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An evaluation of pumice, unloaded clinoptilolite and nutrient-loaded clinoptilolite zeolites, as plant growth substrates in the intensive production of long season glasshouse crops

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**AN EVALUATION OF PUMICE, UNLOADED CLINOPTILOLITE AND
NUTRIENT-LOADED CLINOPTILOLITE ZEOLITES, AS PLANT GROWTH
SUBSTRATES IN THE INTENSIVE PRODUCTION OF LONG SEASON
GLASSHOUSE CROPS**

by

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fulfilment for the degree of

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In collaboration with the States of Jersey Department

of Agriculture and Fisheries,

ADAS and Hazlewood VHB

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Abstract

An evaluation of pumice, unloaded clinoptilolite and nutrient-loaded clinoptilolite zeolites, as plant growth substrates in the intensive production of long season glasshouse crops

by

Paul Francis Challinor

Annual losses of nitrogen from existing glasshouse crop production substrate systems could be as high as 600 kg ha⁻¹, using an average of 30% drainwater containing a nitrate-nitrogen concentration of 200 mg l⁻¹. The use of nutrient recirculation systems such as nutrient film technique (NFT) helped to reduce nutrient losses to the environment but the commercial area of NFT has decreased due to high initial capital costs, concerns over disease transmission within the system and an absence of recent research and development. Most substrate systems rely on the provision of liquid nutrient feeds at every watering. This study examines clinoptilolite which is able to selectively store, supply and exchange cations with plant roots.

The use of the naturally-occurring volcanic aluminosilicates pumice and clinoptilolite zeolite in the intensive production of edible and ornamental protected crops, tomatoes, sweet peppers and standard carnations was studied. Pumice from Sicily, Italy and clinoptilolite (84-87%) from Beli Plast, Bulgaria were used in the experiments. The management of the pumice and unloaded clinoptilolite systems involved provision of all the plant growth nutrients via a drip irrigation system. In comparison, the nutrient-loaded clinoptilolites were examined using only water in the irrigation cycles which allowed relatively unimpeded cation exchange to take place between the clinoptilolite and the surrounding solution, thus providing nutrients for plant roots. The total cation exchange capacity of clinoptilolite was measured as 132.0-158.3 meq 100g⁻¹, compared with 1.8 meq 100g⁻¹ for pumice.

Unloaded clinoptilolite irrigated with nutrient-balanced liquid feeds gave yields and quality equivalent to those of tomatoes, peppers and standard carnations grown on rockwool, pumice and peat / peat alternatives.

For the first nine months of an eighteen month experiment, the yield and quality of standard carnation flowers from high nutrient-loaded clinoptilolite matched those from pumice receiving liquid feeds at every watering. Thereafter, lower concentrations of available nitrogen and, to a lesser extent phosphorus, limited production by up to 25%. Drainwater nutrient concentrations were, however, extremely low and reduced the potential pollution risk to the surrounding environment. Drainwater nitrate-nitrogen concentrations of below 10 mg l⁻¹ were measured, compared with 100-300 mg l⁻¹ for pumice. Drainwater potassium concentrations were also comparatively low at < 20 mg l⁻¹ for clinoptilolite and 200 mg l⁻¹ for pumice. Phosphorus concentrations in the drainwater did not exceed 12 mg l⁻¹, compared with a maximum of 70 mg l⁻¹ in drainwater from pumice.

The inclusion of phosphate rock (apatite) in with the clinoptilolite provided a source of phosphorus available to plants and the dissolution of apatite was regulated by the rate of absorption of phosphorus and calcium by plants. In all the experiments, clinoptilolite adsorbed ammonium-nitrogen and potassium, releasing calcium and sodium. However, concentrations of sodium released into the root zone were not harmful to plant growth. The average nitrate-nitrogen concentration of new, fully-expanded carnation leaves was 51.7% lower than the target levels. The nutrient loading of nitrogen and phosphorus regulated the overall yield of the crops evaluated in the experiments. The use of nutrient-loaded clinoptilolite to produce commercial crops and reduce environmental pollution by regulating the concentration of nutrients in the drainwater over long periods of time is further explored in the study.

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‘The woods are lovely, dark and deep,

But I have promises to keep,

And miles to go before I sleep,

And miles to go before I sleep.’

An extract from ‘Stopping by Woods on a Snowy Evening’ by Robert Frost

From New Hampshire (1923).

Declaration

At no time during the registration for the Degree of Doctor of Philosophy has the author been registered for any other University award.

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Chapter One Introduction

1.1 Development of intensive crop production hydroponic and substrate systems

1.1.1 Introduction - the move from soil to peat

Hydroponic and substrate systems currently in commercial use include: peat, coir, nutrient film technique (NFT), rockwool (stonewool), glasswool, polyurethane foam, pumice and perlite. The move away from soil-based systems in the 1970s to peat was stimulated by the need to control problems with soil pests, diseases and nutritional imbalances. According to Bragg (1990) the advantages of peat as a major constituent of substrates were seen as follows:

- excellent air / water relationships;
- slow rate of decomposition when used in containers;
- generally pathogen (plant and human) free;
- dark brown colour; and
- low pH and nutrient content, allowing easy adjustment for all crops.

Peat-based systems offered a potentially pest and disease-free alternative but practical problems with water content, water availability and nutrient balance limited its applications to certain crops. For example, without an accurate irrigation system, cultivation of solanaceous crops, such as tomatoes and peppers, was disrupted by a loss of marketable fruit as a direct result of water stress, leading to a transient calcium deficiency and, subsequently, blossom-end rot (Ho *et al.*, 1993; Ho and Adams, 1994; Reid *et al.*, 1996; Ho and Hand, 1997). In addition, the presence of weed seeds in the peat was occasionally disruptive to the normal production of crops. Peat is still widely used, often in combination with other inert materials such as rockwool and perlite in potting compost mixes (Bragg, 1990). Peat mixed with a base fertiliser composite is also used in the production of long season flower crops, such as spray and standard carnations (Anon, 1995). The development of alternatives to peat mixes for hanging baskets and

patio plants was thought to be desirable, particularly as the substrate is only acting as a physical support and nutrients are supplied as liquid feeds or from controlled-release fertilisers (Bragg, 1990). All peat systems require a constant supply of nutrients, either in the form of a slow release fertiliser or liquid feeds; depending on the nutrient composition of the background water, nutrient imbalances can quickly occur, such as a low potassium status in the production of carnations (MAFF, 1967). Adams *et al.* (1978) found that microbial decomposition of peat during cropping at first resulted in immobilization of nitrogen and, later, much of the nitrogen was mineralised and became available to crops. Good yields of high quality tomato fruit may be grown in peat, provided that adequate levels of nutrients are maintained throughout the production season (Adams *et al.*, 1973). In addition, although peat proved to be a successful medium for growing tomatoes, the yield was found to decline when the micronutrient status was not maintained (Graves *et al.*, 1978).

The overall professional use of peat grow-bags has declined since the mid-1970s and most of the protected crops are now grown in alternative substrates (Bragg, 1990). Latterly, conservation and environmental groups have exerted pressure on the Industry to utilise other materials such as coir (Carlile, 1999). Other institutions, for example Bridgemere Nurseries in Cheshire, developed their own alternative to peat - 'Fipro' which was based on oil seed rape straw, for use in containerised ornamental plant production (Bragg, N., 1994 - pers. comm.). In the early 1990s, the main additive to peat was pine bark and its introduction was a response to the decline in quality of peat available to the grower (Blackman, 1994). Coir was considered to be the most successful alternative material, although wood waste products dominated in the retail sector (Blackman, 1994).

There has been a marked increase in interest in the use of peat alternatives by commercial growers in the last two years (Holmes and Lightfoot-Brown, 2000). Many growers appear to lack confidence to move away from peat immediately and further research and

demonstration of the potential of peat alternatives is still required (Anon, 2000a). For peat alternatives to be viable competitive products in a commercial market, it is important to develop media with a guaranteed continuity of quality and supply (Dickinson and Carlile, 1995). There are now other materials (Table 1.1) which can be used in place of peat for many sectors of commercial horticulture (Holmes and Lightfoot-Brown, 2000). In the DETR Monitoring and assessment of peat and alternative products for growing media and soil improvers in the UK (1996-1999) planning research report (2000), the following points were highlighted:

- general professional grower experience was that peat-free growing media do not perform as well as peat-based products;
- amateur gardeners showed a greater acceptance of the performance of peat-free growing media;
- price and availability were factors most likely to influence purchasing decisions in relation to peat-free materials;
- professional growers were aware of environmental concerns and some perceived that there was a marketing advantage by using peat alternatives, especially when supplying multiple retailers;
- amateur gardeners and local authorities stated that environmental concern was the main reason for experimenting with peat-free products;
- soil improvers were more likely to be based on alternative materials;
- growing media were more likely to be based on peat; and
- concerns about the conservation of natural peat-bog habitats have been widely canvassed by conservation organisations. Amateur gardeners do have sympathies with environmental issues. The decision by the National Trust to ban the use of peat on its own properties, for example, is likely to increase awareness of the issue amongst the public.

Table 1.1 Alternatives to peat (after Holmes and Lightfoot-Brown, 2000)

Peat alternative	Background	Main problems
Loam	Well defined soil type originally in 'John Innes' mixes. Traditionally lifted as turfs and stacked until stabilised.	Availability and variation between batches. High bulk density. High Mn after sterilisation. Some sources have high pH levels.
Coir	Short to medium length fibres constituting the mesocarp of the coconut fruit. Excellent rooting, due to high air capacity. Well proven as peat alternative. Low bulk density 250-300 g l ⁻¹ .	Non-indigenous product. Sample variation and supply reliability. Salt contamination (and high K early). N lock-up and pre-treatment with calcium nitrate adds to cost.
Coniferous barks Scots pine / Corsican pine (main species).	By-product of forestry industry. Bark is a sustainable material, as timber is a renewable resource. Disease-suppressive activity due to presence of fungi antagonistic to certain root pathogens. Bulk density of chipped bark low 150-250 g l ⁻¹ .	Bark must be matured to allow phytotoxins eg: terpenes to reduce. Low pH and low nutrient status. Barks immobilise nitrogen as they break down. Extra N fertiliser needed, especially for spruce barks. Low water holding capacity: > leaching of nutrients.
Forestry residues	Waste from forestry operations. 50-70% residue from product. Low bulk density 350 g l ⁻¹ . Similar to bark but finer texture with higher water holding capacity.	Low pH. Higher water requirement than peat. Extra N needed.
Chipboard residues	Waste from chipboard sheet processing (milled and composted). Urea formaldehyde added, which releases N during the composting phase.	High pH. Higher water requirement than peat. High bulk density 600 mg l ⁻¹ .

Green compost	European Landfill Directive and Landfill Tax initiative have diverted large volumes of organic wastes (brushwood / grass) away from land-fill into composts. 1 M m ³ green compost available. May contain beneficial micro-organisms.	High pH and EC. High K and Cl. Contaminants. High bulk density 500-600 g l ⁻¹ . Transport costs.
Other organic materials eg: composted sewage-based products, municipal solid waste, spent mushroom substrate, hop waste, coffee bean waste, cocoa bean shells, rice husks, bran, food industry wastes, paper wastes.	Consumer resistance to sewage-based products.	Availability of some products. High bulk density. Poor drainage / aeration. High pH and high nutrient status.
Inorganic materials eg: rockwool, perlite, pumice, lignite, zeolite, polystyrene, urea formaldehyde resins.	Some in use for many years. Low nutritional status allows precise nutritional control in hydroponics.	Good in hydroponics but considered environmentally-unfriendly due to high transport costs and energy used in rockwool production. Disposal problems.

1.1.2 Nutrient film technique

According to Benton Jones (1982), "hydroponics is a widely and frequently used technique for growing plants without soil, providing for a considerable degree of the elemental environment surrounding the root. The technique has an interesting history of development and use dating back into the mid-18th Century, although the growing of plants in nutrient rich water may have dated back into the early history of man." One advantage of horticultural production in hydroponic systems, as compared with growing in soil, is that external properties do not limit nutrient acquisition (Schwarz *et al.*, 1997). Nutrient film technique (NFT) was developed in the early 1970s by Dr. Allen Cooper and remains the ultimate nutrient recirculation system (Anon, 1996a). According to Cooper (1975), the use of water containing dissolved nutrients as a technique for crop production

was first described by Gericke in 1929. The system consists of a water sump tank into which are dosed nutrients in various combinations (Graves, 1983). The quantity of liquid in the sump tank and the pH and conductivity of the solution are constantly monitored by a computer system and the appropriate changes made by the introduction of fresh water, acid and nutrients in liquid form, as required (Graves, 1986). Traditionally, two dosing tanks were used to separate the phosphorus and calcium inputs until the point of introduction into the irrigation system (Drakes *et al.*, 1984). At first, the computer systems were instructed or only able to draw from these tanks evenly. More recently, equipment has been developed to vary the proportions of each tank that can be dosed at any one time. This has allowed a more precise control of the specific nutrient concentration of input feeds. From the sump tank, the complete liquid nutrient feed is pumped to the top end of a series of closed troughs and the liquid feed then enters each trough through a delivery tube and moves evenly, by gravity, down a slope of 1 in 80 or 1 in 100 (Drakes *et al.*, 1984). The root system of each plant in the trough is then bathed with water, feed and dissolved oxygen. A root mat develops in the stream of water, with a proportion of the roots slightly above the solution in moist conditions but in contact with the air (Cooper, 1979). *Lycopersicon esculentum*, for example, can adapt to and efficiently utilise a wide range of nutrient concentrations (10 to 320 mg l⁻¹ nitrogen and 20 to 375 mg l⁻¹ potassium) and, therefore, may be grown in a recirculation hydroponic culture system such as NFT (Davies and Hobson, 1981). The plants can then selectively remove nutrients and water from the solution, as the plant growth stage and environmental conditions dictate. Cooper (1975) stated that as there is no drainage loss of water and little evaporative loss, the water requirement is reduced to the essential plant transpirational loss. Apart from being the first commercially acceptable recirculation system, NFT gave growers the best control of conditions in the root zone (Roe, 1982). In all other substrate systems, the roots are only partially visible and the substrate and

feed have to be managed separately to give the best conditions for root growth in the substrate itself. Since its early introduction, interest in NFT systems has waned for a number of reasons including the high starting capital costs, system failures, nutritional problems and plant losses through root diseases. System failures have included faulty designs, incorrect installation of equipment and plant death due to oxygen starvation. Nutritional problems have included low nutrient solution pH caused by acid overdosing, an accumulation of unwanted ions over time (for example sodium, chloride and sulphate), often as a result of poor background water quality, and general nutrient solution imbalance problems. Attenburrow and Waller (1980), for example, found that 200 mg l⁻¹ sodium chloride in the make-up NFT water significantly reduced the yield of tomatoes compared with a sodium chloride-free control. With increasing sodium chloride concentration and conductivity, fruit quality improved but fruit size declined. In addition, root death and disease problems have been caused as a direct result of stagnant conditions in the root zone and lack of skills on the part of the grower to understand basic plant health and nutritional requirements.

Initially, there was little or no pressure to recirculate nutrients within soil-less crop production systems, although growers were aware of the savings in water and feed costs that NFT, in particular, offered. It is possible to grow tomatoes, for example, in recirculating water culture using treated pig slurry (Garraway, 1982) and, possibly, other liquid animal wastes. More recently, nutrient recirculation systems have been encouraged due to their environmental benefits. NFT is still used for the production of salad crops, especially long season tomatoes, in areas of the UK with good water supply characteristics, such as the Vale of Evesham, Kent and areas on the South Coast of the UK. Tomato and cucumber can produce high yields of fruit when grown under optimal conditions in soilless culture (Adams and Ho, 1995). There is renewed interest in the utilisation of NFT in areas of the world where recirculation of water and nutrients is

becoming a legislative requirement, often in conjunction with pressure from the markets (supermarkets in UK) and consumers. Supermarket assured produce schemes, such as Tesco Stores Ltd 'Nature's Choice,' are pressurising growers to examine their use, re-use and disposal of all materials involved with the production of crops (Ann, D., 2001 - pers. comm.)

1.1.3 Rockwool (Stonewool)

The introduction of rockwool in the early 1970s revolutionised the crop production industry worldwide. The material is a by-product of the loft insulation industry and is produced by the heating and mixing-together of two rocks - basalt and diabase - at temperatures above 1500°C and the resulting flux then being spun into fibres and formed into horizontal, vertical or combination slabs (Smith, 1987). In its prepared state, it has a pore volume of approximately 97% and its function is to provide root anchorage for the plant and to regulate the water and air supply. It does not contain any plant nutrients and the plant must rely entirely on the inclusion of nutrients in the water supply (Bunt, 1988). Unlike the insulation material, rockwool is made to accept water, not repel it, and is pest, disease and weed free. It does, however, require the reduction of pH from approximately 8.0 to 6.0 and a thorough wetting with nutrient solution, prior to use by the grower. Many errors have been made due to insufficient wetting-up prior to planting and, occasionally, quality control problems have resulted in slabs with a poor structure being supplied.

One of the main reasons for the rapid and widespread uptake of rockwool is the fact that the management of the moisture and nutrient contents are simple when compared with NFT. In fact, mistakes with irrigation can be quickly corrected by over-irrigating with a liquid feed at the correct pH and electrical conductivity (EC). Until recently, most growers ignored the fact that they were probably over-irrigating their rockwool substrates by over 30% and thus creating large volumes of drainwater. According to Grylls *et al.*

(1996) typical application rates for rockwool tomatoes range from 1,000-1,500 litres m² year⁻¹. The crop requirement is estimated at approximately 700 litres m² year⁻¹, causing drainwater percentages of 30-53%. Using an average of 30% drainwater and a nitrate-nitrogen concentration of 200 mg l⁻¹, the total annual loss of nitrogen could be as high as 600 kg ha⁻¹ (Grylls *et al.*, 1996). It is now unacceptable to allow drainwater to escape from the glasshouse unit into water courses and the importance of a return to re-use or recirculation of nutrients and water is paramount (Hibberd, 1989). The present situation is that existing rockwool systems are being adapted so that drainwater can be collected away from the slabs and treated to allow recirculation to take place. This involves collection of drainwater in a clean, sealed channel system, transfer of solution to a sump tank, measurement of parameters such as pH and conductivity, followed by a possible solution disinfection prior to returning the drainwater to the slabs. To achieve a failsafe system would involve similar capital expenditure to the setting-up of an NFT system plus the additional cost of the rockwool slabs. The equipment failure and pest / disease pressures associated with prototype NFT systems are the same for such rockwool recirculation systems. Work at Horticulture Research International, Stockbridge House, North Yorkshire, has revealed the presence of beneficial organisms in NFT system solutions, although their commercial exploitation remains to be fully investigated (McPherson, M., 1997 - pers. comm.).

Work at the Department of Agriculture and Fisheries, Jersey, has consistently shown higher yields of long season tomato crops in NFT systems, compared with rockwool systems where the drainwater is recirculated (Anon, 1992, 1993, 1994, 1995a, 1996a, 1997a). Rockwool can be sterilised and re-used for two or three seasons, depending on the type of rockwool (one-year / two year, horizontal / vertical fibres) and how carefully the material has been handled prior to, during and after the end of the crop. Once the material has reached the end of its useful life, there then remains the separate problems of

how to handle and how to dispose of the slabs. A recycling scheme has recently been introduced by one of the main suppliers, Grodania, but it is limited to nurseries close to the recycling centres. Other methods of disposal include dumping at land-fill sites and incorporation of shredded rockwool into a mixture of raw materials for house brick manufacture (Anon, 2000b; Proctor, N., 2000 - pers. comm.). With increasing charges for transport, recycling and landfill, disposal of rockwool may prove extremely difficult and may threaten the long-term use of the material. Other problems, such as the detection and spread of pepino mosaic virus in 2000 (Dungey, N., 2001 - pers. comm.), may also restrict the movement of materials off site (Lang, 2000).

The rockwool slab is totally inert and it does not participate in the process of movement of ions to the plant root, except that it provides air spaces and support for the root mat. If there is an imbalance in the ion content of the input feed, this will be mirrored in the root zone, as the fibres do not interact with the nutrient solution. Rockwool systems are currently successful because they are easy to manage in terms of irrigation but when the complication of having to collect and store drainwater, analyse, monitor and re-use the solution is added, then the system becomes less attractive. Rockwool systems are, therefore, not the complete answer to the requirement for environmentally-friendly production of crops in the 21st Century.

1.1.4 Polyurethane foam

Polyurethane foam can be used to produce slabs that are similar in operation to rockwool slabs *i.e.* the material does not actively participate in the exchange of nutrients from material to plant roots or *vice versa*. Most of the commercial foam products are more free-draining than their rockwool counterparts (Anon, 1996a), especially the bonded types such as 'Aggrofoam,' (Hardgrave, 1995). The main advantage over rockwool is that the foam has a much longer working life of up to ten years (Smith, 1996). Most foam slab types can be effectively and economically steam sterilised between crops

(Hardgrave, 1995). There remains, however, the problem of disposal at the end of the cropping sequence.

Chipped waste polyurethane foam was used to produce some of the first slabs used in production of horticultural crops. Foams of different densities and pore sizes were mixed together to form compressed homogeneous blocks and bonding was effected by applying superheated steam at 120°C, to form a sterile and stable growing material (Smith, 1996). More recently, low density slabs have been produced specifically for intensive glasshouse crop production (Hardgrave, 1995; Smith, 1996).

In experiments involving polyurethane foam for hydroponic cucumber production, Hardgrave (1995) found that there was little variation in slab nutrient concentrations between rockwool and foam and also concluded that nutrient regimes do not need to be formulated differently for a foam substrate. Bohme (1995), however, found that although cucumber yields were high on foam, water consumption and drainwater volumes were also high from the system (maximum recorded levels > 40%).

1.1.5 Perlite

Perlite is a volcanic glass formed when molten lava cools very rapidly trapping small quantities (2-5% w/w) of water. When crushed and heated to 1,000 °C, it expands to form white, lightweight aggregates with a closed cellular structure. These aggregates are virtually inert, stable, have a low bulk density and do not break down when mixed with other materials (Day, 1991). Water is retained only on the surface of the aggregates and peat mixes containing perlite, for example, are well-drained.

Plants grown in perlite are totally dependent on liquid feeding (Bunt, 1988). The internal porosity of expanded perlites has a high effect on water retention and hydraulic conductivity. Internal porosity could act both as an air reservoir and as a water reservoir that may serve as a rhizosphere buffer (Orozco *et al.*, 1995). Perlite has a negligible

cation exchange capacity and has a nominal pH of 7.0 to 7.5. It is resistant to steam temperatures, so it can be sterilised as required (Smith, 1996).

A system based on perlite as the rooting substrate was developed at the West of Scotland College in 1984 (Hall *et al.*, 1989). Early systems relied on the maintenance of a reservoir of water under the perlite bolsters or slabs and the subsequent rise of water through the material by capillarity. Although most UK tomato growers have switched to using rockwool over the last 10 to 15 years, perlite systems have, more recently, started to be utilised by growers in Spain, for example.

1.1.6 Pumice

Pumice is an highly vesicular volcanic glass, silicic in composition and occurs as massive blocks or unconsolidated, fragmented material (Mitchell and Bloodworth, 1989). The vitric ash-sized component of many tuffs consists dominantly of bubble-wall shards mixed with pumice shreds and lapilli. Bubble-wall shards are mostly the broken bubble or vesicle walls of pumice (Fisher and Schmincke, 1984). Volcanic magma contains 2-3% water and, on entering the atmosphere during an eruption, this water evaporates rapidly causing expansion of the material (Gunnlaugsson and Adalsteinsson, 1995). This may solidify on contact with the atmosphere as a vent filling or flow, or may be shattered by a violent eruption (Robbins, 1984). Fragmented pumice with shards under 2 mm in diameter is generally defined as pumicite (Peterson and Mason, 1983). Pumice is a unique geological material since its density is often less than water (Whitham and Sparks, 1986). Silicic pumice usually has a high porosity (up to 90%), a density of $< 1.0 \text{ g cm}^{-3}$ and low permeability (Fisher and Schmincke, 1984). An example of a natural pumice is Hekla-pumice (Plate 3.2), which originated from the Hekla volcano in Iceland over 2,800 years ago. It is inexpensive and biologically inert and contains no pathogens or weed seeds (Gunnlaugsson and Adalsteinsson, 1995).

Pumice is a stable material which can withstand steam sterilisation without a major loss of structure (Smith, 1996). The pore volume of Icelandic pumice has been reported as 85% and the moisture content as 45% (Boertje, 1995). Low bulk density, good heat and sound insulating properties and excellent abrasive capabilities give pumice and pumicite useful industrial applications. The main use of pumice is in the construction industry, particularly in building block aggregate (Peterson and Mason, 1983). Pumice has been used more recently in Holland in plant substrate systems and in compost mixtures although there is very limited use in UK. All plant growth systems involving pumice require liquid feeding to sustain the growth of plants. The Mediterranean island of Lipari, which lies 35 km off the northern coast of Sicily, is the focus of the Italian pumice industry (McMichael, 1990). Physical and chemical properties of Sicilian pumice are described in more detail in Chapter Two.

1.1.7 Zeolites: introduction

At present, the zeolite group includes more than 40 naturally-occurring species and is the largest group of minerals among the silicates (Mumpton and Fishman, 1977; Rinaldi, 1984; Parham, 1989; Tsitsishvili *et al.*, 1992). It was not until the late 1950's that the scientific community became aware of zeolites as major constituents of numerous volcanic rocks that had been deposited in ancient saline lakes of the western United States and in the thick marine deposits of Italy and Japan (Mumpton, 1984b). Zeolites are crystalline, hydrated, framework aluminosilicates of alkali and alkaline earth cations that are characterised by three-dimensional structures containing channels in which are located cations and water molecules (Mumpton, 1984b; Dyer, 1988; Ming and Mumpton, 1989). Water can be lost and re-gained and cation exchange can occur between the zeolite substrate and plant roots. Clinoptilolite is a form of zeolite that has a particular affinity for monovalent ions such as ammonium-nitrogen and potassium (Tsitsishvili *et al.*, 1992). Some clinoptilolites can be rich in sodium (Weber *et al.*, 1984) which can cause

salt stress in plants following the release of the cation (Pirela *et al.*, 1984; Ferguson *et al.*, 1986; Nus and Brauen, 1991; Yi *et al.*, 1991) and sources of materials low in sodium and high in potassium and calcium are essential for applications in glasshouse systems. At present, there is only a minimal use of clinoptilolite in the UK horticultural industry in propagation of specialist hardy ornamental stock and also in herb production (Tucker, 1997). Physical and chemical attributes of Bulgarian clinoptilolite (Plate 3.1) are described in Chapter Two.

1.2 History and uses of zeolites

1.2.1 Discovery and basic properties

Zeolites were discovered in 1756 by Freiherr Axel Fredrick Cronstedt, a Swedish mineralogist, and were termed boiling stones from the Greek ζειν - “to boil” and λιθος - “stone” (Mumpton, 1984b). On heating, water is expelled, causing the zeolite to froth. This property illustrates their easy water loss and is described as intumescence (Dyer, 1988). Another characteristic property, known as molecular sieving, arises from the molecular framework arrangement which allows the selective uptake of some molecules into their porous structure, whilst rejecting others on the basis of their larger molecular dimensions (Breck, 1974). Clay has a layered crystal structure and is subject to swelling and shrinking as water is absorbed and desorbed between the layers. Zeolites, in comparison, have a rigid, three dimensional crystal structure consisting of a network of interconnected tunnels and cages. Water can move in and out of these pores but the zeolite framework remains rigid (Barrer, 1978). Although clinoptilolite and heulandite belong to the same structural group, they differ in composition, properties and thermal stability (Mumpton, 1960).

Zeolites are very common and well known as fine crystals of hydrothermal genesis in geodes and fissures of eruptive rocks, or as microcrystalline masses of sedimentary origin (Gottardi and Galli, 1985; Ogihara, 1996). The rock-forming zeolites are

primarily found as products of the alteration of glasses of volcanic or impact origin and, more rarely, of aluminosilicate gels or other crystalline materials (nepheline, smectite, plagioclase and earlier-formed zeolites) (Ibrahim and Hall, 1996; Stamatakis *et al.*, 1996). Fine-grained volcanic glass is the basic source of natural zeolites due to its high reactive capacity, chemical composition and large surface area (Temel and Gundogdu, 1996). Glasses of alkali origin are easily and completely zeolitized (Aleksiev and Djourova, 1974; de'Gennaro and Langella, 1996). Slag and pumice structures of most ashes promote zeolitization: the thin walls of the glass bubbles are easily bordered by mineralising solutions. Microscopic observations show that particles of zeolitized volcanic glass are coated with a fine film of montmorillonite on which layers of zeolite crystals are grown, in turn (Tsitsishvili *et al.*, 1992). Zeolitic rocks of economic importance, containing analcime, clinoptilolite and mordenite, have been identified in the Lower Oligocene of the north eastern Rhodopes, Bulgaria (Aleksiev and Djourova, 1975; Djourova, 1976; Djourova and Milakovska-Vergilova, 1996). Acidic, vitroclastic material, transported as pyroclastic flows, was deposited in marine environments and underwent alteration processes, resulting in the formation of analcime and clinoptilolite rocks (Gottardi, 1989; Gundogdu *et al.*, 1996). All of the clinoptilolites used in the experiments detailed in Chapters Four, Five and Six were sourced from deposits in the Bulgarian Rhodopes (Beli Plast (Plate 3.1), Han Krum and Kurdjali). Further descriptions of the clinoptilolites follow in Chapter Two.

Sheppard (1984) stated that “agricultural researchers have either failed to characterize the zeolites (or, more correctly, zeolite-rich rocks) or have only poorly characterized the materials used in their studies. This deficiency has contributed to difficulties in interpreting and reproducing the experimental results.” The chemical composition of the zeolite is extremely important in plant growth experiments (Parham, 1989). Soils treated with natural sodic clinoptilolite, for example, were found to have an adverse effect on the

growth of beans and barley in terms of decreased plant yield (Nishita and Haug, 1972). The detrimental effect on the plant growth was apparently due to the release of sodium from the zeolite to the soil, thereby reducing the productivity of the soil.

1.2.2 Ion exchange properties

According to Colella (1996), the ion exchange reaction occurs between two or more phases, one of which is liquid, which exchange two or more ions (cations or anions), more or less strongly bound to each phase. Ion exchange is commonly an equilibrium reaction but there are cases in which exchange proves to be irreversible (Collela, 1996). The quantity of ions exchangeable by a solid exchanger, depending on its chemical and structural features, is called the ion exchange capacity and is usually expressed in milliequivalents g^{-1} .

Zeolites are capable of exchanging ions with the external medium (Semmens, 1984). Ion exchange is possible at low temperatures (100°C at the most) and tetrahedral cations exchange above 400°C (Tsitsishvili *et al.*, 1992). Water is lost at approximately 250°C and reversibly re-absorbed at room temperature (Gottardi and Galli 1985). In zeolites, ion exchange arises from the presence of extra-framework cations, located in the regular array of channels and cages, which constitute the rigid anionic framework (Collela, 1996). Cations are bound to the lattice and to water molecules, which normally fill the zeolite micropores. The substitution of trivalent Al for quadrivalent Si in the silicate tetrahedra of zeolite structures creates fixed, negatively charged sites throughout the structure (Semmens, 1984). To maintain electrical neutrality, the negative charges are neutralised by the presence of an equivalent number of mobile cations or counterions (White, 1988). Such mobile cations are only loosely bonded in the crystal structure and are free to exchange with cations in solution. This cation exchange process occurs when ions from solution replace counterions within the crystal structure and at any concentration of counterion, as predicted via equilibrium thermodynamics (Semmens,

1984). Thus, cation exchange in natural zeolites is not merely a surface phenomenon; it takes place throughout the zeolite particle. According to Tsitsishvili (1992), the cation exchange capacity is theoretically equal to the total sum of cations in the zeolite and is usually expressed in units of meq g⁻¹. Exchange of monovalent ions on clinoptilolite proceeds with a clear selectivity towards the larger cations, for example Cs⁺, Rb⁺ and K⁺ as compared with Na⁺ and towards Na⁺ as compared with Li⁺ (Tsitsishvili *et al.*, 1992). Cations in the channels are easily substituted and are known as exchange or extra-framework cations. Conversely, silicon and aluminium are not exchanged as easily and are termed tetrahedral or framework cations (Tsitsishvili *et al.*, 1992). The silicon / aluminium ratio in natural zeolites lies within the limits of 1 to 6, with the upper limit of 5 to 6 for clinoptilolite, mordenite, ferrierite and dachiardite. In synthetic zeolites, the silicon can be substituted by germanium and the aluminium by gallium, iron, chromium and boron, for example. In natural specimens, only beryllium and iron are observed in tetrahedral sites, in addition to silicon and aluminium (Tsitsishvili *et al.*, 1992). The water content of zeolites depends on the character of the exchange cations and conditions experienced during crystallization. In the zeolite structures, there are various cation sites which differ from each other in framework position and in bond energy. This may affect both the extent and kinetics of cation exchange. Incomplete exchange reactions may arise from cation sieving. This may be due to cation size, both in diameter or in volume, being incompatible with the channel dimensions or with the space available in the specific site (Colella, 1996). Cation sieving may also occur due to the inability of the negative charge distribution on the zeolite structure to accommodate a given cation (Dyer, 1988). Cation exchange capacity of the zeolite substrates used in this study is further explored in the following sections and, at length, in Chapter Two.

1.2.3 Adsorptive properties

The adsorptive properties of zeolites are widely used in the drying of gases and liquids, for example in the drying and purification of effluents to improve the quality of raw materials and final products. Zeolites can adsorb water in much higher quantities than other adsorbents (Tsitsishvili *et al.*, 1992). Among the many different adsorbents, the most selective ones for unsaturated and polar compounds are zeolites. In addition, high-silica zeolites are highly acid-resistant and thermally stable, thus allowing gas purification at high temperatures. Aggressive impurities such as carbon dioxide, hydrogen sulphide, sulphur dioxide, ammonia, oxides of nitrogen and chlorine can all be treated (Whateley *et al.*, 1996). Tsitsishvili *et al.* (1992), continued that such substances as NO₂, NOCl, NO₂Cl and Cl₂ adsorb better on the hydrogen form of clinoptilolite than on the natural zeolite. Synthetic and natural zeolites can adsorb up to 10% ammonia (Breck, 1974). Oxygen enrichment of air is possible using mordenite-clinoptilolite tuffs. Natural zeolites can also be used as preservatives for mineral fertilisers and as grain-drying agents. Girgin *et al.* (1996) studied the vegetable oil decolorization properties of a clinoptilolite from Turkey. In addition, zeolites have applications as diverse as ammonia filters in kidney dialysis units and as inclusions in pet litter materials (Mumpton, 1999).

1.2.4 Selectivity for caesium and strontium: purification of radioactive wastes

One of the main methods of purification of radioactive waste is adsorption deactivation (Howery and Thomas, 1965). Clinoptilolite-containing tuffs are characterised by high ion exchange selectivity for ¹³⁷Cs, ⁹⁰Sr and other radioactive elements (Ames, 1960; Mumpton, 1984a; Colella, 1996; Mumpton, 1999). They also possess chemical, thermal and radiation stability, mechanical strength, show irreversibility of sorption and are of sufficiently high capacity and low initial cost. According to Pansini, (1996), clinoptilolite was used in a variety of different ways in the management of contaminated areas after the Chernobyl nuclear power plant accident:

- in particular, the caesium concentration of low-level radioactive waters was reduced by a factor of 1000 and the radioactivity of milk was reduced by a factor of 100 using clinoptilolite filtration;
- the addition of clinoptilolite to soil reduced the supply of radionuclides to plants by a factor of 2-3 times for caesium and 50-70% for strontium;
- the addition of clinoptilolite to polluted fodder reduced the concentration of radionuclides in meat by a factor of 2-3 and, in milk, by a factor of 5-7; and
- the taking of a clinoptilolite-based medication increased the removal of radionuclides from the human body by a factor of 3-5.

Preliminary data on the removal of americium, yttrium, zirconium, hafnium, niobium and thorium from water by ion exchange using natural zeolites are also available in the literature (Pansini, 1996). It is also necessary to guard against the movement of radioactive nuclides from buried high-level radioactive wastes and mixtures of bentonite, mordenite and clinoptilolite have been used as buffer materials in this respect (Tsitsishvili *et al.*, 1992).

1.2.5 Selective removal of heavy metals and other uses

The contamination of the environment with waste-containing different metals is becoming increasingly more dangerous due to the known toxic effects on animals, plants and man via the food chain (Pansini, 1996). The majority of literature on this subject has concentrated on the mechanisms involved with the selective removal of heavy metals from water rather than actual examples of practical applications. Sodium clinoptilolite is selective for heavy metals, for example Ba^{2+} and Pb^{2+} but less for Cu^{2+} , Cd^{2+} and Zn^{2+} . Tetraethyllead can be fixed by zeolites and clinoptilolite tuff can adsorb lead from soil and decrease the content of lead in plants. Zeolites have also been used in the improvement of soil physical properties and remediation of acidic or contaminated soils.

Clinoptilolite tuff is used in Japan as a paper filler and this produces more porous paper characterised by lower volume weight than in the case of clay (kaolin) fillers (Tsitsishvili *et al.*, 1992). In order to protect rubber mixtures against premature polymerization during vulcanization and to recover components of gas in volatile vulcanizing systems, synthetic zeolites of the A and X type have been used in the rubber industry (Tsitsishvili *et al.*, 1992). Zeolite catalysts are widely used in oil refineries for cracking, hydrocracking, isomerization, selectoforming and other reactions, due to their molecular sieve properties (Breck, 1974).

Other uses include zeolite incorporation into solar energy systems, involving air conditioning and refrigeration systems designed to use zeolites. Dehydration of zeolites during daytime and absorption of water at night leads to a temperature change to an extent sufficient for cooling (or heating) of small rooms. Clinoptilolite tuff can be introduced into detergents (Townsend, 1986) to replace sodium tripolyphosphate, an ecologically undesirable compound (Coghlan, 1994). Zeolite tuffs are widely used as silica additives to concrete and cement grouts, which increases the longevity of cement stone, its stability in aggressive media and decreases impact cracking (Kitsopoulos and Dunham, 1996). Natural zeolites can also be used in the extraction of phosphorus from production solutions obtained as a result of leaching of low grade phosphate ores.

1.2.6 Ammonium-nitrogen adsorption

It is known that both synthetic and natural zeolites possess definite selectivity in ion exchange. Ammonium-nitrogen is extracted by cation exchange or by adsorption in the cavities of the aluminosilicate system. Examination of equilibrium exchange data on clinoptilolite at 23 °C for several cation pairs, including ammonium and the most common alkali and alkaline earth cations found in natural waters, revealed the following selectivity sequence:

$K > NH_4 > Na > Ca > Mg$ (Colella, 1996).

Pretreatment of natural zeolites with sodium chloride or sodium hydroxide solutions improves adsorption capacity in relation to ammonium ions. The exchange capacity of the zeolite is affected by the presence of other cations in the feed solution. These can compete with ammonium ions. As the concentration of Ca^{2+} and Na^{+} increases, less capacity is available for NH_4^{+} ions and the zeolite becomes less effective in the removal of ammonia (Semmens, 1984). The contact time available for exchange to occur also influences the cation exchange performance of natural zeolites (Chapter Two). Exchange is more rapid at elevated temperatures (ion diffusion increases with temperature) and for small particle sizes of the zeolite (where the diffusion path is shorter). Potassium ions are adsorbed first on clinoptilolite and mordenite. Solutions of sodium chloride or nitric acid are the best reagents for regeneration of clinoptilolite in relation to K^{+} and NH_4^{+} ions. Natural zeolites can adsorb more than 1 meq g^{-1} ammonium-nitrogen and potassium ions and then release them gradually into soil solution. Thus zeolites in the soil can prolong the effects of mineral fertilisers by prevention of leaching of cations but the availability of specific nutrients to plants may also be impeded by the adsorption processes.

According to Allen and Ming (1995), MacKown (1978), examined the effects of clinoptilolite from Tilden, Texas on nitrification in soil. Nitrification decreased in a loamy sand by 11% and in a silty clay loam by 4%, when using a rate equivalent to 30 tonnes ha^{-1} of ammonium-nitrogen exchanged clinoptilolite in an incubation experiment. The results were credited to the retention of ammonium-nitrogen by clinoptilolite in sites unavailable to nitrifying bacteria.

Microorganisms can stimulate, inhibit or be without effect on root growth, depending on the type of microorganism, plant species and environmental conditions (Marschner, 1995). According to Marschner (1995), Bowen and Rovira (1991) classified soil microorganisms into two categories in relation to their effects on plant growth:

1. negative (detrimental): root pathogens; subclinical pathogens; detrimental rhizobacteria; cyanide producers; and
2. positive (beneficial): rhizobia; mycorrhizae; antagonists (biocontrol) of detrimental microorganisms; hormone producers; plant growth promoting bacteria.

The most important factors for root-induced changes in rhizosphere pH are imbalances in the cation / anion uptake ratio and corresponding differences in net release of H^+ and HCO_3^- or OH^- and the excretion of organic acids (Marschner, 1995). Nitrate and ammonium are the major sources of inorganic nitrogen 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 nitrate accumulation in vacuoles can be important in cation-anion balance, for example. Some bacteria use nitrate as an electron acceptor under anaerobic conditions (nitrate respiration) and produce nitrogenous gases (N_2 , N_2O and NO_x), a process which causes a considerable loss of combined nitrogen from soils by denitrification. The reduction of nitrate to ammonia is mediated by two enzymes: nitrate reductase, which involves the two-electron reduction of nitrate to nitrite and nitrite reductase, which transforms nitrite to ammonia in a six-electron reduction. Whereas nitrate can be stored in vacuoles without detrimental effect, ammonium and ammonia are toxic at quite low concentrations. The formation of amino acids, amides and related compounds is the main pathway of detoxification of either ammonium ions taken up by roots or ammonia derived from nitrate reduction or nitrogen fixation (Marschner, 1995). The use of clinoptilolite in slowing ammonium-nitrogen losses is further explored in 1.2.9.

1.2.7 Agricultural applications

In agriculture, zeolites have been used as additives to feeds for poultry, cattle and pigs (Mumpton and Fishman, 1977). Its introduction into broiler feed caused more effective feeding and an increase in animal survival rate (Mumpton, 1984a). Mumpton and Fishman (1977) reported that, based on the successful use of montmorillonite clay in slowing down the passage of nutrients in the digestive system of chickens and the resultant improvement in calorific efficiency, clinoptilolite and mordenite have been added to the normal protein diets of pigs, chickens and ruminants at several agricultural stations and livestock farms in Japan. In addition, the physical and chemical properties of many natural zeolites lend themselves to a variety of applications in the treatment of animal wastes including:

- the reduction of malodour and associated pollution;
- the creation of healthier environments for confined livestock;
- the control of the viscosity and nutrient retentivity of the manure; and
- the purification of methane gas produced by anaerobic digestion of the excrement.

Clinoptilolite tuffs on byre floors have deodorising capacity and hydrophilicity, decreasing concentrations of harmful gases by a factor of two and relative humidity by 5%. Poultry manure can be turned into deodorized fertiliser by the application of zeolite at a rate of 2.3 kg m^{-2} .

Witter and Lopez-Real (1988) found that a cover of clinoptilolite (unspecified source) and of a clay soil placed on top of a compost pile, consisting of a mixture of sewage sludge and straw, proved very effective in adsorbing volatilized ammonia. In comparison, they found that a layer of matured sewage sludge and straw compost proved to be ineffective.

1.2.8 Aquaculture

Ammonia produced by the decomposition of excrement and unused food is a primary cause of disease and mass mortality of fish and clinoptilolite is therefore used in fish farming and fish hatcheries to remove ammonia (Mumpton and Fishman, 1977). Natural zeolites are better sorbents of NH_4^+ ions than ion exchange resins (Tsitsishvili *et al.*, 1992). However, the ability of clinoptilolite to remove a given ion, such as NH_4^+ , from water is adversely affected by the presence of competing ions, such as Na^+ and Ca^{2+} (Semmens, 1984). Ion size, valence and hydration energies are important factors in determining selectivity of a given ion in a specific system. For example, large cations, such as K^+ , Pb^{2+} , Ba^{2+} and NH_4^+ , are extremely well removed by clinoptilolite but smaller ions, such as Li^+ , Na^+ and Ca^{2+} , are very poorly removed. The contact time available for exchange to occur also influences the cation exchange performance of natural zeolites. Due to the time required for ions to physically diffuse into the pores and channels of the zeolite structure to the exchange sites and exchanged ions to move out to the surrounding solution, cation exchange is not an instantaneous process. For this reason, exchange is more rapid at elevated temperatures (ion diffusion increases with temperature) and for small particle sizes of the zeolite (where the diffusion path is shorter) (Semmens, 1984).

Research work has examined slow release fertilization with specific emphasis on ion exchange and, more recently, mineral-dissolution reactions.

1.2.9 Experimental work: unloaded clinoptilolite

Hershey *et al.* (1980) used leaching experiments to compare the release of potassium ions from untreated clinoptilolite with the release from soluble potassium nitrate, when each was added to a sand-peat-sawdust potting mix. Clinoptilolite was naturally high in exchangeable potassium (160 meq 100 g⁻¹). Potassium release curves indicated that clinoptilolite behaved similarly to a slow-release fertiliser.

Hershey *et al.* (1980) also completed a glasshouse experiment in which all the potassium required by a three month crop of pot chrysanthemums was supplied by clinoptilolite in the place of liquid potassium feeds. They found that 50 g of clinoptilolite per 1.5 litre potting media (30% sand, 35% peat and 35% composted sawdust) produced yields equal to those obtained from daily irrigation of unamended potting soil with 234 mg l⁻¹ potassium.

Lewis (1981) showed that ammonium-charged zeolite increased radish growth in both medium and light textured soils, when applied as a band treatment. A decrease in nitrate-nitrogen loss also occurred in the leached light soil. In two glasshouse experiments, Lewis (1981) also found that radish 'Improved Scarlet Globe' responded positively to charged and naturally potassic zeolites, equalling growth obtained by liquid feeding.

Pirela *et al.* (1984) evaluated clinoptilolite from the Washakie Basin, Wyoming as a potential enhancer of nitrogen availability to plants. Four successive harvests of radish (*Raphanus sativus*) in a Nunn loam soil amended with different rates of zeolite and ammonium sulphate increased dry matter production in the third harvest and exchange of ammonium-nitrogen as a slow release over time from the clinoptilolite was speculated to be the cause.

Ferguson *et al.* (1986) provided data indicating that zeolite had potential as a medium for the growth of turfgrass and, in 1987, Ferguson and Pepper demonstrated that clinoptilolite slowed ammonium-nitrogen losses from volatilization, nitrification and denitrification. Ammonium-nitrogen retention increased with increasing quantities of clinoptilolite. They concluded that clinoptilolite was a beneficial amendment to golf-course greens, as it could improve nitrogen fertiliser-use efficiency.

Chen and Gabelman (1990) researched the development of a sand-zeolite medium for simulating controlled levels of potassium deficiency in soil-root systems. Coarse sand acted as a well-aerated physical support and allowed easy root recovery and a synthetic

zeolite (IE-96) served as a controlled potassium source and pH buffer. An increase in the amount of loaded zeolite per culture pot resulted in a linear increase of tomato plant dry matter accumulation, indicating that potassium bioavailability is diffusion-limited in the sand-zeolite culture system as in soils (Chen and Gabelman, 1990).

Nus and Brauen (1991) compared clinoptilolite to sphagnum peat and sawdust as sand amendments to enhance the establishment of creeping bentgrass (*Agrostis palustris*) in the construction of golf putting greens. The study showed that coarse-grade clinoptilolite compared favourably with peat and sawdust and suggested that enhanced establishment of the creeping bentgrass was due to both increased moisture and nutrient status provided by the clinoptilolite treatment.

Experimental work on potential amendments for better fertilizer utilization in sandy soils by Yuan in 1992 concluded that zeolites may effectively retain soluble cations from fertilisers, especially potassium and ammonium-nitrogen, against leaching loss in sandy soils.

1.2.10 Experimental work: nutrient-loaded clinoptilolite

Stoilov and Popov (1982) reported the use of clinoptilolite as a raw material for plant substrates. The substrate acted as a reservoir for nutrient cations and was sterile, with respect to pathogenic microorganisms. Depending on the plant species, 20 to 150% increases in yield over control plots were observed for tomato (*Lycopersicon esculentum*), strawberry (*Fragaria chiloensis*), pepper (*Capsicum frutescens*) and rice (*Oryza sativa*). In addition, ripening of rice, cotton and tomato was found to be accelerated in the zeolite substrate. According to Tsitsishvili *et al.* (1992), a Bulgarian soil substitute ("Balkanin"), based on clinoptilolite, turf, vermiculite and additional nitrogen and phosphorus, can be successfully used in greenhouses and in the open.

Rivero and Rodriguez Fuentes (1988) described the use of natural zeolitic rocks as substrates for open-air hydroponic culture of crops in Cuba. Their work examined two

aspects of cultivation of plants using zeolites: application of nutrient solutions to natural Cuban zeolitic rock (Tasajeras deposit) in the cultivation of tomato and other vegetable crops; and the use of nutrient-loaded (including microelements) "Nerea" substrates receiving inputs of irrigation water only and no supplementary liquid feeds. According to their results with the nutrient-loaded substrates, the "optimum development of plants and high crop yields are guaranteed, as are significant reductions in installation costs." In addition, plants showed no nutritional deficiencies, as they were able to selectively access nutrients by ion exchange with the zeolite, and there was no contamination by excess of any element (Rivero and Rodriguez Fuentes, 1988).

Myt'ko *et al.* in 1989 found that the application of ion-exchanging substrates, based on synthetic ion-exchanging materials, for growing vegetable and ornamental crops in a range of controlled environment systems were highly effective as media for root growth. The authors quoted that it was possible to obtain 12-17 kg of biomass m⁻² from each of three successive 30-day "green" crops (cabbage, leaf-beet and borage). However, only 40-50% of potassium, 15-30% of nitrogen, 12-15% of phosphorus and 1-2% of calcium and magnesium were found to be utilised from the substrates, depending on the crop species grown. Nutrient uptake was greater by longer-season crops with well-developed root systems, such as tomatoes and potatoes. They concluded that the continuance of the ion-exchange process, taking place between the substrate and the root system, was limited by the degree of blocking of the exchange radicles of the surface layer of ion-exchangers by accumulating organic materials of biotic origin, in proportion to the substrate's period of use and by the activity of the plant root system. Finally, Myt'ko *et al.* (1989) demonstrated that a new substrate (IS-2 mixed with clinoptilolite from formations at Dzegvi and Tedzami) not only stabilised the productivity of a vegetable production line (see plant species above) for an extended period but increased the yield of useful biomass, for example 160 kg m⁻² obtained from thirteen 30-day crops.

1.2.11 Zeoponics and inclusion of the mineral apatite

In general, the term zeoponics can be applied to the cultivation of plants in any artificial soil in which zeolite minerals constitute an important component (Allen and Ming, 1995; Allen *et al.*, 1996). Bulgarian scientists, for example Petrov *et al.* in 1982, were some of the first to demonstrate that zeoponics can be used successfully for growing plants. Petrov *et al.* (1982) patented zeoponic substrates composed of specific particle-size ranges of clinoptilolite (0.8 to 2.0 mm, 2.0 to 5.0 mm and 5.0 to 8.0 mm), vermiculite and / or peat supplemented with nitrogen and phosphorus fertilisers (ammonium nitrate, ammonium sulphate and superphosphate). They reported success using the zeoponic substrates to grow strawberries and peppers and also to stimulate the rooting of softwood fruit cuttings. In America, Allen (1991) and Allen *et al.* (1991) concluded that if zeoponic mixtures of clinoptilolite and rock phosphate were properly formulated, then they could supply sufficient nitrogen, phosphorus, potassium and calcium for the intensive cultivation of wheat. In addition to ion exchange mechanisms, dissolution of materials such as the mineral apatite have been studied (Mumpton, F., 1995 - pers. comm.). The two reactions drive each other in that dissolution provides cations for ion exchange and ion exchange captures dissolving cations, thereby increasing dissolution (Allen *et al.*, 1993; Allen and Ming, 1995; Allen *et al.*, 1995a; Allen *et al.*, 1996) (Figure 1.1).

Ming *et al.* (1995) and Allen *et al.* (1995b) advanced these systems by synthesizing carbonate hydroxyapatites having balanced quantities of secondary and micronutrients incorporated into their crystal structures. The synthetic apatites were mixed with ammonium-nitrogen and potassium saturated clinoptilolites to form zeoponic substrates for growing wheat. Pot experiments in growth chambers indicated that the substrates were capable of supplying N, P, K, Ca, Mg, S, Fe, Zn, Cu, Mn, B, Mo and Cl. Slightly higher levels of dry matter were produced in the zeoponic soils compared with sand and zeolite controls watered with Hoagland's solution (Allen and Ming, 1995).

Zeoponics has great commercial potential increasing fertiliser-use efficiency and environmental protection. Nutrient-loading of the zeolite material, however, does need to meet the specific nutritional needs of the crop (Allen and Ming, 1995; Carlino *et al.*, 1998).

1.2.12 Production of food crops in space using clinoptilolite

Substrate experiments involving natural zeolite dressed with mineral salts (“Balkanin”), as a nutritive medium for plant cultivation, have taken place in the Svet Space Greenhouse (Ivanova *et al.*, 1992). Svet is an automatic system designed by scientists from the Bulgarian Academy of Sciences for use on board the Mir orbital station in microgravity and the first “space” vegetables (radish ‘White-tipped red’ and Chinese cabbage ‘Hibinski’) were grown in 1990 (Ivanova, 1994). One of the main requirements made of substrates for land-based and space hothouses is the possibility of growing highly productive plants on them for a long time. Shaidorov *et al.* (1992) described the growth of lettuce (*Lactuca sativa*) and radish (*Raphanus sativus* var. *radicula*) on “Balkanin” in the presence of “Ecotol” (the end product obtained in aerobic microbiological decomposition of plant materials, such as wheat straw) for 8-9 successive cut crops. US astronaut John Blaha subsequently harvested 32 mature plants of “super dwarf” wheat on 6 December, 1996 from a 6 August sowing in Greenhouse Svet on the Mir space station (Anon, 1996b).

Zeoponic substrates have space applications for plant growth experiments in microgravity (Space Shuttle, Mir Space Station and International Space Station) and hypogravity (example lunar outpost) environments (Ming *et al.*, 1995). The Biomass Production Chamber (BPC) at NASA’s Kennedy Space Center has provided baseline data for using plants in closed, life-support systems in space (Wheeler *et al.*, 1996a). All crops (wheat, soybean, lettuce and potato) were grown satisfactorily using NFT and high pressure sodium lighting (Wheeler *et al.*, 1996b). Regenerative life-support systems for long-

duration space missions (space stations and planetary outposts) require fresh food sources and it is desirable to develop a substrate that provides the essential plant elements in a static watering system, thereby eliminating the pumps and monitors required for hydroponic processes. A self-sufficient lunar base will require the utilization of in-situ resources for construction materials, propellants and life-support systems. Plant growth at a lunar base will be essential to sustain a self-sufficient human colony (Ming, 1989). Experiments at NASA's Johnson Space Center in Houston have aimed to prove that plants, such as wheat, can provide enough oxygen to support astronauts on a trip to Mars (Kiernan, 1995). Most of the plant growth research in controlled ecological life support systems (CELSS) has been aimed toward hydroponic systems (Ming, 1989; Wheeler *et al.*, 1993; Wheeler, 1996). Other human life support system work has been completed by Dixon *et al.* (1997) using sealed environment chambers to further explore lighting, gas exchange, humidity, temperature and nutrient solution effects. Zeoponic systems have the potential to be regenerated with plant-essential nutrients and reused over and over. Plants are being considered as an important component of regenerative life-support systems for long-duration space missions, for example in space stations and planetary outposts (Ming *et al.*, 1995). Research on zeoponic substrates reported by Ming *et al.*, 1995 suggested that clinoptilolite (Fort LeClède deposit, Sweetwater County, Wyoming) and two apatites (one synthetic laboratory apatite and a natural apatite from North Carolina) had the capability to supply plant growth nutrients slowly for long periods of time, with only the addition of water. Mixtures of zeolite and phosphate rock react to release cations and anions into soil solution through dissolution and ion exchange. These mixtures have the potential to serve as slow-release sources of nutrients in synthetic soils (Allen *et al.*, 1993; Allen *et al.*, 1995a; Allen *et al.*, 1995b). Zeoponic substrates were also able to buffer the solution ionic composition and pH without sophisticated monitoring and control systems. According to Ming (1989), the

design of new, plant growth substrates may have tremendous terrestrial applications, for example, zeoponic systems may be used in commercial greenhouses. These systems are only in their design states and will require further research before they can be used to their fullest potential (Ming, 1989). According to Ming *et al.*, (1995) commercial spin-offs from the technology may include:

- substrates for plants in greenhouses;
- substrates for potting mixes for house plants;
- fertiliser on golf greens;
- field agriculture applications as a slow-release fertiliser (example, for iron); and
- slow-release fertilisers in areas in which environmental issues may be a concern (example, sandy soils near surface water or aquifers).

Zeolites have been used in the improvement of soil physical properties and remediation of acidic or contaminated soils.

1.3 Crop production using substrates in the 21st Century

1.3.1 Integrated crop management systems

Farmers and growers in UK are under increasing pressure from Government legislation, NFU protocols and supermarket crop production guidelines to reduce emissions of nitrate-nitrogen, phosphorus and pesticides into the environment. This pressure is forcing growers using hydroponic systems to re-think policies on both fertiliser and water use and the subsequent disposal of drainwater.

1.3.2 Production of glasshouse crops on Jersey

On Jersey, one problem facing growers is background water supply quality; several sites are adversely affected by saline water supplies with sodium and chloride levels in excess of 100 mg l⁻¹ and 150 mg l⁻¹, respectively. This necessitates careful control over the main element balance in both feed and substrate, to prevent sodium ion accumulation. Invariably, high substrate conductivity levels can result, leading to plant nutrient uptake

problems exemplified by transient calcium deficiency, causing blossom end rot in long season tomato and pepper production.

As a large proportion of the Jersey drinking water is still abstracted from boreholes, it is especially important to regulate fertiliser levels in use on agricultural and horticultural sites, to prevent contamination of potable water (Robins and Smedley, 1994; Chilton and Bird, 1995; Lott *et al*, 1999). Heathwaite and Johnes (1996) found that high loads of dissolved inorganic nitrogen (with > 90% transported as $\text{NH}_4\text{-N}$) were recorded in surface runoff from heavily grazed land. The form of the nitrogen load varied with land use and grazing intensity.

1.3.3 Reduction of pollution by managing input nutrients and controlling drainwater volumes

Attempts to reduce the quantity of fertilisers in use include regular soil, water and hydroponic solution analysis, in conjunction with the appropriate fertiliser recommendations and close monitoring of the nutrient profiles in use. In hydroponics, there has been widespread promotion of the use of chloride fertilisers in the partial replacement of nitrate fertilisers in hydroponic feed formulations (Marks, 1993; Hand and Fussell, 1995). Collection of drainwater from glasshouses has been attempted by several intensive salad crop producers but sterilisation and subsequent recirculation back to the same crop is still at a low level. Other methods of drainwater treatment have been explored, for example collection and re-use of drainwater to soil or other substrate crops, following nutrient content or solution EC adjustment. Application of drainwater to grassland and, more recently, the installation of reed beds, using local aquatic plant species, to partially remove some of the components of hydroponic drainwater are more recent diverse treatments (Anon, 1998).

Hydroponic growers are also being encouraged to replace less accurate irrigation dosing and delivery equipment and to carefully monitor application rates and drainwater volumes.

Equally important is the selection of a substrate that is complementary to the nursery location, in relation to water catchment areas and surrounding environments, in addition to the importance of the specific crop in production and irrigation system control.

1.3.4 Thesis objectives

Substrate systems of the future will need to address problems of production ethics and costs, utilisation of nutrients and water, reduction of nutrient content and volume of drainwater, re-use aspects and disposability. Both natural zeolites and pumice have a range of attributes that will address these concerns.

This thesis attempts to investigate the extent to which unloaded natural clinoptilolite can be successfully used in a nutrient recirculation system and how, over time, the clinoptilolite will exchange cations such as ammonium-nitrogen, potassium and calcium allowing input feeds to be adjusted to account for levels of potassium, calcium and magnesium already naturally present in the clinoptilolite. In addition, the thesis continues to develop the theory that nutrient-loaded clinoptilolites can be utilised as part of recirculation systems or, simply, as stand-alone crop production systems. In the former, application of liquid feeds may interfere with the nutrient exchange between substrate and plant root system. In the latter, drainwater nutrient content is low, after the establishment period, and so it may be less important to install expensive recirculation equipment, especially for short-season crops.

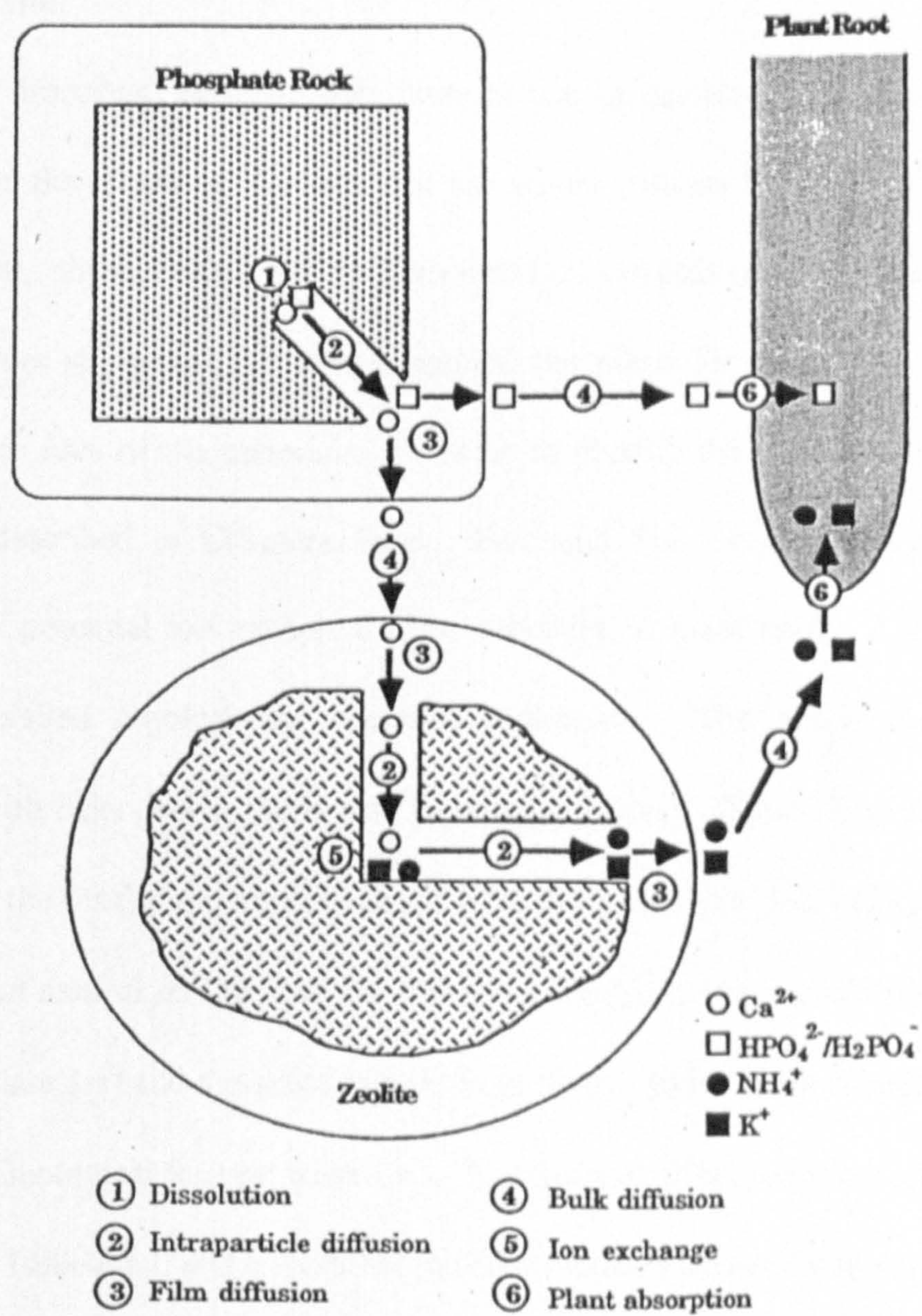


Figure 1.1 Diagrammatic representation of the various transport and reaction processes controlling nutrient release from mixtures of clinoptilolite and phosphate rock. Dashed lines define stagnant water layers surrounding particles (Allen et al., 1995a).

Chapter Two Characterisation of a natural zeolite from Beli Plast, Bulgaria and a pumice from Sicily, Italy

2.1 Introduction

Chapter One described the main substrates in use in current worldwide protected crop production and the sequence of events that has driven growers from the cultivation of crops in soil and peat, through NFT and rockwool and on towards nutrient recirculation systems and participative substrates. It also examined the place for zeolites in horticulture and potential future uses of the materials. In order to classify the zeolite material used in the experiments described in Chapters Four, Five and Six, and to fully understand the mechanism of potential ion exchange from substrate to plant root, it was necessary to perform a detailed physical and chemical evaluation. This work was completed in conjunction with Scientists at the British Geological Survey (Simon Inglethorpe and David Morgan) and the results and interpretations were discussed as a joint effort.

Two samples of natural zeolite from the Beli Plast deposit in the Eastern Rhodopes region of Bulgaria (Plate 3.1) and a pumice sample from Sicily, Italy, were submitted for analysis at the British Geological Survey, Keyworth, Nottingham. The natural zeolite samples were an unmodified (unloaded) and a modified (nutrient-loaded) clinoptilolite supplied by Zeoproducts Ltd via Hawthorn Applied Technology Ltd. The modified zeolite tested is sold under the name 'Hydrocult F'. The pumice sample was supplied by Italpumice SpA via Granite Products Ltd, Jersey and was quarried from the island of Lipari, which lies 35 km off the north coast of Sicily.

2.2 Materials and methods: mineralogy

2.2.1 Whole rock X-ray diffraction analysis

X-ray diffraction (XRD) analysis was carried out using a Philips automated PW1700 X-ray diffractometer. Prior to XRD analysis, samples were ground for 10 minutes with a McCrone micronizing mill. Using the powdered samples obtained, randomly-oriented mounts were prepared by back-loading into standard aluminium sample holders. Instrumental conditions were as follows: CoKa tube at 45 kV voltage and 40 mA current, 3-50° 2 θ angular range and 0.9° 2 θ per minute scan speed. Qualitative mineralogy was determined by conventional Hanawalt search procedures and also by reference to a Joint Committee on Powder Diffractions Standards (JCPDS) database of standard mineral patterns.

2.2.2 < 2 μ m fraction XRD analysis: pumice

Clay minerals were extracted from the pumice sample by separation of a < 2 μ m fraction by sedimentation/decantation procedure carried out in accordance with Stokes' Law (Moore and Reynolds, 1989). An orientated clay mineral mount was then prepared by filtration of 80 mg of the < 2 μ m fraction onto a porous ceramic disc. The orientated mount was analysed using a Philips automated PW1700 X-ray diffractometer over an angular range of 1.5 to 35° 2 θ under conditions identical to those stated above in 2.2.1. The oriented mount was analysed by XRD both in an air-dried state and after glycol-solvation. Separation and clay mineral identification was carried out by reference to Moore and Reynolds (1989).

2.2.3 Thermal analysis: natural zeolite

Clinoptilolite content was measured using an adaptation of the method of de'Gennaro and Colella (1989), which is based on the unusual reversible dehydration/rehydration behaviour of zeolite minerals. Initially, a 100 mg sample was heated at 450°C for 2 hours to dehydrate all mineral phases present. After heating, samples were allowed to cool to ambient temperature and then left for 16 hours in a 300 ml min⁻¹ flow of nitrogen at 40%

relative humidity (equivalent to 12.72 mbar water vapour at 25°C) produced by an ADC Ltd Type WG 600 water vapour generator. The purpose of this was to rehydrate only the clinoptilolite constituent of the sample.

The zeolitic water content of the sample was then determined by thermogravimetric analysis (TGA) using a Stanton Redcroft TG770 microthermobalance. A 10 mg sample was heated at 20°C minute⁻¹ in an inert nitrogen gas flowing at 25-30 ml minute⁻¹. Chart recorder full-scale deflection was set at 20% and chart recorder speed of 2 mm minute⁻¹ was used throughout.

2.3 Materials and methods: petrography

Back-scattered scanning electron microscopy (BSEM) of resin-impregnated polished thin sections was performed using a Cambridge Instruments S250 scanning electron microscope fitted with a KE Developments solid-state four quadrant backscatter detector. A Link Systems 860 Mark 1 energy dispersive X-ray microanalysis system (EDXA) was used for qualitative chemical analyses. In addition, a rock chip specimen of the Beli Plast clinoptilolite was mounted on an aluminium stub and coated with a 25 nm thick layer of conductive carbon in an Emitech Vacuum Evaporation Carbon Coater. This rock chip was examined on the Cambridge Instruments S250 scanning electron microscope using the secondary-electron mode.

2.4 Materials and methods: chemistry

2.4.1 Major element X-ray fluorescence analysis

The BGS X-ray fluorescence (XRF) facility was equipped with three sequential, fully-automatic wavelength-dispersive X-ray fluorescence spectrometers, each fitted with automatic sample changers. Two spectrometers (Philips PW2400) were fitted with 60 kV generators and 3 kW rhodium end-window X-ray tubes. A third (Philips PW1480) was fitted with a 100 kV generator and a 3 kW tungsten side-window X-ray tube. These

spectrometers were computer-operated using software applications supplied by the manufacturer.

A 5 g sample was dried for 24 hours at 105°C. Loss on ignition (LOI) was calculated from the weight loss of 1 g of sample heated at approximately 1050°C for 1 hour. Fused glass beads were prepared by fusing 0.9 g of sample with 9 g of dried lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$) flux at approximately 1200°C in a large muffle furnace. The melt was poured into a platinum casting dish. Lithium iodide (LiI) was added to all samples before fusion to act as a releasing agent.

Analyte channels were calibrated from international and in-house standard reference materials. All standards and unknowns were prepared as fused glass beads. All backgrounds and peaks were drift corrected using an external ratio monitor. Fourteen major elements were calibrated as oxides (Na_2O , MgO , Al_2O_3 , SiO_2 , P_2O_5 , K_2O , CaO , TiO_2 , Mn_3O_4 , total Fe_2O_3 , Cr_2O_3 , SrO , ZrO_2 and BaO) using a standard Philips calibration algorithm and theoretically-generated alpha coefficient corrections. LOI represents the loss of volatiles from the samples due to reactions such as carbonate decomposition, sulphide oxidation and the loss of moisture and structural water. Detection limits for major elements have not been specified but a lower reporting limit of 0.01% was applied to all of the above oxides.

2.4.2 Cation exchange capacity: pumice

Cation exchange capacity (CEC) values were measured using a modified version of the method of Avery and Bascomb (1982), which uses barium as an index ion.

2.4.3 Cation exchange capacity and exchangeable cation content: natural zeolite

Exchangeable cation content was measured using an adaptation of the standard ammonium acetate saturation (AMAS) method.

CEC determinations carried out on natural zeolites using this procedure were discussed by Lieu *et al.* (1988) and more recently by Kitsopoulos (1997). One hundred ml of 1 N ammonium acetate solution (pH 7) was added to 1 g of sample in a 250 ml centrifuge bottle and shaken on a reciprocal shaker. For each sample, two leachate solutions were prepared in this manner using different contact times (1.5 hours and 24 hours).

Theoretically, due to preferred selectivity, ammonium from the leach solution is taken up on exchange sites within the natural zeolite mineral, displacing exchangeable cations into solution. Classically, for measurement of total CEC, the NH_4 -saturated sample is either: boiled in acid and displaced ammonia measured by back-titration; or shaken with NaOH (or NaCl) solution and displaced ammonia measured using an ion-specific electrode. However, rather than analysing the amount of ammonium taken up by the sample, the BGS method instead measured the equivalent quantity of exchangeable cations (K, Na, Mg and Ca) released into solution. A total CEC value was then derived from the sum of individual cation concentrations.

Leachate solutions were analysed by inductively coupled plasma atomic emission analysis (ICP-AES), a multi-elemental technique in which emission intensities of sample solutions are measured against calibration standards. Spectral interferences and instrumental drift were corrected by software routines. Control samples were included in each batch of samples analysed in order to monitor data quality. All cation concentrations reported were corrected back to the solid. Operating conditions were as given in Table 2.1.

Table 2.1 Operating conditions for analysis of leachate solutions by ICP-AES

Equipment	Operating conditions
Spectrometer	Fisons / ARL 3580 Quantovac
Spectrometer	Dual 1 m Paschen Runge with purged light path
Spectrometer	45 fixed channels
Spray chamber	Conical 45 ml minimum volume with impact bead
Nebuliser	Meinhardt glass concentric, TR- 30-K
Torch	Quartz mini torch
Autosampler	ARL plasma autosampler
RF power	650 W
RF frequency	27.12 MHz
Viewing height	9mm above the coil
Coolant gas	7.5 l min ⁻¹
Plasma gas	0.8 l min ⁻¹
Carrier gas	0.8 l min ⁻¹
Solution uptake	2.0 ml min ⁻¹
Pump	Gilson Minipuls 3

2.4.4 Electron probe micro-analysis (EPMA): natural zeolite

Microchemical analyses were completed on polished thin sections using a Cambridge Instruments Microscan 5 electron microprobe fitted with an Oxford Instruments An 10000 energy-dispersive X-ray analyser (EDXA). This instrument is capable of detecting all elements with an atomic number higher than 11 (i.e. sodium and above) at detection limits of circa 0.1 weight % element. In each "spot" analysis, a volume of approximately 3µm diameter was analysed.

2.5 Materials and methods: physical properties

2.5.1 Particle-size analysis

A portion of each sample was dry-screened on a nest of 30 cm diameter metal sieves using a Fritsch Analysette automatic sieve-shaker. For the pumice sample, a British Standard (BS) aggregate series of 14, 10, 5, 2.36, 1.18, 0.6, 0.3, 0.15 and 0.075 mm aperture sieves were used. A set of 2, 1, 0.5, 0.25, 0.125 and 0.063 mm aperture sieves were used for analysis of the two natural zeolites. Particle-size was calculated both as a frequency distribution (i.e. mass % retained between each sieve aperture) and as a cumulative distribution (i.e. mass % finer than each sieve aperture).

2.5.2 Specific gravity (density of the solid phase)

Specific gravity (SG) was determined by using a standard water pycnometry method. A portion of ground powder was placed in a previously weighed 25 cm³ pycnometer bottle, weighed again and then thoroughly wetted with deionized water in an ultrasonic bath. After ensuring no air bubbles were entrapped, deionized water was added up to the 25 cm³ level and the pycnometer bottle was weighed again. The pycnometer bottle was also weighed when filled with deionized water only. SG was calculated as follows:

$$SG = (B-A) / [(B+D)-(A+C)] \text{ where}$$

A = weight of pycnometer bottle;

B = weight of pycnometer bottle + dry powder;

C = weight of pycnometer bottle + wetted powder + deionized water; and

D = weight of pycnometer bottle + deionized water only.

2.5.3 Bulk density (density of the solid phase and voids)

Bulk density in kg m⁻³ was determined by adding a known weight of sample to a graduated measuring cylinder and recording the volume obtained. Both unsettled and settled values were determined.

2.5.4 Relative density: pumice

Relative density (g cm^{-3}) was determined in accordance with BS812: 1975.

2.5.5 Water absorption: pumice

Water absorption (weight %) was determined in accordance with BS812: 1975.

2.5.6 Surface area: natural zeolite

Specific surface area was measured with a Micromeritics Flowsorb 2300 II surface area analyser using the single-point BET procedure. In this method, the quantity of nitrogen required to form a monomolecular layer on the surface of the sample is measured. Prior to analysis, dehydration of the sample ("outgassing") was carried out in a vacuum oven set at 400°C for 16 hours. Previously, outgassing temperatures in the range 300-480°C have been used by other workers (Yucel and Culfaz, 1988, Barrer, 1978 and Ma and Lee, 1978) for gas adsorption experiments on natural zeolites.

2.6 Results and discussion: natural zeolite from Beli Plast, Bulgaria

2.6.1 Mineralogy

2.6.1.1 Whole-rock XRD analysis

The XRD profiles of the natural sample and modified sample are almost identical (Figures 2.1 and 2.2, respectively). Clinoptilolite predominates with subordinate cristobalite and quartz. Figure 2.3 illustrates the very close match between JCPDS pattern 25-1349 for clinoptilolite and the XRD pattern of the natural sample. Trace mica was also tentatively identified in the natural sample. Generally, XRD analyses confirm that both samples are high-grade natural zeolites (Table 2.2).

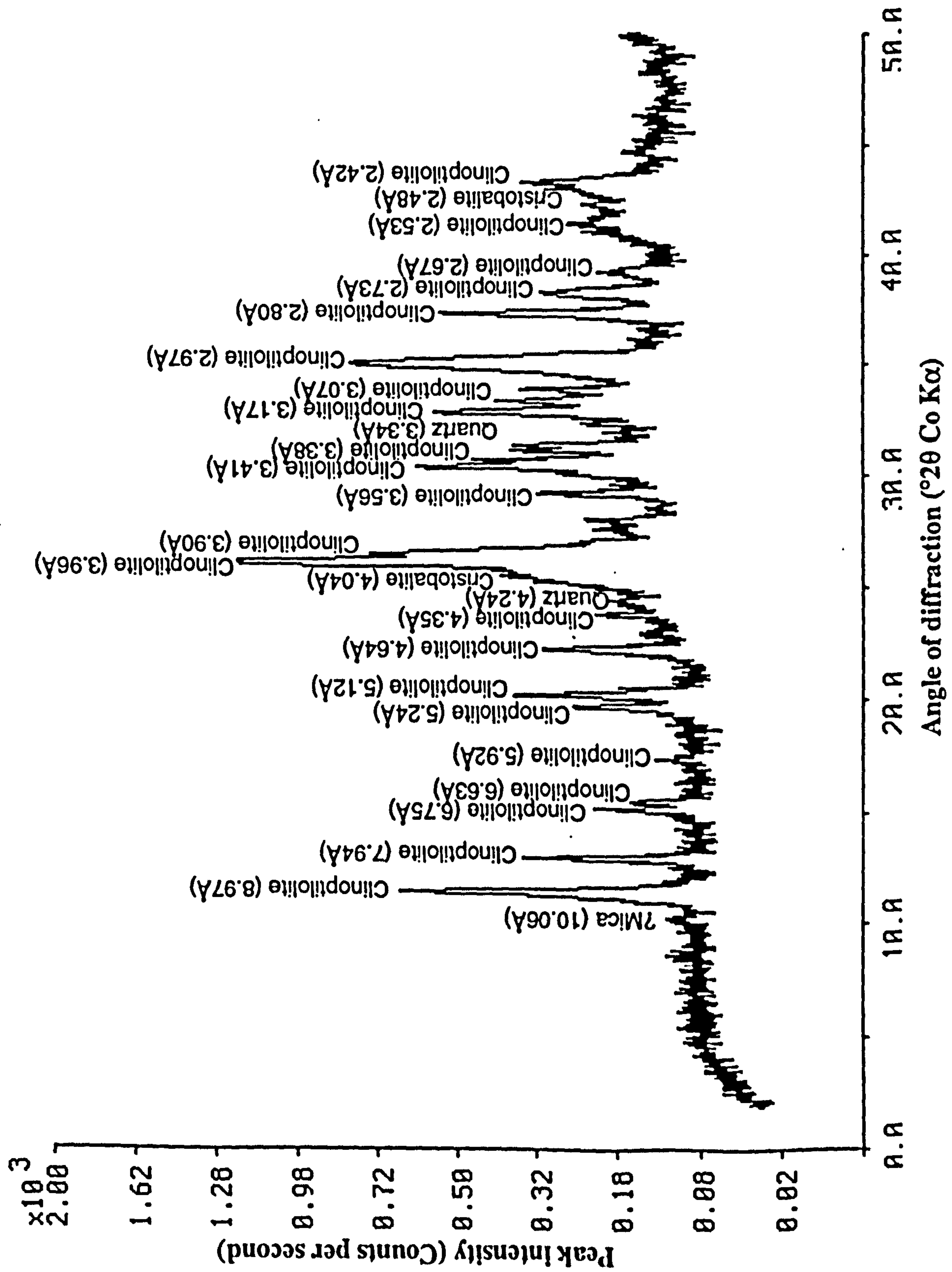


Figure 2.1. Annotated X-ray diffraction (XRD) profile of the natural sample from the Beli Plast natural zeolite deposit, Bulgaria.

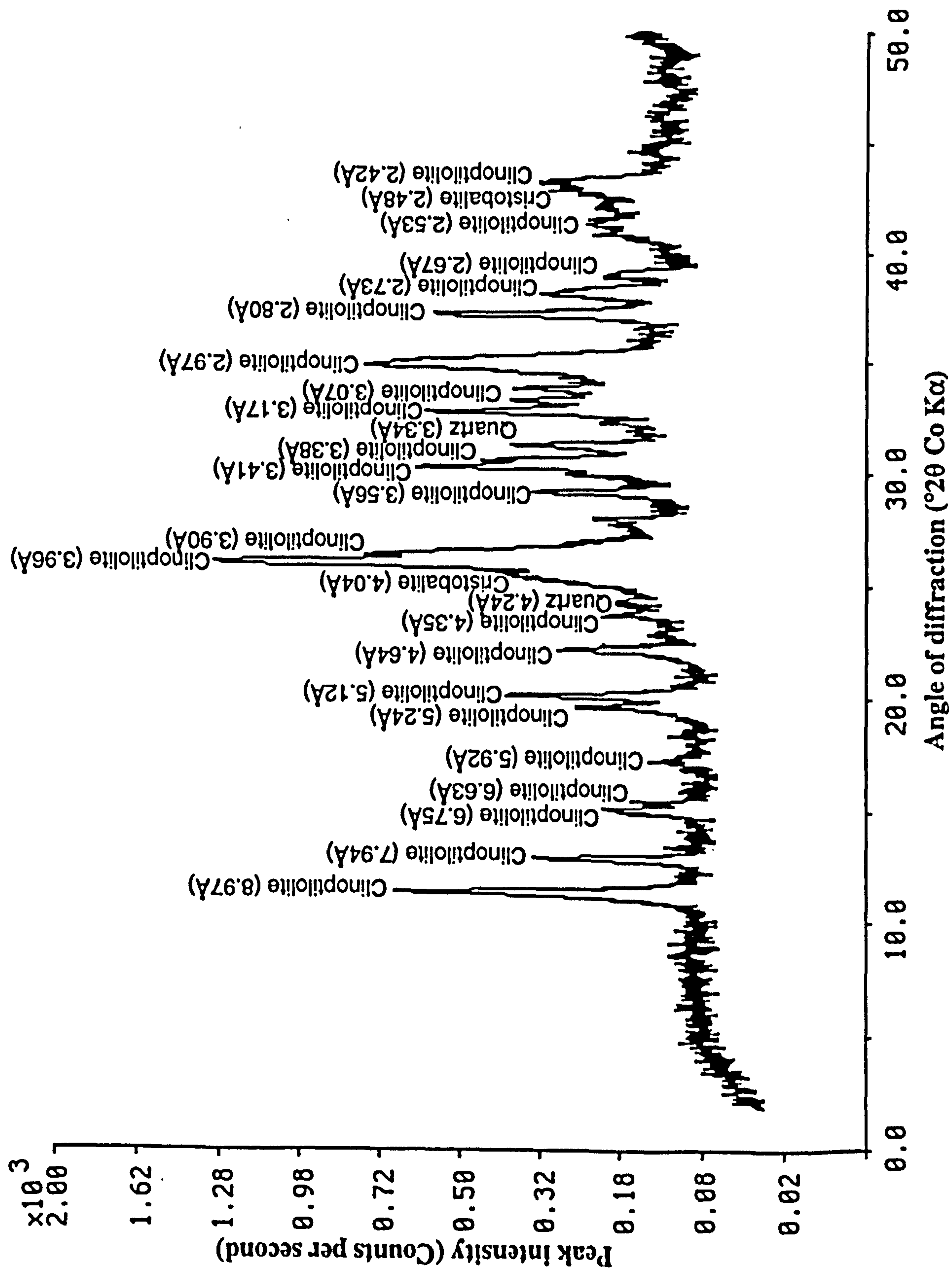


Figure 2.2. Annotated X-ray diffraction (XRD) profile of the modified sample from the Beli Plast natural zeolite deposits, Bulgaria.

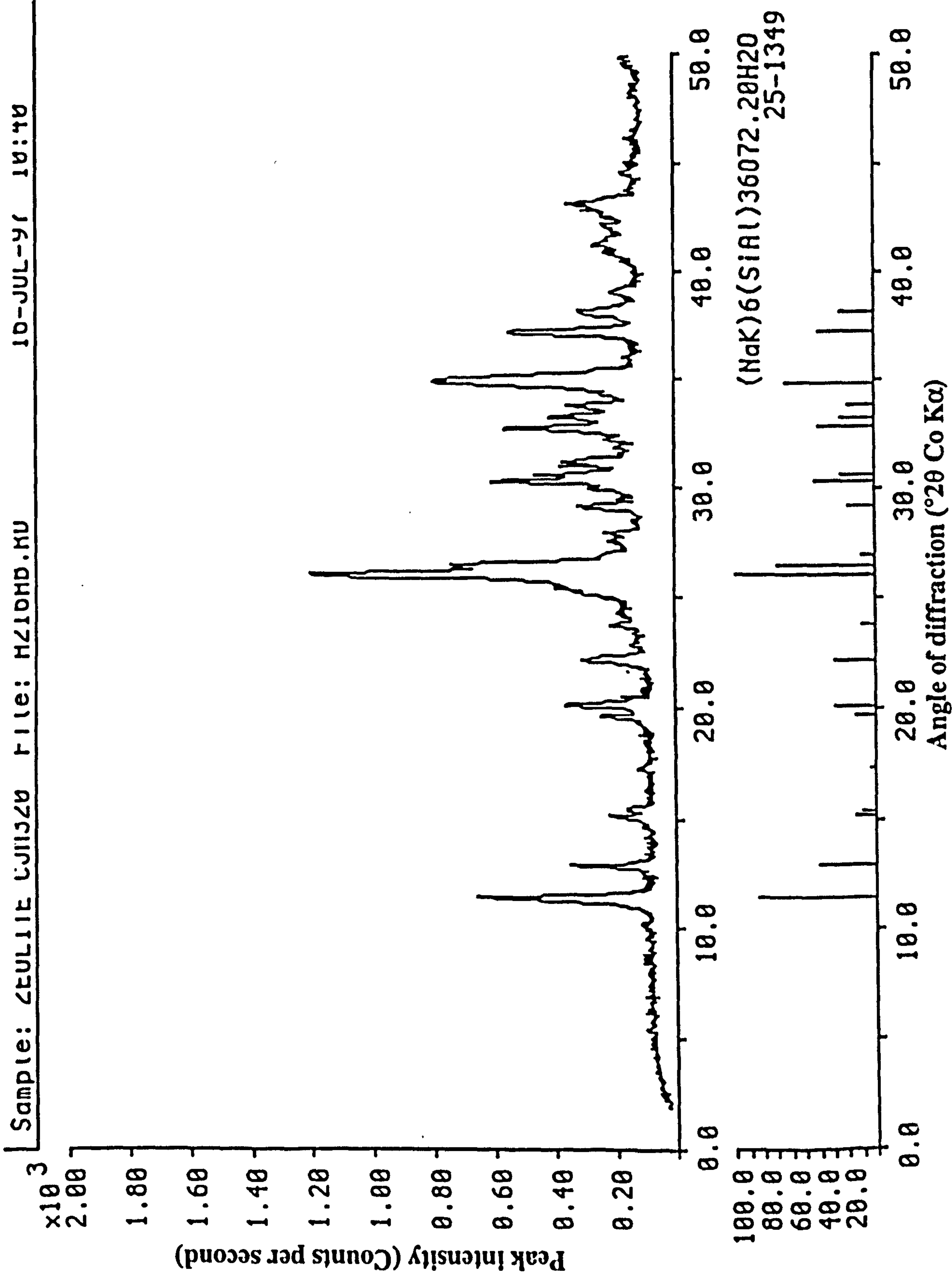


Figure 2.3. X-ray diffraction (XRD) profile of the natural sample from the Beli Plast natural zeolite deposit, Bulgaria, in comparison to the Joint Committee on Powder Diffraction Standards (JCPDS) standard "stick" pattern 25-1349 for clinoptilolite.

Table 2.2 Summary of XRD analyses: mineral contents of natural and modified samples from the Beli Plast natural zeolite deposit, Bulgaria. The minerals are listed in approximate order of concentration

Sample	Major phases	Minor phases	Trace phases
Natural	Clinoptilolite	Cristobalite, quartz	Mica
Modified	Clinoptilolite	Cristobalite, quartz	

Cinoptilolite, example	JCPDS 25-1349 (Na, K) ₆ (Si, Al) ₃₆ O ₇₂ .20H ₂ O
Cristobalite, example	JCPDS 11-695 SiO ₂
Quartz, example	JCPDS 33-1161 SiO ₂
Mica	Undifferentiated

The JCPDS 25-1349 has been superseded by pattern JCPDS 39-1383 (Gottardi and Galli, 1985).

The Zeoproducts Ltd catalogue (Anon, 1997b) indicates that montmorillonite, celadonite, cristobalite, calcite, quartz and feldspar are common minor mineral constituents found in the Beli Plast natural zeolite deposit.

Discrete apatite was not detected by XRD, as it was present at below detection limits.

2.6.1.2 Thermal analysis

Using the thermal analysis method of de’Gennaro and Colella (1989), clinoptilolite content of the natural sample was estimated at 84% and the clinoptilolite content of the modified sample was estimated at 87% (Tables 2.3 and 2.4). This is consistent with the high-grade indicated by XRD analysis. A zeolite grade of 84-87% is also comparable to that of other commercially available clinoptilolites.

Table 2.3. Clinoptilolite content of commercially available zeolites

Commercial product	Clinoptilolite %
St Clouds Mining Company, New Mexico, USA	80-85
American Resource Corporation	90 +/- 5
RBZ, Geoproduct KFT, Hungary	50

Table 2.4 Estimated clinoptilolite content of the natural and modified samples from the Beli Plast natural zeolite deposit, as calculated from thermogravimetric analysis (TGA) measurements of zeolitic water content

(A) Sample	(B) Zeolitic water (%)	(C) Clinoptilolite (%)
(1) Natural sample	12.0	84
(2) Natural sample repeat	12.0	84
(3) Natural sample av	12.0	84
(1) Modified sample	12.5	88
(2) Modified sample rpt	12.3	86
(3) Modified sample av	12.4	87

The clinoptilolite % was calculated on the basis of the $(K_{1.9} Ca_{1.8} Na_{0.4} Mg_{0.1})Al_{6.1} Si_{29.9} O_{72} \cdot 21.3H_2O$ composition for the Beli Plast clinoptilolite quoted in the Zeoproducts Ltd Catalogue (Anon, 1997b).

2.6.2 Chemistry

2.6.2.1 Major element X-ray fluorescence (XRF) analysis

For both the natural and modified samples, in terms of major element composition, the oxides SiO_2 and Al_2O_3 predominated with appreciable K_2O and CaO also present (Table

2.5). The modified sample was also rich in phosphate (0.42% P_2O_5). This is consistent with the statement that Hydrocult F is loaded with phosphate (apatite)(0.25% P_2O_5).

In comparison to chemical data for stratigraphic zones I, II, III and IV of the Beli Plast deposit, as delineated by Aleksiev (1995), both samples correspond most closely with zone III, on the basis of K_2O , CaO and MgO values (Table 2.5).

2.6.2.2 Cation exchange capacity and exchangeable cation content: natural zeolite

Exchangeable cation results are given in Table 2.7. In both samples, exchangeable K predominated with subordinate Ca and Na and only minor Mg. In general, altering contact time from 1.5 hours to 24 hours resulted in an increase in total CEC of between 11.5-16.4 %. In terms of individual cations, increasing contact time resulted in: a reduced quantity of exchangeable K released to solution; and, conversely, increased exchangeable Na, Mg and Ca in solution. This indicated that exchangeable K initially released into solution may subsequently be resorbed, at least partially, on exchange sites within the clinoptilolite lattice as equilibrium is approached. Other researchers have observed a similar re-exchange of monovalent cations at equilibrium (example: Zanetti and Gunter, 1997). This behaviour has been explained by differences in the diffusion coefficients of individual cations (Yang et al, 1997). Typically, hydrated monovalent cations diffuse rapidly into solution but are subsequently resorbed on exchange sites at equilibrium, reflecting the ultimate selectivity of the zeolite.

Total CEC values obtained here (132.0-158.3 meq $100g^{-1}$) were close to the levels reported in the Zeoproducts Ltd. catalogue (Anon, 1997b)(160 meq $100g^{-1}$) and also CEC values reported for other commercial clinoptilolites (Table 2.6).

Table 2.5	Major element chemical composition of natural and modified zeolites from Beli Plast, Bulgaria.																		
	Chemical data for zones I-IV of the Beli Plast from Aleksiev (1995) are																		
	included for comparison.																		
Zone																			
Sample	Natural	Modified	A	B	A	B	C	D	A	B	C	A	B	C	A	B	C		
% Oxide																			
SiO2	67.69	66.82	64.82	65.19	66.79	64.92	66.41	66.23	65.48	65.97	66.39	65.86	67.40	65.61					
TiO2	0.12	0.12	0.13	0.11	0.11	0.11	0.16	0.15	0.13	0.10	0.12	0.12	0.16	0.15					
Al2O3	11.46	11.28	11.54	11.26	10.51	11.41	11.09	11.15	10.72	10.62	10.83	11.37	11.47	12.20					
Fe2O3	0.78	0.77	0.96	0.93	0.71	0.93	0.81	0.54	0.95	1.22	1.19	0.75	0.78	1.24					
CaO	2.92	3.11	3.33	3.88	3.40	3.73	3.67	3.66	3.94	3.81	2.64	2.46	1.86	2.80					
Mn3O4	0.10	0.07	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A					
MgO	0.64	0.66	1.69	0.79	1.05	0.83	0.92	0.68	0.60	0.47	0.60	0.25	0.28	0.66					
Na2O	0.76	0.75	0.53	0.2	0.20	0.25	0.26	0.25	0.53	0.20	1.01	1.00	0.98	1.21					
K2O	3.36	3.35	1.36	2.53	1.90	2.91	2.32	2.27	3.11	3.24	4.56	5.35	5.96	5.58					
P2O5	0.01	0.42	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A					
Cr2O3	0.00	0.00	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A					
SrO	0.04	0.04	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A					
ZrO2	0.01	0.01	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A					
BaO	0.01	0.01	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A					
LOI	11.58	12.10	15.35	14.6	14.94	14.6	14.28	14.66	14.85	13.93	12.67	12.44	11.48	10.58					
Total	99.48	99.51	99.71	99.44	99.61	99.69	99.92	99.59	100.31	99.56	100.01	99.60	100.32	100.03					

Table 2.6 CEC values of commercially available zeolites

Commercial clinoptilolite	CEC (meq / 100 g)
St Clouds Mining Company, New Mexico, USA	185-220
American Resource Corporation	185
Escott Z3, Victoria, Australia	119
MSC, Geoproduct KFT, Hungary	150.4
RBZ, Geoproduct, KFT, Hungary	164.1

Table 2.7 Extractable cation analysis for the natural and modified samples from the Beli Plast natural zeolite deposit, Bulgaria: (1) results for 1.5 hour contact time with ammonium acetate leach solution; (2) results for 24 hour contact time with ammonium acetate leach solution. Exchangeable cation concentration is expressed both on a milliequivalents per 100 g (meq 100g⁻¹) and mg l⁻¹ basis

Sample	Na	Ca	Mg	K	Total CEC (meq 100g ⁻¹)
(1) 15 min:					
Natural meq 100g ⁻¹	16.3	31.5	1.1	50.6	99.4
Natural mg l ⁻¹	3,744	12,617	255	19,771	
Modified meq 100g ⁻¹	12.7	33.8	1.2	49.5	97.1
Modified mg l ⁻¹	2,917	13,534	287	19,344	
(2) 24 hr:					
Natural meq 100g ⁻¹	17.4	38.2	2.8	47.7	106.2
Natural mg l ⁻¹	4,003	15,299	692	18,661	
Modified meq 100g ⁻¹	18.2	40.2	3.1	49.0	110.5
Modified mg l ⁻¹	4,194	16,093	753	19,164	
Beli Plast mg l ⁻¹	5,900	28,000	5,600	28,600	160

2.6.2.3 Electron probe micro-analysis (EPMA)

Results of EPMA determinations of clinoptilolite replacing the rims/cores of vitric shards and within the rock matrix are listed in Table 2.8. Clinoptilolite was identified on the basis of Gottardi and Galli's (1985) criteria for distinguishing clinoptilolite from heulandite, i.e. Si/Al ratio >4 and $\text{Na}+\text{K} > \text{Ca}$. The presence of clinoptilolite was also corroborated using the Mumpton (1960) test, i.e. the crystal structure was not destroyed by 16 hours heating at 450°C . Although, within limits, clinoptilolite composition does vary, there was no evidence of any systematic chemical zonation. Several chemical analyses of other minor mineral phases present including feldspar (grains of K-feldspar, plagioclase and alkali-rich composition) and mica (biotite composition) are also reported in Table 2.9.

The following clinoptilolite formula was calculated on an anhydrous 72 oxygen basis from an average of the data in Table 2.8: $(\text{K}_{1.6} \text{Ca}_{1.6} \text{Na}_{0.6} \text{Mg}_{0.3})\text{Al}_{6.4} \text{Si}_{29.7} \text{O}_{72}$. This corresponds closely to the $(\text{K}_{1.9} \text{Ca}_{1.8} \text{Na}_{0.4} \text{Mg}_{0.1})\text{Al}_{6.1} \text{Si}_{29.9} \text{O}_{72} \cdot 21\text{H}_2\text{O}$ formula quoted for the Beli Plast deposit in the Zeoproducts Ltd catalogue (Anon, 1997b). The average of the BGS analyses of the Beli Plast clinoptilolite are listed against the composition of other known occurrences of clinoptilolite in Table 2.10. In comparison to the other sedimentary types reported by Gottardi and Galli (1985) (i.e. columns 13, 14 and 15 data), Beli Plast clinoptilolite is anomalously Ca-rich and Na-poor. This is particularly important in terms of the suitability of the clinoptilolite for use as a plant growth substrate as a high sodium content would cause plant growth problems.

2.6.3 Petrography

The sample was an highly-altered vitric ash tuff, in which altered vitric shards predominated. The morphology of these shards varied from regular, elongate, blade-like clasts to irregular "horn-shaped" clasts bounded by concave arcuate surfaces (Plates 2.1 and 2.2). Particle-size was between 0.1-2 mm and shards were moderately- to well-sorted. In addition, a uniform distribution of medium sand-to silt-size minor crystal clasts (K-feldspar,

Table 2.8 Electron microprobe analyses of clinoptilolite replacing vitric shards (core and rim) and within the matrix in a natural zeolite from Beli Plast, Bulgaria																
Analysis No	2		4		9		3		5		10		11		12 Average	
% Oxide	Core		Core		Core		Rim		Rim		Rim		Matrix		Matrix	
SiO2	53.31		56.72		66.37		58.42		65.20		64.21		67.28		57.29	61.10
TiO2	0.00		0.00		0.00		0.00		0.00		0.00		0.00		0.28	0.04
Al2O3	10.54		10.78		12.38		10.56		11.43		11.29		11.85		9.90	11.09
FeO	0.00		0.00		0.00		0.00		0.00		0.00		0.00		0.00	0.00
MnO	0.00		0.00		0.00		0.00		0.00		0.00		0.00		0.00	0.00
MgO	0.37		0.30		0.41		0.29		0.27		0.43		0.37		0.38	0.35
CaO	3.16		3.16		3.78		2.88		3.07		2.87		3.19		2.81	3.12
Na2O	0.61		0.43		0.43		0.61		0.73		0.76		0.69		0.44	0.59
K2O	2.23		2.06		2.72		2.37		2.80		2.83		2.81		2.28	2.51
Total	70.20		73.44		86.08		75.12		83.51		82.38		86.19		73.38	78.79
% Element																
Si	29.26		29.58		29.60		29.80		29.94		29.90		29.91		29.90	29.74
Ti	0.00		0.00		0.00		0.00		0.00		0.00		0.00		0.11	0.01
Al	6.82		6.63		6.51		6.35		6.19		6.19		6.21		6.09	6.37
Cr	0.00		0.00		0.00		0.00		0.00		0.00		0.00		0.00	0.00
Fe	0.00		0.00		0.00		0.00		0.00		0.00		0.00		0.00	0.00
Mn	0.00		0.00		0.00		0.00		0.00		0.00		0.00		0.00	0.00
Mg	0.30		0.23		0.27		0.22		0.19		0.30		0.24		0.29	0.26
Ca	1.86		1.76		1.81		1.57		1.51		1.43		1.52		1.57	1.63
Na	0.65		0.44		0.37		0.60		0.65		0.69		0.59		0.45	0.55
K	1.56		1.37		1.55		1.54		1.64		1.68		1.60		1.52	1.56
No of oxygen basis	72.00		72.00		72.00		72.00		72.00		72.00		72.00		72.00	72.00
Si/Al	4.29		4.46		4.55		4.69		4.84		4.83		4.82		4.91	4.67

Table 2.9 Electron microprobe analyses of crystal clasts in a natural zeolite from Beli Plast, Bulgaria									
Analysis No	6	7	13	8					
% Oxide	K-feldspar	Plagioclase feldspar	Alkali-rich feldspar	Biotite					
SiO ₂	67.16	65.18	67.41	36.86					
TiO ₂	0.00	0.00	0.00	4.39					
Al ₂ O ₃	18.54	21.67	21.02	13.89					
FeO	0.00	0.00	0.44	16.73					
MnO	0.00	0.00	0.00	0.76					
MgO	0.00	0.00	0.00	12.77					
CaO	0.41	3.06	2.21	0.00					
Na ₂ O	5.17	10.22	9.74	0.53					
K ₂ O	9.21	0.00	2.00	8.76					
Total	100.48	100.13	102.82	94.69					
% Element									
Si	9.03	8.60	9.86	27.44					
Ti	0.00	0.00	0.00	0.50					
Al	2.94	3.37	2.21	2.49					
Cr	0.00	0.00	0.00	0.00					
Fe	0.00	0.00	0.00	2.13					
Mn	0.00	0.00	0.00	0.10					
Mg	0.00	0.00	0.08	2.89					
Ca	0.06	0.43	0.59	0.00					
Na	1.35	2.61	0.15	0.16					
K	1.58	0.02	0.46	1.70					
No of oxygen basis	24.00	24.00	24.00	22.00					

Table 2.10 Chemical analyses (top) and formulae (bottom) for natural zeolite from Beli Plast, Bulgaria in comparison to other data for clinoptilolite (columns 10-19) from Gottardi and Galli (1985)																
% Oxide	Bulk XRF	Average	Beli Plast	10	11	12	13	14	N/A : Not Available			15	16	17	18	19
		probe	*													
SiO2	67.69	61.1	65.85	54.58	65.17	61.14	61.77	64.70	72.40	69.93	62.29				64.00	66.40
TiO2	0.12	0.04	N/A	N/A	0.16	N/A	0.41	N/A	N/A	N/A	N/A				N/A	N/A
Al2O3	11.46	11.09	10.93	15.86	13.38	14.52	13.26	12.43	13.17	11.89	13.81				12.50	11.17
Fe2O3	0.78	0.00	1.61	1.55	1.06	N/A	0.59	0.44	0.20	0.02	0.75				N/A	0.57
MnO	0.10	0.00	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A				N/A	N/A
MgO	0.64	0.35	1.06	0.90	0.53	0.28	0.51	0.34	0.64	0.47	0.14				0.25	0.17
CaO	2.92	3.12	2.91	3.16	3.22	3.60	0.89	1.26	0.24	1.07	2.65				3.89	1.94
SrO	0.04	N/A	N/A	2.00	N/A	N/A	0.03	N/A	N/A	N/A	0.50				N/A	N/A
BaO	0.01	N/A	N/A	0.60	N/A	N/A	0.10	0.53	N/A	N/A	0.33				N/A	N/A
Na2O	0.76	0.59	0.80	1.01	1.62	4.48	4.19	4.32	2.92	2.96	3.58				1.99	2.27
K2O	3.36	2.51	3.37	3.90	2.82	0.94	4.04	2.28	4.93	3.47	1.68				1.81	3.58
H2O	11.58	N/A	13.24	15.99	11.43	14.16	14.78	13.56	N/A	N/A	14.20				15.56	13.31
Total	99.48	78.79	N/A	99.55	99.39	99.12	100.57	99.86	N/A	N/A	99.93				100.00	99.41
% Element																
Si		29.74	29.90	26.48	28.78	28.00	28.50	29.18	29.17	30.02	28.42				29.20	29.88
Ti		0.01	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A				N/A	N/A
Al		6.37	6.10	9.08	6.96	7.84	7.21	6.61	6.37	6.01	7.43				6.72	5.93
Fe		0.00	N/A	0.56	N/A	N/A	0.20	0.15	0.06	N/A	0.26				N/A	0.19
Mg		0.26	0.1	0.64	0.35	0.19	0.35	0.23	0.39	0.30	0.09				0.17	0.11
Ca		1.63	1.80	1.64	1.52	1.77	0.44	0.61	0.11	0.49	1.29				1.90	0.94
Sr		N/A	N/A	0.56	N/A	N/A	0.01	N/A	N/A	N/A	0.13				N/A	N/A
Ba		N/A	N/A	0.12	N/A	N/A	0.02	0.09	N/A	N/A	0.06				N/A	N/A
Na		0.55	0.4	0.96	1.39	3.98	3.75	3.78	2.32	2.45	3.17				1.76	1.98
K		1.56	1.90	2.40	1.60	0.55	2.38	1.31	2.58	1.88	0.98				1.05	2.06
H2O		N/A	21.3	25.84	16.84	21.74	22.72	20.40	N/A	N/A	21.60				23.70	19.98
No of oxygen basis		72.00	72.00	72.00	72.00	72.00	72.00	72.00	72.00	72.00	72.00				72.00	72.00
Si/Al		4.67	4.90	2.92	4.14	3.57	3.95	4.41	4.58	5.00	3.83				4.35	5.04
10	Type 1 clinoptilolite, Albero Bassi, Vicenza, Italy.						Hydrothermal origin									
11	Type 2 clinoptilolite, Shizuma, Japan.						Hydrothermal origin									
12	Type 2 clinoptilolite, Challis, Idaho.						Hydrothermal origin									
13	Type 3 clinoptilolite, Waitemata Group, New Zealand.						Sedimentary origin									
14	Type 3 clinoptilolite, San Bernardino County, California.						Sedimentary origin									
15	Type 3 clinoptilolite, deep sea sample.						Sedimentary origin									
16	Type 3 clinoptilolite, Agoura, California.						Hydrothermal origin									
17	Type 3 clinoptilolite, Alp di Siusis, Italy.						Hydrothermal origin									
18	Type 3 clinoptilolite, Kuruma Pass, Japan.						Hydrothermal origin									
19	Holotype of clinoptilolite, Hoodoo Mountains, Wyoming.						Hydrothermal origin									
*	1997 General catalogue, Zeoproducts Ltd. Co.															

quartz and muscovite) was observed. In some instances, muscovite was altered and slightly exfoliated. It was common for feldspar to be partially or completely altered. Rare monazite occurred both as inclusions within feldspar and as discrete crystals. Lithic clasts (vesicular pumice) were infrequent.

Clasts were enclosed by a fine-grained matrix. EDXA of the matrix (Ca, K, Al, Si) was consistent with a predominantly clinoptilolite composition. However, minor clayey (K- and Fe-rich) pockets also occupied part of the pore space. The proportion of matrix varied spatially and both clast-supported and matrix-supported fabrics were apparent. Some alignment of elongate clasts, possibly bedding-parallel, was evident but preferred orientation of more irregular, equant clasts was not noted.

Although relict morphology was preserved, vitric shards were generally highly-altered. Typically, the rim of each shard consisted of a 10-20 μm thick, fine-grained lining. In the centre of each shard, secondary porosity (i.e. void space) was partially infilled by large (10-20 μm size) euhedral, tabular crystals (Plates 2.3 and 2.4). EDXA results for both the fine-textured outer margin of the shards and the coarse crystals within internal voids were very uniform (Ca, K, Al, Si) and consistent with a clinoptilolite composition. Very thin ($<2 \mu\text{m}$) coatings of montmorillonite around the exterior of shards were reported previously by Aleksiev (1995).

Petrographic studies of the Beli Plast natural zeolite deposit completed by Aleksiev (1995) also identified the following constituents:

Table 2.11 Petrographic study of the Beli Plast zeolite deposit (Aleksiev, 1995)

Authigenic phases	Crystal clasts	Lithic clasts
Clinoptilolite	Feldspar (sanidine, orthoclase, andesine, albite)	Pumice
Montmorillonite	Mica (biotite, muscovite, celadonite coatings)	Rhyolite
	Amphibole	Gneiss
	Apatite	Mica schist
	Zircon	
	Rutile	
	Garnet	
	Titanite	
	Tourmaline	

The well-preserved primary texture and the absence of welding, deformation and compaction suggest that the process of alteration, dissolution and cementation occurred soon after deposition. Aleksiev (1995) proposed that the precursor ash was deposited sub-aqueously and that, due to the volume and rapidity of ash accumulation, substantial heat was retained within the system and was responsible for zeolitization of the rock. This is usually referred to as the “geoautoclave” model of zeolite formation.

2.6.4 Physical properties

Results of particle-size analysis (Table 2.12, Figure 2.4) indicated that the grading characteristics of the natural and modified sample were distinctly different: the size of the crushed rock fragments in the modified sample were coarser than those of the natural sample.

Other physical property results are summarised in Table 2.13. Surface area by the single-point BET N₂ adsorption method, for both the natural and modified samples, were relatively high in comparison to other commercial clinoptilolites analysed previously at BGS laboratories. The surface area of circa 40-42 m² g⁻¹ obtained compared to a “specific surface” of 25-42 m² g⁻¹ quoted by the Zeoproducts Ltd catalogue (Anon, 1997b) for micronized clinoptilolite.

The settled and unsettled bulk densities of the natural sample were greater than those of the modified sample. This is likely to be a reflection of the different grading characteristics noted above. The bulk densities obtained for both samples were higher than the specifications listed for the crushed, rounded and spheroidal granular products in the Zeoproducts Ltd catalogue (Anon, 1997b).

2.7 Results and discussion: pumice from Sicily

2.7.1 Mineralogy

2.7.1.1 Whole rock XRD analysis

The pumice was classified as a poorly-ordered volcanic glass (sideromelane), as indicated by the very broad XRD peak at circa 20-40° 2θ (Figure 2.5). Minor quartz (SiO₂) and feldspar (undifferentiated) were also present. Trace pyroxene (undifferentiated) was tentatively identified.

2.7.1.2 < 2 µm fraction XRD analysis

A smectite-group clay mineral was identified from a characteristic 001 basal spacing of 13.53 Å, which expanded to 16.89 Å after glycol-solvation (Figure 2.6).

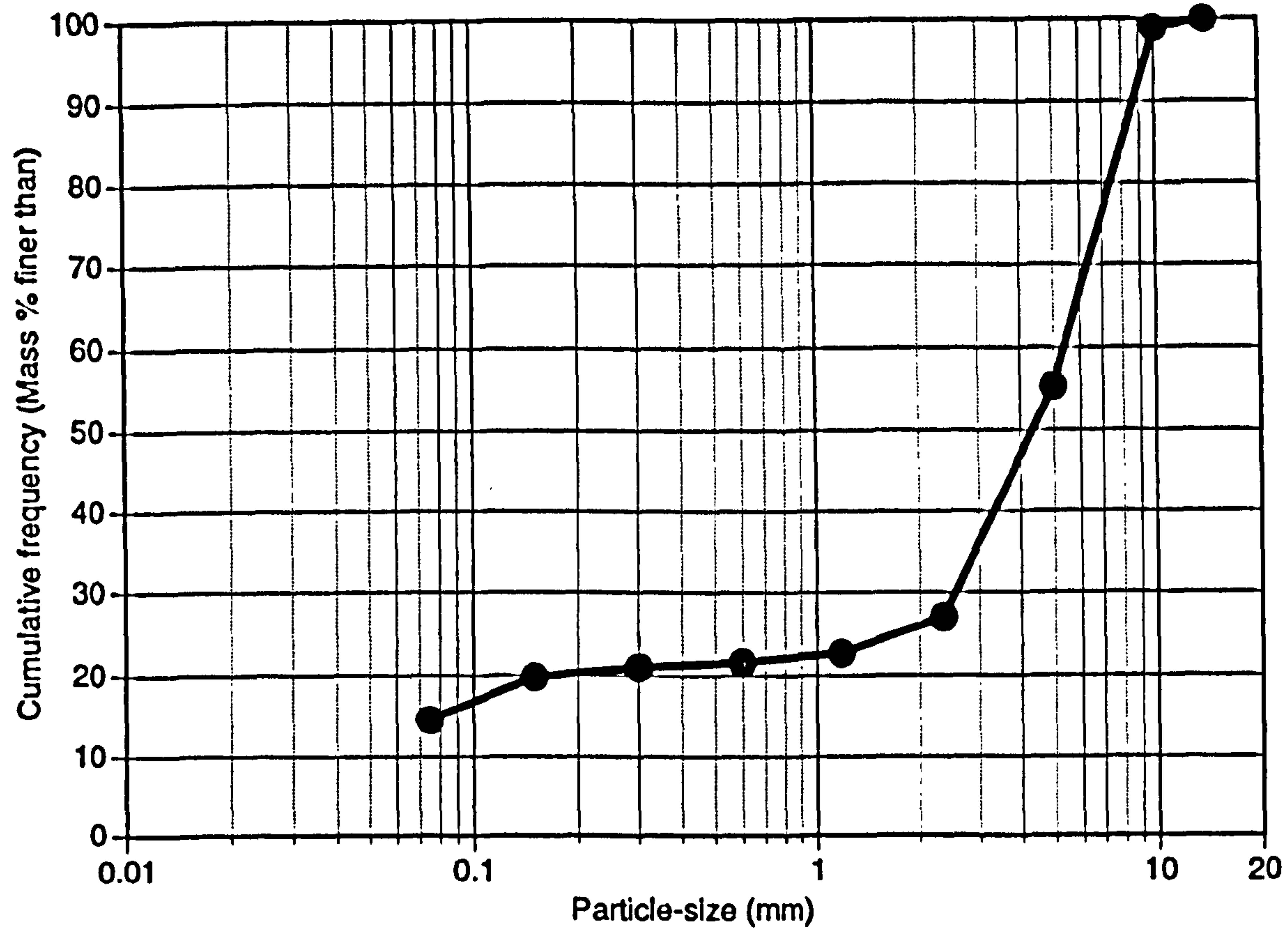


Figure 2.7. Particle-size cumulative frequency distribution for pumice from Sicily.

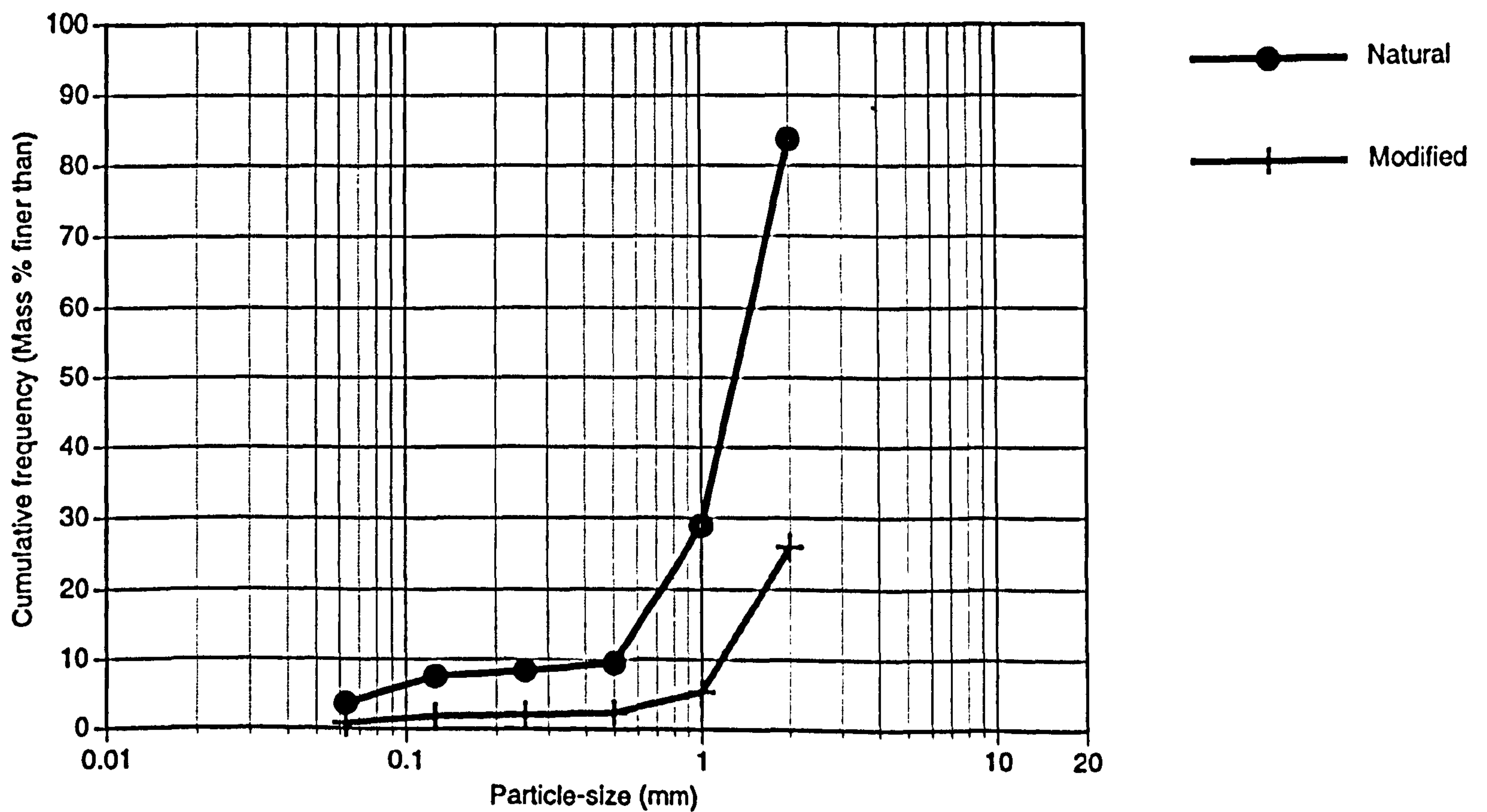


Figure 2.4. Particle-size cumulative frequency distribution of natural and modified samples from Beli Plast natural zeolite deposit, Bulgaria.

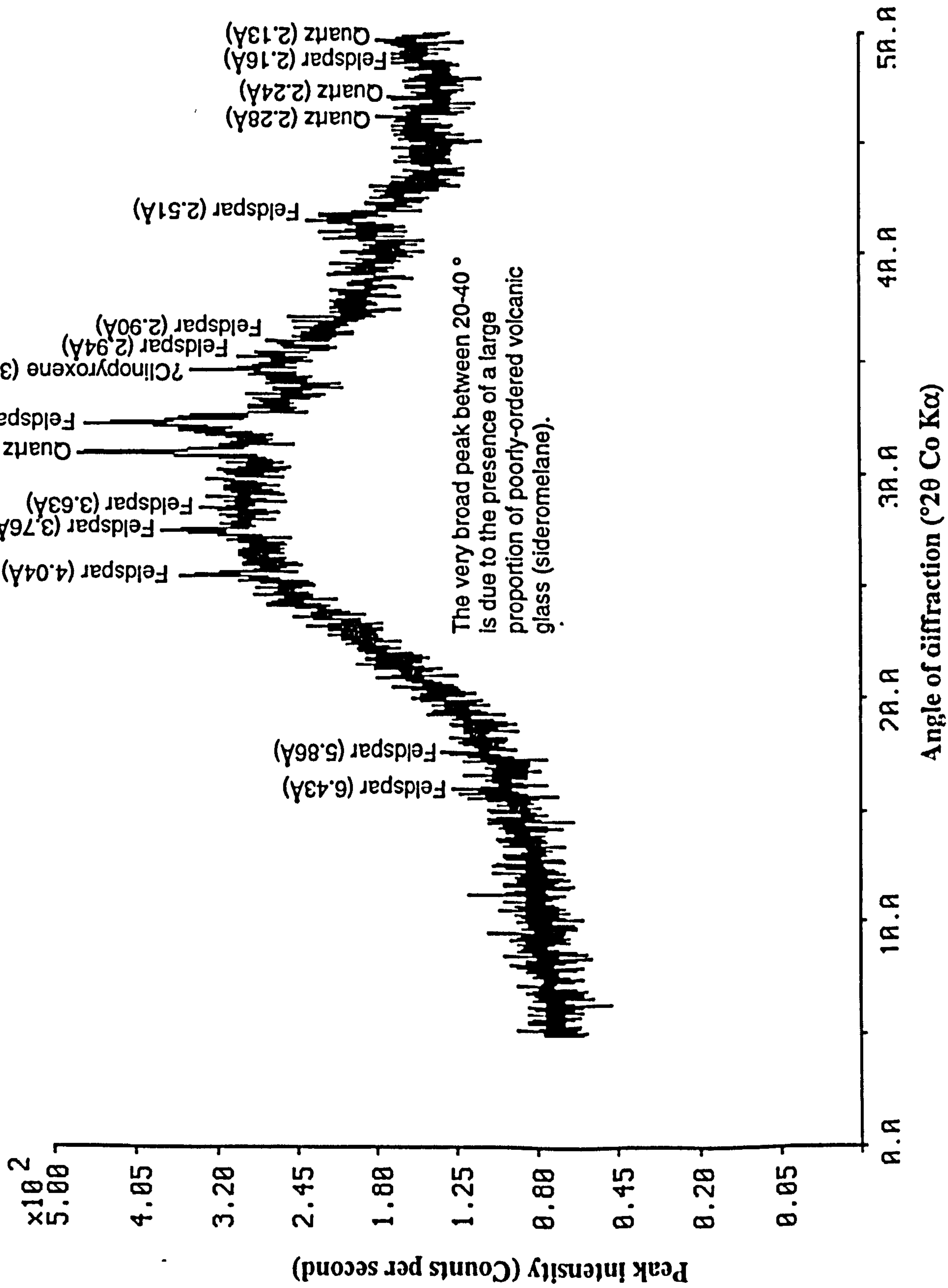


Figure 2.5. Annotated X-ray diffraction (XRD) profile of pumice from Sicily, Italy.

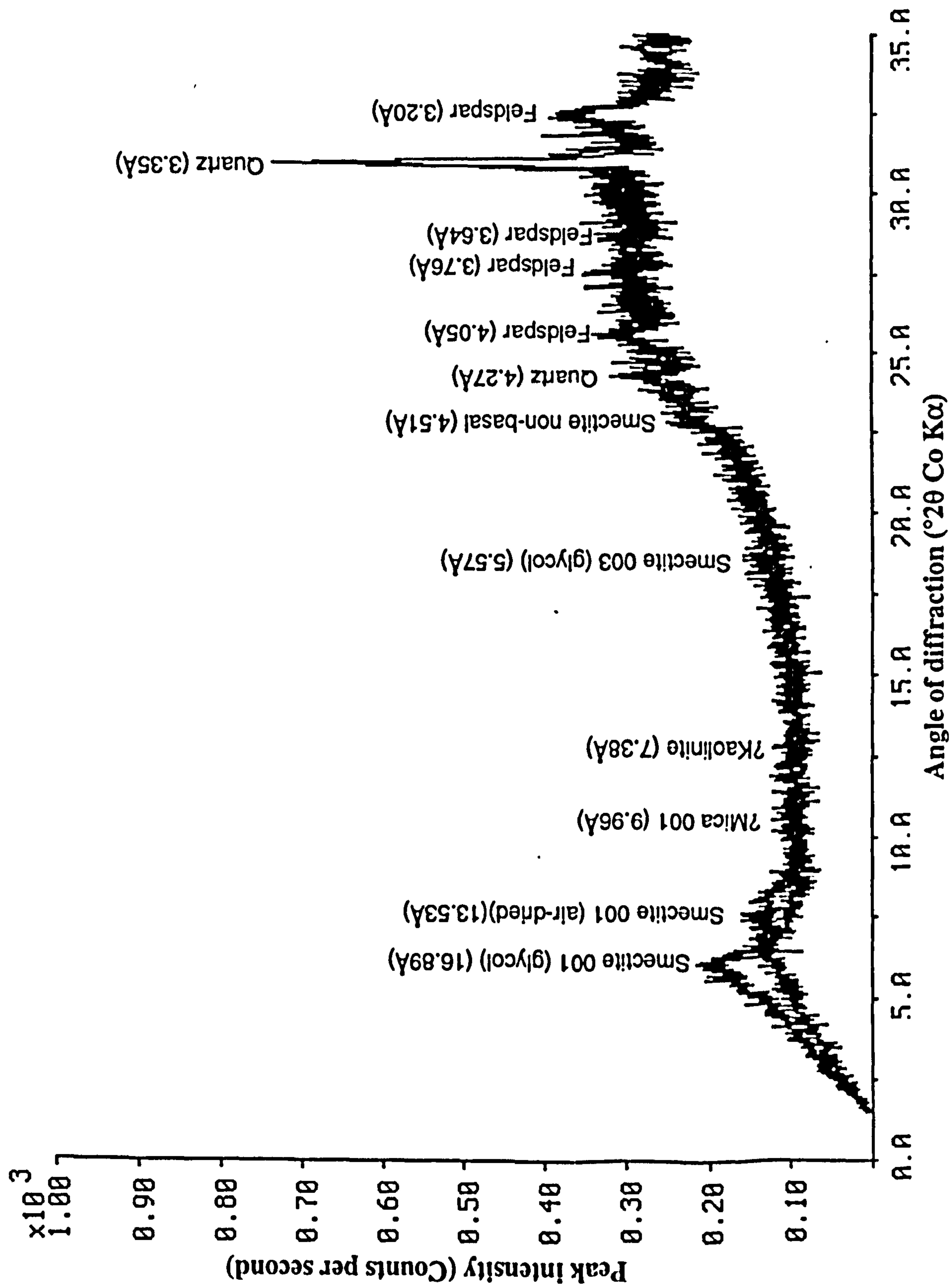


Figure 2.6. Annotated X-ray diffraction (XRD) profile of a $<2\mu\text{m}$ fraction of the pumice from Sicily, Italy. Black profile: air dried pattern. Grey profile: glycol-solvated pattern.

Table 2.12 Particle size frequency distribution of natural (A) and modified (B) samples from the Beli Plast												
natural zeolite deposit, Bulgaria. Particle size cumulative frequency distribution values (i.e. "wt. finer than") are also shown in parentheses												
Size fraction (mm)		(A)			(B)							
		Natural			Modified							
				(wt. %)			(wt. %)					
	2		16.20	83.80		74.00	26.00					
-2	1		54.80	29.00		20.60	5.40					
-1	0.5		19.50	9.50		3.00	2.40					
-0.5	0.25		1.10	8.40		0.30	2.10					
-0.25	0.125		0.80	7.60		0.20	1.90					
-0.125	0.063		3.90	3.70		1.10	0.80					
-0.063			3.70			0.80						
			100.00			100.00						

Table 2.13 Summary of physical property results for natural and modified samples from Beli Plast natural zeolite deposit, Bulgaria.									
Data for other commercial clinoptilolite deposits is included for comparison.									
Sample		Surface area	S.G.	Unsettled bulk density (cm ³ /g)	Settled bulk density (cm ³ /g)				
		(m ² /g)							
(1) Natural									
(i)		41.40	2.11						
(ii)		40.60	2.05						
(iii)		39.40	2.09						
Average		40.50	2.08	1.14	1.12				
(2) Modified									
(i)		40.10	2.17						
(ii)		42.20	2.12						
(iii)		43.00	2.15						
Average		41.70	2.15	1.10	1.05				
Comparative data:									
(3) Inter Rad		36-40							
(4) St. Clouds		12.90							
(5) Biotys		19.40							
(6) Palestra		8.70							
(7) Clinoptilolite			2.15						
(8) Geoprodukt KFT				0.82					
(9) Beli Plast:		25-42	2.16						
crushed				0.78-0.88					
rounded				0.94-0.97					
spherical				0.99-1.02					
Notes:									
(1) Surface area determined on -3.6 mm size fraction									
(2) Surface area determined on -3.6 mm size fraction									
(3) Commercial clinoptilolite, Bulgaria									
(4) Commercial clinoptilolite, New Mexico, -0.710 + 0.300 mm size fraction									
(5) Commercial clinoptilolite, -0.710 + 0.300 mm size fraction									
(6) Clinoptilolite deposit, northern Greece, -0.710 + 0.300 mm size fraction									
(7) Data from Deer et al, 1967									
(8) Commercial clinoptilolite, Hungary									
(9) 1997 General catalogue, Zeoprodukts Ltd. Co.									

2.7.2 Chemistry

2.7.2.1 Major element X-ray fluorescence (XRF) analysis

In terms of its major element composition, the sample essentially consisted of 69.8 % SiO₂, 12.7% Al₂O₃, 8.3 % alkalis (Na₂O and K₂O), 2.1% Fe₂O₃ and 0.5% MgO (Table 2.14).

On the basis of SiO₂ content, the volcanic glass present is of rhyolitic composition. The major element chemistry is broadly in keeping with that quoted by Italpumice (Table 2.14).

2.7.2.2 Cation exchange capacity

The very low CEC value of 1.8 meq 100g⁻¹ obtained is probably derived largely from minor clay minerals identified in the fine-fraction by XRD.

2.7.3 Petrography

In hand-specimen, the sample is composed of dust-coated, pale-grey, well-rounded pumice fragments and very minor (<1% by volume estimated) of darker rock fragments (lithic clasts).

Scanning electron microscopy confirmed the predominance of an highly-vesicular K-, Al- and Si- bearing volcanic glass. Vesicles are between 0.01mm and 2mm in size (Plate 2.5); the smaller size vesicles are typically oval and slightly elongate, whereas the larger vesicles are more spherical but are irregular in outline. The surface and part of the void space of pumice fragments is covered by a 0.1-0.5 mm coating of small, angular pumice particles (Plate 2.7).

The lithic clasts noted in hand-specimen are of porphyritic andesite (Plate 2.8). Phenocrysts of clinopyroxene (diopside and augite) and Ca-plagioclase are present within a fine-grained matrix of clinopyroxene and plagioclase with minor K-feldspar and accessory magnetite / ilmenite. Infrequent highly-altered and corroded olivine (forsterite) was also noted. The lithic clasts examined have been altered as indicated by the presence of large (several mm size) secondary voids which sometimes contain collomorphic kaolinite (Plate 2.10). Kaolinite has also partially replaced the Ca-plagioclase and clinopyroxene phenocrysts.

Table 2.14 Major element chemical composition of pumice sample from Sicily in comparison to other commercial pumice products														N/A : Not Available	
Weight %		Pumice, Sicily	Hess Pumice, USA	Italpumice, Italy	Lava Mining, Greece	Pumice, Costa Rica									
			*	*	*	**									
SiO2		69.75	70.5	71.75	70.55	72.81									
TiO2		0.11	0.20	0.11	N/A	0.31									
Al2O3		12.70	13.5	12.33	12.24	15.32									
Fe2O3		2.08	1.10	1.98	0.89	1.59									
Mn3O4		0.07	N/A	0.07	N/A	0.12									
MgO		0.48	0.50	0.12	0.10	0.41									
CaO		1.39	0.80	0.70	2.36	2.05									
Na2O		3.72	1.60	3.59	3.49	3.68									
K2O		4.62	1.80	4.47	4.21	3.69									
P2O5		0.02	N/A	N/A	N/A	N/A									
Cr2O3		0	N/A	N/A	N/A	0.03									
SrO		0.01	N/A	N/A	N/A	N/A									
ZrO2		0.02	N/A	N/A	N/A	N/A									
BaO		0.01	N/A	N/A	N/A	N/A									
LOI		4.66	N/A	N/A	N/A	N/A									
Total		99.64	N/A	N/A	N/A	100.01									
*	Harben and Kuzvart, 1996														
**	Mitchell and Bloodworth, 1989 (sample JB77)														

2.7.4 Physical properties

Generally, for pumice products, particle-size distribution is a useful means of classification (Figure 2.7). This is because specific applications require pumice products with a well-defined particle-size range, as follows in Table 2.15.

Table 2.15. Particle-size distribution of pumice products

Application	Particle-size range
Lightweight aggregate	-18 mm
Abrasives:	
Stonewashing	-8 + 2 mm
Cleaning	-2 mm
Polishing	-0.053 mm
Pesticide carrier	-0.850 + 0.180 mm
Filler	-0.100 mm

The grading characteristics of the pumice correspond broadly with data quoted for the -10mm product marketed by Italpumice (Table 2.16). The proportion of material finer than 0.075 mm probably resulted from abrasion during transport and handling.

The bulk density of the pumice sample as received was 596 kg m^{-3} (Table 2.17). The bulk density of unsieved pumice products is usually $500\text{-}700 \text{ kg m}^{-3}$, however, for particular pumice sieve fractions, the bulk density range is broader ($400\text{-}900 \text{ kg m}^{-3}$). Bulk density increases with both decreasing particle size and increasing compaction during settling (Table 2.18). If the mean particle size is small, increase in bulk density during settling is more pronounced. In the pumice sample tested here, bulk density varied from 474 kg m^{-3} for the -10+5 mm sieve fraction to 677 kg m^{-3} for the -0.075 mm sieve fraction (Table 2.18). Similar trends were observed for a pumice from Zarcero, Costa Rica, where bulk density

Table 2.16 Particle size frequency distribution of the pumice sample from Sicily (A) in comparison to another commercial pumice product (B)										N/A : Not Available	
Size fraction (mm)	(A)					(B)					
	Pumice (wt. %)					Italpumice (wt. %)					
-14.00	10.00					5.00*					
-10.00	5.00					28.00**					
-5.00	2.36					16.00***					
-2.36	1.18					11.00					
-1.18	0.60					5.00					
-0.60	0.30					2.00					
-0.30	0.15					4.00					
-0.15	0.75					29.00****					
-0.75						N/A					
Total						100.00					
*	-12 9 mm sieve fraction										
**	-9 6 mm sieve fraction										
***	-6 2.36 mm sieve fraction										
****	-0.15 mm sieve fraction										
Table 2.17 Physical properties of the pumice sample from Sicily (A) in comparison to other commercial pumice products										N/A : Not Available	
Physical properties	(A)					(B)		(C)		(D)	
	Pumice					Italpumice		JB77*		JB78*	
SG											
Bulk density (kg/m3)						2.30		N/A		N/A	
Relative density (g/cm3):						400-900		552.00		976.00	
(1) Oven dried											
(2) Surface saturated						N/A		N/A		N/A	
Apparent relative density (g/cm3)						N/A		N/A		N/A	
Water absorption (wt. %)						N/A		1.85		2.23	
								58.90		35.00	
*	Mitchell and Bloodworth, 1989										

Table 2.18 Variation of bulk density versus particle size for the pumice sample from Italy for both unsettled (A) and settled material (B)												
Sieve fraction (mm)				(A) Sicily								
				unsettled (kg/m3)								
Whole sample												
-10	5			596								
-5	2.36			474								
-2.36	1.18			493								
-1.18	0.6			495								
-0.6	0.3			573								
-0.3	0.15			635								
-0.15	0.75			685								
-0.75				660								
2.				677								
Table 2.19 Variation of bulk density versus particle size for pumice from Costa Rica (unsettled)												
Sieve fraction (mm)				(C) Costa Rica						(D) Costa Rica		
				unsettled (kg/m3)*						unsettled (kg/m3)**		
Whole sample												
10				552						976		
-10	5			443						708		
-5	1.18			468						574		
-1.18	0.3			512						690		
-0.3				522						959		
				821						1016		
Mitchell and Bloodworth, 1989				* Sample JB77						** Sample JB78		

varied from 443 kg m^{-3} for the -14+10 mm sieve fraction to 821 kg m^{-3} for the -0.300 mm sieve fraction (Table 2.19). The SG of the sample (2.4) compared with a typical SG of 2.5 for pumice glass quoted in the literature. SG is largely dependant on the chemical composition of the glass phase. According to the literature, pumice has the ability to absorb up to 100 % of its own weight in water. Therefore, the water absorption of the pumice examined here (21 %) was relatively low. For example, the Costa Rican pumice analysed previously was found to have a water absorption of approximately 60 % (Table 2.17).

2.8 Conclusions

2.8.1 Natural zeolite from Beli Plast, Bulgaria (Plate 3.1)

- From thermal analysis, the two natural zeolite samples were estimated to contain 84-87 % clinoptilolite. Clinoptilolite was identified from the very close match between X-ray diffraction (XRD) profiles and the Joint Committee on Powder Diffraction Standards (JCPDS) mineral pattern 25-1349 for clinoptilolite. XRD analysis also indicated the presence of minor cristobalite and quartz. Clinoptilolite was distinguished from heulandite on the basis of the chemical criteria of Gottardi and Galli (1985), i.e. a Si/Al ratio > 4 and $\text{Na}+\text{K} > \text{Ca}$. The presence of clinoptilolite, rather than heulandite, was also corroborated by the Mumpton (1960) heating test.
- For both the natural and modified samples, in terms of major element composition, the oxides SiO_2 and Al_2O_3 predominated with appreciable K_2O and CaO also present. The modified sample was also rich in phosphate (apatite) (0.42 % P_2O_5). In comparison to chemical data for stratigraphic zones I, II, III and IV of the Beli Plast deposit, both samples corresponded most closely with zone III, on the basis of K_2O , CaO and MgO values.
- The following clinoptilolite formula was calculated from an average of the electron microprobe data on an anhydrous 72 oxygen basis: $(\text{K}_{1.6} \text{Ca}_{1.6} \text{Na}_{0.6} \text{Mg}_{0.3})\text{Al}_{6.4} \text{Si}_{29.7}$

O₇₂. This corresponds closely to the (K_{1.9} Ca_{1.8} Na_{0.4} Mg_{0.1})Al_{6.1} Si_{29.9} O₇₂ · 21H₂O formula quoted for the Beli Plast deposit in the Zeoproducts Ltd. Co. 1997 catalogue. In comparison to data for other sedimentary types of natural zeolite, Beli Plast clinoptilolite is anomalously Ca-rich and Na-poor.

- In both samples, exchangeable K predominates with subordinate Ca and Na, and only minor Mg. In general, altering contact time from 15 minutes to 24 hours resulted in an increase in total CEC of between 7-14 %. Results indicated that exchangeable K initially released into solution may subsequently be resorbed, at least partially, on exchange sites within the clinoptilolite lattice, as equilibrium is approached. Total cation exchange capacity (CEC) values obtained here (132.0-158.3 meq 100g⁻¹) were close to those quoted for other commercially-available clinoptilolite products (119-220 meq 100g⁻¹).
- Petrographic analysis was carried out on a separate hand specimen from the Beli Plast deposit. Altered vitric shards predominated. The morphology of these shards varied from regular, elongate, blade-like clasts to irregular, "horn-shaped" clasts bounded by concave, arcuate surfaces. A possible bedding-parallel alignment of the elongate clasts was noted. Particle size was between 0.1-2mm and shards were moderately-to well-sorted. Minor crystal clasts (K-feldspar, quartz and muscovite) were also observed. Lithic clasts of vesicular pumice were infrequent. Clasts were enclosed by a fine-grained matrix, predominantly of clinoptilolite composition with minor clayey pockets. Although relict morphology was preserved, vitric shards were generally highly altered. Typically, the rim of each shard consisted of a fine-grained lining. In the centre of each shard, secondary porosity was partially infilled by large (10-20 µm size) euhedral, tabular crystals. The EDXA composition of both the fine-textured outer margin of shards and the coarse crystals within internal voids are consistent with a clinoptilolite composition.

- In summary, in terms of its behaviour as an hydroponic substrate, the Beli Plast clinoptilolite, due to its large CEC, is capable of releasing a large quantity of nutrients (K, Ca) into solution. However, the effective in-situ CEC of the substrate is likely to be much less than the values quoted here. Efficiency will be limited by the inability of cations to diffuse from (or into) the interior of large rock fragments. Also, an appreciable proportion of clinoptilolite is effectively “locked” within secondary voids in the interior of vitric shards and is, therefore, likely to be only partially available for chemical exchange. The modified and natural samples mainly differ in terms of grading (particle size) and phosphate content. In comparison to the pumice, the Beli Plast natural zeolite does not contain any large scale pores (“macropores”) and is therefore likely to have a lower water retention ability.

2.8.2 Pumice from Sicily

- In hand specimen, the sample was comprised of dust-coated, pale grey, well-rounded pumice fragments and very minor (<1% by volume estimated) darker rock fragments. X-ray diffraction analysis indicated that poorly-ordered volcanic glass predominated in the sample. Minor quartz and feldspar were also identified by XRD. In terms of its major element composition, the sample essentially consisted of 69.8 % SiO₂, 12.7% Al₂O₃, 8.3% alkalis (Na₂O and K₂O), 2.1% Fe₂O₃ and 0.5% MgO.
- Scanning electron microscopy confirmed the predominance of an highly vesicular K-, Al- and Si- bearing volcanic glass. Vesicles were between 0.01mm and 2mm in size. The smaller size vesicles were typically oval and slightly elongate, whereas the larger vesicles were more spherical but irregular in outline. The surface of pumice fragments and part of the void space were covered by a 0.1-0.5 mm thick coating of small angular pumice particles. The lithic clasts noted in hand specimen were of porphyritic andesite.

- A low CEC value of $1.8 \text{ meq } 100\text{g}^{-1}$ was obtained. This CEC is likely to be mostly derived from minor clay mineral constituents, as identified in the $<2\mu\text{m}$ fraction by XRD analysis.
- In summary, in terms of its behaviour as an hydroponic substrate, the pumice will act essentially as an inert porous media. A large number of macropores of between 0.01-2mm size provided the pumice with an appreciable water retention capacity, as demonstrated by the water absorption value of 21% by weight. The CEC of the pumice is almost negligible, being an order of magnitude lower than that of the Beli Plast natural zeolite. Therefore, the influence of this pumice within an hydroponic system is likely to be primarily physical rather than chemical.

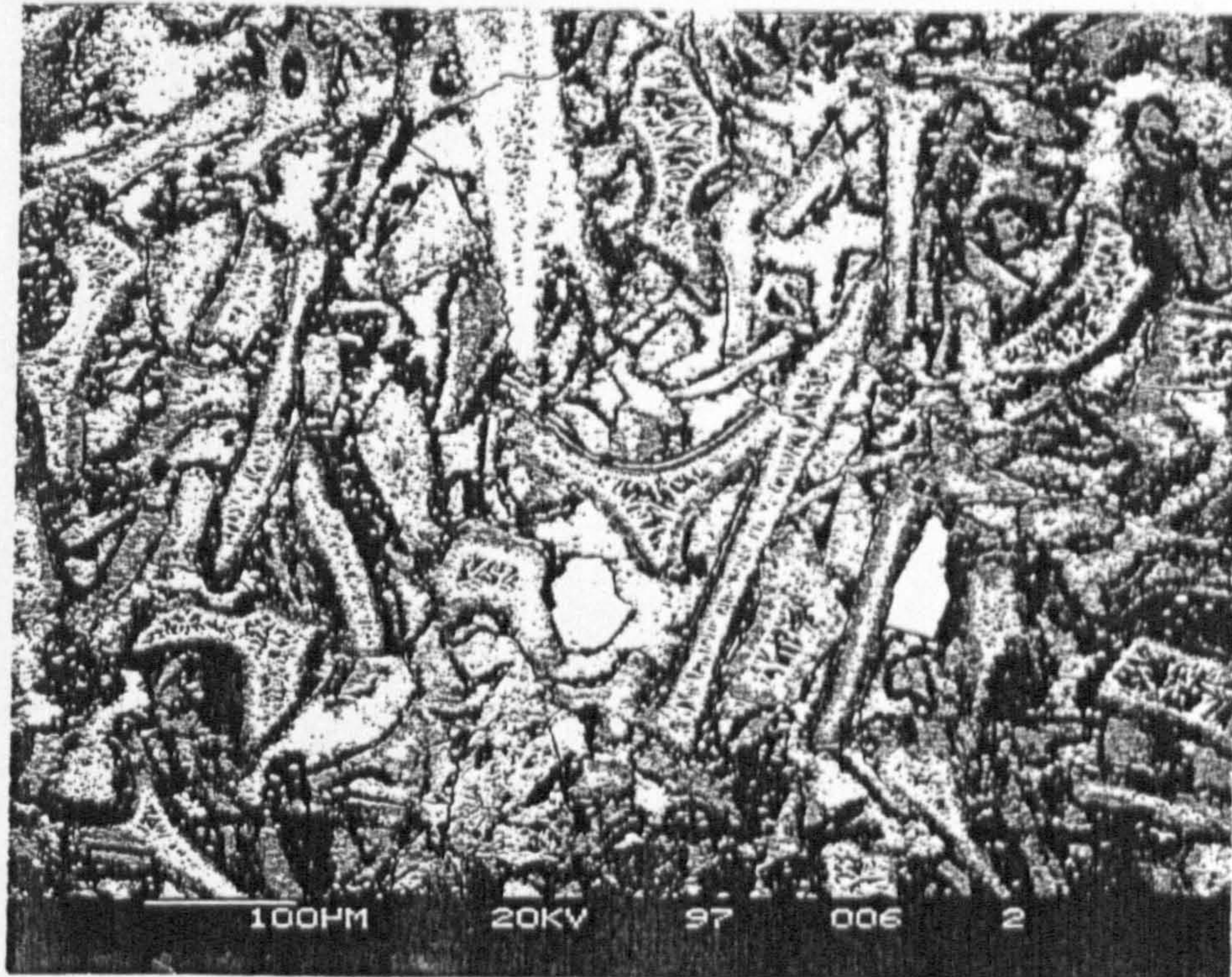


Plate 2.1. Low-magnification BSEM photomicrograph of the resin-impregnated polished thin section of the Beli Plast natural zeolite.

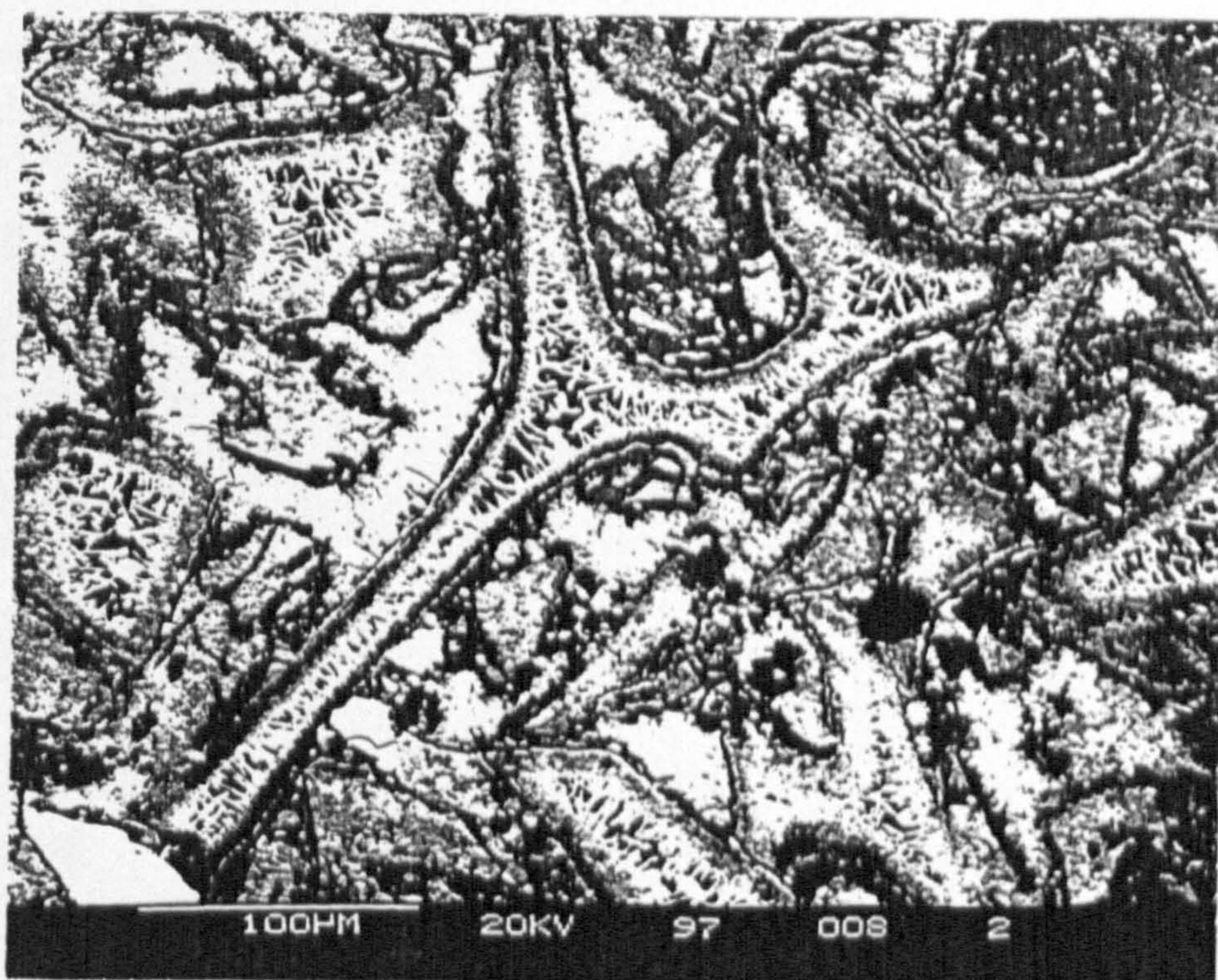


Plate 2.2. BSEM photomicrograph of "horn-shaped" vitric ash clast with a well-preserved relict texture but completely replaced by clinoptilolite.

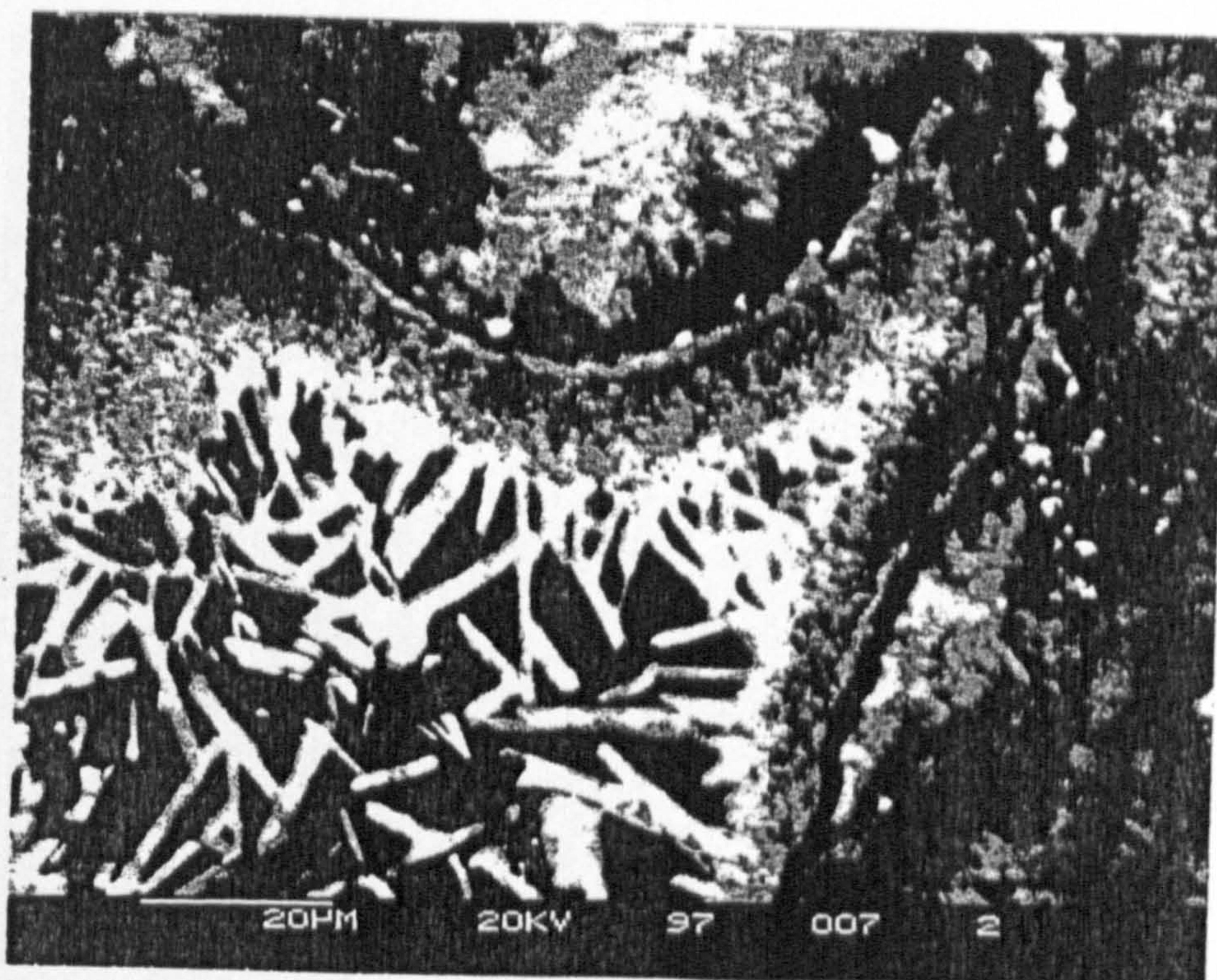


Plate 2.3. High magnification BSEM photomicrograph of the top-right part of clast featured in Plate 2.2. Coarse euhedral clinoptilolite crystal growth within a secondary void. Outer zone of clast consists of fine-grained clinoptilolite.

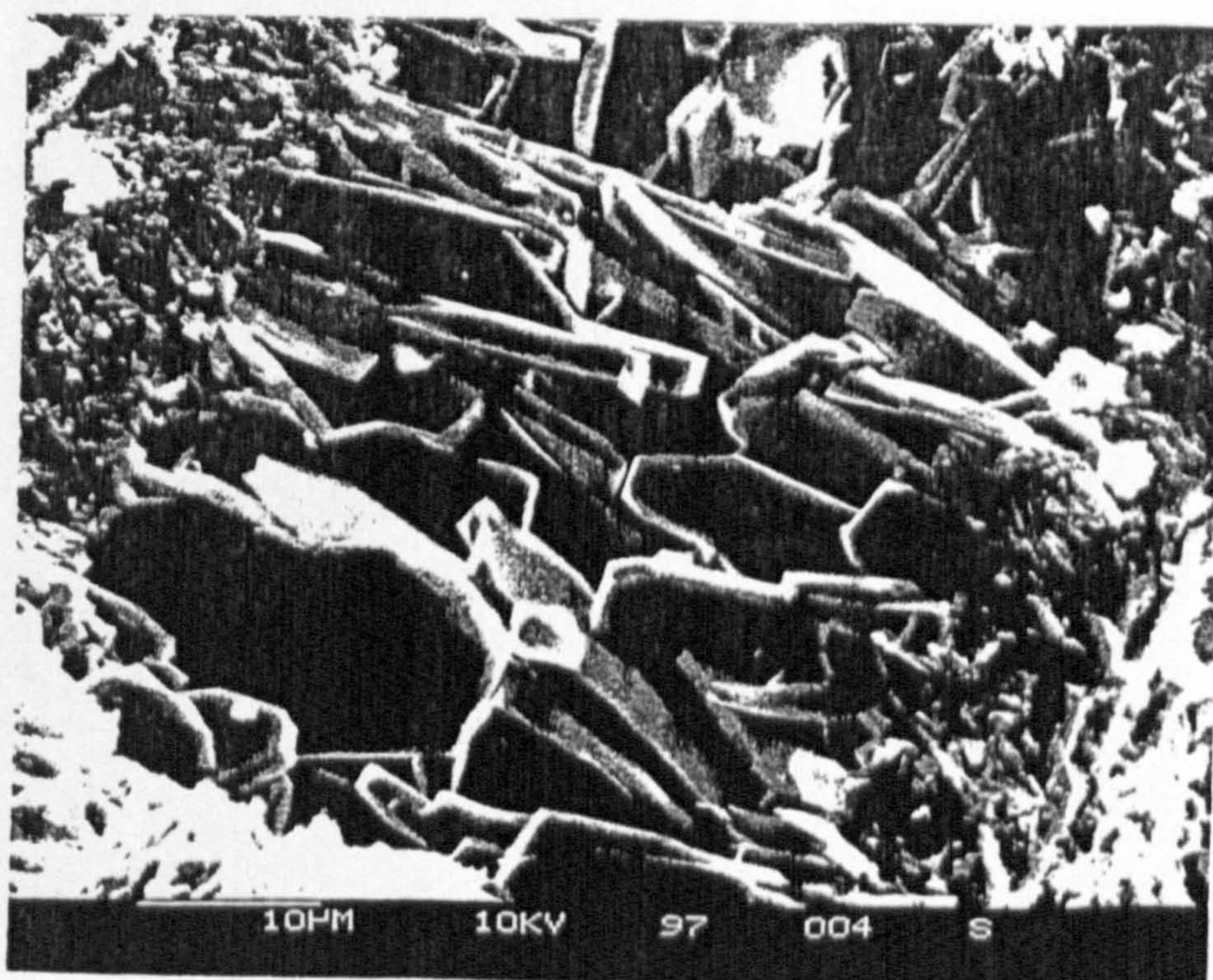


Plate 2.4. Secondary-electron mode photomicrograph of euhedral, tabular clinoptilolite within a secondary void. Finer-grained clinoptilolite surrounds.

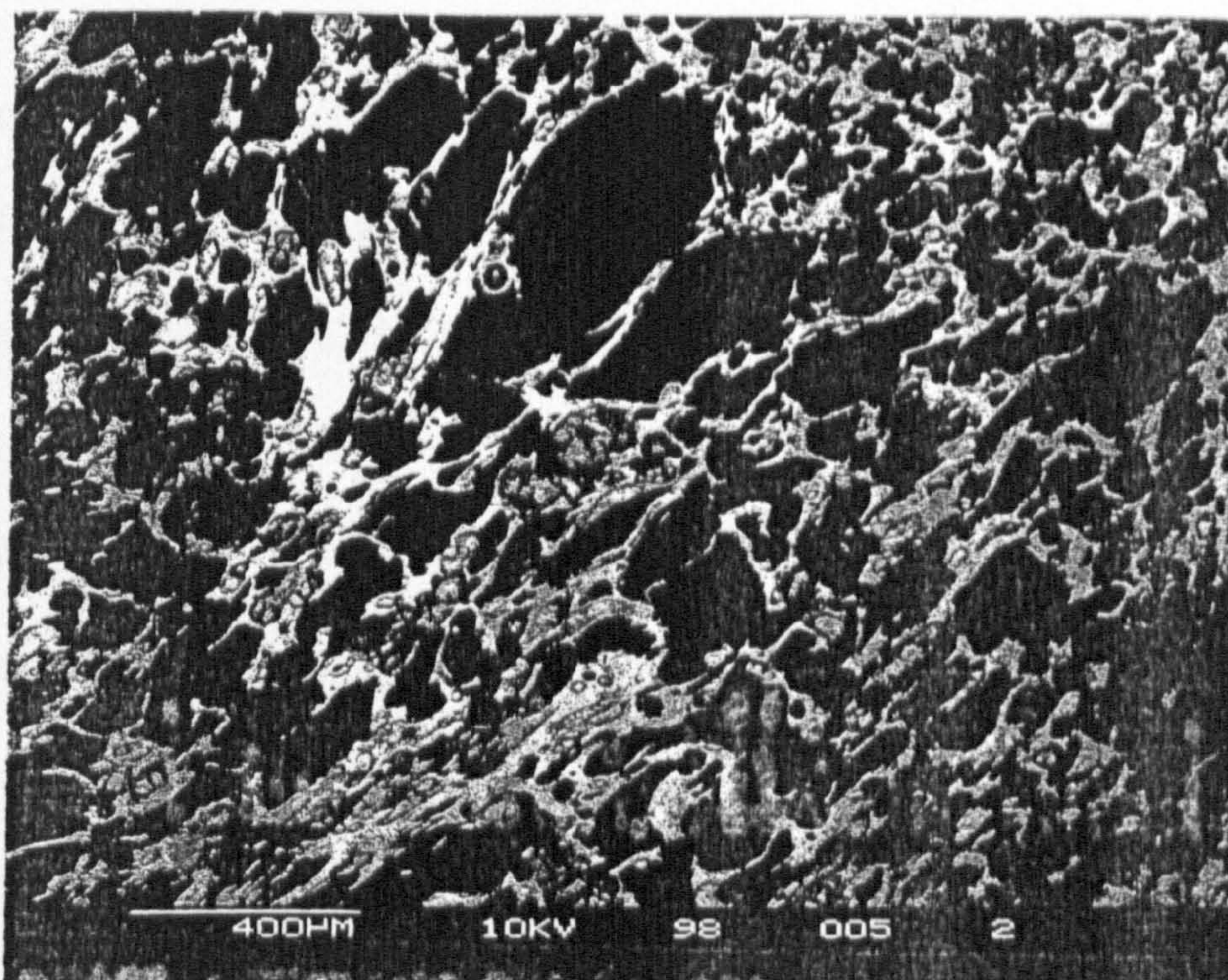


Plate 2.5. BSEM photomicrograph of resin-impregnated thin section. Vesicular glassy appearance is typical of pumice.

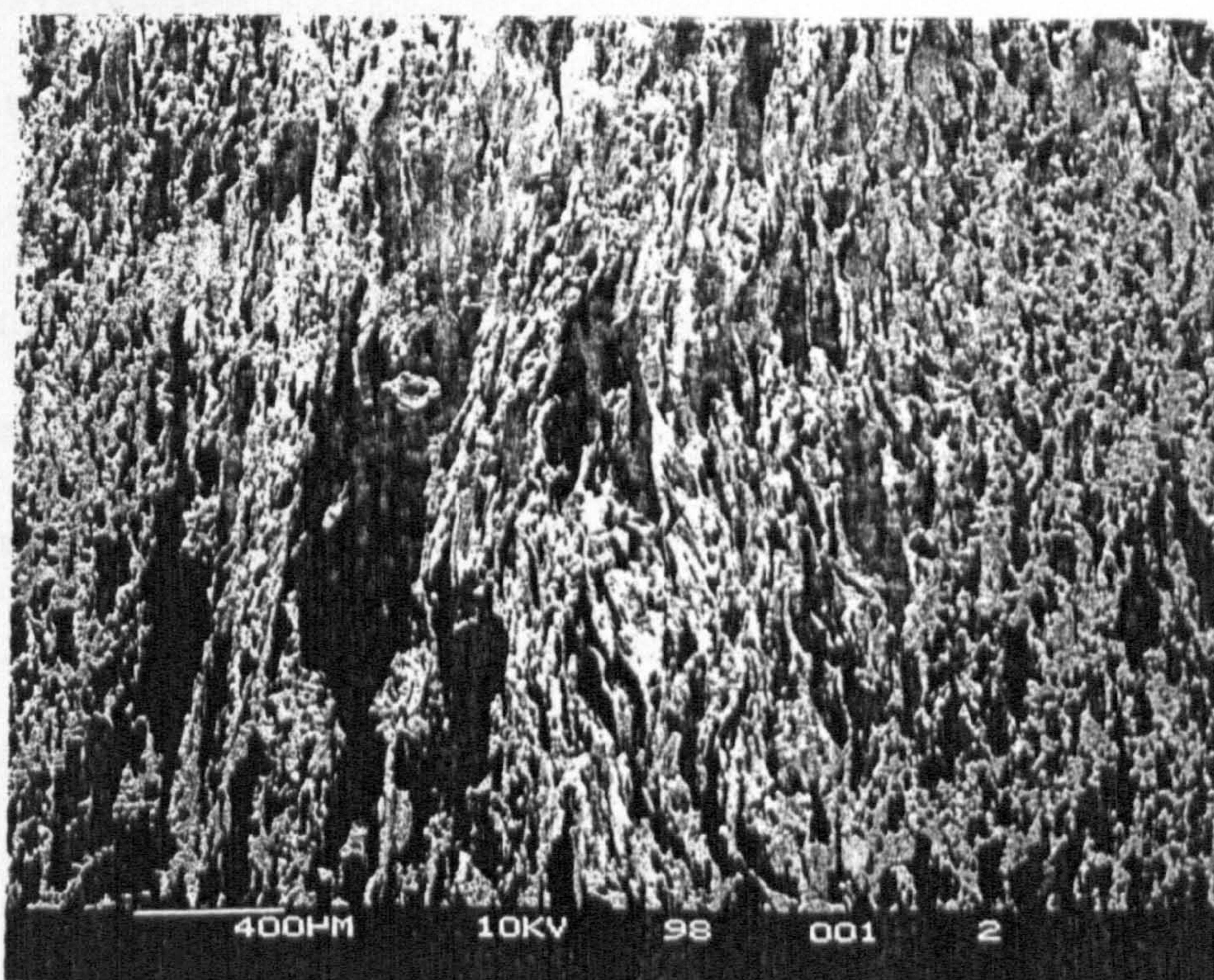


Plate 2.6. BSEM electron photomicrograph of asymmetric pores in pumice resulting from deformation or flow in the molten state.

Chapter Three Plant and Crop Production Materials and Methods

3.1 Introduction

This Chapter describes the procedures used in the growing of the various crops in the substrates described in Chapter Two. Standard operating procedures (SOPs) were created by the author for each crop examined for use in the Experimental Programme at the States of Jersey Department of Agriculture and Fisheries and adapted to include management aspects of the different substrates used. Environmental control of the glasshouse compartments is presented and also the analytical procedures performed at the ADAS Analytical Chemistry Laboratory, Wolverhampton. The zeolite substrates were gradually phased into the experimental programme, so that by the end of the work, the full potential of the materials had been fully explored and the correct handling and management protocols recorded.

3.2 Standard operating procedures for long season tomato crops

3.2.1 Propagation

Prior to sowing, all existing green plant material was removed from the propagation glasshouse compartments, including plant debris from the previous crop and weeds around the internal and external perimeters of the compartments. The garden area to the west of the glasshouses was checked for the presence of insect pests, such as thrips and leafhoppers and the appropriate biological controls ordered prior to crop emergence. The inner glass walls and roof were cleaned with an approved disinfectant / detergent and the external roof area was checked for moss and weeds. After removal of the latter, the glass and gutters were cleaned and any broken glass panes were replaced.

All fixtures and fittings, such as benches, irrigation / feed tanks, carbon dioxide distribution tubes and sodium vapour lamps were cleaned and the operation of the sodium lamps and time clocks were checked prior to use. Polystyrene sheets were placed on the

propagation benches and the polystyrene was covered with black / white polythene sheeting, with the white, reflective side uppermost. Rockwool multiblocks (propagation cubes) were positioned on the propagation benches of the germination compartment and perlite was placed under the propagation cubes to aid drainage of irrigation water. All batches of propagation cubes were labelled with an appropriate variety label, complete with the date of sowing.

Each batch of propagation cubes was centred under the sodium lamps to ensure that supplementary light was received evenly over the seedlings from emergence.

Before sowing, the propagation cubes were thoroughly wetted with a pre-warmed liquid feed solution at pH 5.0 and a conductivity of $1,500 \mu\text{S cm}^{-1}$, to achieve pH 6.0 and a conductivity of $2,000 \mu\text{S cm}^{-1}$ in the root zone. One seed was inserted into each cube to a depth of 3 to 5 mm, to give the required number of seeds in each batch. The cubes were then covered with a thin layer of vermiculite, to aid shedding of seed coats following seedling emergence. A final covering of clear, horticultural polythene sheeting was then applied to the cubes. The germination compartment had the following dedicated computer settings: a day / night temperature (until seedling emergence) of 24°C ; and a ventilation temperature of 28°C . The lighting system was engaged at the first sign of seedling emergence, to give 16 hours of supplementary light from 06:00 to 22:00 hours. Carbon dioxide enrichment provided a constant level of 1,000 parts per million by volume (ppmv) during the daily light period, from seedling emergence.

The propagation cubes were regularly examined for signs of seedling emergence and to monitor the moisture status of the rockwool. On recording 10% emergence, the polythene sheet was removed. Where necessary, the manual removal of seed coats from expanding cotyledons was performed. On full emergence, the computer settings were adjusted to: a day / night temperature of 20°C ; a ventilation temperature of 26°C ; a supplementary

lighting period of 06:00 to 22:00 hours; and a carbon dioxide enrichment level of 1,000 ppmv.

The moisture status of the propagation cubes was checked on a daily basis and, when necessary, a feed solution of pH 5.5 and conductivity $2,500 \mu\text{S cm}^{-1}$ was applied. The propagation cubes were blocked-on into 7.5 cm rockwool blocks after 10 days, using a sideways placement of the multiblocks. The blocks were thoroughly wetted with the starter feed solution, to achieve a pH of 6.0 before transplanting. Feed and rockwool drainwater samples were taken and sent for laboratory analysis at regular intervals. Computer settings were maintained as outlined above.

Once the first true leaf had appeared, a daily feed of pH 5.5 and conductivity $3,500 \mu\text{S cm}^{-1}$ was applied. As the first true leaf expanded, the temperatures were reduced to 20°C day, 18°C night in stages of 0.5°C per 24 hour period. The plants were ready for moving into the production compartments 21 to 28 days from sowing.

3.2.2 Establishment

All recirculation pipes were covered during the clean-up phase, to prevent contamination by soil and plant debris. Alterations to irrigation pipework were completed before the floor covers were installed and a mobile propane burner was utilised to flame the soil surface prior to laying the floor covers. The floor was covered with black / white polythene, with the white side uppermost and the polythene was raised to meet the concrete support walls.

Recirculation stands and trays were constructed to allow a smooth passage of drainwater away from the slabs down a slope of between 1 in 100 and 1 in 80. The trays were lined with a black / white polythene protector sheet and then polystyrene insulation slabs were positioned onto the liner. After placement of irrigation lines down all cropping rows, polythene channels were constructed to house the recirculation drainage rails and the rockwool slabs themselves. In each cropping row were placed two, 3 cm square polystyrene rails, with a between-row distance of 10 cm. Rockwool slabs were then placed

on the rails and irrigation tubing inserted into the outer wrapping of the slabs to effect slab wetting-up. Carbon dioxide layflat tubing was then installed down each cropping row and secured to the top rail of each stand. The rockwool recirculation irrigation system was tested and the slabs were filled with a dilute nutrient solution at the required pH and conductivity level, in order to thoroughly soak the rockwool well in advance of planting. In addition, the sump tank feed warming system was tested to ensure that the correct slab temperatures could be maintained.

Glasshouse temperatures were set at: 18°C day; 16°C night; and 23°C vent. Carbon dioxide enrichment was set to provide an atmospheric content of 1,000 ppmv. Two daily ventilation purges were programmed for ten minutes at midday and 16:00 hours. Overhead thermal screens were set to close when the outside temperature fell below 10°C.

Plants were transferred from the propagation house to the main glasshouse when the weather conditions were suitable (not cold, windy or raining) and all transport trays were labelled with the correct glasshouse number and variety. The plants were graded before planting and any unusual, blind or damaged plants were discarded. Squares were scored in the polythene wrapping of the rockwool slabs to accommodate the propagation blocks. The blocks were then positioned onto the surface of the slabs and an attendant dripper inserted to secure the blocks to the slabs.

Two to five days after planting, a total of four, 3 cm vertical slits were made at two places on each side of each 1.2 m slab, between the plants. Care was taken to avoid cutting into the rockwool and it was important to ensure that the slits were to the base of the slabs, to allow free drainage to occur.

Drip line feed and drainwater samples were taken at twice weekly intervals for pH and conductivity measurements and samples were sent to the ADAS analytical laboratory for a full hydroponic analysis. The plants were checked daily for unusual plant development such as blindness and jacks; affected plants were removed and replaced. Plant cotyledons were

removed before closing the polythene channels in an attempt to avoid the start of disease problems, such as *Botrytis cinerea*. The channels were stapled to a central wire, ensuring that the polythene was secure but preventing contact between plant stem and support wire. All plants were then supported by attaching a loop of string below the second true leaf on each plant. The string was twisted clockwise around the plant, avoiding trapping leaves and any developing trusses. Developing sideshoots were removed to maintain a cordon plant habit. The strings were twisted around the plants on a weekly basis. As soon as trusses were sufficiently developed (two to three open flowers), a truss support was carefully attached to each truss stem. The supports were used over the winter period until there was a marked improvement in light levels. Once the first flowers were open in sufficient numbers, bumble bees were introduced to effect pollination. A careful check on the early flowers was made to ensure that the bees were not over-biting or damaging the flowers. All plant heads were spaced equidistantly, to ensure even light interception. Temperatures were raised by 2°C for two hours over the midday period to assist pollination and provide optimum conditions for establishment of biological control organisms.

3.2.3 Main season

The crop was checked for the presence of unusual plant development, such as jacks and chimera symptoms. On detection, an abnormal plant was removed and a sideshoot taken from an adjacent plant to replace it and maintain plant head density. Support strings were twisted around the plants, in a clockwise direction, on a weekly basis. It was important to avoid trapping leaves, leaflets and flower trusses under the string. Sideshoots were removed once a week to maintain a cordon plant habit.

Dripline feed and drainwater samples were taken from the rockwool slabs daily for pH and conductivity measurement and samples were sent to ADAS on a weekly basis. Changes to the feed regime were made, where necessary, using the ADAS Rockstar computer program.

A regular check was made to ensure that bumble bees used for pollination were not repeatedly visiting and thus damaging the same tomato flowers. Glasshouse temperatures were maintained at 18°C day, 16°C night and 23°C vent. A 2°C midday lift was maintained for two hours each day. A modulating night lift of up to 1.5°C was introduced when the light level reached a total of 350 MJ m⁻² during the previous day. Carbon dioxide enrichment was maintained at 1,000 ppmv during daylight hours with the vents closed. The carbon dioxide level was set at 600 ppmv with the vents over 5% open and a modulating control was programmed between 0 and 5% opening. Waste heat from the burning process was distributed throughout the glasshouse compartments to give a maximum pipe temperature of 50°C. Carbon dioxide levels equivalent to 12 m³ 1,000 m⁻² hour⁻¹ natural gas burning rate were maintained during the spring and summer months.

Side screens were set to open when the light levels reached 72 J cm⁻² and settings were regularly revised. The overhead shade screen was set to open to 85% when the light levels reached 89 J cm⁻² and settings were regularly revised.

Once plant layering commenced, stems were laid flat in a clockwise direction around each double row. Great care was taken to ensure that each variety was confined to its own plot. Finished fruit trusses were removed from the plant stems by cutting cleanly with a sharp knife. Older plant leaves were removed regularly to one leaf below the ripening fruit truss. The crop was picked three times per week, at the colour stage required by the market outlet. Each fruit was carefully removed, ensuring that the calyx remained attached. All containers were taken to the packing shed after harvest, to facilitate recording and cool storage. The fruit was stored at 8-10°C prior to marketing.

3.3 Standard operating procedures for long season sweet pepper crops

3.3.1 Propagation

The propagation compartments were prepared as described for tomatoes in 3.2.1. The germination compartment had the following dedicated computer settings: a day / night temperature (until seedling emergence) of 28°C; and a ventilation temperature of 30°C. The lighting system was engaged at the first sign of seedling emergence, to give 16 hours of supplementary light from 06:00 to 22:00 hours. Carbon dioxide enrichment provided a constant level of 1,000 ppmv during the daily light period, from seedling emergence.

The propagation cubes were regularly examined for signs of seedling emergence and to monitor the moisture status of the rockwool. On recording 10% emergence, the polythene sheet was removed. Where necessary, the manual removal of seed coats from expanding cotyledons was performed. On full emergence, the computer settings were adjusted to: a day / night temperature of 24°C; a ventilation temperature of 26°C; a supplementary lighting period of 06:00 to 22:00 hours; and a carbon dioxide enrichment level of 1,000 ppmv.

The moisture status of the propagation cubes was checked on a daily basis and, when necessary, a feed solution of pH 5.5 and conductivity 1,500 $\mu\text{S cm}^{-1}$ was applied. The propagation cubes were blocked-on into 7.5 cm rockwool blocks after ten days, using a sideways placement of the multiblocks. The blocks were thoroughly wetted with the starter feed solution, to achieve a pH of 6.0 before transplanting. Feed and rockwool drainwater samples were taken and sent for laboratory analysis at regular intervals. Computer settings were maintained as outlined above.

Once the first true leaf had appeared, a daily feed of pH 5.5 and conductivity 2,000 $\mu\text{S cm}^{-1}$ was applied. As the first true leaf expanded, the temperatures were reduced to 23°C day and night in stages of 0.5°C per 24 hour period. The plants were ready for moving into

the production compartments in five to six weeks from sowing with two to three shoots visible in the head of each plant.

3.3.2 Establishment

The production compartments were prepared as described as in 3.2.2. Glasshouse temperatures were set at: 23°C day; 23°C night; and 26°C vent. Carbon dioxide enrichment was set to provide an atmospheric content of 1,000 ppmv. Two daily ventilation purges were programmed for ten minutes at midday and 16:00 hours. Overhead thermal screens were set to close when the outside temperature fell below 14°C.

Plants were transferred from the propagation house to the main glasshouse when the weather conditions were suitable and all transport trays were labelled with the correct glasshouse number and variety. The plants were graded before planting and any unusual, blind or damaged plants were discarded. Squares were scored in the polythene wrapping of the rockwool slabs to accommodate the propagation blocks. The blocks were then positioned onto the surface of the slabs and an attendant dripper inserted to secure the blocks to the slabs. Each plant was orientated on the slabs to allow easy training of the two main shoots along each side of the row.

Two to five days after planting, a total of four, 3 cm vertical slits were made at two places on each side of each 1.2 m slab, between the plants. Care was taken to avoid cutting into the rockwool material and it was important to ensure that the slits were to the base of the slabs, to allow free drainage to occur. Clear polythene sheeting of 60 cm width was installed from ground to wire height at the south end of each row, to prevent low humidity leaf rolling.

Drip line feed and drainwater samples were taken at twice weekly intervals for pH and conductivity measurements and samples were sent to the ADAS analytical laboratory for a full hydroponic analysis. The plants were checked daily for unusual plant development such as virus symptoms and shoot blindness; affected plants were removed and replaced. Plant

cotyledons were removed before closing the polythene channels. The channels were stapled to a central wire, ensuring that the polythene was secure but preventing contact between plant stem and support wire. All plants were then supported by attaching a loop of string below the head of each pepper plant. The loop was made large enough to allow for stem expansion during the growth of the pepper plants over the season. The string was twisted clockwise around the plant, avoiding trapping any leaves. Two main shoots of equal vigour were selected from the head of each pepper plant (stage 1). Any shoots forming adjacent to the slabs were discarded and two main shoots per plant were allowed to remain, growing in parallel with the line of slabs. All crown flowers forming in the position between the two main shoots were removed. Stage two is where the next flower normally forms at a leaf node on each of the shoots selected in conjunction with an attendant side shoot. In order to establish a strong, catapult-shaped framework, this second flower was removed but the side shoot was allowed to develop. Once it was large enough to handle, the same side shoot was cut to remove any subsequent flowers and growing points, whilst retaining two to three leaves on the side shoot. Temperatures were then gradually reduced to 21°C day, 19°C night and 24°C vent before stage 3. Under-substrate heating was set at 22°C. Stage 3 trimming took place where the next flower formed, again at a leaf node on each main shoot with a developing side shoot. This flower was allowed to set and, where plants were growing rapidly, a second flower was retained on the side shoot. Three to four leaves were retained on each side shoot to facilitate plant transpiration, movement of calcium into developing fruitlets and also to provide shade for fruit forming below the leaf canopy. Trimming side shoots carefully helped to prevent both sun scorch and blossom end rot. Once the first fruit flowers were open in sufficient numbers, bumble bees were introduced to effect pollination. A careful check on the early flowers was made to ensure that the bees were not over-biting or damaging the flowers. All plant heads were spaced equidistantly, to ensure even light interception. Temperatures were raised by 2°C for two hours over the

midday period to assist pollination and provide optimum conditions for establishment of biological control organisms (Challinor, 1993).

3.3.3 Main season

The crop was checked for the presence of unusual plant development, such as blindness, genetic disorders and virus symptoms. On detection, the abnormal plant was removed and a sideshoot taken from an adjacent plant. The existing support string was twisted around one main stem in a clockwise direction and a second string was tied under the king flower position for support of the second main stem. The strings were twisted around the stems with at least one twist every 15 cm. Flowers form at each leaf node on each main shoot. In addition, a side shoot also develops. The main aim is to ensure that every flower at the leaf node position on each main shoot sets properly and develops a quality fruit. Each sideshoot forming on each main stem will also produce at least one flower. One flower on each side shoot was allowed to set and produce a quality fruit. On occasions when the plants became overloaded with fruit, the side shoot fruitlets were thinned, to relieve plant stress and to encourage vegetative growth. Only four to six fruitlets were allowed to swell on each main stem at any one time.

In order to prevent one stem from developing a dominance over the other, it was important to match the direction angle of each main shoot from the plant stem. An overhead wire spacing of 60 cm between the wires helped to achieve this. All plant heads were spaced evenly along the rows. Where stems or plant heads had been broken, damaged or removed, another shoot was trained-in using a different-coloured string.

Dripline feed and drainwater samples were taken from the rockwool slabs daily for pH and conductivity measurement and samples were sent to ADAS on a weekly basis. Changes to the feed regime were made, where necessary.

A regular check was made to ensure that bumble bees used for pollination were not over-pollinating and thus damaging the pepper flowers. Glasshouse temperatures were

maintained at 21°C day, 19°C night and 24°C vent. The under-substrate heating system was set at 22°C. A 2°C midday lift was maintained for two hours each day. A modulating pre-midnight temperature drop of up to 2°C was utilised when the plants became too vegetative or when the plants failed to set flowers at any stage. Carbon dioxide enrichment was maintained at 1,000 ppmv during daylight hours with the vents closed. The carbon dioxide level was set at 600 ppmv with the vents over 5% open and a modulating control was programmed between 0 and 5% opening. Waste heat from the propane gas burning process was distributed throughout the glasshouse compartments to give a maximum pipe temperature of 50°C. Carbon dioxide levels equivalent to 12 m³ 1,000 m⁻² hour⁻¹ natural gas burning rate were maintained during the spring and summer months. The overhead shade screen was set to open to 87% when the light levels reached 60 J cm⁻² and settings were regularly revised.

The crop was assessed for the need to remove senescent leaves from the bases of the plants in August and September. In a cool, wet autumn, increasing the airflow around the stem bases was thought to be beneficial in the control of diseases, such as *Botrytis cinerea*.

The crop was picked twice a week, at the colour stage required by the market outlet. Green fruit were cut when they had reached their full size and were firm to the touch. It was important to harvest green fruit before any ripening colour change. Coloured fruit were cut when at least 95% of the fruit surface had turned colour. It was important to leave the correct amount of fruit stalk on each fruit to match the market specification, including avoidance of torn or damaged cut ends. All containers were taken to the packing shed after harvest, to facilitate recording and cool storage. The fruit was stored at 8-10°C at a relative humidity of 90-95% prior to marketing. Fruit were handled carefully at all times and it was important to avoid exposing green fruit to any sources of ethylene gas, to prevent ripening in store.

3.4 Standard operating procedures for long season standard and spray carnation crops

3.4.1 Preparation

The production compartments were prepared as described for tomatoes in 3.2.1. Any gaps in the structure between neighbouring compartments were sealed with expandable foam.

The soil floor was profiled and the heating system pipework rearranged to accommodate metal stands and the latter were installed so that metal trays could be joined together creating an uninterrupted, smooth fall of 1 in 100. The bare earth was covered with woven, polypropylene floor matting to prevent pest and disease transfer from the soil.

A trench and sump area were excavated at the north end of the glasshouse compartment in order to accommodate the irrigation mains and waste water collection system and sump barrel, respectively. Once earthworks had been completed at the north end, the waste water collection system and the sump barrel operation were tested and, finally, the remaining exposed soil was covered with woven, polypropylene floor matting. Rigid 2.5 cm thick polystyrene slabs were placed in the centre of each row of metal trays to form a continuous line. Black / white polythene sheeting was laid on the polystyrene slabs on the metal trays, with the white surface uppermost. Netafim irrigation lines were placed on the metal stands. Each metal row contained one irrigation line to supply liquid feeds and one irrigation line to supply water only.

3.4.2 Planting and establishment

Plots containing pumice, foam, peat, cocofibre or woodchips received the liquid feed irrigation drippers and the nutrient-loaded zeolites received the water only drippers. Five litre, black, polypropylene pots were filled to just below the rim with the various substrates as supplied (Plate 3.3). In some experiments, three litre pots of the same make were

utilised. Each substrate was moistened with water before the plant cuttings were inserted. The aim was to achieve an evenly moist substrate at planting.

Carnation cuttings were inserted at a density of 32 plants m⁻² (four cuttings to a three or five litre pot). All plant cuttings were propagated in Europe or Israel by the supplying companies and transported to Jersey. Each cutting was checked for signs of disease (for example, soft rots at the stem bases) and any suspect cuttings were sealed in a labelled plastic bag and sent to the plant pathology laboratory at Howard Davis Farm for disease identification. Cuttings raised in peat plugs were checked for signs of dryness; any dry plugs were carefully re-wetted by placing the cuttings in a shallow bath of water. On insertion of the cuttings into the substrates, it was ensured that: no damaged or diseased cuttings were planted; the roots were covered by the substrate materials but that the cuttings were not planted too deeply; and cuttings inserted into the foam plots had their roots in intimate contact with the foam, to prevent drying-out. A post-planting drench of water was applied to each substrate using a hand-held hose and the subsequent aim was to maintain an evenly moist substrate at all times during the establishment phase. Eight cropping nets were installed after planting to support the growing crop over a two year period. The plots were labelled using floor markers and labels over the cropping beds (Plate 3.4). An initial temperature regime of 19°C day, 16°C night and vent at 21°C was computed for the first three to four weeks. The temperatures were then reduced to 16°C day, 14°C night and 18°C vent. The established plants were then stopped, by pinching-out the growing points, to allow six side-shoots of equal vigour to develop.

External lime-wash shading was applied to the glass panes when necessary over the period from June to September, to prevent summer flower quality problems. Regular bursts of water from the overhead irrigation system were programmed to keep compartment relative humidity levels above 60% during the establishment phase. The frequency of the applications was directly linked to the incident light levels received.

3.4.3 Main season

Drainwater was collected from all treatments at predetermined points in the glasshouse and samples were sent for laboratory analysis every two weeks. The first crop support net was positioned between 7.5 and 12.5 cm above the tops of the pots, with subsequent layers spaced evenly at 15 cm intervals. The actual position of each net varied slightly as there were several plots of each variety in any cropping row and each variety had a different growth habit. The crop was examined regularly and the nets were carefully raised a little at a time. The adjustment of the nets was performed by at least two people, with one on either side of the net. The net was never forced upwards, as this would have broken shoots and may have disturbed root systems. A morning heat boost starting just before sunrise was provided by direct-fired kerosene burners, in order to reduce condensation within the glasshouse and to provide supplementary carbon dioxide. Enrichment continued for two to four hours each day, depending on the weather conditions. At least one purge setting was included in the daily ventilation cycle, to ensure that unwanted products of combustion were removed. To maintain flower size, standard carnation varieties were disbudded early in the terminal bud development phase, to leave a single central bud on each flower stem. Conversely, the central bud was removed from each spray carnation plant to encourage the even development of side-shoot flowers. A tungsten bulb supplementary lighting programme was employed each September to stimulate the formation of flower buds in time for the pre-Christmas market.

Stems were harvested by cutting with a sharp knife and standard varieties were picked when the bud had opened and the outer petals were past the vertical in summer or horizontal in winter. All flowers from both sides of each marked plot were placed carefully into the correct container for subsequent marketing. Stems were placed in water containing an appropriate flower conditioner as soon as they had been cut. All containers were taken to the packing shed as soon as possible after harvesting was completed, to facilitate recording

and cool storage. The cool stores were maintained at a minimum of 2°C. The flower stems were handled carefully at all times and the flowers were kept away from potential ethylene sources, such as ripening vegetables and fruit.

3.5 Environmental control

3.5.1 Glasshouse compartments

The Wilco Venlo glasshouse was constructed in 1990 to a high specification prepared and quality controlled by ADAS. It had a ground to gutter height of 4.5 metres and a ground to ridge height of 5.3 metres. It was fitted with overhead and side wall thermal / side screens and all environmental control settings were implemented by a Priva CD 750 environmental computer system. Each compartment had its own irrigation system, complete with acid and nutrient dosing tanks and solution recirculation equipment. Two compartments had under-slab heating facilities for long season pepper crops.

The Robinson widespan glasshouse was built in 1988 and had a ground to gutter height of 3.5 metres. Each compartment was fitted with a tungsten light system, complete with individual time controller. As with the Wilco glasshouse, each compartment had its own irrigation system, complete with acid and nutrient dosing tanks. Individual drainwater collection systems were installed in each compartment and drainwater storage or transfer to a series of reed beds for nutrient removal was possible. There were facilities to fit an individual compartment with two irrigation systems, one to provide nutrient feeds and one to supply water only.

3.5.2 Heating systems

The main heating fuel was oil and propane gas was introduced towards the end of the experimental programme, in order to provide additional carbon dioxide and heat for the compartments. A new, dedicated propane boiler was added to the system in 1996, allowing very high dosing rates of carbon dioxide to be introduced into all compartments. Unwanted heat released from the burning processes during the day was stored in an

insulated water tank and released into the heating system at night. Direct-fired kerosene burners were used to provide heat and carbon dioxide during the winter months in the Robinson glasshouse compartments until 1996. A new, propane-fuelled combined heat and power unit (CHP), installed in 1996, complemented the new heating / carbon dioxide system, providing additional heat and electricity to the protected crop unit, farm and offices.

3.6 Analytical procedures

3.6.1 Electrical conductivity of waters and nutrient solutions

The electrical conductivity of a solution is a measure of its ability to conduct electricity and depends on its ionic concentration. Samples were always brought up to 20° +/- 1°C before the conductivity was measured by standing in a constant temperature room for at least 30 minutes and the temperature of the standards and solutions were checked before analysis. The samples were filtered through 0.45 µm millipore filters prior to analysis. Quality control samples were analysed on a basis of one in ten samples. If the batch size was less than ten, then the quality control frequency was one per batch.

The Philips PW9526 is designed for routine measurements in the range 1 to 200 mS cm⁻¹ using two electrode cells in the Philips range.

3.6.2 Preparation and analysis of nutrient and water samples

Irrigation water and drainwater samples were collected from the crop plots every 2 weeks and analysed at the ADAS Analytical Chemistry Laboratory, Wolverhampton. An inductively coupled plasma atomic emission spectrometer (ICP-AES) was used to determine the concentration of elements present. The method uses a spectrophotometric technique based on very high temperature atomization / ionisation of a sample solution. In ICP-AES, the plasma is produced by passing a flow of argon gas through a strong radio frequency field. This induces ionisation in the argon which immediately reverts, shedding the excess energy as intense heat and light in a continuous and constant process. When a sample solution is nebulised into the plasma, atomisation is assured and a complex spectra,

characteristic of the elements present, is emitted. Argon plasmas are so hot (8,000-10,000°C), that chemical interferences, associated with atomic absorption and flame emission, are eliminated. Other types of spectral interferences occur, however, necessitating careful selection of wavelengths (Barrett, M., 1997 - pers. comm.). All calibration graphs are linear but background noise levels are sometimes high, especially for potassium. An ultrasonic nebuliser sometimes gives greater sensitivity (Barrett, M., 1997 - pers. comm.). The reaction sequence includes nebulisation, ionisation and emission from excited atoms measured sequentially or simultaneously. Three ICP spectrophotometers manufactured by Thermo Jarrel Ash were used: Atomscan 25; Enviro; and Iris. The analytical reporting range was 0 to 900,000 mg kg⁻¹ and the concentrations given were for a 95% probability level. Quality control samples were analysed on a basis of one per ten samples and, if the batch size was less than ten samples, the quality control sample frequency was one per batch. The absolute difference between two single test results obtained under reproducibility conditions was not greater than 10% of the mean of two results (Wood, G., 1997 - pers. comm.).

Ammonia, nitrate-nitrogen and chloride were all determined using continuous flow analysis. Samples for NH₄ ECN were filtered through a 0.45 µm millipore filter prior to analysis. The principle is that ammonia in the sample reacts with hypochlorite ions which are generated in situ by alkaline hydrolysis of sodium dichloroisocyanurate. This reaction forms monochloramine, which then reacts with salicylate ions in the presence of sodium nitroprusside to form a blue, indophenol-type compound, which is measured colourmetrically at 630 nm. Magnesium interferes by forming a precipitate of magnesium hydroxide at the high pH value (>12) required for full colour development. Trisodium citrate is used as a complexing agent to prevent this interference. At the concentration of trisodium citrate specified, the method will tolerate magnesium at concentrations normally encountered in most non-saline waters. The tolerance of the chemistry to magnesium can

be increased, to deal with partially-saline water, by increasing the concentration of trisodium citrate in the reagents (up to the limit of solubility, which is 390 g l⁻¹).

Ammonia is volatile and will leave the sample slowly, even through polyethylene bottles.

The samples were run within a 24 hour period. The apparatus involved was a Lachat Quikchem Automatic Flow Injection Analyser and quality control samples were analysed on the basis of 1 per 15 samples. If the batch size was less than 15, then the quality control frequency was one per batch.

3.6.3 Nitrate-nitrogen in water

Nitrate was quantitatively reduced to nitrite by passage of the sample through a copperized cadmium column. The nitrite (reduced nitrate plus original nitrite) was then determined by diazotizing with sulfanilamide followed by coupling with N-(1-naphthyl)ethylenediamine dihydrochloride. The resulting water soluble dye had a magenta colour which was read at 520 nm. One potential problem with the method is that the build-up of suspended matter in the reduction column can restrict the sample flow. Since nitrate-nitrogen is soluble, the sample may be filtered. Low results would be obtained for samples that contain high concentrations of iron, copper or other metals. In this method, EDTA was added to the buffer to reduce this interference. A Lachat Quikchem Automated Flow Injection Analyser was used in the determinations. Quality control samples were included at 1 in 10 samples. Nutrient solutions were analysed on Lachat 3 using nitrate, ammonium and chloride multi-standards.

3.6.4 Chloride in water

Thiocyanate ion is liberated from mercuric thiocyanate by the formation of soluble mercuric chloride. In the presence of ferric ions, free thiocyanate ions form the highly-coloured ferric thiocyanate, of which the absorbance is proportional to the chloride concentration. Ferric thiocyanate absorbs strongly at 480 nm. The calibration curve is non-linear. Interferences are caused by substances such as sulphate and thiosulphate which reduce Fe^{III}

to iron Fe^{II} and Hg^{III} to Hg^{II} . Halides which also form strong complexes with mercuric ion (example: Br^- , I^-), give a positive interference. Quality control samples were included at 1 per 10 samples or 1 per batch.

3.6.5 Nitrogen by Leco instrumentation (Leco FP428)

The sample was combusted in an oxygen atmosphere and the gaseous products were cleaned. The nitrogen compounds were converted to nitrogen, which was measured by a thermal conductivity cell. Results were expressed on a "sample as received" basis and reported to two decimal places. Duplicate analysis carried-out on the same sample by the same analyst within a short period of time was targetted to agree to within 0.1 % nitrogen absolute.

3.6.6 Plant sap analysis

Plant sap analysis was performed, at the States of Guernsey Horticultural Advisory Service Laboratory, on leaf tissue samples using a 1:10 macerated water extract (Smith, 1988). Fully-expanded, new leaves were sampled from the crops and were received at the processing laboratory within 24 hours.

3.6.7 Solid substrate analysis

The total nutrient content of each substrate was determined by nitric acid digestion on samples before and after use. Acid digestion of the zeolite samples involved drying at 105°C and milling to $45\ \mu\text{m}$, followed by treating one gram of zeolite with 10 ml of concentrated nitric acid. This was boiled-down to 50 % volume and then a further 5 ml of concentrated hydrochloric acid was added. After warming gently and cooling, the solution was made-up to 100 ml, filtered and then analysed by ICP-AES. This digestion does not dissolve silica but causes lattice disruption by leaching of aluminium.

The sodium exchange process involved sampling five grams of zeolite and adding 100 ml of 1M sodium chloride. This mixture was shaken for one hour and the supernatant was then decanted, followed by the addition of a fresh 100 ml aliquot of sodium chloride. This was

repeated a total of four times. The 400 ml sample (sodium chloride plus ions exchanged out of the zeolite) was made-up to 500 ml and then analysed by ICP-AES.

3.6.8 Statistical analysis and interpretation

Where appropriate, data were analysed for statistical differences using Minitab 11. Differences between treatments were subjected to Fisher's Variance Ratio test (F-test) and the calculated probability of significance value (p-value) determined. The p-values were then assigned a significance indicator (*, ** or ***) associated with the standard convention where: $p > 0.05$ n.s. (not significant)

$0.05 > p > 0.01$ *

$0.01 > p > 0.001$ **

$0.001 > p$ ***

Where an F-test indicates that a significant difference exists between the levels of a treatment, it is appropriate to calculate a Least Significant Difference statistic (LSD). Where the F-test is not significant, LSDs are not calculated due to the risk of making Type 1 errors (i.e. adjudging differences to be significant which are in fact not significant) (Parker, 1973). In several experiments, due to extremely large numbers and cost of analyses undertaken, a strategic decision was made for single sample analyses of water samples over time. In order to minimise errors, representative samples from plots were collected and bulked prior to analysis. During analysis, it was routine for a minimum of duplicate measurements to be taken on each sample to ensure consistency of results and remain within the quality control system of the laboratory (see page 91).

In unreplicated experiments, varieties were used as surrogate replicates to compare between substrates (for example, Experiments 2 and 5).



Plate 3.1 Clinoptilolite zeolite at Beli Plast, Bulgaria

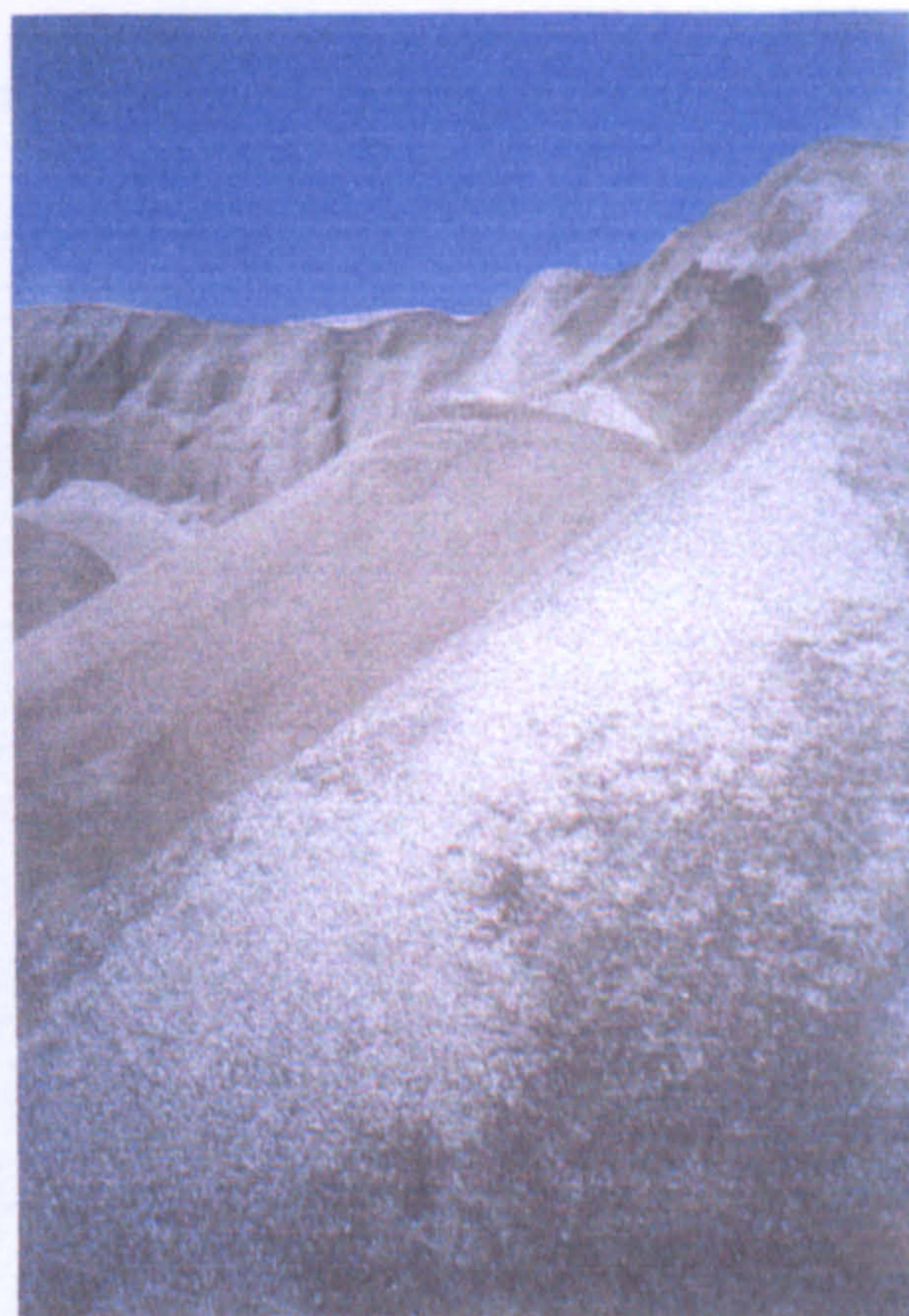


Plate 3.2 Icelandic pumice in storage

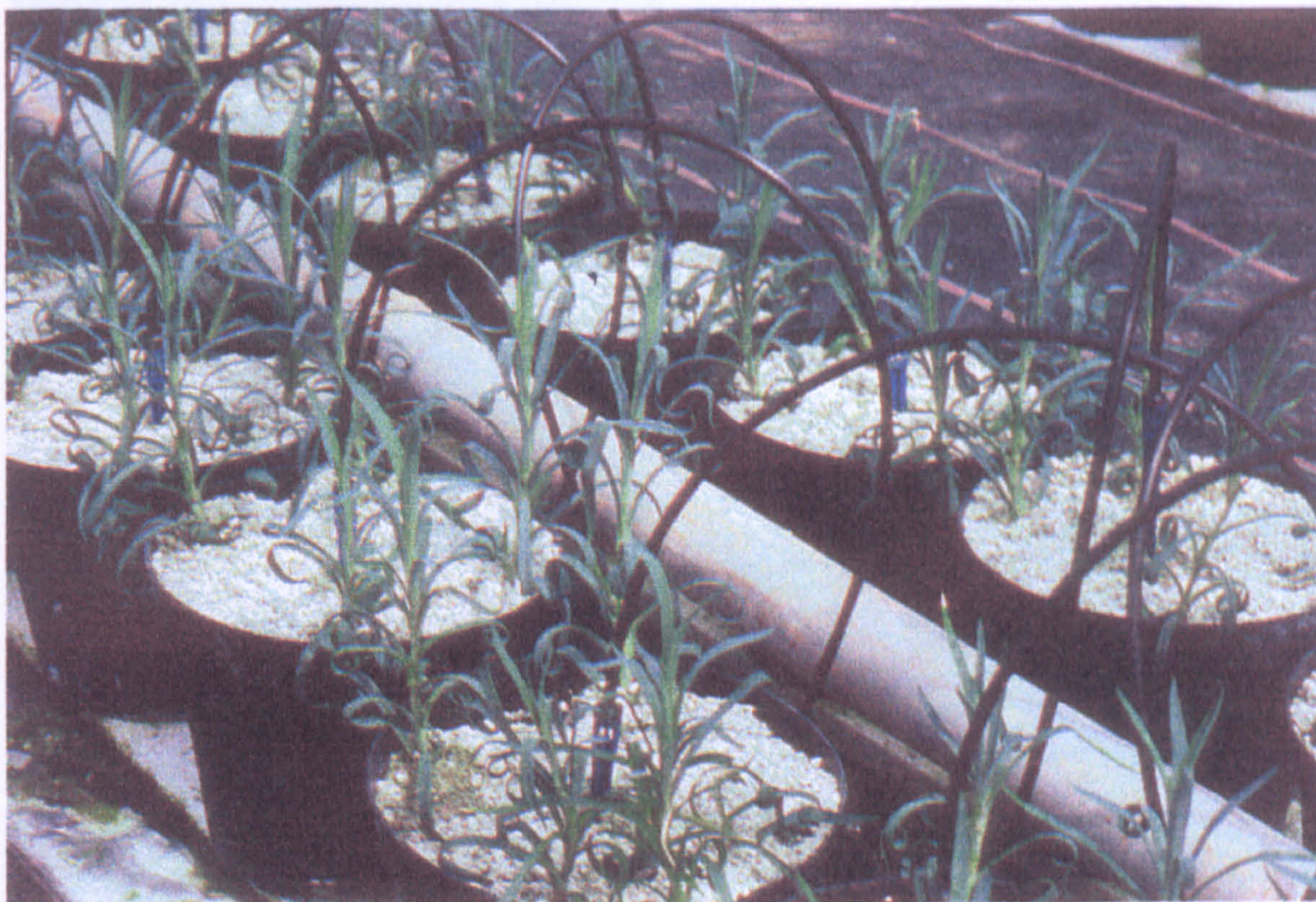


Plate 3.3 Standard carnation cuttings in nutrient-loaded zeolite



Plate 3.4 Layout of standard carnation plots

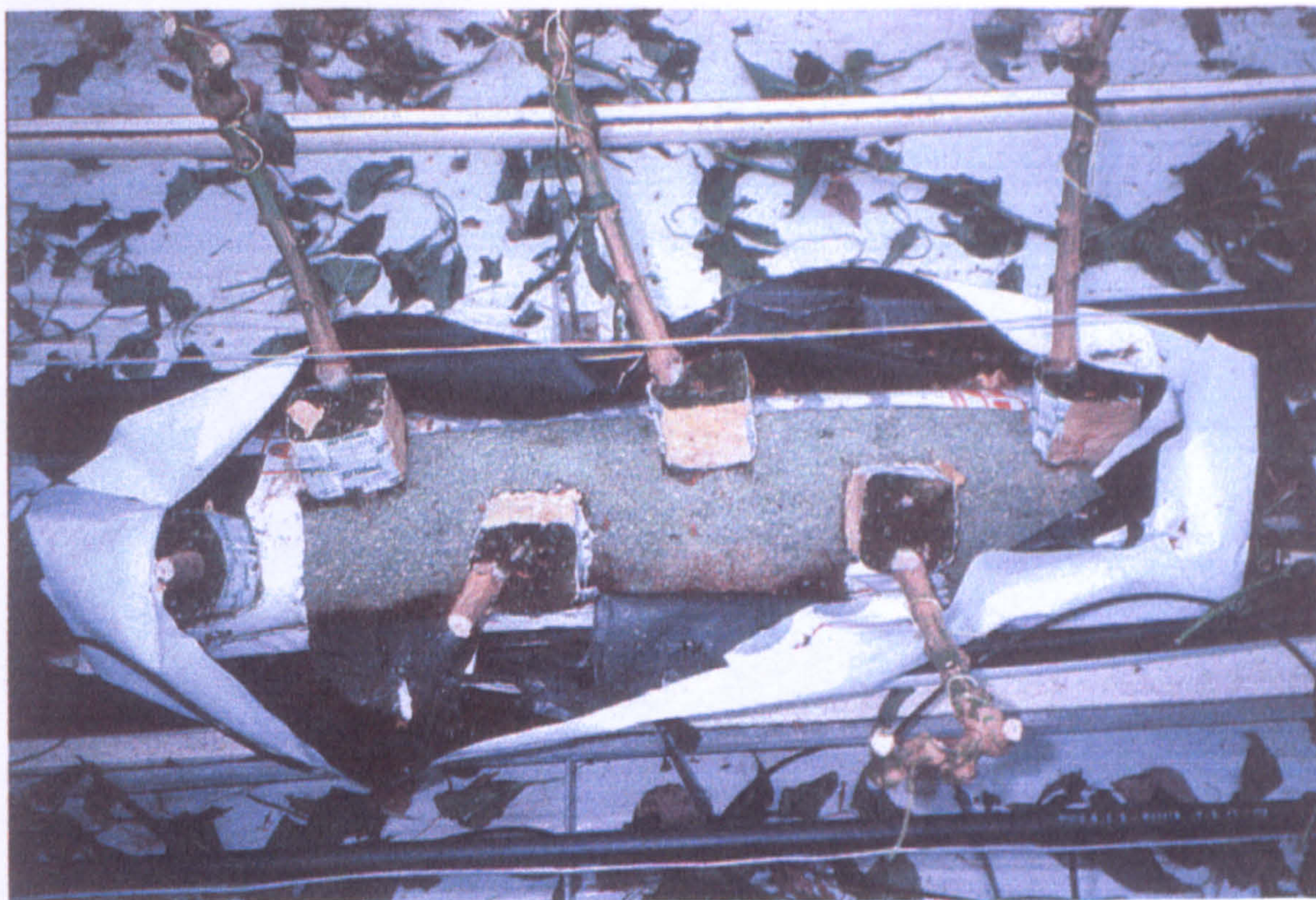


Plate 3.5 Sweet pepper plants in unloaded zeolite



Plate 3.6 Sweet pepper root distribution in nutrient-loaded zeolite



Plate 3.7 Sweet peppers in unloaded and nutrient-loaded zeolites



Plate 3.8 Mature sweet pepper plants in high nutrient-loaded zeolite (left), low nutrient-loaded zeolite (centre) and unloaded zeolite (right)

Chapter Four Unloaded clinoptilolite zeolite as a plant growth substrate

4.1 Introduction

Having established the physical characteristics of clinoptilolite and described the protocols utilised in the culture of salad and flower crops on aluminosilicate substrates, this Chapter details four experiments involving unloaded clinoptilolite zeolite. The unique physical and chemical properties of natural zeolites make them useful for many agronomic and horticultural applications, such as hydroponics (zeoponics), soil improvement and as slow release fertilisers (Allen and Ming, 1995). These applications have broad appeal across the technological spectrum ranging from potential uses in developing countries to applications in outer space (Ming, 1989).

The aim of the experiments was to prove that it is possible to grow a range of crop plants on clinoptilolite using liquid feeds at each watering. Plant growth characteristics were examined to ascertain if there were any differences in growth rate or development, especially with flowering and fruiting. The nutritional profiles of plants grown on standard and clinoptilolite substrates were also assessed. Further, the performance of crops grown on clinoptilolite was measured against standard substrates such as peat, rockwool and pumice in an attempt to show that yield and quality of produce was not compromised by using clinoptilolite. Drainwater nutrient content was examined with the aim of highlighting any differences which may be important in the possible contamination of water courses by waste nutrient solution after movement through the substrate. Contamination of potable water by nutrients is not only an issue of human health but also one of significant ecological concern. Nutrients are essential to the health and diversity of surface waters but, in excessive amounts, can be harmful to aquatic life. Pollution of surface water by nitrogen and phosphorus causes hyper-eutrophication resulting in an over-abundance of primary producers leading to a decline in dissolved oxygen and suffocation of other aquatic life (Lott

et al., 1999). Therefore, the aim to reduce nutrient losses from these systems is important and laudable.

Following pot trials, in which a range of plants were grown in clinoptilolite substrates, a series of larger scale experiments was designed and the initial experiment involved a comparison of the growth of tomato plants on unloaded clinoptilolite and two types of rockwool slab.

4.2 Experiment 1 A comparison of unloaded clinoptilolite zeolite with new and steam sterilised rockwool as substrates in the long season production of the speciality tomato (*Lycopersicon esculentum*) variety 'Manhattan'

4.2.1 Objectives

1. To assess the growth and development of tomato cv. 'Manhattan' plants on unloaded clinoptilolite receiving nutrient-balanced liquid feed inputs at each watering.
2. To measure the changes in nutrient concentration of drainwater from the nutrient recirculation system.
3. To compare the fruit yield and quality of tomato cv. 'Manhattan' grown on three substrate systems.

4.2.2 Materials and methods

The experiment was conducted over the period October 1991 to October 1992. The seeds were sown into rockwool cubes on 23 October and the seedlings were blocked-on into rockwool blocks on 31 October. The blocks were planted on the rockwool slabs or clinoptilolite modules on 30 November and the first fruit harvest was on 10 February. Harvesting continued until 2 October.

Unloaded clinoptilolite was placed in 0.8 metre long polyethylene bags and two plants were positioned on each substrate module at planting. Three plants were positioned on each new

or steam sterilised Grodan 1.2 metre rockwool slabs and a traditional double row layout was used to give a final plant density across each compartment of 29,500 plants hectare⁻¹. The steam sterilised rockwool had originally been used as the substrate in the production of long season tomatoes during season 1990/1991. Sterilisation was effected by using steam to hold a mid-stack slab temperature of 90°C for two hours. The trial was replicated twice, using two compartments (houses I and IV in Appendix I) on the east and west edges of the main research glasshouse block at Howard Davis Farm. It was not possible to randomise the layout of the substrates within each glasshouse and each substrate occupied one double row in each compartment. The drainwater from the three systems was collected, monitored and recirculated back to the crop throughout the main growing period. Weekly crop management programmes were identical for all three substrates but irrigation requirements were calculated using water use and water drainage data from plants on the new rockwool slabs.

4.2.3 Results and discussion

There were no visible differences with tomato plant leaf, stem, root, flower and fruit development characteristics between plants grown on unloaded clinoptilolite and the two rockwool substrates. Tomato plants grown in unloaded clinoptilolite had an average stem length of 9.86 metres and developed 37.8 fruit trusses per plant by the end of the production season. In comparison, plants on new rockwool and steam sterilised rockwool had average stem lengths of 9.62 metres and 9.94 metres, respectively. The number of trusses produced was 38.0 and 38.2 for the new rockwool and steam sterilised rockwool systems, respectively.

The drainwater nutrient analysis data showed that there were no marked differences between the concentration of most nutrients in the unloaded clinoptilolite and rockwool substrates (Table 4.1). Drainwater potassium and calcium concentrations, however, were different

during the crop establishment period and beyond the start of fruit harvesting, with potassium much lower and calcium much higher in the unloaded clinoptilolite drainwater samples (Figure 4.1). Thereafter, potassium concentrations in the unloaded clinoptilolite and new rockwool drainwater samples showed no differences. This suggests that potassium from the applied liquid feeds was preferentially adsorbed by the clinoptilolite and that there was a corresponding release of calcium from the clinoptilolite. This calcium would have been available for plant uptake but high conductivity levels in the root zone could have prevented a balanced uptake of nutrients. Hershey *et al* (1980), found that clinoptilolite has a high affinity for the cations ammonium-nitrogen and potassium and that the addition of clinoptilolite (unspecified source) to potting mixes for *Chrysanthemum morifolium* can serve as a slow-release source of potassium, ammonium-nitrogen, iron, manganese, copper and zinc. They also commented that, in leaching experiments, large concentrations of calcium and magnesium ions were also present in solution and that their affinity for clinoptilolite is much less than that of ammonium-nitrogen. Depending on the source of the clinoptilolite, there could have been a release of calcium and magnesium ions from the clinoptilolite used in their experiments, as part of the overall cation exchange process.

Ammonium-nitrogen concentrations were consistently lower in the clinoptilolite drainwater samples (Table 4.1) and, initially, magnesium and phosphorus concentrations were lower (Figure 4.2) and sodium higher (Figure 4.3) in drainwater from the clinoptilolite treatment. Semmens (1984) summarised by stating that in real systems, specific ions, such as ammonium-nitrogen, compete with other ions for exchange sites in the zeolite. In addition, the ability of clinoptilolite to remove a given ion, such as ammonium-nitrogen, from water is adversely affected by the presence of competing ions, such as sodium and calcium. Mumpton (1984a) stated that sodium zeolites may release detrimental amounts of sodium into soil, as they exchange with the soil and / or fertiliser constituents. As stated in Chapter Two, samples of clinoptilolite from the Beli Plast deposit in the Rhodopes, Bulgaria were

Figure 4.1 Comparison of unloaded clinoptilolite (Z) and new rockwool (NR) drainwater potassium and calcium concentrations

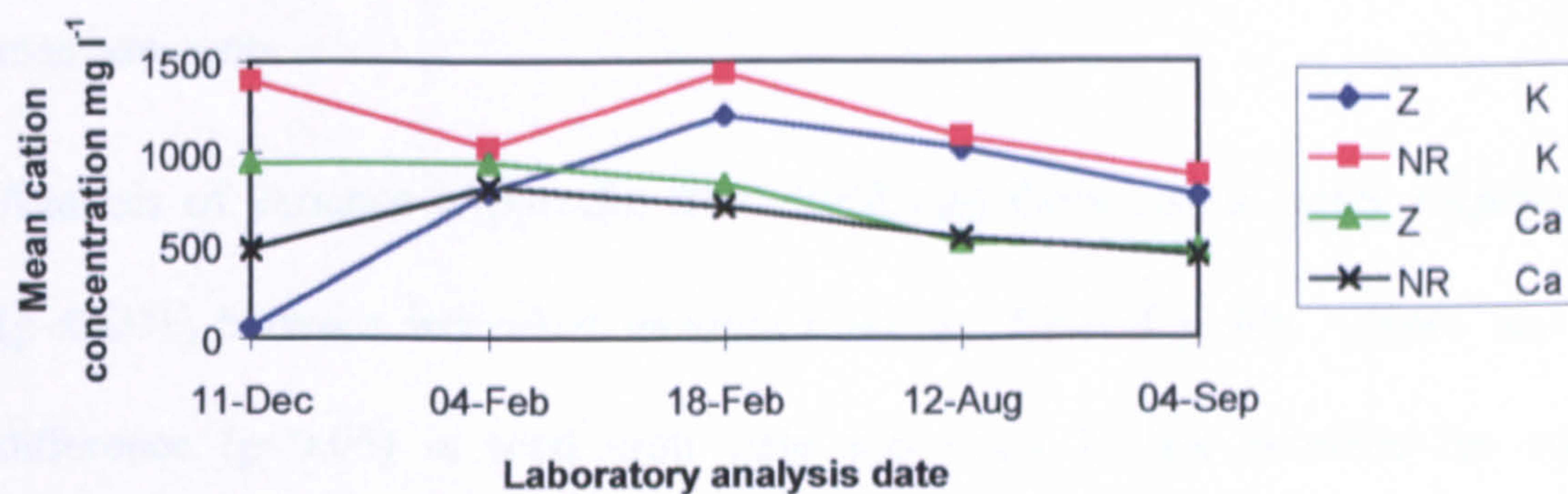


Figure 4.2 Comparison of unloaded clinoptilolite (Z) and new rockwool (NR) drainwater magnesium and phosphorus concentrations

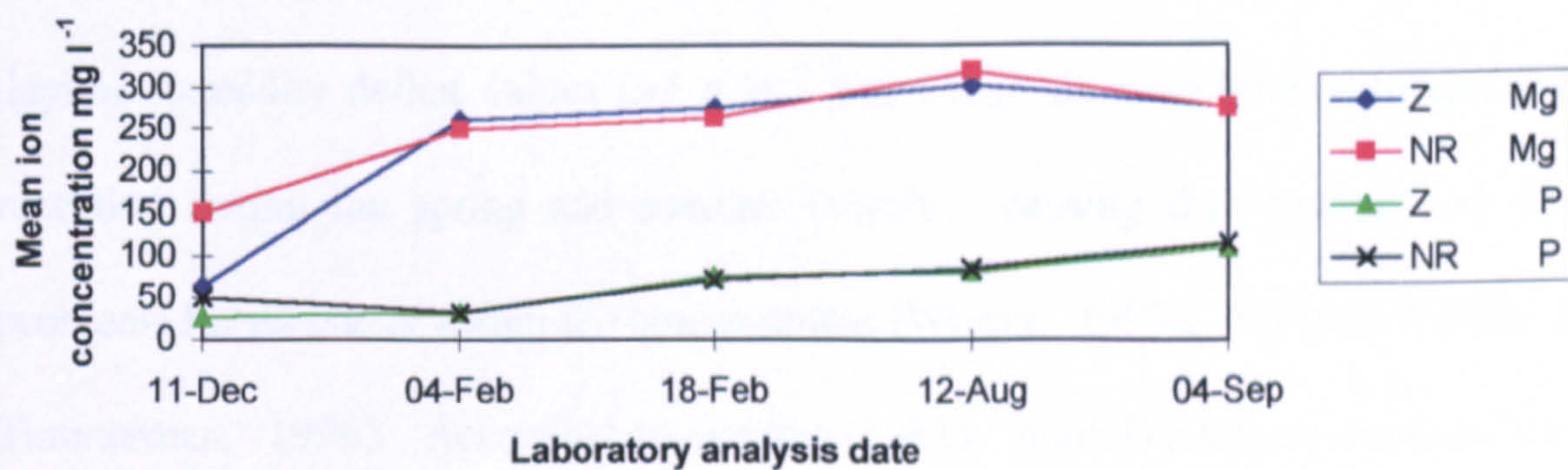
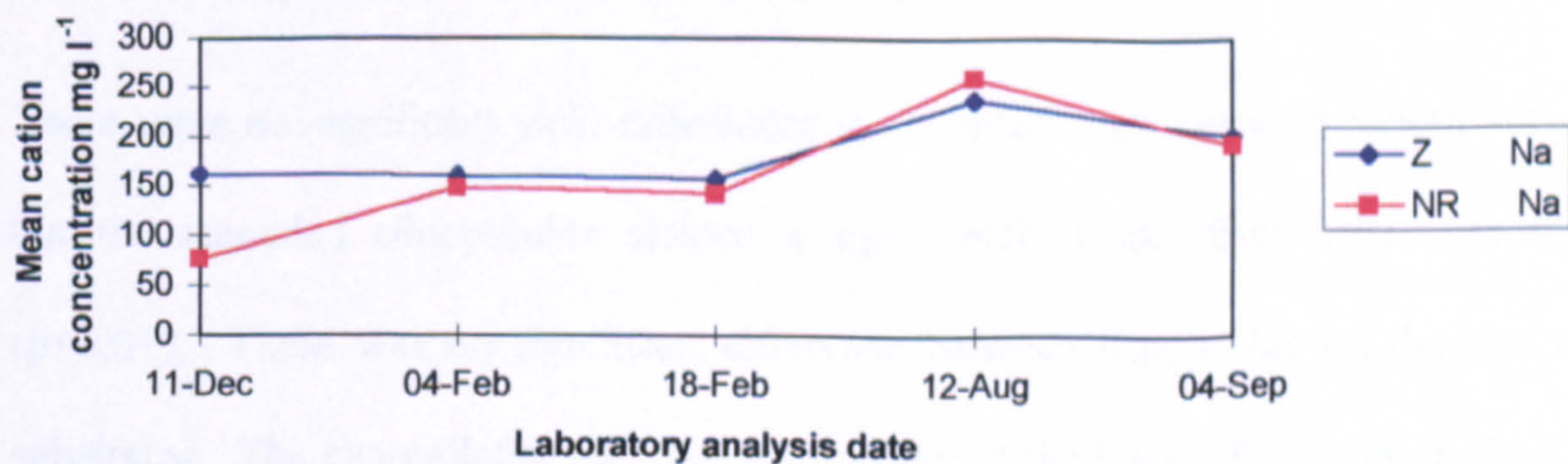


Figure 4.3 Comparison of unloaded clinoptilolite (Z) and new rockwool (NR) drainwater sodium concentrations



rich in potassium and calcium and poor in terms of sodium content. There were no other major differences with pH levels, conductivity, nitrate-nitrogen or trace element measurements.

Analysis of variance (Appendix II) showed that there was a highly significant difference ($p < 0.001$) between individual monthly total and Class I yields. There was a significant difference ($p < 0.05$) in total crop yield and Class I yield between the two replicates, presumably due to the east and west orientations of the glasshouse compartments, with the total yield higher and the quantity of Class II fruit lower in the west compartment (Table 4.2). It was noted that control of summer temperatures and humidity levels was uneven in the outer compartments of the glasshouse, leading to variable flower setting and fruit quality problems. Environmental control in the east compartment was also difficult and high daytime humidity deficit values ($>5 \text{ g kg}^{-1}$) and high daytime temperatures ($>24^{\circ}\text{C}$) were recorded during the spring and summer months, causing fruit setting and development problems for all plants within the compartment (Wright, 1993a; Wright, 1993b; Kamp and Timmerman, 1996). According to Bakker (1991), humidity affects stomatal conductance and crop photosynthesis. Humidity also affects transpiration to a large extent, not only through the effect on the vapour pressure gradient between the leaf and surrounding air but also due to the response of leaf conductance (Stanghellini, 1987). The number of fruits that develop on a truss is determined by the number of flowers per truss and the relative number of flowers that become fruits (percentage fruit set) (de Koning, 1994).

There were no significant yield differences in the interaction between month and substrate but the unloaded clinoptilolite yielded a significantly lower fruit total over the season ($p < 0.01$). There was no significant difference between fruit yields on the two rockwool substrates. The clinoptilolite substrate also produced the lowest fruit total in the 33-40 mm size range and this difference was significant ($p < 0.05$). There were no other significant

differences between substrates at fruit size grades 20-25 mm and 25-33 mm. Although the new rockwool substrate produced the highest Class II fruit total, the difference was not significant. The clinoptilolite substrate fruit yield and size could have been compromised by gearing irrigation regimes to the requirements of tomato plants on new rockwool slabs. If the feed composition had been adjusted in favour of the clinoptilolite substrate (that is, lower potassium and calcium inputs), it is possible that total yield could have been higher and fruit size increased.

4.2.4 Conclusions

- Growth and development of tomato plants on unloaded clinoptilolite was virtually identical to production on rockwool slabs.
- The clinoptilolite adsorbed potassium and released calcium into the root zone throughout the early plant growth and fruit production phases.
- Concentrations of sodium released from the clinoptilolite did not adversely affect the growth and development of the plants.
- Fruit quality was very similar from all substrates although the fruit from the clinoptilolite substrate was slightly smaller than from the rockwool plots.
- Unloaded clinoptilolite can be successfully used as a substrate to produce acceptable yields of Class I long season speciality tomatoes in an hydroponic system.
- Rockwool slabs can be utilised for a second production season, following steam sterilisation to control pest, disease and virus problems, with no loss of production or adverse effect on fruit quality.

Table 4.1 Comparison of substrate nutrient concentrations for unloaded clinoptilolite zeolite (Z) and new rockwool (R/W). Measurements were in mg litre⁻¹ except for: pH; and EC (μS cm⁻¹), (n=1)

Substrate sample means	11/12/91		04/02/92		18/02/92		12/08/92		04/09/92	
Determinand	Z	R/W	Z	R/W	Z	R/W	Z	R/W	Z	R/W
pH	6.1	6.2	5.7	5.5	5.9	5.7	6.2	6.2	5.8	5.8
EC	5250	6850	7870	7900	8345	8210	6800	7245	6750	6850
NH ₄ -N	0.4	1.6	0.7	0.8	1.1	2.85	0.65	0.9	0.7	0.85
NO ₃ -N	642	740	987	924	990	989	709	770	677	690
P	28	50	33	32	76	72	81	84	110	115
K	60	1395	782	1026	1200	1435	1020	1083	759	873
Ca	948	481	941	806	826	703	516	539	474	441
Mg	65	152	262	251	277	265	303	321	278	277
Na	163	77	162	149	159	143	239	261	202	194
Fe	2.14	2.89	3.22	3.16	4.51	4.27	2.84	3.01	3.72	3.79
Mn	0.37	0.42	0.86	0.86	0.64	0.63	0.14	0.18	0.69	0.73
Cu	0.11	0.16	0.13	0.13	0.12	0.12	0.07	0.08	0.09	0.10
Zn	0.94	1.01	1.50	1.42	1.69	1.58	1.02	1.08	1.10	1.11
B	0.55	0.63	0.77	0.76	0.80	0.69	0.85	0.92	0.91	0.92

Table 4.2 Mean yield profile for tomato cv. 'Manhattan' on three substrates (substrate fresh weight means kg plot⁻¹). L.S.D. = least significant difference, n.s. = not significant

Fruit quality / fruit size	Class I 20-25 mm	Class I 25-33 mm	Class I 33-40 mm	Class II	Total marketable yield
Unloaded clinoptilolite	0.297	65.333	23.039	0.007	88.677
New rockwool	0.098	67.195	30.226	0.022	97.541
Steamed rockwool	0.284	65.797	30.575	0.009	96.666
L.S.D. 5%			5.430		5.697
L.S.D. 1%					7.701
F-test significance level	p = n.s.	p = n.s.	p = *	p = n.s.	p = **

4.3 Experiment 2 A comparison of nine sweet pepper varieties (*Capsicum annuum*) with the standard variety 'Mazurka' on an unloaded clinoptilolite zeolite substrate

4.3.1 Introduction

As part of the preliminary investigation into the suitability of unloaded clinoptilolite zeolite in the production of long season salad crops under glass, a range of sweet pepper varieties were planted on clinoptilolite modules. Pepper fruits were harvested green and fully coloured (ripe) from two separate compartments. Unused drainwater from both compartments was collected, monitored and recirculated back to the crop throughout the main growing period, allowing an assessment of clinoptilolite as an interactive or participative substrate within a nutrient recirculation system.

4.3.2 Objectives

1. To compare the fruit yield and quality of each variety harvested both green and coloured on unloaded clinoptilolite.
2. To assess the growth of sweet pepper plants on unloaded clinoptilolite receiving nutrient-balanced liquid feed inputs at each watering.
3. To measure the changes in the drainwater nutrient concentration of the clinoptilolite nutrient recirculation system.

4.3.3 Materials and methods

Nine varieties were compared with the standard variety 'Mazurka' and are listed in Table 4.3.

Table 4.3 Varieties of sweet pepper

Variety	Seed supplier	Colour range	Comments
Mazurka	Rijk Zwaan	Green / red	Standard variety
Sirtaki	Rijk Zwaan	Green / yellow	Ripens to yellow
Reflex	Pinetree De Ruiter	Green / red	Ripens to red
Daphne	Pinetree De Ruiter	Green / yellow	
Kelvin	Pinetree De Ruiter	Green / yellow	
066	Pinetree De Ruiter	Green / red	
Augusta	Enza Zaden	Green / red	
6155	Enza Zaden	Green / orange	Ripens to orange
Helena	Enza Zaden	Green / red	
Tasty	Breeders	Green / red	

The experiment ran from November 1992 to October 1993. The seeds were sown into rockwool cubes on 4 November and seedling emergence occurred on 11 November. All varieties were blocked-on by placing the propagation cubes on their sides in the rockwool blocks on 17 November. The plants were placed on modules each containing 9 litres of

unloaded, clinoptilolite zeolite on 14 December. Following the removal of the crown flowers on 7 January and the second stage flowers on 11 January, the first harvest was recorded on 5 March. No summer carbon dioxide enrichment system was available for this crop. Nutrient recirculation was engaged on 14 December and continued until the final harvest on 14 October.

The standard plant spacing was 3 plants per 0.95 metre module, in traditional double rows, to give 30,000 plants hectare⁻¹ or 60,000 heads hectare⁻¹. The experiment was conducted in two identical glasshouse blocks (houses II and III), within the main research unit at Howard Davis Farm (Appendix I). Fruit from house II was harvested green throughout the season whilst ripe fruit from house III was picked over the period March to October inclusive. Initially, however, in order to prevent overloading of the plants, sweet pepper fruit from house III were picked green and side-shoot fruit were also harvested green during the main production season.

4.3.4 Results and discussion

4.3.4.1 Green fruit yield

The variety 'Helena' produced the highest total Class I and total marketable yields of green fruit to the end of week 41, with 20.92 kg m⁻² and 22.48 kg m⁻², respectively (Table 4.4). 'Mazurka' yielded a Class I total of 20.24 kg m⁻² and a marketable fruit total of 21.10 kg m⁻². The varieties 'Tasty' and 'Mazurka' had the highest waste fruit totals of 1.58 kg m⁻² and 1.57 kg m⁻², respectively.

4.3.4.2 Coloured fruit yield

'Reflex' produced the highest total marketable yield of ripe fruit at 20.29 kg m⁻² (Table 4.5). 'Mazurka' had a total marketable fruit yield of 19.84 kg m⁻² and a higher

Class I total of 18.96 kg m⁻², compared with 18.51 kg m⁻² from 'Reflex.' 'Mazurka' had the highest waste fruit total of 1.02 kg m⁻².

The differences in Class I and total marketable yields between varieties harvested green and ripe were statistically significant ($p < 0.05$) and the difference between the two compartments was highly significant ($p < 0.001$) (Table 4.6) (Appendix II).

The absence of a summer carbon dioxide enrichment system resulted in compartment carbon dioxide levels dropping below external ambient levels (350 ppm) during the spring and summer months. This will have probably decreased fruit yield and quality over the same period (Nederhoff, 1994).

4.3.4.3 Drainwater nutrient concentration

There were highly significant differences ($p < 0.01$) between potassium, magnesium, sodium and manganese concentrations from the two compartments over the period December to September inclusive (Table 4.7). There were also significant differences ($p < 0.05$) between compartment system conductivity levels and calcium, nitrate-nitrogen and zinc concentrations (Appendix II). Concentrations of ammonium-nitrogen, phosphorus, iron, copper, boron and pH levels were not significantly different.

Analyses of drainwater samples taken from both compartments throughout the season revealed that potassium was being preferentially adsorbed by the clinoptilolite (Hershey *et al.*, 1980) and that calcium was being released into the root zone (Figure 4.4). There were no visible plant potassium deficiency symptoms present at any time during the vegetative or generative growth phases and pepper fruit quality was unaffected by this. Replacement feed stock nutrient levels were regularly adjusted to take account of the potassium and calcium analytical results. Levels of blossom end rot were low in the crop and this was thought to

be partly due to the good availability of calcium in the root zone, unimpeded uptake and good distribution of calcium within the plant (Marschner, 1995; Ho *et al.*, 1999).

Measurements of drainwater magnesium revealed initial concentrations below 20 mg l⁻¹, followed by a slow increase to >40 mg l⁻¹ from January to March inclusive. Further increases in drainwater magnesium concentrations above 50 mg l⁻¹ were measured from July (Figure 4.5). Drainwater nitrate-nitrogen concentrations were maintained (150-250 mg l⁻¹) throughout the crop establishment phase until the start of picking (Figure 4.6). Although input feeds were adjusted in an attempt to increase nitrate-nitrogen availability, plant anion demand outstripped supply to the end of the season. Drainwater nitrate-nitrogen concentrations fell below 150 mg l⁻¹ in April and may have reduced vegetative growth and also total fruit yield. According to Marschner (1995), when the supply of nitrogen is suboptimal, plant growth is retarded, nitrogen is mobilised in mature leaves and retranslocated to areas of new growth. Conversely, there were no foliar nitrate-nitrogen deficiency symptoms present in the crop at any time with the possible exception of the lowest leaves, which were removed in September to increase air flow around the plant bases and reduce the possibility of a late infection by *Botrytis cinerea*. Measured concentrations of ammonium-nitrogen were very low in the drainwater samples (<1.0 mg l⁻¹) throughout most of the season, suggesting rapid plant uptake and, possibly, adsorption by the clinoptilolite (Semmens, 1984); (Figure 4.6). Measurements of drainwater revealed that the sodium concentration did not drop below 100 mg l⁻¹ during the experiment (Figure 4.7). There were no major differences between trace element, pH and conductivity measurements from the two compartments (Figures 4.8, 4.9, 4.10 and 4.11).

4.3.5 Conclusions

- Commercially acceptable yields and quality fruit were produced from plants growing on clinoptilolite when used as a substrate for the production of long season peppers to be

Figure 4.4 Drainwater potassium and calcium concentrations from two glasshouse compartments with sweet peppers on unloaded clinoptilolite

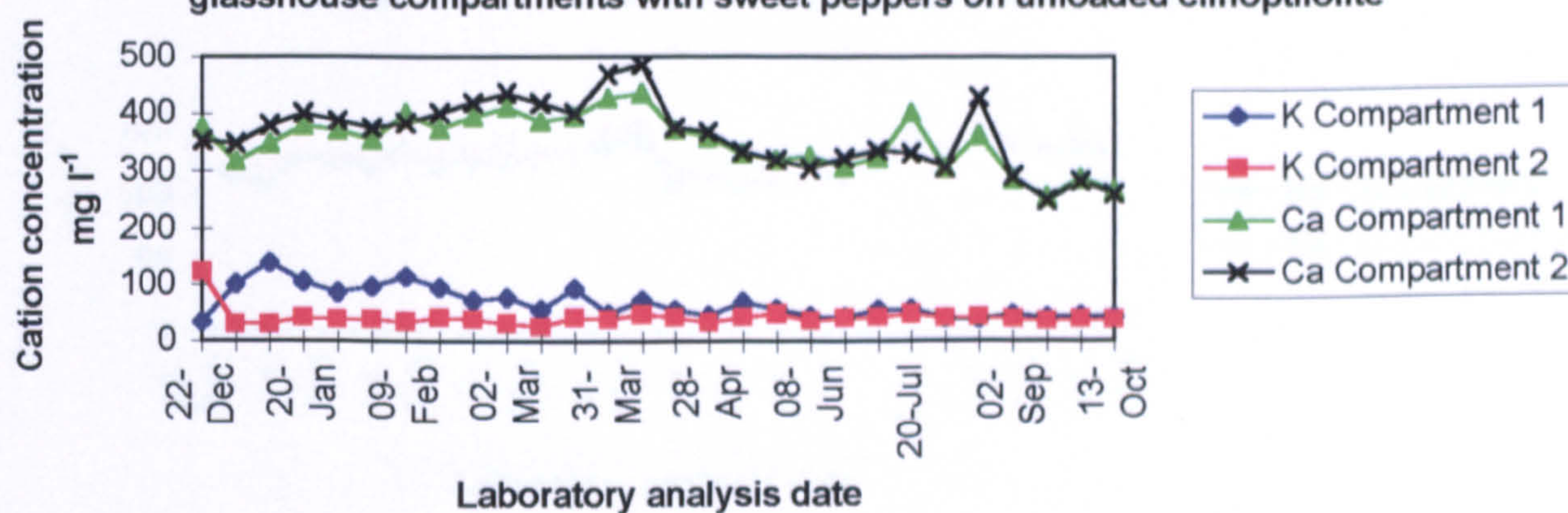


Figure 4.5 Drainwater magnesium and phosphorus concentrations from two glasshouse compartments with sweet peppers on unloaded clinoptilolite

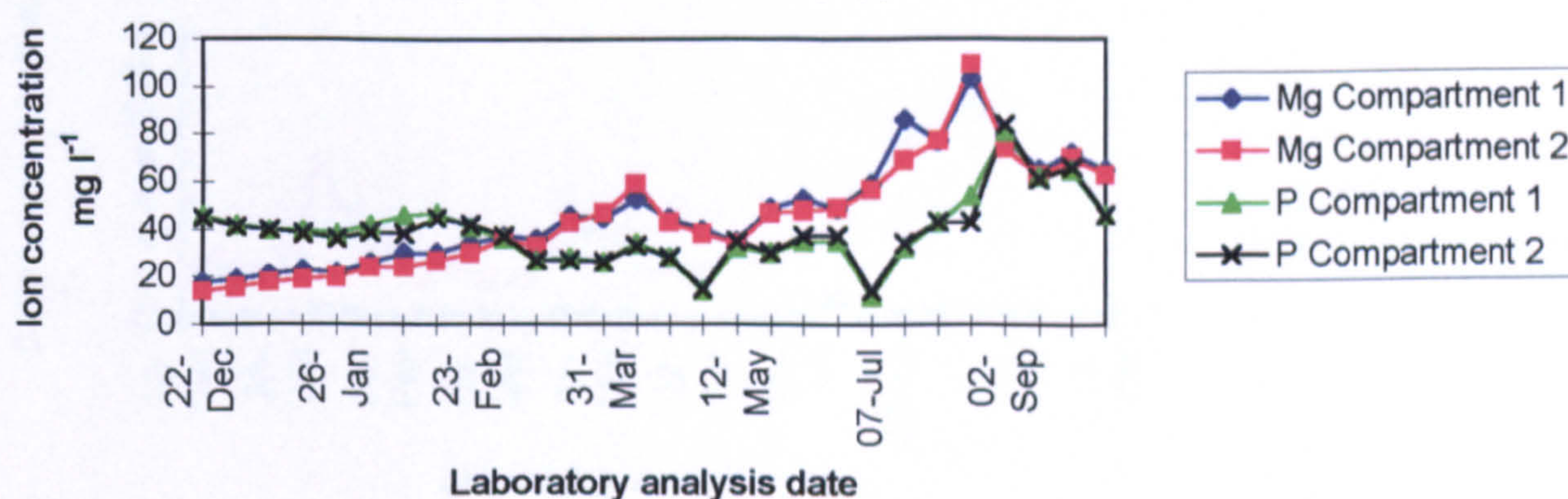


Figure 4.6 Drainwater nitrogen concentrations from two glasshouse compartments with sweet peppers on unloaded clinoptilolite

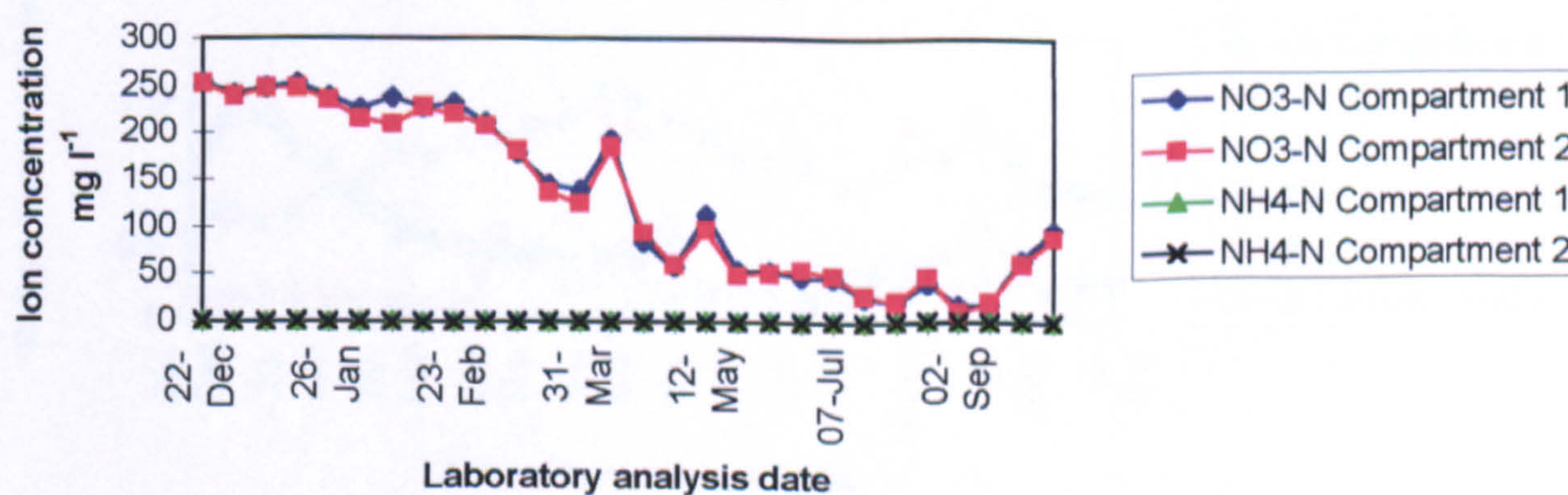


Figure 4.7 Drainwater sodium concentrations from two glasshouse compartments with sweet peppers on unloaded clinoptilolite

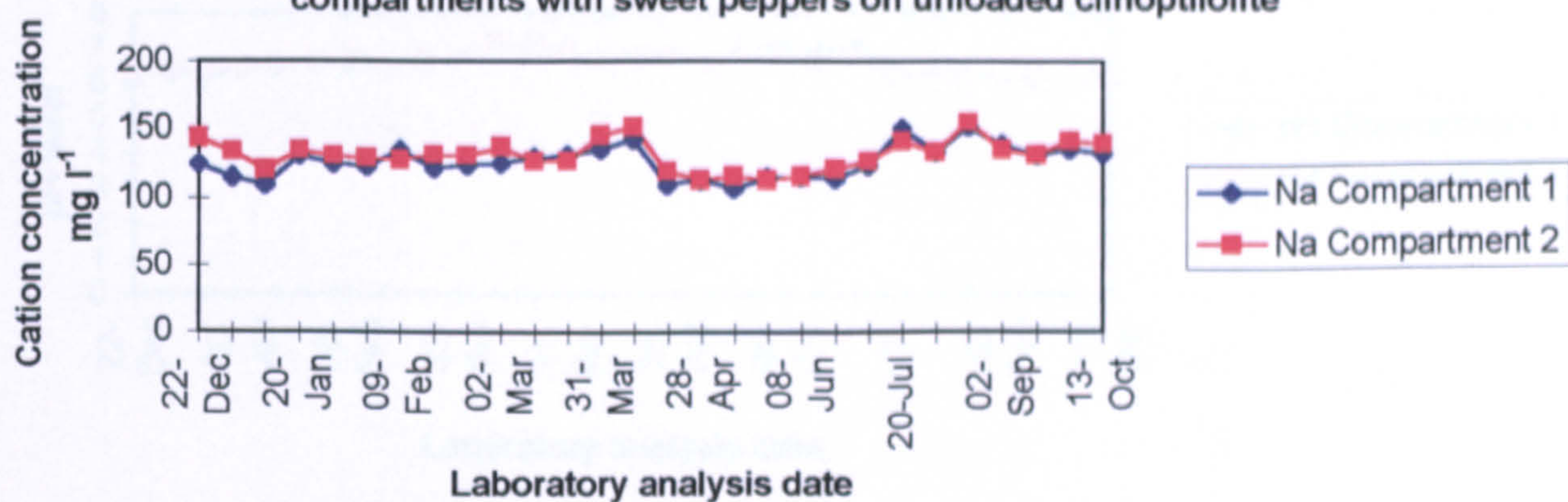


Figure 4.8 Drainwater iron and manganese concentrations from two glasshouse compartments with sweet peppers on unloaded clinoptilolite

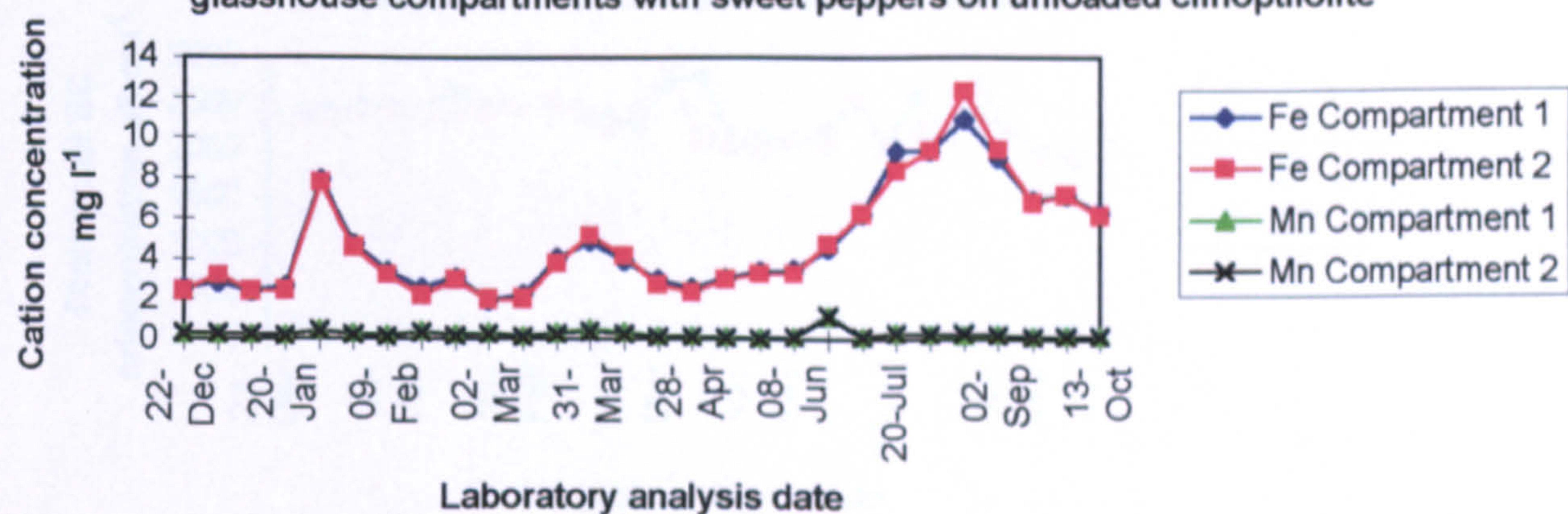


Figure 4.9 Drainwater copper, zinc and boron concentrations from two glasshouse compartments with sweet peppers on unloaded clinoptilolite

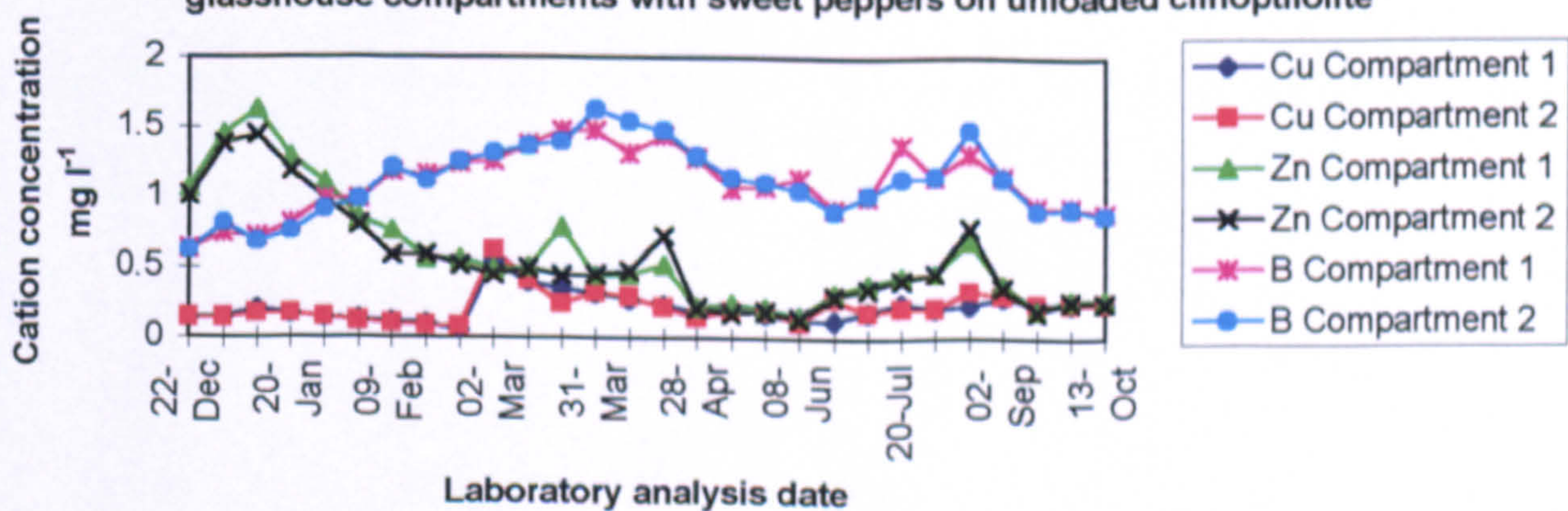


Figure 4.10 Drainwater pH levels from two glasshouse compartments with sweet peppers on unloaded clinoptilolite

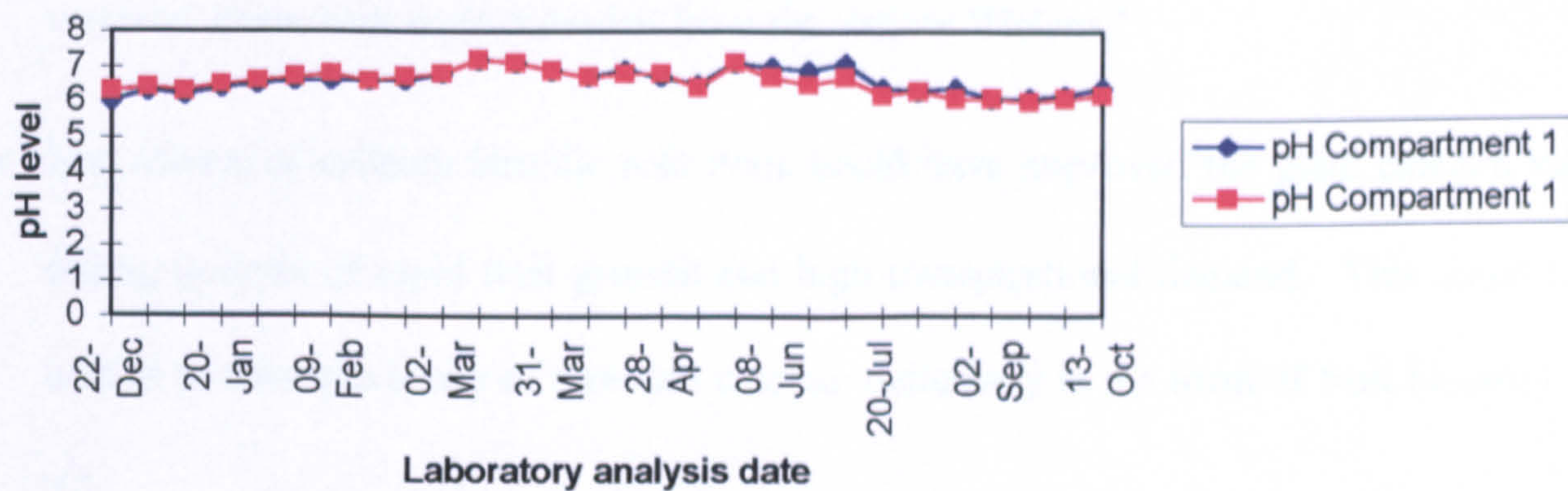
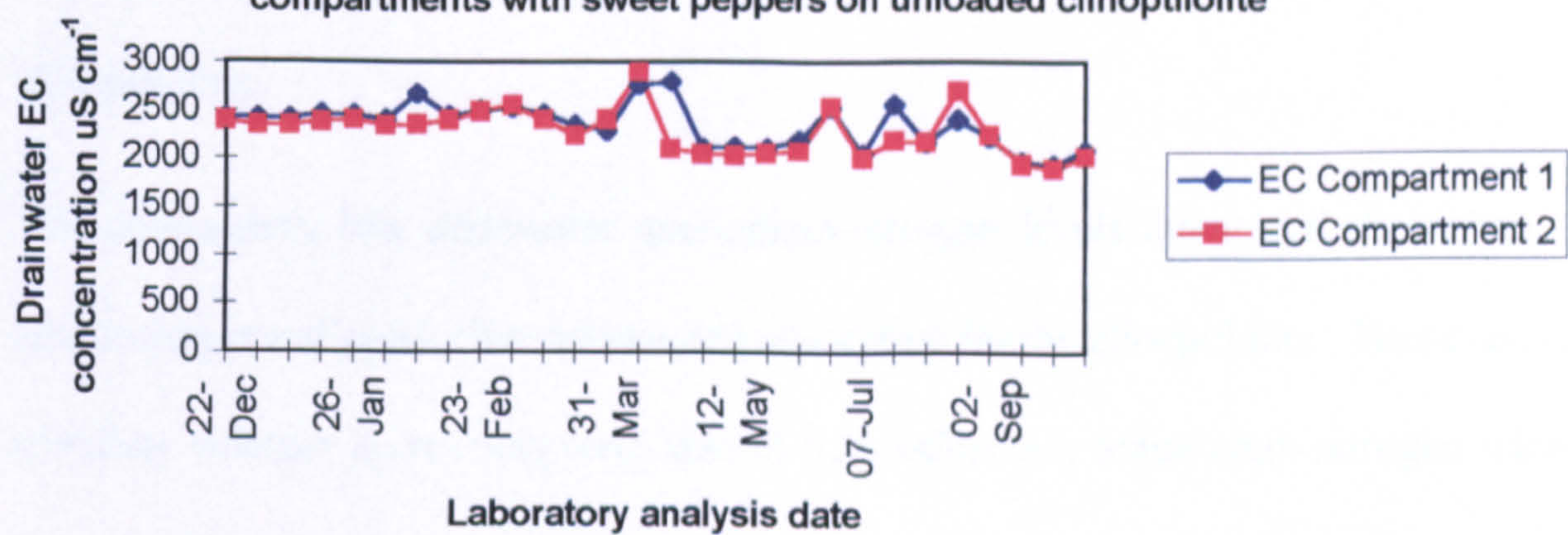


Figure 4.11 Drainwater EC concentrations from two glasshouse compartments with sweet peppers on unloaded clinoptilolite



harvested green or ripe. 'Mazurka' and 'Reflex' produced consistent yields of high quality green and red fruit over the season. The highest total class I and total marketable yields of green fruit were recorded from the variety 'Helena.'

- The release of calcium into the root zone could have improved the plant calcium status during periods of rapid fruit growth and high transpirational demand. This could have helped to decrease levels of transient calcium deficiency in the form of fruit blossom end rot.
- The absence of plant potassium deficiency symptoms suggests that the plant uptake of potassium was unimpeded by the clinoptilolite adsorption processes. It is not clear, however, whether there would have been any antagonistic effects on nutrient availability or plant uptake in the root zone, as a result of the cationic equilibrium surrounding the clinoptilolite.
- The consistently low drainwater ammonium-nitrogen levels monitored throughout the season suggested rapid plant uptake and adsorption by the clinoptilolite. However, it is not clear whether plant roots were able to fully utilise any ammonium-nitrogen released from the clinoptilolite or whether zeolite levels became depleted from March.
- Clearly, availability of nitrate-nitrogen is a limiting factor to sweet pepper plant cultivation in nutrient recirculation systems.
- The use of unloaded clinoptilolite as a substrate in recirculation systems may help to provide a buffer of potassium and calcium, especially during periods of high plant nutrient demand.

Table 4.4 Yield results for ten pepper varieties harvested green from plants growing on unloaded clinoptilolite zeolite (kg m⁻² fresh wt)

Fruit size / quality	60-70 mm	70-80 mm	90+ mm	Class I	Class II	Total	Waste
Helena	1.99	16.87	2.06	20.92	1.56	22.48	0.51
Reflex	3.48	16.32	0.56	20.36	1.46	21.82	0.98
Tasty	3.20	17.18	0.40	20.78	0.94	21.72	1.58
Mazurka	2.31	16.77	1.16	20.24	0.86	21.10	1.57
Kelvin	1.72	15.13	2.38	19.23	1.26	20.49	0.68
Daphne	2.43	15.45	0.93	18.81	1.11	19.92	0.47
Augusta	2.29	15.62	0.54	18.45	1.28	19.73	0.72
Sirtaki	1.16	14.07	3.19	18.42	1.11	19.53	0.95
066	3.16	14.16	0.64	17.96	1.41	19.37	0.69
6155	3.50	12.09	0.40	15.99	1.31	17.30	1.06

Table 4.5 Yield results for ten pepper varieties harvested ripe from plants growing on unloaded clinoptilolite zeolite (kg m⁻² fresh wt)

Fruit size / quality	60-70 mm	70-80 mm	90+ mm	Class I	Class II	Total	Waste
Helena	0.79	8.53	5.67	14.99	2.90	17.89	0.40
Reflex	1.99	13.52	3.00	18.51	1.78	20.29	0.55
Tasty	1.85	13.70	1.84	17.39	0.96	18.35	0.65
Mazurka	1.31	12.88	4.77	18.96	0.88	19.84	1.02
Kelvin	0.87	9.05	8.12	18.04	0.95	18.99	0.35
Daphne	1.24	11.05	4.35	16.64	0.85	17.49	0.31
Augusta	1.39	11.33	3.18	15.90	1.82	17.72	0.29
Sirtaki	0.72	7.98	8.28	16.98	0.98	17.96	0.43
066	1.90	11.96	2.32	16.18	1.66	17.84	0.35
6155	2.15	10.06	2.21	14.42	1.69	16.11	0.62

Table 4.6 Yield profile for sweet pepper varieties harvested green and ripe from plants growing on unloaded clinoptilolite zeolite (kg m⁻² fresh wt). L.S.D. = least significant difference.

Fruit quality	Class I	Total marketable yield
Green fruit	19.116	20.346
Ripe fruit	16.801	18.248
L.S.D (5%)	1.025	0.783
L.S.D (1%)	1.472	1.125
L.S.D (0.1%)	2.166	1.654
F-test significance level	p = ***	p = ***

Table 4.7 Sweet pepper production on unloaded clinoptilolite drainwater

nutrient analysis replicate means. L.S.D. = least significant difference,

n.s. = not significant, n = 1

	Replicate I (NE)	Replicate II (NW)	L.S.D. 5%	L.S.D. 1%	F-test significance level
pH	6.593	6.557			p = n.s.
EC	2352.500	2285.400	66.549		p = *
NH₄-N	0.554	0.484			p = n.s.
NO₃-N	134.690	130.710	3.103		p = *
P	39.357	38.821			n.s.
K	67.321	42.321	13.982	18.882	p = **
Ca	351.610	361.930	10.221		p = *
Mg	47.036	44.679	1.541	2.081	p = **
Na	126.360	131.040	2.657	3.588	p = **
Fe	4.789	4.763			p = n.s.
Mn	0.276	0.242	0.021	0.028	p = **
Cu	0.215	0.219			p = n.s.
Zn	0.597	0.557	0.037		p = *
B	1.115	1.119			p = n.s.

4.4 Experiment 3 A comparison of standard carnation (*Dianthus caryophyllus*) flower yield and quality from plants grown on six substrates: peat, cocofibre, woodchips, pumice, unloaded clinoptilolite and nutrient-loaded clinoptilolite 'Hydrocult S'

4.4.1 Introduction

This experiment was designed to test the responses of standard carnation varieties to cut flower production on a range of substrates under glasshouse conditions. In addition to the standard substrates in use in commercial production (peat and pumice), peat alternatives were screened (cocofibre and woodchips) and two types of clinoptilolite zeolite were also included.

The principal environmental concerns regarding growing media are the acquisition of constituents and production of the substrates and the accompanying release of nutrients and pesticides into groundwater during crop production using these systems (Carlile, 1999). Although naturally-occurring, peat is an example of a semi-finite resource, whereas rockwool, perlite and vermiculite all require energy inputs during their manufacture. In addition, there are widespread concerns over the disposal of these materials at the end of their useful periods as substrates. Inorganic materials, such as rockwool, are particularly stable and do not break down in soil, whereas organic substrates degrade more easily, releasing carbon dioxide and making a potential contribution to global warming (Carlile, 1999). One of the problems with the use of peat is the sustainability of the raw material itself and another problem is loss of structure over time. All peats have inherent water holding properties depending on their degree of humification (Bragg, 1995). Young sphagnum peats, for example, have a high air capacity and retain the ability to absorb water easily (Bunt, 1988). On milling to a fine particle size, the moisture retention properties are increased at the expense of the air holding capacity. Carnations are extremely

sensitive to waterlogging and oxygen starvation, necessitating good substrate drainage. The performance of peat substrates over time may ultimately depend on the balance between air and water contents in the root zone, coupled with the management of irrigation programmes, particularly during the winter months (Holmes, 1993).

Cocofibre is a waste ligno-cellulose material produced during preparation of coconuts for food use (Verdonck et al., 1983). The outer husks of coconut are rendered down in water to extract long fibres which are used in coconut matting. It is the spherical particles that comprise coir dust. One advantage of using cocofibre is that it has a relatively uniform particle size range and this is useful in avoiding waterlogging when used as a substrate. Cocofibre has little buffering capacity, however, and can be easily leached of soluble nutrients (Bragg, 1995).

Woodfibre is shredded timber which may have been treated with alkali to dissolve sugars involved with microbial breakdown of the wood (Bragg, 1995). As a result, the initial pH level may be higher than 6.5. There is little buffering capacity and a good starting air-filled porosity (AFP) - however, this reduces as the fibres become fully wetted and the woodfibre partially slumps.

In the light of these important considerations in the selection of a suitable substrate in protected crop cultivation, an experiment was designed to test several alternative materials, each with its own environmental benefits.

4.4.2 Objectives

1. To compare a range of substrates in the production of *Dianthus caryophyllus* grown under modern, computer-controlled, glasshouse environmental conditions.
2. To compare the flower production and quality of a range of varieties over a 19 month harvest period.
3. To measure the changes in the drainwater nutrient concentrations of the substrate systems, with particular emphasis on drainwater nitrogen content.

4.4.3 Materials and methods

The experiment was subdivided so that the peat, cocofibre and woodchip substrates occupied plots in house VII and the pumice and clinoptilolite substrates were positioned in house VIII (Appendix I). The glasshouse compartments were identical in terms of plant layout and equipment although house VII was situated on the eastern edge of the Robinson glasshouse block (Appendix I).

4.4.3.1 Peat / peat alternative substrates

The dry peat boards were supplied in plastic sleeves measuring one metre by 15 cm in width. Once wetted-up, the slabs had a 45 litre volume and 16 plant cuttings were inserted into each hydrated board. The cocofibre was supplied loose and, after pH adjustment, was transferred to five litre, black polypropylene pots. The cocofibre was modified by the addition of ground limestone at a rate of 2.6 kg m^{-3} in order to increase the initial root zone pH from 5.0 to 6.2. Cuttings were inserted at four per pot. The woodchip substrate was utilised as supplied. Each woodchip bag measured one metre by 15 cm and comprised an outer plastic wrapper with an inner liner of clear plastic netting enclosing the woodchips. Eight cuttings were inserted into each substrate module. All sleeves were subsequently slit

to allow drainwater movement out of the plastic modules. Substrate types and volumes are summarised in Table 4.8.

Table 4.8 Substrate types and volumes used in the comparison of standard carnation varieties

Substrate type	Substrate volume (litres)	Substrate volume per plant (litres)
Peat (Vapo boards)	45	2.81
Cocofibre (Golden Grow / Dutch Plantin)	5	1.25
Woodchips (Hortifibre)	16	2.00

The following varieties were compared on the peat, cocofibre and woodchip substrate systems.

1. Yellow Candy (Selecta)
2. Master (Barbaret and Blanc)
3. Sahara (Shemi)

The cuttings were planted over the period 19-21 February 1992 and the final flower harvest was on 31 December 1993.

In each metre length of bed there were eight cocofibre pots, four woodchip bags or two peat boards and all were planted with a total of 32 cuttings. The varieties were replicated three times on each substrate in a fully randomised design. A polypropylene, spun-fibre, crop cover (UV17) was installed as a tent from 21 February-10 March 1992 in order to maintain heat, moisture and humidity levels around the cuttings. Developing plantlets were

then “stopped” by removal of the plant growing points at five to seven pairs of leaves on 12 March, to encourage the formation of side shoots.

4.4.3.2 Aluminosilicate substrates

All substrates were placed in five litre, black polypropylene pots and plant cuttings were inserted at four per pot. The volume of pumice, unloaded clinoptilolite and nutrient-loaded clinoptilolite was 1.25 litres per plant. Eight pots per metre length of bed were positioned in a double row layout, to give a plant density of 32 plants m². Three varieties were replicated three times on each substrate in a fully randomised design in this compartment (Plate 3.4). A polypropylene, spun-fibre, crop cover (UV 17) was positioned as a tent over the pots from 19 February to 3 March 1992 and the cuttings were stopped at five to seven pairs of leaves on 5 March.

The following varieties were compared on the pumice and clinoptilolite substrates.

1. Yellow Candy (Selecta)
2. Forever (Lek and Zonen)
3. Omagio (Shemi)

The cuttings were planted over the period 19-21 February 1992 and the final flower harvest was on 31 December 1993.

4.4.4 Results: peat / peat alternative substrates

As the overall crop irrigation requirements were based on the moisture content of the cocofibre pots, it was more difficult to accurately gauge the moisture content of the two sleeved substrates. As a result, there were problems with overwatering during the winter and, in particular, the woodchip bags became waterlogged and a rapid decomposition of the contents ensued. Each woodchip bag slumped over the growing season, causing a reduction in AFP (Table 4.9). The peat boards were also susceptible to overwatering,

particularly during the winter months. As a result, disease problems, such as *Fusarium culmorum* (stub rot), contributed to poor crop growth following the winter period (MAFF, 1967) and caused subsequent plant losses.

A series of three air-filled porosity measurements were taken before and after use for each substrate and these revealed that AFP values of the woodchips and cocofibre reduced by more than 50 % over the 22 month growing period (Table 4.9).

Table 4.9 Air-filled porosity measurements of peat and peat-alternatives

Substrate	Mean original AFP %	Mean final AFP %	% reduction
Peat	16.4	13.8	15.9
Cocofibre	25.4	11.1	56.3
Woodchips	63.8	30.3	52.5

Examination of the root systems at the end of the experiment revealed that the peat boards contained healthy roots at the top and middle areas of the boards but the peat was very wet towards the bases, with poor root development. The cocofibre root systems were more healthy by comparison. The woodchips had partially decomposed and some rooting through the drainage slits and into the glasshouse soil had occurred. It is possible that movement of roots into the glasshouse soil could have predisposed the root systems to infection by diseases such as *Fusarium culmorum* and *Fusarium oxysporum*.

The first flower harvest from the peat and peat alternative substrates was on 15 June. There were no significant differences between Class I flower yields m² of the varieties 'Yellow Candy,' 'Master' and 'Sahara' grown on peat, cocofibre and woodchips (p>0.05)

(Appendix II). The highest total marketable production of 'Yellow Candy' flowers was recorded from the woodchip plots at 503 stems m^{-2} and, in comparison, the highest marketable flower totals from the peat and cocofibre plots were 459 and 432 blooms m^{-2} , respectively. The mean total Class I blooms m^{-2} for the three combined varieties on peat, cocofibre and woodchips were 506, 490 and 525, respectively.

4.4.5 Results: aluminosilicate substrates

The crop irrigation requirements were based on the moisture content of the clinoptilolite substrates. Particle size distribution in the clinoptilolite substrates was very even, resulting in rapid surface drying. Evaporation of moisture at the pot surface, particularly at the start of the trial before full crop cover had been reached, was a particular problem related to the zeolite substrates (Plate 3.3).

The first flowers were harvested on 10 June and there were no significant differences between Class I flower yields m^{-2} of the varieties 'Yellow Candy,' 'Forever' and 'Omaggio' grown on pumice, unloaded clinoptilolite zeolite and nutrient-loaded clinoptilolite zeolite 'Hydrocult S' ($p>0.05$) (Appendix II). The highest total production of 'Yellow Candy' flowers was recorded from the pumice plots with 447 stems m^{-2} . In comparison, the total marketable flower totals for the clinoptilolite and nutrient-loaded clinoptilolite were 421 and 423 stems m^{-2} , respectively. The mean total Class I blooms m^{-2} for the three combined varieties on pumice, clinoptilolite and nutrient-loaded clinoptilolite were 425, 452 and 451, respectively.

Statistical analysis of the combined Class I flower yields m^{-2} for the variety 'Yellow Candy' on all six substrates indicated that there were no significant differences between the substrates ($p>0.05$)(Table 4.10).

4.4.6 Nutrient concentration changes: peat / peat alternative substrates

The peat and cocofibre drainwater nutrient concentrations for potassium showed little variation over the 22 month sampling period (Figure 4.12). Carnations have a high requirement for potassium (MAFF, 1967) and drainwater potassium concentrations from the woodchips were lower during the main flower flush periods (for example, July 1992). Conversely, the woodchip substrate leached more potassium between flower flushes (for example, September 1992).

Calcium drainwater concentrations for all three substrates were very closely matched during the first year of flower production (Figure 4.13). In the second year, however, higher calcium concentrations were measured in the cocofibre and woodchip drainwater samples. It was noticeable that the calcium drainwater concentrations were lower during the major flower flushes in July of both years, perhaps due to high demand for calcium by rapidly expanding cells in flower stems and buds (Marschner, 1995).

Drainwater nutrient concentrations for nitrate-nitrogen showed similar concentrations for all three substrates in the first year of the experiment (Figure 4.14). Higher drainwater nitrate-nitrogen concentrations were recorded from the cocofibre and woodchip substrates in the second year, however.

Drainwater samples taken from the woodchip substrate contained concentrations of ammonium-nitrogen above 1.0 mg l^{-1} in March, May and June in 1992 and also in February, July, August and September in 1993 (Figure 4.15). Decomposition of the woodchips over the experimental period may have released ammonia causing low pH conditions in the root zone. Ammonium-nitrogen concentrations in drainwater from peat and cocofibre substrates were comparatively lower and more consistent, being within the range 0.5 to $1.0 \text{ mg litre}^{-1}$.

Figure 4.12 Drainwater potassium concentrations for peat, cocofibre (coco) and woodchip (wood) substrates

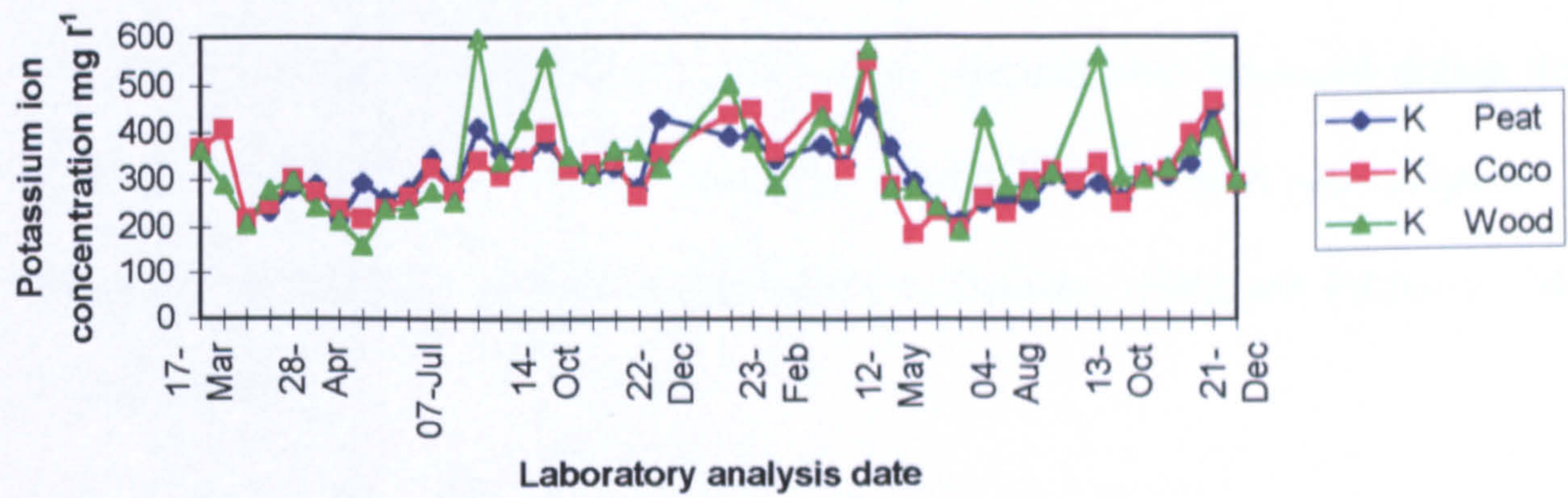


Figure 4.13 Drainwater calcium concentrations for peat, cocofibre (coco) and woodchip (wood) substrates

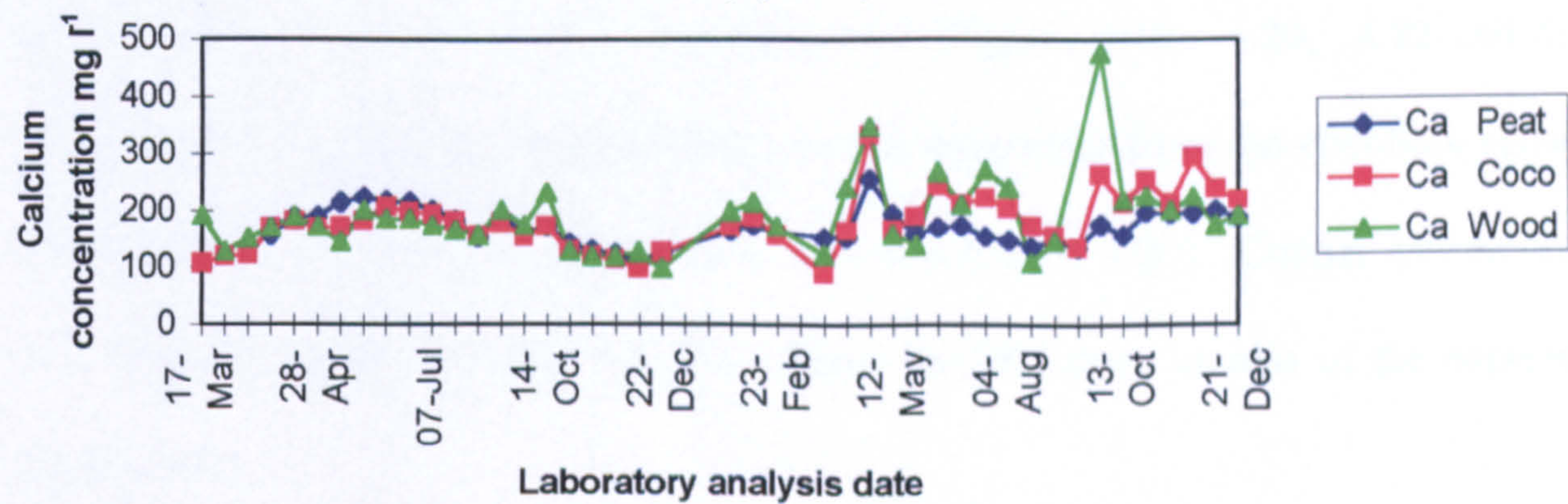
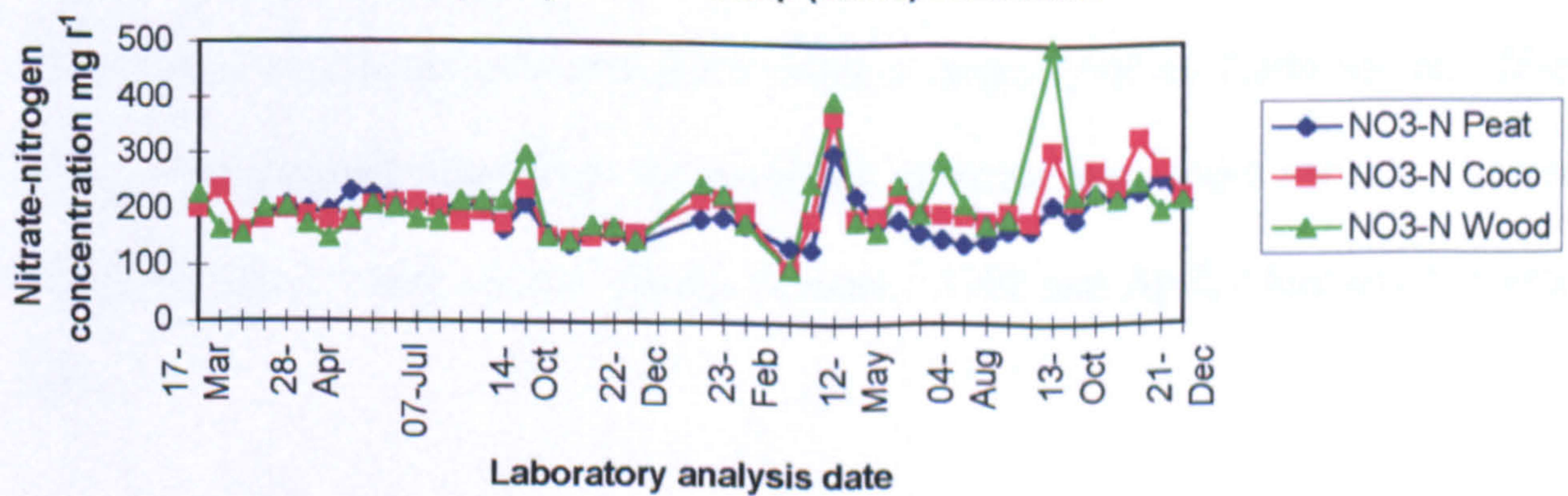


Figure 4.14 Drainwater nitrate-nitrogen concentrations for peat, cocofibre (coco) and woodchip (wood) substrates



Magnesium drainwater concentrations were very similar for all three substrates in the first year (Figure 4.16). Higher concentrations of magnesium were detected during periods of vegetative growth, for example October, 1992, April, 1993 and September, 1993.

Low concentrations of phosphorus in drainwater samples were measured during flower flushes in the peat substrate, for example July and December in both years (Figure 4.17). Phosphorus drainwater concentrations increased in October, 1992 and February, March and April, 1993.

Sodium concentrations were very similar in drainwater taken from all three substrates, with the exception of an isolated sample from the woodchip substrate in September, 1993 which showed a concentration approximately three times higher than other readings (Figure 4.18).

Iron, manganese, zinc and boron concentrations in drainwater were generally higher from the woodchip substrate over the sampling period (Figures 4.19, 4.20, 4.22 and 4.23). Manganese concentrations were extremely low in drainwater from the cocofibre substrate throughout the 22 month sampling period, however (Figure 4.20). Copper concentrations were lower from the woodchip substrate during the first three months of the experiment (Figure 4.21).

Drainwater pH levels started at pH 7.0 from the cocofibre and woodchip substrates and remained within a pH range of 6.0 to 7.5 for most of the production season (Figure 4.24). Woodchip samples had the lowest pH readings overall but rarely dropped below pH 6.0.

Measurements of drainwater EC from the peat and cocofibre substrates revealed a steady concentration profile over the two years within a range 1,500 to 2,500 $\mu\text{S cm}^{-1}$ (Figure 4.25). Measurements taken from the woodchip substrate were more variable, however, with peaks above 3,000 $\mu\text{S cm}^{-1}$ during October, 1992 and April, July and September, 1993.

Figure 4.15 Drainwater ammonium-nitrogen concentrations for peat, cocofibre (coco) and woodchip (wood) substrates

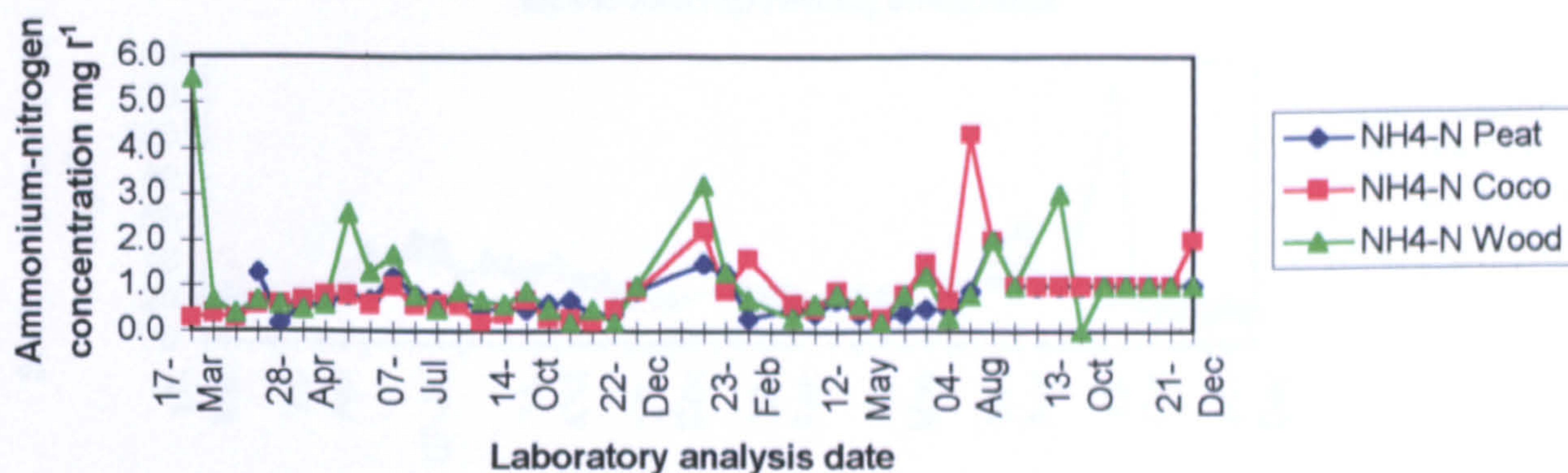


Figure 4.16 Drainwater magnesium concentrations for peat, cocofibre (coco) and woodchip (wood) substrates

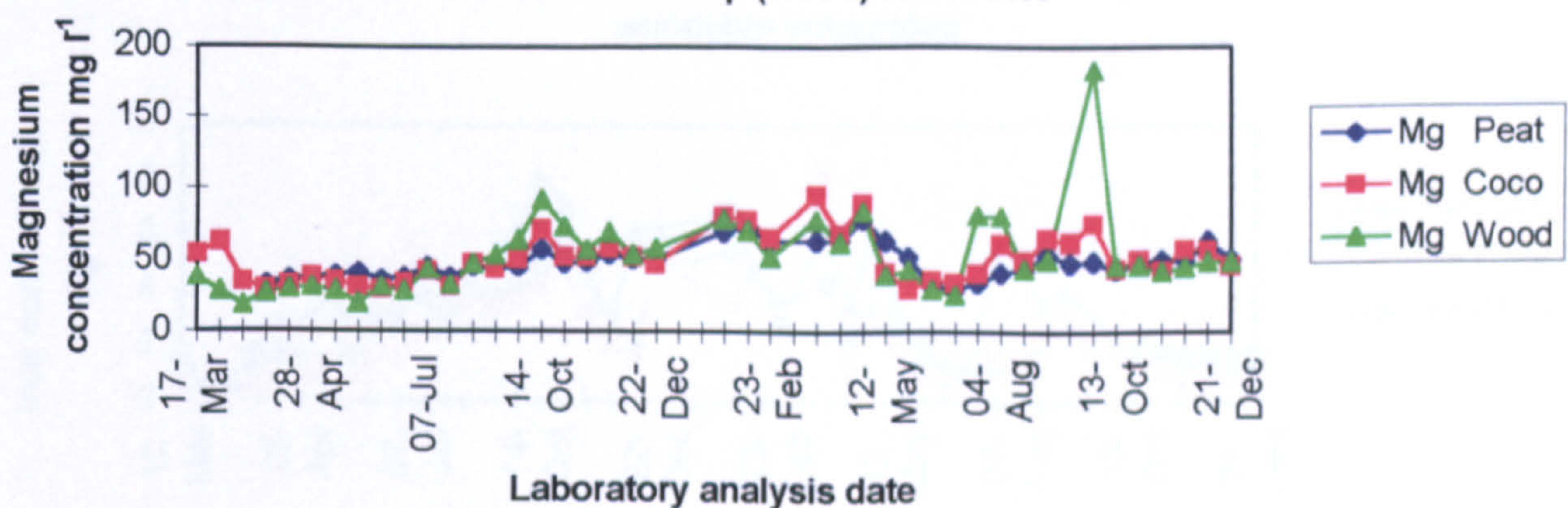


Figure 4.17 Drainwater phosphorus concentrations for peat, cocofibre (coco) and woodchip (wood) substrates

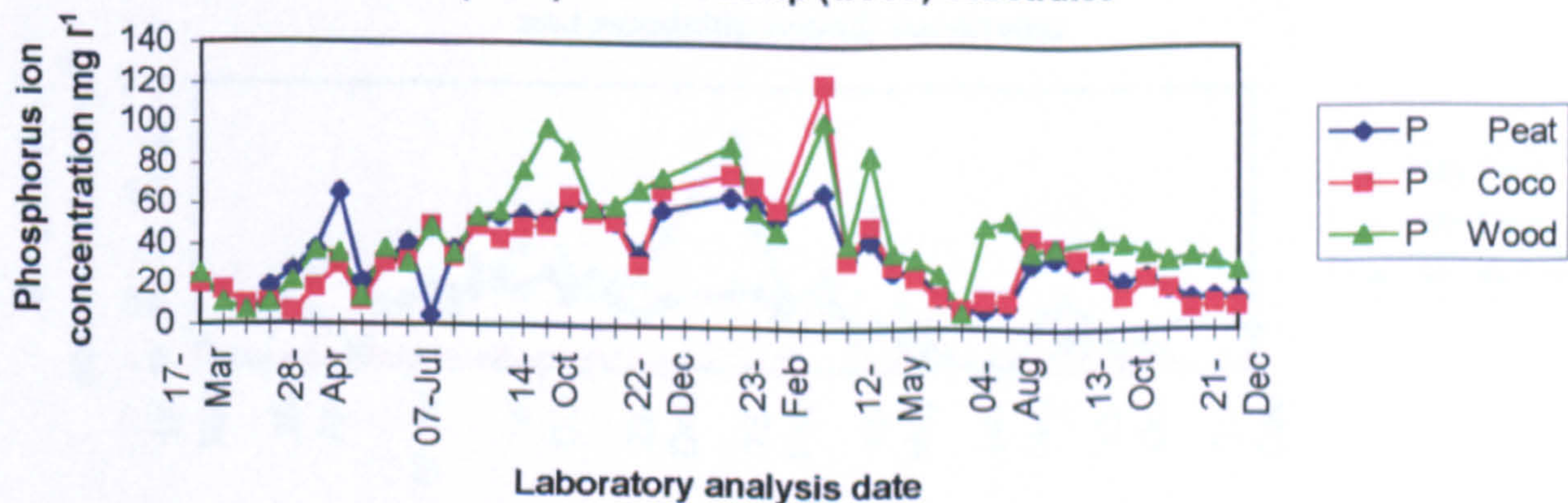


Figure 4.18 Drainwater sodium concentrations for peat, cocofibre (coco) and woodchip (wood) substrates

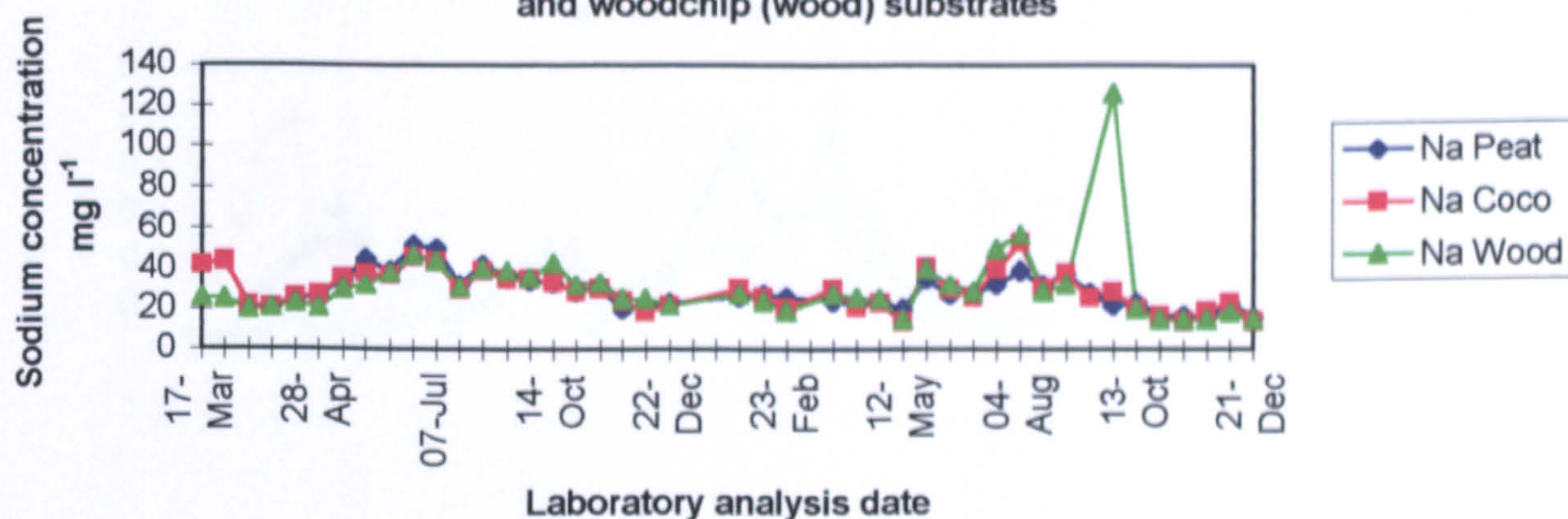


Figure 4.19 Drainwater iron concentrations for peat, cocofibre and woodchip substrates

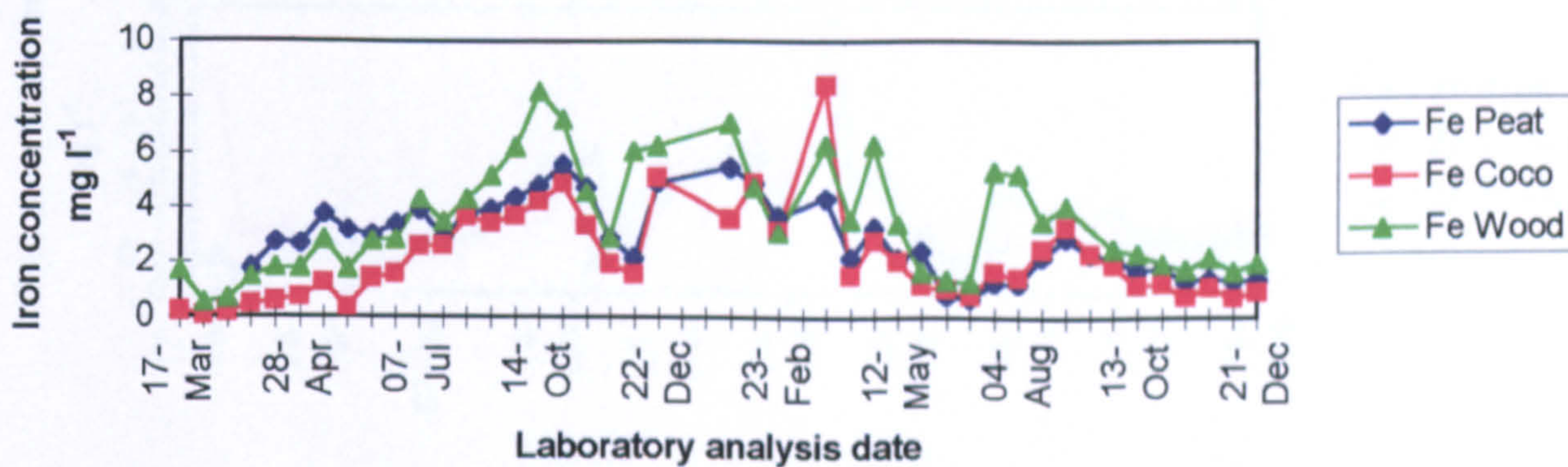


Figure 4.20 Drainwater manganese concentrations for peat, cocofibre (coco) and woodchip (wood) substrates

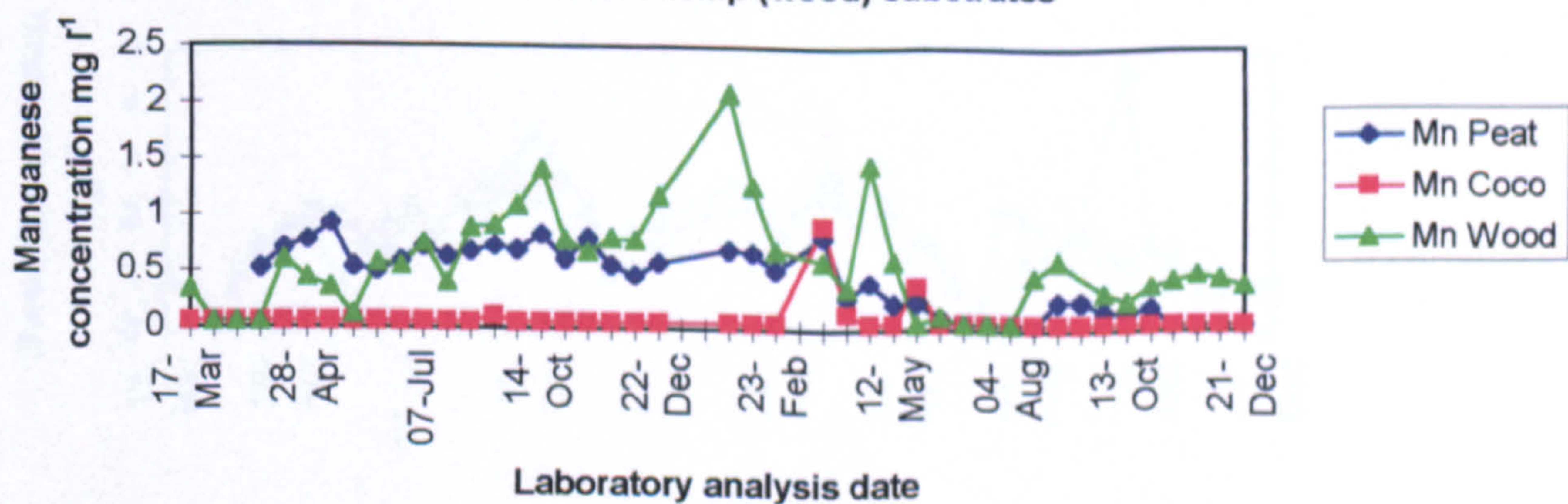


Figure 4.21 Drainwater copper concentrations for peat, cocofibre (coco) and woodchip (wood) substrates

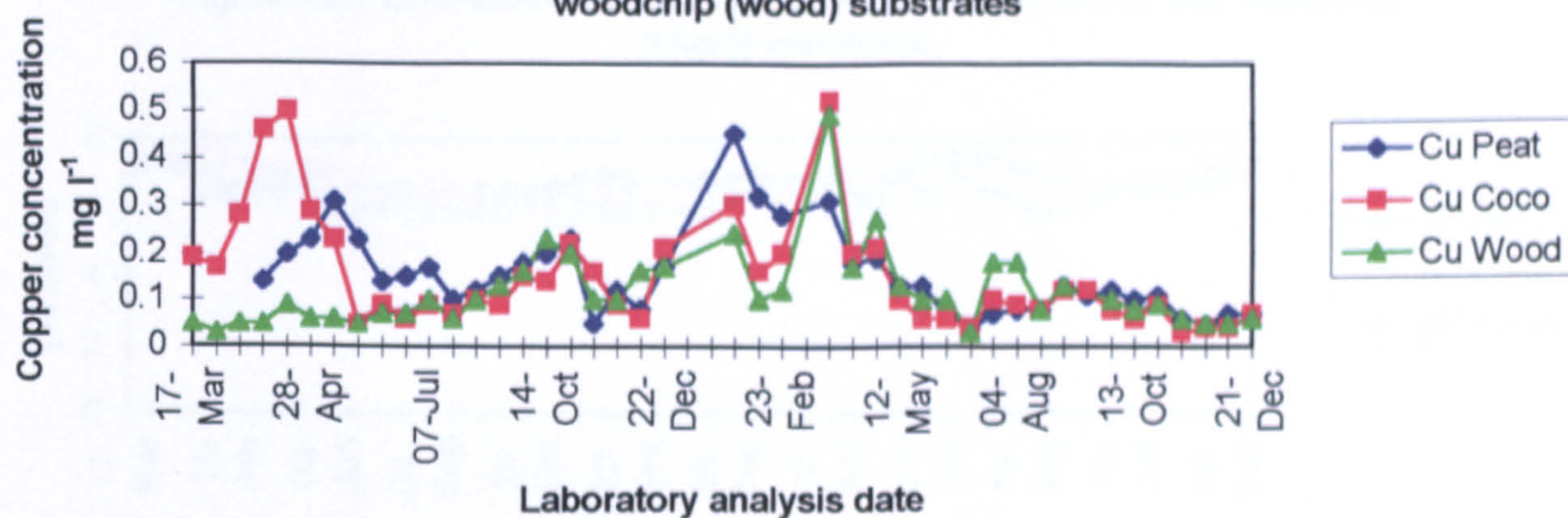


Figure 4.22 Drainwater zinc concentrations for peat, cocofibre (coco) and woodchip (wood) substrates

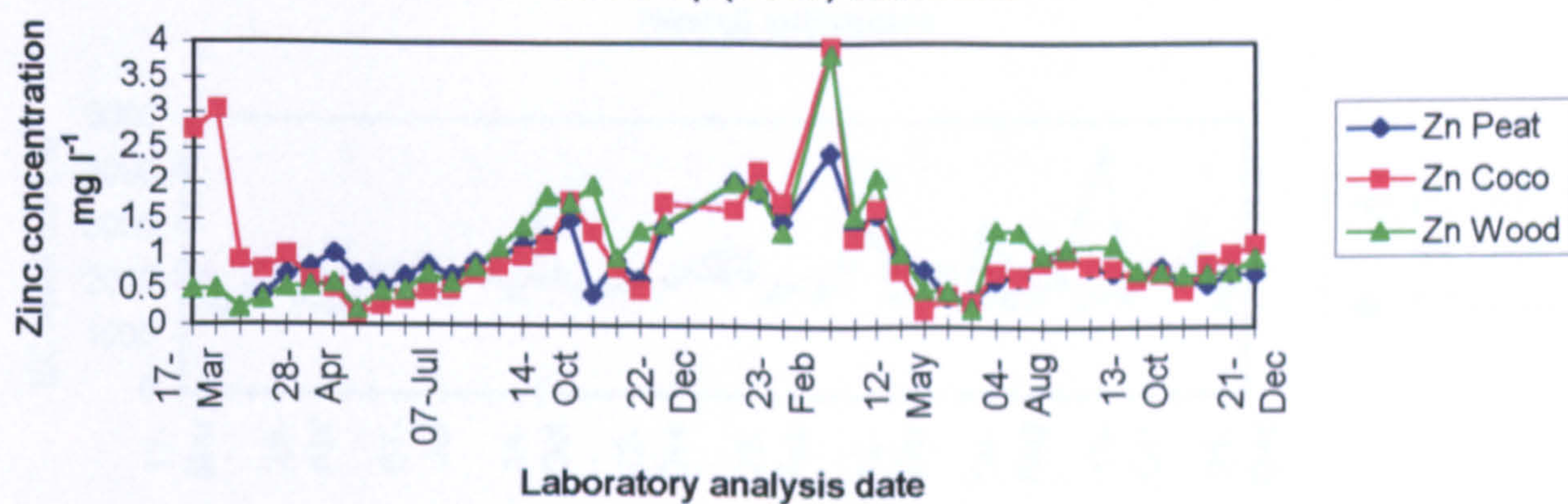


Figure 4.23 Drainwater boron concentrations for peat, cocofibre (coco) and woodchip (wood) substrates

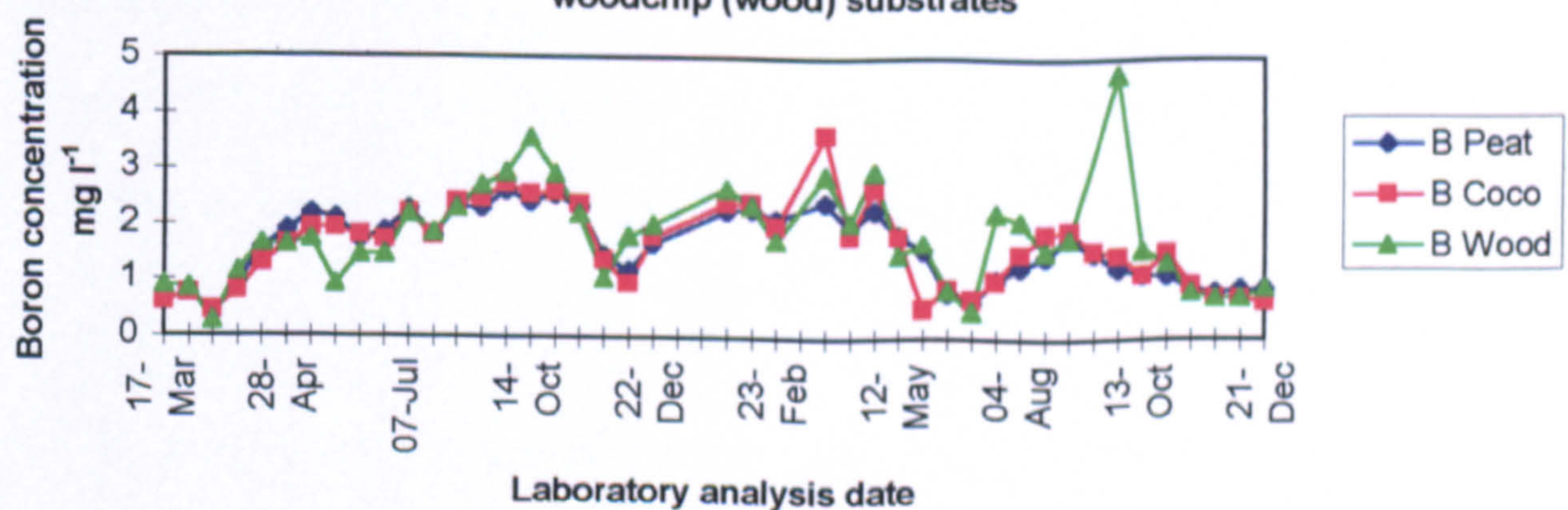


Figure 4.24 Drainwater pH levels for peat, cocofibre (coco) and woodchip (wood) substrates

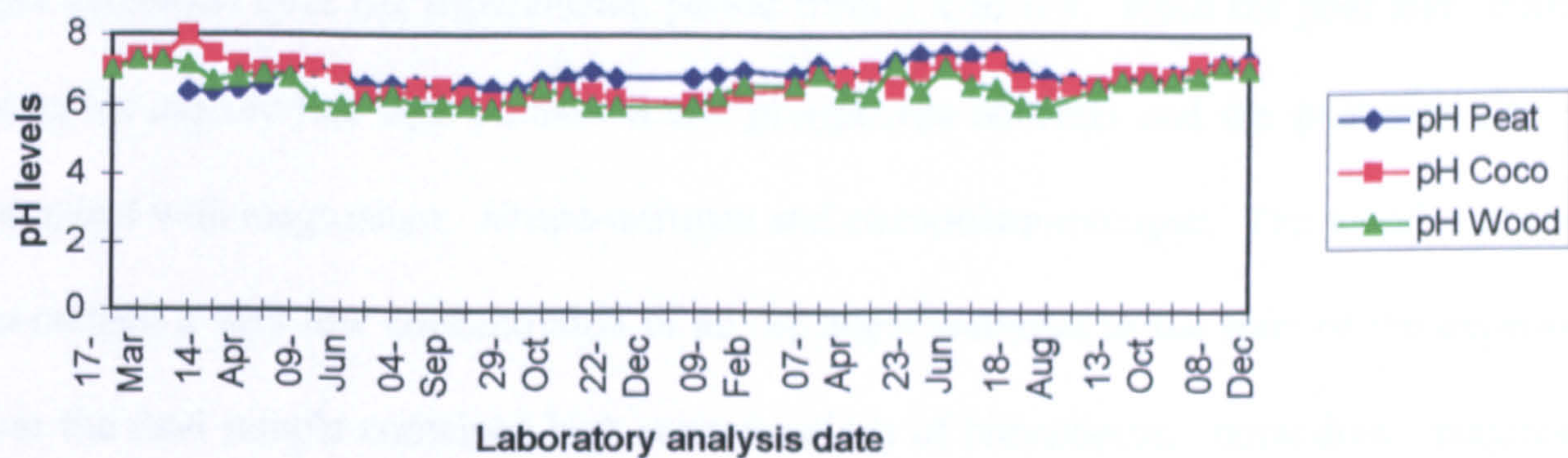
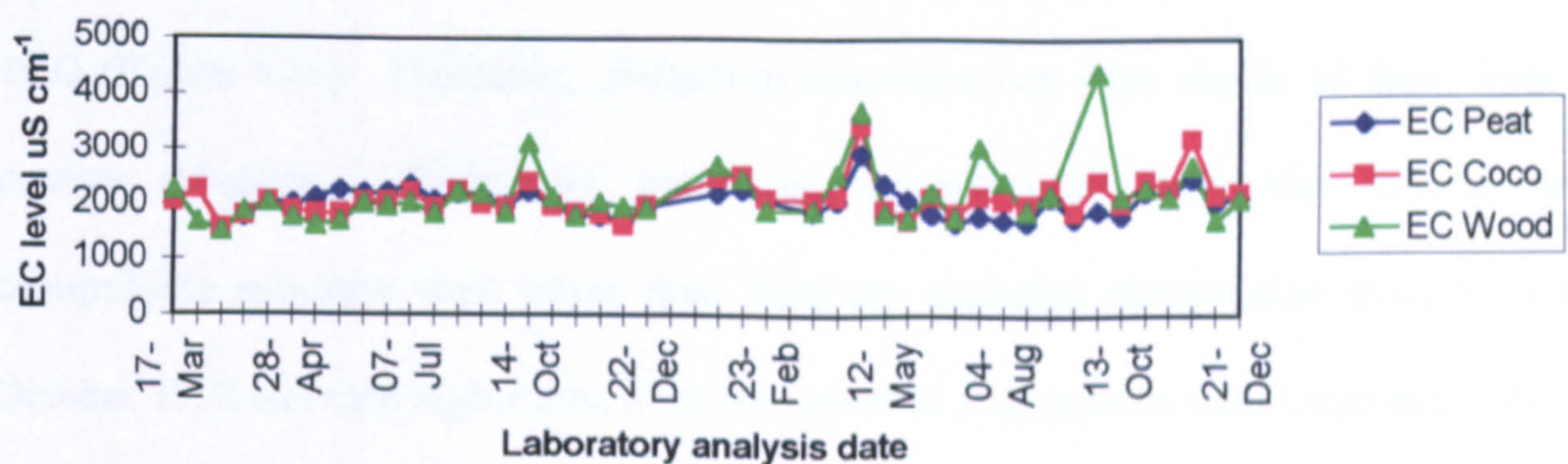


Figure 4.25 Drainwater EC levels for peat, cocofibre (coco) and woodchip (wood) substrates



All three substrates were bulk-sampled before and after the experiment and analysed for major element content (Tables 4.11 and 4.12). The starting pH value of the woodchip material was low at pH 5.0 and ended at pH 7.2. In comparison, the cocofibre substrate pH decreased over the experimental period from 7.2 to 6.4. Both the peat and cocofibre samples initially had high potassium and phosphorus contents and the peat was also well supplied with magnesium, nitrate-nitrogen and ammonium-nitrogen. The woodchip sample contained a very low concentration of all the major elements at the start of the experiment but the final sample contained high concentrations of phosphorus, potassium, magnesium and nitrate-nitrogen.

4.4.7 Nutrient concentration changes: aluminosilicate substrates

Potassium concentrations in the unloaded and nutrient-loaded clinoptilolite drainwater samples were lower than from the pumice substrate over the period March, 1992 to May, 1993 (Figure 4.26). Thereafter, potassium concentrations were similar to those from the pumice substrate. Drainwater potassium concentrations from the nutrient-loaded clinoptilolite substrate were lower than from the unloaded clinoptilolite from March to October 1992 and then higher than from the unloaded clinoptilolite until December 1993.

Conversely, calcium concentrations in the unloaded and nutrient-loaded clinoptilolite drainwater samples were higher than from the pumice substrate from March, 1992 until February, 1993 (Figure 4.27). Thereafter, calcium concentrations were similar from all three substrates. Drainwater calcium concentrations were higher from the nutrient-loaded clinoptilolite compared with the unloaded clinoptilolite from March to September 1992 and then lower than the unloaded clinoptilolite until July 1993.

Nitrate-nitrogen concentrations from nutrient-loaded clinoptilolite were higher than from pumice and unloaded clinoptilolite from March to September 1992 (Figure 4.28). Thereafter, drainwater nitrate-nitrogen concentrations were similar from all three

Figure 4.26 Drainwater potassium concentrations for pumice (Pum), unloaded clinoptilolite (Ulz) and nutrient-loaded clinoptilolite 'Hydrocult S' (HyS)

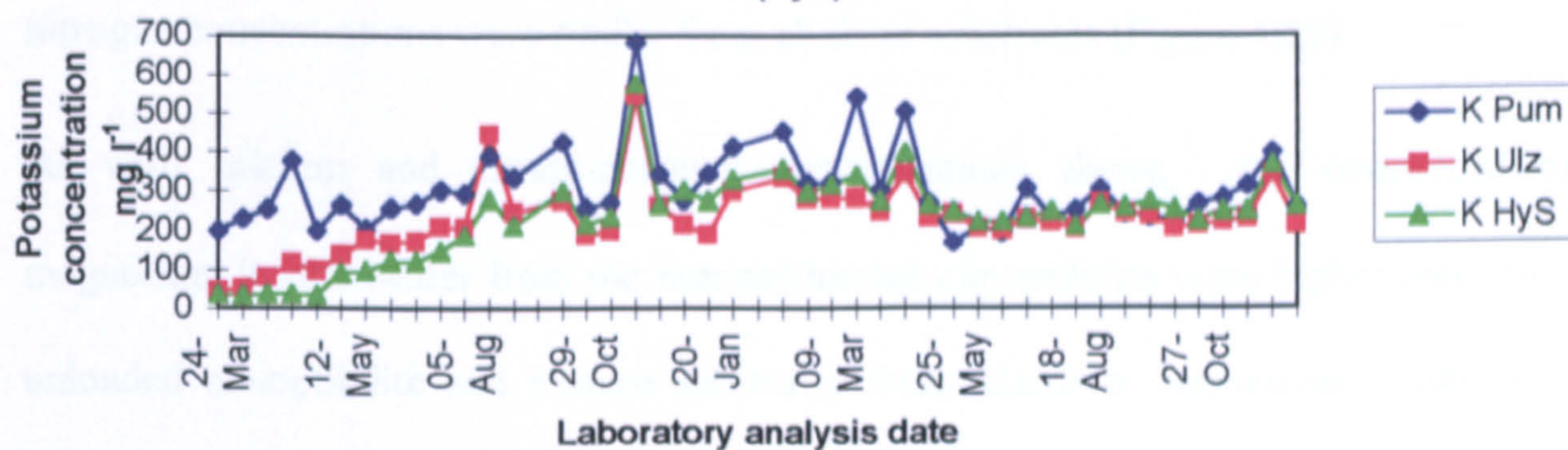


Figure 4.27 Drainwater calcium concentrations for pumice (Pum), unloaded clinoptilolite (Ulz) and nutrient-loaded clinoptilolite 'Hydrocult S' (HyS)

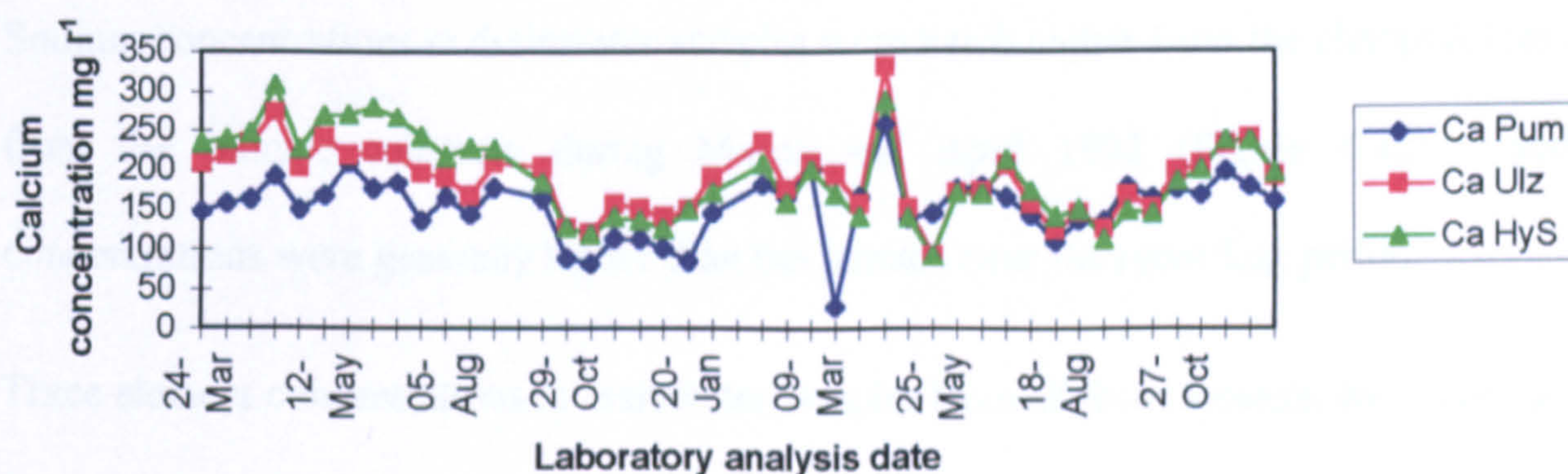
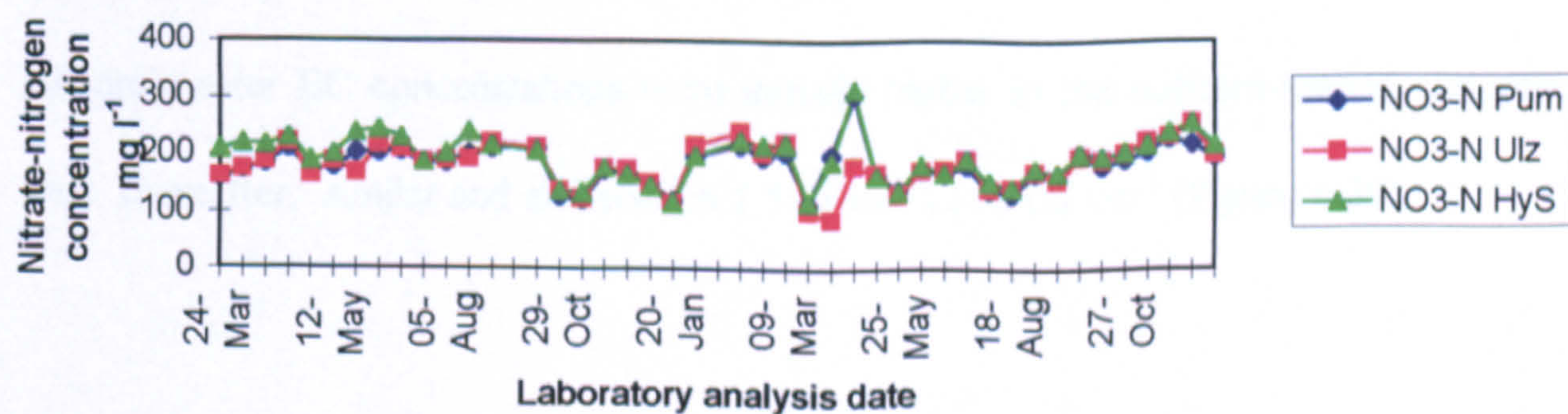


Figure 4.28 Drainwater nitrate-nitrogen concentrations for pumice (Pum), unloaded clinoptilolite (Ulz) and nutrient-loaded clinoptilolite 'Hydrocult S' (HyS)



substrates. Drainwater samples from the nutrient-loaded clinoptilolite substrate initially contained higher concentrations of ammonium-nitrogen and, subsequently, ammonium-nitrogen concentrations were similar from all three substrates (Figure 4.29).

As with calcium and nitrate-nitrogen concentrations above, the concentrations of magnesium in drainwater from the nutrient-loaded clinoptilolite were higher than from the unloaded clinoptilolite and pumice substrates from March to September, 1992 (Figure 4.30). Thereafter, concentrations were similar from all three substrates.

Phosphorus drainwater concentrations from all three substrates were similar throughout the recording period, except that drainwater from the nutrient-loaded clinoptilolite contained more phosphorus from the first four sampling dates (Figure 4.31).

Sodium concentrations in drainwater samples were much higher from the clinoptilolites than from the pumice substrate during March and April 1992 (Figure 4.32). Sodium concentrations were generally higher than the pumice over the recording period.

Trace element concentrations in drainwater samples from all three systems were very similar over the 22 month sampling period (Figures 4.33 to 4.37).

All drainwater pH levels were lower than 5.0 from June to October, 1992 (Figure 4.38). Subsequently, pH levels were below 6.0 for all substrates during the first year and above 6.0 for the second year. There was less fluctuation in pH levels over the 22 months from the nutrient-loaded clinoptilolite, however.

All drainwater EC concentrations were initially higher in the nutrient-loaded clinoptilolite and, thereafter, similar and all between 1,500 and 2,500 $\mu\text{S cm}^{-1}$ (Figure 4.39).

Figure 4.29 Drainwater ammonium-nitrogen concentrations for pumice (Pum), unloaded clinoptilolite (Ulz) and nutrient-loaded clinoptilolite 'Hydrocult S' (HyS)

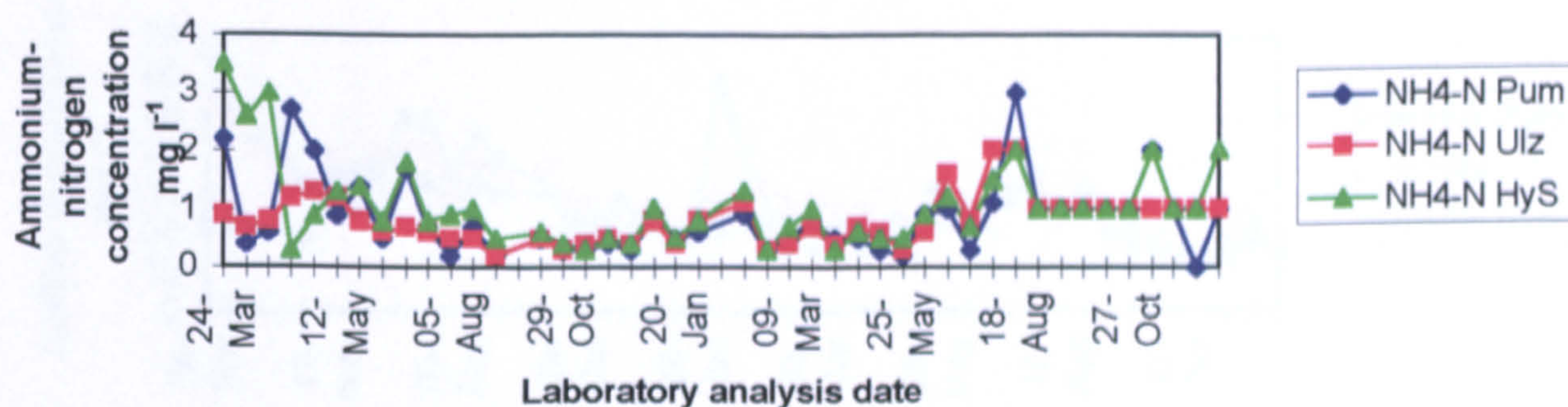


Figure 4.30 Drainwater magnesium concentrations for pumice (Pum), unloaded clinoptilolite (Ulz) and nutrient-loaded clinoptilolite 'Hydrocult S' (HyS)

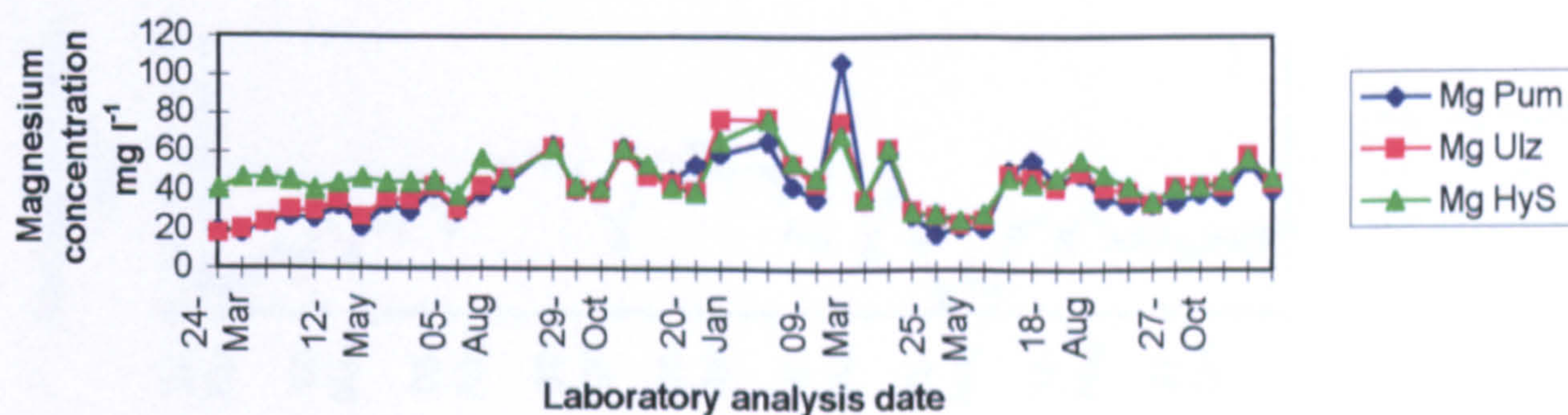


Figure 4.31 Drainwater phosphorus concentrations for pumice (Pum), unloaded clinoptilolite (Ulz) and nutrient-loaded clinoptilolite 'Hydrocult S' (HyS)

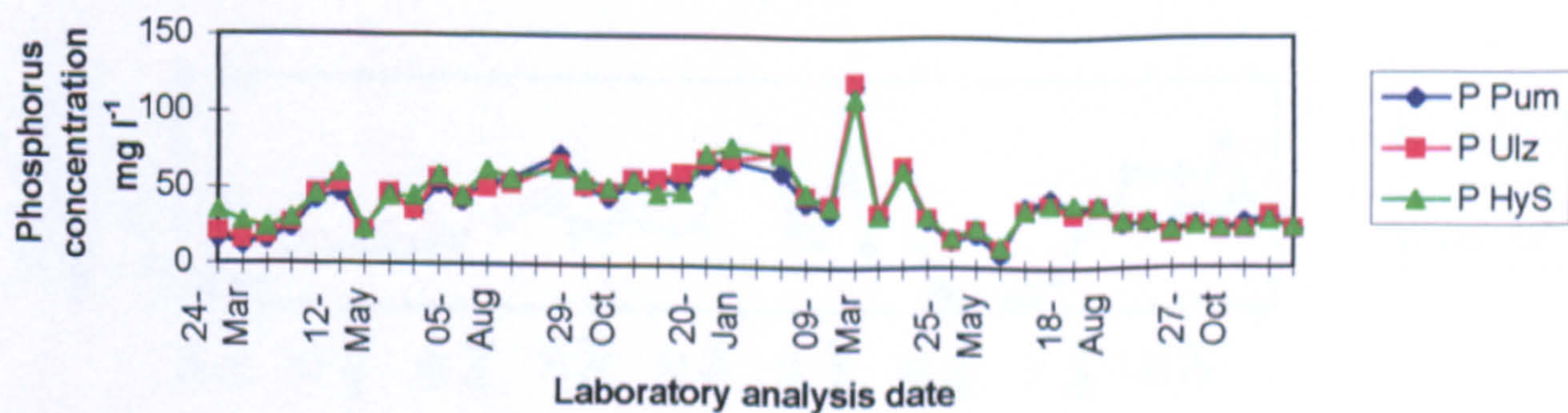


Figure 4.32 Drainwater sodium concentrations for pumice (Pum), unloaded clinoptilolite (Ulz) and nutrient-loaded clinoptilolite 'Hydrocult S' (HyS)

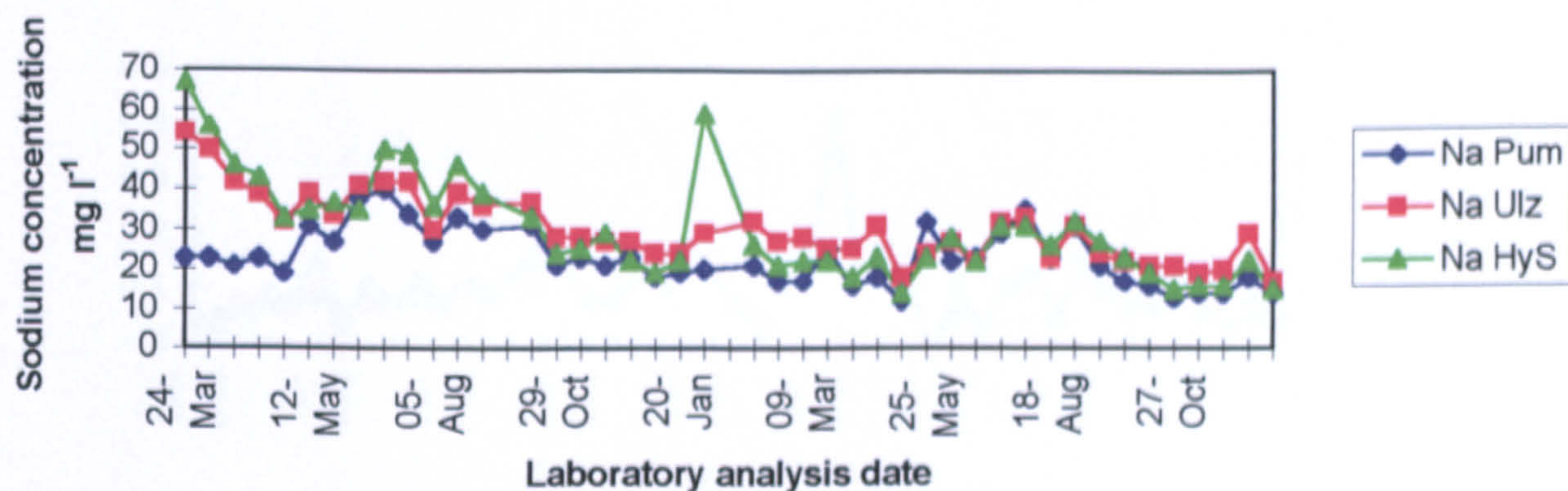


Figure 4.33 Drainwater iron concentrations for pumice (Pum), unloaded clinoptilolite (Ulz) and nutrient-loaded clinoptilolite 'Hydrocult S' (HyS)

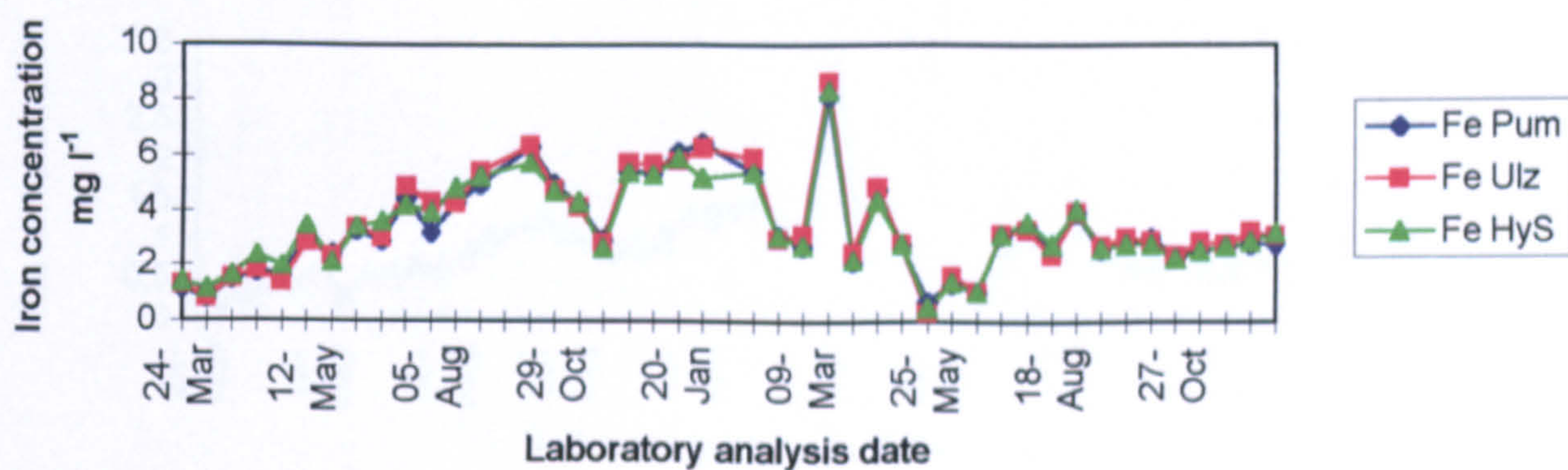


Figure 4.34 Drainwater manganese concentrations for pumice (Pum), unloaded clinoptilolite (Ulz) and nutrient-loaded clinoptilolite 'Hydrocult S' (HyS)

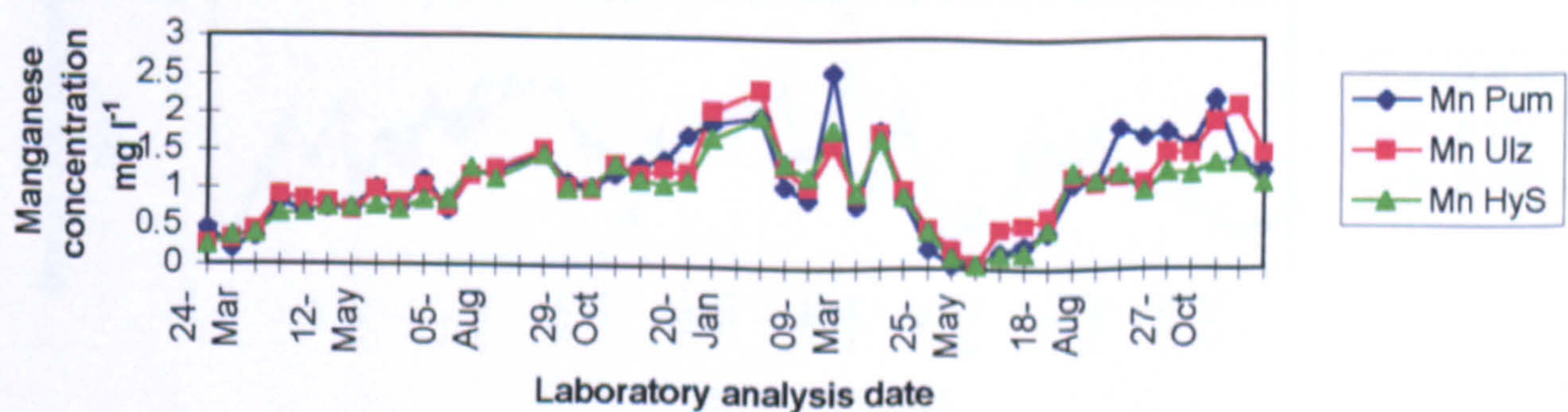


Figure 4.35 Drainwater copper concentrations for pumice (Pum), unloaded clinoptilolite (Ulz) and nutrient-loaded clinoptilolite 'Hydrocult S' (HyS)

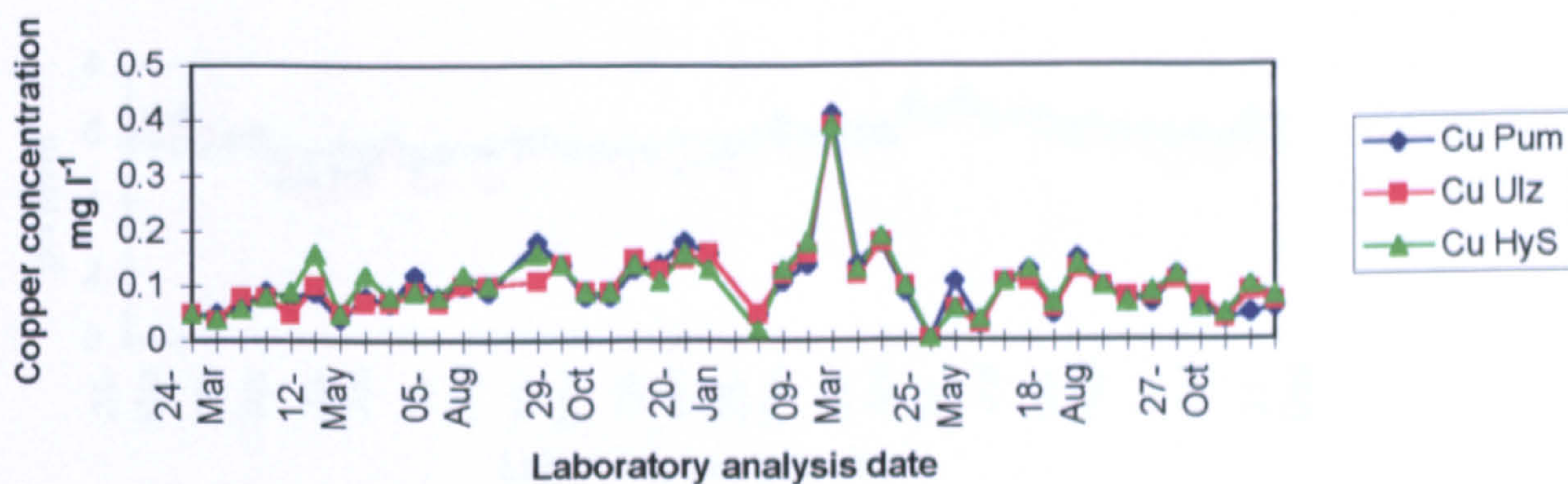


Figure 4.36 Drainwater zinc concentrations for pumice (Pum), unloaded clinoptilolite (Ulz) and nutrient-loaded clinoptilolite 'Hydrocult S' (HyS)

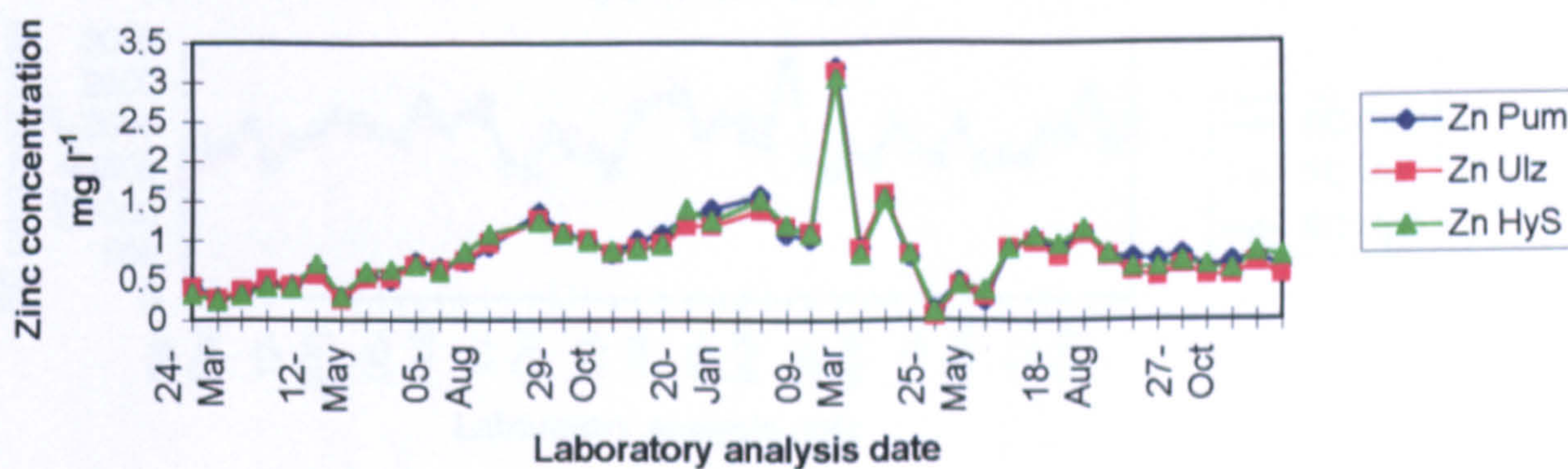


Figure 4.37 Drainwater boron concentrations for pumice (Pum), unloaded clinoptilolite (Ulz) and nutrient-loaded clinoptilolite 'Hydrocult S' (HyS)

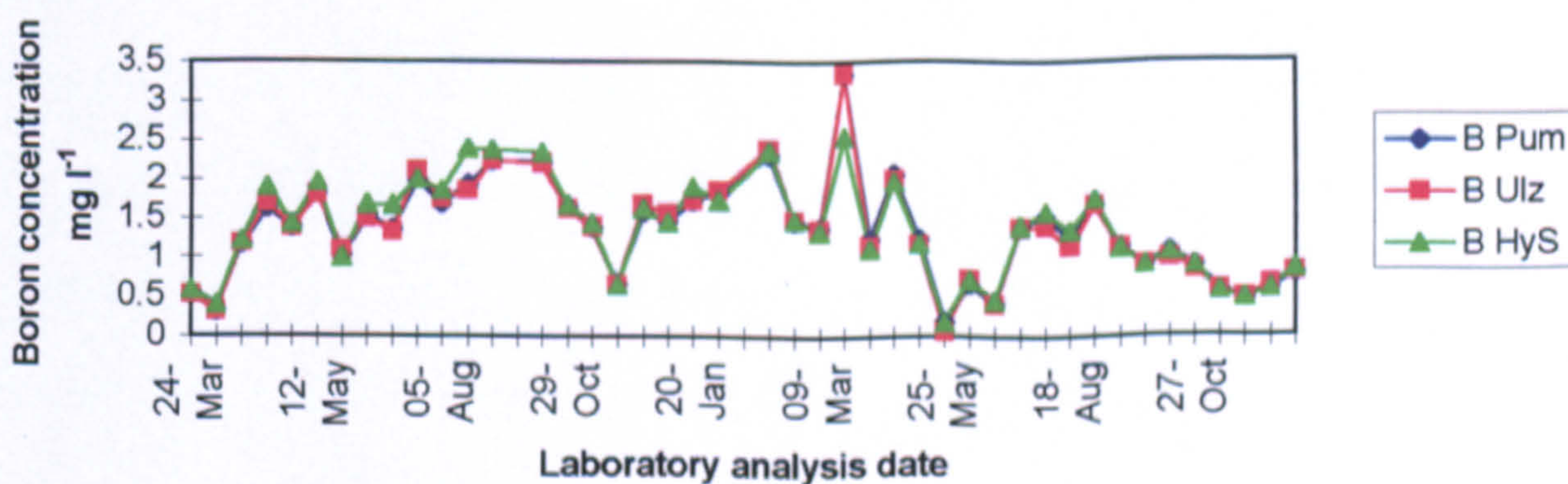


Figure 4.38 Drainwater pH levels for pumice (Pum), unloaded clinoptilolite (Ulz) and nutrient-loaded clinoptilolite 'Hydrocult S' (HyS)

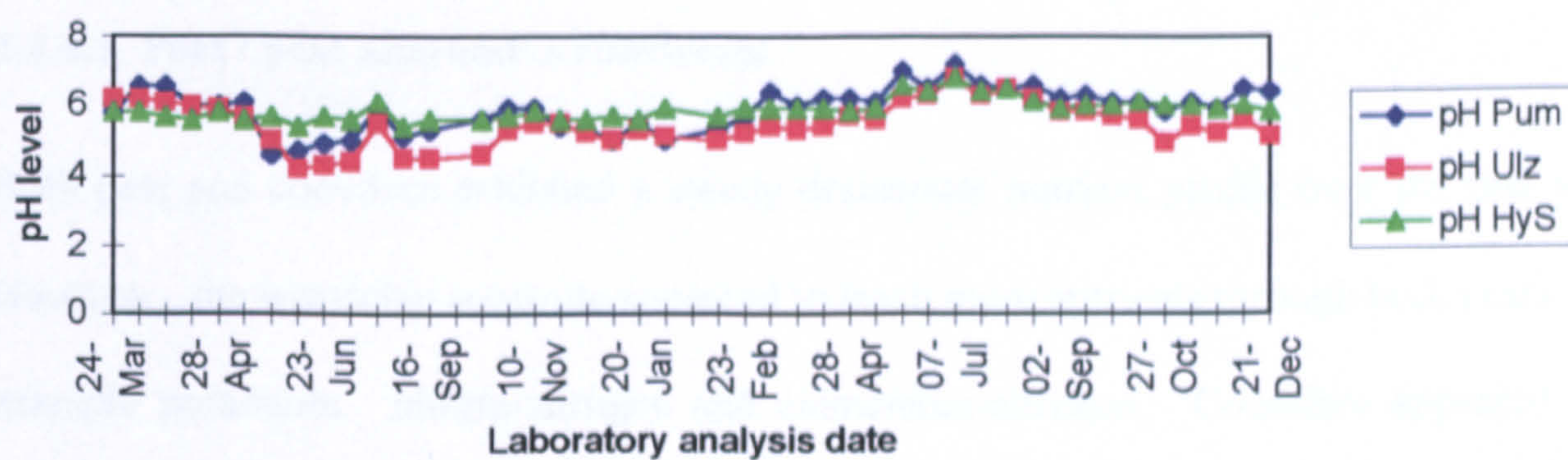
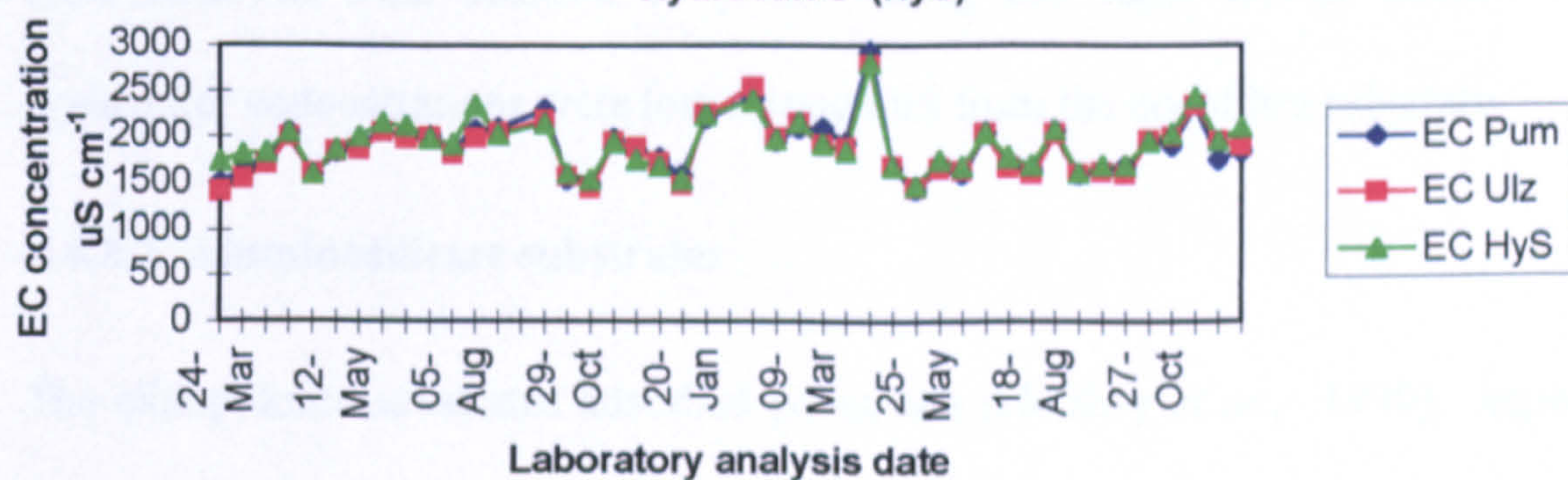


Figure 4.39 Drainwater EC concentrations for pumice (Pum), unloaded clinoptilolite (Ulz) and nutrient-loaded clinoptilolite 'Hydrocult S' (HyS)



4.4.8 Summary and discussion on nutrient concentration changes

4.4.8.1 Peat / peat alternative substrates

Both peat and cocofibre exhibited a steady drainwater nutrient profile over the first year. However, the woodchip substrate appeared to leach more nutrients through both years, for example potassium, nitrate-nitrogen and ammonium-nitrogen. Cocofibre appeared less stable during the second year, with more variation in concentrations of nutrients in drainwater samples. The woodchip substrate leached more sodium and this coincided with higher EC concentrations in September, 1993. This was due to temporary drying-out of the woodchip substrate. It was apparent that more potassium, calcium and phosphorus were removed from solution by plants during the major flower flushes. Manganese drainwater concentrations were low throughout from the cocofibre substrate.

4.4.8.2 Aluminosilicate substrates

The clinoptilolite substrates adsorbed potassium (Hershey *et al.*, 1980), especially in the first year and released calcium into the drainwater over the same period. The nutrient-loaded clinoptilolite appeared to adsorb more potassium and release more calcium than the unloaded clinoptilolite. In addition, the nutrient-loaded clinoptilolite also appeared to release more nitrate-nitrogen, magnesium and phosphorus into drainwater during the first six months. Initially, there was a higher concentration of ammonium-nitrogen in drainwater from the nutrient-loaded clinoptilolite. Both clinoptilolite substrates released more sodium at the start of the experiment compared with pumice. The higher release of nutrients, for example, calcium, magnesium and sodium, coincided with higher EC readings over the first six months from the nutrient-loaded clinoptilolite. According to Semmens (1984), ion size, valence and hydration energies are important factors in determining selectivity of a given ion in a specific system. For example, large cations, such as K^+ , Pb^{2+} , Ba^{2+} and

NH_4^+ , are extremely well removed by clinoptilolite but smaller ions, such as Li^+ , Na^+ and Ca^{2+} , are very poorly removed. The contact time available for exchange to occur also influences the cation exchange performance of natural zeolites (Semmens, 1984). This helps to explain the apparent preference shown by clinoptilolite for adsorption of potassium and ammonium-nitrogen in relation to calcium, magnesium and sodium recorded during the experiment.

4.4.9 Conclusions

- It was possible to grow standard carnation plants and produce commercially-acceptable yields of quality flowers over a two year period on all substrates in the experiment.
- The provision of liquid feeds resulted in an even supply of available nutrients to plants growing on all substrates during the crop establishment period.
- The nutrient-loaded clinoptilolite produced a good yield of standard carnations and the additional availability of nutrients during the first six months could have helped to improve growth and flower quality.
- Unloaded clinoptilolite performed as well as pumice in five litre pots, over a 22 month growing period.
- The moisture content of the aluminosilicates was critical to the early rooting and establishment of the carnation cuttings. However, the excellent air-filled porosity and drainage characteristics of the aluminosilicates ensured a better winter performance and plant survival rate, in comparison with the peat, cocofibre and woodchip substrates.
- Of the peat and peat alternative substates, the variation in concentration and release of nutrients from the woodchips into the drainwater was the most marked, especially in the second year of production.
- As part of the cation exchange processes involved, the nutrient-loaded clinoptilolite also released quantities of nutrients into the drainwater, particularly at the start of the experiment.

Table 4.10 Fresh weight yield profile for ‘Yellow Candy’

on six substrates (substrate means blooms m⁻² per month)

n.s. = not significant

Substrate	Mean Class I blooms m⁻² per month, n = 3
Peat	24.158
Cocofibre	22.737
Woodchips	26.474
Pumice	23.526
Unloaded clinoptilolite	22.158
Hydrocult S	22.263
F-test significance level	p=n.s.

Table 4.11 Peat, cocofibre and woodchip substrate analysis : 17 February, 1992
(start of experiment). Water extractable nutrients (mg l⁻¹, except: pH; EC in μ S
cm⁻¹; and ADAS index in brackets), (n=1)

	pH	P	K	Mg	EC	NO ₃ -N	NH ₄ -N	Na
Peat	7.1	57 (7)	300 (5)	26 (4)	288 (1)	84 (4)	57 (2)	---
Coco	7.2	21 (4)	486 (6)	8 (1)	285 (1)	32 (2)	1 (0)	---
Wood	5.0	2 (0)	78 (2)	2 (0)	32 (0)	5 (0)	1 (0)	---
ADAS target	5.5 - 6.5	30 - 55	250 - 400	25 - 35	800 - 1,000	80 - 130	Low	Low

Table 4.12 Peat, cocofibre and woodchip substrate analysis : 7 February, 1994
(end of experiment). Water extractable nutrients (mg l⁻¹, except: pH; EC in μ S
cm⁻¹; and ADAS index in brackets), (n=1)

	pH	P	K	Mg	EC	NO ₃ -N	NH ₄ -N	Na
Peat	7.4	19 (4)	220 (4)	20 (3)	239 (1)	92 (4)	4 (0)	41
Coco	6.4	44 (6)	263 (5)	18 (3)	268 (1)	102 (4)	10 (0)	30
Wood	7.2	41 (6)	386 (5)	79 (6)	550 (4)	215 (6)	9 (0)	77
ADAS target	5.5 - 6.5	30 - 55	250 - 400	25 - 35	800 - 1,000	80 - 130	Low	Low

4.5 Experiment 4 Comparison of unloaded clinoptilolite zeolite and pumice with four other substrates in the production of long season green peppers (*Capsicum annuum*)

4.5.1 Introduction

Experiment Two confirmed that it was possible to grow sweet pepper plants on unloaded clinoptilolite over a production season spanning eight months. As the drainwater was recirculated in Experiment Two, it was not clear whether changes in the nutrient content of the drainwater were interfering with ion availability to the plants. This experiment aimed to monitor nutrient concentration changes using fresh feed applications during each irrigation sequence. In addition, summer carbon dioxide was available in this compartment and so it was projected that spring and summer yields and also fruit quality would be improved as a direct result (Nederhoff, 1994). Replicating the plots and comparing the clinoptilolite with pumice, rockwool and glasswool substrates were also improvements in the experimental design.

The aim of this investigation was to assess the growth and development of long season peppers on a range of substrates using a drainwater to waste system. Nutritional changes were recorded in substrate and plant leaf tissue samples throughout the production season. Fruit yield and quality characteristics of the variety 'Mazurka' (Rijk Zwaan) were also noted for each substrate.

4.5.2 Objectives

1. To compare fruit yield and quality of the sweet pepper variety 'Mazurka' on unloaded clinoptilolite and pumice. To utilise a summer carbon dioxide enrichment system in order to improve spring and summer production.

2. To assess plant growth and development on the substrates using nutrient-balanced liquid feeds at each watering, with no nutrient recirculation.
3. To measure changes in the drainwater nutrient concentrations in order to indicate which ions may be being adsorbed and released by the aluminosilicate substrates pumice and clinoptilolite.
4. To measure changes in the plant leaf tissue nutrient concentrations and compare with changes in drainwater nutrient concentrations.

4.5.3 Materials and methods

The substrates were:-

1. Rockwool (Grodan N-series slabs)
2. Glasswool (Cultilene AG mix slabs)
3. Foam (Richgrow high density slabs)
4. Pumice (Sicilian)
5. Unloaded clinoptilolite zeolite (Bulgarian)

The experiment took place from November 1995 to October 1996. The seeds were sown into rockwool cubes on 1 November and seedlings were blocked-on into 7cm rockwool blocks on 15 November. Plants were placed on the substrates on 3 January, the first harvest was on 27 February and the final harvest was completed on 14 October.

A V-system planting arrangement was utilised for this crop, with six plants per slab or module, to give a plant density of 30,000 plants hectare⁻¹ or 60,000 heads hectare⁻¹ (Plate 3.5). The individual rockwool, glasswool and foam slab volume was 13.5 litres compared with a 12 litre module volume for the pumice and clinoptilolite substrates. The experiment

was conducted in house III within the main research unit (Appendix I) The trial layout incorporated three replicates of each substrate in a randomised block design.

4.5.4 Results and discussion

4.5.4.1 Plant growth, fruit yield and quality

Sweet pepper plants grown in glasswool and rockwool had the longest main shoot lengths (Table 4.15) and correspondingly high total yields (Table 4.16). There were no significant differences between size grades on the various substrates ($p>0.05$) (Appendix II). Glasswool produced the highest total of 60-70mm and 70-90mm fruit. Rockwool produced the highest total of 90+mm fruit, foam yielded the highest Class II total and rockwool produced the highest blossom end rot and total waste fruit. Conversely, clinoptilolite yielded the lowest blossom end rot and waste fruit totals. Pepper plant leaf, stem, root, flower and fruit development characteristics were very similar with all the substrates. Weekly crop management programmes were identical for all treatments in the experiment but irrigation requirements were calculated using water use and water drainage data from plants on the rockwool slabs.

4.5.4.2 Nutrient concentration changes : major elements in the drainwater

In summary, the nutrient analysis data highlights the preferential adsorption of potassium and release of calcium by the clinoptilolite throughout the experimental period (Hershey *et al.*, 1980; Semmens, 1984); (Figures 4.40 and 4.41). In addition, magnesium appeared to be adsorbed by the clinoptilolite until April when, subsequently, drainwater concentrations of magnesium increased in comparison with the applied liquid feed (Figure 4.44). The clinoptilolite appeared to release sodium into the root zone throughout, with differences in applied feed and drainwater concentrations measuring over 100 mg litre⁻¹ until early March (Semmens, 1984); (Figure 4.46). Drainwater nutrient concentration changes

Figure 4.40 Pepper input feed and drainwater potassium concentrations for three substrates

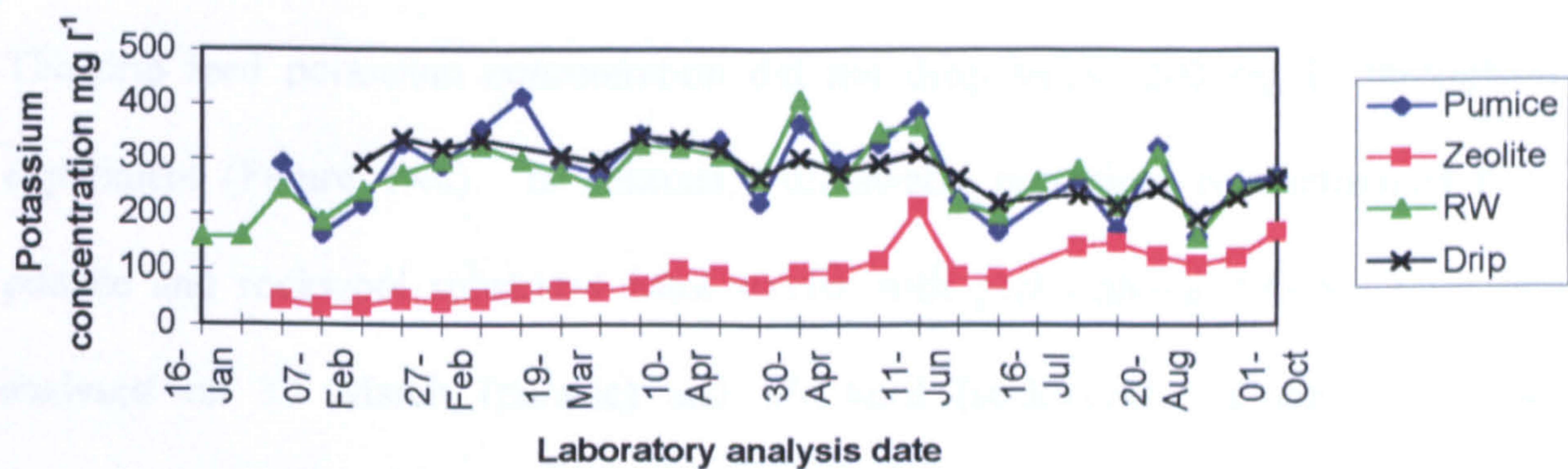


Figure 4.41 Pepper input feed and drainwater calcium concentrations for three substrates

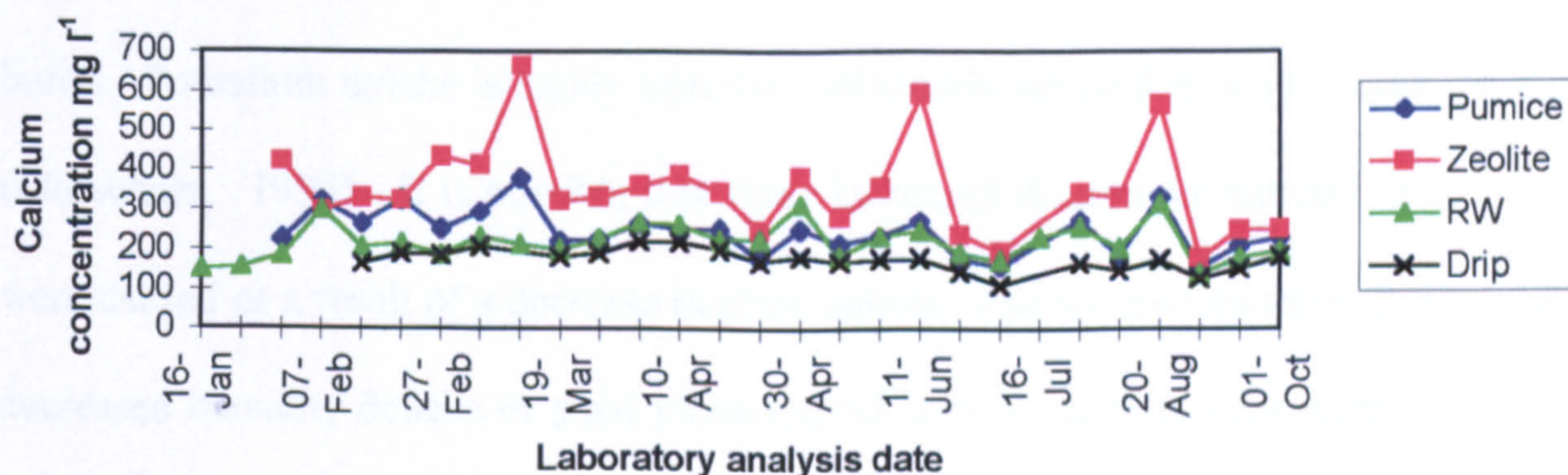
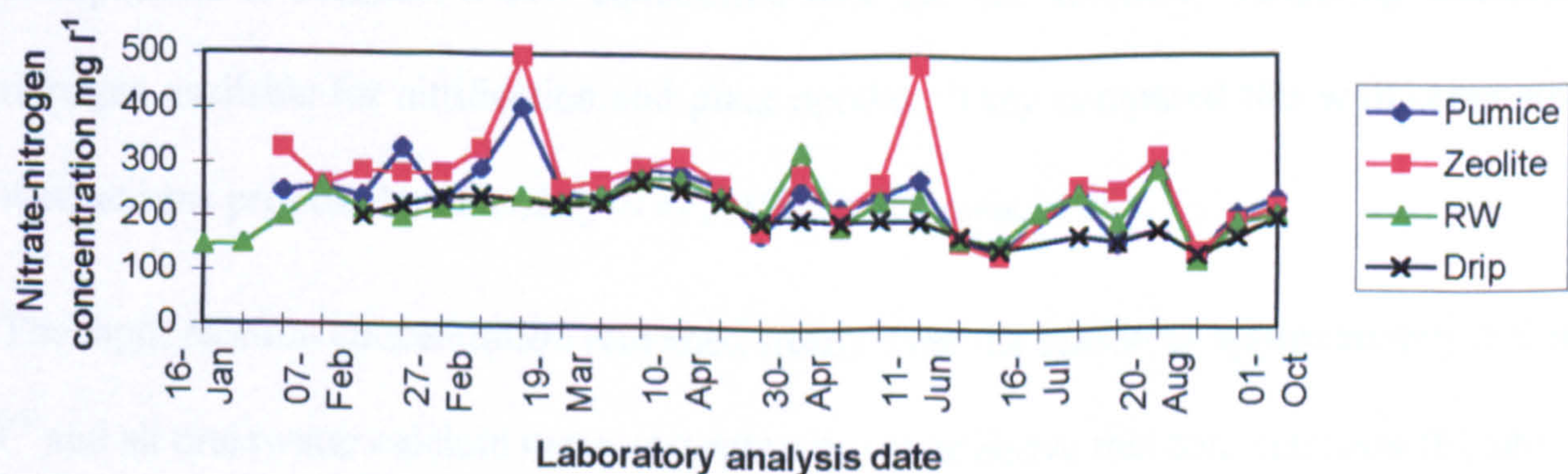


Figure 4.42 Pepper input feed and drainwater nitrate-nitrogen concentrations for three substrates



were similar for the rockwool, glasswool and foam substrates and are represented by data as discussed for rockwool below.

The drip feed potassium concentration did not drop below 200 mg l⁻¹ throughout the experiment (Figure 4.40). In contrast, drainwater potassium concentrations from the pumice and rockwool substrates were similar with peaks above 400 mg l⁻¹ in samples analysed on 12 March (pumice) and 30 April (rockwool). Drainwater potassium concentrations from the unloaded clinoptilolite were below 100 mg l⁻¹ for the first four months of the year, reflecting the very active adsorption of potassium by the clinoptilolite. One particular increase in drainwater potassium concentration was recorded at 220 mg l⁻¹ on 11 June. This also coincided with increased drainwater nutrient concentrations of calcium, magnesium, nitrate-nitrogen, ammonium-nitrogen, sodium, iron, copper, zinc and boron. Potassium uptake is highly selective and closely coupled to plant metabolic activity (Marschner, 1995). It is possible that these increased drainwater nutrient concentrations were caused as a result of a decrease in plant uptake, due to environmental factors such as decreased humidity deficits or plant physiological factors, such as high plant fruit loading. There was a gradual rise in clinoptilolite drainwater potassium content from 50 mg l⁻¹ (30 January) to 160 mg l⁻¹ (1 October), possibly as a result of exchange sites becoming occupied or blocked by other organic materials of biotic origin (Myt'ko *et al.*, 1989). Pirela *et al.* (1984), found over time that ammonium nitrogen may have been released from clinoptilolite to establish a new equilibrium with the soil solution, rendering ammonium-nitrogen available for nitrification and plant uptake. They compared this with other similar mechanisms proposed by Hershey *et al.*, 1980 and Lewis, 1981.

The input calcium concentration remained steady over the season at approximately 200 mg l⁻¹ and all drainwater calcium measurements were at or above this concentration (Figure 4.41). For the first two months, pumice drainwater concentrations were higher than for rockwool and similar thereafter. This suggests an initial release of calcium from the pumice

and the existence of an ion exchange mechanism. Clinoptilolite drainwater contained higher concentrations of calcium throughout, with peaks above 500 mg l⁻¹ on 12 March, 11 June and 20 August. Clinoptilolite was clearly releasing calcium ions into the root zone throughout the experiment. Examination of equilibrium exchange data on clinoptilolite at 23 °C for several cation pairs, including ammonium and the most common alkali and alkaline earth cations found in natural waters, revealed the following selectivity sequence: K > NH₄ > Na > Ca > Mg (Colella, 1996).

Drip nitrate-nitrogen concentrations remained close to 250 mg l⁻¹ during the first four months of the experiment (Figure 4.42). Subsequently, inputs were decreased to nearer 200 mg l⁻¹, causing a general reduction in drainwater nitrate-nitrogen content. Drainwater nitrate-nitrogen concentrations were higher from the pumice than from the rockwool during the first three months of the year. Drainwater samples taken from the clinoptilolite substrate contained concentrations of nitrate-nitrogen in excess of 450 mg l⁻¹ on 12 March, 11 June and 20 August. As nitrate-nitrogen is not adsorbed by the clinoptilolite, it is possible that there was preferential uptake of ammonium-nitrogen by the pepper plants from the clinoptilolite, thus causing an accumulation of nitrate-nitrogen in the drainwater. Nitrate-nitrogen and ammonium-nitrogen are the major sources of inorganic nitrogen taken-up by the roots of higher plants. Most of the ammonium-nitrogen is incorporated into organic compounds in the roots, whereas nitrate-nitrogen is readily mobile in the xylem and can be stored in the vacuoles of roots, shoots and storage organs. When plants are supplied with ammonium nitrate fertiliser, ammonium-nitrogen is usually taken-up in preference to nitrate-nitrogen (Marschner, 1995).

Drip ammonium-nitrogen concentrations were measured above 3 mg l⁻¹ in samples analysed on 20 February, 10 April, 30 April and 3 September (Figure 4.43). All drainwater concentrations were no higher than 2 mg l⁻¹, with the exception of a clinoptilolite drainwater ammonium-nitrogen peak of 3 mg l⁻¹ on 24 July. In order to be incorporated

into organic structures and to fulfil its essential functions as a plant nutrient, nitrate-nitrogen has to be reduced to ammonia. The importance of the reduction and assimilation of nitrate-nitrogen for plant life is similar to that of the reduction and assimilation of carbon dioxide in photosynthesis. The ammonium-nitrogen assimilation in roots produces approximately one proton per molecule of ammonium-nitrogen taken-up which has to be excreted into the external medium (Marschner, 1995). There were no major decreases in pH measured in the drainwater samples, however.

There was a steady drip magnesium concentration of approximately 50 mg l^{-1} throughout the experiment and pumice drainwater measurements peaked above 90 mg l^{-1} on 12 March, before mirroring the rockwool drainwater concentrations for the remainder of the season (Figure 4.44). It is possible that there was a release of magnesium from the pumice into the drainwater at the start of the experiment. Low drainwater magnesium concentrations below 20 mg l^{-1} were measured from all substrates on 7 February and clinoptilolite drainwater concentrations below 40 mg l^{-1} were recorded for the first month. Plant demand for magnesium could have been particularly high at the end of January and early February, prior to the start of cropping. Clinoptilolite drainwater concentrations, however, peaked above 150 mg l^{-1} on 11 June and 20 August. This suggests that clinoptilolite initially adsorbed magnesium and then released magnesium into the drainwater from April (Bunt, 1988). The rate of plant magnesium uptake can be depressed by other cations such as potassium, ammonium-nitrogen, manganese and also by protons (low pH conditions). No magnesium deficiency symptoms were recorded at any time during the experiment, however.

Feed phosphorus concentrations remained close to 35 mg l^{-1} during the experiment and both the pumice and rockwool drainwater concentrations were comparable for most of the season (Figure 4.45). Low concentrations below 5 mg l^{-1} of phosphorus were measured from all three substrates on 7 February and, in comparison, clinoptilolite concentrations

Figure 4.43 Pepper input feed and drainwater ammonium-nitrogen concentrations for three substrates

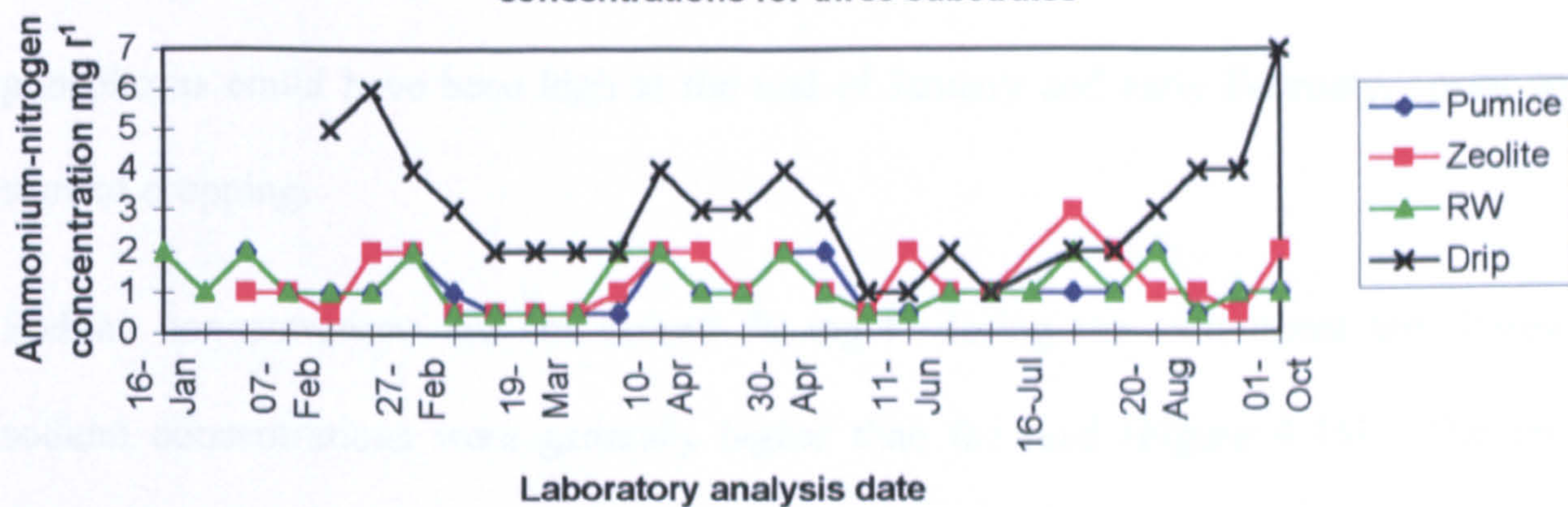


Figure 4.44 Pepper input feed and drainwater magnesium concentrations for three substrates

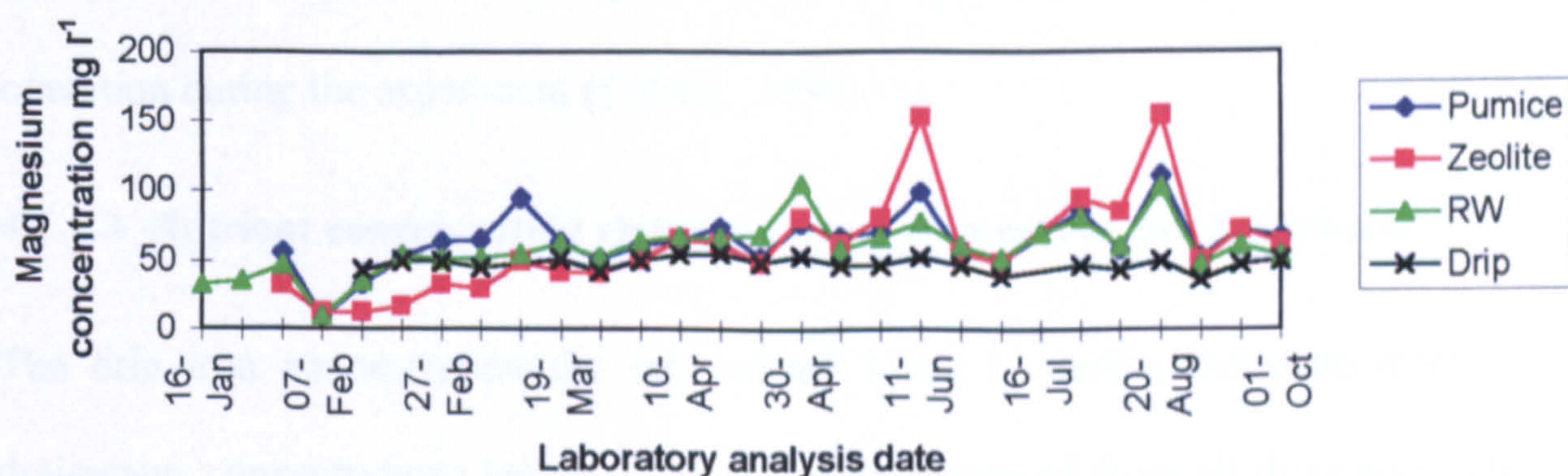
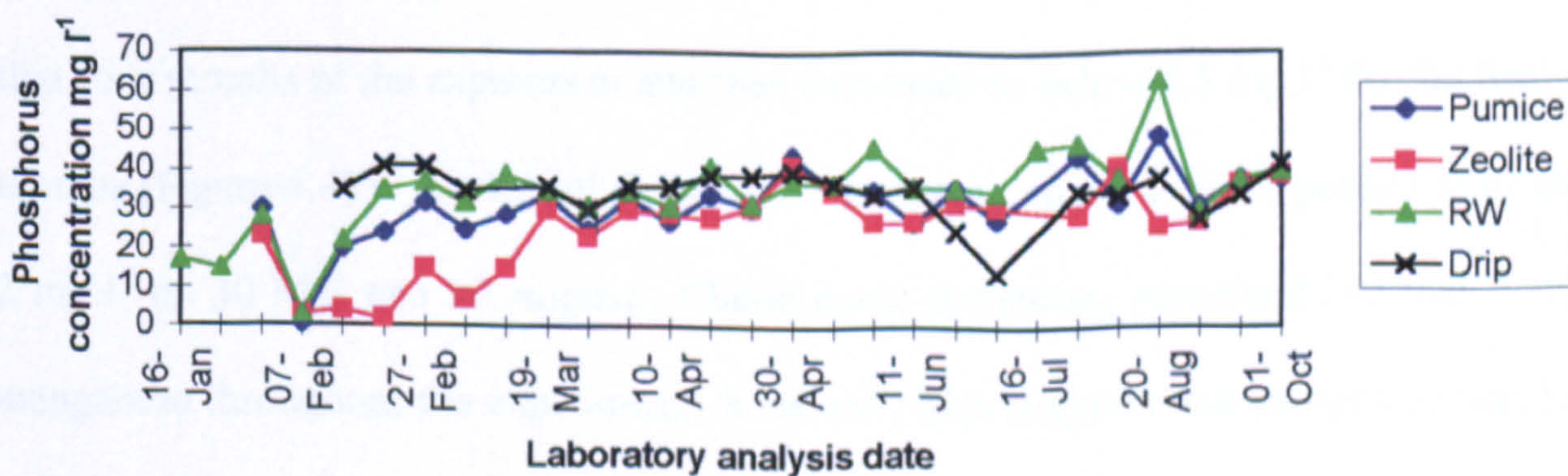


Figure 4.45 Pepper input feed and drainwater phosphorus concentrations for three substrates



below 30 mg l⁻¹ were recorded for the first two months before the nutrient profile returned to closely match those of the pumice and rockwool substrates. Plant demand for phosphorus could have been high at the end of January and early February, prior to the start of cropping.

Sodium concentrations did not exceed 50 mg l⁻¹ during the experiment but drainwater sodium concentrations were generally higher than the feed (Figure 4.46). The pumice drainwater sodium concentration was slightly higher than the rockwool for the first three months and, subsequently, similar to the rockwool nutrient profile. Drainwater from the clinoptilolite contained 180 mg l⁻¹ sodium on 30 January and exceeded 130 mg l⁻¹ on 12 March, 11 June and 20 August. It is possible that direct ion exchange of sodium out of the clinoptilolite and potassium adsorption by the clinoptilolite was one of the mechanisms in operation during the experiment (Colella, 1996).

4.5.4.3 Nutrient concentration changes : trace elements in the drainwater

The drip iron concentration did not exceed 3 mg l⁻¹ during the experiment but low drainwater concentrations below 0.5 mg l⁻¹ were measured from all three substrates on 7 February (Figure 4.47). The clinoptilolite drainwater iron content peaked above 6 mg l⁻¹ on 20 August, however. Plant demand for iron could have been high at the end of January and early February, prior to the start of cropping.

Input feed concentrations of manganese remained at approximately 1.5 mg l⁻¹ during the first four months of the experiment and then decreased to below 0.5 mg l⁻¹ for the final four months (Figure 4.48). Rockwool drainwater manganese concentrations peaked at or above 2 mg l⁻¹ on 30 May and 20 August. Clinoptilolite drainwater contained less than 1 mg l⁻¹ manganese throughout the experiment, however. This suggests that manganese was being adsorbed by the clinoptilolite during the season (Hershey *et al.*, 1980).

Figure 4.46 Pepper input feed and drainwater sodium concentrations for three substrates

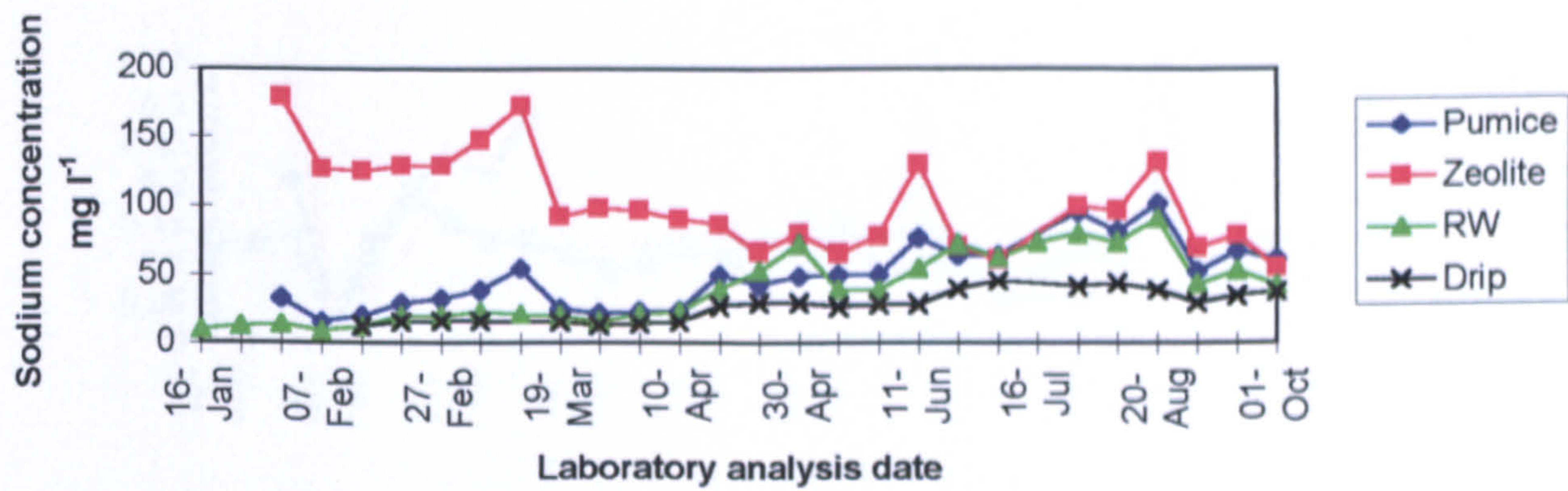


Figure 4.47 Pepper input feed and drainwater iron concentrations for three substrates

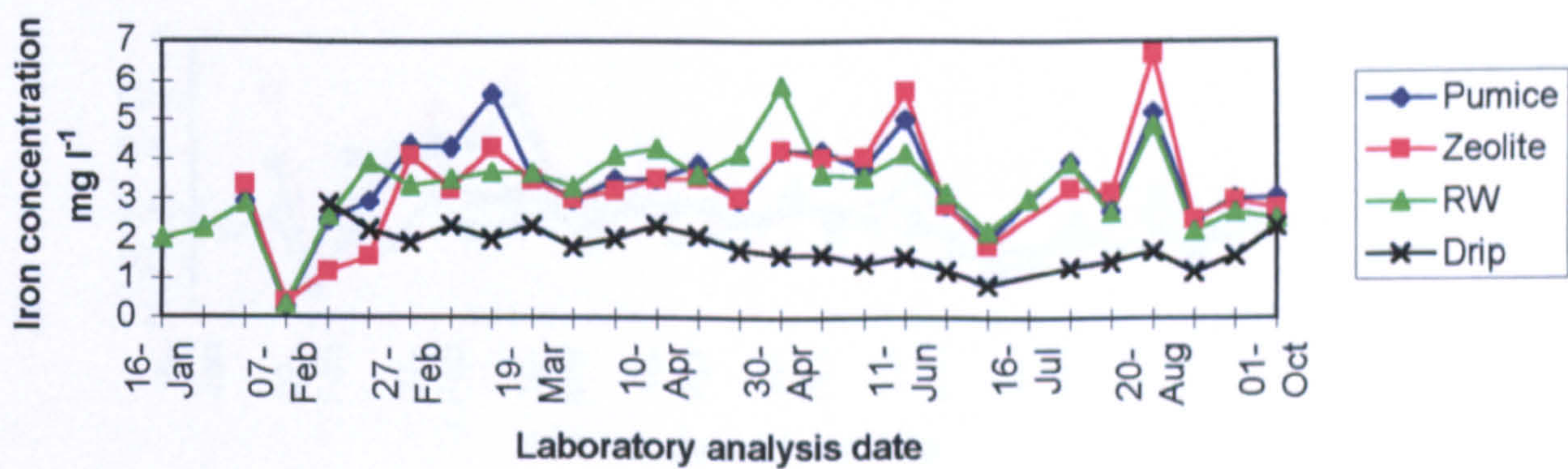


Figure 4.48 Pepper input feed and drainwater manganese concentrations for three substrates

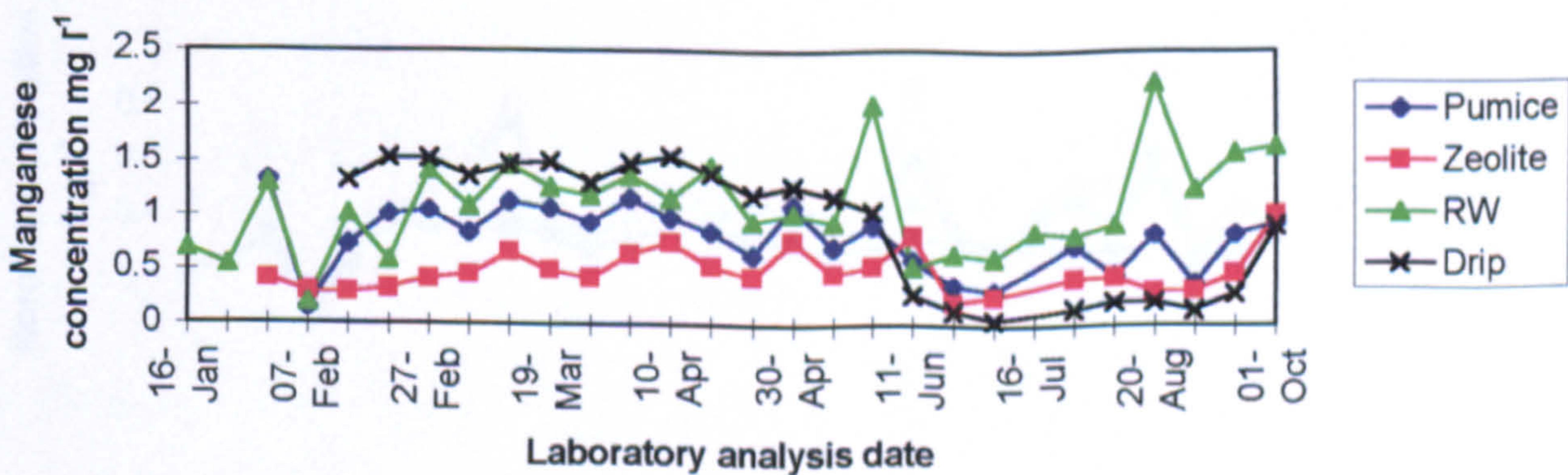


Figure 4.49 Pepper input feed and drainwater copper concentrations for three substrates

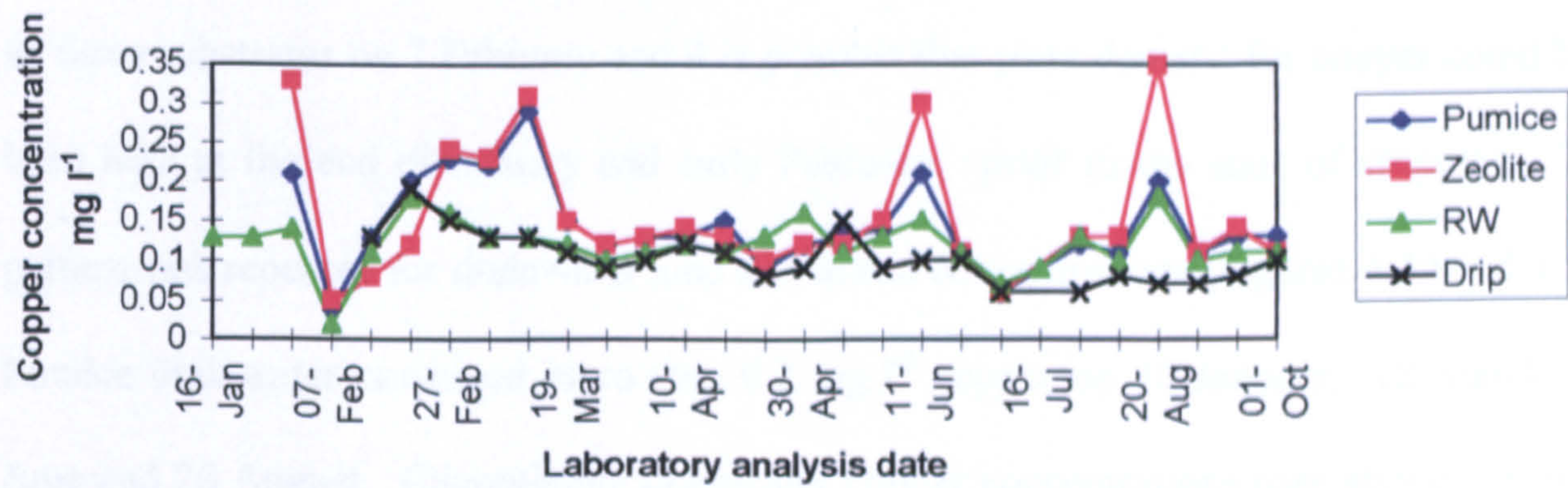


Figure 4.50 Pepper input feed and drainwater zinc concentrations for three substrates

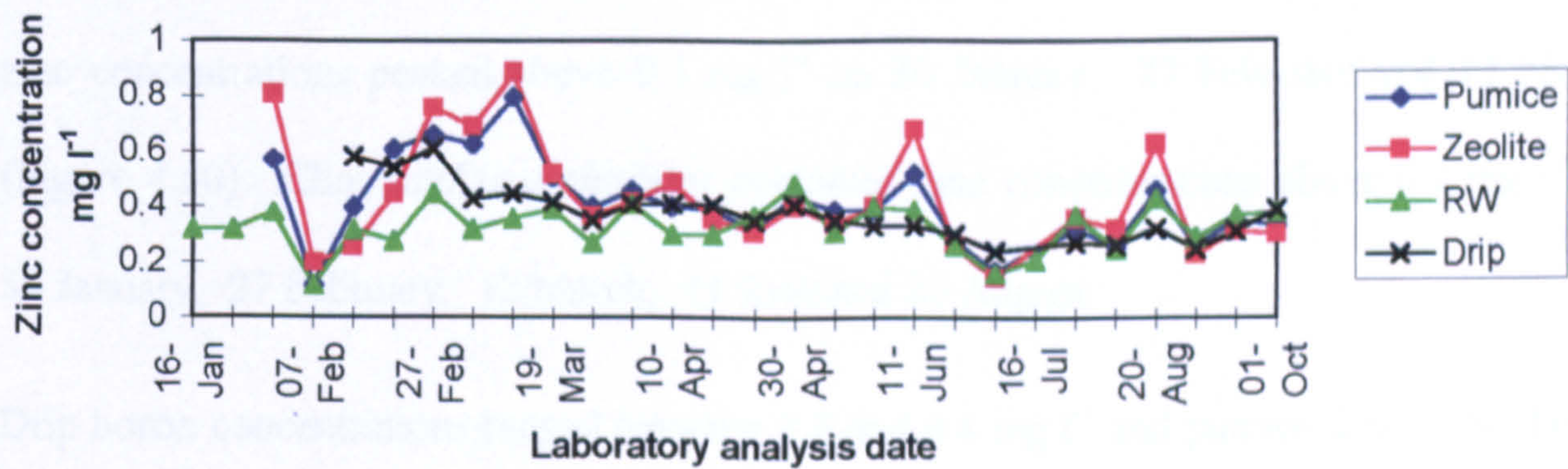
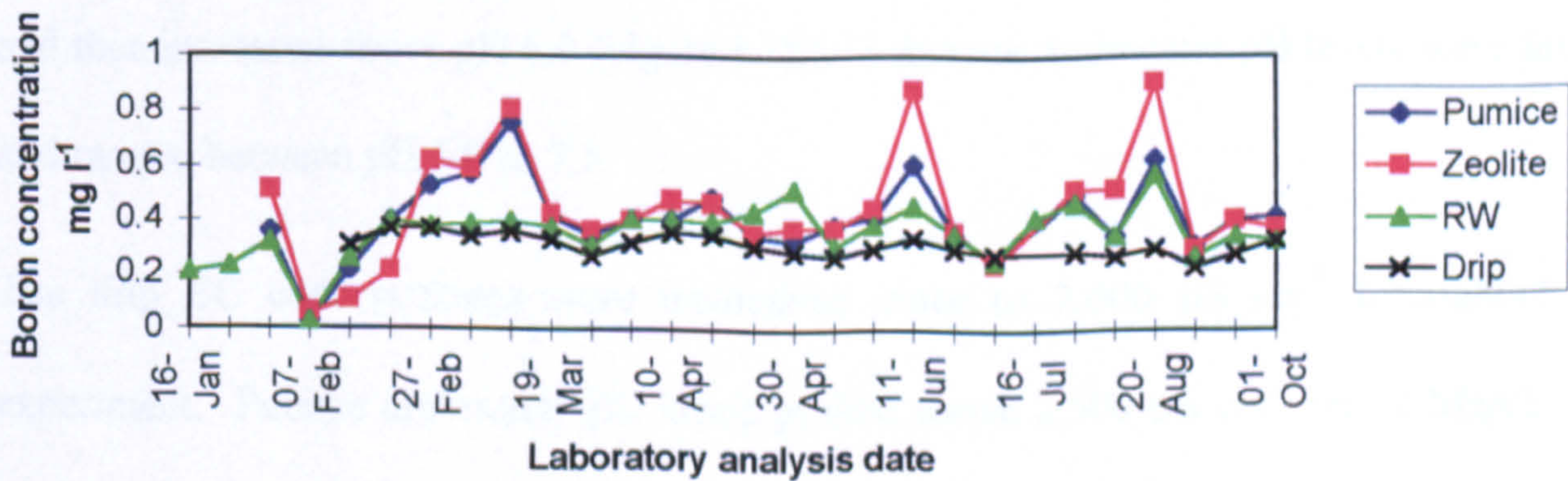


Figure 4.51 Pepper input feed and drainwater boron concentrations for three substrates



Drip copper content measured between 0.1 and 0.2 mg l⁻¹ during the eight month sampling period (Figure 4.49). Low concentrations below 0.1 mg l⁻¹ of copper were measured from all three substrates on 7 February and it is possible that plant demand for copper could have been high at the end of January and early February, prior to the start of cropping. This pattern was repeated for drainwater zinc and boron concentrations (Figures 4.50 and 4.51). Pumice drainwater contained more than 0.2 mg l⁻¹ copper on 30 January, 12 March, 11 June and 20 August. Clinoptilolite drainwater copper concentrations rose above 0.3 mg l⁻¹ on 30 January, 12 March, 11 June and 20 August. Measurements from the aluminosilicate substrates suggest that copper was involved in ion exchange mechanisms between plant roots and pumice and clinoptilolite during the experiment (Hershey *et al.*, 1980).

The zinc drip concentration range was between 0.2 and 0.6 mg l⁻¹ and pumice drainwater zinc concentrations peaked above 0.5 mg l⁻¹ on 30 January, 27 February and 12 March (Figure 4.50). Clinoptilolite drainwater contained zinc concentrations above 0.6 mg l⁻¹ on 30 January, 27 February, 12 March, 11 June and 20 August.

Drip boron concentrations ranged between 0.2 and 0.4 mg l⁻¹ and pumice drainwater boron concentrations peaked above 0.6 mg l⁻¹ on 12 March, 11 June and 20 August (Figure 4.51). By comparison, clinoptilolite drainwater boron concentrations also rose above 0.8 mg l⁻¹ on the same sampling dates.

Input pH levels ranged between 5.0 and 6.0 during the first five months of the experiment and then increased above pH 6.0 (Figure 4.52). Substrate drainwater pH levels were similar and ranged between pH 6.0 to 7.5.

The drip EC concentrations were maintained close to 2,000 $\mu\text{S cm}^{-1}$ throughout the experiment. Pumice drainwater EC levels peaked above 2,500 $\mu\text{S cm}^{-1}$ on 12 March, 30 April, 11 June, 24 July and 20 August (Figure 4.53). In comparison, clinoptilolite drainwater EC levels peaked above 3,000 $\mu\text{S cm}^{-1}$ on 12 March, 11 June and 20 August.

Figure 4.52 Pepper input feed and drainwater pH levels for three substrates

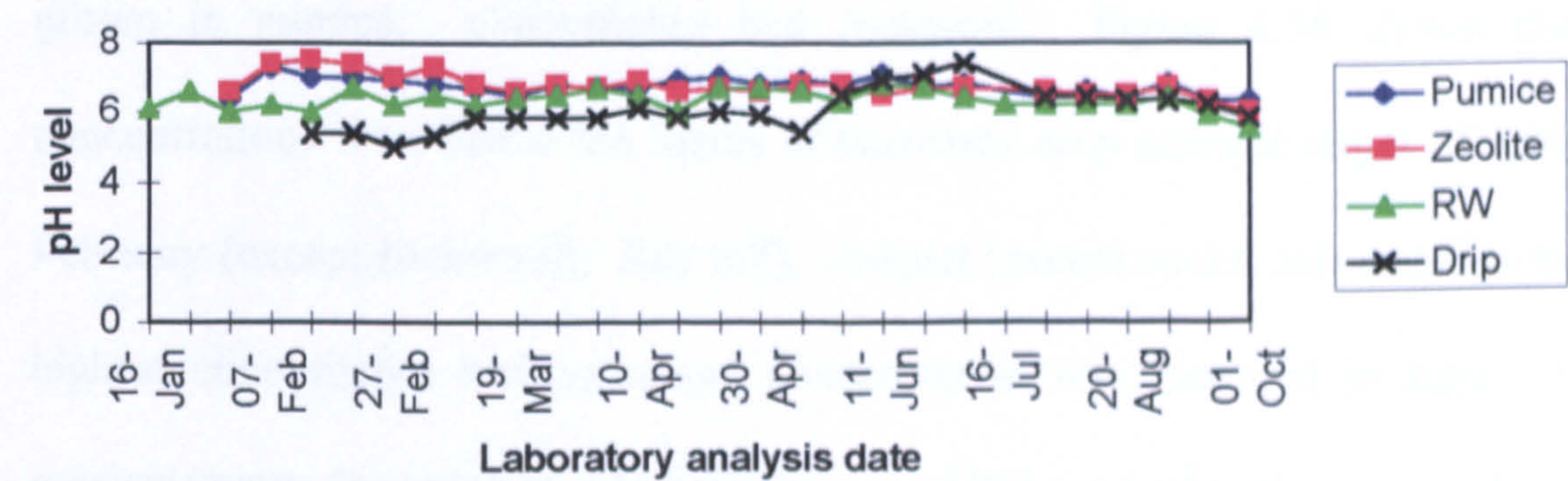
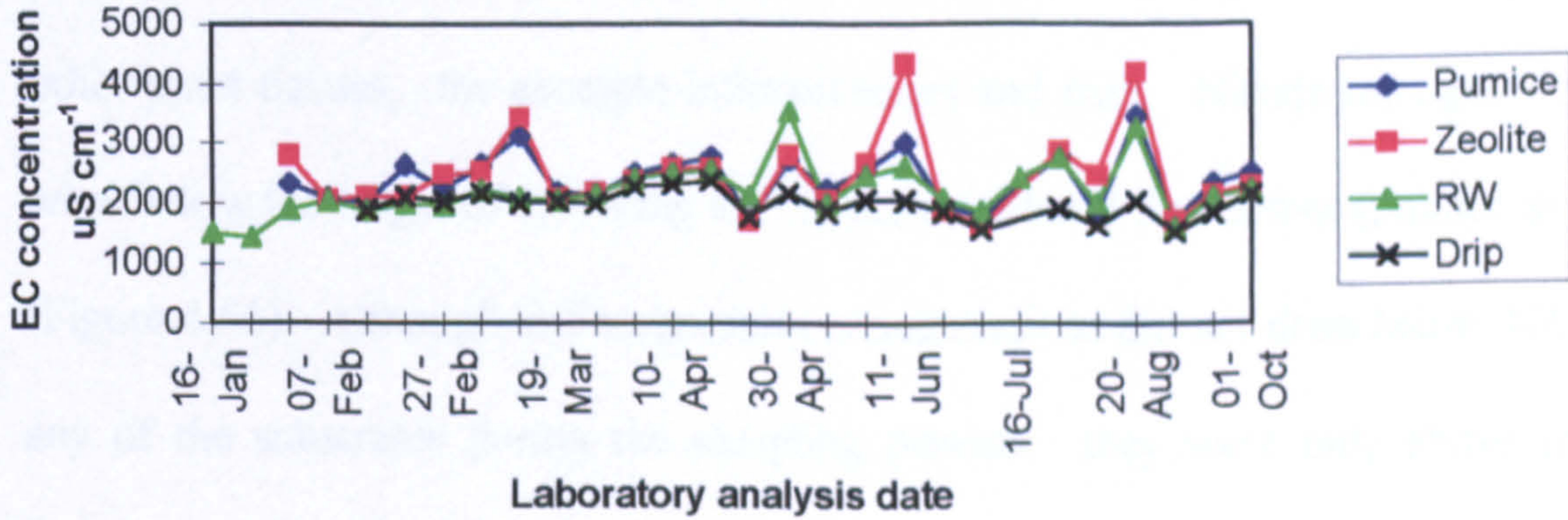


Figure 4.53 Pepper input feed and drainwater EC concentrations for three substrates



4.5.4.4 Nutrient concentration changes : major elements in the leaf tissue

Leaf analysis data revealed comparable concentrations of nutrients in samples from plants grown in pumice, clinoptilolite and rockwool. Figure 4.54 shows that potassium concentrations were below the States of Guernsey crop nutrient target of $6,000 \text{ mg kg}^{-1}$ in February (except rockwool), July (all), August (except rockwool) and October (all). The highest clinoptilolite leaf potassium concentration was recorded in June. Leaf calcium concentrations exceeded the Guernsey target of 280 mg kg^{-1} in February only (Figure 4.55). Clinoptilolite leaf samples had the highest calcium concentrations in May, June, August and October. Drainwater calcium concentrations indicated a good calcium supply for all substrates and low calcium leaf concentrations suggest that plant uptake was inadequate, suppressed by high daytime humidity deficits or that calcium was being partitioned into other plant tissues, for example inflorescences and fruit. Nitrate-nitrogen concentrations were below the target of $1,000 \text{ mg kg}^{-1}$ in April (all) and September (pumice and rockwool) (Figure 4.56). Although leaf magnesium concentrations did not drop below 100 mg kg^{-1} for any of the substrates during the sampling periods, they were only above the Guernsey target level of 450 mg kg^{-1} in April and August (Figure 4.57). As the drainwater magnesium data suggests that the magnesium supply was good during the summer, plant uptake could have been inadequate in May, June, July and September. Potassium and calcium compete effectively with magnesium and strongly depress the plant uptake rate of magnesium. Phosphorus concentrations were below the target of 300 mg kg^{-1} in March and May (Figure 4.58). Clinoptilolite samples had the highest phosphorus leaf contents in June, July and September. The leaf analysis data suggests that there was a very high uptake of phosphorus in February and this correlates well with the low drainwater concentration recorded from all three substrates. Although clinoptilolite drainwater sodium concentrations were high (target of 120 mg kg^{-1}), leaf sodium contents were higher in the pumice and rockwool leaf samples in April and June (Figure 4.59).

4.5.4.5 Nutrient concentration changes : trace elements in the leaf tissue

Leaf manganese measurements were always on or above the target (6.0 mg kg^{-1}) for all three substrates (Figure 4.60). Although the clinoptilolite appeared to be adsorbing manganese throughout the experiment, leaf manganese concentrations were always above the leaf target concentration. This suggests that sufficient manganese was available to the plants growing on clinoptilolite either direct from the liquid feed or from the clinoptilolite itself by ion exchange. Leaf zinc concentrations were consistently higher than the target of 4.5 mg kg^{-1} , with higher concentrations in April and August for all three substrates (Figure 4.61). There were generally low leaf boron concentrations, particularly in May (Figure 4.62). Concentrations were only above the target of 3.0 mg kg^{-1} in July (except pumice) and September (except clinoptilolite and pumice). It is possible that plant uptake was insufficient in March, May and June. Plant boron uptake is closely related to the pH and the external boron concentration and its distribution in plants is primarily governed by the transpiration stream (Marschner, 1995). There was little variation in drainwater pH levels during the experiment and so it is concluded that plant boron uptake and internal distribution were directly linked to the low leaf tissue boron concentrations.

There were no visual plant deficiency symptoms with any of the treatments during the experimental period. Levels of blossom end rot were lowest in the clinoptilolite samples and, correspondingly, clinoptilolite leaf samples had the highest calcium concentrations in May, June, August and October.

4.5.5 Conclusions

- Growth and development of sweet pepper plants on both unloaded clinoptilolite and pumice was very similar to production on rockwool, glasswool and foam slabs.

- Fruit quality was similar from all substrates, although clinoptilolite produced less blossom end rot and total waste fruit.
- Spring and summer yields were improved by the use of a summer carbon dioxide enrichment programme.
- Yields were maintained by provision of fresh nutrient feeds at each irrigation round, rather than by nutrient recirculation.
- The clinoptilolite adsorbed potassium and released calcium into the root zone throughout the experiment. Although clinoptilolite adsorbed potassium, there was sufficient potassium available for plants in order to support normal growth and fruit development.
- Magnesium appeared to be adsorbed and subsequently released from the zeolite over the production season.
- Clinoptilolite released sodium, especially at the start of the experiment but this did not appear to interfere with plant growth and fruit development.
- Manganese was adsorbed by the clinoptilolite throughout the experiment and there was a release of copper, zinc and boron from the clinoptilolite at similar times during the season.
- Leaf nutrient content profiles were very similar for pumice, clinoptilolite and rockwool.
- Unloaded clinoptilolite and pumice can be successfully used as substrates to produce acceptable yields of Class I peppers in an hydroponic system.

Figure 4.54 Pepper leaf potassium concentrations from three substrates

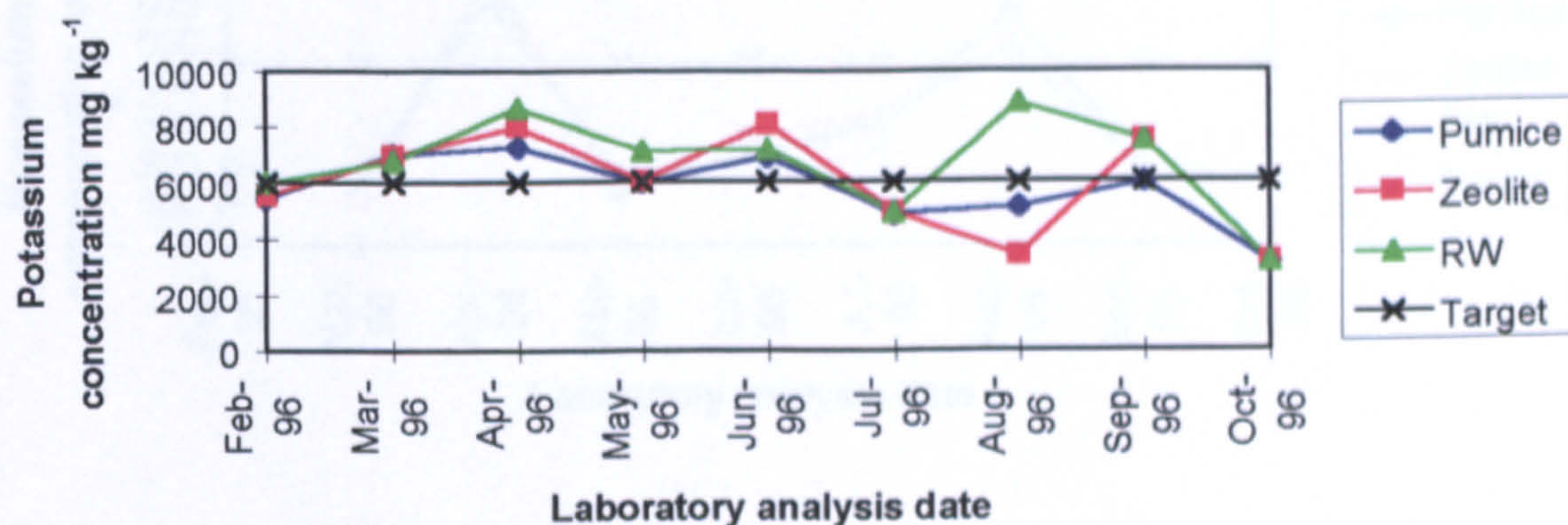


Figure 4.55 Pepper leaf calcium concentrations from three substrates

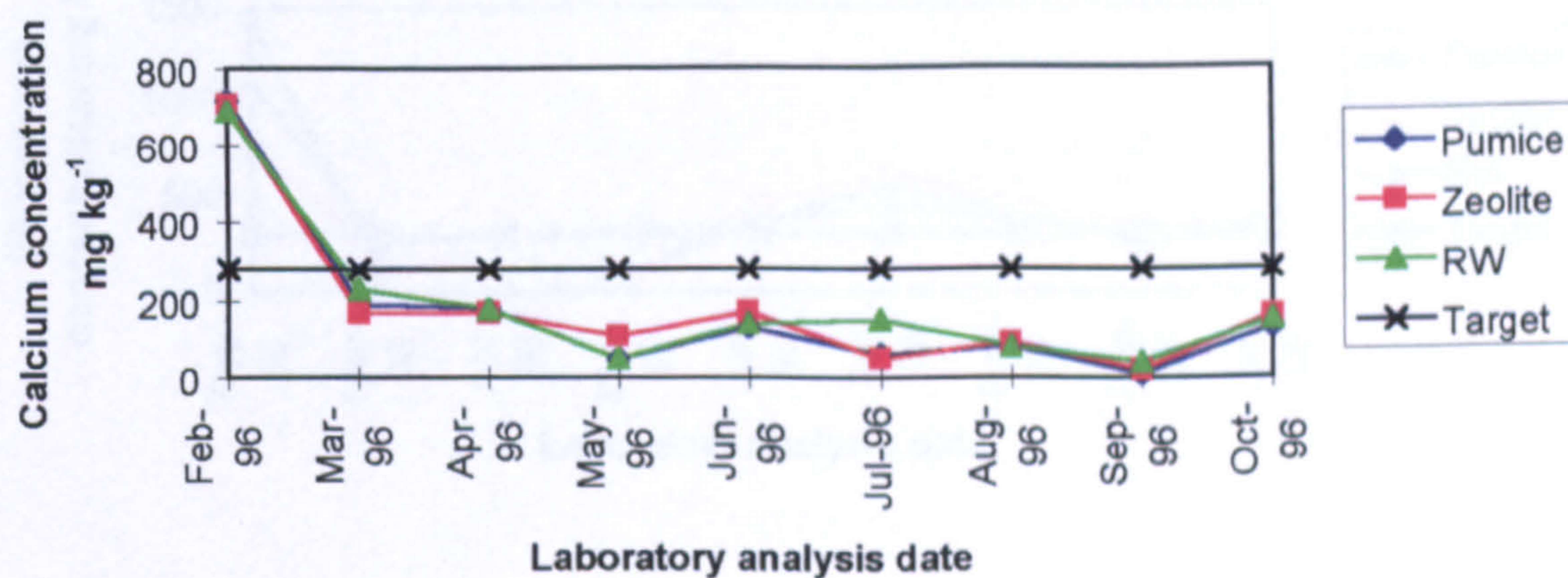


Figure 4.56 Pepper leaf nitrate-nitrogen concentrations from three substrates

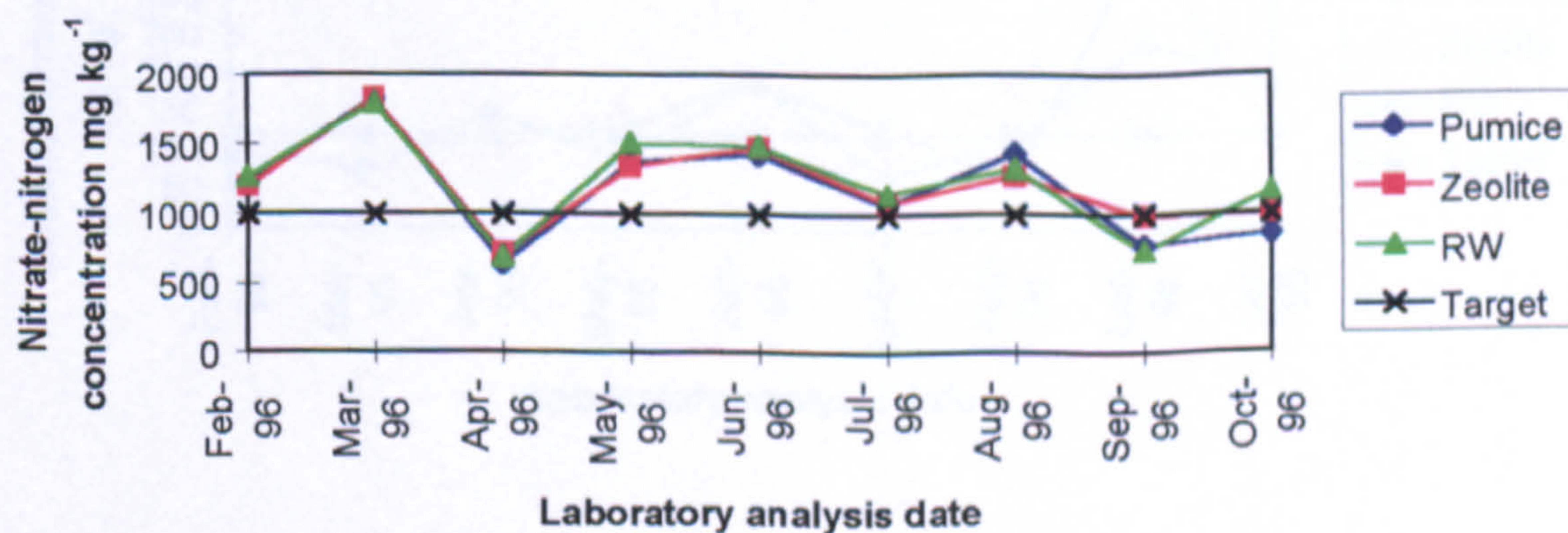


Figure 4.57 Pepper leaf magnesium concentrations from three substrates

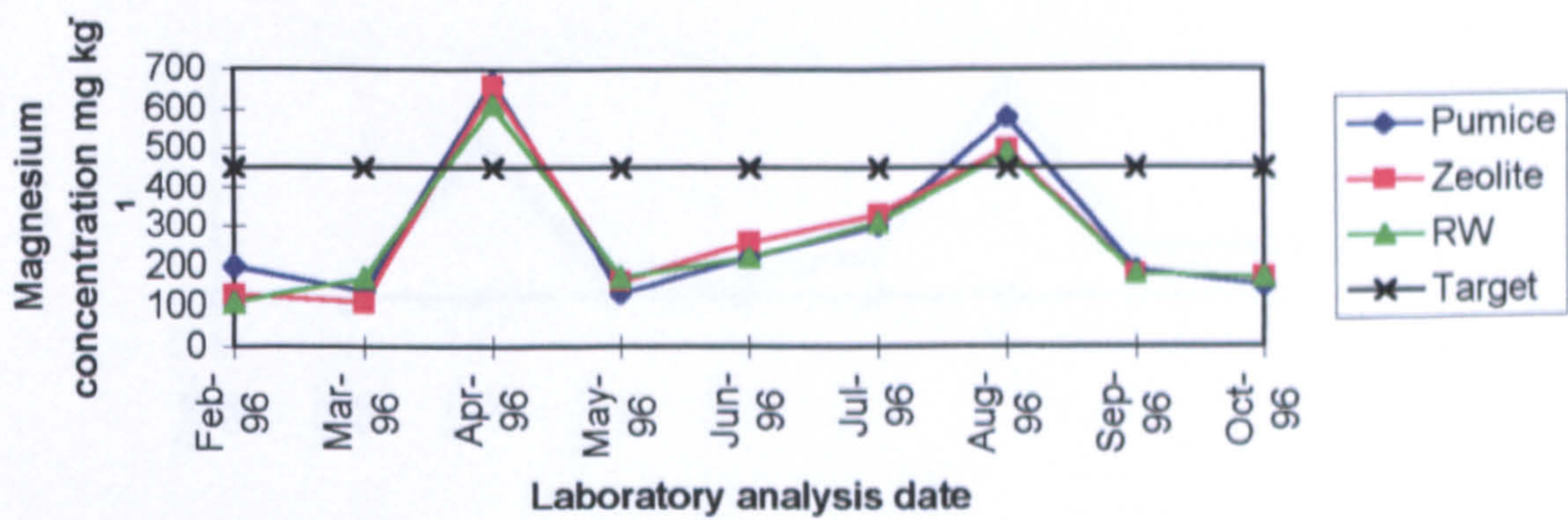


Figure 4.58 Pepper leaf phosphorus concentrations from three substrates

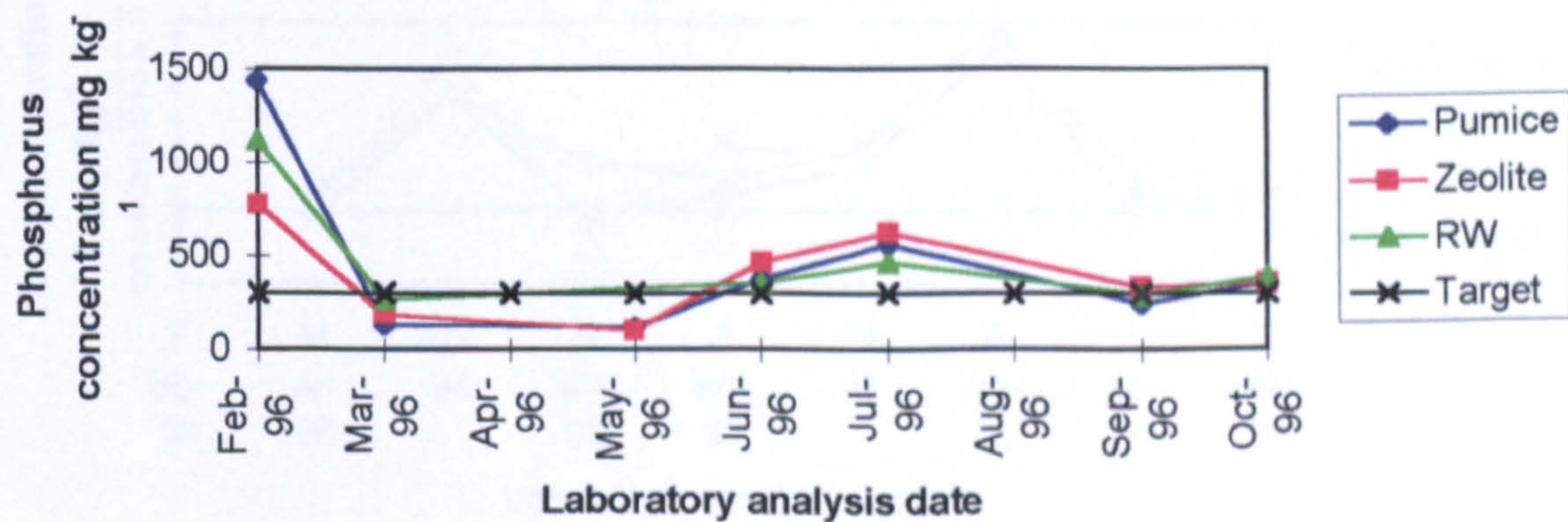


Figure 4.59 Pepper leaf sodium concentrations from three substrates

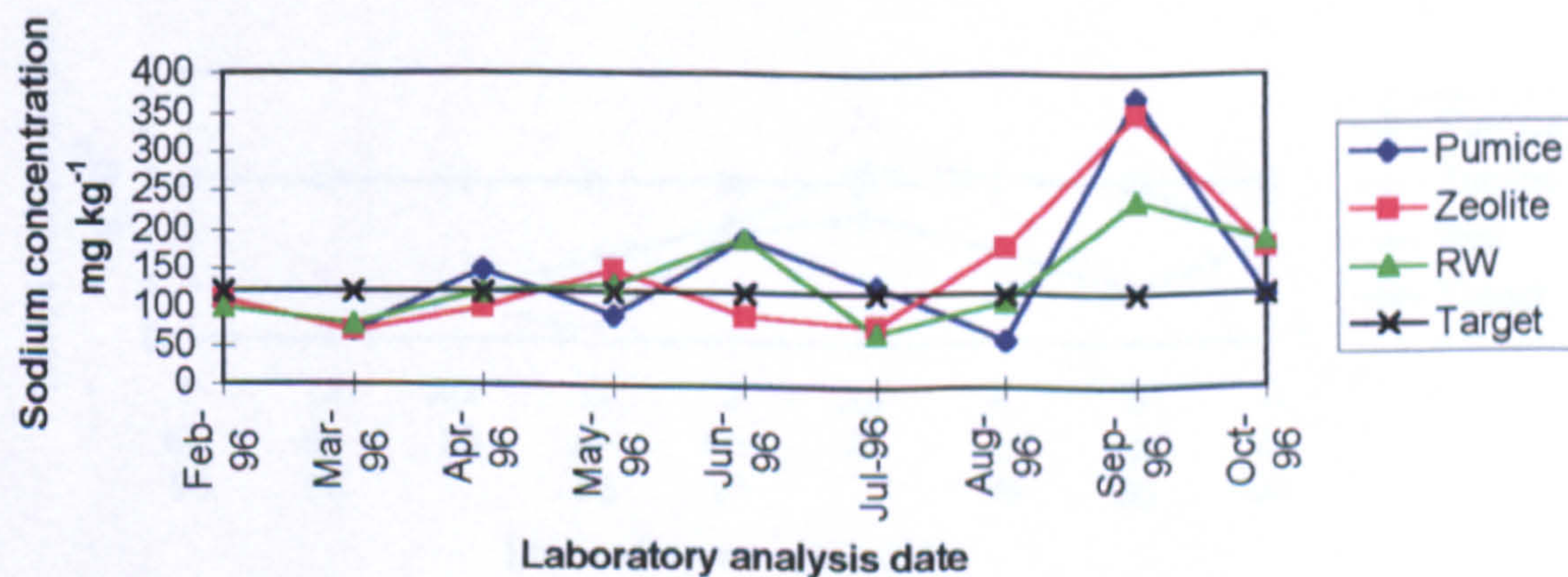


Figure 4.60 Pepper leaf manganese concentrations from three substrates

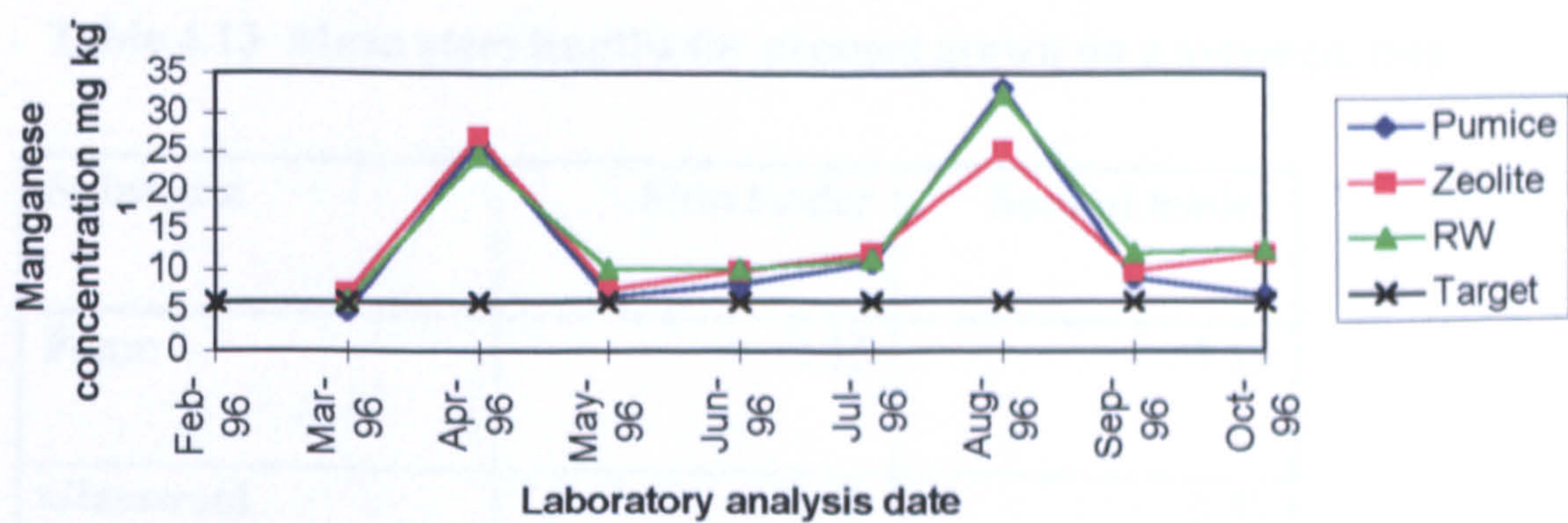


Figure 4.61 Pepper leaf zinc concentrations from three substrates

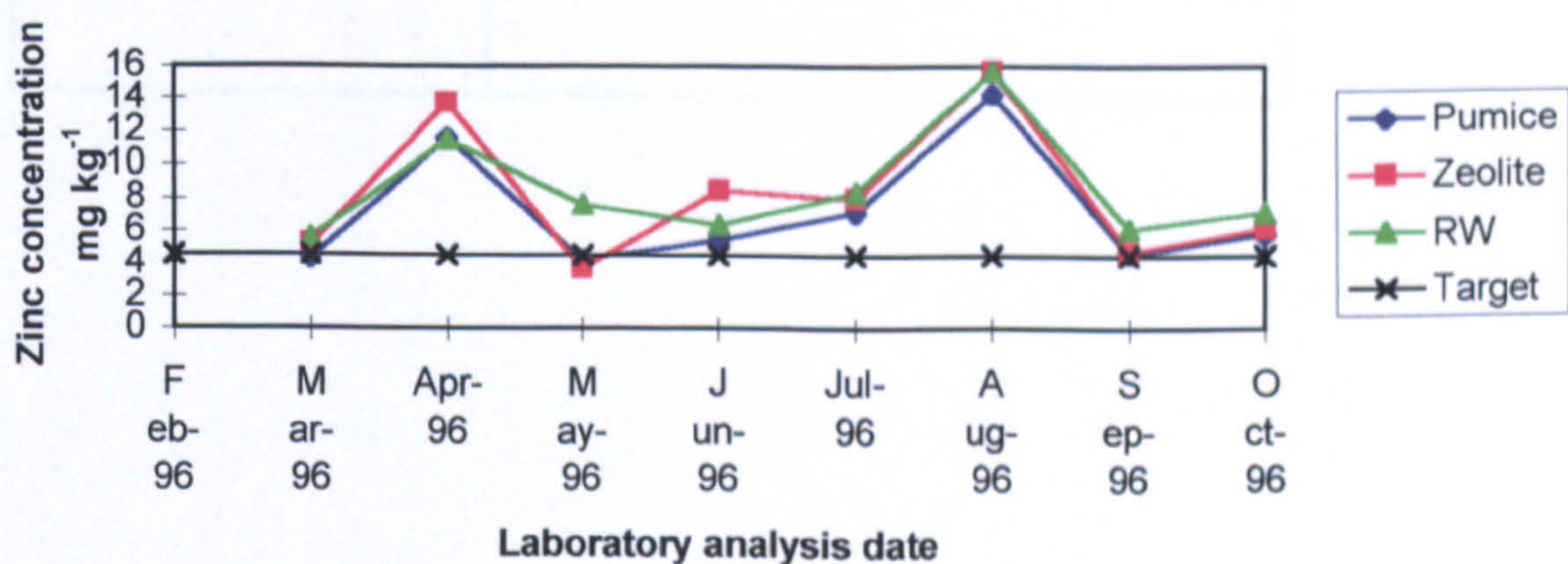


Figure 4.62 Pepper leaf boron concentrations from three substrates

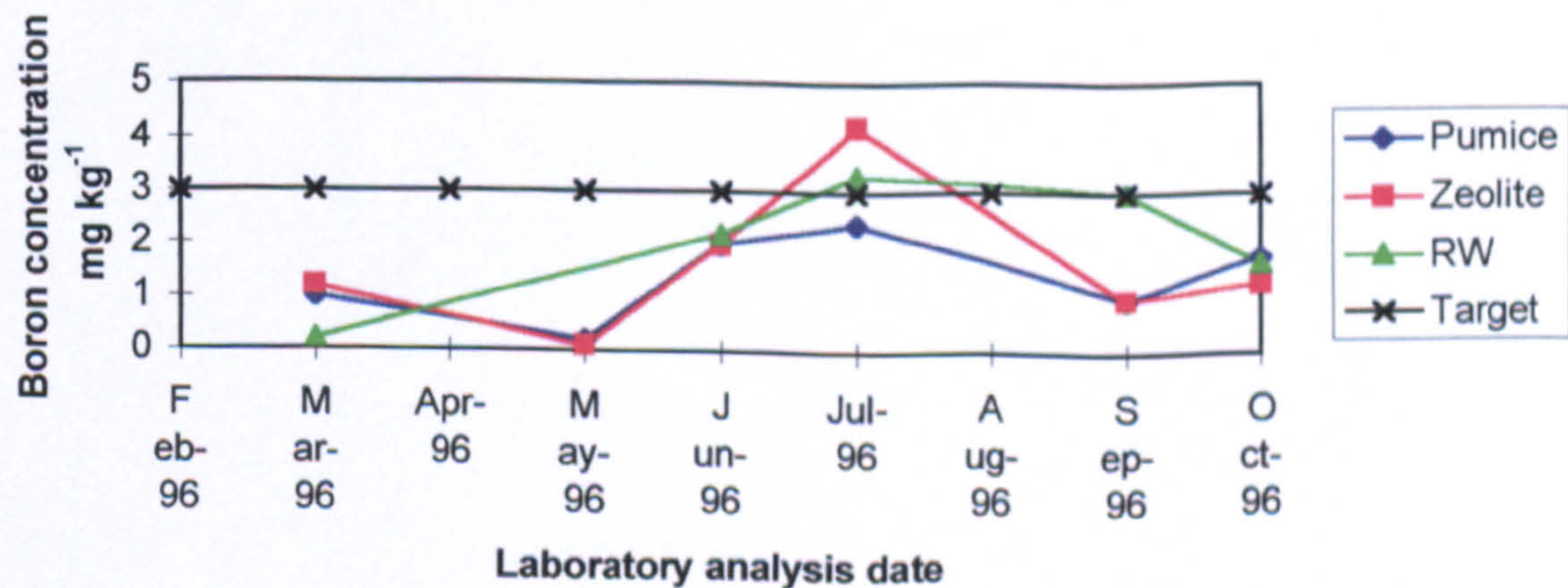


Table 4.13 Mean stem lengths for peppers grown on a v-system (m)

Substrate	First leader	Second leader
Foam	3.25	3.15
Glasswool	3.43	3.35
Pumice	3.19	2.98
Rockwool	3.39	3.27
Clinoptilolite	3.26	3.15

Table 4.14 Yield profile for ‘Mazurka’ on five substrates (n=3)

(substrate means kg m⁻²). B.E.R. = Blossom end rot, n.s. = not statistically significant

Fruit size / quality	60-70mm	70-90mm	90+mm	Total Class I	Total Class II	Total mktble	B.E.R.	Total waste
Foam	1.903	19.483	0.413	21.800	2.137	23.937	1.967	2.017
Glass-wool	2.290	21.050	0.337	23.677	1.963	25.640	2.197	2.243
Pumice	1.820	19.013	0.297	21.130	1.777	22.907	2.183	2.220
Rock-wool	1.800	20.677	0.533	23.010	2.033	25.043	2.500	2.563
Clinop-tilolite	1.850	19.063	0.400	21.313	1.567	22.880	1.750	1.783
F-test significance	p=n.s.	p=n.s.	p=n.s.	p=n.s.	p=n.s.	p=n.s.	p=n.s.	p=n.s.

Chapter Five Evaluation of nutrient-loaded clinoptilolite as a plant growth substrate

5.1 Introduction

Chapter Four detailed the inclusion of unloaded clinoptilolite zeolite into the experimental programme and illustrated its nutritional characteristics when used as a substrate irrigated with liquid feeds. The propensity of clinoptilolite to selectively adsorb cations, particularly ammonium-nitrogen and potassium, and the corresponding release of calcium into the plant root zone were demonstrated. Having established that it is possible to produce commercially acceptable yields and quality of tomatoes, peppers and carnations from plants grown on unloaded clinoptilolite, the experimental focus then switched to the performance of nutrient-loaded clinoptilolite in substrate systems. According to Allen and Ming (1995), much of the work on zeolites in the late 1980's and early 1990's concentrated on the combination of soluble minerals with zeolites to provide slow release fertilisation through a combination of dissolution and ion exchange reactions, rather than by relying on ion exchange or dissolution alone. Dissolution of the mineral apatite (phosphate rock) supplies cations for ion exchange and ion exchange captures dissolving cations, thereby increasing dissolution. At equilibrium, the overall reactions stop unless a sink, such as a plant root, is available to remove reaction products (nutrients). The plant is, therefore, able to regulate the supply of nutrients released and this is further explored in the following experiments, using only water as the solution surrounding substrate and plant roots.

The first experiment shows the initial work with the nutrient-loaded clinoptilolite 'Hydrocult S' using water only in the irrigation programmes. Subsequent experiments investigate if it is possible to produce good yields and quality of standard carnations and also sweet peppers using the nutrient-loaded clinoptilolites 'Hydrocult S' and 'Hydrocult F' irrigated with water only. Chapter Two described the chemical differences between unloaded

clinoptilolite and nutrient-loaded clinoptilolite 'Hydrocult F' and concluded that the latter had 0.42 % phosphate as P_2O_5 .

5.2 Experiment 5 An evaluation of the use of nutrient-loaded clinoptilolite zeolite in the production of standard carnations, using only water in the irrigation programme in place of liquid feeds

5.2.1 Introduction

Following earlier experiments on the suitability of nutrient-loaded clinoptilolites for the production of standard carnations (Chapter Four), this experiment aimed to examine whether the nutrient loading of the clinoptilolite would sustain a crop over a complete flower production cycle using only water in the irrigation pulses. The following objectives were set.

1. To assess plant growth and development characteristics of standard carnation varieties, growing in nutrient-loaded clinoptilolite and using only plain water in the irrigation cycles.
2. To measure actual nutrient concentrations in the irrigation water and drainwater, to determine if there were any changes in the system nitrate-nitrogen and phosphorus concentrations, in particular.
3. To measure nutrient concentration changes in the plant leaf sap over the period of the experiment.

5.2.2 Materials and methods

The varieties, cutting suppliers and flower colours are given in Table 5.1

Table 5.1 Standard carnation varieties used in the experiment

Variety	Supplier	Flower Colour
Angeline	Hilverda	Yellow
Cobra	Hilverda	Yellow
Esty	Hadar	Yellow
Faro	Selecta	Pink
Griselda	WestStek	Cerise
Master	Barbaret and Blanc	Red
Hode	Hadar	White
Napoleon	Shemi	Red
Oregan	Van Staaveren	Red
Oriana	Barbaret and Blanc	Pink
Uniko	Kooij and Zonen	Pale pink
White Giant	Lek and Zonen	White

The cuttings were planted on 30 March, 1993 at a rate of four cuttings per five litre pot, to give a final plant density of 32 plants m². Plot size was 24 pots per variety and the experimental design incorporated two replicates of each variety in a fully randomised design (Plate 3.4). An overhead irrigation system, supplied with water only, was used to maintain an even moisture level at the surface of the nutrient-loaded clinoptilolite ('Hydrocult S') and encourage rapid rooting into the substrate during the eight week establishment phase. Thereafter, the pots were dosed with water through a drip irrigation system during the life

of the crop at a rate of two litres per hour and no liquid feed was applied to the system at any time.

Shoot tips were removed approximately three weeks after planting (14 April), to encourage the formation and development of side shoots. The first flowers were picked 16 weeks after planting (19 July) and harvesting continued for 18 months. The final pick was on 30 December 1994.

5.2.3 Results

5.2.3.1 Crop yields

Yields to December 1994 are given in Table 5.2 and Figure 5.1. Average marketable yields were similar to those recorded in previous experiments using pumice (Anon, 1992). The standard varieties 'White Giant' and 'Master' performed in a similar manner in this experiment to previous experiments. Timing of flower flushes was normal with a first flush starting in July 1993 and a second season main flush starting in May 1994. Variety performance gave a rank order with 'White Giant' as the highest yielding (526 marketable Class I blooms m^{-2}) with 78% marketable (Table 5.3). In comparison, the variety 'Hode' as the lowest yielding (203 marketable blooms m^{-2}) with 36% marketable and there were highly significant differences between varieties ($p < 0.01$) (Appendix III).

5.2.3.2 Chemical analysis of irrigation water

The analysis of the irrigation water revealed a potassium range of 1 to 51 mg l^{-1} (Figure 5.2), a calcium range of 1 to 24 mg l^{-1} (Figure 5.3), a sodium range of 5 to 31 mg l^{-1} (Figure 5.4), a nitrate-nitrogen concentration range of <1 to 35 mg l^{-1} (Figure 5.6), a phosphorus range of <1 to 10 mg l^{-1} (Figure 5.7) and a conductivity range of <10 to 391 $\mu\text{S cm}^{-1}$ (Figure 5.9). The concentration ranges were taken over a 21 month sampling period.

There were no major fluctuations in the micronutrient concentration of the irrigation water throughout the sampling period.

5.2.3.3 Chemical analysis of drainwater and discussion

Analysis of the drainwater was expressed as the difference between the concentration of the irrigation water and the drainage water (Δ concentration). Data are presented for the major nutrients at six month intervals during the experiment; other samples did not yield any differences from these results (Table 5.4).

Apart from an initial release of calcium (Figure 5.3), sodium (Figure 5.4), ammonium-nitrogen (Figure 5.5) and phosphorus (Figure 5.7) from the nutrient-loaded clinoptilolite in the early stages of the experiment, the concentration of nutrients in the drainwater were low. In addition, low concentrations of nitrate-nitrogen (Figure 5.6) and magnesium (Figure 5.8) were also recorded at the start of the sampling period. The conductivity of the drainwater was $189 \mu\text{S cm}^{-1}$ higher than that of the irrigation water in samples taken four weeks after planting. However, 28 weeks after planting, the conductivity of the drainwater was $80 \mu\text{S cm}^{-1}$ lower than the irrigation water. After 54 and 72 weeks, the drainwater conductivity was 15 and $17 \mu\text{S cm}^{-1}$ lower than the irrigation water, respectively. Most importantly, there were virtually no losses of ammonium-nitrogen or nitrate-nitrogen in the drainwater, after the initial establishment period. The concentration of calcium in the drainwater was higher than in the irrigation water after four weeks; later in the experiment, concentrations of calcium were generally less in the drainwater than in the irrigation water. With sodium, the drainwater concentration was higher than in the irrigation water after four weeks. Subsequently, the concentrations of drainwater sodium were similar to the irrigation water concentrations. As in previous experiments, the selectivity of clinoptilolite for ammonium-nitrogen and potassium (Allen and Ming, 1995; Colella, 1996) was demonstrated. As part of the ion exchange balancing mechanism,

Figure 5.1 Mean Class I, waste and total blooms m⁻² for all standard carnation varieties growing in nutrient-loaded clinoptilolite 'Hydrocult S'

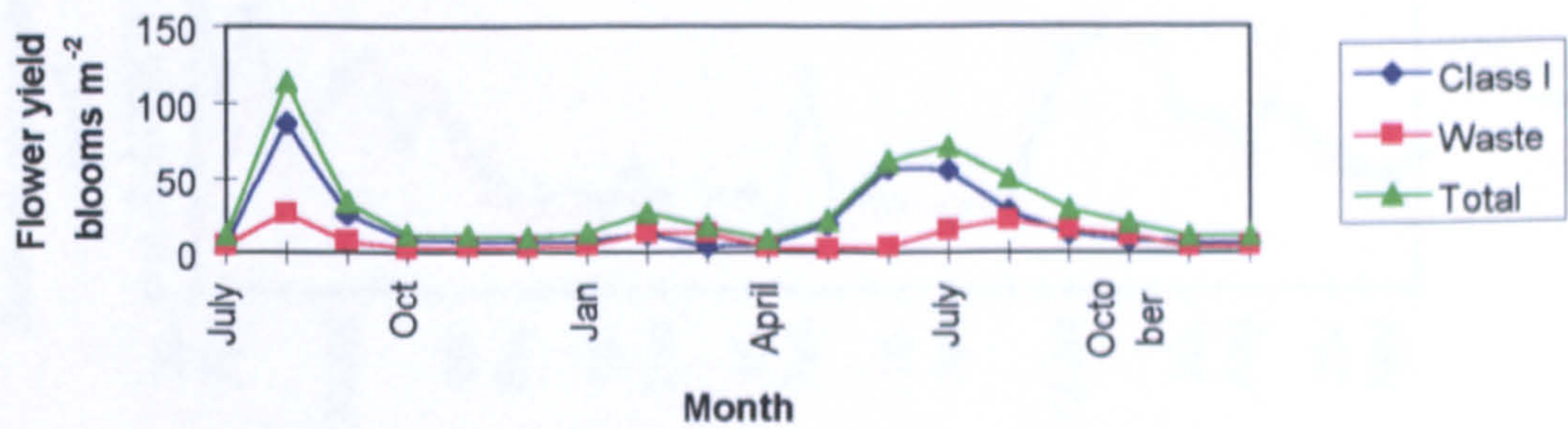


Figure 5.2 Potassium concentrations in irrigation and drainwater samples

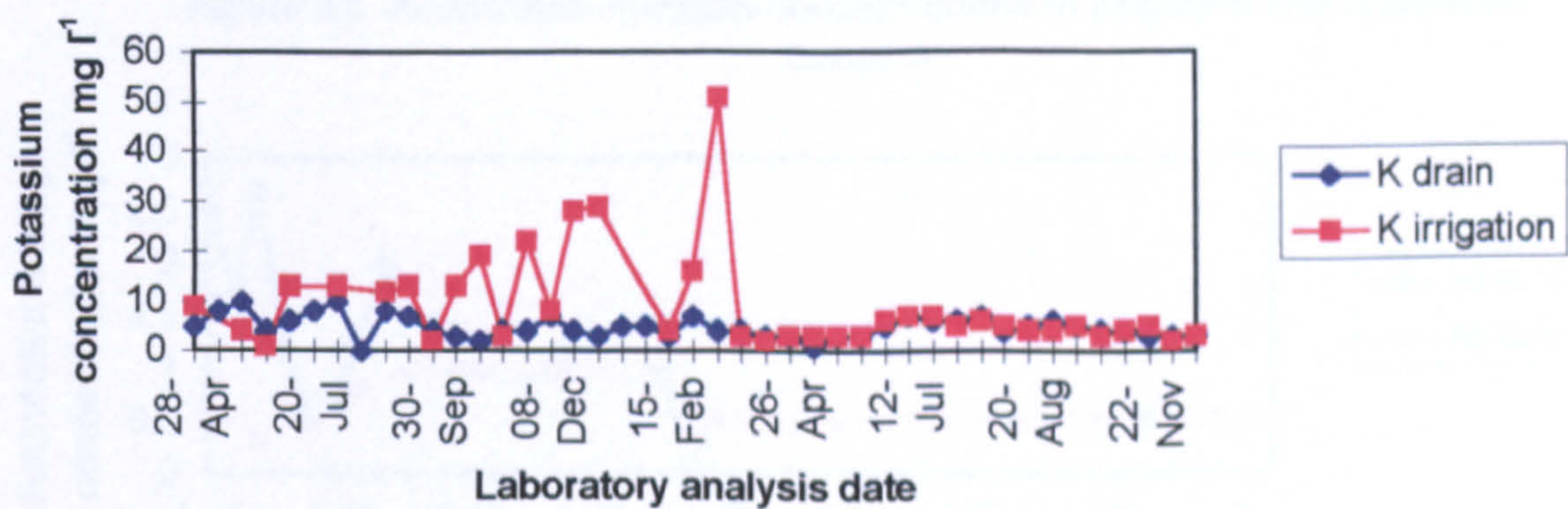


Figure 5.3 Calcium concentrations in irrigation and drainwater samples

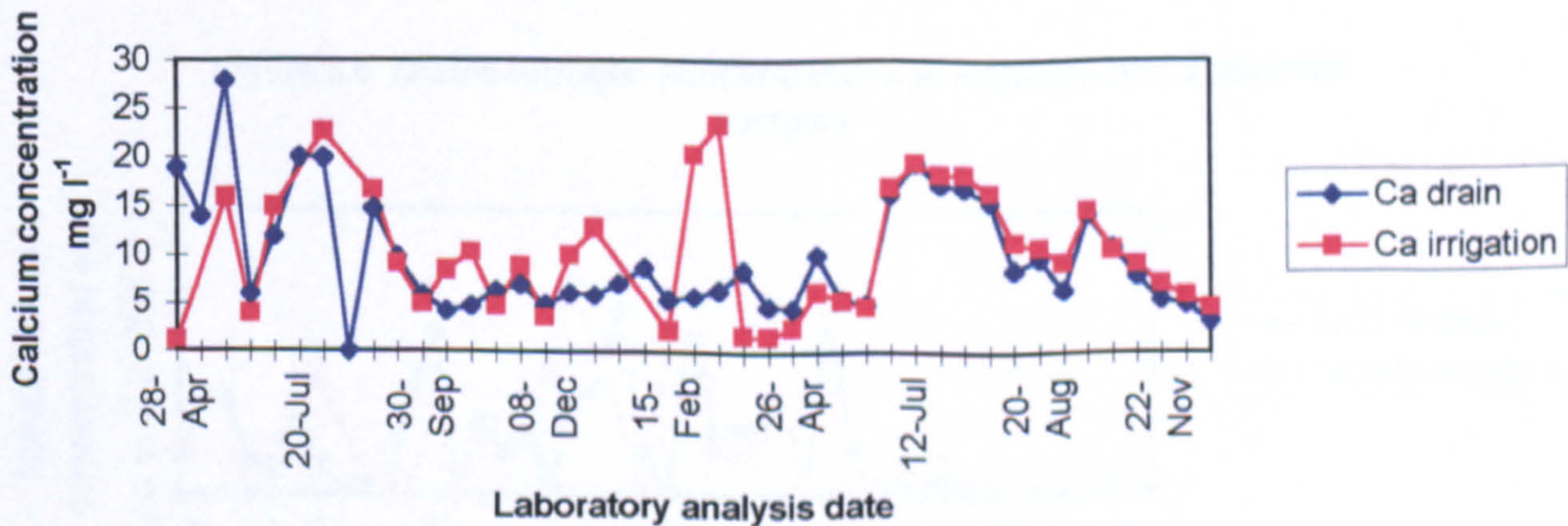


Figure 5.4 Sodium concentrations in irrigation and drainwater samples

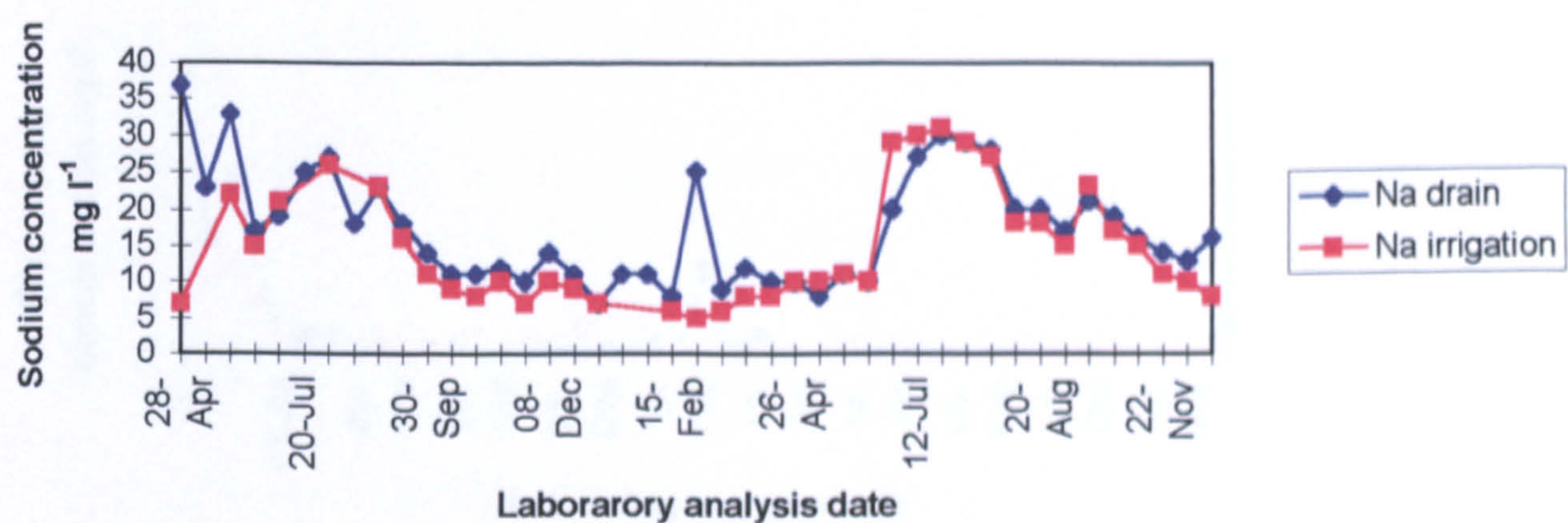


Figure 5.5 Ammonium-nitrogen concentrations in irrigation and drainwater samples

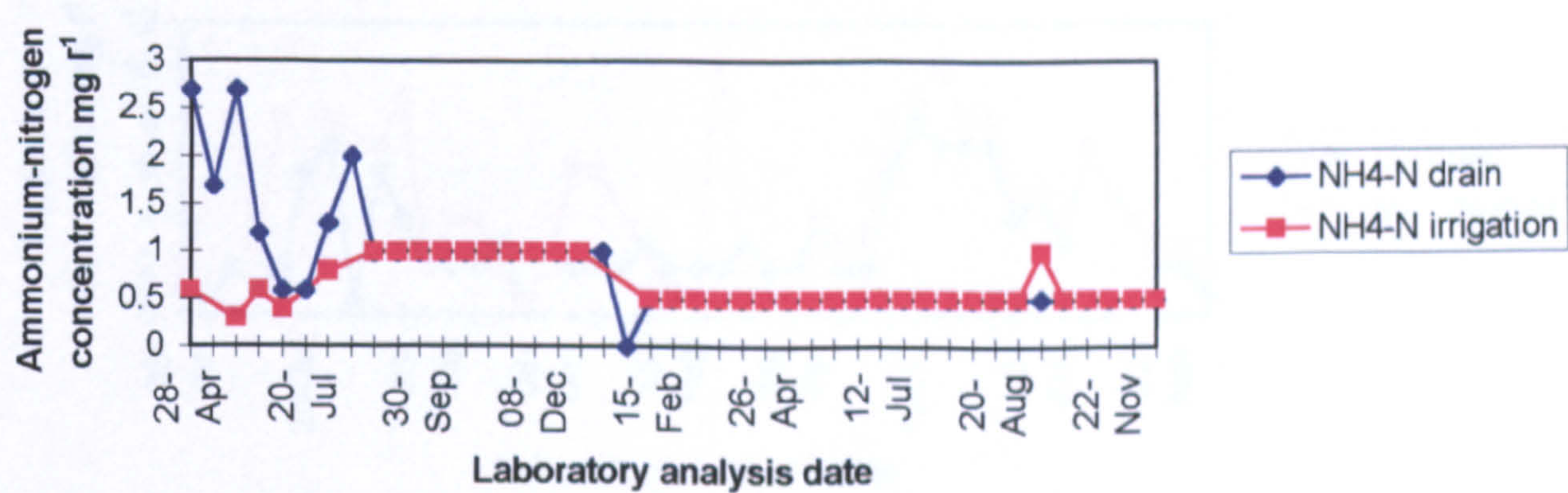


Figure 5.6 Nitrate-nitrogen concentrations in irrigation and drainwater samples

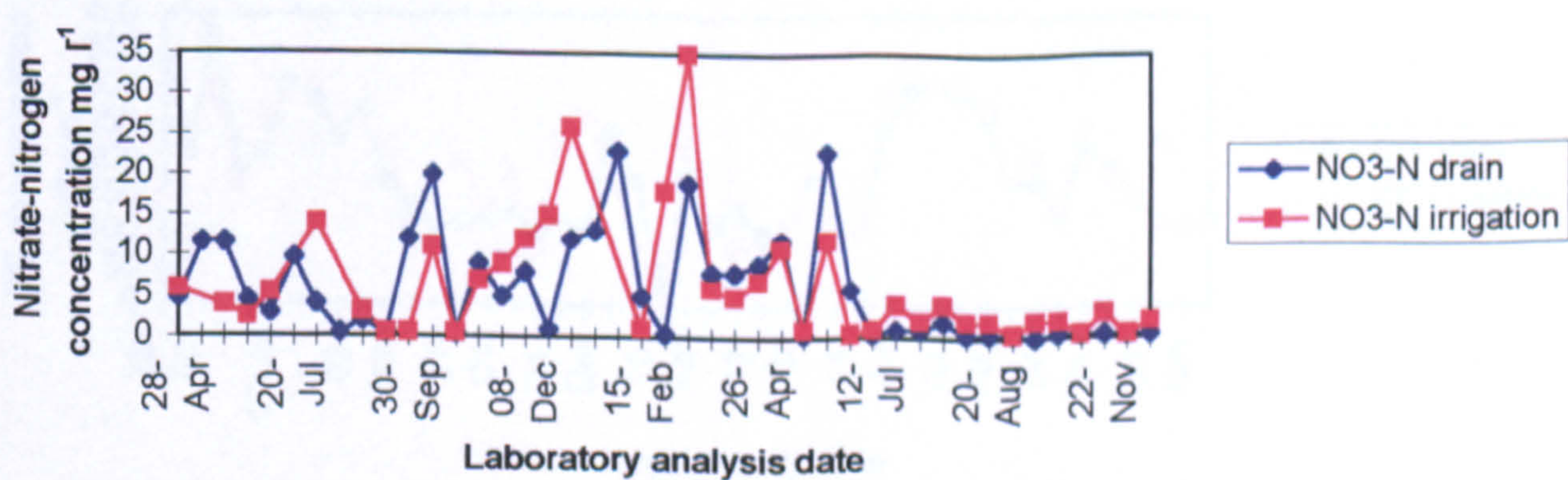


Figure 5.7 Phosphorus concentrations in irrigation and drainwater samples

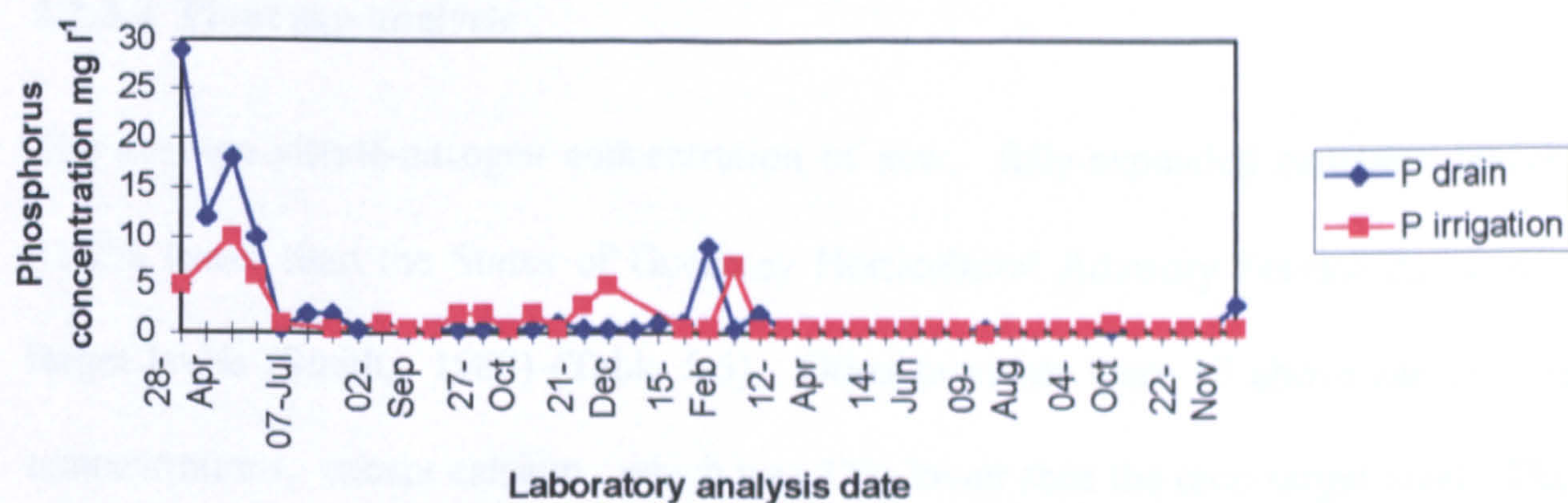


Figure 5.8 Magnesium concentrations in irrigation and drainwater samples

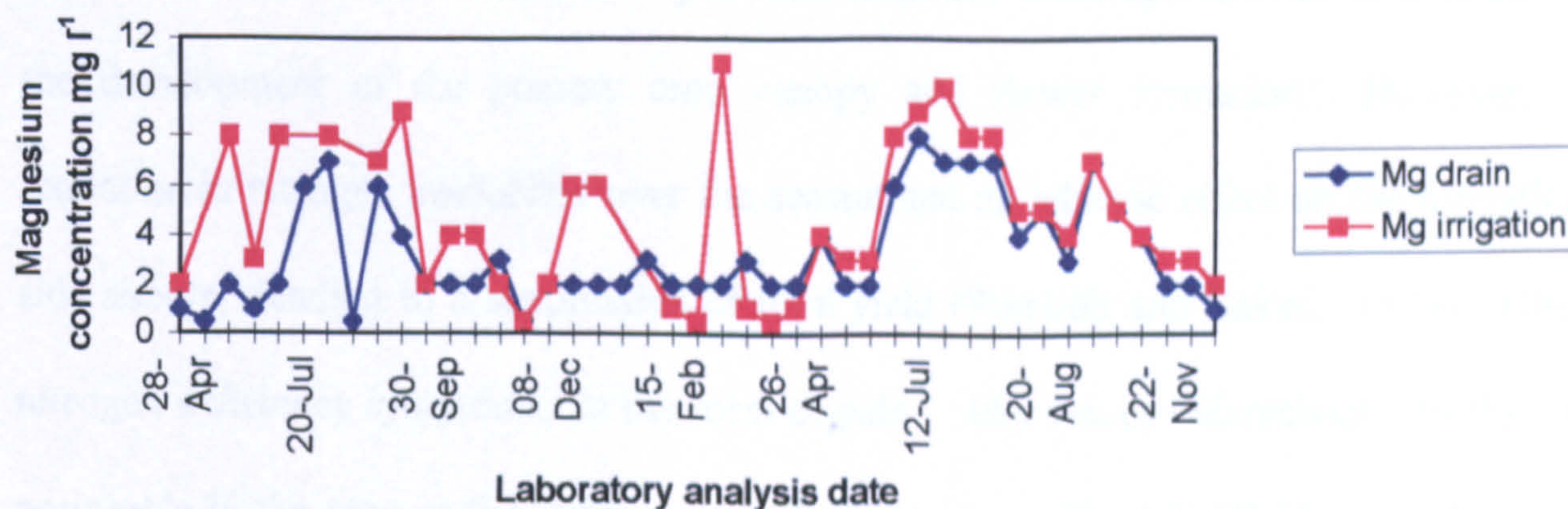
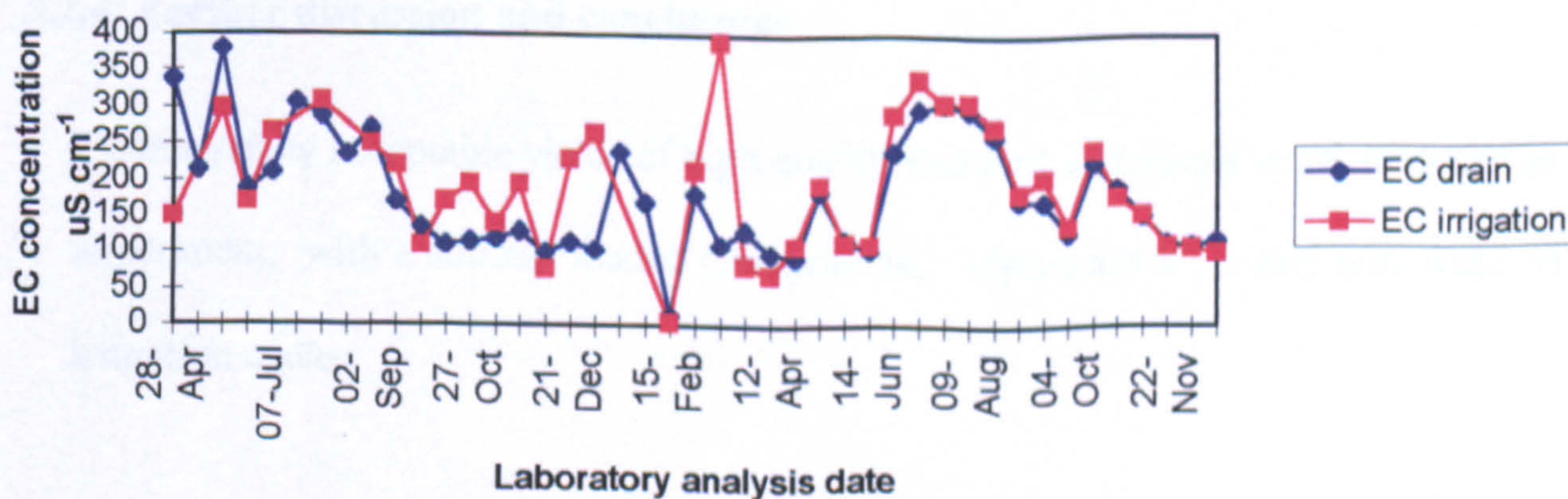


Figure 5.9 EC concentrations in irrigation and drainwater samples



sodium, calcium and magnesium were released from the clinoptilolite, particularly at the start of the experiment.

5.2.3.4 Plant sap analysis

The average nitrate-nitrogen concentration of new, fully-expanded carnation leaves was 51.7% lower than the States of Guernsey Horticultural Advisory Service carnation crop target levels (Smith, 1988) (Table 5.5). Other nutrients were all above the crop target concentrations, except calcium, which was 32% lower than the crop target level. The leaf analysis data show no marked differences from previous data collected at the experimental site, including an adjacent glasshouse compartment containing carnation varieties growing on pumice and receiving regular inputs of liquid fertiliser.

Despite the difference in nitrate-nitrogen concentration, there appeared to be little effect on the development of the primary crop canopy and flower formation. However, the reduction in nitrogen availability over the season had an adverse effect on the formation of side shoots, leading to a suppression of total yield (Sutcliffe and Baker, 1974). Nitrate-nitrogen deficiency symptoms, in the form of pale, older leaves (Marschner, 1995), were noticeable in the crop in the latter stages of production. The MAFF Manual of carnation production (1967) also detailed the symptoms of severe nitrogen deficiency as an excessive loss of leaves from the base of the plant upwards and premature yellowing to browning of mid-leaves, with the appearance of purple-red pigments.

5.2.4 Further discussion and conclusions

- Commercially acceptable yields of high quality standard carnations were produced in this experiment, with a nutrient loaded clinoptilolite, 'Hydrocult S', using only water in the irrigation cycles.

- Fast plant establishment relied on the careful maintenance of moist conditions in the rooting zone. This was complicated by rapid drying of the substrate at the pot surface. Early rooting was satisfactory but it is possible that dry substrate conditions and high initial EC concentrations in the drier zones could have impeded further root development. This could have been improved by increasing the proportion of fine grade clinoptilolite and, possibly, a water absorbent gel or proportion of bentonite in the substrate mix.
- The main nutritional limiting factor to plant growth was nitrogen and the substrate became depleted in ammonium-nitrogen by the end of the first flower flush. Subsequent production of shoots was limited by the availability of nitrogen from the substrate and from the irrigation water.
- As phosphorus is not held as a cation within the clinoptilolite matrix, an initial release of phosphorus as phosphate was expected in the first drainage flushes. The sap analysis results indicated that there was an adequate concentration of phosphorus in the new leaf tissue and that there were no phosphorus deficiency symptoms evident in the crop canopy, however.
- Potassium was readily absorbed by the plants from the zeolite and it is likely that an interaction with calcium and magnesium was involved in the cation exchange process.
- As indicated in the sap analysis results, there was a lower concentration of calcium present and this was probably more related to plant uptake from the root zone and subsequent internal plant transport under the influence of glasshouse humidity levels. Any cations released into the root zone later in the experiment were probably absorbed quickly by active plant roots or re-adsorbed by the clinoptilolite.
- It was noticeable that there was a low level of root and stem base disease problems over the winter period in this crop. This could have been due to a combination of dry

substrate surface conditions and the lower availability of nitrogen thus preventing soft, luxuriant growth.

Table 5.2 Standard carnation yield results (monthly and (total) cumulative blooms m⁻² to the end of December, 1994 meaned over replicates n=3).

L.S.D. = least significant difference, F-test = significance level

Variety	Mean Class I blooms m ⁻²	Mean waste blooms m ⁻²	Mean total blooms m ⁻²	Marketable % of total
Angeline	21.778 (392)	3.444 (62)	25.222 (454)	86
Cobra	16.222 (292)	12.333 (222)	27.722 (514)	57
Esty	23.833 (429)	13.667 (246)	37.500 (675)	64
Faro	19.778 (356)	6.667 (120)	26.444 (476)	75
Griselda	23.500 (423)	5.889 (106)	29.389 (529)	80
Master	21.444 (386)	6.389 (115)	27.833 (501)	77
Hode	11.278 (203)	19.722 (355)	31.000 (558)	36
Napoleon	21.722 (391)	8.000 (144)	29.722 (535)	73
Oregan	19.556 (352)	4.444 (80)	24.000 (432)	81
Oriana	24.333 (438)	9.500 (171)	33.833 (609)	72
Uniko	15.056 (271)	15.722 (283)	30.778 (554)	49
White Giant	29.222 (526)	8.111 (146)	37.333 (672)	78
L.S.D. (5%)	7.663	5.803	7.787	
L.S.D. (1%)	10.128	7.670	10.293	
L.S.D. (0.1%)		9.886		
F-test	p=**	p=***	p=**	

Table 5.3 Class I, waste and total fresh wt blooms m⁻² meened over twelve standard carnation varieties grown in nutrient-loaded clinoptilolite, 'Hydrocult S').

L.S.D. = least significant difference, F-test = significance level

Month	Mean Class I blooms m⁻²	Mean waste blooms m⁻²	Mean total blooms m⁻²
July, 1993	6.667	5.667	12.330
August	86.917	27.167	114.08
September	26.250	8.250	34.500
October	9.250	3.250	12.500
November	8.250	4.167	12.420
December	8.167	3.917	10.830
January, 1994	8.333	5.333	13.670
February	13.333	13.667	27.000
March	4.500	13.583	18.080
April	6.000	3.583	9.580
May	19.083	2.667	21.750
June	56.833	4.333	61.170
July	55.167	15.750	70.920
August	27.583	22.167	49.750
September	13.000	16.167	29.170
October	8.667	11.333	20.000
November	7.083	4.500	11.580
December	6.500	5.333	11.830
L.S.D. (5%)	9.385	7.108	9.538
L.S.D. (1%)	12.405	9.395	12.606
L.S.D. (0.1%)	15.988	12.109	16.248
F-test	p=***	p=***	p=***

Table 5.4 Δ concentration (drainwater minus irrigation water) of pH, EC and nutrients at six monthly intervals in the experiment (n=1)

	Sample date 28/04/93	Sample date 27/10/93	Sample date 26/04/94	Sample date 25/10/94
pH	0.100	0.200	0.000	-0.200
EC $\mu\text{S cm}^{-1}$	189.000	-80.000	-15.000	-17.000
NH ₄ -N mg l^{-1}	2.100	0.000	0.000	-0.500
NO ₃ -N mg l^{-1}	-1.100	0.000	2.000	-2.000
P mg l^{-1}	24.000	-1.500	0.000	-0.500
K mg l^{-1}	-4.000	-17.000	0.000	0.000
Ca mg l^{-1}	17.800	-5.600	2.000	-0.300
Mg mg l^{-1}	-1.000	-2.000	1.000	0.000
Na mg l^{-1}	30.000	3.000	0.000	-2.000
Cl mg l^{-1}	N/A	-1.000	-1.000	0.000
Fe mg l^{-1}	-0.010	-0.130	0.090	-0.090
Mn mg l^{-1}	-0.080	0.000	0.000	0.000
Cu mg l^{-1}	0.010	-0.015	0.000	0.000
Zn mg l^{-1}	0.070	-0.030	0.010	0.020
B mg l^{-1}	0.050	-0.030	0.040	-0.010

Table 5.5 Standard carnation plant sap analytical data from nutrient-loaded clinoptilolite ('Hydrocult S') and comparable data collected from a parallel experiment involving standard carnations growing in pumice (mean monthly measurements mg kg⁻¹). Each sample consisted of 25 leaves from separate plants within each plot

Nutrient	Target concentration mg kg ⁻¹	'Hydrocult S' mg kg ⁻¹	Pumice mg kg ⁻¹
NO ₃ -N	300	145	235
P	300	569	591
K	3200	3344	2966
Ca	300	204	210
Mg	200	253	231
Na	180	191	184
Fe	4.0	5.8	5.2
Mn	6.0	16.6	13.6
Cu	1.6	7.7	8.1
Zn	4.0	12.4	6.8
B	10.0	14.8	8.8

5.3 Experiment 6 An examination of the growth and flower production of standard carnations grown on nutrient-loaded clinoptilolite irrigated with water only compared with pumice and foam substrates fertigated with liquid feeds

5.3.1 Introduction

Experiment Five illustrated how it was possible to grow standard carnation varieties on nutrient-loaded clinoptilolite using only water in the irrigation cycles over a production season spanning 18 months. This experiment examined the performance of two standard carnation varieties on four substrates pumice, foam, nutrient-loaded clinoptilolite ('Hydrocult F') and a combination of nutrient-loaded clinoptilolite ('Hydrocult F') and a crosslinked polyacrylamide gel ('Alcosorb 400'). 'Hydrocult F' (high nutrient-loaded clinoptilolite) contained approximately twice the initial concentration of ammonium-nitrogen, nitrate-nitrogen and phosphorus compared with 'Hydrocult S' (low nutrient-loaded clinoptilolite). Synthetic water imbibing polymers, such as 'Alcosorb 400' can be used to aid water management by improving the water retention properties of soils or substrates. The super-absorbant polymers are able to absorb water, usually in the region of 200-400 times their weight of deionised water, forming discrete gel particles into and around which roots can grow and extract water (Bunt, 1988). The ability to absorb water is influenced, however, by the root zone nutrient concentration and absorption may be reduced by up to 60% (Bragg, 1995).

In Experiment Five, there was no comparison with other substrates grown with liquid feed inputs and so there was no opportunity to check if yields were comparable with standard substrates, such as pumice, and if there was any reduction in drainwater nutrient concentration by using nutrient-loaded clinoptilolite. One of the practical problems identified in the experiments with the use of clinoptilolite in pots is that the surface can dry rapidly and that this may cause rooting difficulties, high EC zones or reduced potential

opportunity for root ion exchange. Therefore, in an attempt to reduce drying at the pot surface, a separate treatment involving a polyacrylamide gel was included.

In addition, flue-gas carbon dioxide was available throughout this experiment and so it was projected that yields and quality would be improved as a direct result (Nederhoff, 1994). Replicating the plots and adding in pumice and foam as comparative substrates were also improvements in the experimental design. Nutrient concentrations were measured in drainwater, leaf and substrate samples.

5.3.2 Objectives

1. To obtain information on the growth and development of standard carnations on pumice and foam cylinders receiving liquid feed inputs throughout the life of the crop, compared with a nutrient-loaded clinoptilolite ('Hydrocult F') and a mixture of nutrient-loaded clinoptilolite ('Hydrocult F') and a polyacrylamide gel ('Alcosorb 400'), receiving only water in the irrigation cycles.
2. To assess flower yield and quality. To utilise a flue-gas low level carbon dioxide enrichment system in order to improve production, especially during the spring and summer months.
3. To measure changes in drainwater nutrient concentration to determine if there was less leaching of nutrients from the nutrient-loaded clinoptilolite systems, with particular reference to ammonium-nitrogen, nitrate-nitrogen and phosphorus.
4. To measure changes in plant leaf sap nutrient concentration to monitor the nutrient concentration profile of the nutrient-loaded clinoptilolite, with particular regard to leaf sap nitrate-nitrogen.
5. To measure changes in substrate nutrient concentration at the end of the experiment by using analytical methods involving acid digestion and sodium extraction techniques.

5.3.3 Materials and methods

The varieties, cutting suppliers and flower colours are listed below.

1. White Giant (Lek and Zonen) - white.
2. Master (Barbaret and Blanc) - red.

Two varieties of standard carnation cuttings were planted into pumice, foam and nutrient-loaded clinoptilolite on 23 February 1995. One treatment consisted of nutrient-loaded clinoptilolite plus 10% by volume of a polyacrylamide gel ('Alcosorb 400') at a rate of three grams per five litre pot. Each plot contained 24, five litre, black polypropylene pots per variety and a plant density of 32 plants m² was achieved by using four cuttings per pot. The experimental design was a two-way factorial randomised block, in which the factors were substrate and variety. The design incorporated three replicates of each variety and, as the yield was assessed at monthly intervals, these assessments comprised repeated measures.

The pumice and foam pots were irrigated with nutrient-balanced liquid feeds and the nutrient-loaded plots were irrigated, using a separate irrigation system, with water only over the 22 month growing period. An irrigation programme, based on light levels received by the crop, was managed by a Priva environmental computer system. Side shoot formation was encouraged by the removal of the main stem apical meristem three weeks after planting.

A biological control programme was utilised as the main defence against carnation pests and compatible chemicals were integrated into the programme to control both pests and diseases, as required. The first flowers were picked four months after planting and harvesting was performed three times each week until the final harvest on 31 December 1996.

5.3.4 Results and integral discussion

5.3.4.1 Plant growth, flower yield and quality

The flower yield pattern over the 18 month production period was similar for the two varieties growing on each substrate, with a major flush of flowers in July 1995 and also over the period June to August, 1996 inclusive (Figure 5.10). These two major production periods were interspersed with smaller flushes of flowers in November 1995, February 1996 and December 1996 (Figure 5.10).

Initially, flower yields were similar from both varieties in all of the treatments. Following the first flower flush, however, the production of side shoots from plants in the nutrient-loaded clinoptilolites was visibly slower and weaker than in pumice. This resulted in a lower number of Class I flower stems being produced in the nutrient-loaded clinoptilolite treatments, especially over the period covering June to August, 1996 (Figure 5.11; Table 5.6).

The data were analysed for a two-way factorial randomised block design, with yield being the response variable (Appendix III). Mean cumulative Class I yields were highest for both 'White Giant' and 'Master' in pumice at 755 blooms m⁻² and 624 blooms m⁻², respectively, to the end of December 1996 (Figure 5.11). In comparison, the mean cumulative Class I yields for 'White Giant' and 'Master' in nutrient-loaded clinoptilolite were 564 blooms m⁻² (25.3 % lower than on pumice) and 464 blooms m⁻² (25.6 % lower than on pumice), respectively, to the end of December 1996 (Tables 5.6 and 5.7).

5.3.4.2 Major element concentrations in the drainwater

Drainwater nutrient concentrations from samples taken from all four substrates ('White Giant' plots) are given in Appendix III. The drainwater nutrient concentration from the pumice and foam systems was very high in comparison to the equivalent samples from the

nutrient-loaded clinoptilolite. Pumice and foam drainwater potassium concentrations were consistently above 200 mg l⁻¹ and similar in profile from May 1995 until December 1996 (Figure 5.12). Clinoptilolite drainwater potassium concentrations were comparatively very low at <20 mg l⁻¹ throughout the recording period. On examination of the potassium concentrations measured in samples of irrigation water and drainwater, it was apparent that the drainwater contained up to 5 mg l⁻¹ more than the input irrigation water during the first five months (Figure 5.13). From September, however, potassium concentrations were similar, except during the period January to April 1996 when the potassium drainwater concentration was approximately 2 mg l⁻¹ above the irrigation water. As stated in Chapter Two, this suggests that clinoptilolite was releasing and selectively adsorbing potassium during the experiment.

Pumice and foam drainwater calcium concentrations gave similar profiles between 90 - 200 mg l⁻¹ and more calcium was measured in samples taken from the pumice substrate over the period April to December 1996 (Figure 5.14). Clinoptilolite drainwater concentrations contained <30 mg l⁻¹ throughout and the nutrient profiles showed higher calcium concentrations from May to October 1995 and April to October 1996. This latter trend was consistent with the fluctuating calcium concentrations in the irrigation water (Figure 5.15). In May 1995, it was apparent that there was a 5-12 mg l⁻¹ difference in favour of the clinoptilolite drainwater calcium concentration but the nutrient profiles were subsequently similar. This suggests that clinoptilolite released calcium into the root zone initially and also during flower flushes. This is consistent with other results in this study (Chapters Four and Five).

Nitrate-nitrogen drainwater concentrations were slightly higher from the pumice substrate, although the nutrient concentration profiles for the pumice and foam were very similar over the 18 month recording period between the 100-300 mg l⁻¹ range (Figure 5.16). The clinoptilolite drainwater nitrate-nitrogen concentrations were below 10 mg l⁻¹ throughout.

There was, however, a 7 mg l^{-1} difference between the clinoptilolite and irrigation water nitrate-nitrogen concentration in the sample taken on 2 May 1995 (Figure 5.17).

Ammonium-nitrogen concentrations were generally lower from the pumice compared with the foam substrate, suggesting that the pumice was adsorbing some of the ammonium-nitrogen (Figure 5.18). Bunt (1988), stated that cation exchange can occur with pumice and plant roots. There was a consistently higher concentration (3 mg l^{-1}) of ammonium-nitrogen in the clinoptilolite drainwater during the first three months, after which time concentrations were generally below those of the pumice and foam substrates. After the first three months, the clinoptilolite drainwater ammonium-nitrogen concentrations did not rise above the irrigation water concentrations (approximately 2 mg l^{-1}) (Figure 5.19).

Drainwater magnesium concentrations from the pumice were very similar to those from foam until September 1995 ($40\text{-}120 \text{ mg l}^{-1}$) and were then generally higher than the foam (Figure 5.20). In comparison, the clinoptilolite drainwater magnesium concentrations were below 10 mg l^{-1} throughout. The clinoptilolite drainwater magnesium concentrations were generally $1\text{-}5 \text{ mg l}^{-1}$ below the irrigation water concentration during the experiment, suggesting that magnesium was being actively adsorbed throughout (Figure 5.21).

Drainwater pumice and foam phosphorus concentrations were similar at the start and then less than the foam, generally, from January 1996 (Figure 5.22). The nutrient-loaded drainwater concentration started at 12 mg l^{-1} and gradually reduced over a two month period to 0.5 mg l^{-1} . The clinoptilolite and polyacrylamide gel mixture had a phosphorus concentration of 7 mg l^{-1} and then gradually reduced over the same time. Both clinoptilolites had drainwater phosphorus concentrations of $<2 \text{ mg l}^{-1}$ from July 1995 to December 1996. In comparison with the irrigation water, the clinoptilolite drainwater phosphorus was identical from the end of March to December, 1996 (Figure 5.23).

Figure 5.10 Mean monthly yield of Class 1 blooms from 'White Giant' and 'Master' on pumice and nutrient-loaded clinoptilolite

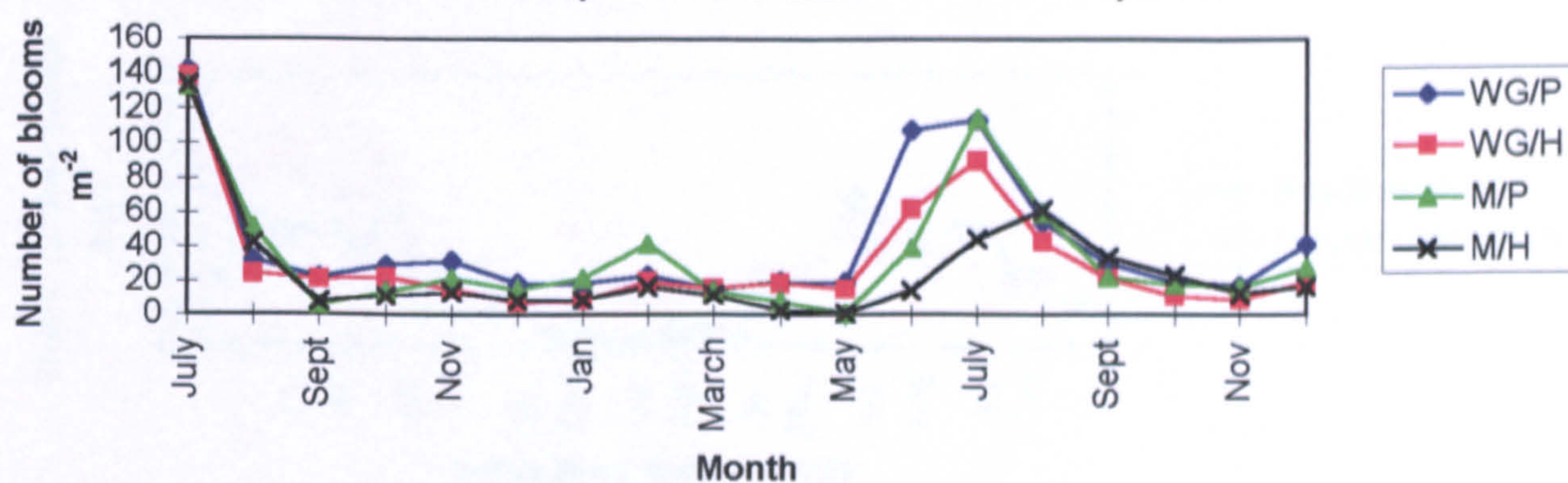


Figure 5.11 Cumulative mean monthly yields of Class 1 blooms for 'White Giant' and 'Master' on pumice and nutrient-loaded clinoptilolite

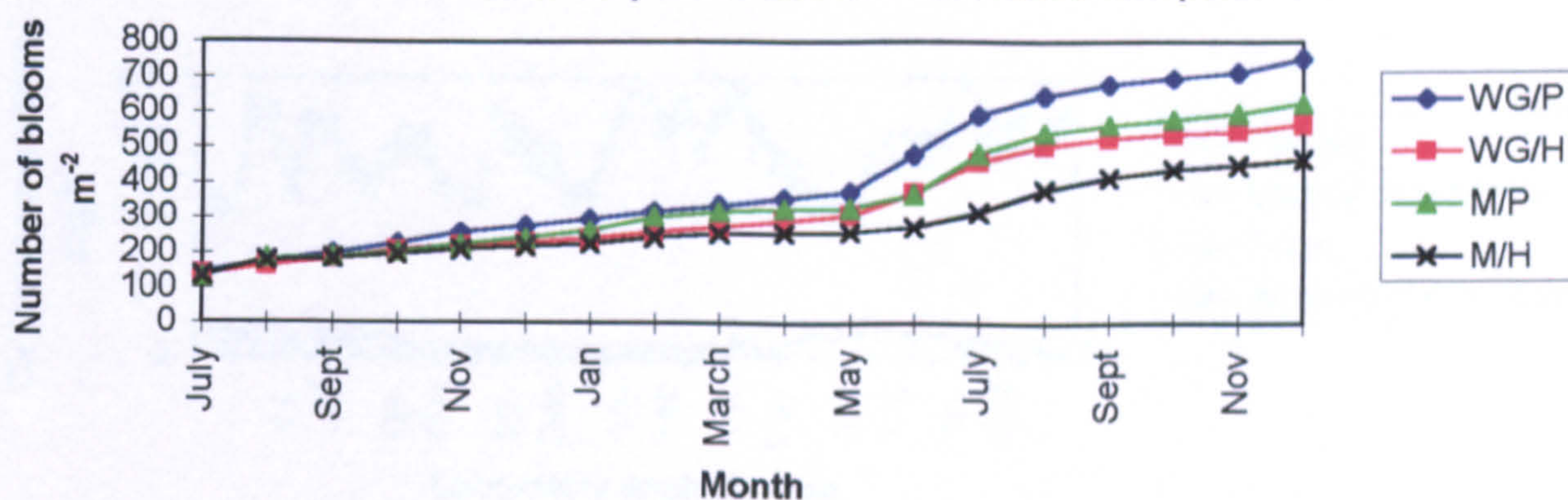


Figure 5.12 Drainwater potassium concentrations from fertigated and irrigated substrates

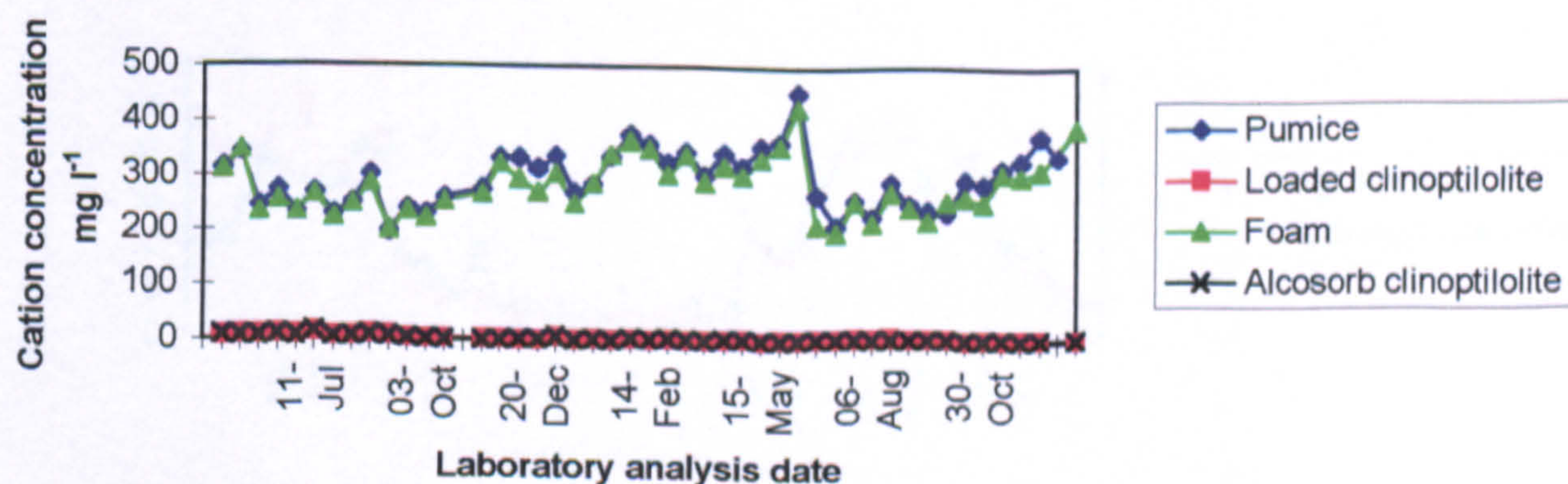


Figure 5.13 Comparison of irrigation water and drainwater potassium concentrations from the nutrient-loaded clinoptilolite

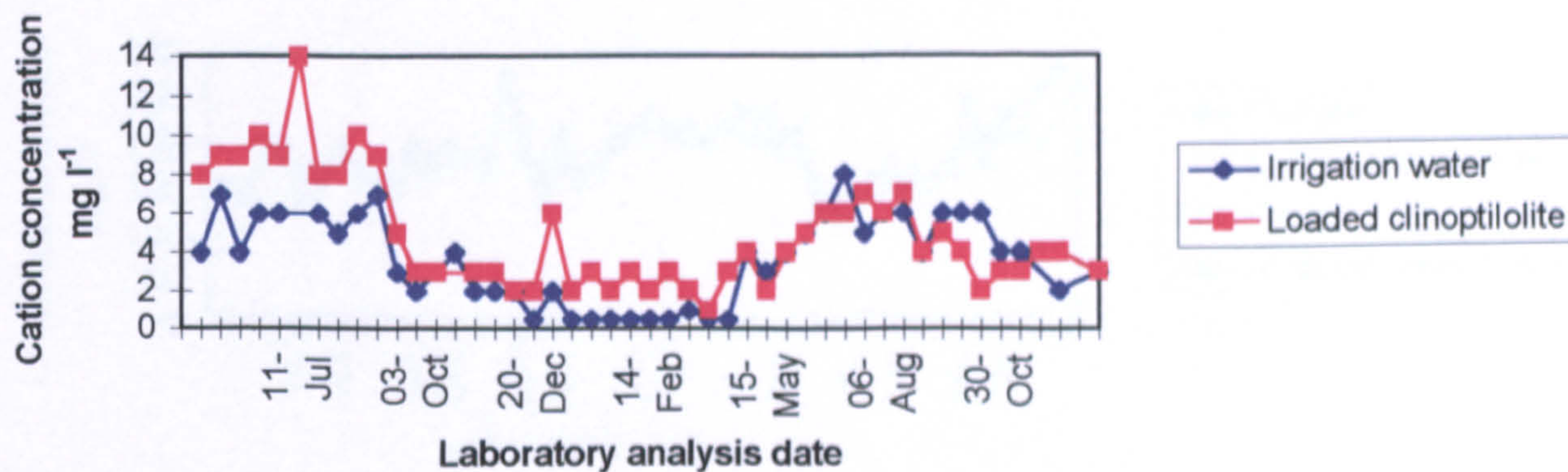


Figure 5.14 Drainwater calcium concentration from fertigated and irrigated substrates

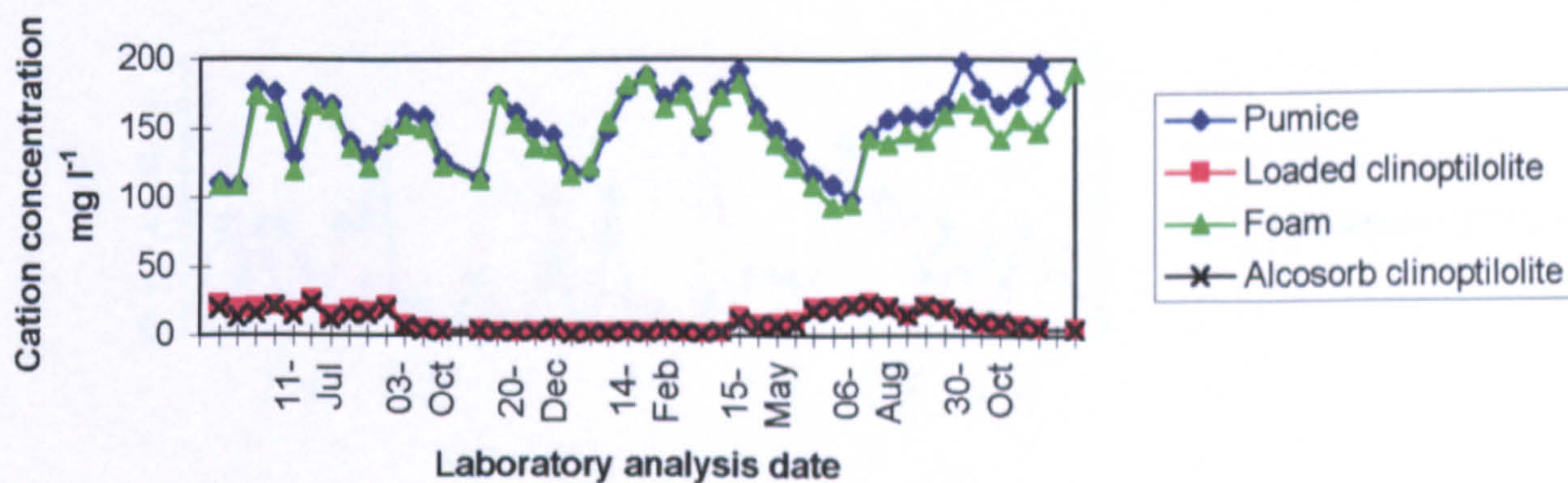


Figure 5.15 Comparison of irrigation water and drainwater calcium concentrations from the nutrient-loaded clinoptilolite

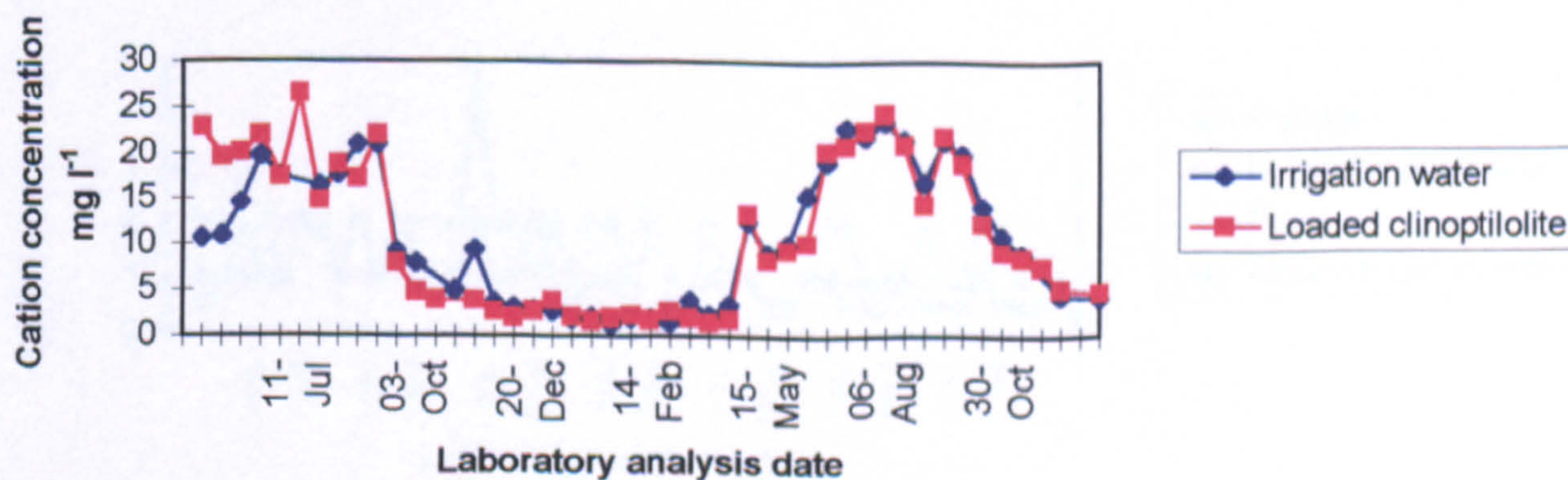


Figure 5.16 Drainwater nitrate-nitrogen concentrations from fertigated and irrigated substrates

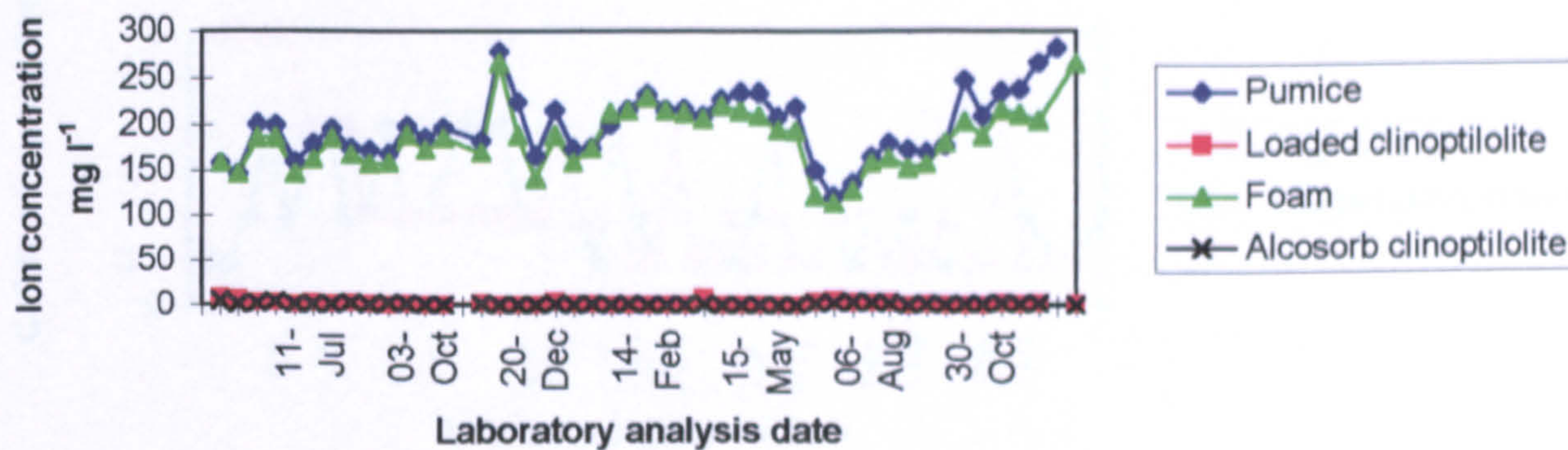


Figure 5.17 Comparison of irrigation water and drainwater nitrate-nitrogen concentrations from the nutrient-loaded clinoptilolite

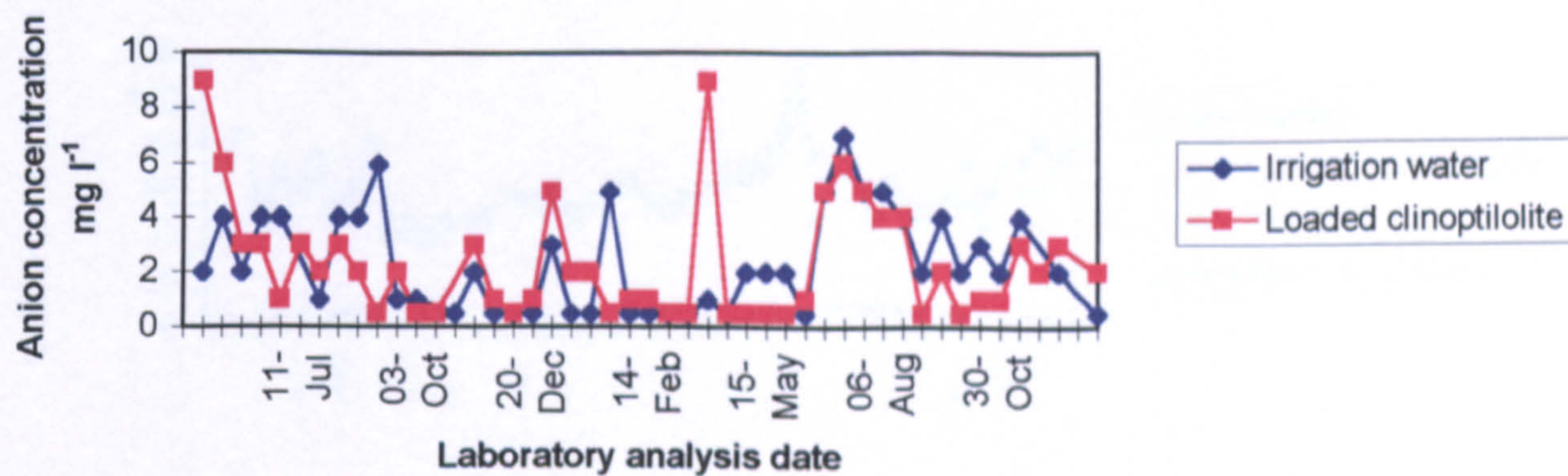


Figure 5.18 Drainwater ammonium-nitrogen concentrations from fertigated and irrigated substrates

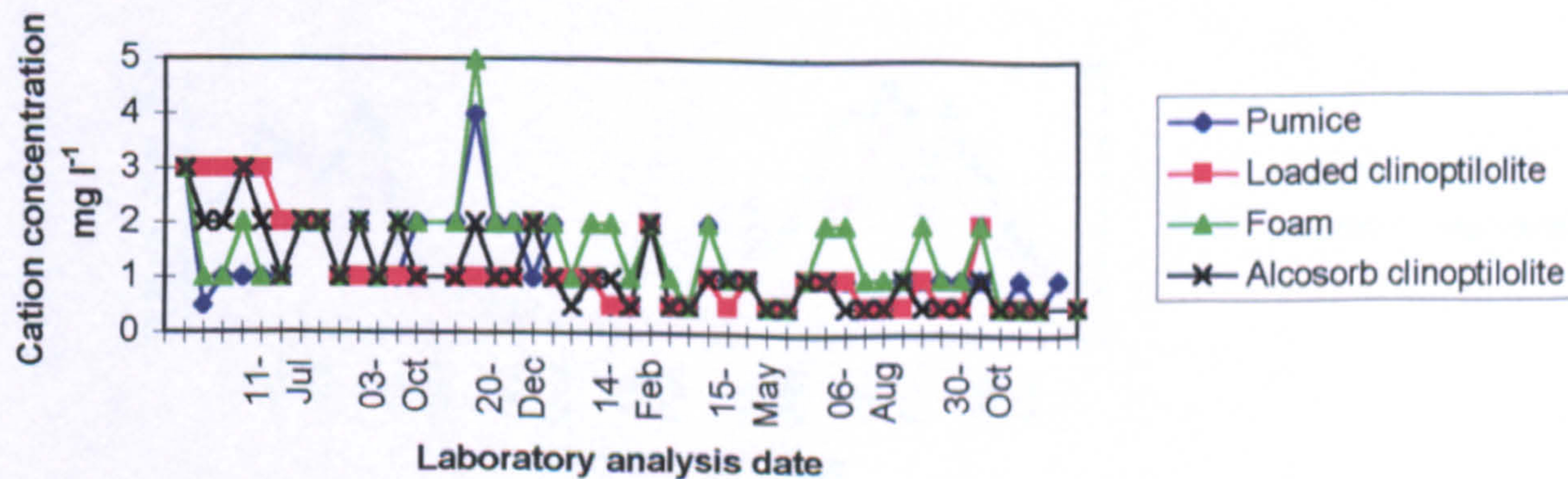


Figure 5.19 Comparison of irrigation water and drainwater ammonium-nitrogen concentrations from the nutrient-loaded clinoptilolite

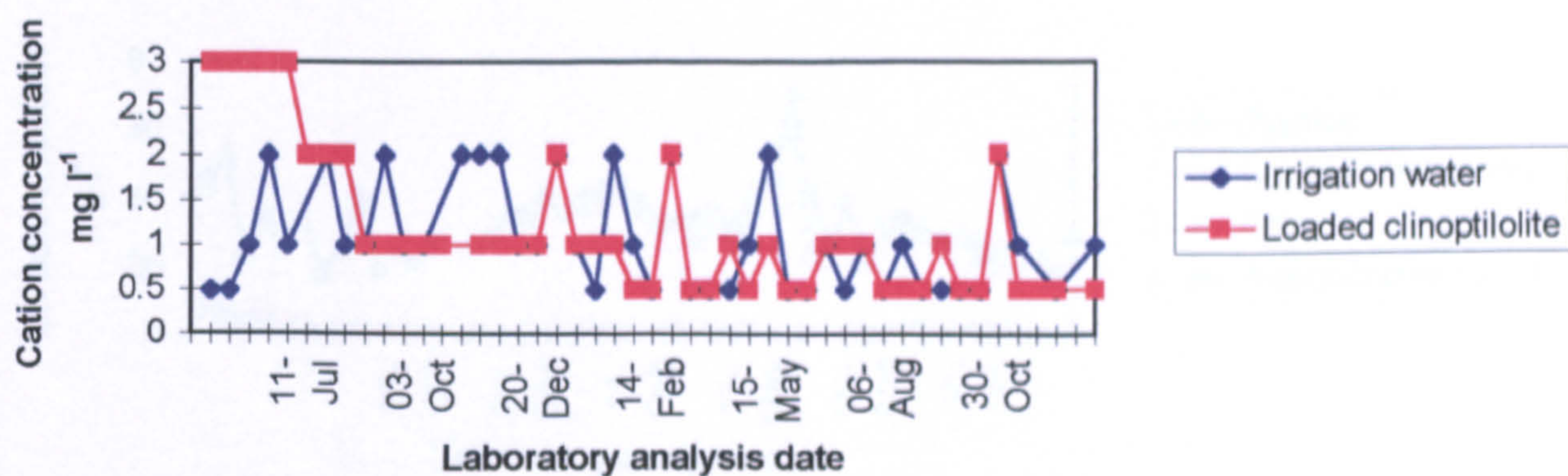


Figure 5.20 Drainwater magnesium concentrations from fertiligated and irrigated substrates

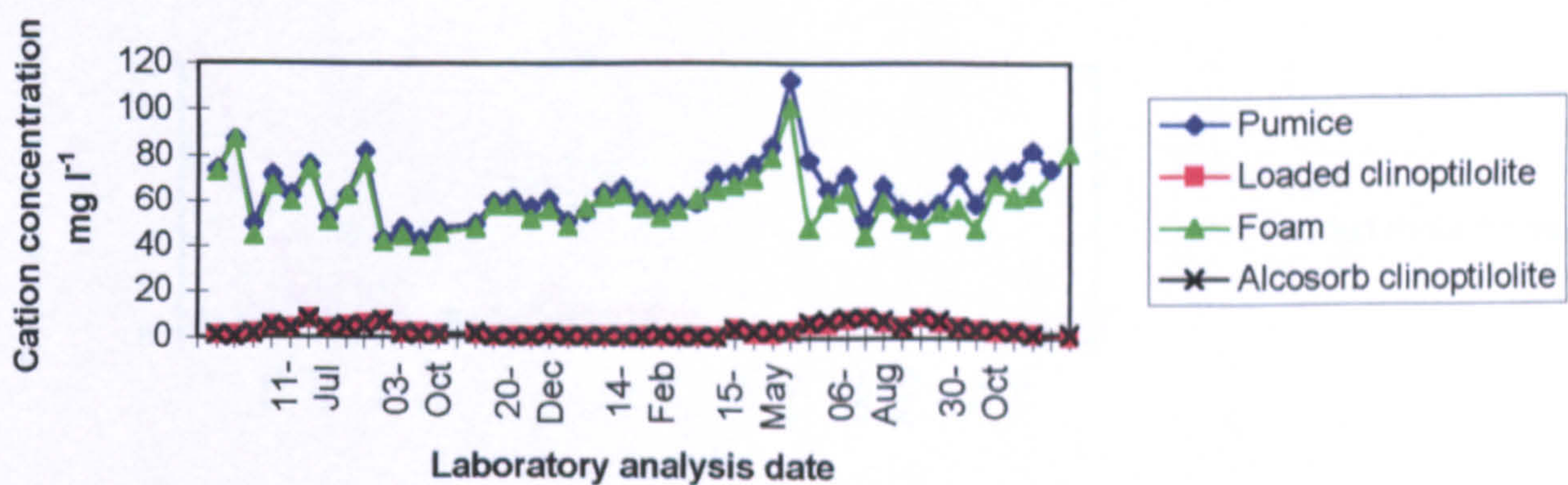


Figure 5.21 Comparison of irrigation water and drainwater magnesium concentrations from the nutrient-loaded clinoptilolite

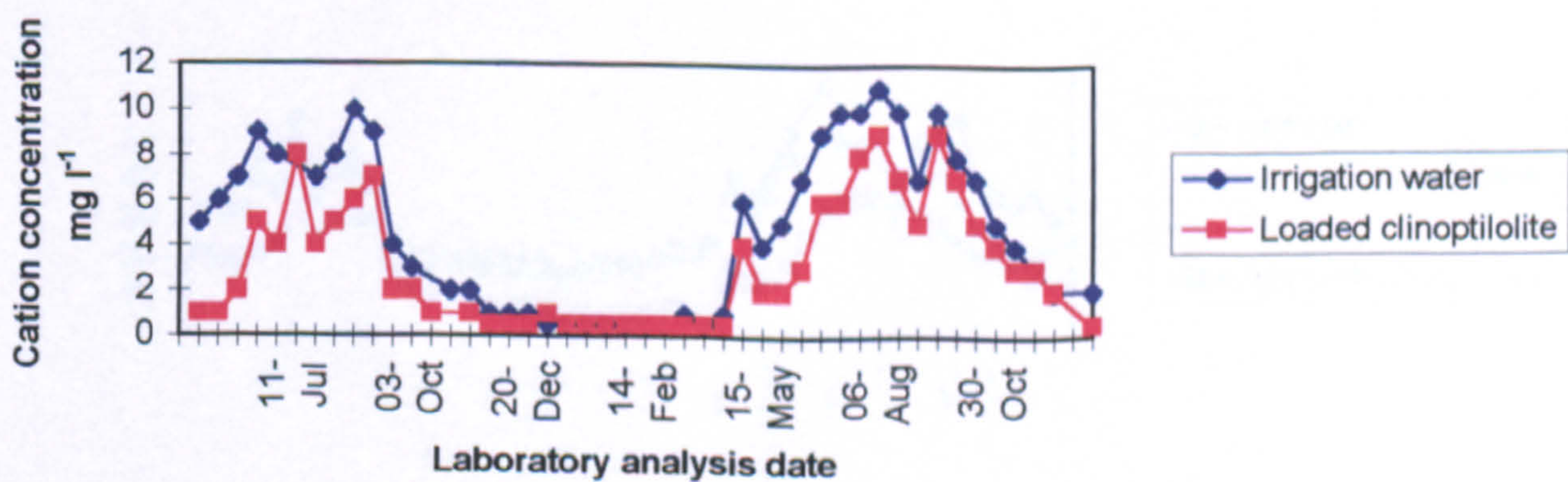


Figure 5.22 Drainwater phosphorus concentrations from fertigated and irrigated substrates

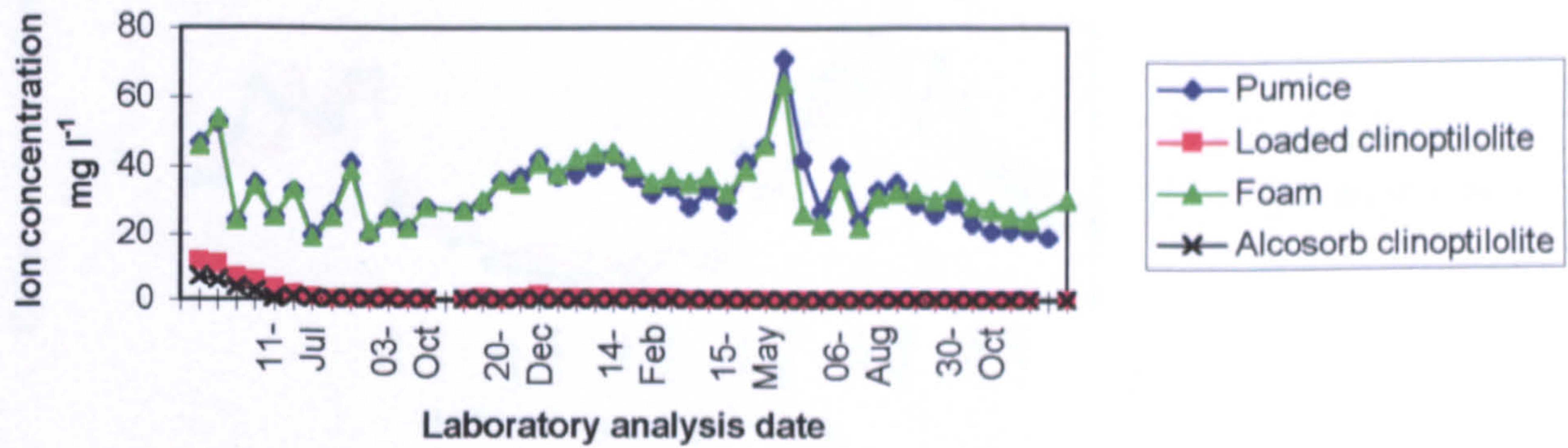


Figure 5.23 Comparison of irrigation water and drainwater phosphorus concentrations from the nutrient-loaded clinoptilolite

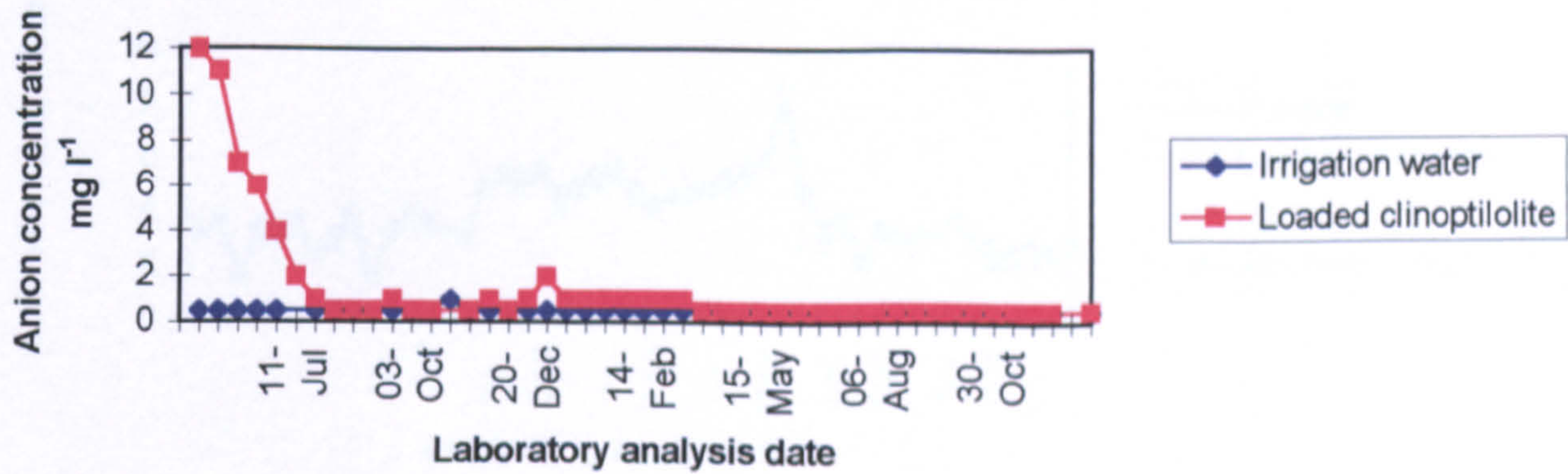


Figure 5.24 Drainwater sodium concentrations from fertigated and irrigated substrates

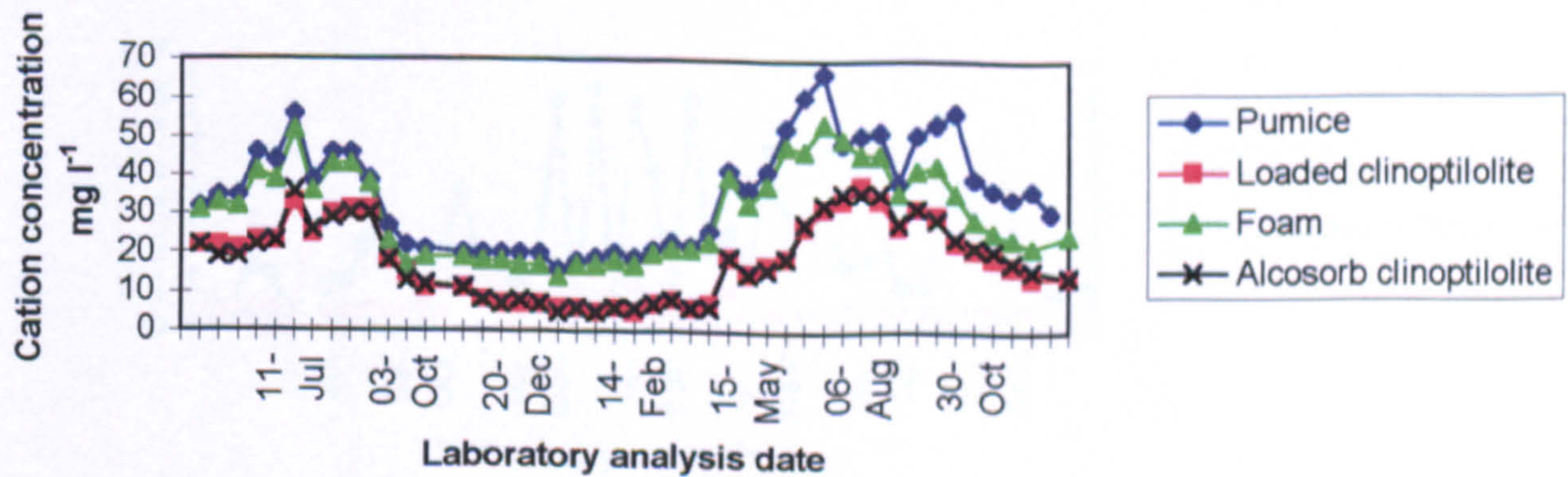


Figure 5.25 Comparison of irrigation water and drainwater sodium concentrations from the nutrient-loaded clinoptilolite

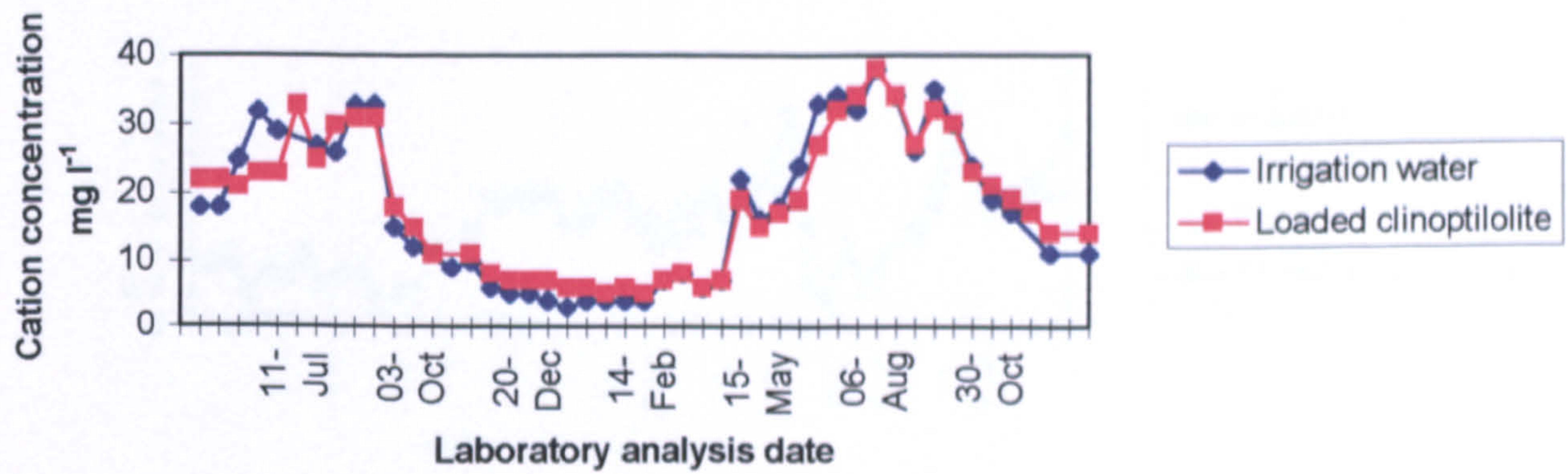


Figure 5.26 Drainwater iron concentrations from fertigated and irrigated substrates

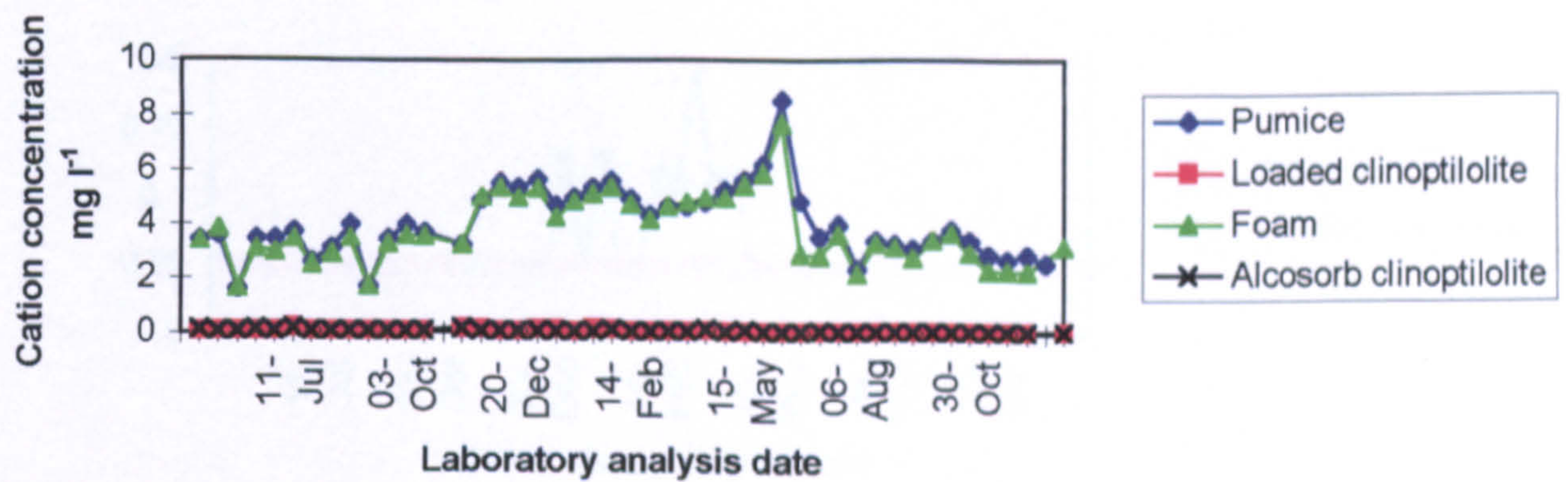


Figure 5.27 Comparison of irrigation water and drainwater iron concentrations from the nutrient-loaded clinoptilolite

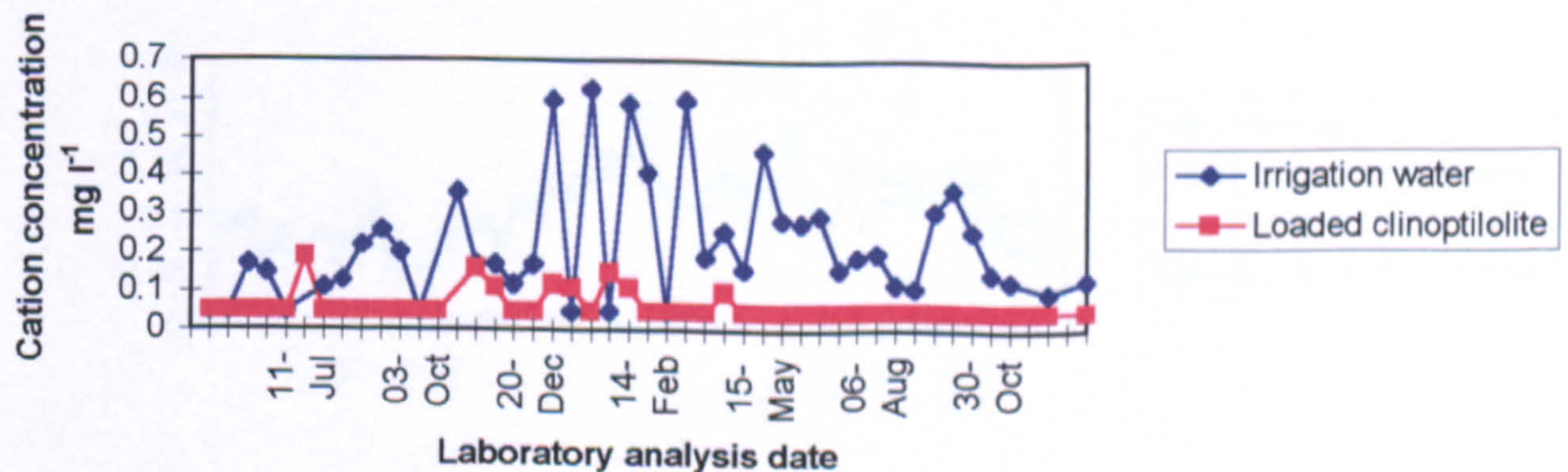


Figure 5.28 Drainwater manganese concentrations from fertigated and irrigated substrates

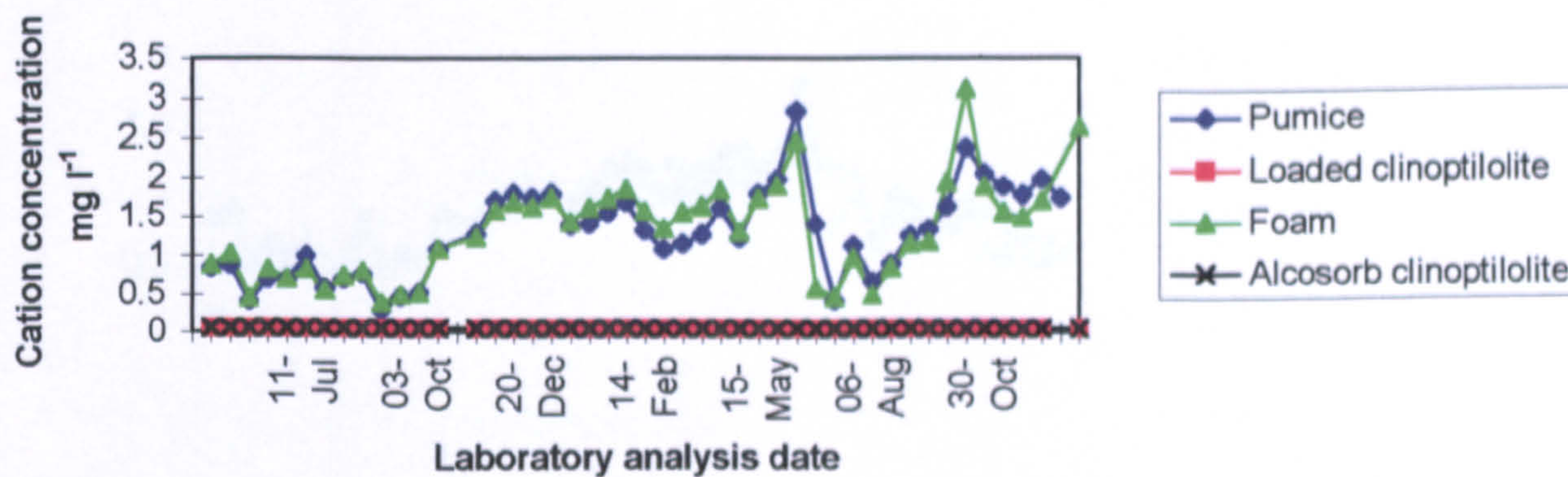


Figure 5.29 Comparison of irrigation water and drainwater manganese concentrations from the nutrient-loaded clinoptilolite

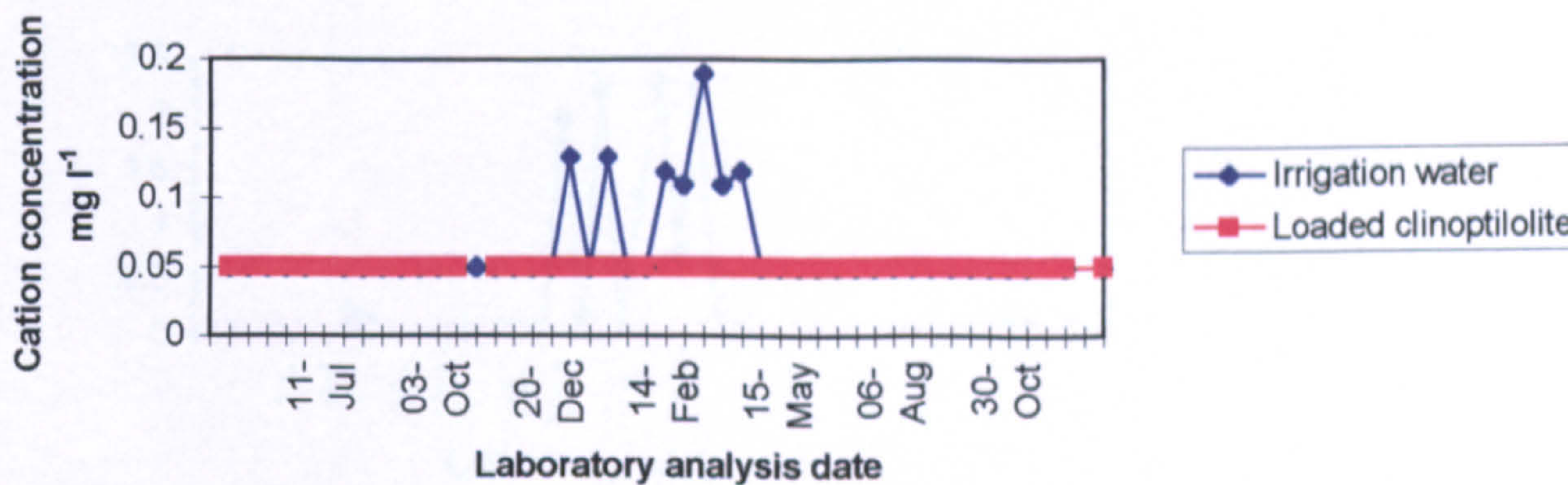


Figure 5.30 Drainwater copper concentrations from fertigated and irrigated substrates

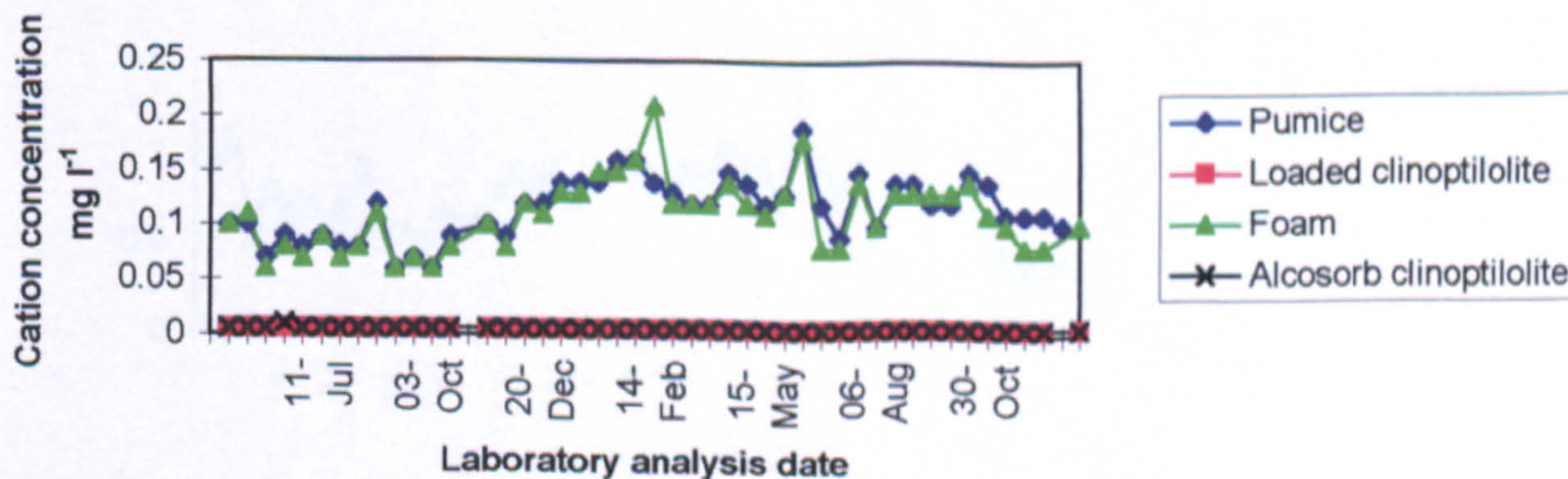


Figure 5.31 Drainwater zinc concentrations from fertigated and irrigated substrates

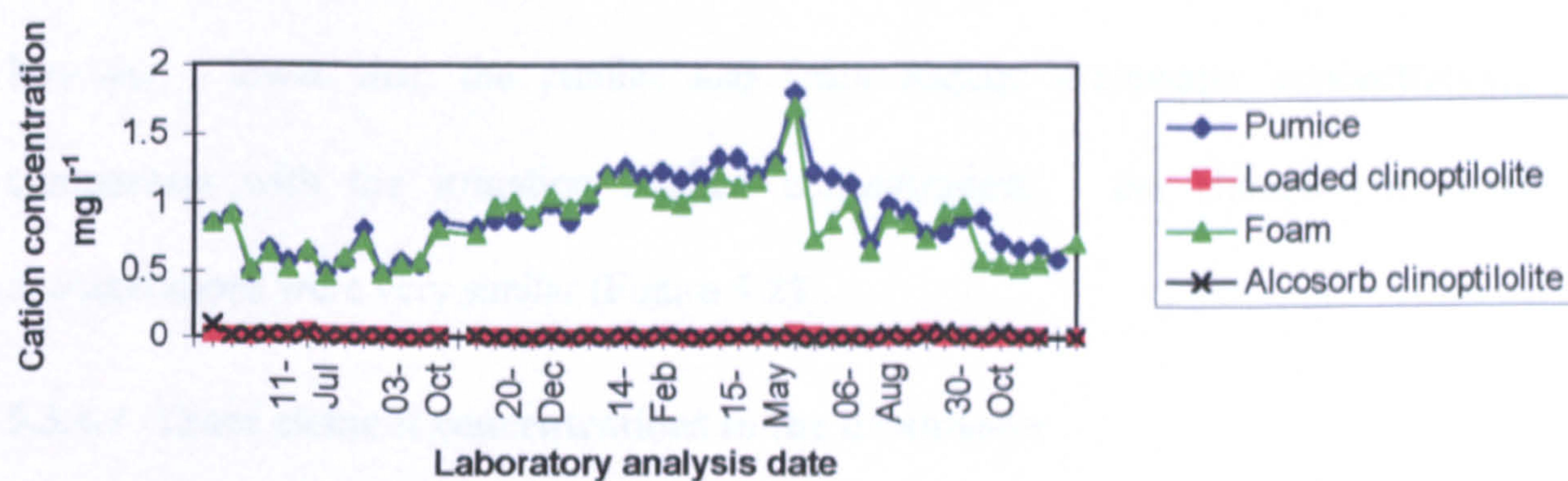


Figure 5.32 Comparison of irrigation water and drainwater zinc concentrations from the nutrient-loaded clinoptilolite

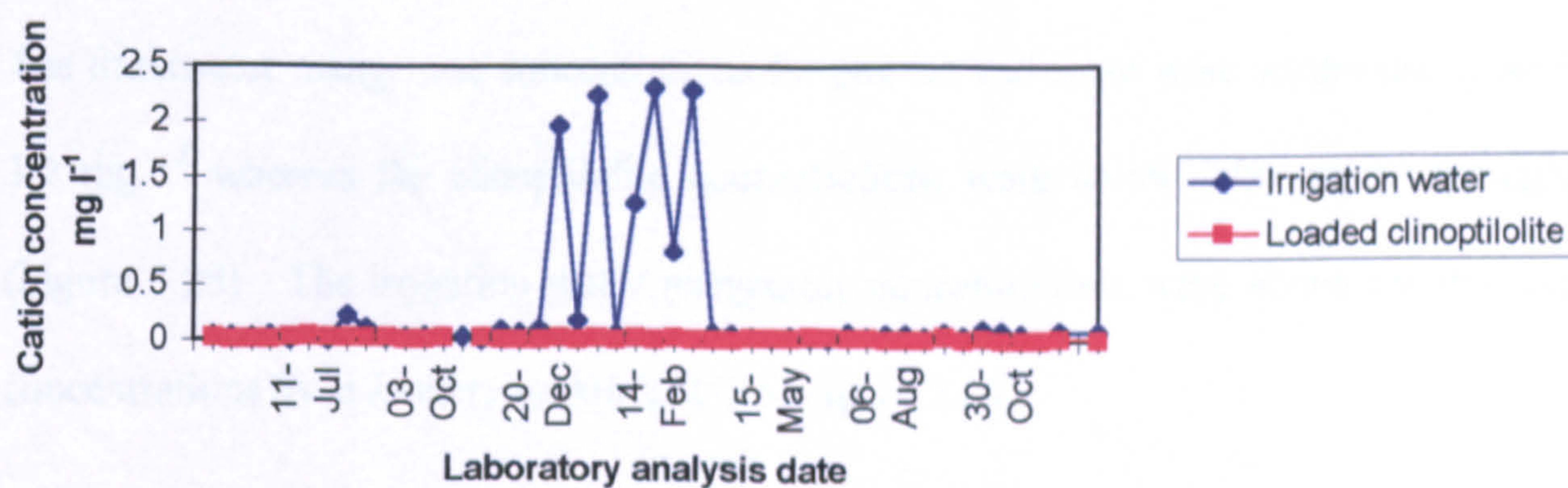
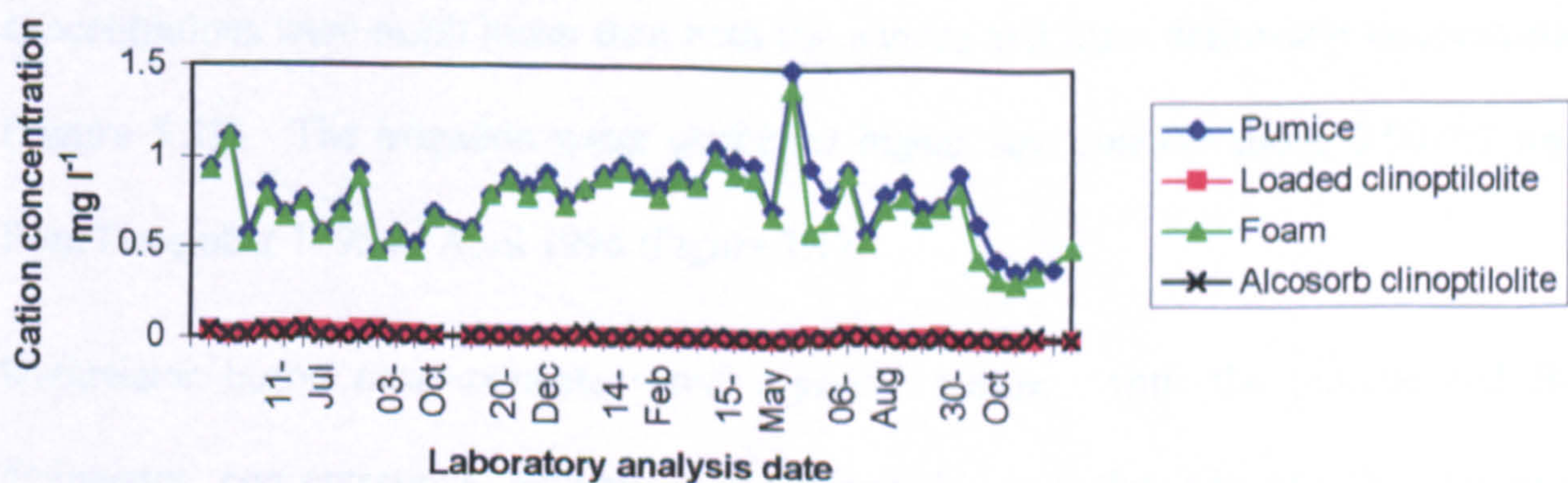


Figure 5.33 Drainwater boron concentrations from fertigated and irrigated substrates



Sodium drainwater concentrations were 1-21 mg l⁻¹ higher from the pumice substrate compared with the foam. Both sets of drainwater clinoptilolite measurements were almost identical and followed the same nutrient concentration profile (Figure 5.24). They were, however, lower than the pumice and foam sodium drainwater concentrations. In comparison with the irrigation sodium concentrations, the clinoptilolite drainwater concentrations were very similar (Figure 5.25).

5.3.4.3 Trace element concentrations in the drainwater

Both the pumice and foam drainwater iron concentrations were similar over a range 1-9 mg l⁻¹ and the clinoptilolite concentrations were very low at <0.2 mg l⁻¹ throughout (Figure 5.26). The irrigation water iron concentrations were up to 0.58 mg l⁻¹ higher than the clinoptilolite drainwater concentrations, however (Figure 5.27).

The drainwater manganese concentrations for pumice and foam were within the range 0.3-3.2 mg l⁻¹ whereas the clinoptilolite concentrations were below 0.06 mg l⁻¹ throughout (Figure 5.28). The irrigation water manganese concentrations were above the drainwater concentrations from January to April, 1996 (Figure 5.29).

There was a similar pattern with drainwater copper concentrations i.e. pumice and foam measurements were similar 0.06-0.19 mg l⁻¹ whereas the clinoptilolite drainwater concentrations were below 0.005 mg l⁻¹ throughout (Figure 5.30).

Zinc drainwater concentrations showed similar trends to copper in that the clinoptilolite concentrations were much lower than both the pumice and foam drainwater concentrations (Figure 5.31). The irrigation water contained higher zinc concentrations 0.06-2.3 mg l⁻¹ from December 1995 to April 1996 (Figure 5.32).

Drainwater boron measurements showed similar trends, with the pumice and foam drainwater concentrations between 0.3-1.5 mg l⁻¹ and the clinoptilolite drainwater

concentrations always below 0.05 mg l^{-1} (Figure 5.33). Irrigation water and drainwater concentrations were similar throughout.

The pH of pumice and foam drainwater dropped to 4.0 over the period November, December 1995 (both) and October, November and December 1996 (foam) (Figure 5.34). Both sets of clinoptilolite drainwater pH levels were more stable with the exception of the loaded clinoptilolite, which dropped below pH 5.0 during May to June 1996. The drainwater pH levels were slightly lower than the input water and there was no obvious deleterious effect on plant growth as a result, however.

Drainwater EC concentrations were slightly higher from the pumice substrate and both the pumice and foam were in the range $1,500\text{-}2,800 \mu\text{S cm}^{-1}$ (Figure 5.35). EC concentrations from the clinoptilolite substrates were always below $500 \mu\text{S cm}^{-1}$, by comparison. The drainwater EC concentration closely tracked the irrigation water EC concentration profile, with the clinoptilolite EC starting slightly higher and ending slightly lower than the irrigation water.

Chloride concentrations were all very similar from the four substrates and the irrigation water concentration closely matched the clinoptilolite drainwater concentrations (Figure 5.36).

Pumice drainwater sulphate concentrations were higher than from the foam substrate from March 1996 ($50\text{-}170 \text{ mg l}^{-1}$) and the clinoptilolite drainwater concentrations were below 30 mg l^{-1} throughout (Figure 5.37). The irrigation water and clinoptilolite drainwater concentrations were very similar, however.

Figure 5.34 Drainwater pH levels from fertigated and irrigated substrates

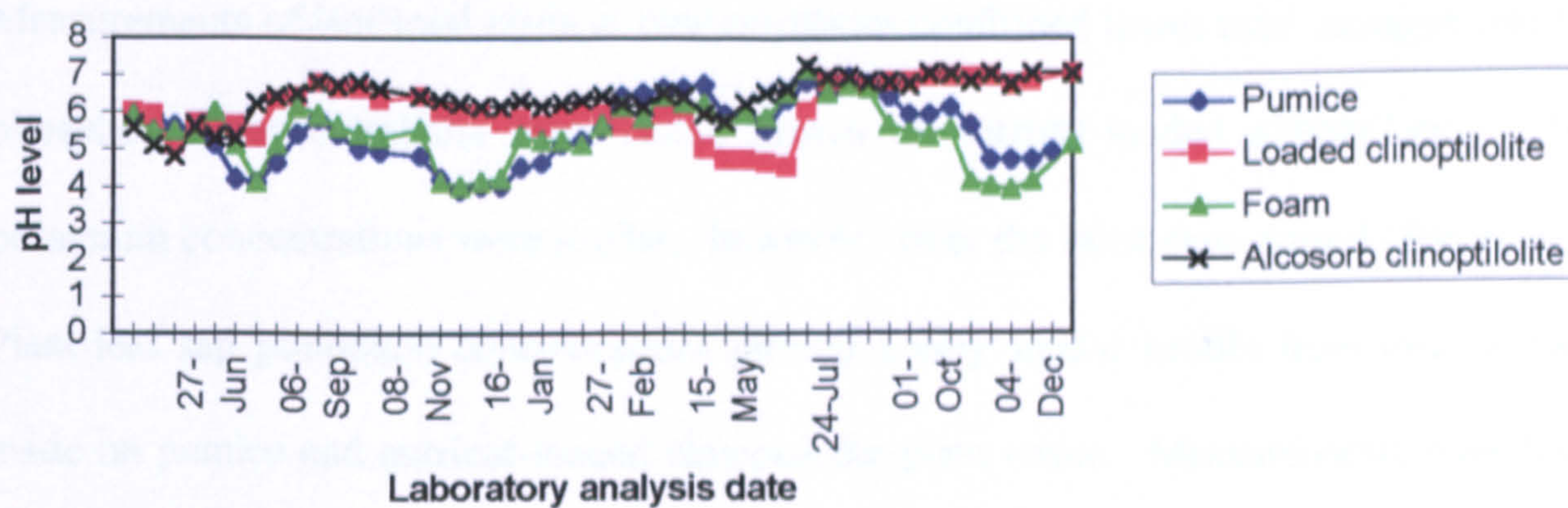


Figure 5.35 Drainwater EC concentrations from fertigated and irrigated substrates

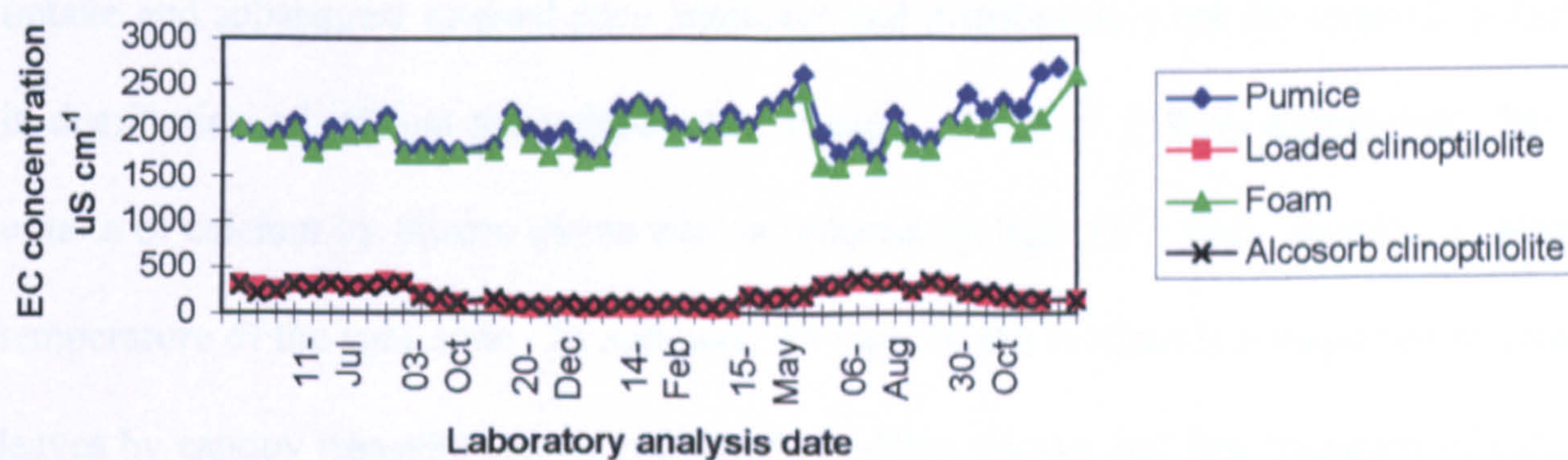
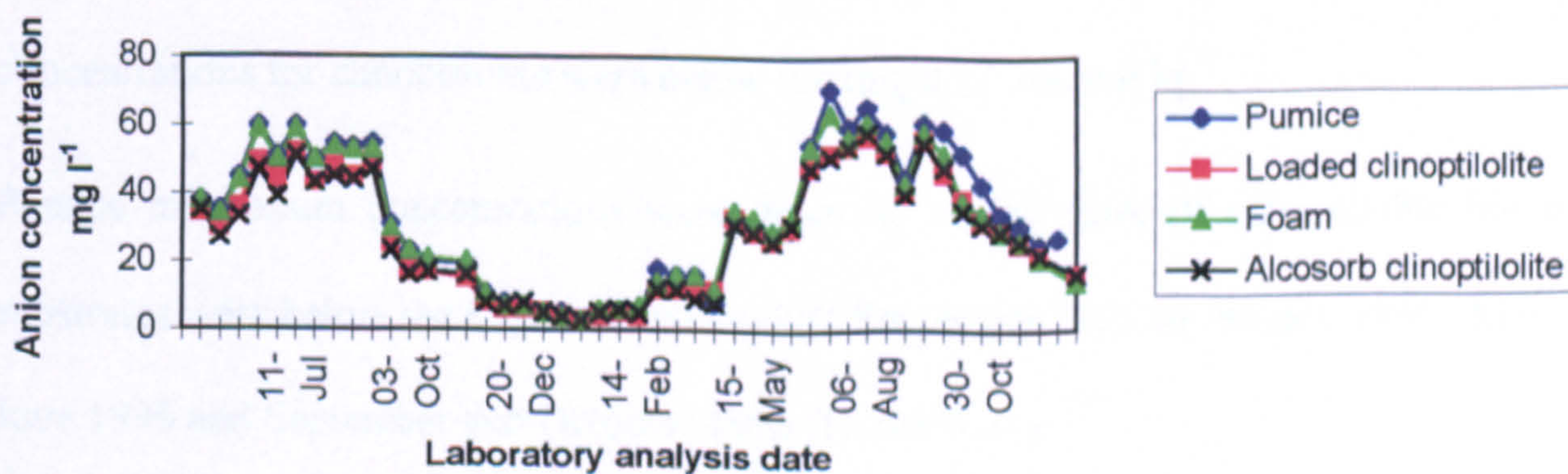


Figure 5.36 Drainwater chloride concentrations from fertigated and irrigated substrates



5.3.4.4 Major element concentrations in the leaf tissue (pumice and nutrient-loaded clinoptilolite only)

Measurements of leaf total element concentrations confirmed lower total nitrogen and total phosphorus concentrations from plants grown in nutrient-loaded clinoptilolite. Total potassium concentrations were similar, however, over the same time period (Figure 5.38). Plant leaf sap potassium concentrations plotted a very similar profile from measurements made on pumice and nutrient-loaded clinoptilolite plant tissue. Measurements were below 1,000 mg kg⁻¹ in December 1995 (both) and below 2,000 mg kg⁻¹ in September 1996 (nutrient-loaded clinoptilolite).

Both substrates revealed leaf sap calcium concentrations below the target concentration of 300 mg kg⁻¹ during the warmest months of each year (Figure 5.39). This suggests that plant uptake and subsequent internal plant transport and distribution were the overriding factors in distribution of calcium throughout plant tissues. Ho *et al.* (1999) summarised that the uptake of calcium by tomato plants can be reduced by high EC, poor aeration or adverse temperature of the root zone. In addition, as most of the calcium is transported to tomato leaves by canopy transpiration, a combination of low uptake and low transport of calcium to the fruit can cause a low calcium status in the fruit.

Pumice nitrate-nitrogen leaf sap concentrations were generally higher than the nutrient-loaded clinoptilolite, except in September 1996 (Figure 5.40). With the exception of three measurements (March, September and November 1996), the leaf sap nitrate-nitrogen concentrations for clinoptilolite were below the target of 300 mg kg⁻¹.

Pumice magnesium concentrations were generally above those of clinoptilolite but both substrates were below the target of 200 mg kg⁻¹ September 1995 to January 1996, May and June 1996 and September and October, 1996 (Figure 5.41).

Figure 5.37 Drainwater sulphate concentrations from fertigated and irrigated substrates

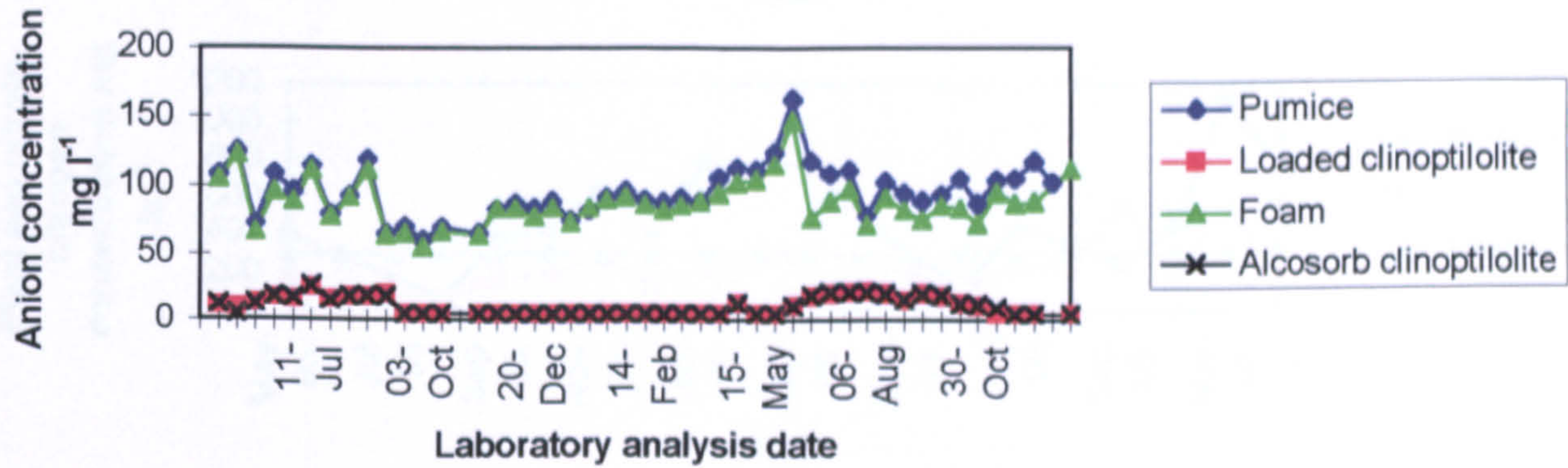


Figure 5.38 Plant leaf sap potassium concentrations from pumice irrigated with liquid feeds and nutrient-loaded clinoptilolite irrigated with water

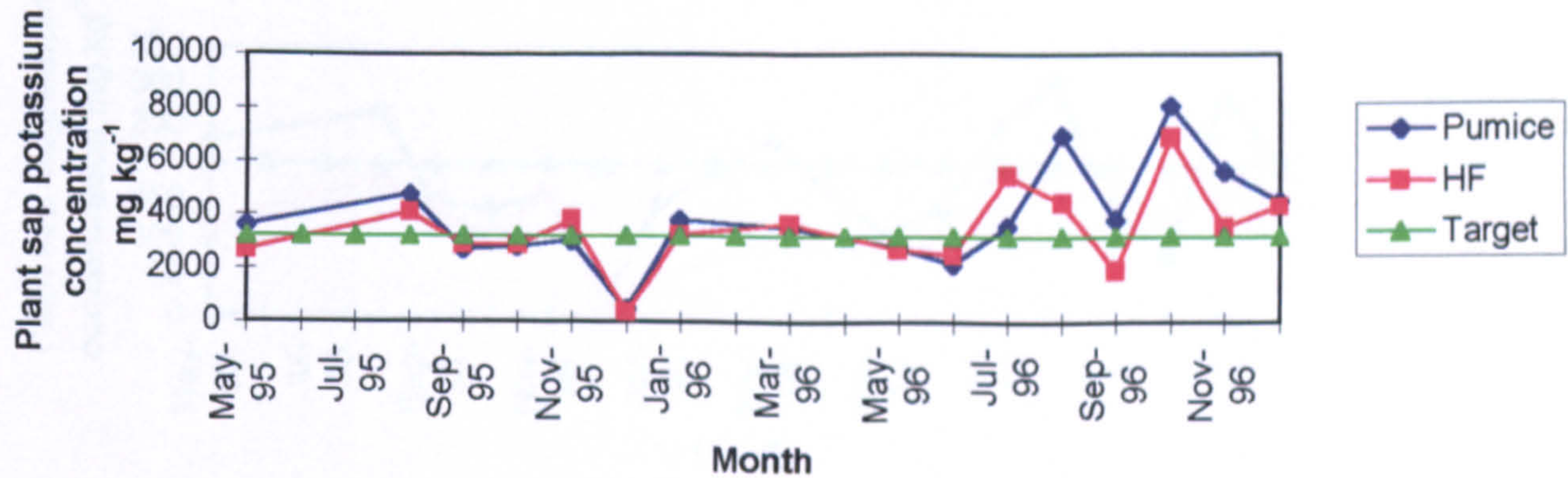


Figure 5.39 Plant leaf sap calcium concentrations from pumice irrigated with liquid feeds and nutrient-loaded clinoptilolite irrigated with water

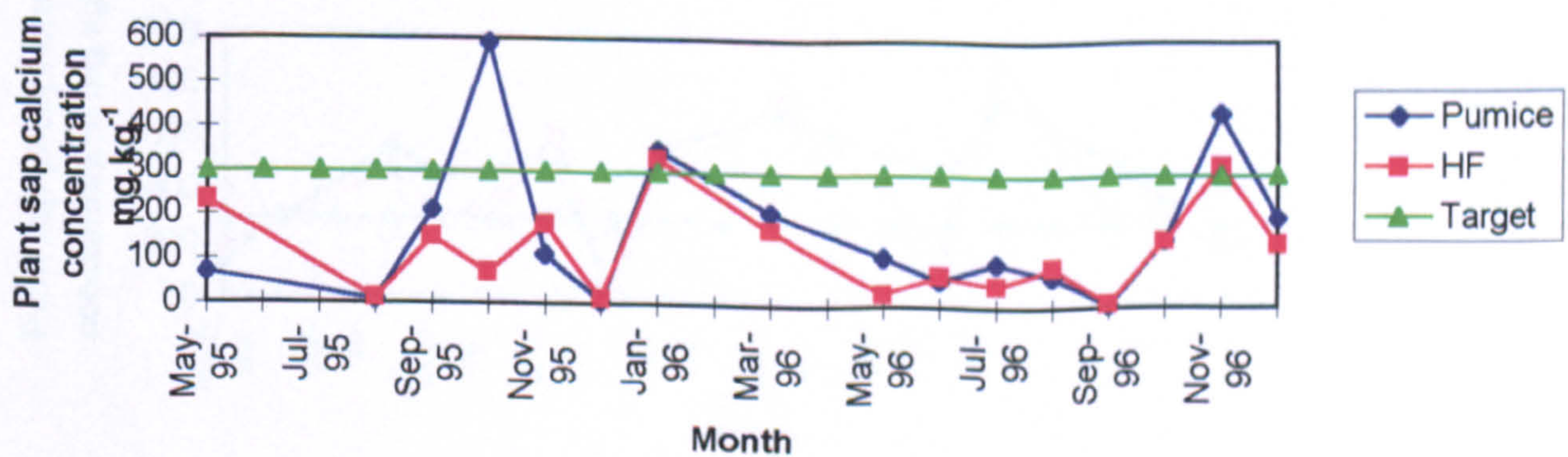


Figure 5.40 Plant leaf sap nitrate-nitrogen concentrations from pumice irrigated with liquid feeds and nutrient-loaded clinoptilolite irrigated with water

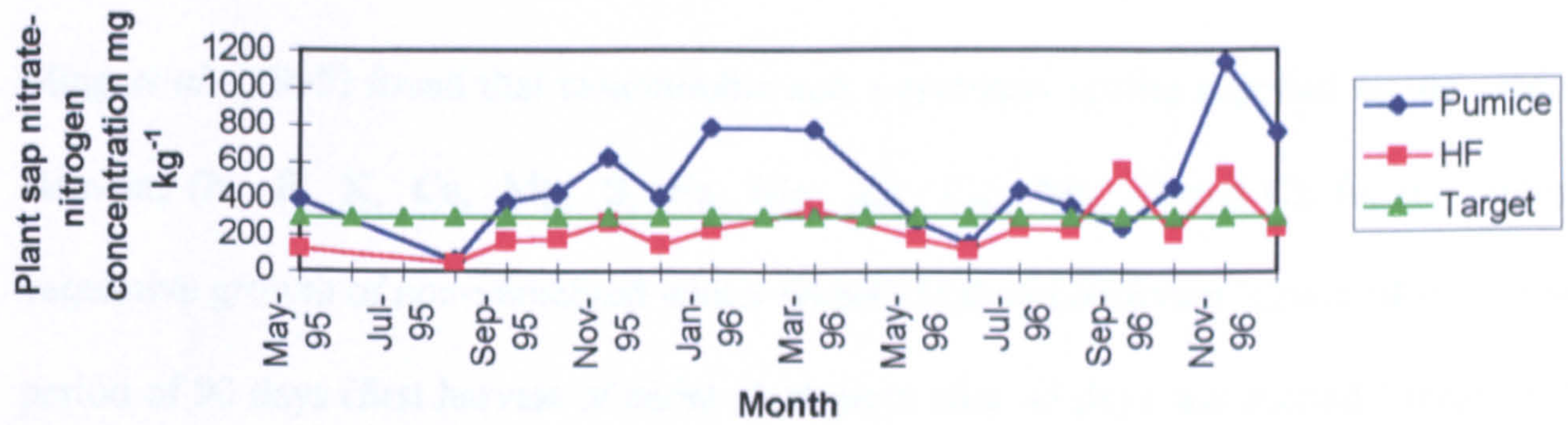


Figure 5.41 Plant leaf sap magnesium concentrations from pumice irrigated with liquid feeds and nutrient-loaded clinoptilolite irrigated with water

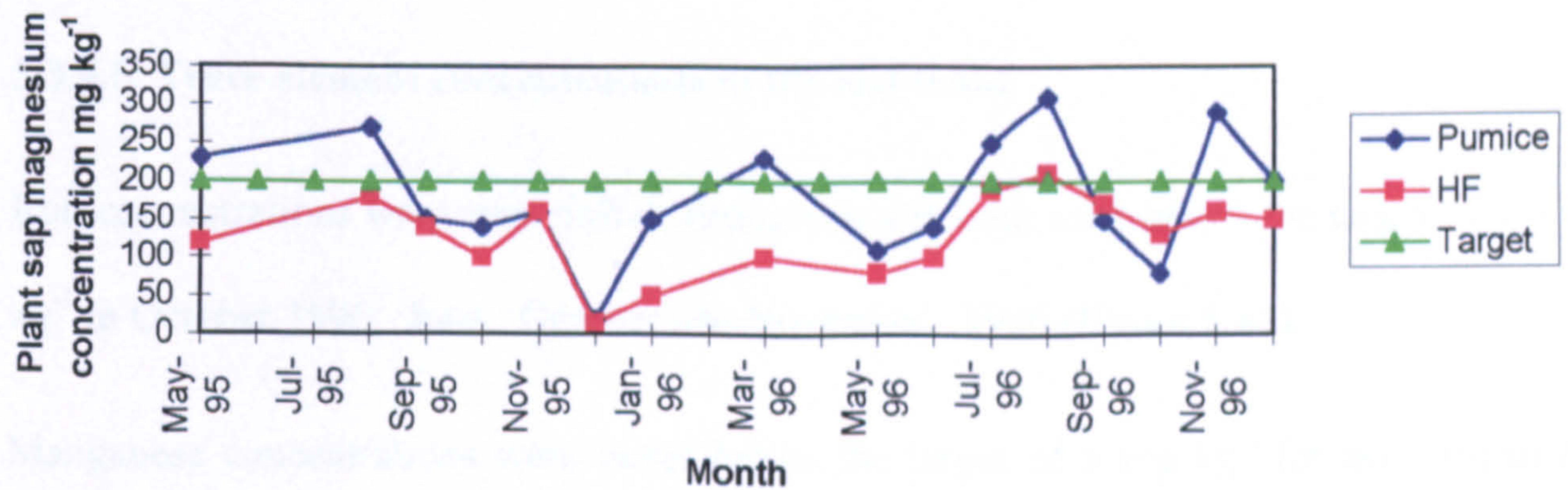
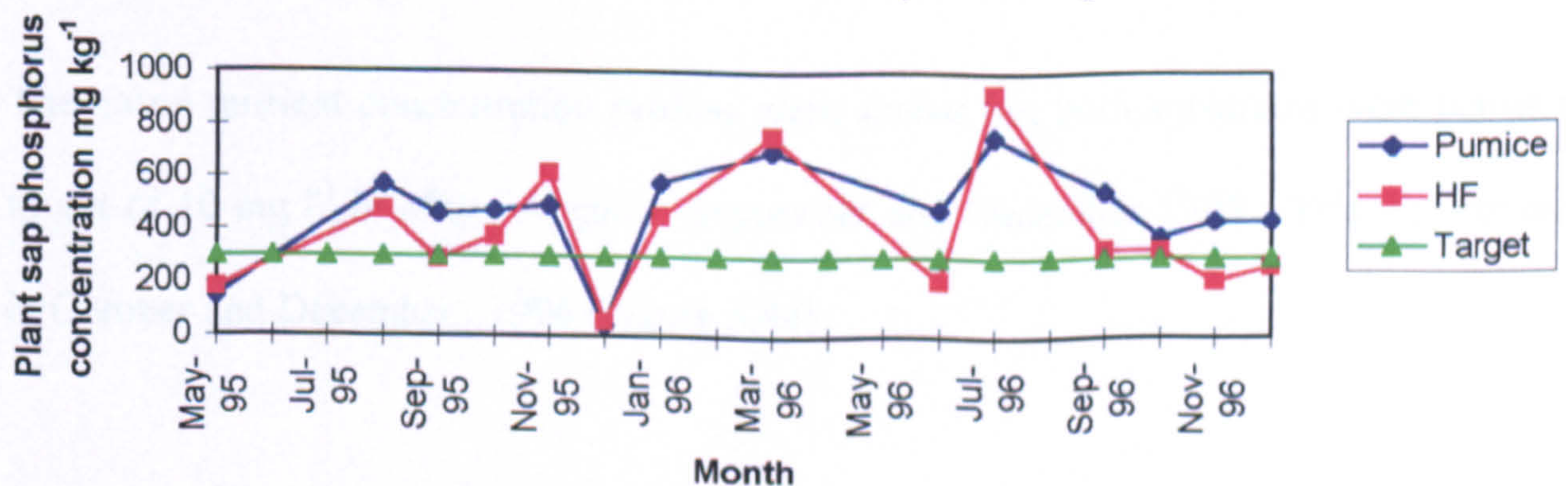


Figure 5.42 Plant leaf sap phosphorus concentrations from pumice irrigated with liquid feeds and nutrient-loaded clinoptilolite irrigated with water



Phosphorus was below the target of 300 mg kg⁻¹ in May 1995, December 1995 (both), June 1996 (clinoptilolite) and November and December 1996 (clinoptilolite) (Figure 5.42).

Sodium concentrations were very similar throughout (Figure 5.43).

Ming *et al.* (1995) found that clinoptilolite and a synthetic apatite supplied all the essential elements (N, P, K, Ca, Mg, S, Fe, Mn, Zn, Cu, Mo, B and Cl) for the intensive vegetative growth of non-vernalised winter wheat (*Triticum aestivum* 'Coker 68-15') over a period of 90 days (first harvest of aerial plant parts after 45 days and second harvest of the re-growth after an additional 45 days). In the same experiment, they found that clinoptilolite and natural apatite supplied all the essential elements as listed, with the exception of magnesium (second harvest only). In the present study, magnesium was not found to be limiting to plant growth.

5.3.4.5 Trace element concentrations in the leaf tissue

Iron concentrations were very similar throughout and both were below the target of 4.0 mg kg⁻¹ in October 1995, June, October and November, 1996 (Figure 5.44).

Manganese concentrations were never below the target of 5 mg kg⁻¹ for both substrates (Figure 5.45). Clinoptilolite copper concentrations were slightly below the target in June and November 1996 (Figure 5.46).

Clinoptilolite zinc concentrations were consistently higher than the pumice concentrations (Figure 5.47).

The boron nutrient concentration profiles were similar but both substrates were below the target of 10 mg l⁻¹ in May, August, September and December 1995. This was repeated in October and December, 1996 (Figure 5.48).

Figure 5.43 Plant leaf sap sodium concentrations from pumice irrigated with liquid feeds and nutrient-loaded clinoptilolite irrigated with water

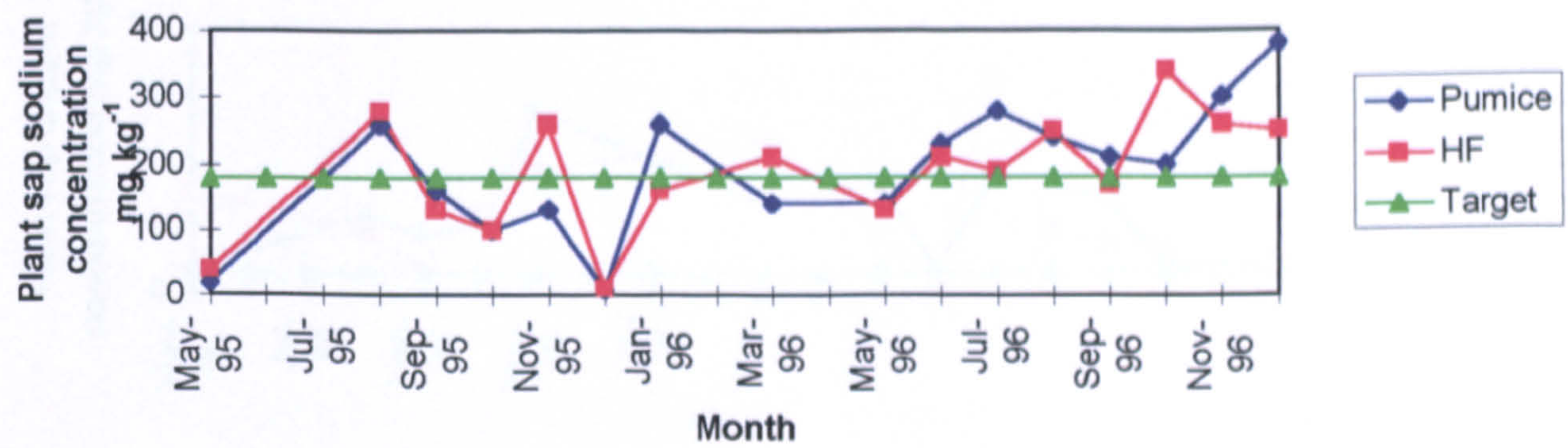


Figure 5.44 Plant leaf sap iron concentrations from pumice irrigated with liquid feeds and nutrient-loaded clinoptilolite irrigated with water

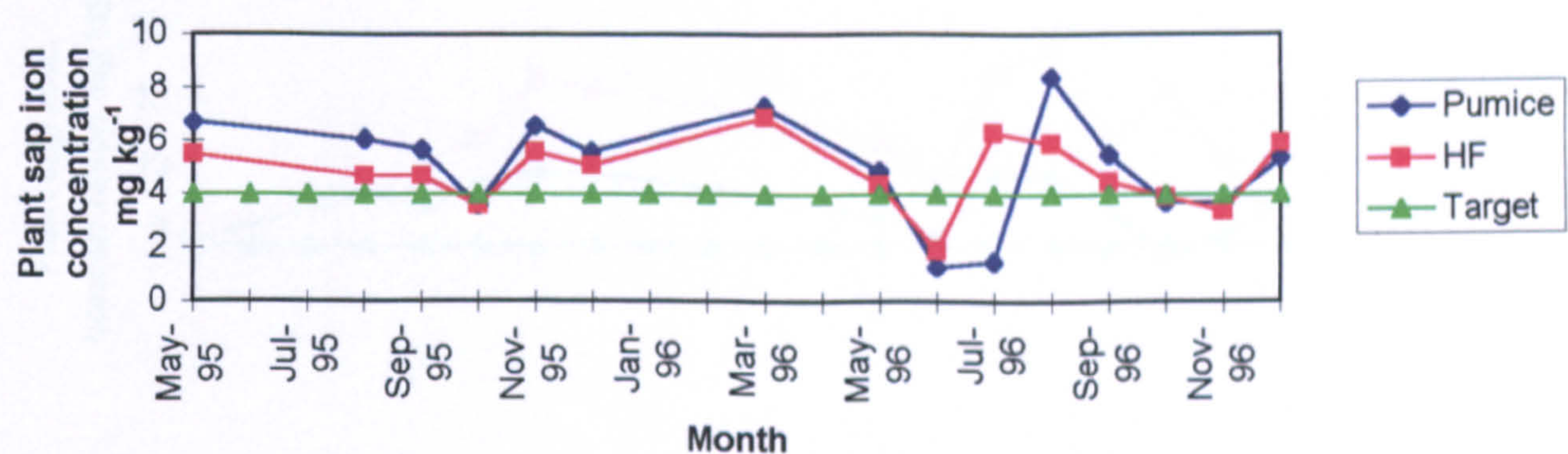


Figure 5.45 Plant leaf sap manganese concentrations from pumice irrigated with liquid feeds and nutrient-loaded clinoptilolite irrigated with water

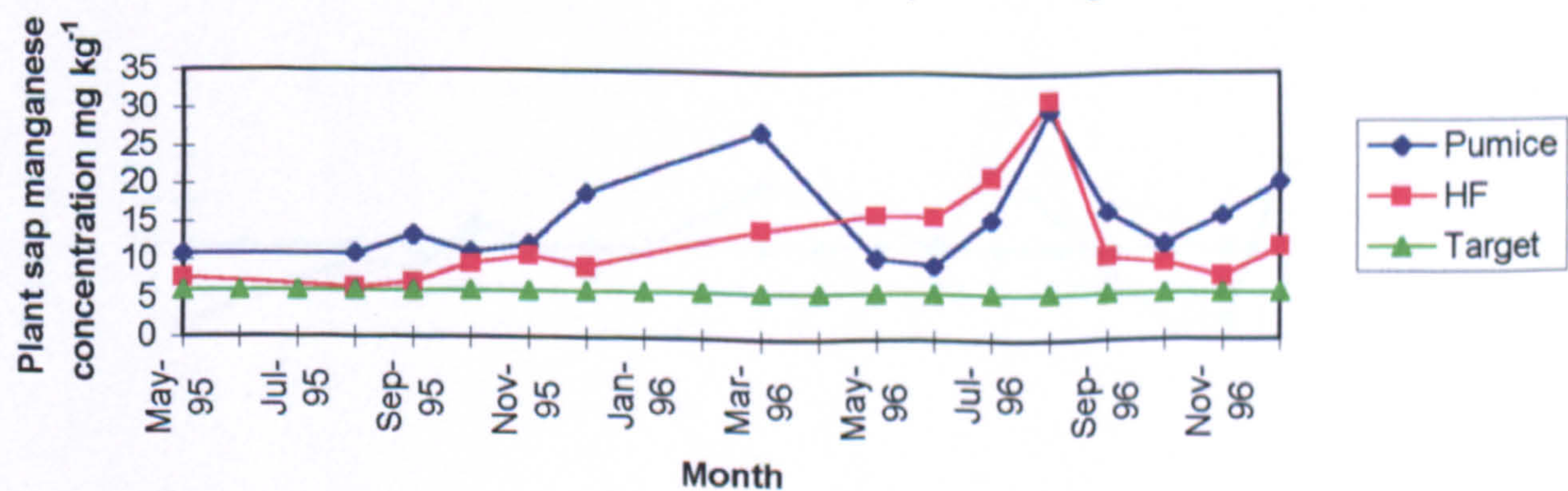


Figure 5.46 Plant leaf sap copper concentrations from pumice irrigated with liquid feeds and nutrient-loaded clinoptilolite irrigated with water

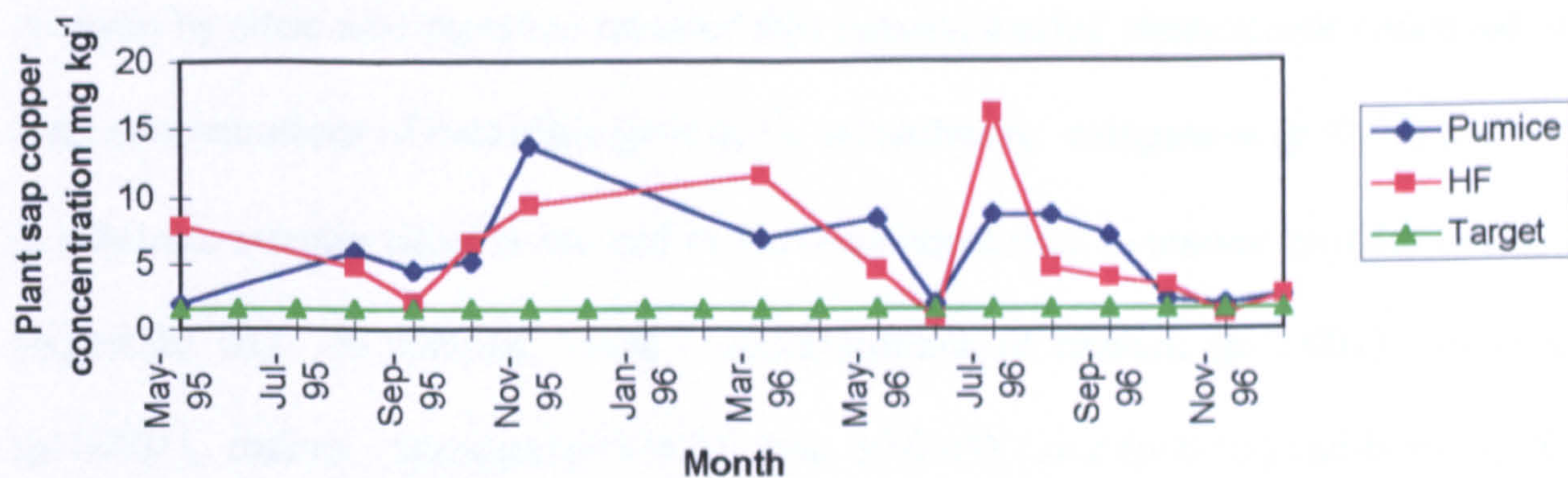


Figure 5.47 Plant leaf sap zinc concentrations from pumice irrigated with liquid feeds and nutrient-loaded clinoptilolite irrigated with water

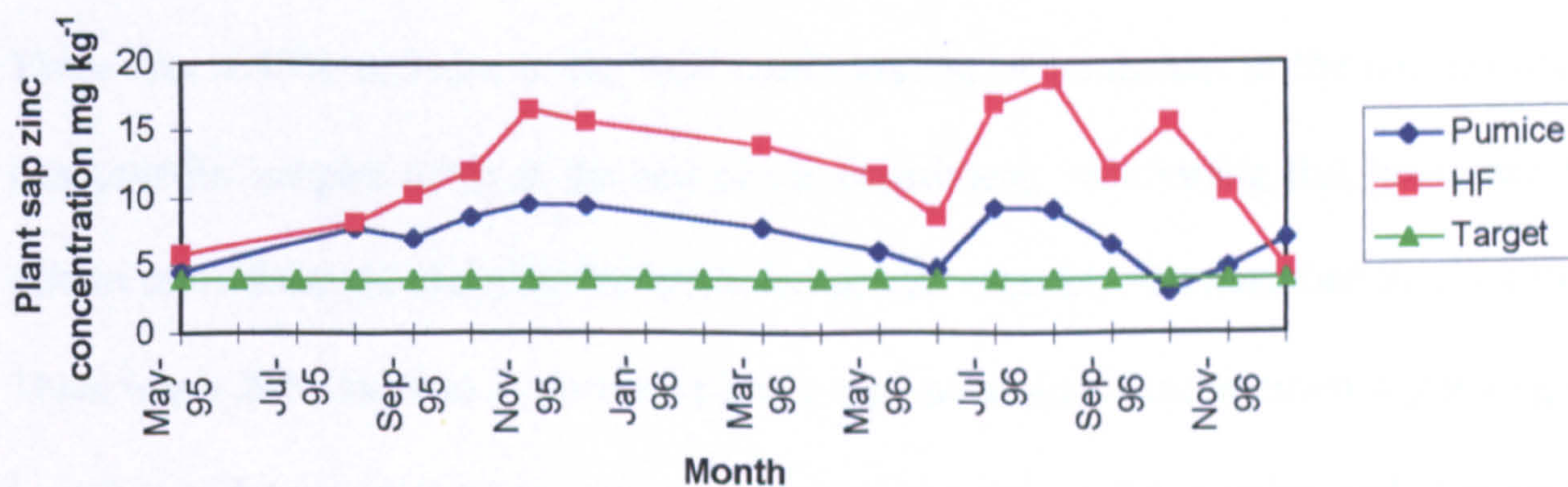
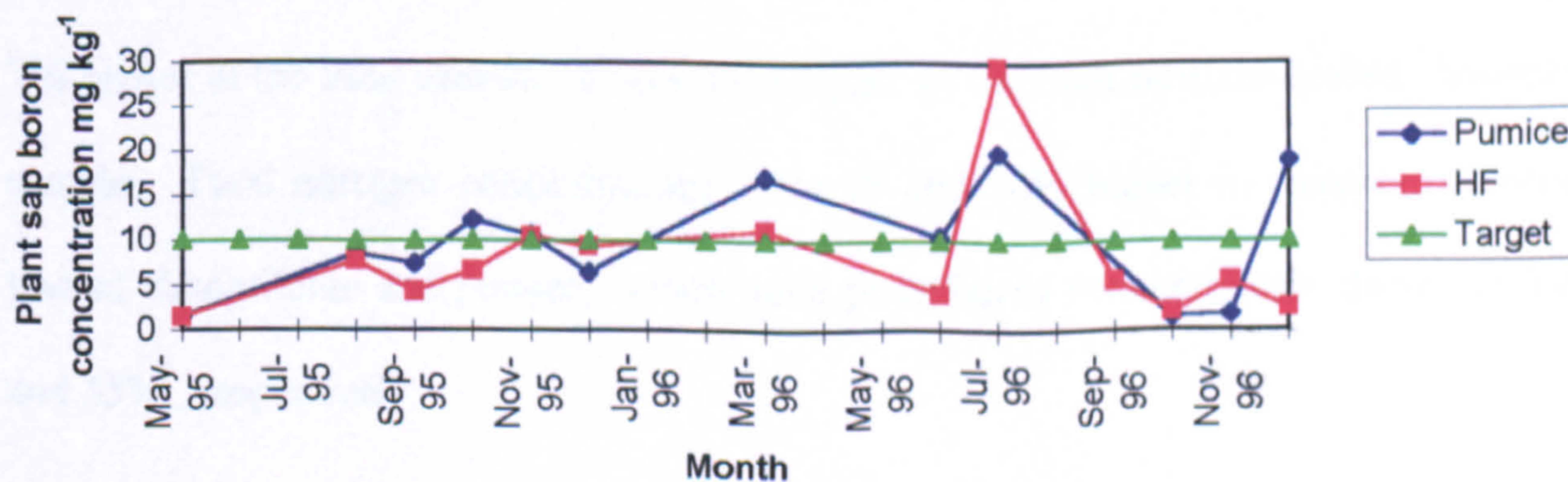


Figure 5.48 Plant leaf sap boron concentrations from pumice irrigated with liquid feeds and nutrient-loaded clinoptilolite irrigated with water



5.3.4.6 Major and trace element concentrations in the substrate

Analysis by nitric acid digestion revealed that nutrient-loaded clinoptilolite contained lower total concentrations of potassium ($p<0.001$), phosphorus, manganese ($p<0.01$) and copper in substrate samples taken at the end of the experiment than in unused samples (Table 5.8) (Appendix III). In contrast, total concentrations of calcium ($p<0.001$), magnesium ($p<0.001$), sodium, nitrogen ($p<0.001$), iron ($p<0.05$), zinc ($p<0.05$) and boron ($p<0.01$) were higher in the used substrate samples. Total potassium, phosphorus, copper and zinc concentrations were lower in samples of pumice taken at the end of the experiment compared with unused samples. Pumice total concentrations of calcium, magnesium, sodium, nitrogen, iron and manganese were higher in the used material.

There was a 43% decrease in the total concentration of potassium in the nutrient-loaded clinoptilolite samples taken at the end of the experiment, confirming that potassium was able to move from the clinoptilolite into solution and, possibly, be absorbed by plant roots. There was a 22% decrease in the used pumice total potassium concentration suggesting that a cation exchange mechanism was also operating between the pumice and surrounding nutrient solution. There were similar % increases in total calcium concentration of used nutrient-loaded clinoptilolite and pumice (56 and 54%, respectively). Used nutrient-loaded clinoptilolite and pumice total magnesium sample concentrations were 18 and 16% higher, respectively, than the unused materials. Whilst the pumice total sodium concentration was 7% higher in the used sample, it was 57% higher in the used nutrient-loaded clinoptilolite sample. Total nitrogen concentrations were 25 and 44% higher in samples of nutrient-loaded clinoptilolite and pumice, whilst total phosphorus concentrations decreased by 40 and 35%, respectively.

Experimental work completed by Allen *et al.* (1993, 1995a, 1995b and 1996) utilised mixtures of clinoptilolite and either natural or synthetic apatites in attempts to provide zeoponic substrates for the intensive growth of wheat. Early work indicated that slow release fertilisation using clinoptilolite and phosphate rock media may provide adequate levels of N, P and K to support plant growth, although solution calcium concentrations were lower than the optimum for plant growth (Allen *et al.*, 1993). However, properly formulated zeoponic mixtures of San Miguel or Wyoming clinoptilolite and North Carolina phosphate rock were capable of supplying sufficient levels of N, P, K and Ca for intensive growth of wheat (Allen *et al.*, 1995b). Models studied by Allen *et al.*, (1995a) suggested that nutrient release was diffusion controlled. Further work by Allen *et al.* in 1996 confirmed that clinoptilolite and phosphate rock may be used to obtain a controlled release of ammonium-nitrogen, phosphorus and potassium in a synthetic soil. The work in this study confirms that all plant nutrients required by standard carnations can be supplied by nutrient-loaded clinoptilolite but that the nutrient-loading of ammonium-nitrogen and phosphorus are the main limiting factors to flower yield and growth after a period of eight months.

5.3.5 Further discussion and conclusions

- The nutrient-loaded clinoptilolite substrate loadings of ammonium-nitrogen and phosphorus were the main limiting nutritional factors affecting plant growth and flower yield.
- Drainwater nutrient concentrations were low throughout the experiment from the nutrient-loaded clinoptilolite plots, whilst drainwater from the fertigated pumice plots contained notably higher concentrations of nitrate-nitrogen, phosphorus and potassium.

- Leaf tissue analysis in 1996 revealed lower total nitrogen and total phosphorus concentrations in leaves sampled from plants growing in nutrient-loaded clinoptilolite.
- The clinoptilolite cation exchange mechanism involved potassium, calcium, magnesium and sodium as the major participating ions. The clinoptilolite total potassium concentration decreased and the total calcium, magnesium and sodium concentrations increased over the experimental period. The clinoptilolite total phosphorus concentration decreased during the experiment and the release of phosphorus could have been related to and regulated by the accumulation of calcium in the substrate.
- It is clear that loading of ammonium-nitrogen in nutrient-loaded clinoptilolite is sufficient to produce commercially-acceptable yields of standard carnations over an eight month period. Thereafter, in order to compete with flower production from a fertigated pumice crop, it would be necessary to supplement the nitrogen and, possibly, the phosphorus contents of the nutrient-loaded zeolite by the introduction of a liquid feed of ammonium nitrate or mono-ammonium phosphate, for example. Careful nutritional monitoring of the system would be required, however, as the introduction of NH_4^+ into the root zone would tend to decrease the pH by release of H^+ ions and also encourage cation exchange with the clinoptilolite, with the possible release of high concentrations of accumulated sodium ions.
- Future work should examine higher loading start values of nutrient-loaded clinoptilolite and the supplementation of nitrogen by the addition of liquid feeds containing ammonium-nitrogen. Liquid feeding frequency and control of the concentration of the applied supplementary feed would also be additional areas of research on which to focus.

Table 5.6 Mean total monthly fresh wt standard carnation flower production averaged over the 18 month production period from ‘White Giant’ and ‘Master’ on four substrates, n=3. L.S.D. = least significant difference

Substrate	Mean monthly blooms per plot
Pumice	114.980
Nutrient-loaded clinoptilolite	85.670
Foam	104.35
Nutrient-loaded clinoptilolite / Alcosorb 400	82.32
L.S.D. (5%)	10.512
L.S.D. (1%)	13.894
L.S.D. (0.1%)	17.907
F-test significance level	p=***

Table 5.7 Mean monthly carnation flower production for two varieties and two substrates (fresh wt blooms m⁻²). Pum = pumice, clin = nutrient-loaded clinoptilolite (‘Hydrocult F’), WG = ‘White Giant’, M = ‘Master’, L.S.D. = least significant difference, F-test = significance level, n.s. = not significant, n=3

Year 1	July	August	Sept	October	Nov	Dec
PumWG	142.340	32.780	22.557	29.337	31.663	18.890
Clin WG	138.450	24.557	21.777	22.557	15.110	7.557
Pum M	132.660	51.890	5.667	14.110	21.777	15.333
Clin M	133.890	42.223	7.997	11.110	13.220	8.557
F-test	p=n.s.	p=n.s.	p=n.s.	p=n.s.	p=n.s.	p=n.s.

Year 2	Jan	Feb	Mar	Apr	May	June
PumWG	18.333	23.223	15.333	19.443	19.110	106.670
Clin WG	8.667	19.780	15.667	18.780	15.553	61.780
Pum M	21.333	41.443	14.443	8.110	1.110	39.450
Clin M	9.110	16.443	11.443	3.110	0.777	14.220
L.S.D. (5%)		3.558		2.834		
L.S.D. (1%)		5.390				
L.S.D. (0.1%)		8.664				
F-test	p=n.s.	p=***	p=n.s.	p=*	p=n.s.	p=n.s.
Year 2	July	August	Sept	October	Nov	Dec
PumWG	112.560	54.780	30.000	19.777	17.333	41.333
Clin WG	89.560	43.110	21.780	11.223	9.223	19.110
Pum M	113.330	60.110	22.223	17.557	16.443	27.333
Clin M	44.780	61.333	34.223	22.780	12.220	16.223
L.S.D. (5%)	23.300		7.943	9.184		
L.S.D. (1%)			12.033			
F-test	p=*	p=n.s.	p=**	p=*	p=n.s.	p=n.s.

Table 5.8 Interaction between substrate and element - nitric acid digestion of unused and used pumice and nutrient-loaded clinoptilolite ('Hydrocult F'). L.S.D. = least significant difference, n.s. = not significant, n=3

Substrate / Total Element	Mean Total Concentration mg kg⁻¹	L.S.D. (5%)	L.S.D. (1%)	L.S.D. (0.1%)	F-test significance level
Unused Pumice K	1586.000				
Used Pumice K	1233.000	3407.741	5162.442	8298.623	p=***
Unused Zeolite K	34867.000				
Used Zeolite K	20000.000				
Unused Pumice Ca	2910.000				
Used Pumice Ca	4530.000	3052.126	4623.715	7432.619	p=***
Unused Zeolite Ca	12200.000				
Used Zeolite Ca	18767.000				
Unused Pumice Mg	812.700				
Used Pumice Mg	960.700	671.102	1016.663	1634.286	p=***
Unused Zeolite Mg	3543.300				
Used Zeolite Mg	4123.300				
Unused Pumice Na	1970.000				
Used Pumice Na	2103.300				p=n.s.
Unused Zeolite Na	2473.300				
Used Zeolite Na	3883.300				
Unused Pumice N	533.300				
Used Pumice N	766.700	233.096	353.121	567.642	p=***
Unused Zeolite N	1466.700				
Used Zeolite N	1833.300				

Unused Pumice	P	402.330				
Used Pumice	P	262.670				p=n.s.
Unused Zeolite	P	274.000				
Used Zeolite	P	164.670				
Unused Pumice	Fe	1670.300				
Used Pumice	Fe	5076.700	1699.745			p=*
Unused Zeolite	Fe	4420.000				
Used Zeolite	Fe	4516.700				
Unused Pumice	Mn	61.070				
Used Pumice	Mn	61.530	273.670	414.587		p=**
Unused Zeolite	Mn	630.000				
Used Zeolite	Mn	477.670				
Unused Pumice	Cu	14.200				
Used Pumice	Cu	7.933				p=n.s.
Unused Zeolite	Cu	9.567				
Used Zeolite	Cu	0.933				
Unused Pumice	Zn	16.567				
Used Pumice	Zn	14.367	16.160			p=*
Unused Zeolite	Zn	32.733				
Used Zeolite	Zn	39.233				
Unused Pumice	B	2.133				
Used Pumice	B	2.300	0.607	0.919		p=**
Unused Zeolite	B	0.867				
Used Zeolite	B	1.000				

Chapter Six Comparison of unloaded and nutrient-loaded clinoptilolites as plant growth substrates

6.1 Experiment 7 Growth analysis of sweet pepper plants on unloaded and nutrient-loaded clinoptilolite zeolites

6.1.1 Introduction

In this experiment, unloaded clinoptilolite was compared with two nutrient-loaded clinoptilolites in the production of sweet peppers under a commercial glasshouse environmental regime. Only water was supplied to all the treatments throughout the seven month growing period. The following objectives were set.

1. To assess plant growth and sweet pepper fruit yield from the clinoptilolite substrates supplied with water only.
2. To measure nutritional changes in individual substrate drainwater samples, in order to detect differences between nutrient concentrations in the applied irrigation water and the drainwater.
3. To measure total plant nitrogen, phosphorus and potassium concentrations over the period April to October.
4. To measure the concentration of fixed and exchangeable major and trace elements before and after the experiment in all three substrates.

6.1.2 Materials and methods

The three treatments were : 1. Unloaded clinoptilolite; 2. Low nutrient-loaded clinoptilolite : 'Hydrocult S'; and 3. High nutrient-loaded clinoptilolite : 'Hydrocult F'.

6.1.3 Plant growing conditions

Sweet pepper plants of the variety 'Mazurka' (Rijk Zwaan) were raised at a commercial nursery site in 0.65 litre rockwool propagation blocks, using a standard hydroponic liquid feed regime (Table 6.1). The plants were planted over the period 29 March to 1 April in three litre pots, in single rows at a density of three plants m⁻² (Plate 3.7). Each plot

consisted of three pots and there were three treatments. The experimental design incorporated four replicates of each treatment and seven harvests in a randomised block design.

The rockwool blocks were inserted into the substrate with the plant base level with the surface of the substrate to ensure that the roots were in intimate contact with the clinoptilolite. This resulted in an actual substrate volume of 2.35 litres per pot. Loose clinoptilolite was prevented from moving out of the pots by incorporating a lining of spun, polypropylene fibre inside the base of each pot. The same material was used to cover the top of the pots to prevent rapid evaporation of moisture from the substrate surface. Initial waterings were by hand using an equal quantity of water to maintain moisture levels within each pot. The zeolite particle-size distribution was 0.8-2.5 mm for the unloaded clinoptilolite, compared with 0.8-5.0 mm for the nutrient-loaded clinoptilolites. All pots were placed on polystyrene boards, to allow efficient drainage away from the pots and to provide heat insulation to the pot bases (Plate 3.7). The pots were dosed with water via a drip irrigation system throughout the life of the crop at a rate of one litre hour⁻¹ and no liquid feed was applied to the system at any time. The number of irrigation cycles per day was determined by the amount of light received by the crop but was manually controlled until May and, thereafter, allowed to operate on a continuous basis day and night.

Destructive sampling of plant material took place each month and weekly plant trimmings were collected and frozen-stored, prior to bulking-up with the main sample. Data collected included the number and fresh weight of each fruit per plot and the fruit was quality graded to MAFF standards.

6.1.4 Chemical analysis of water, plant and substrate samples

Samples of input irrigation water and drainwater were taken on a monthly basis. The drainwater was sampled from modified pots in the final harvest plots, to provide data on changes in the concentration of nutrients involved with all three treatments. Modifications

to the pots involved the addition of an inner well contained within an outer polypropylene collar extension to the pot base. Samples of the drainwater were collected from the inner well under the pots using a syringe and were transferred to plastic bottles. Samples from the four replicates were combined to provide one representative sample per treatment.

Four plants from each treatment were destructively harvested each month and divided into leaves (including petioles), stems, fruits (including inflorescences and flower buds) and roots (Plate 3.6). Roots were manually separated from the substrates and a range of entomological sieves were used to capture all root pieces broken during the separation process. Samples of each substrate were taken before filling the pots and from the final harvest pots after completion of the experiment. Nitric acid digestion and sodium exchange determinations were performed on the resulting substrate samples.

6.1.5 Results

6.1.5.1 Crop yields

Yields to October, 1994 are given in Tables 6.2 and 6.3. The first peppers were picked on 8 May and subsequent harvesting operations were performed monthly thereafter, according to good commercial practice (Anon, 1995b). The highest monthly fruit weights were recorded from plants growing in the nutrient-loaded clinoptilolite 'Hydrocult F'. The analysis of variance of fruit weights demonstrated that the treatments were highly statistically significant ($p < 0.001$) for all six harvest dates (Appendix IV). There were no quality defects in fruit harvested from the nutrient-loaded clinoptilolite plants. It was noticeable, however, that levels of blossom end rot were particularly low from all treatments (Plate 3.8).

6.1.5.2 Chemical analysis of irrigation water

The analysis of irrigation water over the sampling period revealed potassium concentrations of 3.0 to 9.0 mg l⁻¹ (Figure 6.1), a calcium concentration range of 1.3 to 21.8 mg l⁻¹ (Figure 6.2), sodium concentrations of 8.0 to 40.0 mg l⁻¹ (Figure 6.4), a nitrate-nitrogen

Figure 6.1 Drainwater and irrigation water potassium concentrations of samples taken from unloaded clinoptilolite (ULZ), low nutrient-loaded clinoptilolite (HS) and high nutrient-loaded clinoptilolite (HF)

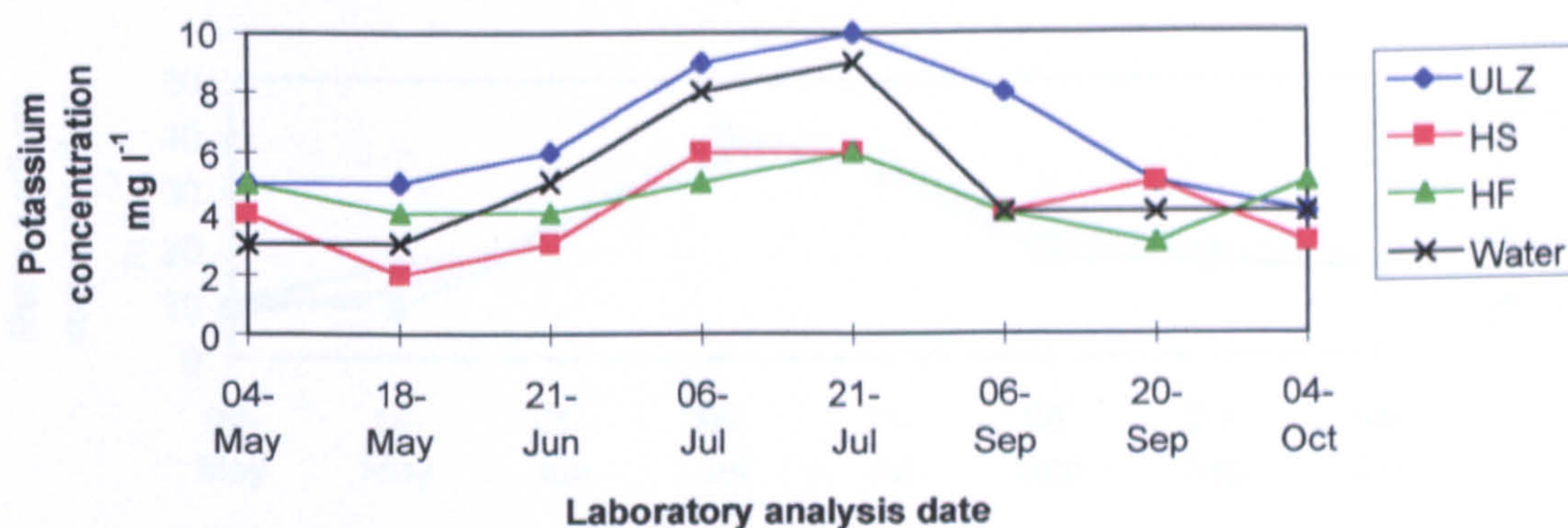


Figure 6.2 Drainwater and irrigation water calcium concentrations of samples taken from unloaded clinoptilolite (ULZ), low nutrient-loaded clinoptilolite (HS) and high nutrient-loaded clinoptilolite (HF)

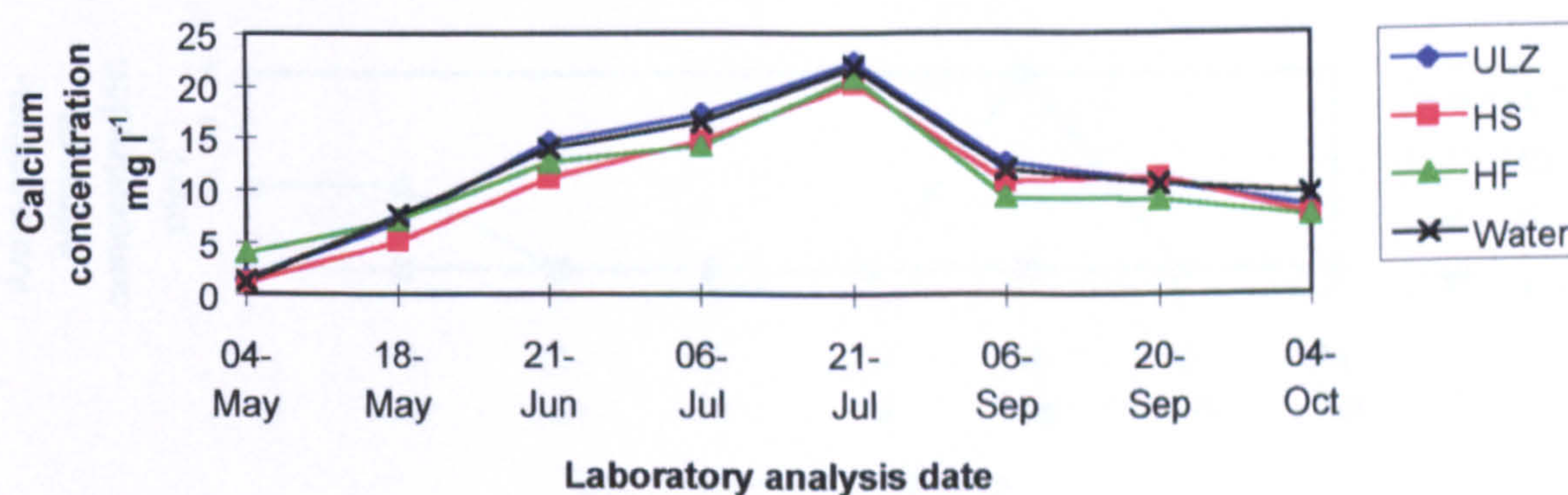


Figure 6.3 Drainwater and irrigation water magnesium concentrations of samples taken from unloaded clinoptilolite (ULZ), low nutrient-loaded clinoptilolite (HS) and high nutrient-loaded clinoptilolite (HF)

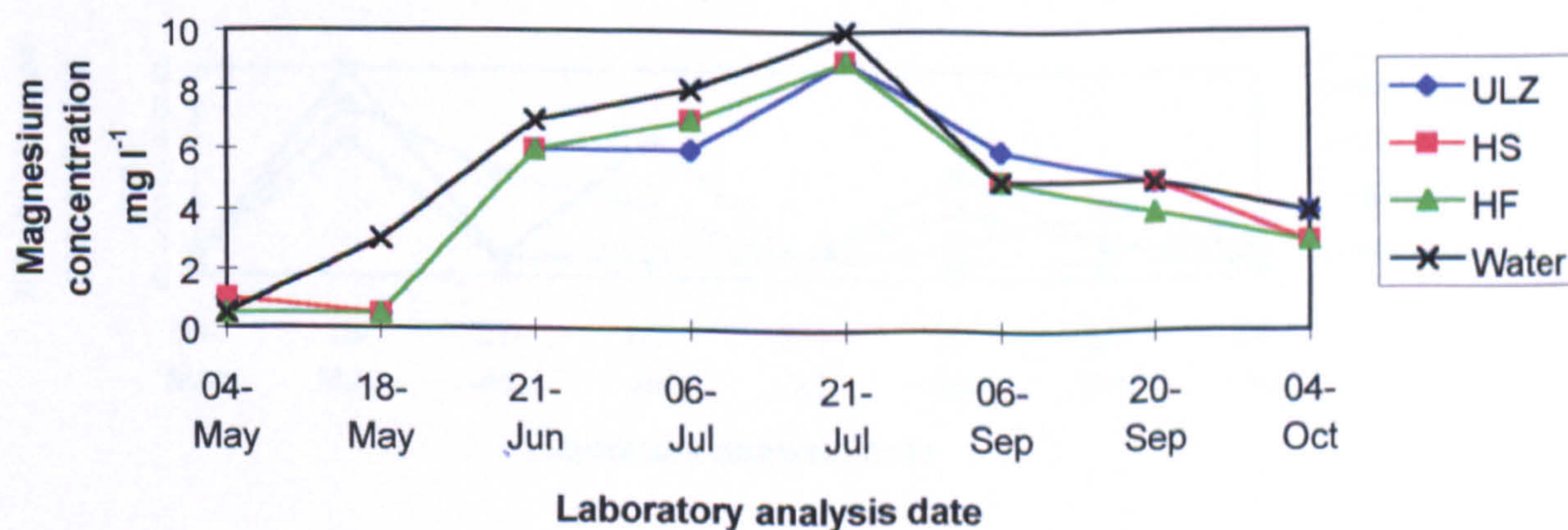


Figure 6.4 Drainwater and irrigation water sodium concentrations of samples taken from unloaded clinoptilolite (ULZ), low nutrient-loaded clinoptilolite (HS) and high nutrient-loaded clinoptilolite (HF)

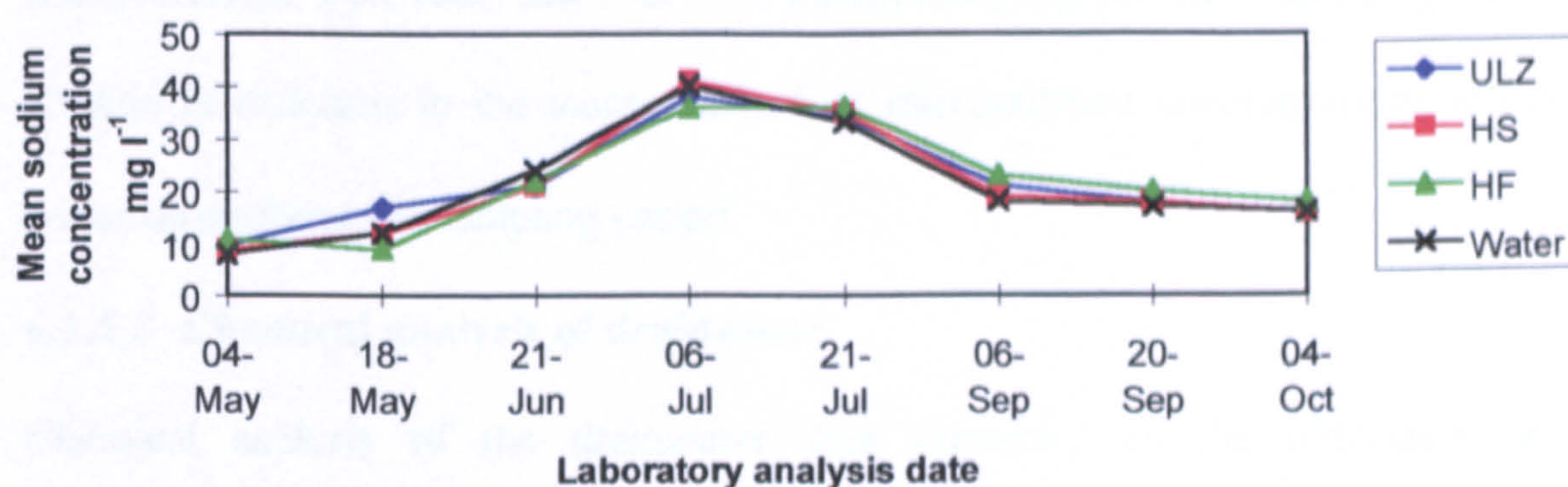


Figure 6.5 Drainwater and irrigation water ammonium-nitrogen concentrations of samples taken from unloaded clinoptilolite (ULZ), low nutrient-loaded clinoptilolite (HS) and high nutrient-loaded clinoptilolite (HF)

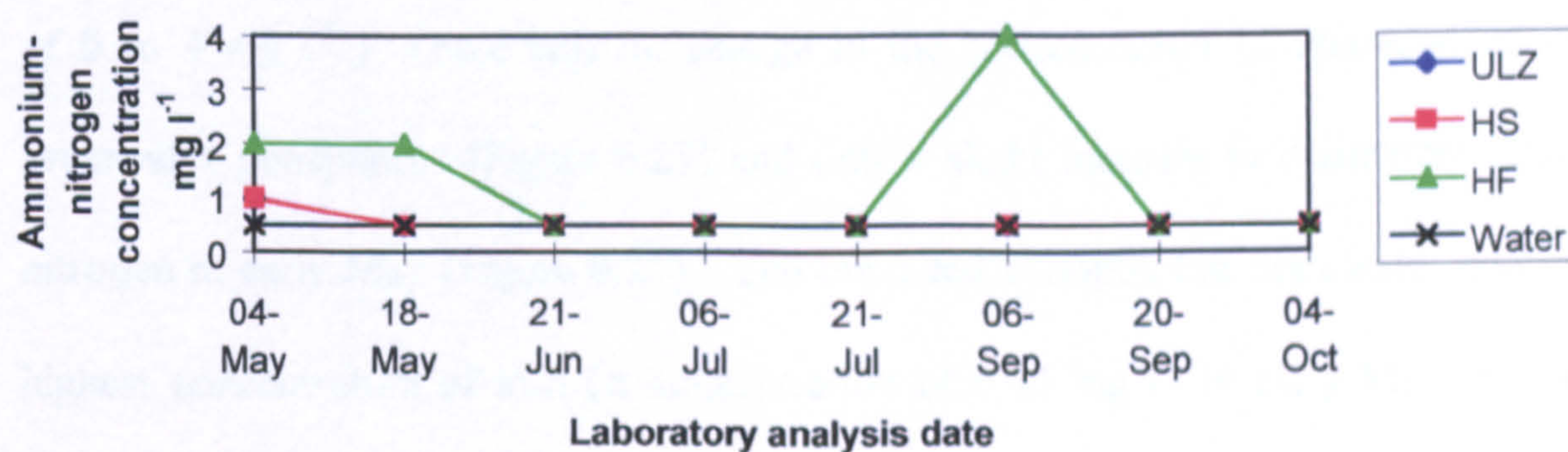
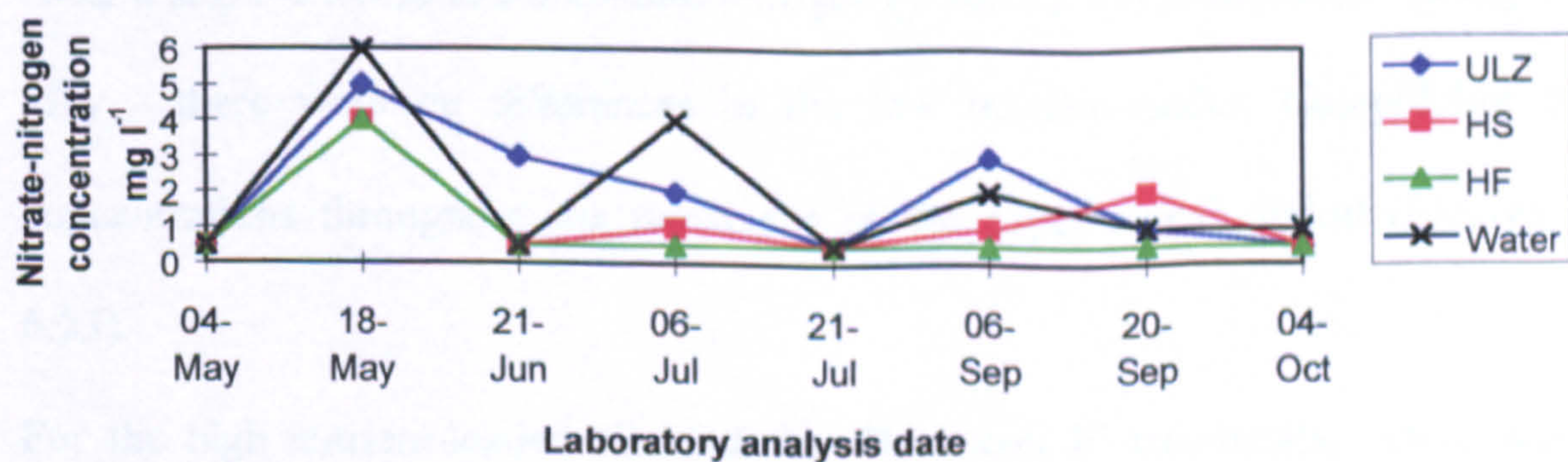


Figure 6.6 Drainwater and irrigation water nitrate-nitrogen concentrations of samples taken from unloaded clinoptilolite (ULZ), low nutrient-loaded clinoptilolite (HS) and high nutrient-loaded clinoptilolite (HF)



concentration range of 0.5 to 6.0 mg l⁻¹ (Figure 6.6), a phosphorus concentration of 0.5 mg l⁻¹ (Figure 6.7), and a conductivity range of 55 to 405 μ S cm⁻¹ (Figure 6.15). The concentrations were recorded over a six month sampling period (Table 6.4). There were no notable fluctuations in the macronutrient or micronutrient concentrations in the irrigation water throughout the sampling period.

6.1.5.3 Chemical analysis of drainwater

Chemical analysis of the drainwater was expressed as the difference between the concentration of the irrigation water and the drainage water (Δ concentration). Data were recorded for the major nutrients at intervals during the experiment (Table 6.5).

The concentration of potassium in the unloaded clinoptilolite drainwater (Figure 6.17) was consistently higher than in the irrigation water but of a low concentration (Δ concentration of 0 to 4 mg l⁻¹). There was no change in the concentration of unloaded clinoptilolite drainwater phosphorus (Figure 6.23) and only a slight increase in drainwater ammonium-nitrogen in early May (Figure 6.21). The unloaded clinoptilolite drainwater contained the highest concentration of iron (Δ concentration of 0.45 mg l⁻¹ in early May) and this had decreased to 0.05 mg l⁻¹ by mid-June (Figure 6.24).

With the low nutrient-loaded clinoptilolite 'Hydrocult S' treatments, there was a slight increase in the conductivity of the drainwater in early May, thereafter, drainwater conductivity concentrations were consistently lower than the irrigation water (Figure 6.25). After a slight increase in ammonium-nitrogen (1 mg l⁻¹) and phosphorus (2 mg l⁻¹) in early May, there were no differences in the low nutrient-loaded clinoptilolite drainwater concentrations throughout the remainder of the experimental period (Figures 6.21 and 6.23).

For the high nutrient-loaded clinoptilolite 'Hydrocult F' treatments, there was a larger increase in the conductivity of the drainwater in early May (Δ concentration of 35 μ S cm⁻¹); thereafter, drainwater conductivity concentrations were consistently lower (Figure 6.25).

Figure 6.7 Drainwater and irrigation water phosphorus concentrations of samples taken from unloaded clinoptilolite (ULZ), low nutrient-loaded clinoptilolite (HS) and high nutrient-loaded clinoptilolite (HF)

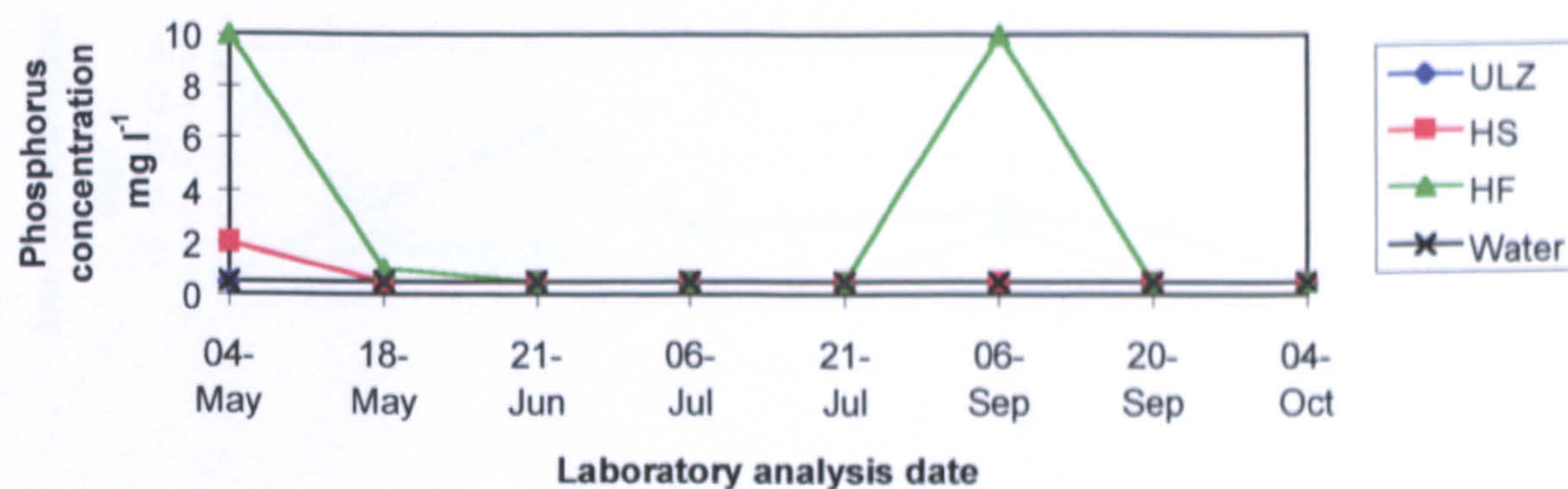


Figure 6.8 Drainwater and irrigation water chloride concentrations of samples taken from unloaded clinoptilolite (ULZ), low nutrient-loaded clinoptilolite (HS) and high nutrient-loaded clinoptilolite (HF)

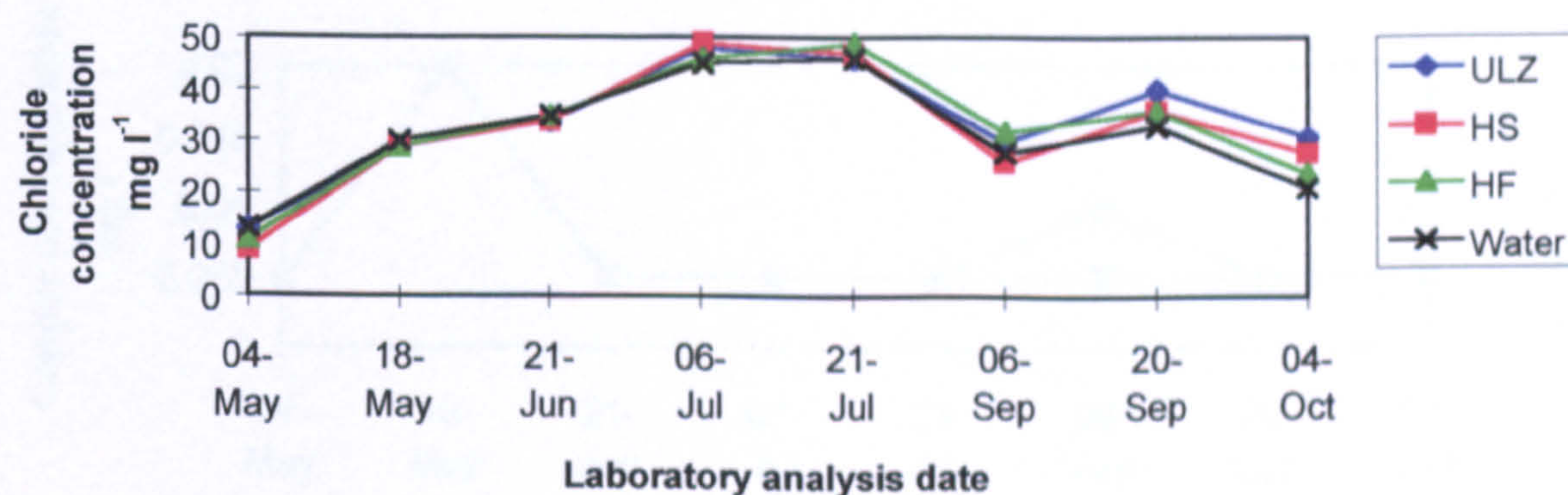


Figure 6.9 Drainwater and irrigation water sulphate concentrations of samples taken from unloaded clinoptilolite (ULZ), low nutrient-loaded clinoptilolite (HS) and high nutrient-loaded clinoptilolite (HF)

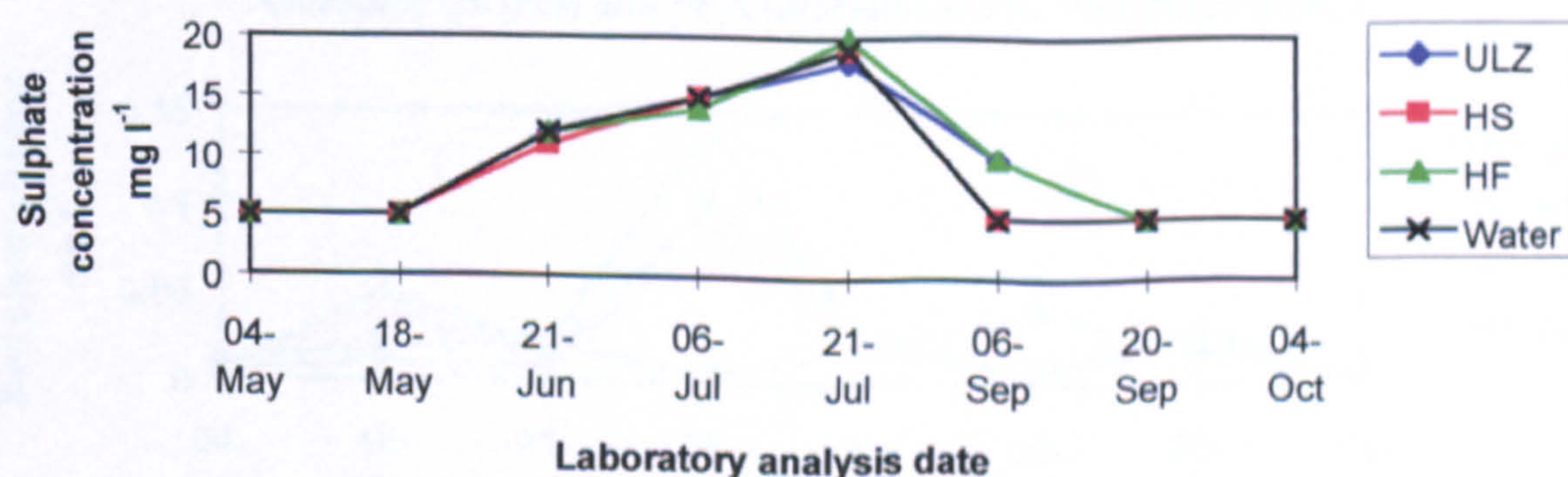


Figure 6.10 Dainwater and irrigation water iron concentrations of samples taken from unloaded clinoptilolite (ULZ), low nutrient-loaded clinoptilolite (HS) and high nutrient-loaded clinoptilolite (HF)

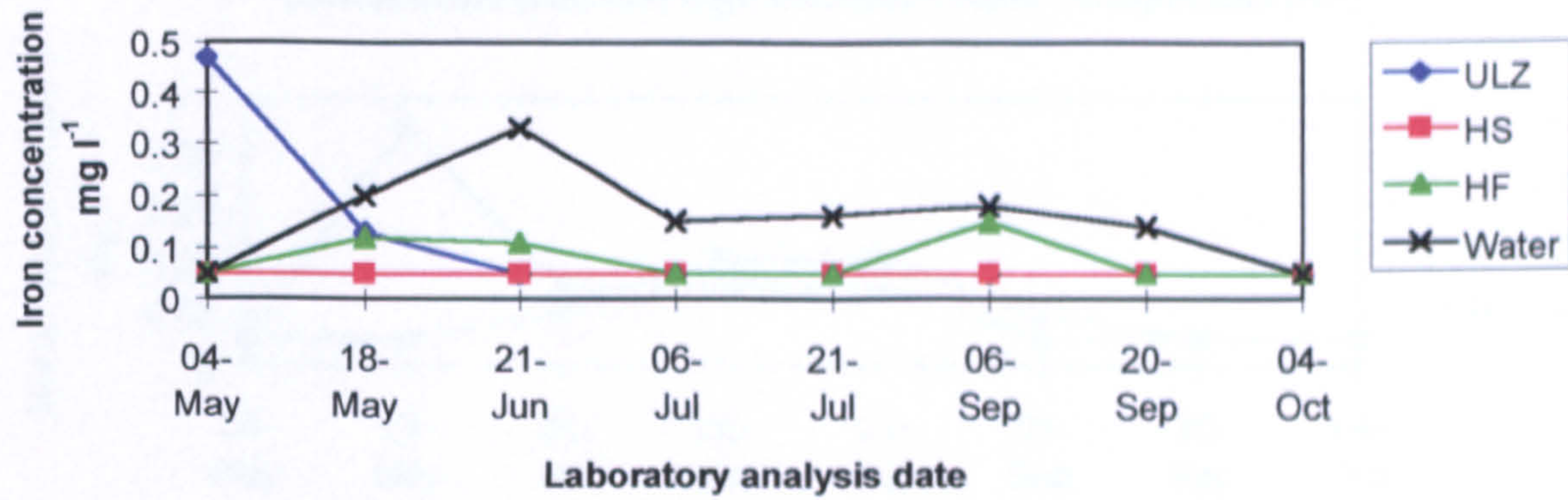


Figure 6.11 Drainwater and irrigation water copper concentrations of samples taken from unloaded clinoptilolite (ULZ), low nutrient-loaded clinoptilolite (HS) and high nutrient-loaded clinoptilolite (HF)

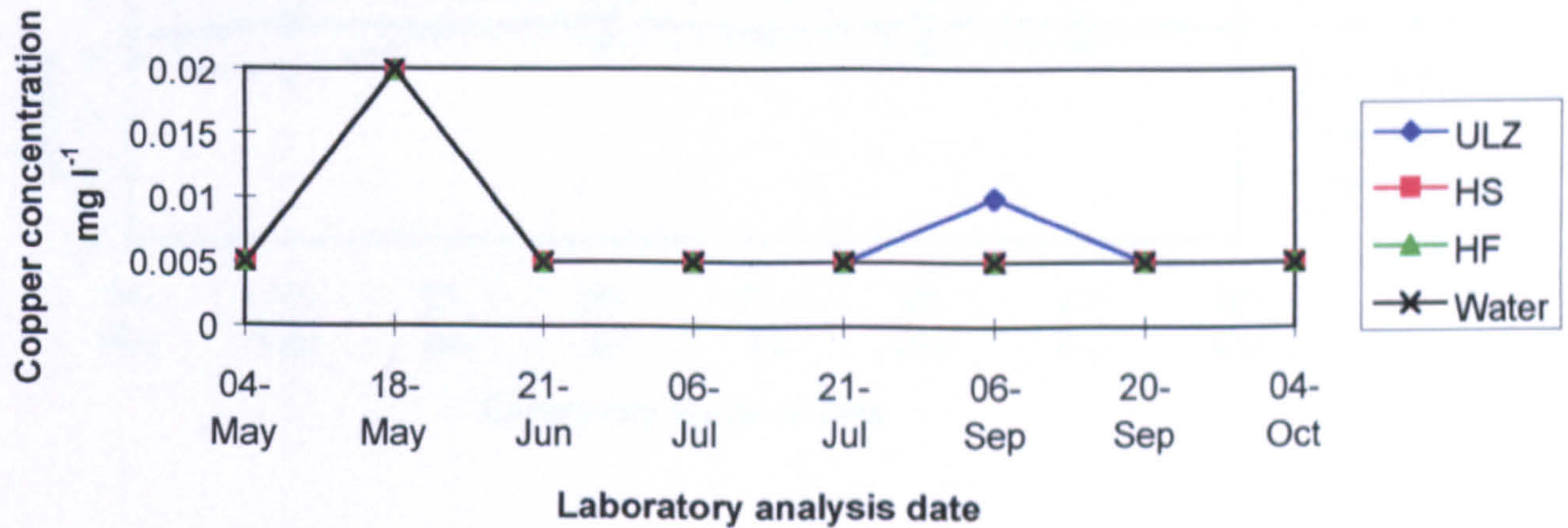


Figure 6.12 Drainwater and irrigation water zinc concentrations of samples taken from unloaded clinoptilolite (ULZ), low nutrient-loaded clinoptilolite (HS) and high nutrient-loaded clinoptilolite (HF)

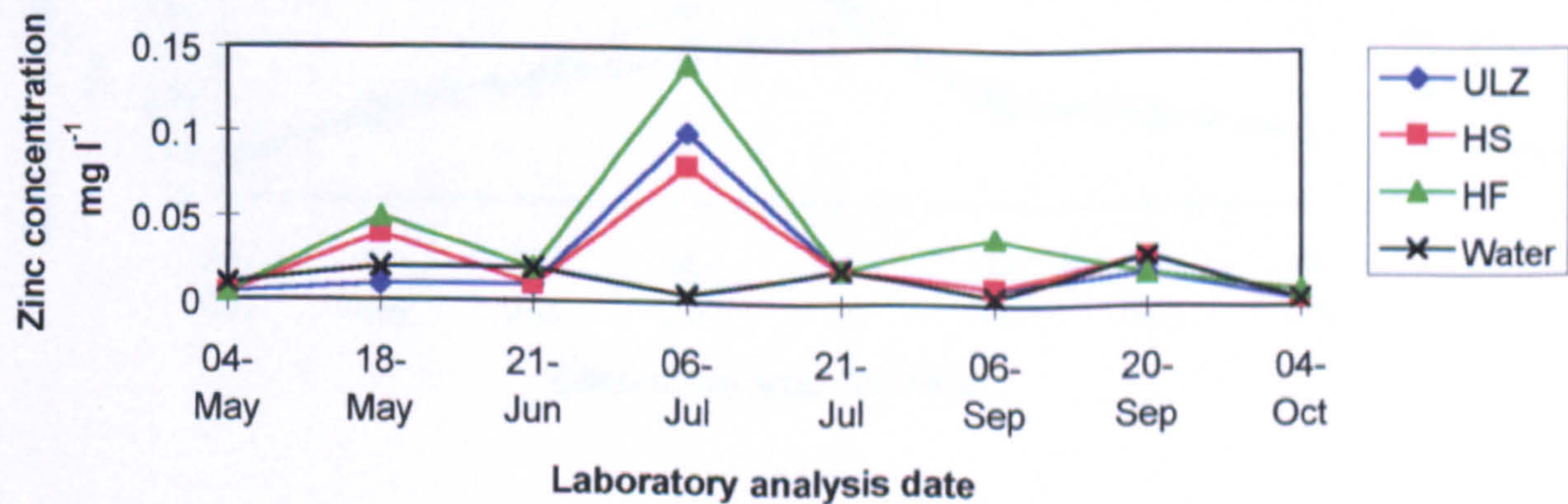


Figure 6.13 Drainwater and irrigation water boron concentrations of samples taken from unloaded clinoptilolite (ULZ), low nutrient-loaded clinoptilolite (HS) and high nutrient-loaded clinoptilolite (HF)

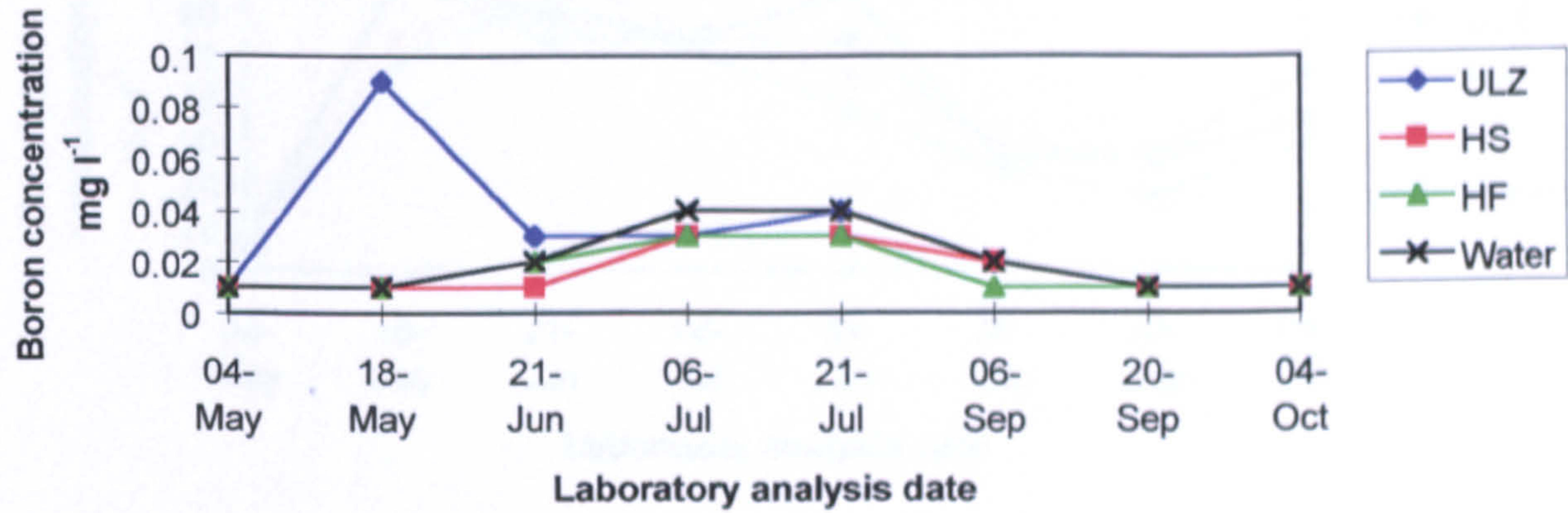


Figure 6.14 Drainwater and irrigation water pH levels of samples taken from unloaded clinoptilolite (ULZ), low nutrient-loaded clinoptilolite (HS) and high nutrient-loaded clinoptilolite (HF)

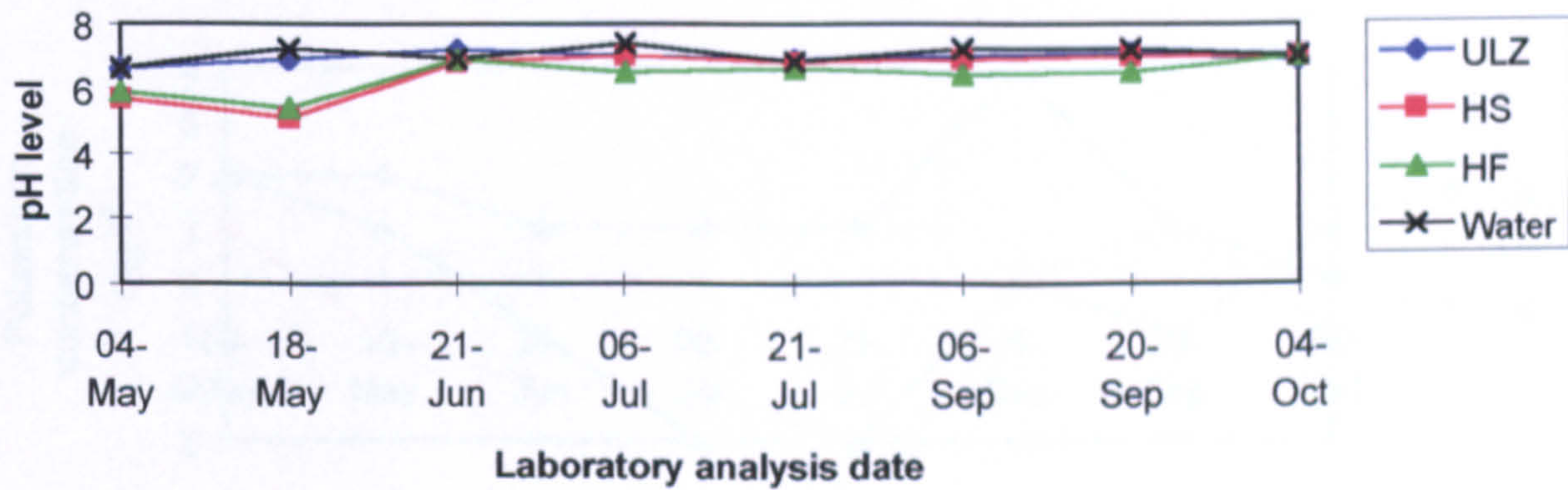


Figure 6.15 Drainwater and irrigation water EC concentrations of samples taken from unloaded clinoptilolite (ULZ), low nutrient-loaded clinoptilolite (HS) and high nutrient-loaded clinoptilolite (HF)

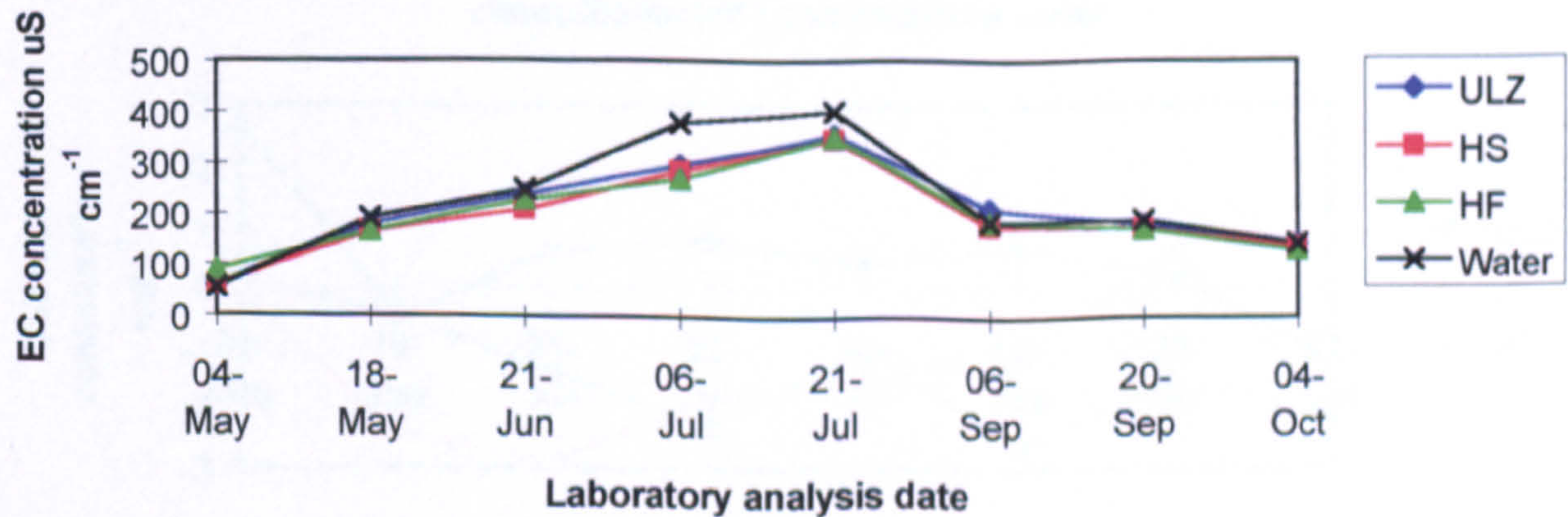


Figure 6.16 Drainwater and irrigation water bicarbonate concentrations of samples taken from unloaded clinoptilolite (ULZ), low nutrient-loaded clinoptilolite (HS) and high nutrient-loaded clinoptilolite (HF)

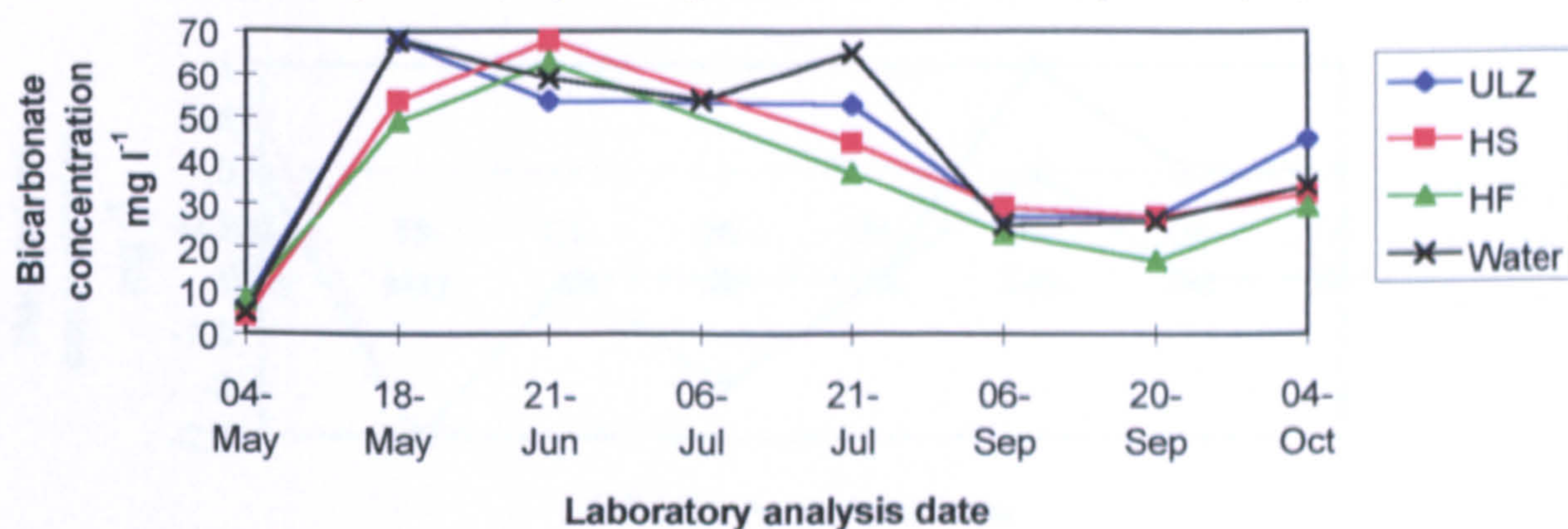


Figure 6.17 Δ concentration of potassium between unloaded clinoptilolite (ULZ), low nutrient-loaded clinoptilolite (HS), high nutrient-loaded clinoptilolite (HF) and irrigation water

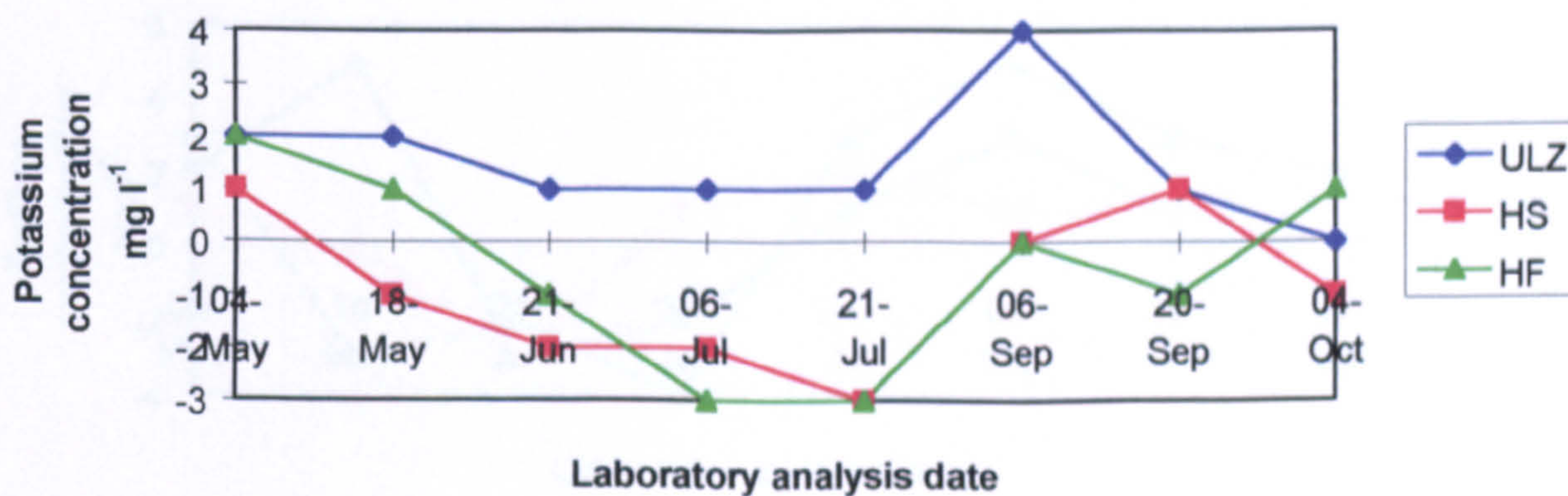


Figure 6.18 Δ concentration of calcium between unloaded clinoptilolite (ULZ), low nutrient-loaded clinoptilolite (HS), high nutrient-loaded clinoptilolite (HF) and irrigation water

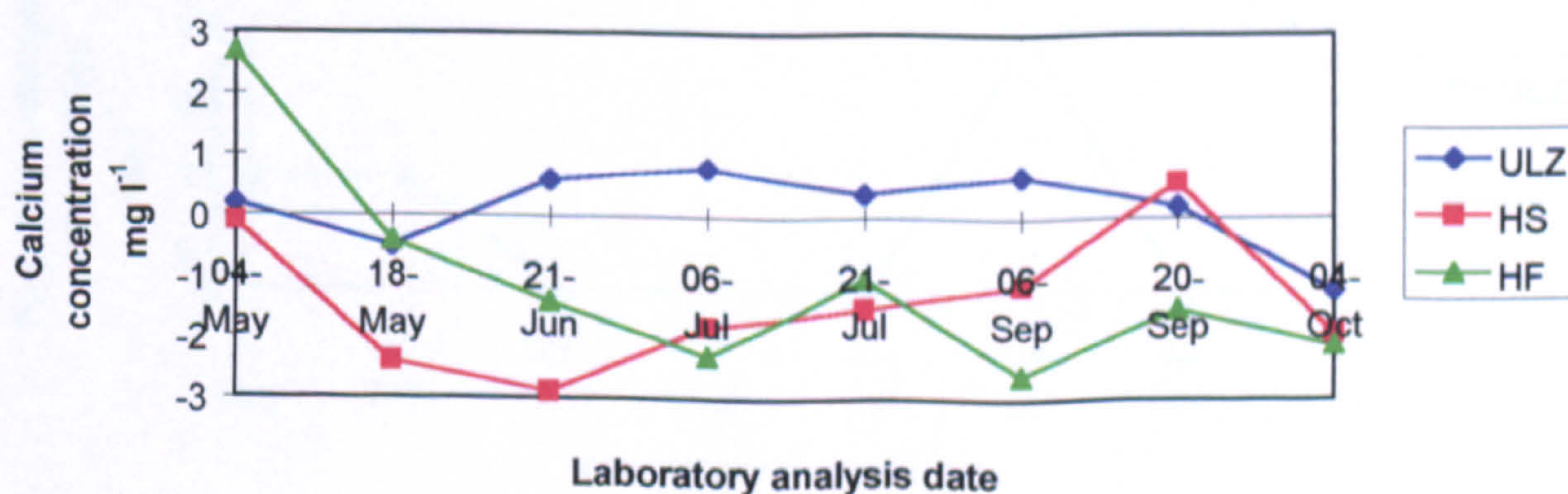


Figure 6.19 ^ concentration of magnesium between unloaded clinoptilolite (ULZ), low nutrient-loaded clinoptilolite (HS), high nutrient-loaded clinoptilolite (HF) and irrigation water

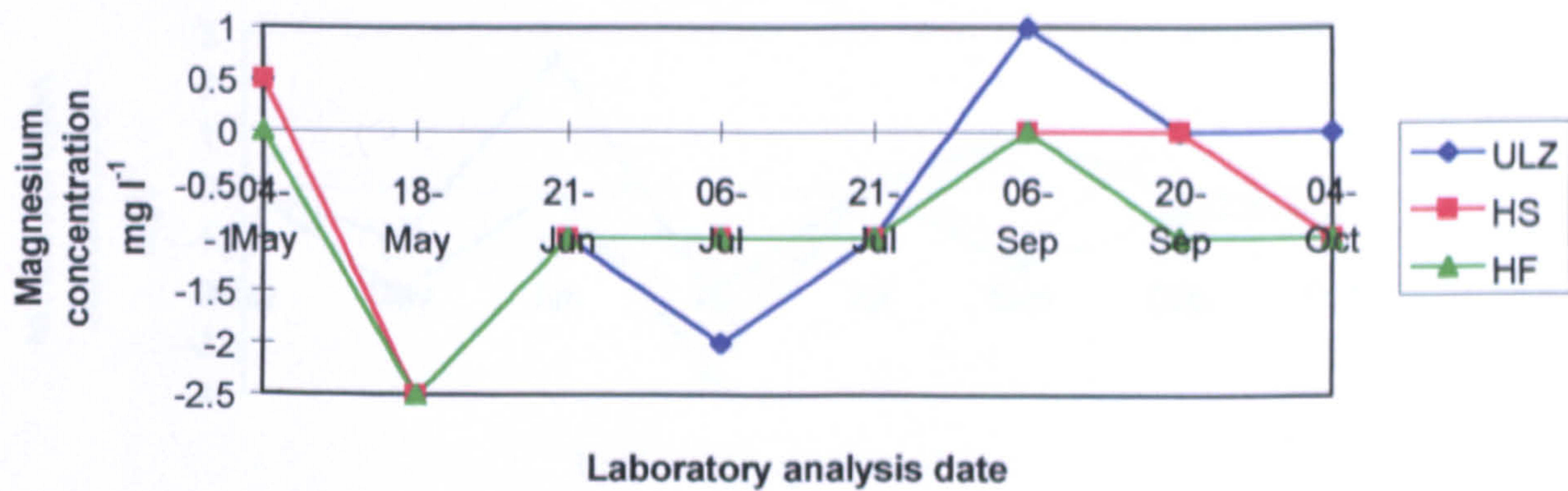


Figure 6.20 ^ concentration of sodium between unloaded clinoptilolite (ULZ), low nutrient-loaded clinoptilolite (HS), high nutrient-loaded clinoptilolite (HF) and irrigation water

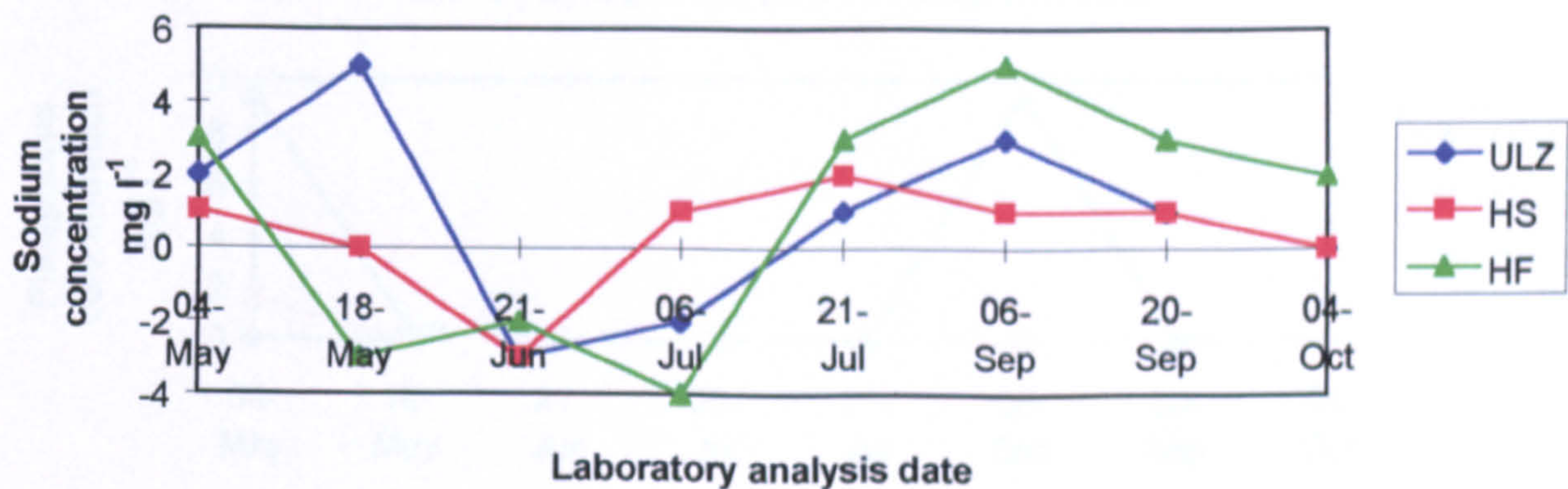


Figure 6.21 ^ concentration of ammonium-nitrogen between unloaded clinoptilolite (ULZ), low nutrient clinoptilolite (HS), high nutrient-loaded clinoptilolite and irrigation water

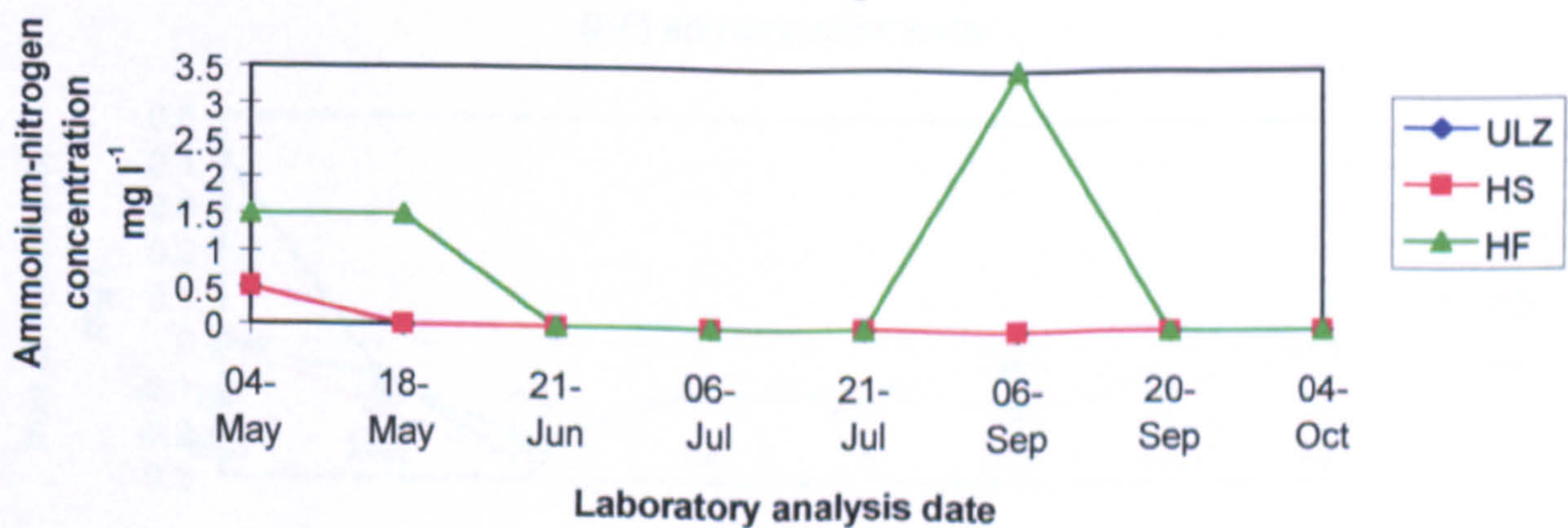


Figure 6.22 ^ concentration of nitrate-nitrogen between unloaded clinoptilolite (ULZ), low nutrient-loaded clinoptilolite (HS), high nutrient-loaded clinoptilolite (HF) and irrigation water

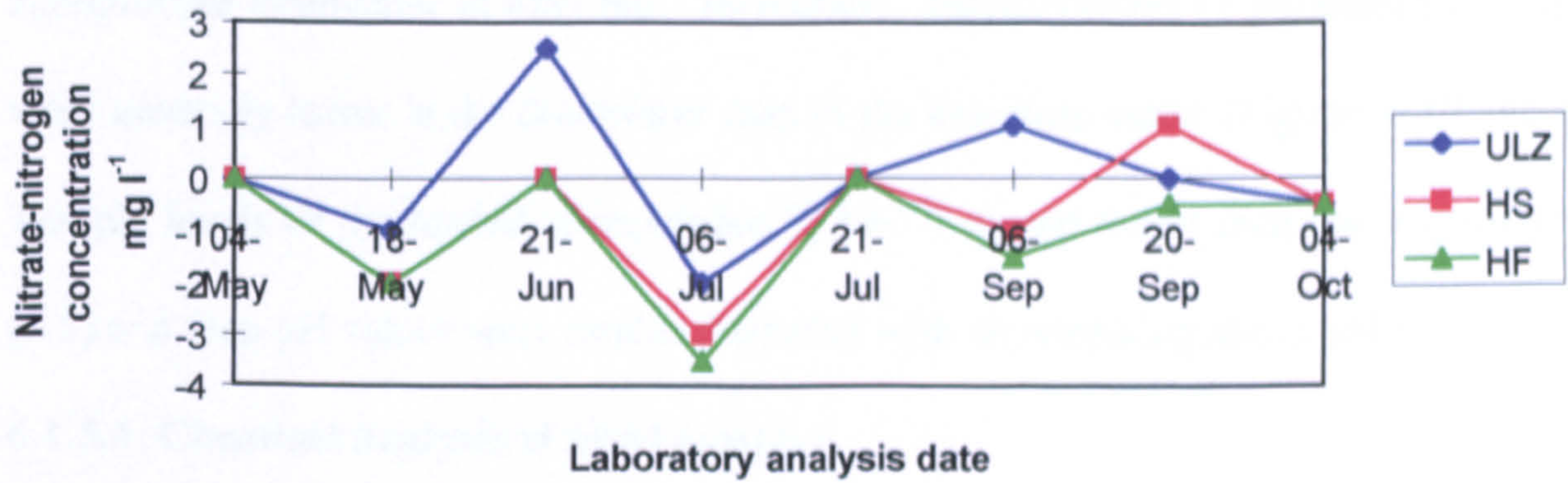


Figure 6.23 ^ concentration of phosphorus between unloaded clinoptilolite (ULZ), low nutrient-loaded clinoptilolite (HS), high nutrient-loaded clinoptilolite (HF) and irrigation water

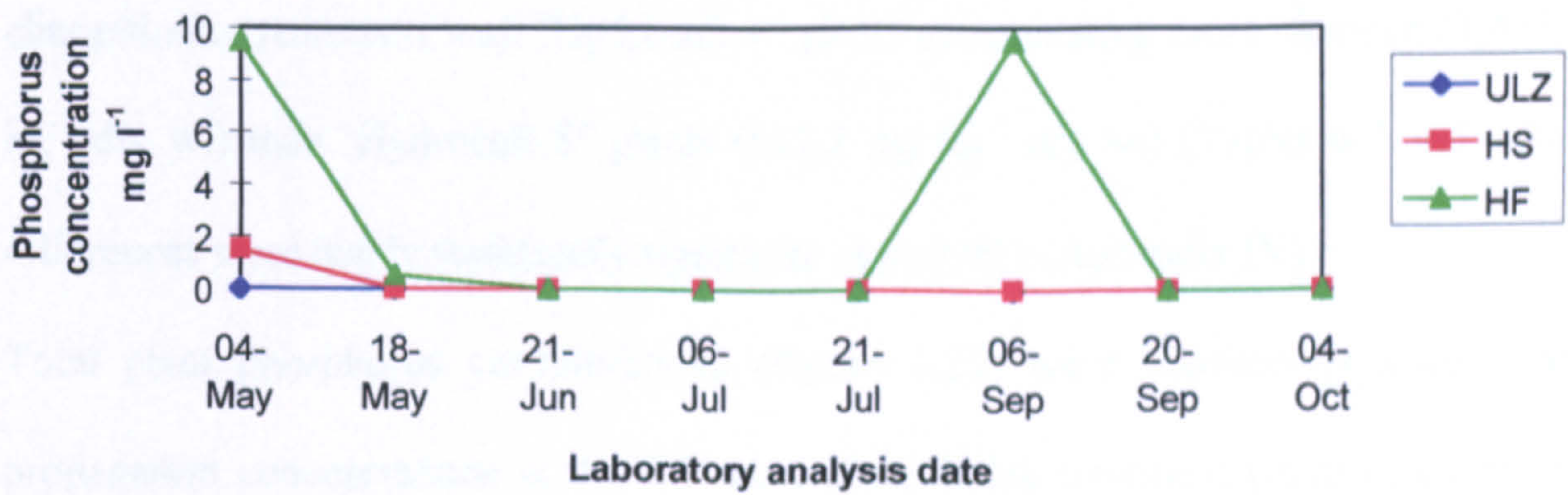
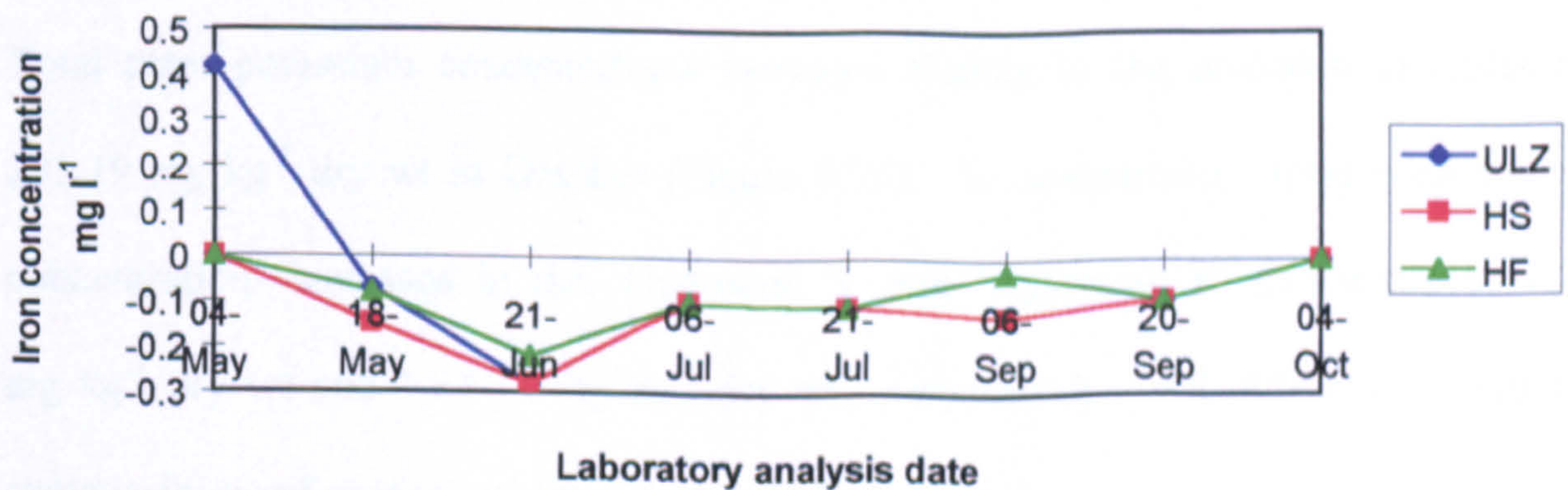


Figure 6.24 ^ concentration of iron between unloaded clinoptilolite (ULZ), low nutrient-loaded clinoptilolite (HS), high nutrient-loaded clinoptilolite (HF) and irrigation water



Higher concentrations of phosphorus (10 mg l^{-1}) and calcium (4 mg l^{-1}) were present in the high nutrient-loaded clinoptilolite drainwater compared with the low nutrient-loaded clinoptilolite drainwater in May but, thereafter, concentrations of potassium and calcium were generally lower in the drainwater than in the irrigation water (Figures 6.17 and 6.18). The pH levels of the loaded clinoptilolite (5.8-6.0) started lower than the irrigation water (6.5) and then pH values were similar thereafter with all remaining above pH 6.0.

6.1.5.4 Chemical analysis of plant samples

Unloaded clinoptilolite total plant nitrogen concentrations decreased in May (Figure 6.26) and then increased slightly over the period June to August, resulting in a total concentration of $198.87 \text{ mg kg}^{-1}$ dry wt in October (Table 6.6). Total plant nitrogen concentrations increased consistently over the period May to August in the nutrient-loaded clinoptilolite treatments with 'Hydrocult F' plants accumulating more nitrogen ($1,425.5 \text{ mg kg}^{-1}$ dry wt) than 'Hydrocult S' plants (912.2 mg kg^{-1} dry wt) (Tables 6.7 and 6.8). All differences were highly statistically significant at $p < 0.001$ (Appendix IV).

Total plant phosphorus concentrations (Figure 6.27) were consistently lower than the propagation concentrations in the unloaded clinoptilolite treatment (total concentration in October of 10.07 mg kg^{-1} dry wt), whereas it increased consistently in the low nutrient-loaded clinoptilolite and the high nutrient-loaded clinoptilolite treatments to 53.6 mg kg^{-1} dry wt and 121.4 mg kg^{-1} dry wt, respectively (Tables 6.6, 6.7 and 6.8). All differences were highly statistically significant at $p < 0.001$ (Appendix IV).

Total plant potassium concentrations increased slightly in the unloaded clinoptilolite to $291.19 \text{ mg kg}^{-1}$ dry wt in October (Figure 6.28). In comparison, total plant potassium concentrations increased in the 'Hydrocult S' and 'Hydrocult F' treatments to $1,212.7 \text{ mg kg}^{-1}$ dry wt and $1,841.7 \text{ mg kg}^{-1}$ dry wt, respectively. All differences were highly statistically significant at $p < 0.001$ (Appendix IV).

Figure 6.25 Δ concentration of EC between unloaded clinoptilolite (ULZ), low nutrient-loaded clinoptilolite (HS), high nutrient-loaded clinoptilolite (HF) and irrigation water

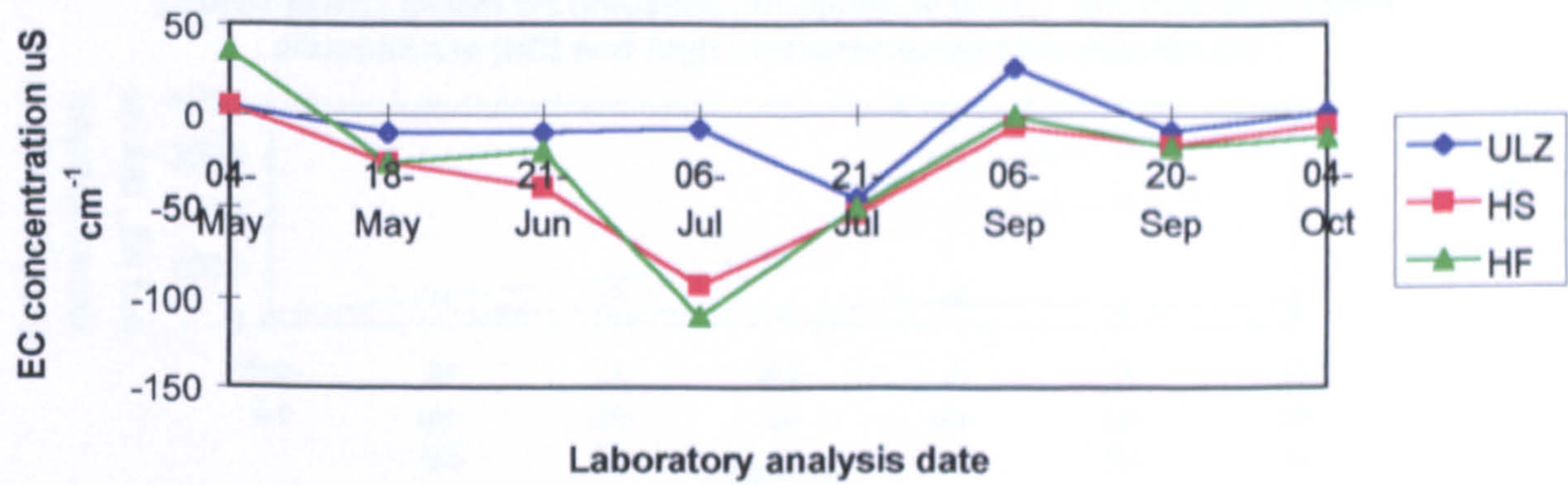


Figure 6.26 Mean monthly total nitrogen concentrations of sweet pepper plants grown on unloaded clinoptilolite (ULZ), low nutrient-loaded clinoptilolite (HS) and high nutrient-loaded clinoptilolite (HF)

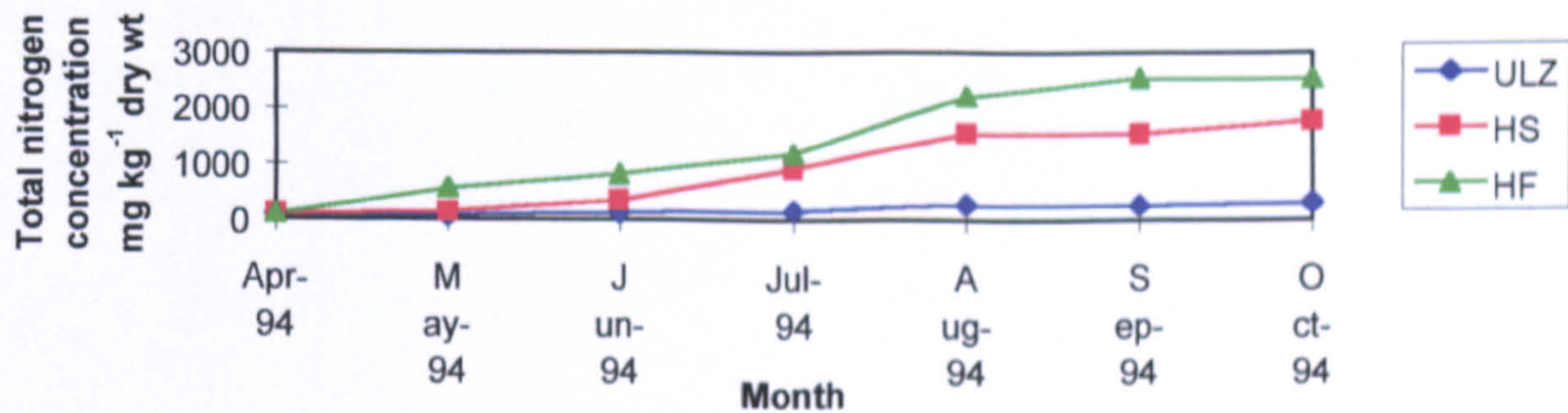


Figure 6.27 Mean monthly total phosphorus concentrations of sweet pepper plants grown on unloaded clinoptilolite (ULZ), low nutrient-loaded clinoptilolite (HS) and high nutrient-loaded clinoptilolite (HF)

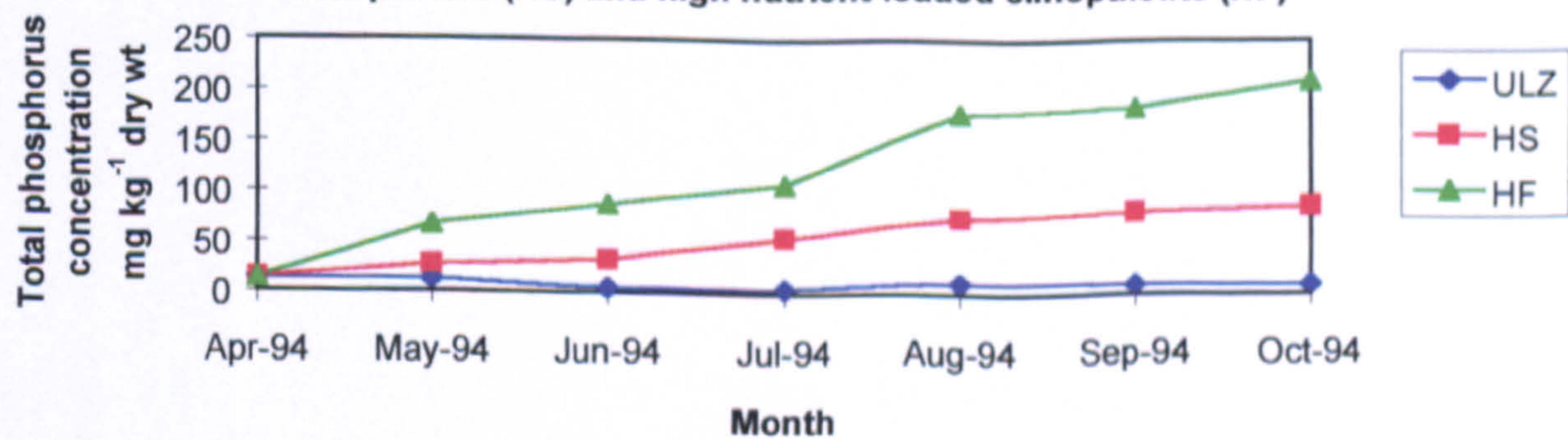
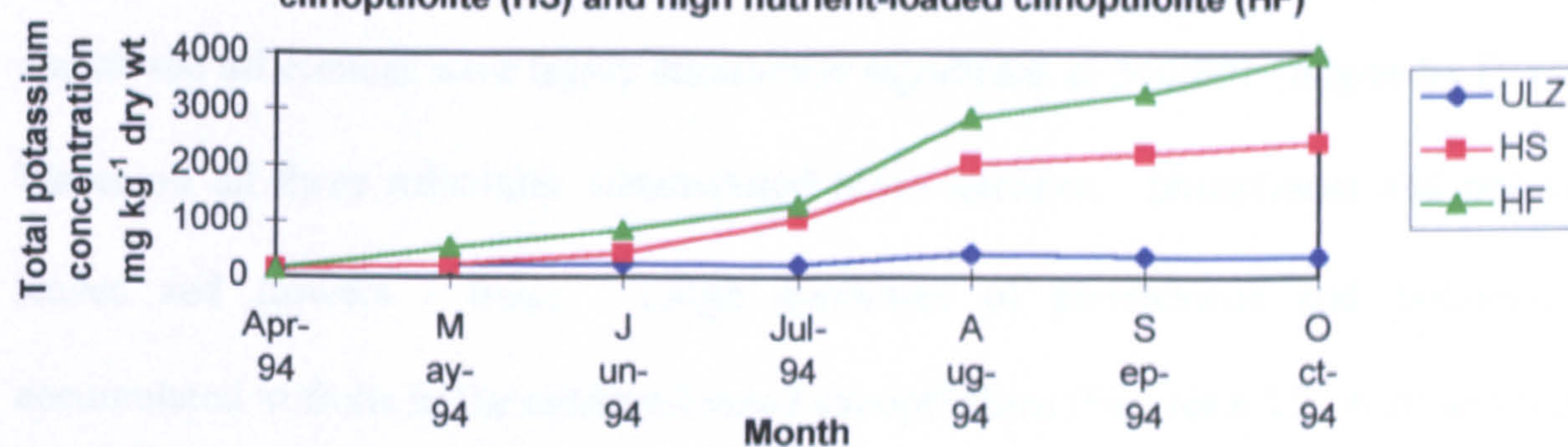


Figure 6.28 Mean monthly total potassium concentrations of sweet pepper plants grown on unloaded clinoptilolite (ULZ), low nutrient-loaded clinoptilolite (HS) and high nutrient-loaded clinoptilolite (HF)



6.1.5.5 Total element plant partitioning

Plants growing on the high nutrient-loaded clinoptilolite had higher concentrations of nitrogen, phosphorus and potassium compared with the other two clinoptilolite substrates and all the differences were highly statistically significant at $p < 0.001$ (Appendix IV).

Plants on all three substrates accumulated more nitrogen, phosphorus and potassium in leaves and flowers / fruits. Large quantities of phosphorus and potassium were accumulated in fruits in the nutrient-loaded clinoptilolites (Figures 6.29, 6.30 and 6.31).

6.1.5.6 Substrate sodium extraction analysis

Sodium extraction analysis results showed 90 and 97 % lower concentrations of ammonium-nitrogen in the used, low and high nutrient-loaded samples ($p < 0.001$), respectively, and an increase in ammonium-nitrogen concentration in the used, unloaded clinoptilolite (Table 6.10) (Appendix IV). There was a 100 % decrease in the phosphorus concentrations of the low and high nutrient-loaded clinoptilolite over the period of the experiment ($p < 0.01$). Decreases of 14 %, 15 % and 28 % in potassium concentrations were recorded for the unloaded, low and high nutrient-loaded clinoptilolites, respectively ($p < 0.001$). Calcium concentrations also decreased in all three clinoptilolites during the experiment ($p < 0.001$).

In contrast, final magnesium concentrations of 565 mg kg⁻¹ (> of 292 %), 468 mg kg⁻¹ (> of 167 %) and 470 mg kg⁻¹ (> of 112 %) were measured for the unloaded, low and high nutrient-loaded clinoptilolites, respectively ($p < 0.001$).

The differences in the iron, copper and boron concentrations of the clinoptilolite substrates were not significantly different, whereas used unloaded and low nutrient-loaded clinoptilolite manganese concentrations were lower at the end of the experiment ($p < 0.001$).

The high nutrient-loaded clinoptilolite accumulated manganese, however. Measurements of sulphate concentrations revealed lower results for each substrate at the end of the experiment. All differences were highly statistically significant at $p < 0.001$.

Figure 6.29 Mean total nitrogen concentrations partitioned in sweet pepper plant tissue grown on unloaded clinoptilolite (ULZ), low nutrient-loaded clinoptilolite (HS) and high nutrient-loaded clinoptilolite (HF)

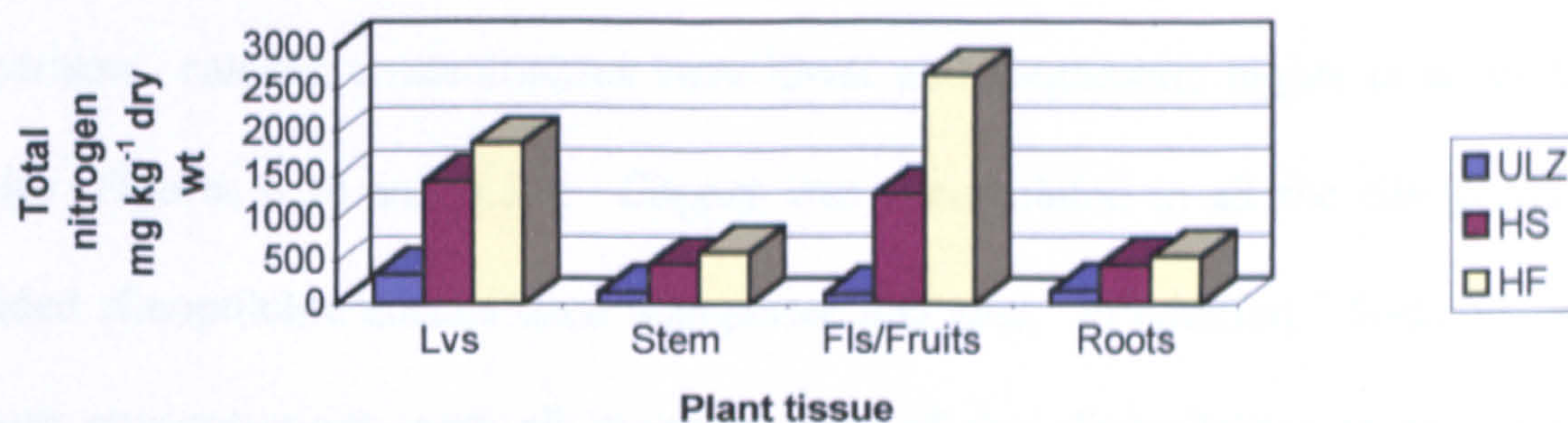


Figure 6.30 Mean total phosphorus concentrations partitioned in sweet pepper plant tissue grown on unloaded clinoptilolite (ULZ), low nutrient-loaded clinoptilolite (HS) and high nutrient-loaded clinoptilolite (HF)

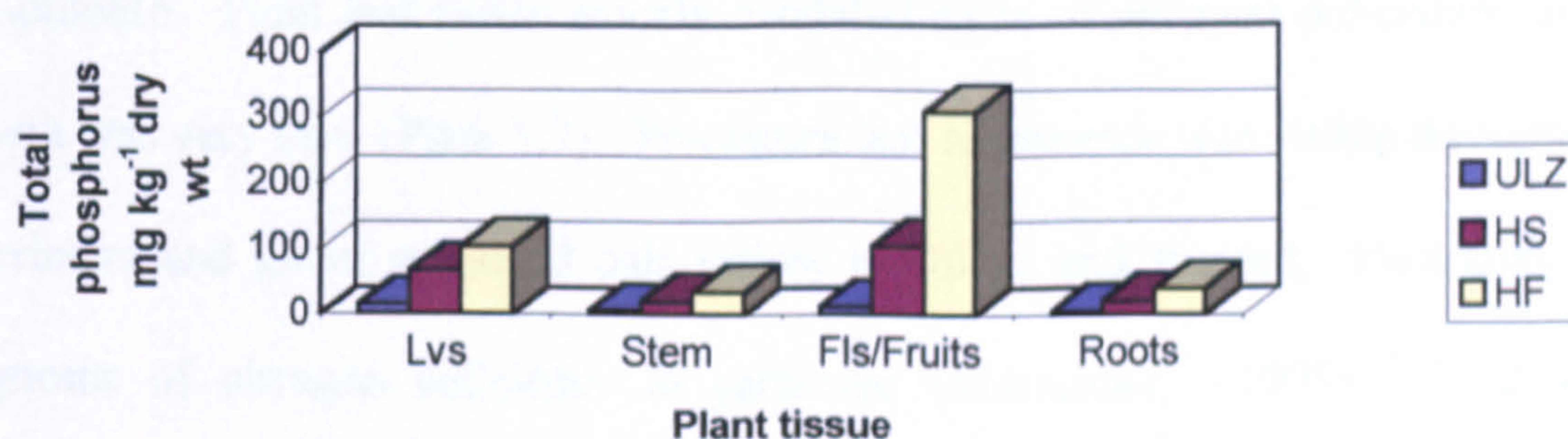
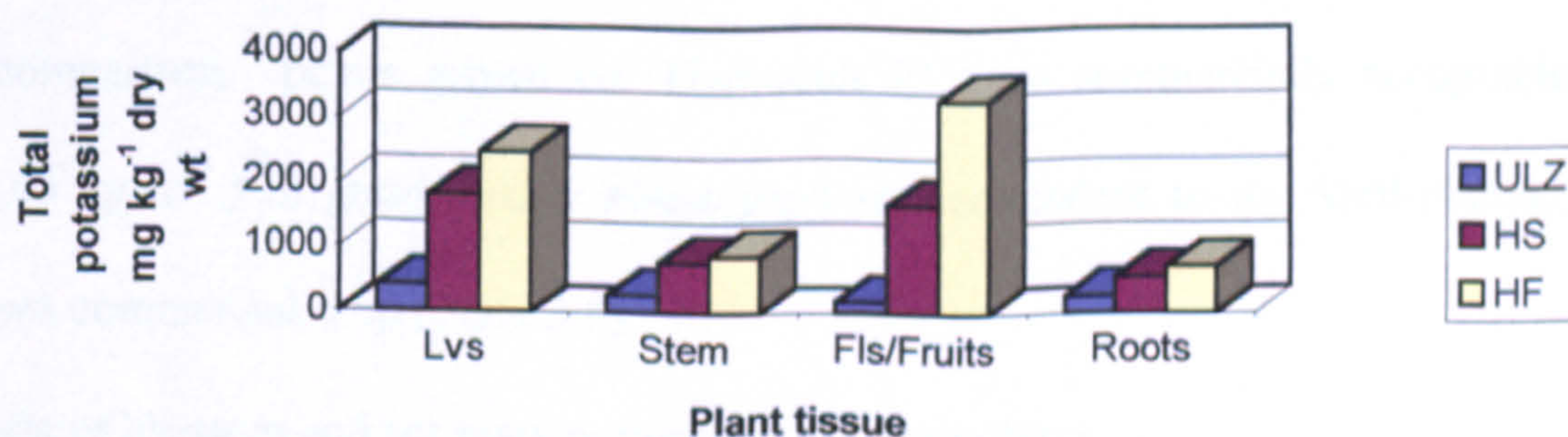


Figure 6.31 Mean total potassium concentrations partitioned in sweet pepper plant tissue grown on unloaded clinoptilolite (ULZ), low nutrient-loaded clinoptilolite (HS) and high nutrient-loaded clinoptilolite (HF)



6.1.5.7 Substrate nitric acid digestion analysis

Nitric acid digestion analysis results from all three substrates revealed lower concentrations of potassium and phosphorus in the used samples (Table 6.9) (Figures 6.32 and 6.33). In comparison, calcium concentrations were lower and magnesium higher in all of the used samples (Figures 6.34 and 6.35). Copper was accumulated in all the clinoptilolites and unloaded clinoptilolite accumulated manganese and zinc, in addition. Sodium, iron and sulphate concentrations were all lower in each of the clinoptilolites at the end of the experiment (Figures 6.36, 6.37 and 6.38). All differences were highly statistically significant at $p < 0.001$, with the exception of iron and manganese at $p < 0.05$ (Appendix IV).

6.1.6 Discussion and conclusions

- As expected, a very low fruit yield resulted from the pepper plants grown on unloaded clinoptilolite. Plant leaf tissue quickly exhibited signs of nitrogen deficiency and plant growth was very slow (Plate 3.7). Premature leaf senescence was visible throughout the experiment and plants remained pale yellow in colour and stunted, illustrating classic symptoms of nitrogen deficiency in particular (Marschner, 1995). Plant analysis determinations revealed deficiencies in all major nutrients. Crop yield was only 4% of a commercial late-season crop at 0.40 kg m^{-2} .
- Availability of nitrogen was a limiting factor to plant growth and the yield of pepper plants grown on 'Hydrocult S'. Fruit yields were 3.89 kg m^{-2} , only 39% of a late-season commercial crop.
- In comparison, plants grown on 'Hydrocult F' gave commercially acceptable yields (10.46 kg m^{-2}) of good quality sweet peppers, equivalent to an April-planted, soil-grown commercial crop (Plate 3.8).
- Levels of blossom end rot were noticeably low throughout.
- It is concluded that the substrate loading of ammonium-nitrogen was the main limiting nutritional factor affecting plant growth and crop yield. Results suggest that even on the

Figure 6.32 Comparison of nitric acid digestion and sodium extraction potassium determinations on unloaded and nutrient-loaded clinoptilolites

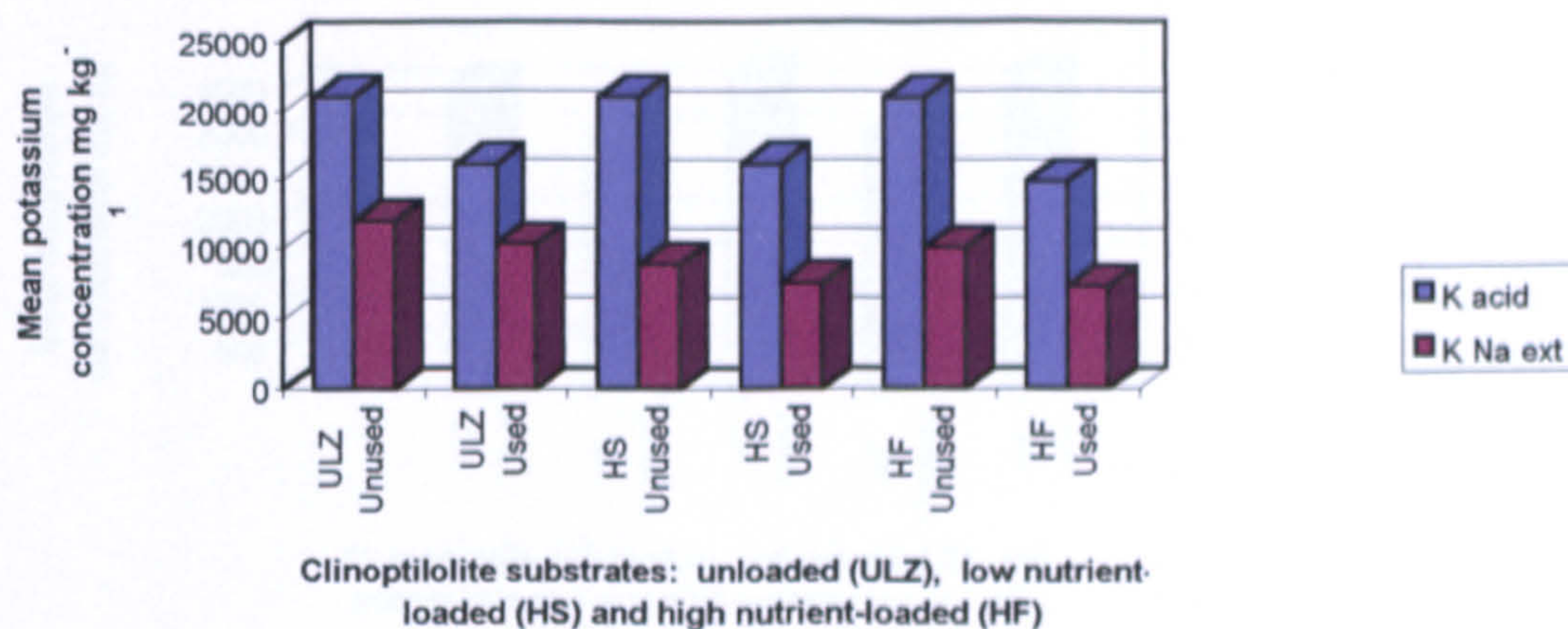


Figure 6.33 Comparison of nitric acid digestion and sodium extraction phosphorus determinations on unloaded and nutrient-loaded clinoptilolites

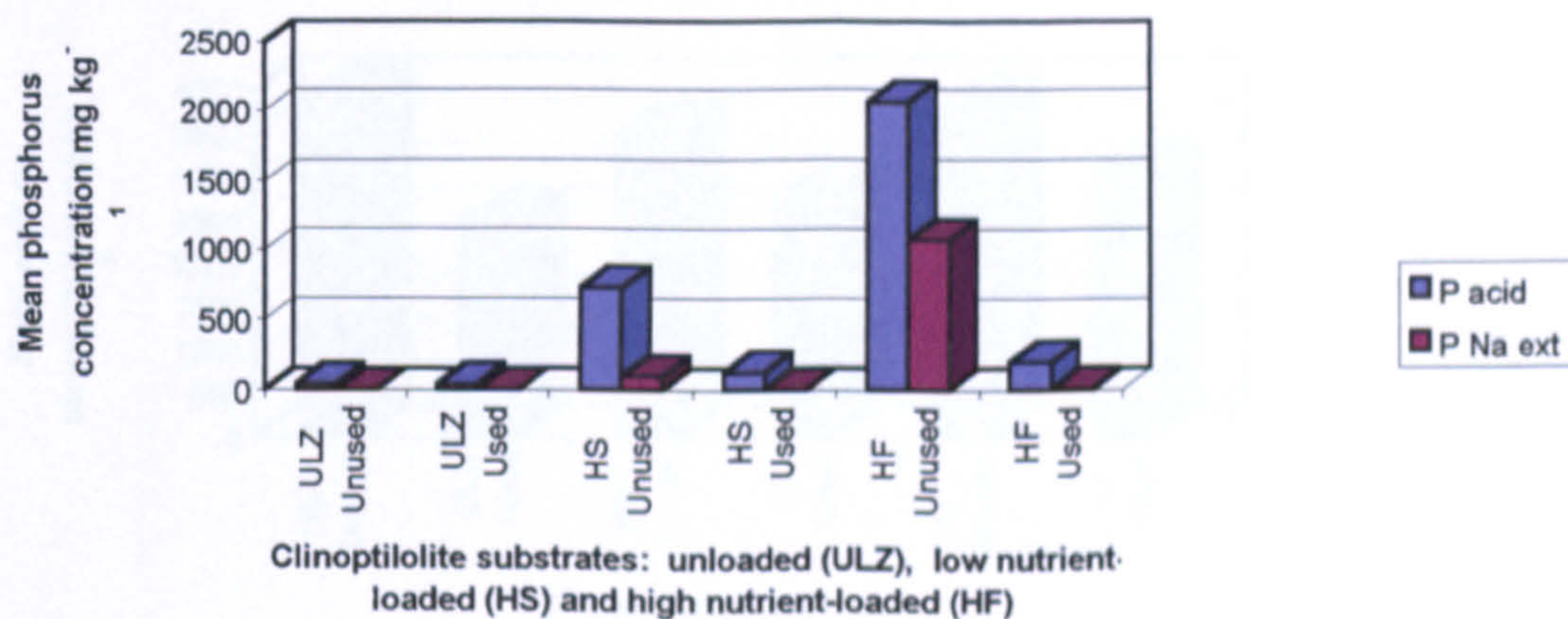


Figure 6.34 Comparison of nitric acid digestion and sodium extraction calcium determinations on unloaded and nutrient-loaded clinoptilolites

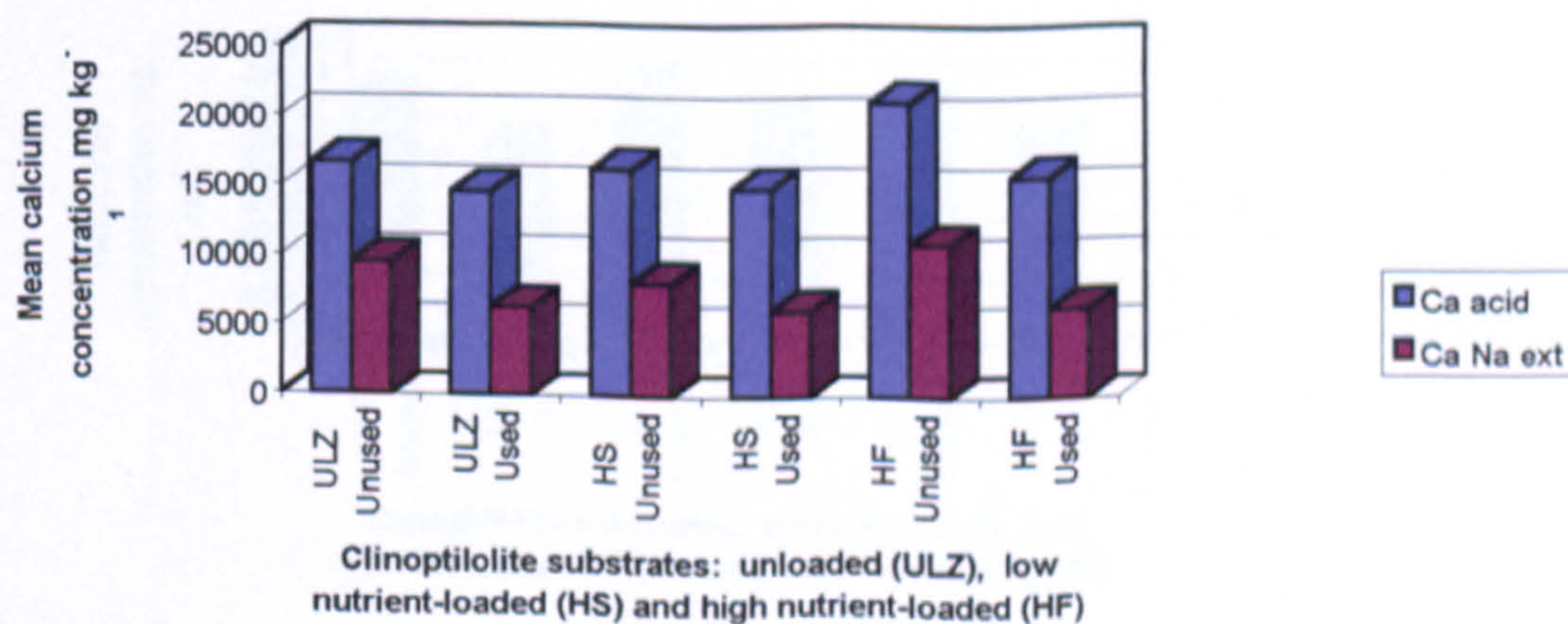


Figure 6.35 Comparison of nitric acid digestion and sodium extraction magnesium determinations on unloaded and nutrient-loaded clinoptilolites

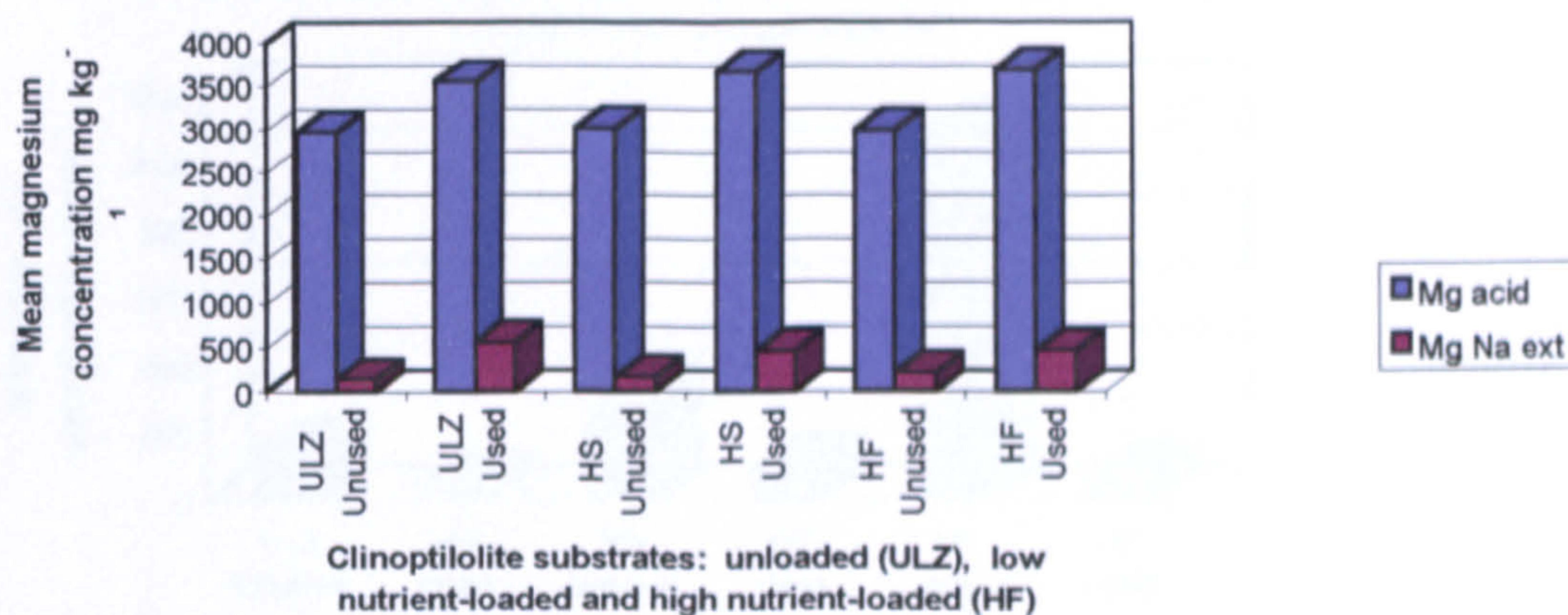


Figure 6.36 Sodium concentrations following nitric acid digestion on samples of unused and used unloaded clinoptilolite (ULZ), low nutrient-loaded clinoptilolite (HS) and high nutrient-loaded clinoptilolite (HF)

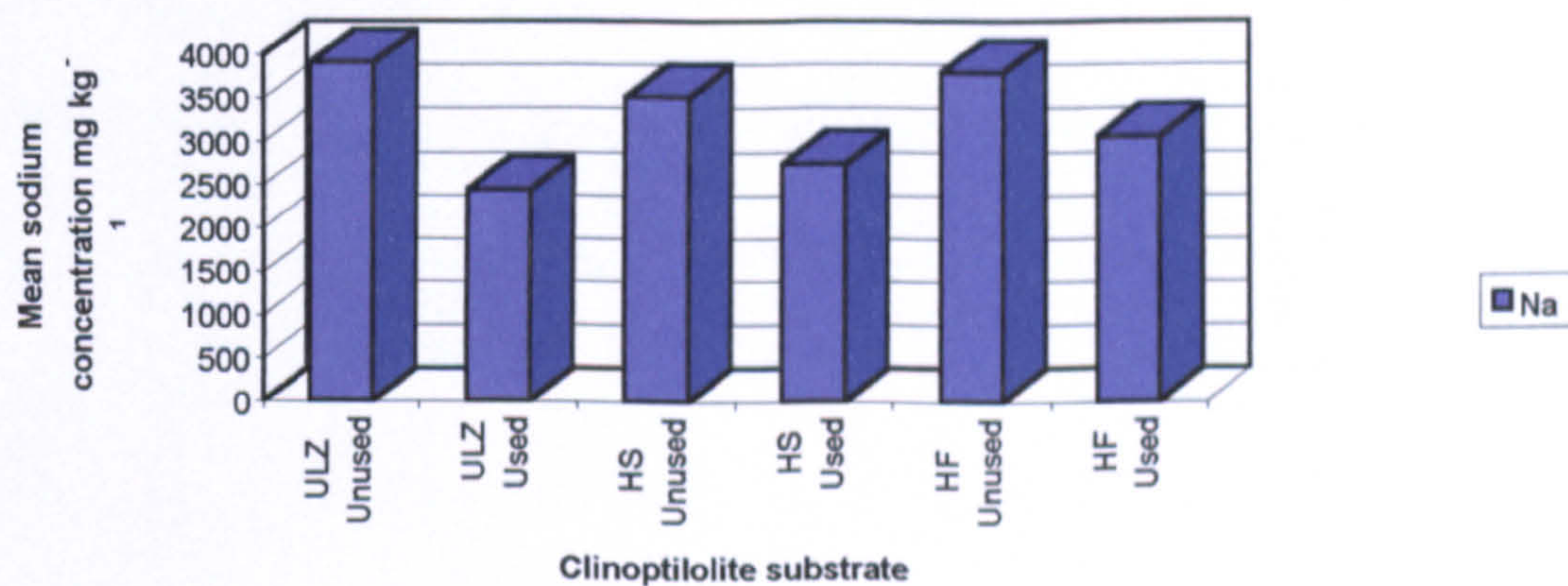


Figure 6.37 Comparison of nitric acid and sodium extraction iron determinations on unloaded and nutrient-loaded clinoptilolites

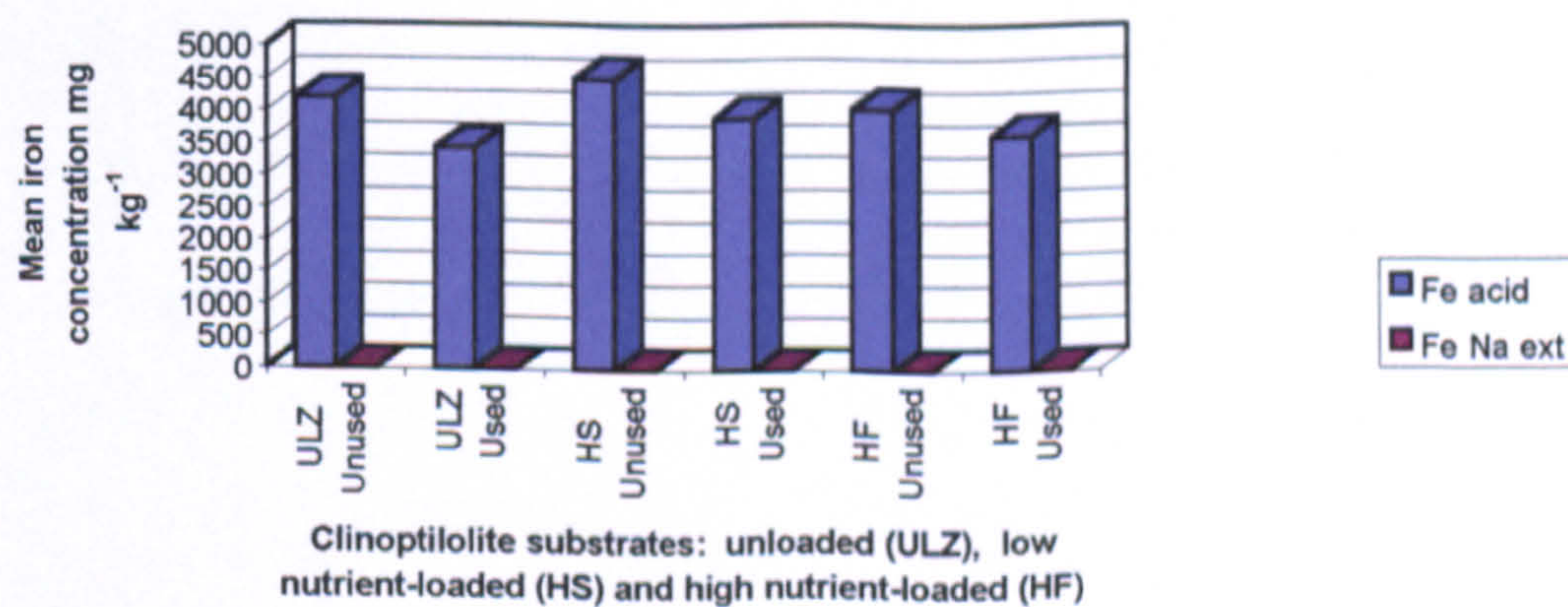
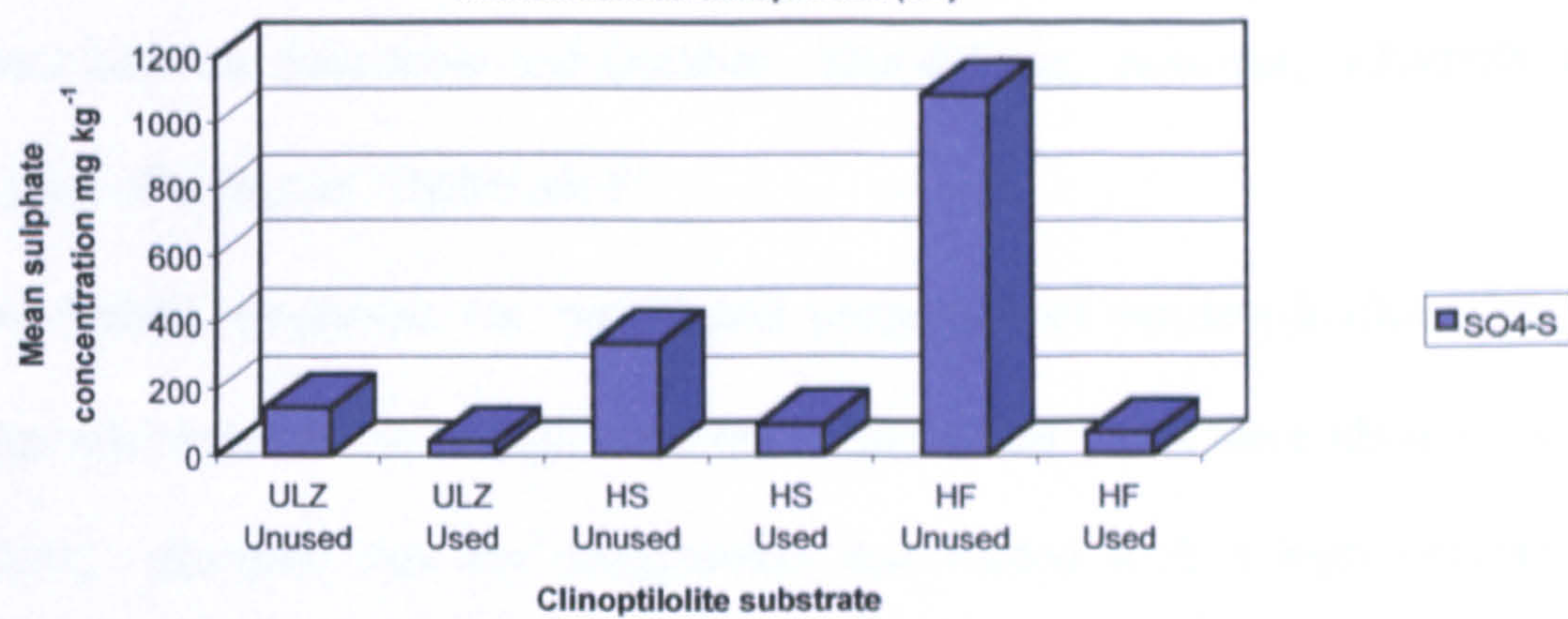


Figure 6.38 Sulphate concentrations following sodium extractions on samples of unused and used unloaded clinoptilolite (ULZ), low nutrient-loaded clinoptilolite (HS) and high nutrient-loaded clinoptilolite (HF)



high nutrient-loaded clinoptilolite ('Hydrocult F'), there was a restriction of plant available nitrogen towards the end of the experiment, with a plateauing of plant nitrogen content between September and October. This did not, however, adversely affect the cropping of plants on 'Hydrocult F'.

- These results emphasise the remarkable properties of nutrient-loaded clinoptilolites. Using only water in the irrigation system, commercial yields were obtained with sweet peppers, provided that the clinoptilolite was loaded with a high concentration of ammonium-nitrogen prior to use.
- One problem with such a substrate is that it could have a high potential leaching risk. However, analyses of drainwater showed that there was little or no loss of nutrients in the drainwater. Indeed, for most cations, an uptake from the irrigation water to the clinoptilolite was recorded, resulting effectively in a deionisation of the irrigation water. Such cations then became available for plant uptake via root exchange, as inferred by the increase in plant nitrogen of plants grown on unloaded clinoptilolite.
- As phosphorus is not held as a cation within the zeolite matrix, an initial release of phosphorus from the root zone was expected and detected on the nutrient-loaded clinoptilolite treatments. No phosphorus deficiency symptoms, however, were evident on plants grown in the nutrient-loaded clinoptilolites. After the initial release of phosphorus, the concentration of all drainwater nutrients was small. The breakdown and dissolution of the mineral apatite, present in the clinoptilolite substrates, would have provided a slow release supply of phosphorus to the plants (Ming *et al.*, 1995; Allen *et al.*, 1991; Allen *et al.*, 1993; Allen *et al.*, 1995a; Allen *et al.*, 1995b; Allen *et al.*, 1996).
- There was a consistently higher concentration of drainwater potassium from the unloaded clinoptilolite substrate, compared to the nutrient-loaded clinoptilolite substrates. This was possibly due to the necessary release of potassium to allow a cation

exchange mechanism to operate, coupled with the preferential selectivity of clinoptilolite for ammonium-nitrogen (Mumpton, 1984b; Tsitsishvili *et al.*, 1992; Colella, 1996).

- The results also indicated that manganese and zinc could have been adsorbed by the unloaded clinoptilolite in the cation exchange mechanism (Hershey *et al.*, 1980).
- The cation exchange process mechanism would appear to involve potassium, calcium, sodium and magnesium as major participants (Colella, 1996) with both unloaded and loaded clinoptilolites containing higher magnesium concentrations at the end of the experiment.
- There would have been some movement of nutrients from the propagation blocks into the substrates at the beginning of the experiment in April and the small reservoir of nutrients held in the rockwool would have diminished rapidly.
- Plant establishment relied on the control and maintenance of moisture in the root zone. Particle size distribution was slightly different in the three substrates, resulting in differences in moisture holding capacity. Prevention of drying of the substrates at the pot surface was partly aided by the polypropylene pot covers but there remained a layer of clinoptilolite at the surface that was continuously dry and, therefore, not contributing to the root zone ion exchange mechanisms. Positioning the rockwool propagation blocks on the substrate surface, thus maintaining the pot volume at three litres, would have reduced the exposed substrate surface area from which water could evaporate. The additional volume of clinoptilolite would have also provided more potential nutrient sites for root ion exchange. Early rooting into the substrates was rapid but it is possible that uneven distribution of water throughout the substrate volume could have impeded root development in April, before the full-time engagement of the irrigation system. Better control over water distribution in the compartment, the use of accurate, pressure-compensated irrigation lines and computer-aided adjustments to the environmental parameters could have improved water management to the overall benefit of the plants.

- It can be further concluded that nutrient-loaded clinoptilolite is a potentially useful substrate for glasshouse systems. It offers the opportunity for growing crops in an environmentally-friendly, water-only delivery system without jeopardising crop yield or producing polluted waste water (Pansini, 1996). The material has been shown to be acceptable in a high nitrogen demanding crop, sweet peppers, and other results detailed in Chapter Four and Chapter Five show that it is equally useful for low and high nutrient demanding crops such as standard carnations and speciality tomatoes, respectively.

Table 6.1 Nutrient analysis results and target concentrations of drainwater samples taken from sweet pepper rockwool propagation blocks on 22 March 1994

Nutrient	Actual results mg l⁻¹ (n=1)	Target concentration mg l⁻¹
pH	6.5 * ¹	6.0-6.2
EC µS cm⁻¹	2,180	2,200
NH₄-N mg l⁻¹	1	Low as possible
NO₃-N mg l⁻¹	193	188
P mg l⁻¹	22 * ²	30
K mg l⁻¹	316	300
Ca mg l⁻¹	155	188
Mg mg l⁻¹	45	50
Na mg l⁻¹	97	Low as possible
Cl mg l⁻¹	171	Low as possible
Fe mg l⁻¹	3.59	3.0-4.0
Mn mg l⁻¹	0.50	0.60
Cu mg l⁻¹	0.10	0.10
Zn mg l⁻¹	0.10 * ²	0.30
B mg l⁻¹	0.50	0.50
K:N ratio	1.6	1.6
K:Ca ratio	2.0	1.6
K:Mg ratio	7.0	6.0

*¹ High concentration result

*² Low concentration result

Table 6.2 Monthly total mean fruit fresh weight marketable yield kg m⁻²

ULZ: unloaded clinoptilolite zeolite, **HS:** low nutrient-loaded clinoptilolite,

HF: high nutrient-loaded clinoptilolite, **n = 4**

	May kg m ⁻²	June kg m ⁻²	July kg m ⁻²	August kg m ⁻²	Sept kg m ⁻²	October kg m ⁻²	Total kg m ⁻²
ULZ	0.06	0.10	0.04	0.20	0.00	0.00	0.40
HS	0.14	0.35	0.81	2.33	0.26	0.00	3.89
HF	0.44	1.23	0.84	3.86	0.80	3.28	10.46

Table 6.3 Total mean fruit fresh weight for each destructive harvest date g plant⁻¹

ULZ: unloaded clinoptilolite zeolite, **HS:** low nutrient-loaded clinoptilolite,

HF: high nutrient-loaded clinoptilolite, **L.S.D. = least significant difference, n = 4**

Harvest date	Mean fruit weight ULZ g	Mean fruit weight HS g	Mean fruit weight HF g
May	20.300	45.800	146.800
June	53.500	164.000	557.000
July	66.200	433.800	836.200
August	132.900	1210.000	2122.500
September	102.200	1296.600	2390.500
October	129.000	1240.000	2435.000
L.S.D. (5%)	220.440		
L.S.D. (1%)	293.185		
L.S.D. (0.1%)	381.361		
F-test	p=***		

All treatments for each date were significantly different at p <0.001

Table 6.4 Concentration of nutrients in the irrigation water

	18 May	20 June	11 July	4 Sept	19 Sept	2 Oct
pH	7.2	6.9	6.8	7.2	7.2	7.0
EC (μ S)	192	250	405	189	190	143
	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
NH ₄ -N	0.5	0.5	0.5	0.5	0.5	0.5
NO ₃ -N	6.0	0.5	0.5	2.0	1.0	1.0
P	0.5	0.5	0.5	0.5	0.5	0.5
K	3	5	9	4	4	4
Ca	7.5	14.0	21.8	11.9	10.6	9.6
Mg	3	7	10	5	5	4
Na	12	24	33	18	17	16
Cl	30	35	46	28	33	21
S	5	12	19	5	5	5
Fe	0.20	0.33	0.16	0.18	0.14	0.05
Mn	0.05	0.05	0.05	0.05	0.05	0.05
Cu	0.020	0.005	0.005	0.005	0.005	0.005
Zn	0.020	0.020	0.020	0.005	0.030	0.005
B	0.01	0.02	0.04	0.02	0.01	0.01
HCO ₃	68	59	65	25	26	34

Table 6.5 Drainwater minus irrigation water, data for Hydrocult F

	4 May	18 May	21 June	6 July	21 July	6 Sept	20 Sept	4 Oct
pH	-0.7	-1.8	0	-0.9	-0.2	-0.8	-0.7	0
EC (μ S)	35	-26	-20	-110	-51	-1	-18	-13
	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
NH ₄ -N	1.5	1.5	0	0	0	3.5	0	0
NO ₃ -N	0	-2	0	-3.5	0	-1.5	-0.5	-0.5
P	9.5	0.5	0	0	0	9.5	0	0
K	2	1	-1	-3	-3	0	-1	1
Ca	2.7	-0.4	-1.4	-2.3	-1	-2.6	-1.5	-2.1
Mg	0	-2.5	-1	-1	-1	0	-1	-1
Na	3	-3	-2	-4	3	5	3	2
Cl	-2	-1	0	1	3	4	3	3
S	0	0	0	-1	1	5	0	0
Fe	0	-0.08	-0.22	-0.1	-0.11	-0.03	-0.09	0
Mn	0	0	0	0	0	0	0	0
Cu	0	-0.015	0	0.005	0.005	0	0	0
Zn	-0.005	0.03	0	0.135	0	0.35	-0.01	0.005
B	0	0	0	-0.01	-0.01	-0.01	0	0
H ₂ CO ₃	3	-19	4	-	-28	-2	-9	-5

Table 6.6 Mean plant total nitrogen, phosphorus and potassium concentrations for unloaded clinoptilolite (ULZ).

Total element	Concentration mg kg⁻¹ dry weight
Nitrogen	198.870
Phosphorus	10.070
Potassium	291.190

Table 6.7 Mean plant total nitrogen, phosphorus and potassium concentrations for low nutrient-loaded clinoptilolite (HS).

Total element	Concentration mg kg⁻¹ dry weight
Nitrogen	912.200
Phosphorus	53.600
Potassium	1212.700

Table 6.8 Mean plant total nitrogen, phosphorus and potassium concentrations for high nutrient-loaded clinoptilolite (HF).

Total element	Concentration mg kg ⁻¹ dry weight
Nitrogen	1425.500
Phosphorus	121.400
Potassium	1841.700

Table 6.9 Comparison of major and trace element concentrations of unused and used clinoptilolites after nitric acid digestion (ULZ: unloaded, HS: low nutrient-loaded and HF: high nutrient-loaded). L.S.D. = least significant difference, utilised = plant uptake and drainage losses, n = 4

Substrate / Element		Unused Mean conc mg kg ⁻¹	Used Mean conc mg kg ⁻¹	Utilised (gains) mg kg ⁻¹	L.S.D. 5% F-test	L.S.D. 1% F-test	L.S.D. 0.1% F-test
ULZ	P	39.000	37.400	1.600			
HS	P	732.200	120.700	611.500	244.528	338.162	467.369
HF	P	2055.000	199.500	1855.500			p=***
ULZ	K	21025.000	16150.000	4875.000			
HS	K	21075.000	16225.000	4850.000	691.801	956.705	1322.247
HF	K	21250.000	14925.000	6325.000			p=***
ULZ	Ca	16700.000	14600.000	2100.000			
HS	Ca	16275.000	14925.000	1350.000	1001.042	1384.359	1913.300
HF	Ca	21125.000	15775.000	5350.000			p=***
ULZ	Mg	2975.000	3552.500	(577.500)			
HS	Mg	3020.000	3660.000	(640.000)	242.565	335.448	463.617
HF	Mg	2997.500	3690.000	(692.500)			p=***
ULZ	Na	3905.000	2445.000	1460.000			
HS	Na	3502.500	2747.500	755.000	149.078	206.163	284.935
HF	Na	3790.000	3050.000	740.000			p=***
ULZ	SO ₄ -S	44.000	30.000	14.000			
HS	SO ₄ -S	653.700	51.400	602.300	166.007	229.574	317.291
HF	SO ₄ -S	1715.000	41.900	1673.100			p=***

Substrate / Element		Unused Mean conc mg kg ⁻¹	Used Mean conc mg kg ⁻¹	Utilised (gains) mg kg ⁻¹	L.S.D. 5% F-test	L.S.D. 1% F-test	L.S.D. 0.1% F-test
ULZ	Fe	4197.500	3432.500	765.000			
HS	Fe	4505.000	3912.500	592.500	583.623		
HF	Fe	4047.500	3635.000	412.500	p=*		
ULZ	Mn	414.250	456.750	(42.500)			
HS	Mn	374.500	286.500	88.000	88.903		
HF	Mn	359.750	319.750	40.000	p=*		
ULZ	Cu	2.875	10.850	(7.975)			
HS	Cu	4.050	6.475	(2.425)	2.442	3.377	4.668
HF	Cu	2.575	6.000	(3.425)			p=***
ULZ	Zn	31.925	35.850	(3.925)			
HS	Zn	54.000	42.975	11.025			
HF	Zn	36.525	33.925	2.600			p=n.s.
ULZ	B	1.525	1.300	0.225			
HS	B	3.100	1.625	1.475			
HF	B	1.925	1.975	(0.05)			p=n.s.

Table 6.10 Comparison of major and trace element concentrations of unused and used clinoptilolites after sodium extraction (ULZ: unloaded, HS: low nutrient-loaded and HF: high nutrient-loaded). L.S.D. = least significant difference, utilised = plant uptake and drainage losses, n = 4

Substrate / Element	Unused Mean conc mg kg ⁻¹	Used Mean conc mg kg ⁻¹	Utilised (gains) mg kg ⁻¹	L.S.D. 5% F-test	L.S.D. 1% F-test	L.S.D. 0.1% F-test
ULZNH ₄ -N	19.700	104.500	(84.800)			
HS NH ₄ -N	1215.000	116.300	1098.700	175.863	243.204	336.128
HF NH ₄ -N	2690.000	90.300	2599.700			p=***
ULZNO ₃ -N	0.500	0.500	0.000			
HS NO ₃ -N	1.125	0.500	0.625			
HF NO ₃ -N	0.500	0.500	0.000			p=n.s.
ULZ P	0.000	2.400	(2.400)			
HS P	95.100	0.000	95.100	600.281	830.140	
HF P	1073.000	4.600	1068.400		p=**	
ULZ K	12000.000	10325.000	1675.000			
HS K	8872.000	7550.000	1322.000	901.456	1246.640	1722.960
HF K	10078.000	7298.000	2780.000			p=***
ULZ Ca	9507.000	6305.000	3202.000			
HS Ca	8123.000	6177.000	1946.000	1001.945	1385.609	1915.027
HF Ca	11017.000	6378.000	4639.000			p=***
ULZ Mg	144.250	565.250	(421.000)			
HS Mg	175.500	468.250	(292.750)	50.675	70.080	96.856
HF Mg	222.000	470.500	(248.500)			p=***

Substrate / Element	Unused Mean conc mg kg ⁻¹	Used Mean conc mg kg ⁻¹	Utilised (gains) mg kg ⁻¹	L.S.D. 5% F-test	L.S.D. 1% F-test	L.S.D. 0.1% F-test
ULZ SO ₄ S	143.300	42.000	101.300			
HS SO ₄ -S	334.500	93.500	241.000	131.510	181.868	251.357
HF SO ₄ -S	1082.800	67.300	1015.500			p=***
ULZ Fe	1.650	0.350	1.300			
HS Fe	4.075	0.325	3.750			
HF Fe	8.800	0.375	8.425			p=n.s.
ULZ Mn	7.525	5.025	2.500			
HS Mn	25.675	16.700	8.975	4.871	6.737	9.311
HF Mn	4.600	14.150	(9.550)			p=***
ULZ Cu	0.000	0.375	(0.375)			
HS Cu	0.350	0.275	0.075			
HF Cu	0.000	0.000	0.000			p=n.s.
ULZ Zn	0.000	1.575	(1.575)			
HS Zn	6.850	1.575	5.275	2.596	3.589	4.961
HF Zn	0.325	0.275	0.050			p=***
ULZ B	0.050	0.000	0.050			
HS B	0.175	0.000	0.175			
HF B	0.000	0.000	0.000			p=n.s.

Chapter 7 General discussion and conclusions

7.1 Introduction

The reasons behind the move by growers from soil to alternative substrate systems, such as peat, and hydroponics for the production of food crops and ornamentals under intensive controlled environments included the need to improve yields and to control pests, diseases and nutritional imbalances. Peat was then replaced by NFT and, subsequently, by inert substrates such as rockwool. Coir and wood waste products are now competing with peat as substrates in the hardy ornamental and containerised plant sectors of horticulture. One of the existing problems with substrate systems is the potential for environmental pollution, due to the concentration of nutrients in drainwater. Robins and Smedley (1994), Chilton and Bird (1995) and Lott *et al.* (1999) all indicated that, as a large proportion of the Jersey drinking water is still abstracted from boreholes, it is especially important to regulate fertiliser levels in use on agricultural and horticultural sites, to prevent contamination of potable water. Therefore, the need for a substrate system capable of providing a full range of nutrients for normal plant growth over a time period of six to nine months, with minimal need for supplementation of the nutritional regime by liquid feeding and minimal risk of producing high concentrations of drainwater nutrients, has been highlighted. The increasing pressure on the fresh food industry by legislation and food chain protocols in the control of environmental protection (Grylls *et al.*, 1996) and overall food safety (Hilborn, R., 2001 - pers. comm.) was also indicated as one of the driving forces behind the need to further examine any alternative methods of production of salad crops, in particular. This study has introduced the group of silicate minerals known as zeolites and focussed on one species called clinoptilolite. Clinoptilolite has a range of physical and chemical properties that allow cation exchange, molecular sieving and selective nutrient

adsorption (Jorgensen *et al.*, 1976). It has been used in a variety of agricultural processes, such as soil amendments, slow release fertilisers, dietary supplements in animal nutrition, carriers of pesticides and deodorisers / moisture-control agents for animal manures (Ming and Mumpton, 1989). Its selectivity for ammonium-nitrogen and potassium have particular relevance for the use of clinoptilolite as a plant growth substrate and many research workers have partly exploited these attributes (for example: Hershey *et al.*, 1980; Pirela *et al.*, 1984 and Myt'ko *et al.*, 1989). The majority of experimental work has concentrated on the use of clinoptilolite in combination with other nutrients or soil amendments (Ferguson and Pepper, 1987) or the short duration use of amended clinoptilolite in order to produce successive harvests of, for example, radish (Lewis, 1981; Pirela *et al.*, 1984; Shaidorov, 1992), Chinese cabbage (Ivanova *et al.*, 1992) or winter wheat (Ming *et al.*, 1995). This study has concentrated on the production of long-season salad (speciality tomato and sweet pepper) and ornamental (standard carnation) crops using unloaded pumice and clinoptilolite with applied liquid feeds and also nutrient-loaded clinoptilolites with irrigation water only. As Colella (1996) indicated, incomplete exchange reactions may arise from cation sieving. This may be due to cation size, both in diameter or volume being incompatible with the zeolite channel dimensions or with the space available in the specific site. Cation sieving may also occur due to the inability of the negative charge distribution on the zeolite structure to accommodate a given cation (Dyer, 1988). In order to fully exploit the mechanisms involved in cation exchange, it was important to examine the nutrient-loaded clinoptilolites with irrigation water alone and no added nutrients. Semmens (1984) stated that as the concentrations of Ca^{2+} and Na^{+} increase, less capacity is available for NH_4^{+} ions and the zeolite becomes less effective in the removal of ammonia. Chapter Two highlighted that the contact time available for exchange to occur will also have an influence on the cation exchange performance of natural zeolites. In addition,

smaller particle sizes will increase the potential for cation exchange, as the diffusion path is theoretically shorter.

7.2 Classification of the aluminosilicate substrates

The pumice, natural clinoptilolite and nutrient-loaded clinoptilolite samples were classified and analysed to determine their physical and chemical properties prior to inclusion in the plant growth experiments. As stated by Sheppard (1984), many experimental papers have omitted to carefully classify the type of zeolite in use and various errors have been made with regard to the physical and chemical properties of the individual clinoptilolite deposits used. Sodium content, in particular, is one of the most important considerations in the selection of a particular clinoptilolite, in order to avoid crop salt stress problems, following release of sodium from the zeolite during cation exchange with ammonium-nitrogen or potassium. Although sodium release from the clinoptilolite systems was detected in the experiments reported in this thesis, concentrations of sodium in the root zone did not cause any adverse growth effects on the crops examined. The clinoptilolite used in the experiments was classified as rich in both potassium and calcium but low in sodium. The pumice, by comparison, was categorised as an inert porous substrate with a physical rather than chemical mode of action.

The incorporation of an accessible, soluble source of phosphorus in a formulation of nutrient-loaded clinoptilolite is essential, as the phosphorus anion is not held in the crystal structure of the clinoptilolite (Bunt, 1988).

7.3 Experimental work

It was considered a fundamental requirement to provide a detailed account of the experimental procedures used in the cultivation of crops in the various substrates from crop culture to analysis of the substrates themselves. This allowed new information to be incorporated into the procedures following each experiment. A rigorous programme of analytical work helped to provide essential data in answer to many of the issues raised by Sheppard (1984). The incorporation of plant leaf tissue and substrate sample testing helped to complement the suite of analyses on feed, recirculation and drainwater samples.

Four experiments using unloaded clinoptilolite and unloaded pumice (Experiments 4.3 and 4.4 only), were described and all demonstrated that the zeolite was a potential source of cations such as K^+ , Na^+ , Ca^{2+} and Mg^{2+} . This corroborates the studies by Hershey *et al.* (1980), Lewis (1981) and Chen and Gabelman (1990). All experiments produced commercially-acceptable yields and quality of crops, in comparison to standard substrates such as rockwool (Experiments 4.1 and 4.4 only) and peat (Experiment 4.3 only). Analysis of drainwater nutrient concentrations further revealed the selective adsorption of ammonium-nitrogen and potassium, coupled with the release, by cation exchange, of calcium and sodium from the clinoptilolite. The adsorption of ammonium-nitrogen by clinoptilolite concurs with the work reported by Ferguson and Pepper (1987). In contrast to a study completed by Nus and Brauen (1991) where establishment of creeping bentgrass was thought to be due to both increased moisture and nutrient status provided by a coarse-grade clinoptilolite treatment, the moisture content of the clinoptilolite in this study was found to be difficult to manage and extremely critical to the initial rooting and establishment of carnation cuttings in five litre pots.

The performance of standard carnations was reviewed using nutrient-loaded clinoptilolites as substrates receiving only water in the irrigation cycles in two separate experiments. The successful production of crops on nutrient-amended clinoptilolite corroborates the studies completed by Petrov *et al.* (1982), Rivero and Rodriguez Fuentes (1988) and Myt'ko *et al.* (1989). The cation selectivity of the clinoptilolite was clearly demonstrated in these experiments with ammonium-nitrogen, calcium, sodium, magnesium, iron and zinc being imported into the clinoptilolite, with the corresponding release of potassium, phosphorus (from apatite), manganese and copper. This study also demonstrated that pumice behaved in a similar way to clinoptilolite but with higher concentrations of manganese and lower concentrations of zinc in samples analysed at the end of the experiment (5.2). Analysis of leaf samples confirmed that there were lower concentrations of nitrate-nitrogen and phosphorus in leaf tissue from plants grown on clinoptilolite, which were insufficiently low as to cause nutrient deficiency symptoms but may have decreased overall growth and yield of standard carnations, particularly in the second year of production.

In experiments with non-vernalised winter wheat over a period of 90 days, Ming *et al.* (1995) found that clinoptilolite and a synthetic apatite supplied all the essential elements (N, P, K, Ca, Mg, S, Fe, Mn, Zn, Cu, Mo, B and Cl) for the intensive vegetative growth of the crop. However, in the same experiment, they found that the magnesium supply was insufficient for the re-growth of the crop after 45 days (second harvest only). However, in this study, magnesium was not found to be limiting to plant growth.

The growth of sweet pepper plants on three clinoptilolite substrates with different nutrient-loadings were also studied: unloaded; low nutrient-loaded; and high nutrient-loaded. The results confirmed conclusions reached in earlier experimental work in this study, for example nitrogen and phosphorus were growth limiting in sweet pepper plants and that the higher the ammonium-nitrogen loading, the more productive the growth

over an eight month period. This expands upon and corroborates the studies of Allen *et al.* (1993, 1995a, 1995b and 1996). A point of vital importance has been demonstrated in this study in that it is essential that the nutrient-loading of the zeolite material does need to meet the specific nutritional needs of the crop and this concurs with work completed by Allen and Ming (1995).

Unlike other experimental work detailed above, this study has concentrated on the performance of aluminosilicate substrates supporting a range of edible and ornamental crops over long periods of time (up to 22 months) under intensive glasshouse conditions. The majority of the large scale experiments have included comparisons with the existing standard, commercial substrates and all have been grown to a consistently high standard of culture. With reference to the cost of the zeolite substrates, the major element of cost of the unloaded clinoptilolite is transport from Bulgaria. At approximately £50 per tonne, this is a cost effective material, bearing in mind the potential for re-use of the substrate. However, additional cost would be incurred in the preparation of the material for containerisation and sleeving. At a cost of approximately £250 per tonne of the nutrient-loaded clinoptilolite, this is an expensive substrate to ship and prepare for use in hydroponics systems. However, cost savings are potentially high in reduced fertiliser inputs throughout the crop production period.

7.4 Critique of the present study

Early experimental work involved the integration of the clinoptilolite substrates into the research and development programme at Howard Davis Farm, States of Jersey Department of Agriculture and Fisheries. As a result, the experimental design and, in particular, the replication of the experimental plots was limited during the preliminary period. Once the initial data had been collected, analysed and early reports written, it was then possible to define an experimental programme specifically designed for the comparison of the clinoptilolite substrates with the existing crop production systems.

All liquid nutrient samples were collected and despatched to the ADAS Laboratory within a maximum of two days and, although there may have been slight changes in pH and EC concentrations during this time period, it is not thought that there would have been any major changes in nutrient concentration overall. However, it is possible that concentrations of ammonium-nitrogen could have changed during the sampling and transport period, following conversion to nitrate-nitrogen by microbial activity. The latter process was not measured during the experiments.

Sampling of liquid nutrients was restricted to single point samples, except where detailed. It is not thought likely that there was a large variation in results, taking into account information received from quality checks completed in the laboratory.

The measurement of the initial release of nutrients from the nutrient-loaded clinoptilolites was not sampled and analysed sufficiently close enough to the date of crop planting and it is possible that the initial release of phosphorus, for example, could have been in excess of 12 mg l^{-1} .

Molybdenum was not included in the suite of analyses completed on the liquid nutrient samples. However, there were no molybdenum deficiency symptoms recorded during any of the experiments and an analysis for molybdenum is not normally included in commercial hydroponic sample testing procedures.

7.5 Directions for future study

1. The introduction of supplementary ammonium-nitrogen and, possibly, phosphorus liquid feeds should be investigated for a range of long season crops. The suitability of the fertiliser compound, concentration of the applied liquid feed and the timing of application should all receive attention, in order to produce a blueprint for commercial production. In addition, the resulting effects on ion exchange between the root zone and clinoptilolite should be measured.
2. The initial concentration of ammonium-nitrogen and phosphorus (as fertiliser and apatite) in the nutrient-loaded clinoptilolite substrate should be adjusted for each crop to be tested. This may avoid having to apply supplementary liquid feeds at all, primarily depending on the crop demand for nutrients and the length of the cropping period.
3. At the end of the cropping period, it may be necessary to remove the substrate and replenish its nutrient content. The most practical and cost effective method to re-charge the clinoptilolite with the correct concentration of nutrients for the following crop should be studied. In addition, the microflora and microfauna present during cropping should be identified and quantified, in order to determine the need for substrate sterilisation from one crop to the next.
4. In terms of its final disposal, experiments should be designed to test the usefulness of nutrient-loaded clinoptilolite as a soil amendment and also as a component of green waste compost mixtures.
5. The replacement of slow release fertilisers with specific nutrient-loaded clinoptilolites in hardy ornamental nursery stock and containerised plants should be studied.
6. One of the criticisms of intensively produced herbs in pots and bedding plants in packs is their short shelf-life characteristics. One method of extending the nutrient availability to plants in artificial environments, such as on the supermarket shelf or in the

garden centre, would be to incorporate the correct formulation of nutrient-loaded clinoptilolite in the compost.

7. It may be possible to incorporate clinoptilolite into rockwool substrates at the point of manufacture in order to improve buffering capacity, nutrient retention and subsequent nutrient supply to plants.

8. Nutrient-loaded clinoptilolite may also be useful as a fertiliser for production of leafy winter salads and, as indicated above, may keep leaf nitrate-nitrogen concentrations to a minimum, depending on the formulation used. This should also receive further attention.

9. The use of amended clinoptilolite as a water or liquid nutrient filter should receive further scrutiny. It is possible that sodium could be removed from water containing high concentrations of sodium (for example, on Jersey) and also to remove unwanted cations during nutrient recirculation.

7.6 Conclusions

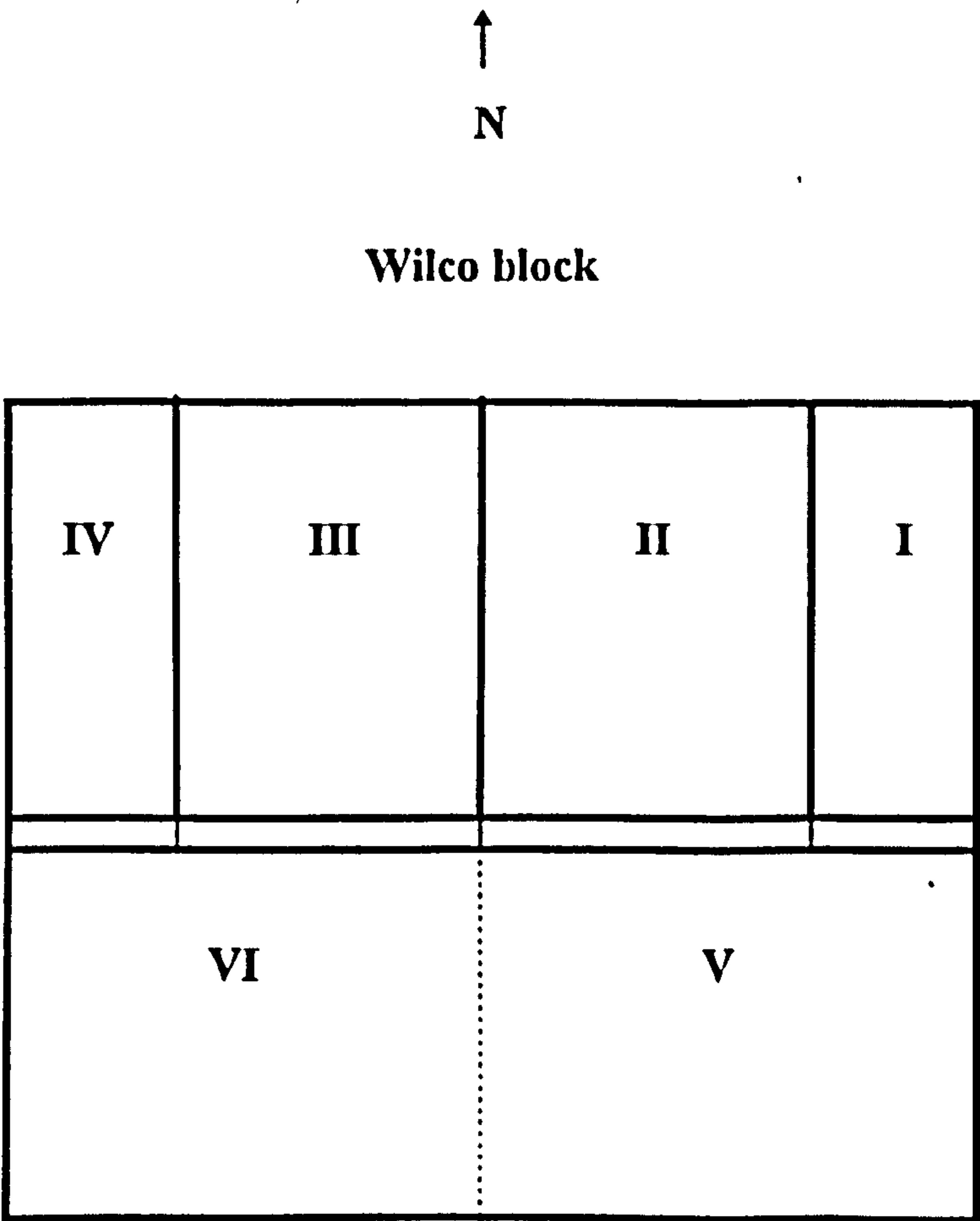
- Unloaded clinoptilolite given nutrient-balanced liquid feeds at every irrigation may be used as a plant growth substrate for the production of commercial crops of edible salads and ornamentals.
- Unloaded pumice may be used in the same way with equally satisfactory results.
- Unloaded clinoptilolite has added advantages over pumice in that the composition of the applied feeds may be adjusted to reduce the overall potassium and calcium concentrations. These cations are held on and within the crystalline structure of the clinoptilolite and may be released into solution during cation exchange processes with the surrounding nutrient solution and plant roots.
- Concentrations of ammonium-nitrogen in applied liquid feeds may be reduced on contact with clinoptilolite, as the mineral has a particular affinity for NH_4^+ . This has desirable consequences, drainwater produced from the crop production system may contain less ammonium-nitrogen and may reduce the potential pollution risk to the surrounding environment.
- Disposal of the clinoptilolite substrate at the end of the cropping period should be easier than other materials, such as rockwool, in that the clinoptilolite may be recycled (cations removed or re-charged) or incorporated into soil (intrinsic fertiliser value or ammonium-nitrogen trap).
- Nutrient-loaded clinoptilolite may be used by plants to supply a full range of plant growth nutrients either in the presence of applied liquid feeds or only water in the irrigation cycles. The presence of liquid feeds may alter or interfere with the cation selectivity processes within the substrate / root zone, creating higher concentrations of nutrients in the drainwater. Application of low nutrient-containing irrigation water to nutrient-loaded clinoptilolite allows the selective release of cations into the surrounding water phases and increases nutrient availability to plant roots.

- The presence of phosphate rock, such as the mineral apatite, provides a source of phosphorus available to plants and the dissolution of apatite may be regulated by the presence of plant roots and the rate of absorption of phosphorus and calcium by plants.
- The concentrations of ammonium-nitrogen in the clinoptilolite and phosphorus in the apatite are plant growth and yield limiting.
- Edible salad and ornamental plants may be grown in nutrient-loaded clinoptilolite for long periods of time with normal growth and yield characteristics. After a period of approximately nine months, however, the ammonium-nitrogen loading of 'Hydrocult F' may become totally exhausted, depending on crop species, and supplementary liquid feeds would be required to maintain pace with other substrate systems, for example with rockwool where soluble nutrients are provided at every watering.
- Crops may be produced in these nutrient-loaded materials for at least 18 months but crop growth and yield will reduce over time, in the absence of supplementary feeding.
- Leaf tissue analysis is a useful method of monitoring concentrations of nitrate-nitrogen and phosphorus in line with other conclusions made above.
- Analysis of substrate samples is essential to provide information on starting and remaining reserves of potassium, calcium, sodium, magnesium and trace elements.
- The analysis of the nutrient content of the clinoptilolite prior to use is fundamental. A clinoptilolite containing high starting concentrations of sodium will release sodium cations which may cause crop growth problems in non-tolerant plant species.
- The regular analysis of input water supply and / or nutrient solutions is essential to allow a prediction of cation exchange and to help adjust subsequent feeding regimes, in order to regulate the supply of soluble nutrients to plant roots.

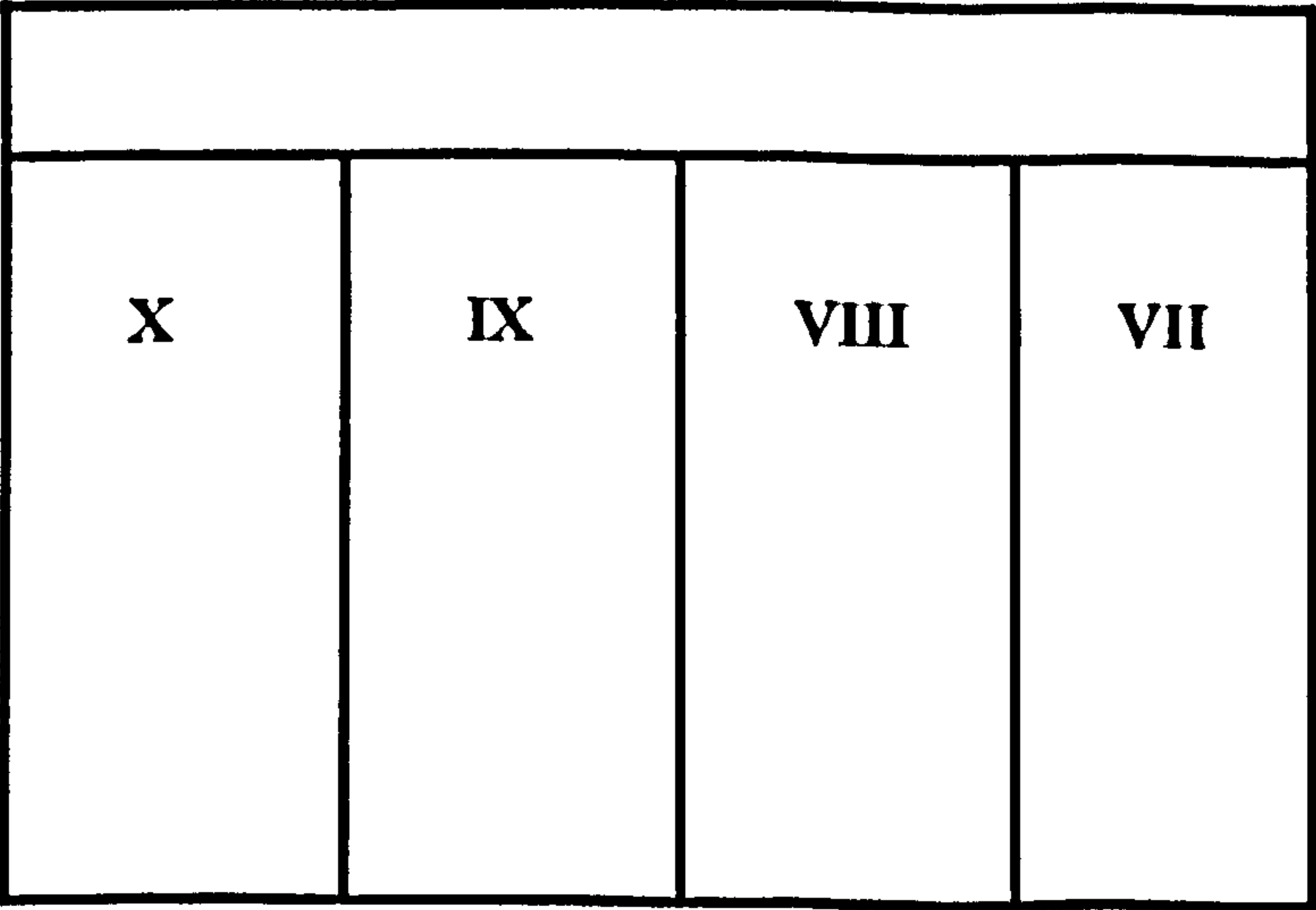
- The use of nutrient-loaded clinoptilolite to produce commercial crops and reduce pollution of the environment by regulating the concentration of nutrients in the drainwater is possible over long periods of time with these materials.

Appendix 1 Howard Davis Farm research unit layout

(main glasshouse blocks)



Robinson block



Appendix II: Chapter 4, Experiment 1

Analysis of Variance: Example 1, Table 4.2

Analysis of Variance for Total Yield

Source	DF	SS	MS	F	P	
Month	8	141036.7	17629.6	255.05	0.000	***
Sub	2	859.0	429.5	6.21	0.006	**
Month*Sub	16	354.7	22.2	0.32	0.989	n.s.
Rep	1	243.0	243.0	3.51	0.072	n.s.
Error	26	1797.2	69.1			
Total	53	144290.5				

LSD Total Yield:

$$LSD_{0.05} = t \sqrt{\frac{2 \times ems}{\text{No values in each mean}}}$$

Substrates $LSD_{0.05} = 5.697$

$LSD_{0.01} = 7.701$

Appendix II: Chapter 4, Experiment 1

Analysis of Variance for 20-25 mm. Example 2, Table 4.2

Source	DF	SS	MS	F	P	
Month	8	3.0735	0.3842	3.78	0.005	**
Sub	2	0.4487	0.2244	2.21	0.130	n.s.
Month*Sub	16	1.4924	0.0933	0.92	0.560	n.s.
Rep	1	0.0888	0.0888	0.87	0.358	n.s.
Error	26	2.6420	0.1016			
Total	53	7.7454				

Appendix II: Chapter 4, Experiment 2

Analysis of Variance: Example 1, Table 4.6

Analysis of Variance for Class I

Source	DF	SS	MS	F	P	
Variety	9	31.415	3.491	3.40	0.041	**
Rep	1	26.796	26.796	26.13	0.000	***
Error	9	9.230	1.026			
Total	19	67.441				

LSD Class I:

$LSD_{0.05} = 1.025$

$LSD_{0.01} = 1.472$

$LSD_{0.001} = 2.166$

Analysis of Variance. Example 2, Table 4.6

Analysis of Variance for Total Yield

Source	DF	SS	MS	F	P	
Variety	9	28.3512	3.1501	5.27	0.011	*
Rep	1	22.0080	22.0080	36.84	0.000	***
Error	9	5.3772	0.5975			
Total	19	55.7364				

LSD Total Yield:

$LSD_{0.05} = 0.783$

$LSD_{0.001} = 1.654$

Appendix II: Chapter 4, Experiment 2

Analysis of Variance. Example 1, Table 4.7

Analysis of Variance for Potassium Concentration.

Source	DF	SS	MS	F	P	
Sdate	27	10348.2	383.3	0.59	0.912	n.s
Rep	1	8750.0	8750.0	13.46	0.001	**
Error	27	17552.0	650.1			
Total	55	36650.2				

LSD Potassium Concentration:

$LSD_{0.05} = 13.982$

$LSD_{0.01} = 18.882$

Analysis of Variance. Example 2, Table 4.7

Analysis of Variance for Calcium Concentration.

Source	DF	SS	MS	F	P	
Sdate	27	150514.5	5574.6	16.05	0.000	***
Rep	1	1491.4	1491.4	4.29	0.048	*
Error	27	9380.1	347.4			
Total	55	161386.0				

LSD Calcium Concentration:

$LSD_{0.05} = 10.221$

Appendix II: Chapter 4, Experiment 2

Analysis of Variance.. Example 3, Table 4.7

Analysis of Variance for Magnesium Concentration

Source	DF	SS	MS	F	P	
Sdate	27	26823.86	993.48	125.81	0.000	***
Rep	1	77.79	77.79	9.85	0.004	**
Error	27	213.21	7.90			
Total	55	27114.86				

LSD Magnesium Concentration:

$LSD_{0.05} = 1.541$

$LSD_{0.01} = 2.081$

Appendix II: Chapter 4, Experiment 3

Analysis of Variance. Example 1, Table 4.10

Analysis of Variance for Blooms.

Source	DF	SS	MS	F	P	
Month	18	80925.7	4495.9	97.83	0.000	***
Sub	5	250.3	50.1	1.09	0.372	n.s.
Error	90	4136.2	46.0			
Total	113	85312.2				

Appendix II: Chapter 4, Experiment 4

Analysis of Variance. Example 1, Table 4.14

Analysis of Variance for Total Marketable.

Source	DF	SS	MS	F	P	
Substr	4	18.597	4.649	2.94	0.091	n.s
Rep	2	2.016	1.008	0.64	0.554	n.s.
Error	8	12.656	1.582			
Total	14	33.269				

Analysis of Variance. Example 2, Table 4.14

Analysis of Variance for 60-70 mm.

Source	DF	SS	MS	F	P	
Substr	4	0.4970	0.1243	0.72	0.601	n.s
Rep	2	0.1709	0.0854	0.50	0.626	n.s.
Error	8	1.3774	0.1722			
Total	14	2.0453				

Appendix III: Chapter 5, Experiment 5

Analysis of Variance. Example 1, Table 5.2 and 5.3

Analysis of Variance For Class I

Source	DF	SS	MS	F	P	
Month	17	106511.5	6265.4	46.48	0.000	***
Variety	11	4483.1	407.6	302	0.001	**
Error	187	25207.0	134.8			
Total	215	136201.5				

LSD Class I (Monthly):

$LSD_{0.05} = 9.385$

$LSD_{0.01} = 12.405$

$LSD_{0.001} = 15.988$

LSD Class I (Variety):

$LSD_{0.05} = 7.663$

$LSD_{0.01} = 10.128$

Appendix III: Chapter 5, Experiment 5

Analysis of Variance. Example 2, Table 5.2 and 5.3

Analysis of Variance for Waste.

Source	DF	SS	MS	F	P	
Month	17	10518.15	618.71	8.00	0.000	***
Variety	11	4783.54	434.87	5.62	0.000	***
Error	187	14462.30	77.34			
Total	215	29763.98				

LSD Waste (Monthly):

$$\text{LSD}_{0.05} = 7.108$$

$$\text{LSD}_{0.01} = 9.395$$

$$\text{LSD}_{0.001} = 12.109$$

LSD Waste (Variety):

$$\text{LSD}_{0.05} = 5.803$$

$$\text{LSD}_{0.01} = 7.670$$

$$\text{LSD}_{0.001} = 9.886$$

Appendix III: Chapter 5, Experiment 5

Analysis of Variance. Example 3, Table 5.2 and 5.3

Analysis of Variance for Total

Source	DF	SS	MS	F	P	
Month	17	157119.1	9242.3	66.39	0.000	***
Variety	11	3745.4	340.5	2.45	0.007	**
Error	187	26032.6	139.2			
Total	215	186897.1				

LSD Total (Monthly):

$LSD_{0.05} = 9.538$

$LSD_{0.01} = 12.606$

$LSD_{0.001} = 16.248$

LSD Total (Variety):

$LSD_{0.05} = 7.787$

$LSD_{0.01} = 10.293$

Appendix III: Chapter 5, Experiment 6

Analysis of Variance. Example 1, Table 5.6

Analysis of Variance for Blooms.

Source	DF	SS	MS	F	P	
Month	17	3575004	210294	138.15	0.000	***
C2 Reps	2	3024	1512	0.99	0.371	n.s.
C3 Vars	1	46480	46480	30.53	0.000	***
C4 Subs	3	77878	25959	17.05	0.000	***
C3*C4	3	718	239	0.16	0.925	n.s.
Error	405	616500	1522			
Total	431	4319604				

LSD substrate:

$$\text{LSD}_{0.05} = 10.512$$

$$\text{LSD}_{0.01} = 13.894$$

$$\text{LSD}_{0.001} = 17.907$$

LSD Variety: substrate interaction

$$\text{LSD}_{0.05} = 14.866$$

Appendix III: Chapter 5 Experiment 6

Analysis of Variance. Example 2 Table 5.7

Analysis of Variance for Yield/m²

Source	DF	SS	MS	F	P	
Rep	2	216.56	108.28	3.05	0.122	n.s.
Pum/hydr	1	5.32	5.32	0.15	0.712	n.s.
Var	1	151.87	151.87	4.28	0.084	n.s.
Pum/hydr*var	1	19.64	19.64	0.55	0.485	n.s.
Error	6	212.78	35.46			
Total	11	606.17				

Example 3, Table 5.7

Analysis of Variance for Yield/m²

Source	DF	SS	MS	F	P	
rep	2	66.46	33.23	2.02	0.214	n.s.
Pum/hydr	1	1.80	1.80	0.11	0.752	n.s.
Var	1	705.49	705.49	42.86	0.001	**
pum/hydr*var	1	7.25	7.25	0.44	0.531	n.s.
Error	6	98.75	16.46			
Total	11	879.75				

Appendix III: Chapter 5, Experiment 6

Analysis of Variance. Example 4, Table 5.7

Analysis of Variance for Yield.

Source	DF	SS	MS	F	P	
Rep	2	0.57	0.28	0.02	0.982	n.s.
Pum/hydr	1	10.72	10.72	0.68	0.442	n.s.
Var	1	16.33	16.33	1.03	0.349	n.s.
Pum/hydr*var	1	306.64	306.64	19.41	0.005	**
Error	6	94.80	15.80			
Total	11	429.05				

LSD substrate: Variety Interaction

$LSD_{0.05} = 7.943$

$LSD_{0.01} = 12.033$

Appendix III: Chapter 5, Experiment 6

Analysis of Variance. Example 1, Table 5.6

Analysis of Variance for Blooms.

Source	DF	SS	MS	F	P	
Rep	2	18.03	9.02	0.43	0.671	n.s.
Pum/hydr	1	8.32	8.32	0.39	0.554	n.s.
Var	1	65.38	65.38	3.09	0.129	n.s.
Pum/hydr*var	1	142.35	142.35	6.74	0.041	*
Error	6	126.80	21.13			
Total	11	360.87				

LSD substrate: Variety Interaction

$LSD_{0.05} = 9.184$

Appendix III: Chapter 5, Experiment 6

Analysis of Variance. Example 6, Table 5.8

Analysis of Variance For Potassium Concentration

Source	DF	SS	MS	F	P	
Sub	3	2363381248	787793728	270.80	0.000	***
Rep	2	2837050	1418525	0.49	0.636	n.s.
Error	6	17454524	2909087			
Total	11	2383672832				

LSD Substrate:

$LSD_{0.05} = 3407.741$

$LSD_{0.01} = 5162.442$

$LSD_{0.001} = 8298.623$

Appendix III: Chapter 5, Experiment 6

Analysis of Variance. Example 7, Table 5.8

Analysis of Variance For Calcium Concentration

Source	DF	SS	MS	F	P	
Sub	3	483746304	161248768	69.10	0.000	***
Rep	2	6447017	3223508	1.38	0.321	n.s.
Error	6	14001650	2333608			
Total	11	504194976				

LSD Substrate:

$LSD_{0.05} = 3052.126$

$LSD_{0.01} = 4623.715$

$LSD_{0.001} = 7432.619$

Appendix III: Chapter 5, Experiment 6

Analysis of Variance. Example 8, Table 5.8

Analysis of Variance For Magnesium Concentration

Source	DF	SS	MS	F	P	
Sub	3	26585990	8861996	78.55	0.000	***
Rep	2	302725	151362	1.34	0.330	n.s.
Error	6	676944	112824			
Total	11	27565658				

LSD Substrate

$LSD_{0.05} = 671.102$

$LSD_{0.01} = 1016.663$

$LSD_{0.001} = 1634.286$

Appendix IV : Chapter 6, Experiment 7

Analysis of Variance. Example 1, Table 6.3

Analysis of Variance For Treatment:Month Interaction

Source	DF	SS	MS	F	P	
Treat	2	21253204	10626602	437.37	0.000	***
Rep	3	120662	40221	1.66	0.188	n.s.
Month	5	17895374	3579075	147.31	0.000	***
Treat*month	10	9584144	958414	39.45	0.000	***
Error	51	1239134	24297			
Total	71	50092520				

LSD Fruit Weight:

$LSD_{0.05} = 220.440$

$LSD_{0.01} = 293.185$

$LSD_{0.001} = 381.361$

Appendix IV : Chapter 6, Experiment 7

Analysis of Variance. Example 5, Table 6.9

Analysis of Variance For Phosphorus Concentration (Nitric Acid Digestion)

Source	DF	SS	MS	F	P	
Sub	5	12507917	2501583	94.99	0.000	***
Rep	3	86675	28892	1.10	0.381	n.s.
Error	15	395015	26334			
Total	23	12989607				

LSD Phosphorus Concentration (Nitric Acid Digestion)

$LSD_{0.05} = 244.528$

$LSD_{0.01} = 338.162$

$LSD_{0.001} = 467.369$

Appendix IV : Chapter 6, Experiment 7

Analysis of Variance. Example 3, Table 6.9

Analysis of Variance For Potassium Concentration (Nitric Acid Digestion)

Source	DF	SS	MS	F	P	
Sub	5	176108336	35221668	167.10	0.000	***
Rep	3	148333	49444	0.23	0.871	n.s.
Error	15	3161667	210778			
Total	23	179418336				

LSD K

$LSD_{0.05} = 691.801$

$LSD_{0.01} = 956.705$

$LSD_{0.001} = 1322.247$

Appendix IV : Chapter 6, Experiment 7

Analysis of Variance. Example 4, Table 6.9

Analysis of Variance For Calcium Concentration (Nitric Acid Digestion)

Source	DF	SS	MS	F	P	
Sub	5	112283336	22456666	50.88	0.000	***
Rep	3	1170000	390000	0.88	0.472	n.s.
Error	15	6620000	441333			
Total	23	120073336				

LSD Ca

$LSD_{0.05} = 1001.042$

$LSD_{0.01} = 1384.359$

$LSD_{0.001} = 1913.300$

Appendix IV : Chapter 6, Experiment 7

Analysis of Variance. Example 5, Table 6.10

Analysis of Variance For Ammonium-nitrogen Concentration (Sodium Extraction)

Source	DF	SS	MS	F	P	
Sub	5	23019284	4603857	337.99	0.000	***
Rep	3	42319	14106	1.04	0.405	n.s.
Error	15	204321	13621			
Total	23	23265924				

LSD_{NH4-N} :

LSD_{0.05} = 175.863

LSD_{0.01} = 243.204

LSD_{0.001} = 336.128

Appendix IV : Chapter 6, Experiment 7

Analysis of Variance. Example 6, Table 6.10

Analysis of Variance For Phosphorus Concentration (Sodium Extraction)

Source	DF	SS	MS	F	P	
Sub	5	3721027	744205	4.69	0.009	***
Rep	3	464930	154977	0.98	0.430	n.s.
Error	15	2380487	158699			
Total	23	6566444				

LSD P :

$LSD_{0.05} = 600.281$

$LSD_{0.01} = 830.140$

Appendix IV : Chapter 6, Experiment 7

Analysis of Variance. Example 7, Table 6.10

Analysis of Variance For Potassium Concentration (Sodium Extraction)

Source	DF	SS	MS	F	P	
Sub	5	64732236	12946448	36.17	0.000	***
Rep	3	912546	304182	0.85	0.488	n.s.
Error	15	5368379	357892			
Total	23	71013160				

LSD K :

$LSD_{0.05} = 901.456$

$LSD_{0.01} = 1246.640$

$LSD_{0.001} = 1722.960$

Appendix V

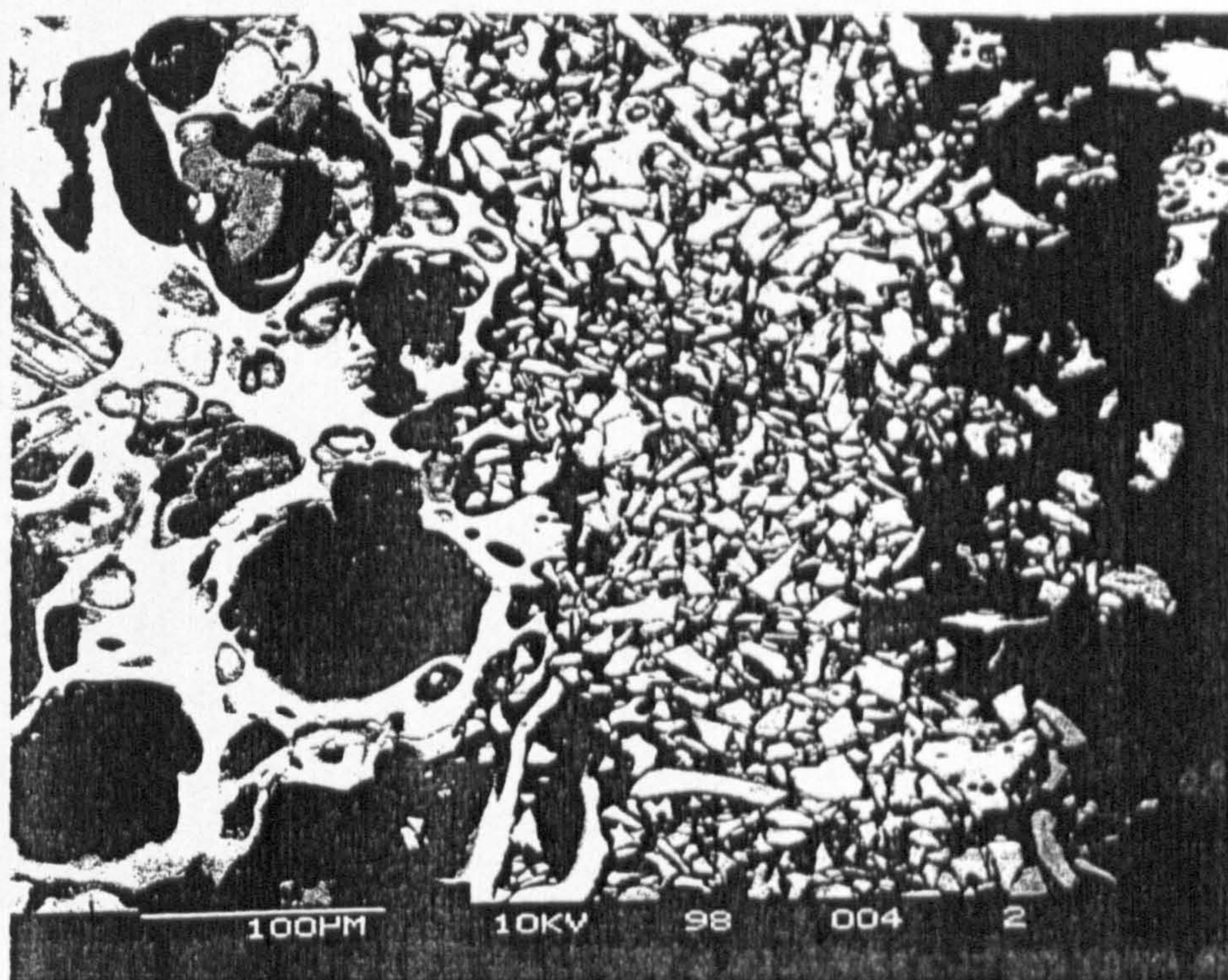


Plate 2.7. BSEM photomicrograph of exterior of pumice fragment coated by a fine-grained angular pumice.

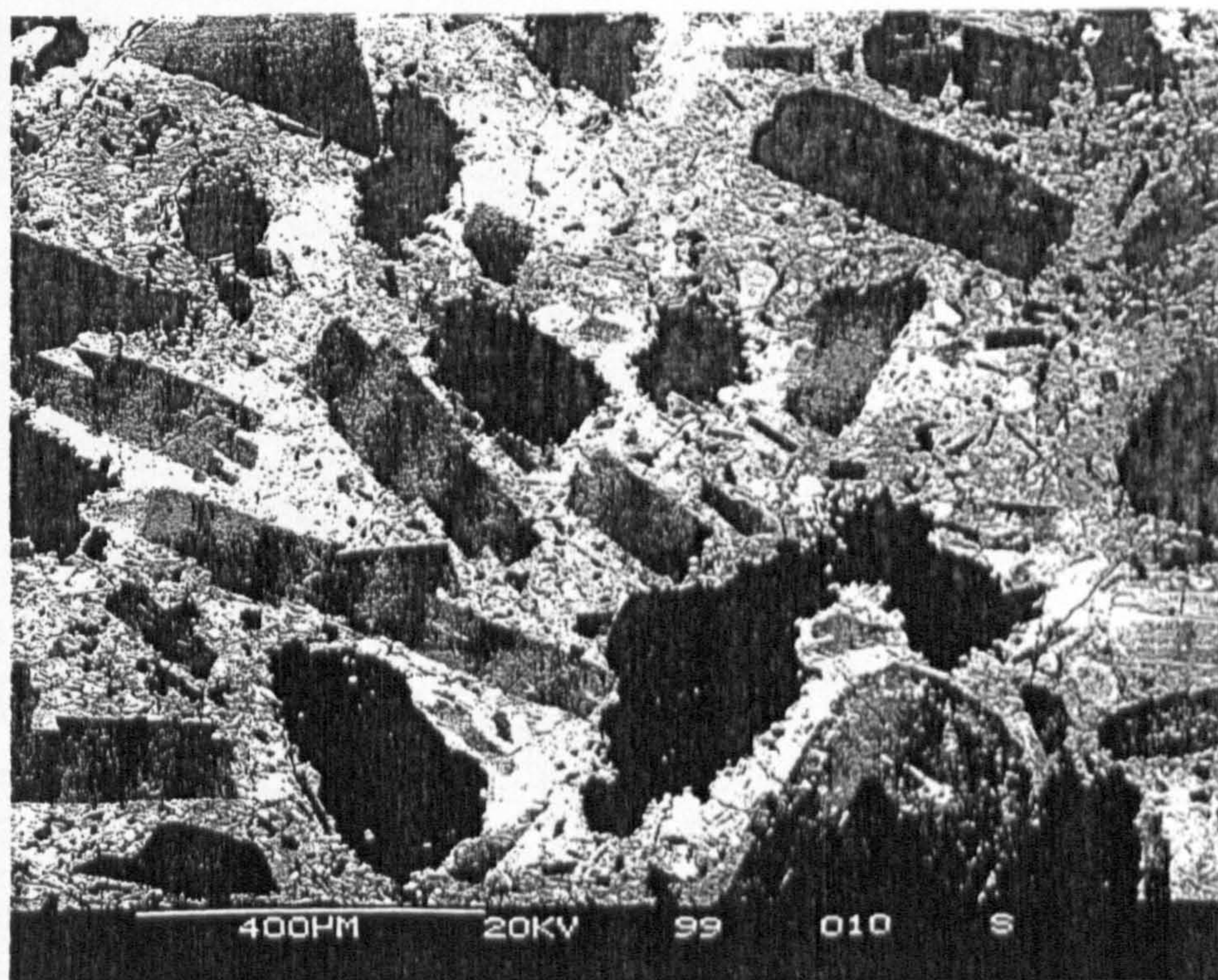


Plate 2.8. BSEM photomicrograph of lithic clast (porphyritic andesite). Phenocrysts of Ca-plagioclase and clinopyroxene. Note minor vesicles and secondary voids of up to several mm dimensions.

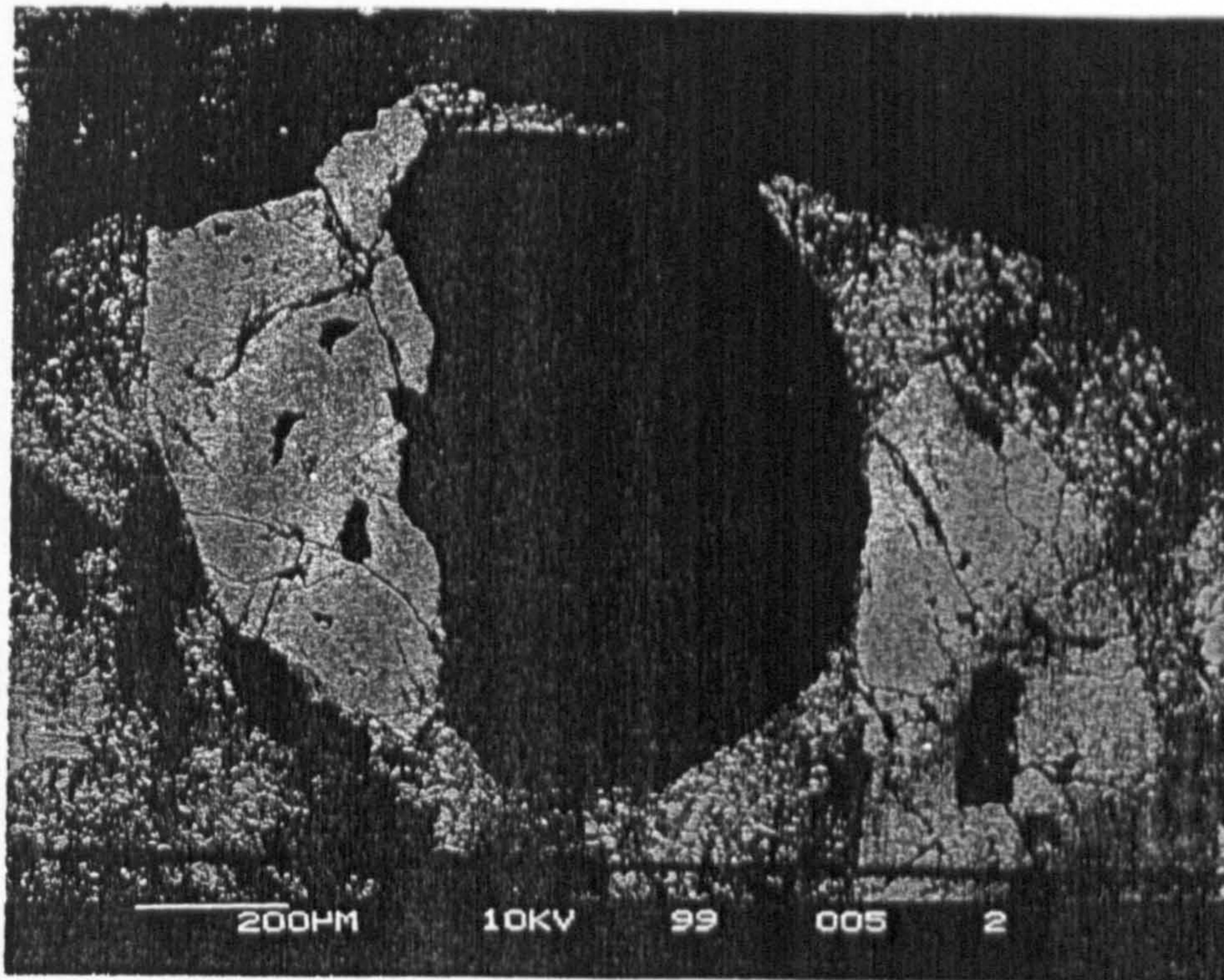


Plate 2.9. BSEM photomicrograph of lithic clast cut by quartz vein, which also partially replaces a phenocryst. Replacement of phenocrysts by kaolinite also apparent.

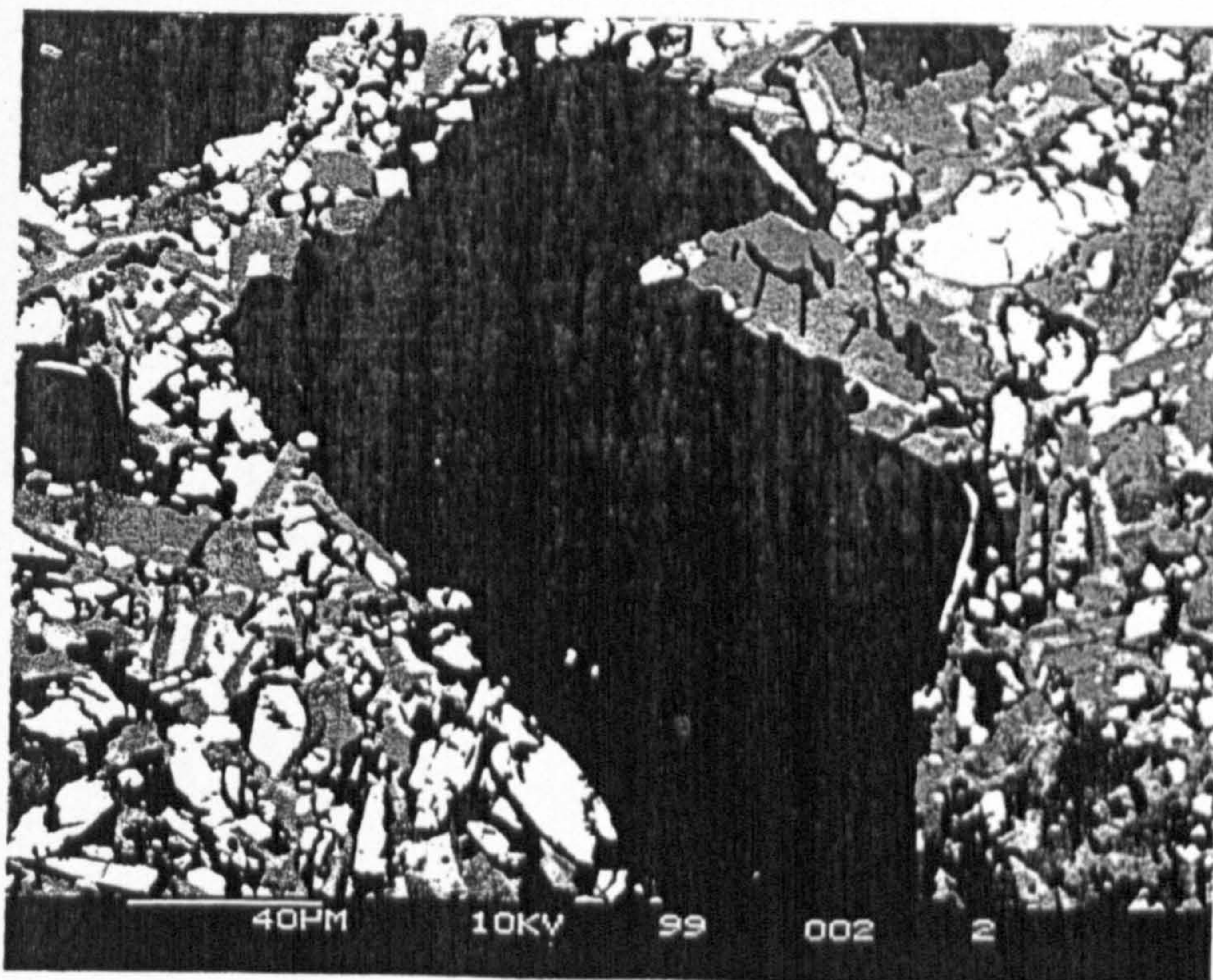


Plate 2.10. BSEM photomicrograph of secondary void in lithic clast lined by collomorphic kaolinite.

Appendix VI

THE PRODUCTION OF STANDARD CARNATIONS ON NUTRIENT-LOADED ZEOLITE

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Abstract

The majority of modern hydroponic systems rely on calculated inputs of liquid nutrient solutions to provide crops with a full nutritional package. Existing substrate systems for the production of carnations on Jersey include containerised pumice and the traditional peat module, both of which are irrigated with liquid fertilisers throughout the life of the crop.

The use of a modified zeolitic substrate in 5 litre pots was examined using mixtures of reservoir and borehole waters only in the irrigation cycles. At no time did the carnation plants receive any liquid fertiliser inputs.

Zeolites are crystalline, hydrated aluminosilicates with 3 dimensional crystal structures, which lose and gain water reversibly and can exchange cations without a major change of structure. The zeolite clinoptilolite shows a preferential absorption for potassium and ammonium-nitrogen.

Twelve standard carnation varieties were selected and 4 cuttings were planted in each 5 litre pot to give a density of 32 plants per square metre.

Analyses completed on the input irrigation water and drain water from the pots showed little differences in nutrient content. After an initial release of nitrate-nitrogen and phosphorus, the drain water contained low levels of nutrients throughout the main growing period.

Leaf tissue analyses performed on fully expanded leaves revealed a significantly lower leaf nitrate-nitrogen content, in comparison to corresponding leaf samples from pumice systems irrigated with liquid feeds.

Yields over a 12 month period are tabulated for a number of commercial standard carnation varieties including 'Master', 'White Giant', 'Esty' and 'Griselda'.

The experimental work is continuing in an attempt to refine a new crop production system for flower crops and investigate a possible alternative to recirculation of liquid nutrient - supplied substrate systems.

1. Introduction

The majority of glasshouse standard carnation crops on Jersey are grown in peat bags or pumice-filled pots and the plants are irrigated with liquid fertiliser throughout the production cycle. Excess liquid draining through the substrates contains a high concentration of nutrients including nitrate-nitrogen, phosphorus and potassium. Overwatering can increase the quantity of drain water released from such systems, further heightening potential environmental pollution problems.

In order to reduce the amount of nutrients in the drain water from rockwool systems, techniques such as partial fertiliser substitution have been developed. In long season tomato production, for example, nitrate-nitrogen fertilisers have been

partially replaced by potassium and calcium chlorides (Hand and Fussell, 1993). Further work has revealed that reduction of nitrate-nitrogen levels below 120 mg per litre (rockwool slab) can lead to plant growth problems and yield losses, however (Fussell and Hand, 1994).

Attempts have also been made to prevent drain water losses from crop production systems by the use of recirculation equipment but such systems may be expensive to install and operate.

Provision of a balanced nutrient package within the substrate and prevention of major nutrient loss to the external environment, by confining plant nutrient uptake to a cation exchange process with the substrate, could reduce the need for recirculation systems for flower crops. One substrate that has high cation exchange properties is the zeolite, clinoptilolite.

Zeolites are crystalline, hydrated aluminosilicates with 3 dimensional crystal structures. They can lose and gain water reversibly and exchange cations without a major change of structure. Natural zeolites are major constituents of numerous volcanic rocks and, consequently, mining locations include USA, Japan, Bulgaria, Hungary, Italy, Mexico, Germany, China and Russia. Each zeolite species has its own unique crystal structure and, therefore, its own set of physical and chemical properties.

Inside the zeolite granules are channels with exchangeable cation sites, where cations such as potassium and calcium can substitute for one another. Loosely bound water is also present and it surrounds the exchangeable cations in the large pore spaces of the structure. Clinoptilolite is highly selective for potassium and ammonium nitrogen. To avoid problems with sodium accumulation in salt sensitive crops, it is extremely important that zeolite material low in exchangeable sodium is utilised. Consequently, a Bulgarian clinoptilolite, which was reported as being rich in potassium, whilst not causing any plant growth problems due to the release of sodium ions, was used in the experimentation.

Clinoptilolite can be used as a substrate for plant growth (Mumpton, 1984). When a balanced hydroponic feed is added, the clinoptilolite selectively adsorbs cations and releases others to the system. Clinoptilolite can act as a reservoir of potassium and it allows cheap nitrogen fertilisers to be used since free ammonia is also adsorbed.

A nutrient loaded form of clinoptilolite (Hydrocult S) containing balanced proportions of ammonium-nitrogen, phosphorus and potassium has been developed in Bulgaria, using a novel, patented production technique.

The work reported in this paper gives the results of a large scale glasshouse trial where Hydrocult S was used as a substrate for standard carnation production and plants were irrigated with water only throughout the trial.

2. Material and Methods

2.1 Plant Growing Conditions

Twelve varieties of standard carnation cuttings were planted into Hydrocult S on 30 March, 1993. Plot size was 24, five litre, black, polypropylene pots per variety and a plant density of 32 plants/m² was achieved using 4 cuttings per pot. The trial

design incorporated two replicates of each variety in a fully randomised design.

An overhead irrigation system supplied with water was only used to maintain an even moisture level at the surface of the Hydrocult S and encourage rapid rooting into the substrate during the establishment phase (8 weeks).

Thereafter, the pots were dosed with water through a drip irrigation system throughout the life of the crop at a rate of two litres per hour; no liquid feed was applied to the system at any time. The number of irrigation cycles per day was determined by the amount of light received by the crop and controlled by a Priva environmental computer system.

Shoot tips were removed ("stopped") approximately 3 weeks after planting, to encourage the formation and development of side shoots. A total of seven support nets were used to maintain the upright plant habit and ensure both good flower stem yield and quality.

A routine, broad spectrum insecticide and fungicide programme was used throughout the trial period.

The first flowers were picked 16 weeks after planting and subsequent harvesting operations were performed three times per week thereafter. Data collected included the number of blooms per variety per week and the flowers were subsequently quality graded to MAFF standards. Data was analysed using two-way analysis of variance and presented as cumulative totals over the 18 month flowering period for each variety.

2.2 Chemical Analysis of Water and Crop Samples

Irrigation water and drain water samples were collected from the carnation plots and analysed every two weeks at the ADAS Analytical Chemistry Laboratory, Wolverhampton.

An inductively coupled plasma atomic emission spectrometer (ICP-AES) was used to determine the concentration of elements present. In ICP-AES, the plasma is produced by passing a flow of argon gas through a strong radio frequency field. This induces ionisation in the argon which immediately reverts, shedding the excess energy as intense heat and light in a continuous and constant process. When a sample solution is nebulised into the plasma, atomisation is assured and a complex spectra characteristic of the elements present is emitted. Argon plasmas are so hot (8,000 - 10,000 °C) that chemical interferences are eliminated. Ammonia, nitrate-nitrogen and chloride were determined using continuous flow analysis.

Plant sap analysis was performed, at the States of Guernsey Horticultural Advisory Service, on leaf tissue samples using a 1:10 macerated water extract (Smith, 1988). Fully expanded, new leaves were sampled from the carnation crop every four weeks.

3. Results

3.1 Crop Yields

Yields to September 1994 are given in Table 1. Average marketable yields were similar to those in previous trials using pumice (Jersey Department of Agriculture and Fisheries, 1992). The standard varieties 'White Giant' and 'Master' performed

in a similar manner in this trial to previous trials. Timing of flower flushes was normal with a first flush starting in July 1993 and a second season main flush starting in May 1994. Variety performance gave a rank order with 'White Giant' as the highest yielding (marketable blooms per m²) with 79% marketable and 'Hode' as the lowest yielding (marketable blooms per m²) with 36% marketable, with significant differences between varieties ($P < 0.005$) (Table 1).

3.2 Chemical Analysis

Irrigation Water

The analysis of the irrigation water revealed a conductivity range of < 10 to $391 \mu\text{S}$, a nitrate-nitrogen range of < 1 to 35 mg per litre , a phosphorus range of < 1 to 10 mg per litre , a potassium range of 1 to 51 mg per litre , a calcium range of 1 to 24 mg per litre and a sodium range of 5 to 31 mg per litre . The ranges are given over a 17 month sampling period.

There were no major fluctuations in the micronutrient content of the irrigation water throughout the sampling period.

Drainwater

Analysis of the drain water was expressed as the difference between the concentration of the irrigation water and the drainage water (Δ concentration). Data are only presented for the major nutrients at 6 month intervals during the trial; other samples did not yield any major differences from these results (Table 2).

Apart from an initial release of phosphorus, calcium and sodium in the early stages of the trial, the levels of nutrients in the drain water were small. The conductivity of the drain water was $189 \mu\text{S}$ higher than of the irrigation water in samples taken 4 weeks after planting. However, 28 weeks after planting, the conductivity of the drain water was $80 \mu\text{S}$ lower than the irrigation water. After 54 and 72 weeks, the drain water conductivity was $15 \mu\text{S}$ and $17 \mu\text{S}$ lower than the irrigation water, respectively.

Most importantly, there were virtually no losses of nitrogen in the drain water, after the initial plant establishment period.

The level of calcium in the drain water was higher than in the irrigation water after 4 weeks; later in the trial, levels of calcium were generally less in the drain water than in the irrigation water. With sodium, the drainwater content was higher than in the irrigation water after 4 weeks. Subsequently, the levels of drain water sodium were similar to the irrigation water concentrations.

3.3 Plant Sap Analysis

The average nitrate-nitrogen value of new, fully expanded carnation leaves was 51.7% lower than the States of Guernsey Horticultural Advisory Service carnation crop target levels (Table 3). Other nutrients were all above the crop target levels. The calcium level, however, was 32% lower than the crop target level.

The leaf analysis data show no marked differences from previous data collected at this site, including an adjacent glasshouse compartment containing carnation varieties growing on pumice receiving regular irrigations of liquid fertiliser.

Despite the difference in nitrate-nitrogen content, there appeared to be little

effect on the development of the crop canopy and flower formation. Nitrate-nitrogen deficiency symptoms, in the form of pale, older leaves, were not noticable in the crop in the latter stages of production, however.

4. Discussion

Commercially acceptable yields of high quality standard carnations were produced in this trial with a nutrient loaded zeolite, Hydrocult S, using only water in the irrigation cycles.

Fast plant establishment relied on the careful maintenance of moist conditions in the rooting zone. This was complicated by rapid drying of the substrate at the pot surface. Early rooting was satisfactory in the trial but it is possible that dry substrate could have impeded further root development. This could be improved by increasing the proportion of fine zeolite material in the substrate mix.

As phosphorus is not held as a cation within the zeolite matrix, an initial release of phosphorus was expected. The sap analysis results indicated that there was an adequate level of phosphorus in the new leaf tissue, however, and there were no phosphorus deficiency symptoms evident in the crop canopy.

Potassium was readily absorbed by the plants from the zeolite and it is possible that an exchange with calcium was involved in the cation exchange process.

The trial has also indicated that it is possible to grow standard carnations at lower nitrogen levels than previously indicated.

The lower level of calcium present in the sap analysis results were probably more related to plant uptake from the root zone and influenced by glasshouse humidity levels. Any cations released into the rooting zone later in the trial were probably absorbed quickly by plant roots.

It was noticeable that there were less root and stem base disease problems over the winter period in this crop. This could be due to a combination of dry substrate surface conditions and the lower levels of nitrogen available, thus preventing soft, luxuriant growth.

It is important to design a system so that excess drain water can be removed during times of high irrigation requirement in order to prevent pot waterlogging.

The experimental work is continuing in an attempt to refine a new crop production system for flower crops and investigate a possible alternative to recirculation of liquid nutrient supplied substrate systems.

Acknowledgements

The supply of standard carnation varieties from the following companies is gratefully acknowledged. Barbaret and Blanc (Master, Oriana), Hadar (Esty, Hode), Hilverda (Angeline, Cobra), Kooij and Zonen (Uniko), Lck and Zonen (White Giant), Selecta (Faro), Shemi (Napoleon), Van Staaveren (Oregon), West Stek (Griselda). The supply of Hydrocult S is also acknowledged from Hawthorn Applied Technology Ltd.

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Table 1 - Standard carnation yield (cumulative to the end of December 1994)

Variety	Colour	Total Blooms/m ² ¹⁾	Marketable Blooms/m ²	% Marketable
White Giant	White	642	505 a	79
Esty	Yellow	671	427 ab	64
Oriana	Pink	592	423 ab	71
Griselda	Cerise	493	415 abc	84
Napoleon	Red	498	370 abc	74
Angeline	Yellow	449	388 abc	86
Master	Red	493	378 abc	77
Faro	Pink	472	354 bc	75
Oregan	Red	417	338 bcd	81
Cobra	Yellow	522	290 bcd	56
Uniko	Pale Pink	537	263 cd	49
Hode	White	554	202 d	36

¹⁾ including non-marketable stems

Figures followed by the same letter are not significantly different from each other $p > 0.05$.

Table 2 - Δ(Drainwater - Irrigation Water) concentration of nutrients in the trial

Timing of Sample After Planting	4 Weeks 28/04/93	28 Weeks 27/10/93	54 Weeks 26/04/94	79 Weeks 25/10/94
pH	0.1	0.2	0	-0.2
Conductivity (μS at 20°C)	189	-80	-15	-17
NH ₄ -N (mg/l)	2.1	0	0	-0.5
NO ₃ -N	-1.1	0	2.0	-2.0
P	24.0	-2.0	0	-0.5
K	-4.0	-17.0	0	0
Ca	17.8	-5.6	2.0	-0.3
Mg	-1.0	-2.0	1.0	0
Na	30.0	3.0	0	-2.0

Table 3 - Carnation plant sap analyses from nutrient-loaded zeolite (Hydrocult S) and comparable data collected from a parallel trial grown on a pumice substrate. (Guernsey Horticultural Advisory Service Technique) mg/kg. Mean of monthly measurements 1994

	NO ₃ -N	P	K	Ca	Mg	Na
Crop Target Level	(300)	(300)	(3200)	(300)	(200)	(180)
Hydrocult S	145	569	3344	204	253	191
Pumice	235	591	2966	210	231	184
	Fe	Cu	Zn	Mn	B	
Crop Target Level	(4.0)	(1.6)	(4.0)	(6.0)	(10.0)	
Hydrocult S	5.8	7.7	12.4	16.6	14.8	
Pumice	5.2	8.1	6.8	13.6	8.8	

THE USE OF PUMICE IN HORTICULTURE

Paul F. Challinor, Jersey

INTRODUCTION

Pumice, pumicite and perlite are direct products of acidic volcanism. Pumice is an highly-vesicular volcanic glass, silicic in composition and occurs as massive blocks or unconsolidated, fragmented material. The vesicles are glass-walled bubble casts, which give pumice a low density (S.G. 1 g/cm³), compared to natural glass (S.G. 2.5 g/cm³).

Pumicite, the commercial term for fine-grained, fragmented pumice with shards under 2 mm in diameter, may be deposited some distance from the source. Scoria is the mafic equivalent of pumice and, being denser, tends to occur as localised cinder cones. Perlite is a partially-hydrated volcanic glass, found capping acidic lava domes which formed from highly-viscous rhyolitic melts.

Pumice is formed from silicic lavas (rhyolitic to dacitic) rich in dissolved volatiles, particularly water vapour. On eruption, sudden release of pressure leads to expansion of volatiles which, in turn, generates a frothy mass of expelled lava. This mass may solidify on contact with the atmosphere as a vent filling or flow, or may be shattered by a violent eruption.

Most industrial applications of pumice take advantage of properties such as high strength-to-weight ratio, insulation and high surface area which result from the vesicular nature of this rock. It is, therefore, used as a light-weight aggregate, as it lessens the weight of building products, facilitating easier handling and reducing foundation requirements and mortar consumption. It is also used in the clothing industry for stone-washing garments, in cosmetics and for cleaning and polishing metal, glass and wood products.

HORTICULTURAL APPLICATIONS: CARNATIONS IN PUMICE

Production of standard and spray carnations has traditionally involved planting rooted cuttings into prepared glasshouse soil beds. There are

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several potential problems with soil-based production systems which must be rectified before planting takes place. Diseases such as *Fusarium culmorum* (stub rot) and, in particular, *Fusarium oxysporum* (carnation wilt) are the main causes of plant losses during the life of the carnation crop. Pests and diseases can remain in the soil after the removal of one crop, to be transmitted to the next, in the absence of a thorough sterilisation programme. Weeds, especially perennial plants, will compete with and disrupt the establishment of carnation cuttings and can also harbour pests and diseases. Any herbicide residues from previous crops could also adversely affect the growth of carnation cuttings. Chemical properties of soils are equally important; an accurate ADAS soil analysis is essential prior to planting to correct nutrient imbalances and deficiencies. In addition, problems can occur with high soil conductivities, high sodium levels and steaming toxicities. Soil physical properties, including structure and drainage, are also extremely important in carnation production. Irrigation methods, in conjunction with soil characteristics, also require careful consideration to enable quality continuity carnation production over 18-20 months.

Carnation trials at Howard Davis Farm have included a number of established and potentially new substrate systems over several years. Rock-wool, perlite, foam slabs, peat, coco-fibre and wood chips have all been compared with pumice. Pumice has proved to be a reliable substrate well suited to the production of quality carnations grown in isolated systems.

Though continuous troughs have been used for individual peat and pumice systems, the risk of disease contamination and nutrient imbalances have forced the use of smaller containers, such as 3 and 5 litre rigid, black pots.

Long season tomato crops have also performed well on the substrate in trials and pumice is currently being examined in comparison with stone-wool, glasswool and zeolite substrates in a long season pepper crop trial at Howard Davis Farm.

CHEMICAL AND PHYSICAL PROPERTIES OF PUMICE

Pumice is inexpensive and biologically inert, containing no pathogens or weeds (Gunnlaugsson and Adalsteinsson, 1995).

CHALLINOR *The use of pumice in horticulture*

1. *Sicilian pumice (after Challinor, 1993)*

pH range	7.0 to 8.0
Conductivity (μ S at 20 °C)	200
Air filled porosity range	20 to 35 %
Extractable sodium	30 to 35 mg/litre

2. *Icelandic pumice (after Boertje, 1995)*

pH range	7.0
Conductivity (μ S at 20 °C)	200
Cation exchange capacity	0.0
Moisture (% by weight)	45
Bulk density (kg/m ³)	400
Pore space (%)	85
Water at -10 cm volume (%)	45
Air space at -10 cm volume (%)	40

3. *Substrate analysis: acid digestion (using nitric acid) mean values, mg/kg*

	Unused pumice	Unused clinoptilolite (unloaded)
P	16.81	39.03
K	502.00	21,025.00
Ca	1,503.75	16,700.00
Mg	507.50	2,975.00
Na	1,637.50	3,905.00
SO ₄ -S	64.80	43.95
Fe	1,419.75	4,197.50
Mn	23.48	414.25
Cu	18.30	2.88
Zn	12.18	31.93
B	2.34	1.52

Air filled porosity is the proportion of the volume of medium that contains air after it has been saturated with water and allowed to drain. A good air filled porosity will help to prevent root waterlogging problems, especially over the winter period (Challinor, 1993).

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The material contains much less potassium and calcium than unloaded clinoptilolite but more copper and boron. It is, however, able to absorb some calcium, potassium, magnesium and phosphorus from the nutrient solution added and release them to the plant later (Bunt, 1988).

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Acta Horticulturae 401, 131-136

SUMMARY

Chemical and physical properties of Silician pumice and Icelandic pumice are compared. For growing carnations rockwool, perlite, foam slabs, peat, coco-fibre and wood chips have all been compared with pumice. Pumice has proved to be a reliable substrate well suited for the production of quality carnations grown in isolated systems.

GROWTH AND DEVELOPMENT OF SWEET PEPPER PLANTS ON UNLOADED AND NUTRIENT-LOADED CLINOPTILOLITE ZEOLITE

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INTRODUCTION

There is increasing pressure on farmers and growers to reduce loss of nitrogen, phosphorus and pesticides from crop systems. The Dutch Government, for example, set an objective of 80 % of glasshouse vegetable production to be grown in closed recirculation hydroponic systems by 1995 and 100 % by the year 2,000 (Vaughan, 1994). Recent European Community directives, specifically the Nitrate Directive, have emphasised the need for UK growers to reduce the uncontrolled loss of nitrate to the environment (Hand and Fussell, 1995).

Of the 16.1 ha of long season tomato crops in production on Jersey, approximately 1.1 ha involve Nutrient Film Technique (NFT) and there is 0.4 ha of stonewool that has been adapted to form a recirculation system (Table 1). The remaining systems allow excess irrigation drainwater to run to waste either within or outside the glasshouse blocks. There are currently 2 ha of peppers being grown on stonewool systems; of these, only 0.4 ha is fully recirculated. There are also 2 ha of standard carnations being grown on pumice, with no recirculation system in operation at the present time.

It is possible to calculate the theoretical amount of feed solution required by substrategrown plants but irrigation system inefficiencies present problems that still need to be overcome. Traditionally, an excess amount of nutrient solution has been applied to ensure that all plants receive a suffi-

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cient supply and excess hydroponic drainwater ranges between 20 - 80 % of the calculated input figure.

Table 1. Soilless culture area in ha (Jersey 1996)

substrate	tomato	cucumber	pepper	standard carnation	total
NFT	1.1	-	-	-	1.1
stonewool	15.0 ¹⁾	0.4	2.0 ¹⁾	-	17.4
pumice	-	-	-	2.0 ²⁾	2.0
-----	-----	-----	-----	-----	-----
total	16.1	0.4	2.0	2.0	20.5

¹⁾ includes 0.4 ha nutrient recirculation

²⁾ includes experimental area of granite chippings and zeolites

For a long-season tomato crop, 20 % drainwater produces in excess 1.3 million litres of water per hectare per season, with approximately 400 kg N per hectare per season wasted (Vaughan, 1994). Whilst watering to excess is wasteful in terms of water and fertiliser, it has been the easiest way for growers to ensure full crop yield. In future, however, growers will not be allowed to run untreated hydroponic solution to waste.

In the UK, Nitrate Sensitive Areas, Nitrate Vulnerable Zones and supermarket protocols are already having an impact on fertiliser policies. These commercial and legislative measures will increase, resulting in the need for new technology to ensure that viable crop production industries are maintained. In order to address the future need of the glasshouse industry, research is being carried-out at Howard Davis Farm, Jersey to address new technology in terms of nutrient recirculation systems. Experimental work has concentrated on attempts to refine existing systems, such as NFT and stonewool. In addition, other materials have been screened to examine their potential as participative substrate, for example pumice and clinoptilolite zeolite. Zeolites are crystalline, hydrated alumino-silicates of alkali and alkaline earth cations that possess infinite, 3-dimensional crystal structures (Mumpton, 1984). In terms of industrial

applications, clinoptilolite is important for its selectivity towards monovalent ions such as ammonium (Tsitsishvili et al., 1992). Earlier work concentrated on Hydrocult S - a nutrient-loaded form of clinoptilolite - and its use in both nutrient-dosed and water only systems (Challinor et al., 1995). In this paper, an unloaded clinoptilolite is compared with two nutrient-loaded clinoptilolites, Hydrocult S and Hydrocult F, using only water in the irrigation cycles.

MATERIALS AND METHODS

Plant growing conditions

Sweet pepper plants, cv. 'Mazurka' (Rijk Zwaan), were raised at a commercial nursery site in 0.65 litre rockwool propagation blocks, using a standard hydroponic liquid feed regime (Table 2). The plants were transferred to Howard Davis Farm on 29 March 1994 and planting took place over the period 29 March to 1 April. Prior to planting, the glasshouse compartment was prepared during early March involving thorough cleaning of the structure, application of black/white polythene to the concrete floor and installation of a drip irrigation system. Three litre, black, poly-propylene pots were positioned in single rows at a density of three plants per m². Each plot consisted of three pots and there were three treatments. The trial design incorporated four replicates of each treatment and seven harvests in a randomised block design.

Planting into the substrate ensured that the rockwool blocks were in intimate contact with the substrate and the plant base was level with the surface of the substrate. The actual volume of substrate was 2.35 l per pot.

The three substrates, unloaded clinoptilolite zeolite, low nutrient-loaded clinoptilolite (Hydrocult S) and high nutrient-loaded clinoptilolite (Hydrocult F) were placed in the pots. Loose material was prevented from moving out of the pots by incorporating a lining of spun, polypropylene fibre inside the bottom of the pots. The same material was used to cover the top of the substrate to prevent rapid drying at the surface. Initial watering was by hand using an equal quantity of water to maintain moisture level within each pot. The unloaded clinoptilolite

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zeolite was the easiest to keep moist, as the zeolite particle size distribution was 0.8 - 2.5 mm, compared with 0.8 - 5 mm for the loaded-clinoptilolites.

Table 2. Nutrient analysis of propagation blocks in mg/l (22 March 1994)

	actual results	targets		actual results	targets
pH	6.5 ¹⁾	6.0 - 6.2	Cl	171	low ³⁾
EC (μS)	2,180	2,200	Fe	3.59	3.0 - 4.0
NH ₄ -N	1	low ³⁾	Mn	0.50	0.60
NO ₃ -N	193	188	Cu	0.10	0.10
P	22 ²⁾	30	Zn	0.10 ²⁾	0.30
K	316	300	B	0.50	0.50
Ca	155	188	K : N	1.6	1.6
Mg	45	50	K : Ca	2.0	1.6
Na	97	low ³⁾	K : Mg	7.0	6.0

¹⁾ = high result ²⁾ = low result ³⁾ = as low as possible

Table 3. Integrated pest management programme

date	agent	pest/disease controlled
7 April	<i>Amblyseius cucumeris</i>	thrips
19 April	pirimicarb ("Pirimor")	aphids (<i>Myzus persicae</i>)
5 May	nicotine (nicotine shreds)	aphids (<i>Myzus persicae</i>)
17 May	nicotine (nicotine shreds)	aphids (<i>Myzus persicae</i>)
weekly ¹⁾	<i>Phytoseiulus persimilis</i>	red spider mite
weekly ¹⁾	<i>Aphidius matricariae</i>	aphids
29 June	<i>Bacillus thuringiensis</i> ("Dipel")	tortix caterpillars
13 July	<i>Bacillus thuringiensis</i> ("Dipel")	tortix caterpillars
18 July	chlorothalonil ("Bravo 500")	<i>Botrytis cinerea</i>
20 Sept.	fenbutatin oxide ("Torque") ²⁾	red spider mite

¹⁾ = weekly introduction ²⁾ = clean-up spray

A biological control programme of pests was used throughout the experiment (Table 3). Guard rows completely surrounded the experimental plots and consisted of peppers planted into 70 % nutrient-loaded Hydrocult F and 30 % Alcosorb 400 at a rate of 6 g per litre of water, with a substrate volume of 1.45 litres. All pots were placed on poly-styrene boards, to allow efficient drainage and to provide some heat insulation to the pot bases.

The pots were dosed with water via a drip irrigation system throughout the life of the crop at a rate of one litre of water per hour; no liquid feed was applied to the system at any time. The number of irrigation cycles per day was determined by the amount of light received by the crop but was manually controlled until May and thereafter was allowed to operate on a continuous basis day and night.

Plant trimming started on 3 April by removal of the king flower and second stage flowers and selection of 2 shoots per plant. The plants were trimmed and trained on a regular basis and the plant material resulting from the operations was collected per treatment, frozen, stored and then bulked together with the subsequent harvest sample. Destructive sampling of plant material took place each month. Each time a harvest was completed, the guard pots were moved to a new position to guard the next set of plots.

Plants were supported by poly-propylene strings attached to overhead wires; two strings per plant were attached below the king flower position. The first peppers were picked on 8 May and subsequent harvesting operations were performed monthly thereafter according to good commercial practice. Data collected included the number and fresh weight of each fruit per plot and the fruit was quality graded to MAFI standards.

Chemical analysis of water, plant and substrate samples

Samples of input irrigation water and drainwater were taken on a monthly basis. The drainwater was sampled from modified pots in the final harvest plots, to provide data on changes in concentration of nutrients involved with all three treatments. Modifications to the pots involved the addition of an inner well contained within an outer collar extension to the pot base. Samples of the drainwater were collected from the inner well under the pots using a syringe and transferred to plastic bottles. Samples from the

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four replicates were combined to provide one representative sample per treatment.

Four plants from each treatment were destructively harvested every month and divided into: leaves including petioles, stems, flowers and fruits (including flower buds), and roots. Roots were manually separated from the substrate and a range of horticultural sieves were employed to capture all root pieces broken during the separation process. Samples of each substrate were taken before filling the pots and from the final harvest pots after completion of the experiment.

Table 4 a. Monthly mean fruit fresh weight marketable yield in kg/m²

substrate	May	June	July	Aug.	Sept.	Oct.	Total
unloaded zeolite	0.06	0.10	0.04	0.20	-	-	0.40
Hydrocult S	0.14	0.35	0.81	2.33	0.26	-	3.89
Hydrocult F	0.44	1.23	0.84	3.86	0.80	3.28	10.46

Table 4 b. Total mean fruit fresh weight for each harvest date in g/plant

harvest	unloaded zeolite	Hydrocult S	Hydrocult F	error ¹⁾
May	20.3	45.8	146.8	13.31
June	53.5	164.0	557.0	15.07
July	66.0	434.0	836.0	55.5
Aug.	133.0	1,210.0	2,123.0	87.9
Sept.	102.0	1,297.0	2,391.0	183.8
Oct.	129.0	1,240.0	2,435.0	201.9

¹⁾ = standard error of differences of means - one replicate in each of the 4 blocks

All treatments for each date were significantly different at P < 0.001

Acid digestion of the samples involved drying the zeolite at 105 °C and milling to 45 µm, followed by treating 1 gram of zeolite with 10 ml of

concentrated nitric acid. This was boiled down to 50 % volume and then a further 5 ml concentrated hydrochloric acid was added. After warming gently and cooling, the solution was made up to 100 ml, filtered and then analysed. This digestion does not dissolve silica but causes lattice disruption by leaching of aluminium. The sodium exchange process involved sampling 5 grams of zeolite (as delivered) and adding 100 ml of 1 M sodium chloride. This mixture was shaken for 1 hour and the supernatant was then decanted, followed by the addition of a fresh 100 ml aliquot of sodium chloride. This was repeated a total of 4 times. The 400 ml sample (sodium chloride plus ions exchanged out of the zeolite) was made up to 500 ml and analysed as outlined below.

An inductively coupled plasma atomic emission spectrometer (ICP-AES) was used to determine the concentration of elements present. Ammonia, nitrate-nitrogen and chloride were determined using continuous flow analysis. All analytical work was completed at the ADAS Analytical Chemistry Laboratory, Wolverhampton. Plant sap analysis was also performed on guard plot leaf samples at the States of Guernsey Horticultural Advisory Service. Leaf tissue samples were analysed using a 1 : 10 macerated water extract (Smith, 1988). Fully expanded, new leaves were sampled from the guard plots every four weeks. The total nutrient content of each substrate was determined by nitric acid digestion on samples before and after use.

RESULTS

Crop yields

Yield to October 1994 is given in Table 4 a and 4 b. The highest monthly fruit weight was recorded from plants growing in Hydrocult F. The analysis of variance of fruit weight demonstrated that the treatments were highly statistically significant ($p < 0.001$) for all six harvest dates.

Chemical analysis

Irrigation water

The analysis of irrigation water over the sampling period revealed a conductivity range of 55 to 405 $\mu\text{S}/\text{cm}$, a nitrate-nitrogen range of 0.5 to

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6.0 mg per litre, a phosphorus content of 0.5 mg per litre, a potassium range of 3.0 to 9.0 mg per litre, a calcium range of 1.3 to 21.8 mg per litre and a sodium range of 8.0 to 40.0 mg per litre. The ranges are given over a six month sampling period (Table 5). There were no notable fluctuations in the macro- or micro-nutrient content of the irrigation water throughout the sampling period.

Table 5. Concentration of nutrients in the irrigation water

	18 May	20 June	11 July	4 Sept.	19 Sept.	2 Oct.
pH	7.2	6.9	6.8	7.2	7.2	7.0
EC (μ S)	192	250	405	189	190	143
<hr/>						
	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
NH ₄ -N	0.5	0.5	0.5	0.5	0.5	0.5
NO ₃ -N	6.0	0.5	0.5	2.0	1.0	1
P	0.5	0.5	0.5	0.5	0.5	0.5
K	3	5	9	4	4	4
Ca	7.5	14.0	21.8	11.9	10.6	9.6
Mg	3	7	10	5	5	4
Na	12	24	33	18	17	16
Cl	30	35	46	28	33	21
S	5	12	19	5	5	5
Fe	0.20	0.33	0.16	0.18	0.14	0.05
Mn	0.05	0.05	0.05	0.05	0.05	0.05
Cu	0.020	0.005	0.005	0.005	0.005	0.005
Zn	0.020	0.020	0.020	0.005	0.030	0.005
B	0.01	0.02	0.04	0.02	0.01	0.01
HCO ₃	68	59	65	25	26	34

Drainwater

Analysis of the drainwater was expressed as the difference between the concentration of the irrigation water and drainwater. Data are presented for the major nutrients at intervals during the experiment (Table 6 a, b and c).

Table 6 a. Nutrients in drainwater minus irrigation water for unloaded zeolite

	4 May	18 May	21 June	6 July	21 July	6 Sept.	20 Sept.	4 Oct.
pH	0	-0.3	0.3	-0.4	0.1	-0.2	-0.1	-0.1
EC (μ S)	5	-10	-10	-8.2	-46	26	-9	1

	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
NH ₄ -N	0.5	0	0	0	0	0	0	0
NO ₃ -N	0	-1	2.5	-2	0	1	0	-0.5
P	0	0	0	0	0	0	0	0
K	2	2	1	1	1	4	1	0
Ca	0.2	-0.5	0.6	0.8	0.4	0.7	0.2	-1.2
Mg	0.5	-2.5	-1	-2	-1	1	0	0
Na	2	5	-3	-2	1	3	1	0
Cl	0	-1	-1	3	0	2	7	10
S	0	0	0	0	-1	5	0	0
Fe	0.42	-0.07	-0.28	-0.1	-0.11	-0.13	-0.09	0
Mn	0	0	0	0	0	0	0	0
Cu	0	0	0	0	0	0.005	0	0
Zn	-0.005	-0.01	-0.01	0.095	.0	0.005	-0.01	0
B	0	0.08	0.01	-0.01	0	0	0	0
H ₂ CO ₃	2	0	-5	-	-12	2	1	11

There was no change in the concentration of unloaded zeolite drainwater phosphorus and only a slight increase in drainwater ammonium-nitrogen in early May. The level of potassium in the drainwater was consistently higher than in the irrigation water but of a low concentration (1 - 4 mg/l).

With the Hydrocult S treatments, there was a slight increase in the conductivity of the drainwater in early May; thereafter, drainwater conductivity level was consistently lower than the irrigation water. After a slight increase of ammonium-nitrogen and phosphorus in early May, there were no differences in drainwater concentration throughout the remainder of the experimental period.

For the Hydrocult F treatments, there was a larger increase in the conductivity of the drainwater in early May; thereafter, drainwater conduc-

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tivity levels were consistently lower. Higher levels of phosphorus and calcium were present in the Hydrocult F drainwater compared with Hydrocult S in May but, thereafter, levels of potassium and calcium were generally lower in the drainwater than in the irrigation water.

Table 6 b. Nutrients in drainwater minus irrigation water for Hydrocult S

	4 May	18 May	21 June	6 July	21 July	6 Sept.	20 Sept.	4 Oct.
pH	-0.9	-2.1	-0.1	-0.4	0	-0.3	-0.2	0
EC (μ S)	5	-26	-40	-93	-54	-7	-17	-6

	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
NH ₄ -N	0.5	0	0	0	0	0	0	0
NO ₃ -N	0	-2	0	-3	0	-1	1	-0.5
P	1.5	0	0	0	0	0	0	0
K	1	-1	-2	-2	-3	0	1	-1
Ca	-0.1	-2.4	-2.9	-1.8	-1.5	-1.1	0.6	-1.9
Mg	0.5	-2.5	-1	-1	-1	0	0	-1
Na	1	0	-3	1	2	1	1	0
Cl	-4	-1	-1	4	1	-2	3	7
S	0	0	-1	0	0	0	0	0
Fe	0	-0.15	-0.28	-0.1	-0.11	0.13	-0.09	0
Mn	0	0	0	0	0	0	0	0
Cu	0	0	0	0	0	0	0	0
Zn	-0.005	0.02	-0.01	0.075	0	0.005	0	0
B	0	0	-0.01	-0.01	-0.01	0	0	0
H ₂ CO ₃	-1	-14	9	-	-21	4	1	-2

Plant samples

Total plant nitrogen levels decreased on the unloaded clinoptilolite treatment in May and then increased slightly over the period June to August. Total plant nitrogen level increased consistently over the period May to August in the Hydrocult treatments (Fig. 1) with Hydrocult F accumulating more plant nitrogen than Hydrocult S.

Total plant phosphorus level was consistently lower than the propagation

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content in the unloaded clinoptilolite treatment, whereas it increased consistently in the Hydrocult S and F treatments from 55.82 mg per plant to 422.9 and 837.61 mg per plant, respectively (Fig. 2).

Table 6 c. Drainwater minus irrigation water, data for Hydrocult F

	4 May	18 May	21 June	6 July	21 July	6 Sept.	20 Sept.	4 Oct.
pH	-0.7	-1.8	0	-0.9	-0.2	-0.8	-0.7	0
EC (µS)	35	-26	-20	-110	-51	-1	-18	-13

	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
NH ₄ -N	1.5	1.5	0	0	0	3.5	0	0
NO ₃ -N	0	-2	0	-3.5	0	-1.5	-0.5	-0.5
P	9.5	0.5	0	0	0	9.5	0	0
K	2	1	-1	-3	-3	0	-1	1
Ca	2.7	-0.4	-1.4	-2.3	-1	-2.6	-1.5	-2.1
Mg	0	-2.5	-1	-1	-1	0	-1	-1
Na	3	-3	-2	-4	3	5	3	2
Cl	-2	-1	0	1	3	4	3	3
S	0	0	0	-1	1	5	0	0
Fe	0	-0.08	-0.22	-0.1	-0.11	-0.03	-0.09	0
Mn	0	0	0	0	0	0	0	0
Cu	0	-0.015	0	0.005	0.005	0	0	0
Zn	-0.005	0.03	0	0.135	0	0.35	-0.01	0.005
B	0	0	0	-0.01	-0.01	-0.01	0	0
H ₂ CO ₃	3	-19	4	-	-28	-2	-9	-5

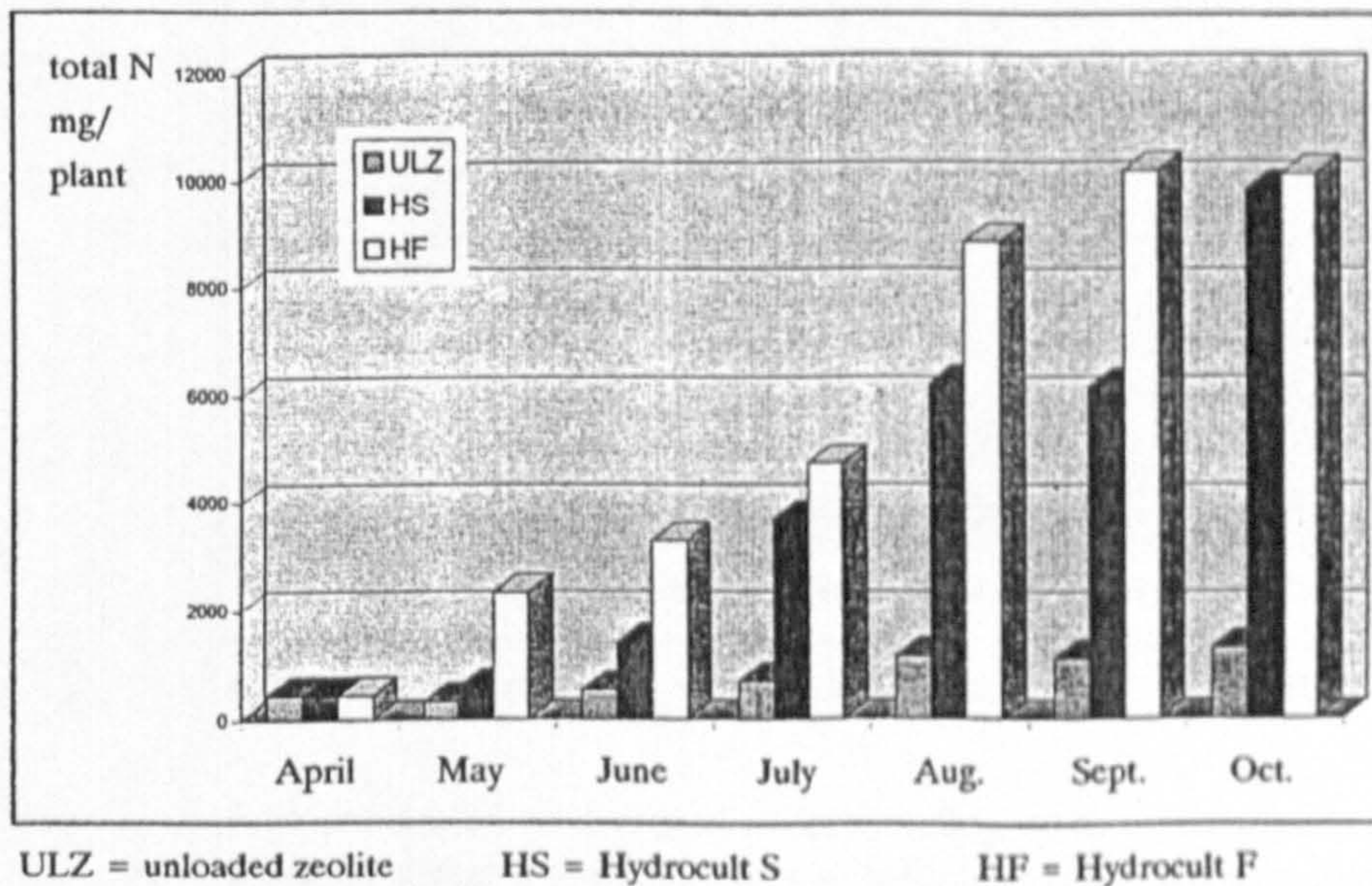
Total plant potassium level increased slightly in the unloaded clinoptilolite from an initial total potassium concentration of 574 mg per plant in April to 1,464 mg per plant in October (Fig. 3). In comparison, total plant potassium content increased in the Hydrocult S and F treatments to 13,39 g per plant and 15,848.46 mg per plant, respectively.

Substrate samples

Sodium extraction analysis results showed lower levels of ammonium-nitrogen in the used, nutrient-loaded samples and an increase in ammo-

nium nitrogen content in the used, unloaded clinoptilolite (Fig. 4). Nitric acid digestion analysis results from all three substrates revealed lower level of phosphorus and potassium in the used samples (Fig. 5 and 6). In comparison, calcium level was lower and magnesium level was higher in all of the used samples.

Fig. 1. Comparison plant nitrogen content unloaded and nutrient loaded zeolite

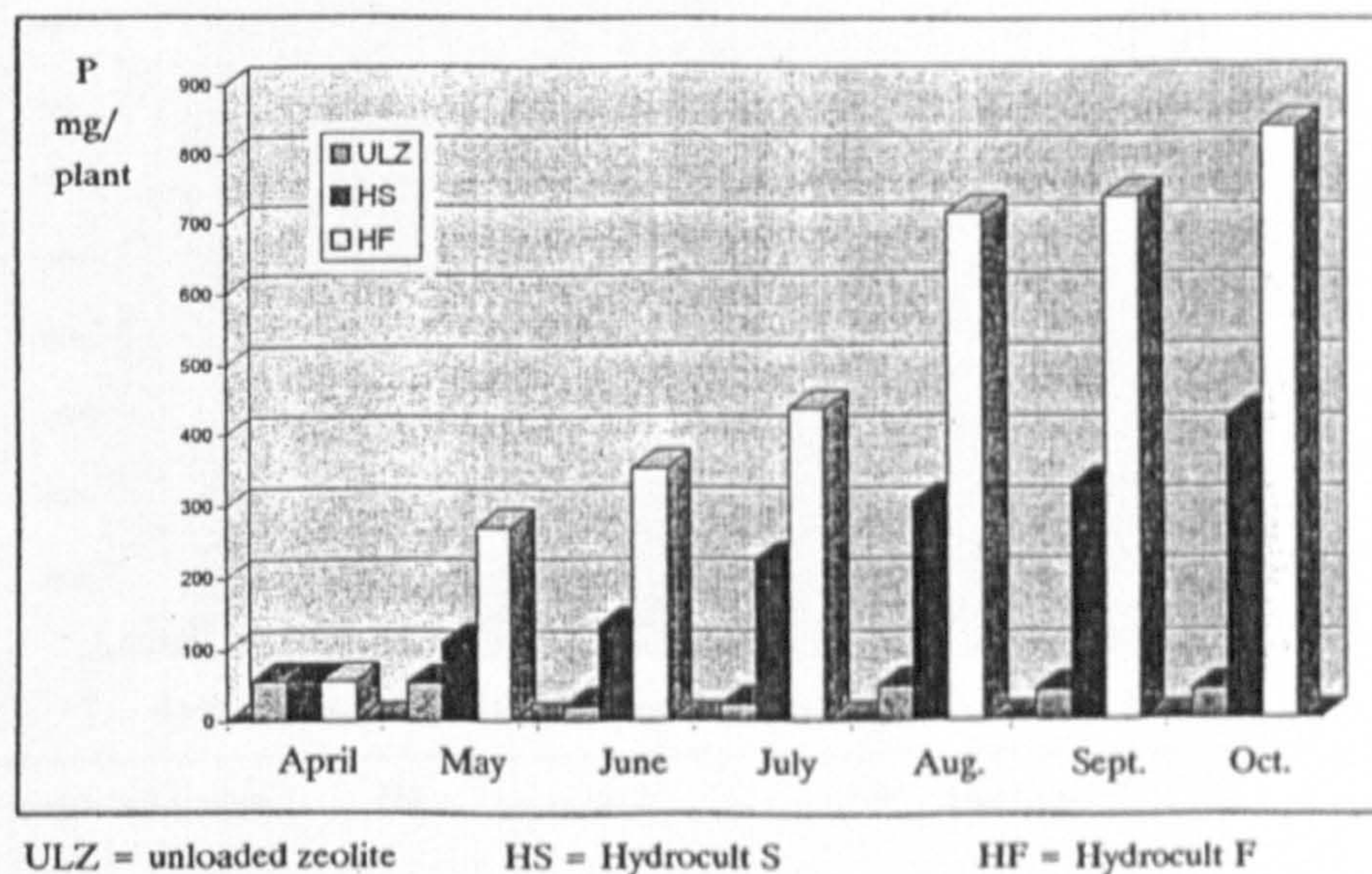


DISCUSSION

As expected, a very low fruit yield resulted from the pepper plants grown on unloaded clinoptilolite. Plant leaf tissue quickly exhibited signs of nitrogen deficiency and plant growth was very slow. Premature leaf senescence was visible throughout the experiment and plants remained pale yellow in colour and stunted. Plant analysis determinations revealed deficiency in all major nutrients. Crop yield was only 4 % of a commercial crop at 0.40 kg/m². Availability of nitrogen was a limiting factor to plant growth and the yield of pepper plants grown on Hydrocult S. Fruit yield

was 3.89 kg/m², only 39 % of a commercial crop. In comparison, plants grown on Hydrocult F gave commercially acceptable yields (10.46 kg/m²) of good quality sweet peppers, equivalent to an April-planted, soil-grown, commercial crop.

Fig. 2. Comparison plant P content unloaded and nutrient loaded zeolite

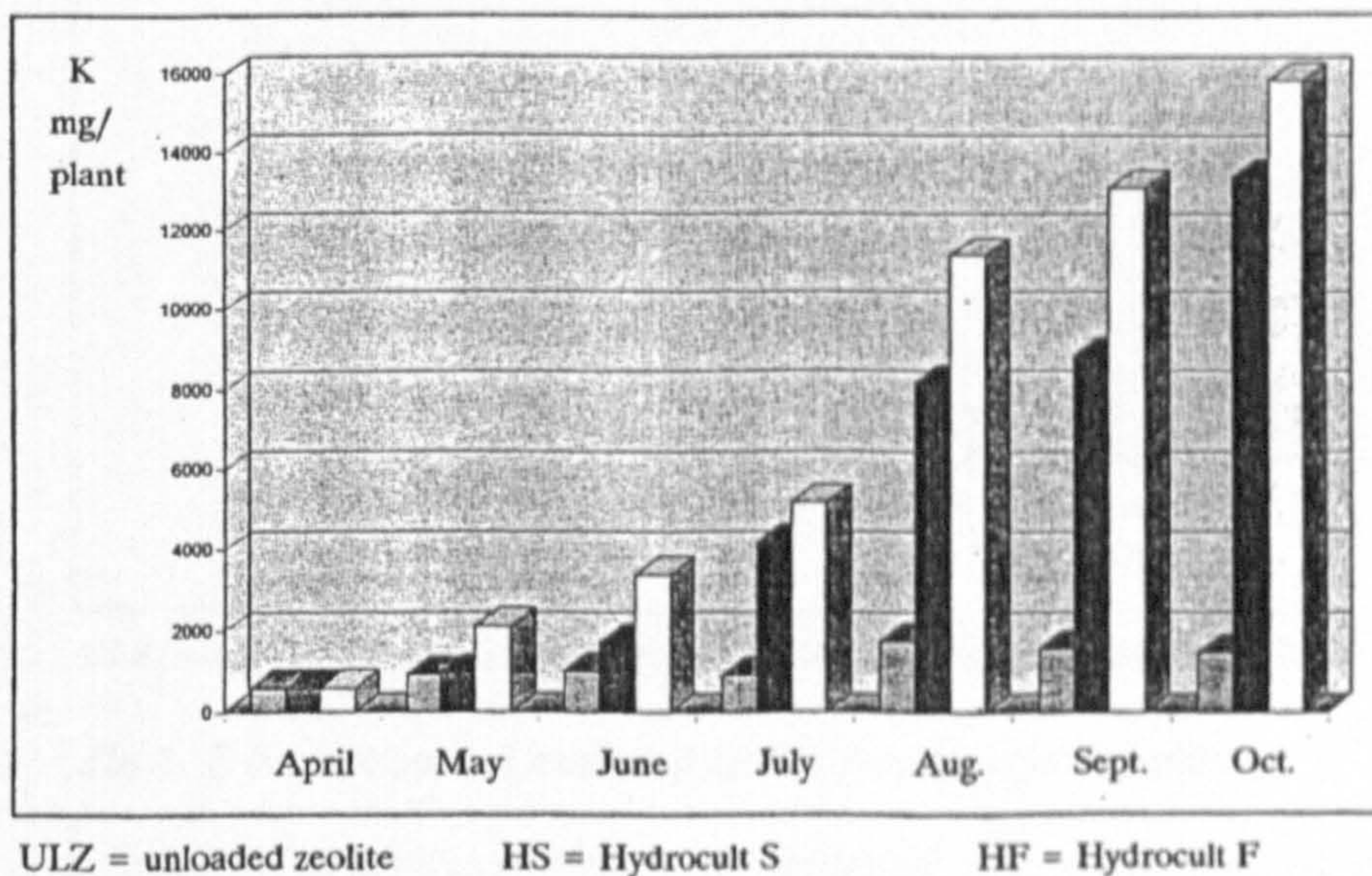


It is concluded that the substrate loading of ammonium-nitrogen was the main limiting nutritional factor affecting plant growth and crop yield. Results suggest that even on the high nutrient-loaded clinoptilolite (Hydrocult F), there was a restriction of plant available nitrogen towards the end of the experiment with a plateauing of plant nitrogen content between September and October. This did not, however, adversely affect the cropping of plants on Hydrocult F.

These results emphasise the remarkable properties of nutrient-loaded clinoptilolites. Using only water in the irrigation system, commercial yields could be obtained with sweet peppers, provided that clinoptilolite was loaded with a high level of ammonium-nitrogen prior to use. One problem with such a substrate is that it could have a high potential leaching risk. However, analyses of drainwater showed that there was

little or no loss of nutrients in the drainwater. Indeed, for most cations, an uptake from the irrigation water to the clinoptilolite was recorded, resulting effectively in a deionisation of the irrigation water. Such cations then became available for plant uptake via root exchange, as inferred by the increase in plant nitrogen of plants grown on unloaded clinoptilolite.

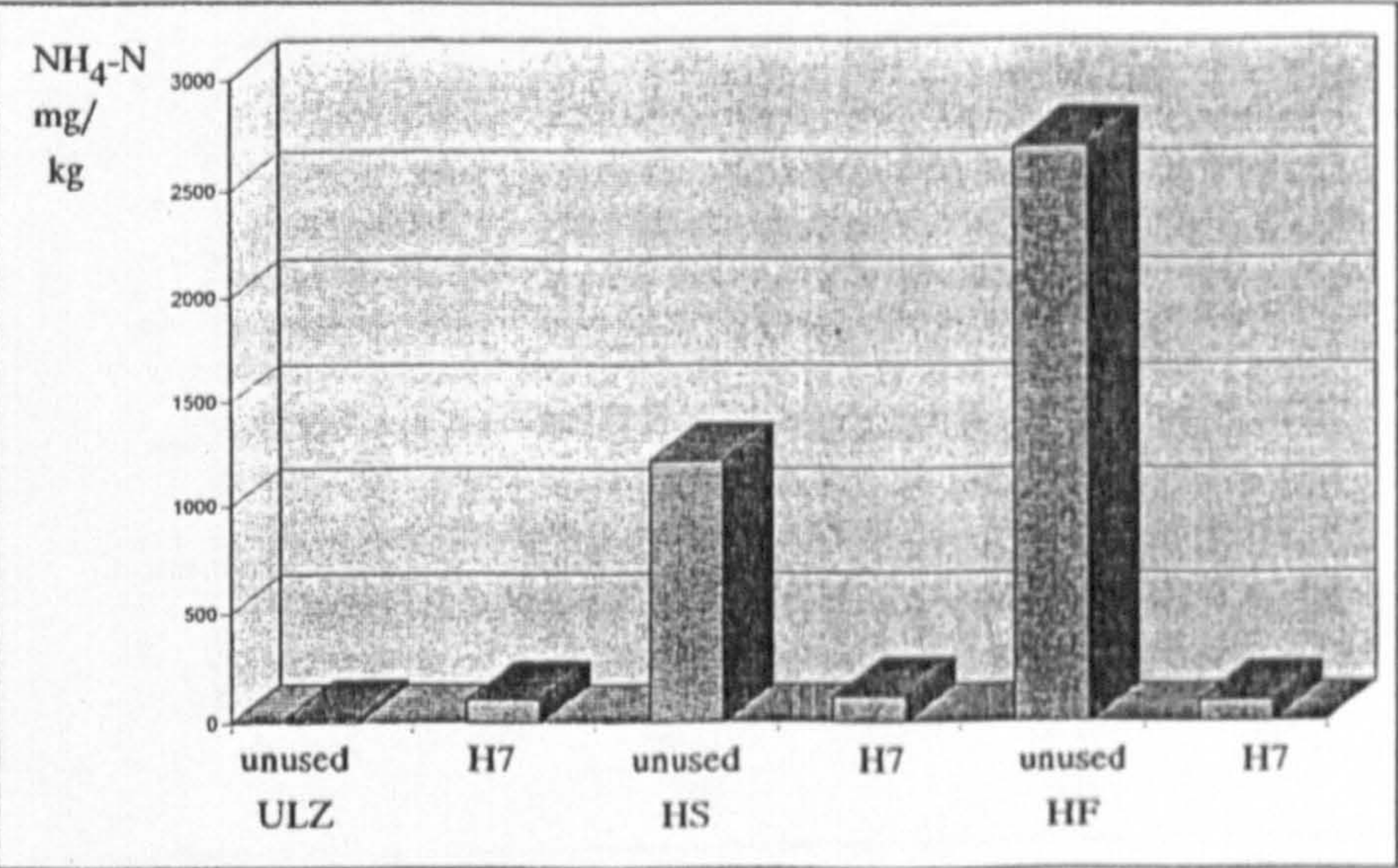
Fig. 3. Comparison plant K content in unloaded and nutrient loaded zeolite



As phosphorus is not held as a cation within the zeolite matrix, an initial release of phosphorus from the root zone was expected and detected on the Hydrocult treatments. No phosphorus deficiency symptoms, however, were evident on the hydrocult grown plants. After the initial release of phosphorus, the level of drainwater nutrients was small. There was a consistently higher level of drainwater potassium from the unloaded clinoptilolite substrate, compared to the Hydrocult substrates. The breakdown of apatite, present in the clinoptilolite substrates, would have provided a slow release supply of phosphorus to the plants.

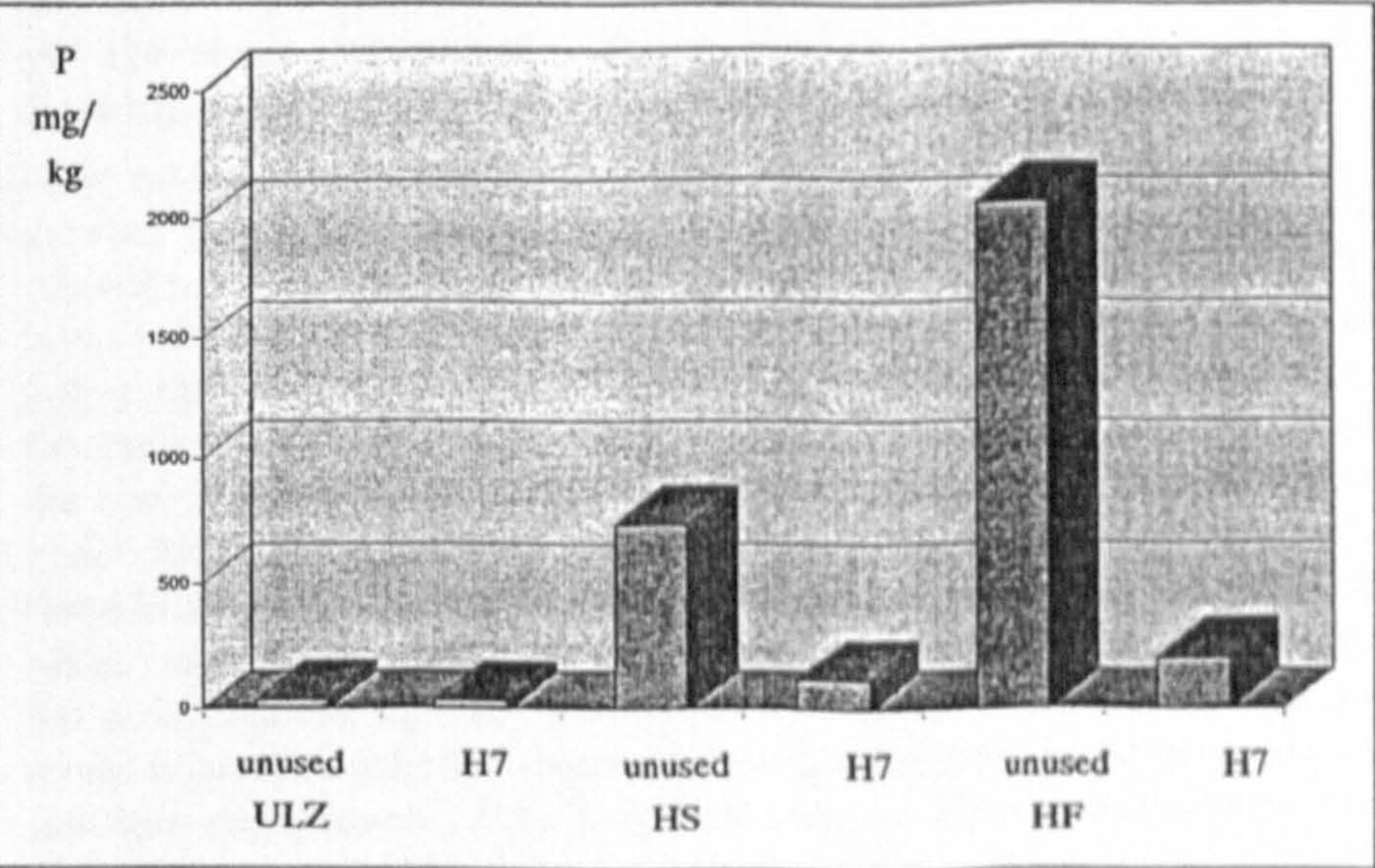
The cation exchange process mechanism would appear to involve potassium, calcium, sodium and magnesium as major participants and both unloaded and loaded clinoptilolites contained higher magnesium levels at the end of the experiment.

Fig. 4. $\text{NH}_4\text{-N}$ content unused and used zeolite by sodium extraction



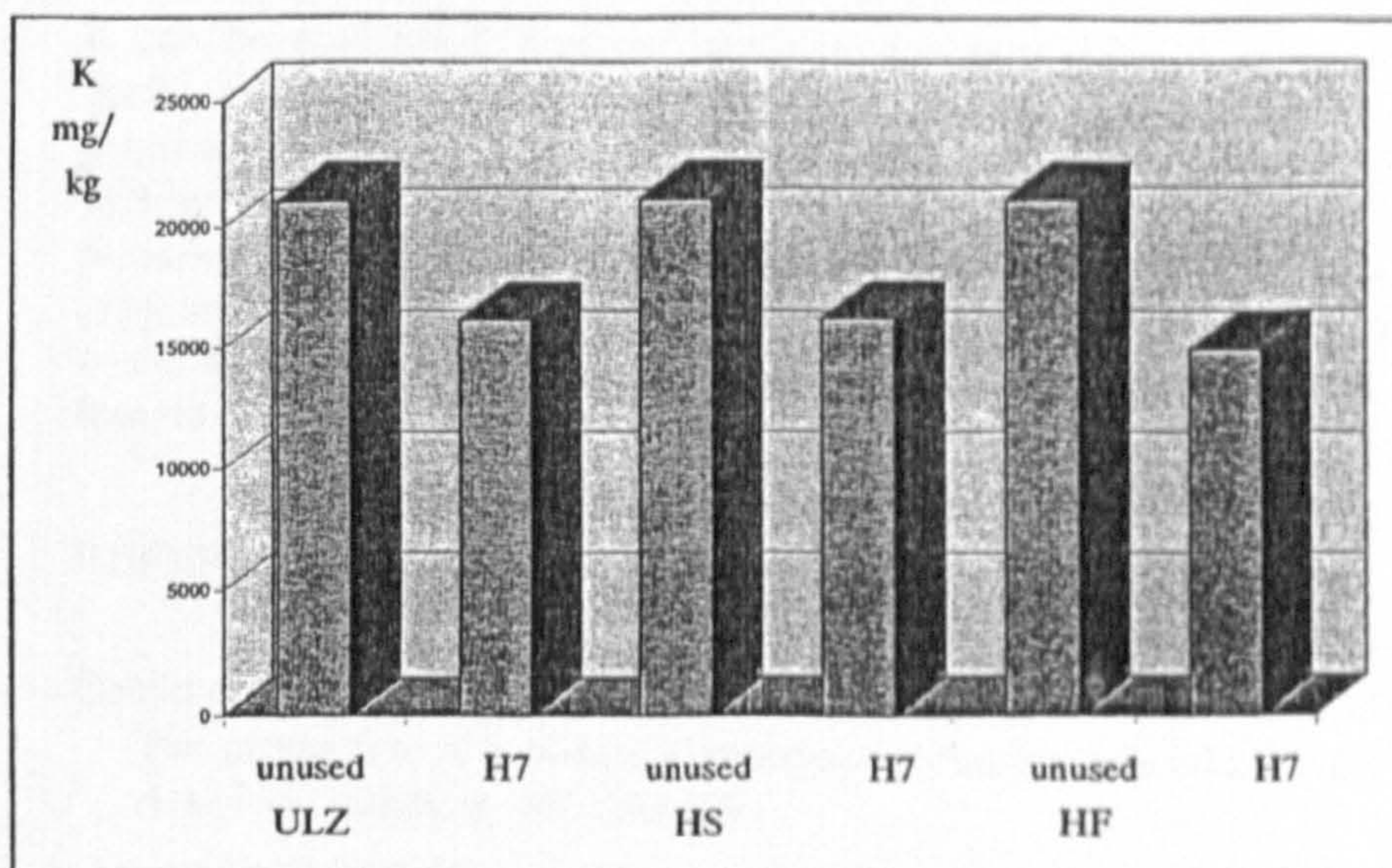
ULZ = unloaded zeolite; HS = Hydrocult S; HF = Hydrocult F; H7 = at final harvest

Fig. 5. P content unused and used zeolite by nitric acid digestion



ULZ = unloaded zeolite; HS = Hydrocult S; HF = Hydrocult F; H7 = at final harvest

Fig. 6. K content unused and used zeolite by nitric acid digestion



ULZ = unloaded zeolite; HS = Hydrocult S; HF = Hydrocult F; H7 = at final harvest

There would have been some movement of nutrients from the propagation blocks into the substrate at the beginning of the experiment in April and the small reservoir of nutrients held in the rockwool would have diminished rapidly.

Plant establishment relied on the control and maintenance of moisture in the root zone. Particle size distribution was slightly different in the three substrates, resulting in differences in moisture holding capacity. Prevention of drying of the substrate at the pot surface was partly aided by the poly-propylene pot covers but there remained a layer of clinoptilolite at the surface that was continuously dry and, therefore, not contributing to the root zone ion exchange mechanisms. Positioning the rockwool propagation blocks on the substrate surface, thus maintaining the pot volume at three litres, would have reduced the exposed substrate surface area from which water could evaporate. Early rooting into the substrate was rapid but it is possible that uneven distribution of water throughout the substrate volume could have impeded root development in April, before the full-time engagement of the irrigation system. Better control over water distribution in the compartment and computer-aided adjustments to the environmental parameters could have improved crop management.

CONCLUSION

It can be concluded that nutrient-loaded clinoptilolite is a potentially useful substrate for glasshouse systems. It offers the opportunity for growing crops in an environmentally-friendly, water-only delivery system without jeopardising crop yield or producing polluted waste water. The material has been shown to be acceptable in a high nitrogen demanding crop, sweet peppers, and other results from our research show it is equally useful for low and high nutrient demanding crops such as carnation and tomato.

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SUMMARY

Pepper plants, cv. 'Mazurka' (Rijk Zwaan) were cultivated in three litre pots containing unloaded clinoptilolite or one of two nutrient-loaded clinoptilolites (Hydrocult S and Hydrocult F). Plants were irrigated with water only over a six month period, using a mixture of reservoir and borehole water. Analyses completed on the input irrigation water and the subsequent drainwater showed an initial release of phosphorus, particularly from Hydrocult F. Thereafter, the drainwater samples contained negligible levels of nutrients. Plants grown on Hydrocult F (high nutrient-loaded clinoptilolite) contained the highest quantities of total nitrogen, phosphorus and potassium. Acid digestions of unused and used substrate samples revealed lower concentrations of phosphorus and potassium in the substrates at the end of the experiment.

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