Recycling waste nutrients in piggery effluent using dietary natural zeolite

by
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Photo source: Jo Brown 2008

A dissertation submitted in partial fulfilment of the requirements for the degree of

Master of Sustainable Agriculture

Charles Sturt University

January 2009

Abstract

Over half of the nutrients fed to pigs are excreted. This is a problem for the pork industry in Australia and overseas as the excretions can have serious environmental impacts, with N, P, K, Cu and Zn being of greatest concern. There is opportunity to recycle excreted waste nutrients by using dietary natural zeolite to effectively treat piggery effluent, enabling safe storage and slurry spreading as fertiliser.

Applications of natural zeolite vary from handling radio-active waste to horticulture and agriculture. This dissertation examines the use of dietary clinoptilolite (a type of natural zeolite) in piggery effluent management to enhance its fertiliser value.

There are many nutrient loss pathways in storing and spreading piggery effluent slurry. The author views lost nutrients as a loss in fertiliser value and a lost opportunity to make use of this valuable organic fertiliser. Understanding and using dietary clinoptilolite technology aids in maximising fertiliser value and minimising environmental impacts. The technology may be considered part of a process known as environmental nutrition, which includes the reduction of waste nutrients through dietary means. This dissertation develops such an understanding using an extensive literature review and case study to explore where, how and why nutrient losses occur. It then explores the value of dietary clinoptilolite in piggery effluent management.

The research shows that formulating pig rations with dietary clinoptilolite powder (particle size $\leq$ 76 µm to 5 µm), is a safe, convenient and effective way of recycling nutrients from piggery effluent and reducing N losses, in particular. Gowrie EcoFarm is a practical demonstration of this technology. Experience and trial work, under veterinary supervision, has led to the following maximum inclusion rates by weight for powdered clinoptilolite in pig diet formulation: weaners 5%, growers 2.5% and breeders 1%.

In summary, the study shows that there is potential for widespread adoption of dietary clinoptilolite technology in the Australian pork industry, especially as fertiliser prices are increasing rapidly, land is usually available on pig farms for slurry spreading, and soils are often infertile and require building up, in terms of chemical, physical and biological fertility.

Declaration

I certify that this dissertation does not incorporate, without acknowledgement, any material previously submitted for a degree or diploma in any university. It does not contain any previously published or written material by another person except where due reference is made in the text.

This dissertation does not exceed 15,000 words

Signed

Ken Crawford

Disclaimer

This dissertation is released as commercial and in confidence.

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Ken Crawford 2009

Acknowledgements

I wish to acknowledge the support of my wife, Sue Crawford, who more than anyone else had to live the zeolite story, sometimes night and day. I extend my thanks to my Supervisor, Dr Judith Crockett and Dr Vera Banks who transformed my journalistic style of writing into an acceptable style of scholarly writing. This was by no means a small task. They also edited my work and gave me much encouragement for which I am grateful.

My daughter, Rachel Gilmore gave me much support and encouragement and her attention to detail was invaluable in the on-farm trial work.

I acknowledge my nine year old grandson, Solomon, and his continual promptings, 'how many words have you written now Pa?' Solomon also provided much stimulus by continually asking questions that required logically sequenced answers. This greatly assisted my writing style and prevented my bipolar mind getting too far ahead of what I was actually saying and eventually wrote. My Life-Coach, Dr Mark Shillito, was extremely impressed with Solomon's strategy. I also thank Mark for his unwavering faith in my ability to complete a Master's degree.

I thank Ian Kruger, from NSW DPI for personal communications and assistance regarding effluent management, particularly in regard to Gowrie EcoFarm.

I thank Bruce Edgerton and Donna Schmid from Australian Pork Limited (APL), for supplying many literature and workshop resources. I truly appreciated this assistance from my own industry. I thank Dr Roger Campbell, CEO of Pork CRC for taking an interest in my zeolite research and sharing his knowledge of balancing energy in pig diets.

Dr Roger Giles of Elizabeth Macarthur Agricultural Institute (EMAI) in Camden, NSW assisted me greatly with pig growth trial work using dietary natural zeolite in 2004. This trial built a strong foundation for other research projects using dietary natural zeolite.

Hanne Hoelaas, Charles Sturt University, Librarian gave me much support with resource material and instruction in EndNote Version 11.

I wish to acknowledge Gordon Heath of Castle Mountain Zeolites who supplied me with powdered natural zeolite for all my research projects and Wolfgang and Nola Bredereck of Crystal Kingdom, Coonabarabran for the beautiful heulandite crystal.

Last of all, and most importantly, I wish to thank my Dad, Bruce Crawford, who taught me to love the land.

Preface

Together with my wife Sue, I have owned and managed Gowrie EcoFarm in Boggabri, NSW (Australia) for over 33 years. I have always had an interest in ecological agriculture and whole-farm sustainability.

Holistic planning and integrating pest management with nutrient management has enabled the soil-building process to continue year after year. At the same time optimal yields have been achieved to give the family a good standard of living.

Piggery effluent treated by formulating pig rations with dietary natural zeolite has, together with other management techniques, transformed the property from a single enterprise farm into an integrated, diversified and highly productive farm. Safe storage and spreading of treated effluent, in a timely manner, has resulted in a connected ecosystem of soil, plant and animal relationships. I have a decade of experience in recycling waste nutrients using dietary clinoptilolite (a volcanogenic form of natural zeolite).

My love of the land is also an integral part of my identity and who I am. I write this dissertation with the hope of inspiring others to reconnect with the land and enjoy the fulfilment that comes from working and living on the land.

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Chapter 1: Introduction

For a number of years the Australian national pig herd has been around 300,000 sows. The impacts of high feed costs and increasing imports of pork product resulting in an industry crisis have reduced this number to approximately 260,000 sows as of the end of June 2008 (Spencer, 2007/08). This has led to a sharp decline in the number of producers. However, the remaining producers are a dedicated group of experienced managers, well equipped to handle all aspects of animal care, feeding, housing, mating, farrowing and weaning. This is one of the main strengths of the industry.

One of the weaknesses in the Australian pork industry is that piggery waste nutrients have not been fully utilised (Crawford, 2005). There remains an opportunity to recycle nutrients in piggery effluent slurry as a valuable fertiliser for cropping. Land is usually available on Australian farms for spreading slurry and conventional housing and collection systems are ideal for storage.

World-wide there are approximately 1 billion pigs grown annually for meat production (Monteny, 2007). However, pig production contributes significantly to all kind of environmental and social issues. Pig slurry is often produced on 'landless' farms and has the potential to pollute surface and groundwater, particularly the nutrients N and P. Slurry has to be transported far away involving high costs and fuel consumption. Intensively housed animals also have the potential to create odour problems which is a social nuisance. And according to Monteny, ammonia contributes to eutrophication through acid rain and the formation of particulate matter (dust). This causes nutrient enrichment of vulnerable ecosystems (Monteny, 2007). Ammonia in the atmosphere is reacting with other chemical substances to form secondary particulate matter or fine dust particles. Since human health research has identified a relationship between particulate matter in the air and some major adverse health impacts, for example respiratory disease, focus is on ammonia as a health issue.

The expansion and concentration of the pig industry in many areas of the globe has caused increased concern about the disposal of effluent (Mullan, Hernandes, Souza & Pluske, 2005). Most attention has been given to the levels of N and P however, trace elements such as Cu and Zn are also important as they too can cause problems for aquatic organisms, grazing livestock and soil micro-organisms. With an estimated 60% of N and 80% of P that is fed to pigs being subsequently excreted, there is scope for improvement (Mullan et al.,2005).

Part of the solution to the problem of managing waste nutrients is to reduce the percentage excreted through dietary means. This concept is termed 'environmental nutrition' (Mullan & Henman, 2008). Replacing inorganic trace minerals with corresponding organic minerals in the diet is a good example of environmental nutrition. According to Mullan and Henman, less organic minerals can maintain or even improve pig performance with lower dietary levels because they are more efficiently utilised by animals, reduce mineral output.

In order to reduce N, P and trace elements in pig manure a better balance between nutrient supply and nutrient requirement is needed (Dourmad & Jondreville, 2006). Lowering the protein and phosphorus content of pig diets and using feed additives like amino acids or phytase are now becoming common in formulating pig rations is one way of achieving this. Feeding pigs with low N diets also allows a reduction in ammonia emission and malodorous compounds. The introduction of the concept of apparent P digestibility allows a reduction of the safety margins when formulating pig diets. Low digestibility remains the main problem although it has been improved by the use of microbial phytase.

Another dietary means of reducing the amount of nutrients excreted is the use of dietary clinoptilolite (a type of natural zeolite). Furthermore, once the manure is excreted the zeolite continues to adsorb the NH_4^+ ion (and thus reduce ammonia emissions) and K^+ us well as Cu^{2+} and Zn^{2+} (Castle Mountain Zeolites, 2004). A recent trial in Canada using clinoptilolite as a feed-additive for pigs to reduce manure mineral content resulted in manure with 15% and 22% less N and P, respectively compared to the control (Leung, Barrington, Wan, Zhao & El-Husseini, 2007). Another Canadian trial concluded that pig diets supplemented with clinoptilolite can lower the nutrient content without altering the physico-chemical properties of the manure in terms of viscosity and other handling characteristics (Tiwari, Barrington & Zhao, 2009).

The research objective of this dissertation is to answer the question: what is the suitability of dietary clinoptilolite, as an absorber and carrier of nutrients, to reduce the amount of nutrients excreted, to retain those nutrients in the effluent stream and to release those nutrients to crops after slurry application to land?

1.1 Structure of the dissertation

Chapter 2 of this dissertation examines the properties and applications of natural zeolites with particular emphasis on clinoptilolite as most of the recent research has been carried out using this type of zeolite (Mumpton, 1999; Tsitsishvili, Andronikashvili, Kirov & Filizova, 1992).

Chapter 3 examines piggery effluent nutrient loss pathways during storage and spreading by way of a literature review. NH_3 emissions will be the main focus of this section (Harper, Weaver & Dotson, 2006).

Chapter 4 develops the concept of blocking the nutrient loss pathways and recycling waste nutrients as valuable fertiliser. The whole-farm approach in nutrient management to minimise environmental impact and maximise fertiliser value is the methodology (Rotz, 2004: Petersen et al., 2007). Dietary solutions are examined, including the use of dietary clinoptilolite to **reduce** the amount of nutrients excreted, to **retain** those nutrients in the effluent stream and to **release** them to crops after slurry application to land.

Chapter 5 is a case-study of a decade of dietary clinoptilolite usage. This practical demonstration on Gowrie EcoFarm supports the view that dietary clinoptilolite has potential for widespread adoption in the Australian pork industry. While much of this evidence is anecdotal, the results achieved on this diversified, integrated farm should encourage further investigation into the use of clinoptilolite as a feed-additive.

Chapter 6 is discussion and Chapter 7 is the conclusion and recommendations.

Chapter 2: Natural zeolites

Background

Natural zeolites are hydrated aluminosilicate rock minerals (Mumpton, 1999). Since their discovery, approximately 250 years ago, geologists considered the zeolite minerals generally to occur as large crystals in the vugs and cavities of basalts and other traprock formations. They were prized by mineral collectors and not used commercially because of lack of quantity and their polymineralic nature (Mumpton, 1999; Colella & Gualtieri, 2006; Pabalan, 2006; Tchernev, 2006; Wise, 2006).

As the synthetic zeolite industry gained momentum in the late 1950s, for industrial use as ‘molecular sieves’, extensive sedimentary beds of natural zeolite were discovered in the western USA Australia and New Zealand (Mumpton, 1999). Natural zeolites were formed by the alteration of volcanic ash in lake and marine environments. Often these deposits contained a high percentage of the one zeolite (for example clinoptilolite) and were able to be mined economically because recovery costs were not prohibitive. The rock mineral is usually blasted from the deposit with explosives and taken to the mill for processing. Here it is crushed and hammer-milled before entering a ball-mill for further refining to a powdered state (Plate 1). The process is relatively cheap compared to producing synthetic zeolites.

Plate 1: Ball mill used to reduce crushed rock to powder (photo source: Gordon Heath, 2009).

Worldwide, there are over 40 types of natural zeolite, the most well-known including clinoptilolite, chabazite, analcime, erionite, faujasite, ferrierite, heulandite, laumonitte, mordenite, and phillipsite (Mumpton, 1999). The main natural zeolite mines in Australia are at Quirindi and Werris Creek in NSW and near Emerald in Qld. These areas are associated with ancient volcanic activity.

Plate 2a is an example of the rock mineral clinoptilolite, a crystal mineral heulandite is shown in Plate 2b (a collectors item). Both specimens are chemically similar, however, this dissertation focuses on clinoptilolite because it can be mined economically in contrast to heulandite. The remainder of this chapter deals with the properties and applications of clinoptilolite.

Plate 2a: Clinoptilolite from Castle Mountain deposit near Quirindi (NSW) (photo source: Ken Crawford, 2008).

Plate 2b: Heulandite from Crystal Kingdom, Coonabarabran (NSW) (photo source: Ken Crawford, 2008).

2.1 Properties of Clinoptilolite

Clinoptilolite has unique chemical and physical properties that make it useful in solving many environmental problems including reducing offensive odours and effluent management (Mumpton, 1999).

2.1.1 Structure and Chemical composition

A feature of all zeolite structures is an aluminosilicate framework composed of three dimensional (Si, Al) O_4 tetrahedra (Dana, 1959). Each oxygen atom is shared by two SiO_4 tetrahedra. The net negative charge of the framework, caused by the presence of aluminium, is balanced by the presence of cations, or positively charged ions (Giles, 2004). Ca^{2+}, Na^+ or K^+ ions are situated within the cavities of the zeolite depending on the environment of formation of the mineral (Deer, Howie, & Zussman, 1970). In the case of volcanic sedimentary crystallised beds the Na^+ is dominant in a marine environment and Ca^+ is dominant in a brackish to fresh water environment. The availability of Na^+ or Ca^{2+} cations to balance the negative charge of the clinoptilolite structure determines whether a Ca-clinoptilolite or a Na-clinoptilolite is formed. They are both used commercially and the fact that they can be modified by exchanging cations, particularly in the presence of surfactants, gives flexibility to their use. Surfactant modified zeolite will be further discussed in chapter 5. Ca-dominated clinoptilolite is typically expressed as $(Ca_{0,5},Na,K)_{4,5}Al_9Si_{27}O_{72}.24H_2O$ (Korbel & Novak, 1999).

Cations with ionic radii smaller than clinoptilolite channels can be selectively adsorbed, for example NH_4^+ and K^+. This is why clinoptilolite is termed a ‘molecular sieve’ (Tsitsishvili, Kirov & Filizova, 1992b). Based on these characteristics, clinoptilolite has many important industrial and specialised applications (Section 2.2).

2.1.2 Physical properties

Clinoptilolite varies in hardness between 3.5 and 5.5 on the Moh’s hardness scale (Mumpton, 1999). Specific gravity varies between 2.0 and 2.4 and pH varies between deposits and ranges from 7-9. Colour varies from green to grey to pink/red. The red colour, for example, is due to the presence of iron hydroxide. Clinoptilolite is micro-porous. When it is heated, the water in the channel-ways is given off easily and continuously as the temperature rises, leaving the structure intact. This contrasts with other hydrated compounds such as gypsum, in which the water molecules play a structural role and dehydration produces structural collapse. After dehydration clinoptilolite may be filled again with water or rehydrated. This reversible rehydration is an important and unique property of clinoptilolite and is one of the reasons for its many applications in agriculture. Water may pass through the channel ways allowing ions in solution to be exchanged for ions in the structure. This process is termed ‘base exchange’ or ‘cation exchange’ (Dana, 1959). This property is very important for effluent treatment, as explained in chapter 4.

2.1.3 Cation Exchange Capacity

The Cation Exchange Capacity (CEC) is a measure of the total of exchangeable cations that a material can adsorb (APL, 2004). The CEC of clinoptilolite samples from deposits world-wide, including Australia, varies with each deposit. For example, samples from Australian deposits have recorded CECs (sum of bases plus NH_4^+ adsorption) approaching 180 meq/100g (Appendix 1). This is good even by world standards. It is important in zeolite research to specify from which deposit the zeolite comes from for the above reason. A particle size analysis of the reference sample is also important as this affects the effectiveness of the zeolite for the purpose of adsorbing cations. The greater surface area in the finer samples aids adsorption (Leung, Barrington, Wan, Zhao & El-Husseini, 2007).

2.2 Applications of clinoptilolite

One of the most respected authors on applications of clinoptilolite worldwide was Fred Mumpton. Much of this section is based on Mumpton (1999).

Applications include dietary use in animal husbandry, in animal housing as bedding or as a component of bedding material. Clinoptilolite is used as a water filtration medium, in treating sewage sludge, in horticulture and mining, aquaculture and liquid effluent treatment. Consequently clinoptilolite often becomes part of the solution to environmental problems.

2.2.1 Animal bedding

Clinoptilolite, with its high moisture absorption property, is widely used for animal bedding and protection of the environment by readily adsorbing NH_3 (Tsitsishvili et al., 1992). Ammonia NH_3 emissions are greatly reduced when clinoptilolite is included as a component of animal bedding and animal health benefits include reduced incidence of pneumonia and other lung diseases in intensively housed animals.

2.2.2 Filtration media

Large scale cation-exchange processes using natural zeolite were first developed to filter municipal wastewater by Ames and Mercer in 1967. Clinoptilolite was used to extract NH_4^+ from waste water streams (Ames, 1967; Mercer, Ames, Touhill, Van Slyke & Dean 1970).

2.2.3 Heavy metal removal

Cu^{2+}, Ni^{2+} Zn^{2+}, Pb^{2+} and other heavy metals can pose a serious threat to the environment if discharged untreated (Morah, Cagun, & Imamaglu, 2006). Clinoptilolite has been used in Turkey, and in other parts of the world, to remove these heavy metals from aqueous solution. The capacities obtained in this study to adsorb heavy metals look promising. However, clinoptilolite exhibits different removal capacities for different heavy metals in the order $Pb^{2+} > Ni^{2+} \sim Cu^{2+} > Zn^{2+}$ (Morah et al., 2006).

2.2.4 Treatment of radio-active waste

The nuclear industry and nuclear energy programs require solutions to problems associated with the development of cheap methods for the purification of radio-active waste. Research is continuing in three areas: extraction of radioactive elements from effluents of high activity, deactivation (decontamination) of low and medium activity effluents and the concentration of radioactive effluents for long-term storage (Tsitsishvili et al., 1992 b).

Cs^+ and Sr^{2+} ion exchange properties of irradiated and chemically modified clinoptilolite were found to be effective in the treatment of radio-active waste (Akhalbedashvili et al., 2006). Clinoptilolite is effective at removing Cs^+ from waste waters and other radiological decontamination applications (Chipera et al., 2006).

2.2.5 Aquaculture

Clinoptilolite is used in aquaculture in Australia and overseas to remove ammonia from fish tanks (Bower & Turner, 1982: Dryden & Weatherly, 1987). Ammonia build-up in fish tanks is detrimental to growth and productivity and can cause high mortality rates if not kept under control.

2.2.6 Agriculture and Horticulture

The addition of clinoptilolite to sandy- clay loam in Ukrainian soils increased the yields of potatoes, barley, clover, and wheat after adding 15 tonne/ ha (Mazur, Medvid & Gvigora, 1986). The addition of NH_4^+ loaded clinoptilolite in greenhouse experiments resulted in 59 % and 53 % increase in root weight of radishes in medium and light clay soils (Lewis, Moore, & Goldsberry, 1984). A 10% addition of clinoptilolite to sand used in golf-course green construction, reduced NO_3^- leaching and increased fertiliser N uptake (Huang & Petrovic, 1994)

2.2.7 Dietary use in animal husbandry

In the 1960's clinoptilolite tuffs were investigated as feed additives to poultry, cattle and pigs (Tsitsishvili, Andronikashvili, Kirov & Filizova, 1992a). Results of these trials appeared promising, in terms of increased daily gain, reduced mortality and general animal health. However further investigations were required to extend this early work. Up until the turn of the century, results from dietary clinoptilolite were varied. This could be a reason why dietary clinoptilolite has not been widely used until recently.

In Australia, KLC Environmental began experimenting with dietary clinoptilolite on Gowrie EcoFarm (northern NSW) in 1999. In preparation for a weaner pig trial at the Elizabeth Macarthur Institute, Giles (2004) undertook a review of the literature which revealed inconclusive results in terms of increase in daily gain with pigs whilst there was good evidence of odour control. Giles cited trials at the Clay Centre, Nebraska that indicated daily live weight of weaner pigs increased by 14% when fed 20 g/kg of clinoptilolite and that the source of the product and particle size affected the growth response (Pond & Yen, 1982; 1987). However, trials in New Zealand (Pearson, Smith & Fox 1985), Denmark (Poulson & Oksbjerg, 1995) and Italy (Malagutti, Zannotti, & Sciaraffia, 2002) showed that growth in pigs was unaffected by dietary clinoptilolite. Reasons as to why results may have varied are covered in the discussion (chapter 6).

The live performance trial of weaner pigs offered dietary zeolite was conducted at EMAI in Camden, NSW in 2004. The main finding was a significant ($P < 0.05$) 16% improvement in daily gain for weaner pigs offered 50g/kg dietary zeolite compared to the zero control diet (Giles, Barker, James & Brewster, 2005). The trial was repeated in a commercial piggery where a non-significant 10% increase in daily gain was recorded when weaner pigs were offered 50g/kg dietary zeolite compared to the zero control diet (Crawford & Gilmore, 2006).

Improvement in health and performance when poultry are fed dietary clinoptilolite is reported by Hale III (2006). According to his work, feeding clinoptilolite and acidogenic compounds to poultry significantly reduced NH_3 emissions. One combination comprising 5.25% $CaSO_4$ and 1.25% dietary clinoptilolite in a 2-months trial resulted in a 66% reduction. In an 11-months trial the reduction was 85%. At the end of the study the amended diet compared to the control increased manure N content by 37% (Hale III 2006, p.126).

2.2.8 Sewage sludge

Addition of powdered clinoptilolite to raw sewage aids in settling and sedimentation. Settling and concentrating nutrients in the sludge facilitates spreading as a fertiliser (Kallo, 1995). The addition of 30-40 g of powdered clinoptilolite of 40-160 μ grainsize to 1 m^3 of raw sewage before aerating the tank was found to (1) increase the oxygen consumption rate, ie the biological activity of the living sludge to a minimum of 25%, (2) cause an increase in the sedimentation rate because of suspended solids in the effluent after the secondary settling tank decreased and (3) decrease the mole ratio of added Fe to P from 2.0-2.5 to 1.2-1.8, ie similar amounts of P were removed using less Fe salts. The resulting sludge could be spread as a fertiliser. This process allows the concentrated sludge to be applied to the land with a spreader, while the diluent portion can be used safely as irrigation water (Kallo, 1995, pp. 341-350). This application is important in managing all types of animal and human effluent allowing large volumes to be handled in a practical manner.

2.2.9 Liquid effluent treatment for improving fertiliser/nutrient management

The high CEC of clinoptilolite allows exposure to effluent N resulting in NH_4^+ being adsorbed and carried by the zeolite crystal. This makes a slow release fertiliser that can be spread on cropping land where plants can use the sequestered NH_4^+ from the clinoptilolite (Barbarick and Pirela, 1984; Lewis, Moore & Goldsberry, 1984; Dwairi, 1998). Furthermore, the clinoptilolite reduces nitrate leaching by inhibiting nitrification of NH_4^+ to soluble NO_3^- (Perrin, Boettinger, Drost & Norton, 1998). Nitrification inhibition occurs because nitrifying bacteria are prevented from accessing the NH_4^+ by the restricted channel dimensions of the clinoptilolite (Mumpton, 1999).

Conventional intensive housing in the Australian pork industry allows the collection of liquid manure under the flooring. It is then flushed and drained into a storage pond to be finally spread on the soil as a slurry fertiliser. Dietary clinoptilolite is suitable for treatment and management of liquid effluent in such a context because of its convenient and effective way of introducing into the effluent stream. This application of clinoptilolite is the focus of this dissertation.

Conclusion: It is apparent from the above discussion on the properties and applications of clinoptilolite in agriculture and animal husbandry that its high CEC and NH_4^+ adsorption capacity and the ability to hydrate and rehydrate without structural collapse are critical factors. The latter property is unique to zeolites and is termed 'reversible rehydration'.

Before assessing the value of these characteristics in the management of piggery effluent it is first necessary to explore the nutrient loss pathways in effluent because it is important to know where losses may occur if clinoptilolite is also going to be successful in blocking them. This, and the potential value of piggery effluent slurry is considered in chapter 3.

Chapter 3: Piggery effluent nutrient loss pathways

There are many pathways by which nutrients may be lost from pig excreta (Rotz, 2004). These nutrients may impact upon the environment as well as representing a lost opportunity to recycle them as plant fertiliser. This chapter deals with nutrient loss pathways from piggery effluent. The focus will be on N losses and explains the four main nutrient loss pathways under field conditions: (1) NH_3 volatilisation (2) NO_3^- leaching below the root-zone of crops (3) denitrification and gaseous emissions 4) removal of N by plant uptake and harvest (Smith, 2001; Bolan, Saggar, Luo, Bhandral & Singh, 2004; Saggar, Bolan, Bhandral, Hedly & Lou, 2004).

3.1 NH_3 volatilisation

Volatilisation of NH_3 is the gaseous release of NH_3 from solution and takes place at the surface of an effluent pond or soil surface. NH_4^+- N often represents a major proportion (50-90%) of the N in piggery effluent and the pH is typically high (>8) (Smith, 2001; Plaza, Garcia-Gil & Polo, 2005). This results in approximately10% being in the NH_3-N form leading to a potential for NH_3 volatilisation (allowing for organic forms of N). Increases in temperature, pH, and NH_4^+ concentration will lead to a greater amount of NH_3 in soil solution. Subsequent volatilisation of NH_3 depends on its concentration at the soil surface and the air pressure between soil and atmosphere as determined by air temperature and wind velocity (Bolan et al., 2004; Saggar et al., 2004).

Mineralisation of urine and faecal N in pig slurries will further increase the amount of NH_4^+ in the soil and a large proportion will dissociate to NH_3 (Bolan et al.,2004; Saggar et al., 2004). Exposure of slurries to the atmosphere will determine the volatilisation loss, particularly with small droplets with a greater surface area (McGahan & Tucker, 2003). It is known that higher NH_3 volatilisation occurs when the pH of the slurry is also high (Kruger, Taylor & Ferrier, 1995; Chadwick, Martinez, Marol, & Beline, 2001; Saggar et al., 2004). Acidifying pig slurry causes a dramatic reduction of NH_3 emission (Pain et al., 1990; Nicks, 2006).

CEC of the soil is a very important factor influencing NH_3 volatilisation (Barkle, Brown, Stenger, & Palmer, 1999). Adsorption of NH_4^+ to negatively charged clay particles and organic matter occurs rapidly after effluent is applied to the land and consequently the amount of freely available NH_4^+ is reduced, thus reducing NH_3 volatilisation.

Adsorption is greatest when the contact between soil particles and effluent is increased, and this may be a significant factor reducing NH_3 loss from slurries with higher liquid fractions or NH_4^+ concentration in urine. Adsorbed NH_4^+ to clay particles will only move back into solution to replace NH_4^+ removed by plants, when the concentration of NH_3 increases due to pH effects or when another ion displaces the NH_4^+ from the exchange complex (Streeten & McGahan, 2000).

3.2 NO_3^- leaching below the root-zone of crops

Factors affecting the rate of nitrate leaching include soil type, annual precipitation and evaporation and the degree of nitrate accumulation in the soil (Morvan, Leterme, Arsene, & Mary, 1997). Organic N is relatively immobile in soil. NH_4^+-N has been reported in leachate (Carey, Rate, & Cameron, 1997) although this is not a common observation in clay soils. In sandy soils this can be a problem. In clays and clay loams $NH_4^+$is generally retained on soil colloids through adsorption. However, NO_3^- is a negatively charged ion that is repelled at the negative charge sites making it susceptible to leaching (Magesan, 1992). It is also soluble in water and moves down the soil profile under gravity depending upon the soil type.

Pig urine makes the greatest N contribution to piggery effluent (Kruger et al., 1995). N in this form rapidly undergoes nitrification after it is applied to land. Nitrification is the process whereby NH_4^+ is converted to NO_3^- by bacteria. Studies show an increase of NO_3^- within the soil profile after the application of piggery effluent (Cameron, Rate, Carey, & Smith, 1995). This means that this is an ideal N loss pathway to target if fertiliser value is to be retained.

As NO_3^- is soluble in water, movement through the soil profile is linked with the downward flow of water. Therefore leaching occurs where field capacity of a soil is exceeded and deep drainage occurs (Barton & Schipper, 2001). Drainage characteristics and hydraulic conductivity are most important when predicting NO_3^- loss. Factors affecting soil nitrate accumulation include; (1) amount applied in effluent (2) the extent of N uptake by the crop and (3) N immobilisation or mineralisation in the soil (McGahan & Tucker, 2003). In piggery slurry net mineralisation usually occurs because of the shortage of available C and high amounts of mineral-N. This means that piggery effluent slurry has the potential to be a premium liquid fertiliser.

3.3 Denitrification and gaseous emissions through microbial activity

Denitrification is one of the terminal steps of the N cycle and is facilitated by microbes in the soil. It is the conversion of NO_3- to NO, N_2O or N_2 gas (Bolan et al., 2004). The amount of N_2, NO and N_2O emissions following application of effluents is mainly dependent upon: (1) high soil NO_3- concentration, (2) reduced oxygen conditions and (3) microbial access to C. Other conditions affecting the rate of denitrification include soil temperature, soil moisture and soil pH. Most gaseous emissions occur between the pH range of 7-8.

Soil management practices such as tillage, soil compaction, irrigation and drainage affect the physical and chemical condition of the soil that promotes denitrification (Bolan et al., 2004; Luo, Tillman & Ball, 2000). For denitrification to occur there must be an excess of NO_3-, above threshold values, and soluble organic carbon for microbial growth (Conen, Dobbie & Smith, 2000). These authors estimate the threshold value to be in the order of 10mg of NO_3^- per kg of dry soil. When waterlogging of soils occurs and oxygen consistency is restricted, increased rates of denitrification are likely which leads to greater N loss (Luo et al., 2000; Bhandral, 2005).

An initially high N_2O-N flux occurs within the first few days of applying manure to soil (Velthof, Kuikman, & Oenema, 2003). Enhanced denitrification of soil NO_3^- due to the addition of readily decomposable organic materials promotes denitrifying bacterial growth. A similarly high flux of N_2O within the first few days of applying piggery slurry was also observed in another trial (Chadwick, Pain & Brookman, 2000).

3.4 Removal of N by plant uptake and harvest

N uptake will vary depending on the type of crop grown, the amount, and nutrient content of the dry matter it produces (McGahan & Tucker, 2003). Potential dry matter yield is one way of predicting the nutrients accumulated by crops and thus indirectly its nutrient requirement. Dry matter yield is the amount of nutrients left after oven drying under controlled laboratory conditions. Estimates of some common plant yields and their nutrient accumulation status are shown in Table 1. These estimated values are useful when calculating nutrient balances of inputs and outputs.

Table 1: Estimates of some common plant yields and their nutrient accumulation status (McGahan & Tucker, 2003).

Crop	**Dry Matter Nutrient Content (%)**			**Normal Yield Range (DM t/ha)**	**Normal Nutrient Removal Range (kg ha $^{-1}$)**		
	N	P	K		N	P	K
Winter Cereals							
Wheat	1.9	0.4	0.5	2-5	38-95	8-20	10-25
Barley	1.9	0.3	0.4	2-5	38-95	6-15	8-20
Oats	1.5	0.3	0.4	1-5	15-75	3-15	4-20
Summer Cereals							
Maize	2.0	0.3	0.4	2-8	40-160	6-24	8-32
Maize (silage)	2.2	0.5	2.0	10-25	220-550	50-125	200-500
Grasses							
Non irrigated pasture	2.0	0.3	1.5	1-4	20-80	3-12	15-60
Irrigated Pasture	2.0	0.3	1.5	8-20	160-400	24-60	120-300
Lucerne	3.1	0.3	2.5	5-15	155-465	15-45	125-375
Vegetable Crops							
Beetroot	4.2	0.3	4.0	5-15	210-630	15-45	200-600
Potato	2.5	0.2	2.2	5-15	125-375	10-30	110-330

Once slurry is applied to soil, organic matter starts to decompose and a significant portion of mineral N will be immobilised by soil microbes and be unavailable to plants (Sorensen & Amato, 2002). Microbes are further stimulated when high volumes of carbon are added as an innate portion of the slurry. This may cause a net immobilisation of N (Plaza et al., 2005). This immobilisation of N usually occurs in the first week spreading (Morvan et al., 1997; Chadwick et al., 2001) extend immobilisation to 14 days and others suggest that 15 %-21 % of applied N may remain immobilised for more than 2.5 years (Sorensen & Amato, 2002). There are many reason why these results may vary including the original composition of the slurry, the weather conditions under which they were applied and the soil type to which they were applied. In chapter 5, which is the case-study, a specific farm situation is be described and the results of residual effects of slurry application will be discussed.

In summary, when slurries are applied to meet plant N requirements, net immobilisation of N may actually cause a plant deficiency in N. Therefore, slurries should be applied based on the N content that is directly available to the plant (Plaza et al., 2005). The N readily available to the plant will be the sum of the mineral N applied in the slurry that is not denitrified, leached or volatilised, plus the amount of mineralised organic N already in the soil. In Australia, models such as PIGBAL (Casey, McGahan, Atezeni, Gardner & Frisso, 1996) and MEDLI (Gardner & Davis, 1998) are useful tools to predict the nutrient composition of piggery effluent slurry. However, it is not within the scope of this work to examine nutrient composition of slurry through modelling.

The residual effect of manure slurry application to land could persist for many years (Smith, Unwin & Williams, 1985). Other studies have found that surface application of slurry leads to a decline in plant N recovery compared to incorporation of slurry into the soil (Sorensen & Amato, 2002; Chantigney, Angers, Morvan & Pomar, 2004a). N recovery also increases when slurries are applied to crops directly through incorporation (Morvan et al., 1997). In this situation up to 60 % recovery of applied N is possible. The process here to reduce N loss is the restriction or reduction of the slurry exposed to the atmosphere; injection of slurry achieves this.

3.5 Blocking nitrogen loss pathways in pig barns and slurry storage systems

Techniques for the reduction of NH_3 emission from pig barns are mainly focused on reducing the NH_3 emitting area exposed to air, reducing the NH_3 concentration in solution or reducing the exchange of air above the emitting surface (Sommer & Thomsen, 1993; Sommer & Hutchings, 1995). Therefore, NH_3 emissions from pig barns are mainly influenced by the floor type, the indoor temperature, the ventilation design and the N concentration in the manure (Nicks, 2006). The emitting surface is smaller on a partly slatted floor compared with a fully slatted one and the expectation is that NH_3 emissions would be less. However, this is not necessarily so because cleanliness of the pen floor is more important than the type of floor. The NH_3 emissions from a dirty partly slatted floor can be higher than a clean fully slatted floor (Nicks, 2006). Higher temperatures favour NH_3 volatilisation from the emitting surfaces to the surrounding air for the reason previously mentioned.

Most of the NH_3 in a piggery originates from slurry stored below the floor. Fast and complete removal of slurry from the pit, reduction of the pit surface area, slurry cooling and acidification of slurry are the most effective means to reduce N losses (Monteny, 2007). Reduced acidity (lowering pH) may be one of the best options, since it requires less control in the manure chain: once NH_4^+ is kept in the slurry it will remain there during storage and spreading in the field because the formation of NH_3 is prevented. This type of solution to N loss is that it will also reduce gas concentration inside the building, meaning a better climate for animals and workers.

A Canadian trial examined the factors influencing the concentration of volatile fatty acids, NH_3 and other nutrients in stored liquid pig manure (Conn, Topp & Lazarovitis, 2007). They concluded that although there were differences between the manure from the finishing pigs unit compared to the manure from the mixed operation unit, and compared to the manure from the sow operation. The main difference was due to manure dilution with hose down water.

An interesting study comparing ammonia and greenhouse gas emissions from pigs on fully slatted floor with pigs on straw-based deep litter was conducted in Belgium (Philippe, Laitat, Canart, Vandenheede & Nicks, 2007). They found that gaseous emissions from pigs raised on the slatted floor and on the deep litter were respectively, 6.2 and 13.1 g/pig/day respectively for NH_3, 0.54 and 1.11g//pig/day for N_2O, 16.3 and 16.0 g/pig//day for CH_4, 1.74 and 1.97kg/pig/day for CO_2 and 2.4 and 3.7 kg/pig/day for H_2O. Their conclusion was that although pigs on straw generally had a good consumer image, this rearing system produces more pollutant gases than keeping pigs on slatted floors (Philippe et al., 2007, p. 144).

3.6 Phosphorus P and K distribution in storage and spreading

Nutrients other than N are briefly discussed in this section, mainly from the environmental impact point of view and their fertiliser value. P is a nutrient necessary for life; however, high levels of P in surface water can trigger algal blooms (Redding & Phillips, 2005). The increased P in surface soils from effluent application has the risk of being mobilised by erosion or dissolution in run-off water. This is the primary pathway for effluent P entry into surface water. Algal blooms have caused problems world-wide, due to toxins produced by algae, and or the oxygen depletion of water supply. The result of algal blooms can be fish kills, stock deaths and human illness (Redding & Phillips, 2005).

Effluent P is particularly valuable as a fertiliser and is concentrated in the sludge during storage over time. After long time storage effluent P shares most of the characteristics of inorganic P (Redding, Shatte, & Bell, 2006). There are risks associated with land application of effluent P in terms of P transport (Redding, 2001). Once the P sorptive capacity of the soil is exceeded P can have environmental impacts due to its presence in solute. Farm plans should include filter strips at the run-off end of fields where P is applied (Karssies & Prosser, 1999). A simple P buffering index for Australian soils has been developed and should be referred to when drawing up environmental management plans for farms (Burkitt, Moody, Gourley & Hannah, 2002).

K is a major essential element for plant growth, however environmental problems can occur when excessive amounts of K are applied to the system (Smiles & Smith, 2003). This is because effluent K may degrade soil structure in much the same way as high concentrations of Na^+ do in sodic soils.

When nutrient loss pathways are examined considering the major plant nutrients, it is interesting to note the way they may interact with each other (Smiles & Smith, 2003). These authors report that piggery effluents worldwide are similar in that they all have high pH, high concentrations of K and initially, very high concentrations of NH_4^+ -N. The NH_4^+ soon disappears from the soil due to volatilisation, uptake by plants and oxidation to NO_3-N. This leaves K^+ as the most important introduced cation; on all farms where effluent has been used in irrigation there is increased exchangeable K^+ (P remains in the sludge of the pond). This sensitivity arises because K^+ is 5-6 times more strongly adsorbed on the clay than is Na^+. Because the physical effects of monovalent cations are determined by the soil solution concentration and not the exchangeable ratios it follows that exchangeable K^+ of 36% is of no more concern than 6% Na^+. The effects of irrigation decrease with increasing clay content in the soil, and decrease with depth in the soil profile (Smiles & Smith, 2003, p. 6).

3.7 Piggery effluent slurry value as a fertiliser

Blocking nutrient loss pathways, as discussed in this chapter, is the key to retaining the fertiliser value. In the case of effluent N, recycling waste nutrients is dependant upon preventing or at least reducing N losses from the piggery effluent slurry (Monteny, 2007). Keeping NH_4^+ in the slurry until the moment of its use as a fertiliser for crop production is the way to get maximum value from nutrients.

Piggery effluent nutrient value is shown in Table 2. For every 100 sows (farrow to finish) the nutrients excreted annually amount to a total value of $32,760, of which N is valued at $14,040.

Table 2: Annual nutrients excreted per 100 sows farrow to finish (Ian Kruger, pers. comm. 2008).

Amount of nutrients	**Value of nutrients**
N: 6 t	$ 14,040 (~30% losses)
P: 2.7 t	$ 13,960
K: 2.8	$ 4,760
Total	$ 32,760

These values only refer to the major plant nutrients and not the trace minerals which also have a value. The organic value, which is more difficult to define in monetary terms, is an important reason why piggery effluent should be applied to cropping land (Kruger, Taylor & Ferrier, 1995). Organic matter is important in soil-building for nutrient retention and improving water holding capacity Treated piggery effluent slurry can be stored and spread safely on cropping land and should not be wasted nor create an environmental hazard. Slurry, in the context of this work, is the mixed or agitated effluent, including the sludge from the bottom of the storage pond.

Slurry spreading with suitable equipment allows nutrients to be distributed evenly. For example the 10,000 l vacuum tanker in Plate 3 is operating on 2 metre raised beds. Spreading width is 10 metres, and one run covers 1 km giving an area of 1 ha (10,000 m^2).

Plate 3: Slurry tanker spreading on Gowrie EcoFarm (photo source: Ken Crawford, 2004).

Having examined piggery effluent nutrient loss pathways and the potential value of these nutrients as organic fertiliser the concept of blocking these pathways requires further examination. This is undertaken in chapter 4.

Chapter 4: Maximizing fertiliser value and minimising environmental impact

The basis of holistic management of nutrients in pork production is that the pig is not just a producer of meat, but considered as an integral part of sustainable farming. Reduction of N loss in animal production requires whole-farm management (Rotz, 2004; Petersen et al., 2007). This chapter takes the holistic approach to Integrated Nutrient Management (INM), first by exploring the nature of INM, then considering the dietary means of reducing the amount of nutrients excreted, and retaining excreted waste nutrients in the pig effluent slurry. The chapter concludes with a description of how those nutrients can be released to plants as fertiliser in sustainable cropping systems (Grant, Aulakh, & Johnston, 2008).

4.1 Integrated Nutrient Management

The challenge of nutrient depletion, and its implications for feeding a hungry world, needs to be balanced by the challenge of nutrient excess, and its implications for adverse environmental impacts (Grant et al., 2008). Integrated Nutrient Management (INM) for sustainable cropping systems attempts to maximise fertiliser value and minimise environmental impact. Recycling of livestock manure in a whole-farm perspective is the key to this approach to sustainable agriculture (Petersen, et al., 2007).

Recycling waste nutrients in such a manner needs site specific planning as there is great diversity in types of production systems. All farm interactions must be taken into account and nutrient balances must account for inputs and outputs. In the context of piggery effluent management strategic planning must begin with manipulating diets fed to pigs in the process known as environmental nutrition (Mullan & Henman, 2008). Dietary clinoptilolite technology, used in combination with other dietary solutions, shows much promise (Tiwari, et al., 2009).

The ultimate goal is to close nutrient cycles on the farm, wherever possible (Petersen, et al., 2007). As more knowledge is gained regarding the farm as an ecosystem refinements will be developed to continually improve the environmental management system for sustainable cropping.

In the piggery context, the process is summarised in figures 1a and 1b. Reducing N loss from the farm must start with nutritional and management techniques to reduce N excretion, (Rotz, 2004). Even with good management large quantities of N are in the effluent stream. In untreated piggery effluent a major portion of this N can quickly volatilise to NH_3 and be lost to the atmosphere. Volatile loss begins soon after excretion, and it continues all through the manure handling processes until the nutrients are incorporated into the soil (Figure 1a). Only by properly managing all farm components can N be used efficiently.

Let us now consider each of these stages in greater detail.

Piggery effluent store and spread systems

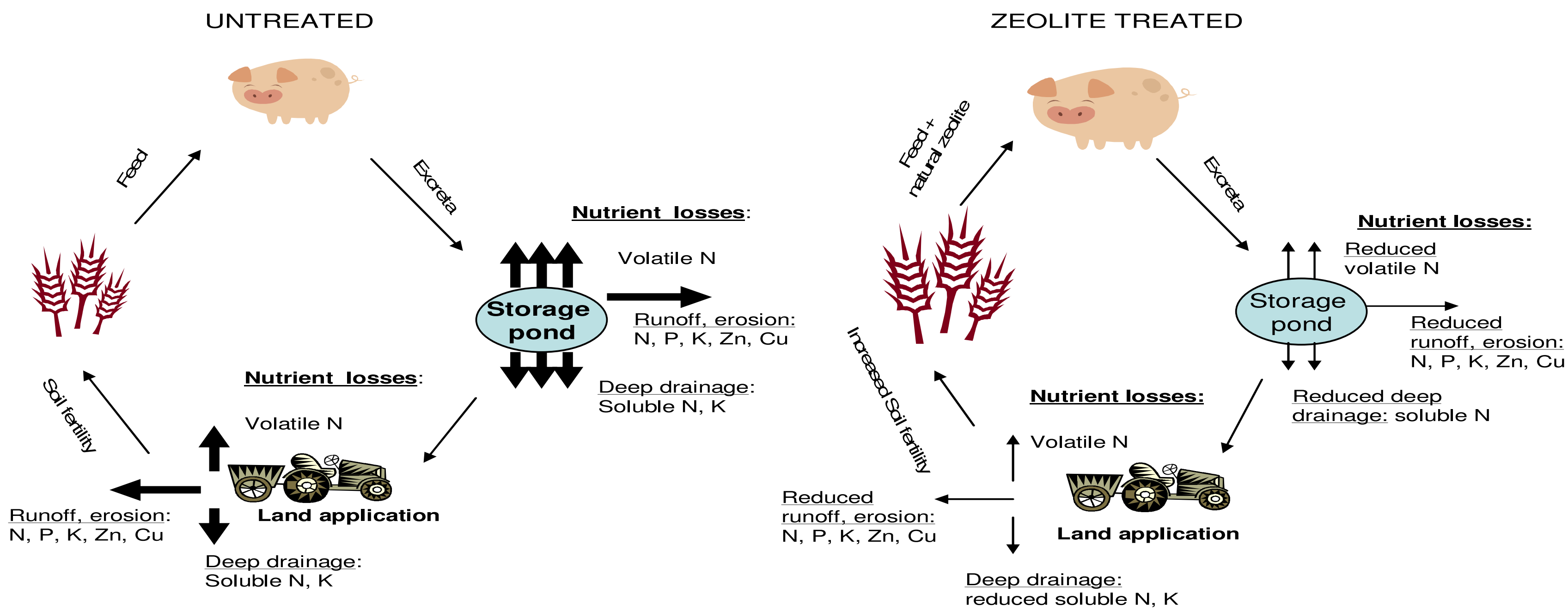

Figure 1a: Untreated pig feed: Nutrient losses of ≥ 30% from pond and land application via 4 pathways. This can lead to socio-economic and environmental problems and reduced fertiliser value.

Figure 1b: Dietary clinoptilolite treatment of feed: increased growth rates (Giles et al. 2005), reduced nutrient loss of 30% leading to increased fertiliser value (Gowrie EcoFarm case study).

4.2 Reducing the amount of nutrients excreted through nutrition

Environmental impacts of waste nutrients can be minimised through nutritional means (i.e. 'environmental nutrition' (Mullan & Henman, 2008). Replacing inorganic minerals with corresponding organic minerals is a good example of environmental nutrition. In order to reduce N, P and trace minerals excreted, research toward a better agreement between nutrient supply and the requirement of the pig has been undertaken in recent years (Dourmad & Jondredville, 2007), particularly by exploring ways to improve the biological availability of these minerals in feedstuffs.

4.2.1 Diet manipulation without clinoptilolite technology

Substantial reduction in N excreted in pigs can be achieved by phase feeding combined with a better adjustment of the amino acid balance. Phase feeding is the feeding of multiple rations specifically designed for each physiological class of pig.

The low digestibility of P in pig diets can also be assisted by supplementing with microbial phytase and the use of highly digestible mineral phosphates (Dourmad & Jondreville, 2006). Reducing phosphorus concentration in pig diets was achieved in a Canadian study by adding an environmental objective into the traditional least cost formulation (Pomar, Dubeau, Letourneau-Montminy, Boucher & Julien, 2007). They also used phytase in their trials at varying rates and at marginally extra costs to the rations to reduce the amount of P excreted. The cost-benefit was acceptable in terms of the sustainability of the pork industry.

In different parts of Europe animal production is highly concentrated and pig production units are common. Surplus nutrients in excreta and gaseous losses to the environment are the main concern (Aarnink & Verstegen, 2007). Nutritional strategies to reduce ammonia emissions include (1) lowering crude protein intake in combination with addition of limiting amino acids, (2) shifting N excretion from urine to faeces by including fermentable carbohydrates in the diet, (3) lowering pH of urine by adding acidifying salts to the diet and (4), lowering the pH of faeces by inclusion of fermentable carbohydrates in the diet. These strategies proved to be independent from each other and the effects are additive (Aarnink & Verstegen, 2007).

4.2.2 Diet manipulation with clinoptilolite technology

Pigs fed diets formulated with clinoptilolite powder produce excreta treated to safeguard against N loss until it is ready to be taken up by plants (Figure 1 b). The dietary use of clinoptilolite in pig diets is expanding (Poulsen & Oksberg, 1995; Sardi, Martelli, Parisini, Cessi & Mordenti, 2002; Leung, 2004; Tiwari, 2007), largely because of its adsorptive and ammonia binding properties and subsequent positive influences on pig health and environmental conditions (Nielsen et al., 1980).

Diet manipulation, such as using dietary clinoptilolite supplementation, can reduce manure nutrient content without adversely affecting manure handling properties (Tiwari et al., 2009). According to their report, the recent trial requires repeating with more pigs and rations containing a better nutrient balance.

In another recent trial, pigs fed dietary clinoptilolite produced manure with 15 % and 22% less N and P, respectively compared to the control diet and that they also demonstrated a better feed conversion, although not statistically significant (Leung et al., 2007, p. 3309). These results show that there is some potential in using high quality clinoptilolite in pig diets to reduce the amount of nutrients excreted, although further investigations are required.

Other reports claiming that dietary clinoptilolite may lead to better digestion as measured by faecal analysis include Cool & Willard (1982) and Shurson, Ku, Miller & Yokoyama (1984). The use of feed additives such as clinoptilolite can manipulate diets to reduce N and P content in piggery effluent slurry and hence minimise the environmental impact, in terms of odour and other gaseous emissions (Jongbloed & Lenis, 1998; Sutton, Kephart, Verstegen, Canh & Hobbs, 1999;).

Clinoptilolite, phytase, yucca extract, modified carbohydrates are the commonly used feed additives for diet manipulation to reduce nutrients in pig manure, Tiwari, (2007) cited (Cromwell, Turner, Taraba, Gates, Lindemann, Traylor, Dozier & Monegue, 1998).

Pond et al (1988) and Paola et al (1999) claimed that clinoptilolite had favourable effects on N metabolism. Better digestion of feed nutrients allows better nutrient retention in the pig and therefore less nutrients excreted. This is the optimal outcome in the first step towards recycling waste nutrients from intensive piggeries.

Dietary clinoptilolite has found to be efficacious in not only prevention of NH_3 and heavy metal toxicities, but adsorbing radioactive elements (Papaionnou, Katsoulos, Panousis & Karatzias, 2005). This comes as no surprise based on the properties and applications of clinoptilolite discussed in Chapter 2. During the last decade, dietary clinoptilolite has been investigated as a mycotoxin binder as well as shifting the effect of N excretion from urine to faeces in monogastric animals (Papaionnou et al., 2005).

Piglets fed clinoptilolite as a feed additive showed a significant ($P<0.05$) improvement of faecal dry matter content (Sardi et al., 2002). At slaughtering, the carcases of these pigs resulted in a trend towards an improvement of lean cuts yield which suggests better digestion of protein in the diet and less N excreted. Carcass quality of heavy pigs fed dietary clinoptilolite through the growing phase showed improved quality, in terms of lean cuts yield and lean to fat cuts ratio (Sardi et al., 2002). Alexopoulos et al. (2007) support these results, showing the long-term dietary use of clinoptilolite at the inclusion rate of 2 % enhanced the performance of growing pigs without adversely affecting their health status in terms of undesirable changes of their biochemical and haematological profiles.

Pig diets supplemented with clinoptilolite can lower the manure mineral content without altering its physico-chemical properties (Tiwari et al., 2009). This means that dietary clinoptilolite can reduce the environmental impact by reducing the amount of nutrients excreted and, at the same time, not have a negative effect on manure slurry handling characteristics.

There appears to be ample evidence in the literature that using dietary clinoptilolite in pig diets reduces the amount of nutrients excreted. However, further investigation is needed to quantify these reductions. Results need repeating with a greater number of pigs and rations containing a better nutrient balance (Tiwari et al., 2009) over the medium to longer term to assure, pork producers and the community that dietary clinoptilolite is a safe and efficacious way of minimising environmental impact from intensive piggeries

4.3 Retaining nutrients in piggery effluent slurry using dietary clinoptilolite

By way of explanation, and as background to this section, most of the early trial work involved treating the effluent directly into the slurry. Dietary use of clinoptilolite to treat slurry is a recent advance in effluent management. Hence, the literature cited in this section will relate to clinoptilolite as a manure additive in most cases. There is much evidence to support its use in this manner (Giles, 2004). However, there is a new wave of research world-wide to consider dietary clinoptilolite as a manure treatment as well as a natural feed-additive to increase daily weight gain (Tiwari, 2007). The early work proves that the concept of adsorbing NH_4^+ and cations works very well. As a manure treatment additive clinoptilolite is effective at adsorbing NH_4^+ and greatly reducing the amount of NH_3 that may form. This has the effect of reducing odour and retaining or maximising the fertiliser value (Cai, Koziel, Liang, Nguyen & Xin, 2007).

Clinoptilolite has a strong affinity for NH_4^+, $K^{+,}$ Cu^{2+} and Zn^{2+} as well as other heavy metals (Barbarick& Pirela, 1984; Langella, Pansini, Cappelletti, de Gennaro & Collella, 2000). This is the consequence of its relatively open structure with a total pore volume of approximately 35% (Godelitas and Armbruster, 2003). A three-dimensional alumino-silicate framework containing narrow four and five membered rings makes up channels capable of hosting exchangeable cations. These channels enhance the selective sorption to clinoptilolite of molecules such NH_3, N_2, CO, and CH_4 which are small enough to enter their channels. The CEC of clinoptilolite is high and selectively adsorbs cations in the following order: $NH_4^+ > Pb^{2+} > Na^+ > Cd^{2+} > Cu^{2+} > Zn^{2+}$ (Langella et al., 2000).

This is a particularly useful property in managing effluent and sewage because it allows adsorption to the zeolite and settling out in the primary storage pond. The pond sludge can then be spread evenly over land and the secondary pond can be used for irrigation. This enables large volumes to be managed as described in chapter 2.

In an effluent management context the amount of NH_4^+ adsorbed by clinoptilolite increases as pH increases (Kithome, Paul, Lavkulich & Bomke, 1999). They reported that at a pH of 4 and 7, the respective NH_4^+ adsorption was 9,660 mg N kg $^{-1}$ and 13,830 mg N kg $^{-1}$. The best range of pH for heavy metal removal is between 4 and 5

(Kesraoui-Ouki & Kavannagh, 1997, pp. 383-394). Nutrients are effectively retained in the slurry because the nutrient loss pathways are blocked, NH_4^+ is contained, and cannot volatilise to NH_3. Another N loss pathway that is effectively blocked is the formation of soluble NO3-. This is due to the greater percentage of NH_4^+ being already taken up from the slurry.

Further investigations are required in the dietary use of clinoptilolite in effluent management (Tiwari, 2007; Tiwari et al., 2009).

4.4 Releasing nutrients from piggery effluent slurry with dietary clinoptilolite for sustainable crop production

As noted in chapter 1 clinoptilolite has special physical and chemical properties that could improve soil properties (Pleso & Tatras, 2002). It has been used to improve soil fertility, particularly through the development of slow release fertilisers enriched with ammonium. Inherent pore size makes clinoptilolite ideal for sorption of what is later beneficially used to enhance plant nutrition. Saturated material can be regenerated or recycled. Nutrients were also slowly released to plants over a long period. (Pleso & Tatras, 2002). NH_4^+ sorption by clinoptilolite in piggery slurry creates a balanced liquid N fertiliser that contains a number of other valuable nutrients, which can then be spread on cropping land in utilising the process described in chapter 1.

Section 2.2.6 deals with other agricultural and horticultural applications of clinoptilolite and should be referred to for additional background information on the release of nutrients to plants. Clinoptilolite becomes a storehouse for nutrients that are slowly released to plants as required (Castle Mountain Zeolites, 2004).

Dietary clinoptilolite is an effective and convenient means of introducing clinoptilolite into the piggery effluent slurry (Giles, 2004).

Chapter 5: Case study - Gowrie EcoFarm

5.1 Location

Gowrie EcoFarm is located at the northern end of the Liverpool Plains near Boggabri (Figure 2) in the North West of NSW.

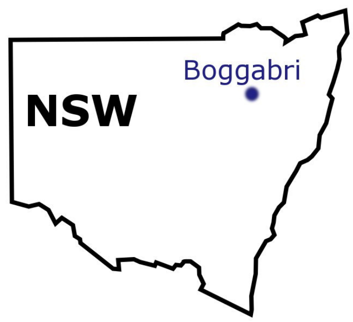

Figure 2: Location of Boggabri (source: Lyon, 2004).

5.2 Soils

The soils are Black Earths derived from weathered basalt. The soils are naturally fertile and well structured and can store large amounts of water and nutrients for the next crop. Plate 3 shows a typical soil profile on the farm.

Plate 3: Typical soil profile at Gowrie EcoFarm (photo source: Aaron Goddard, 2004).

5.3 Climate and available irrigation water

The annual average rainfall is approximately 600 mm and is slightly summer dominant. The annual access licence to the groundwater is 281 ML with the supplementary licence being 22 ML at the commencement of the Namoi Water Sharing Plan. Depth to groundwater is approximately 12 m which means that pumping is very efficient. The main bore is located near the highest point on the property which allows irrigation water to be distributed under gravity to all fields without additional lift-pumping. Most irrigation fields have a constant grade of 1:1000. Plate 4 shows the raised beds with farrow irrigation. All aspects of nutrient management are integrated including applied water through irrigation including quantity and quality. A total, holistic farm management approach is taken where the farm is considered as an ecosystem where its own natural resources are used wherever possible. This promotes resilience and sustainability.

Plate 4: Raised bed furrow irrigation (photo source: Ken Crawford, 2003).

5.4 Piggery layout and effluent storage ponds

Gowrie EcoFarm has three sheds with partly slatted floors over conventional vee drain pits. Treated effluent is pumped into the first anaerobic pond which has a pond cover. The second and third ponds are in reserve for wet weather when spreading cannot be carried out (Plate 5). Treated slurry is agitated and sucked into a 10,000 l vacuum tanker in readiness for land application. Each tanker load is valued at $100 and spreads over 1 ha. In this manner a systematic fertiliser program is achieved without the use of any artificial fertiliser. The tanker takes 5 minutes to fill and 8 minutes to empty allowing a turnaround of approximately 4 loads per hour, depending on the distance from the storage pond.

The tractor drawing the tanker has an on-board computer linked to a true groundspeed sensor and can be calibrated in the same way as a boom spray. Application rates to all fields are logged in the tractor log book. The anti-caking property of dietary clinoptilolite enables even spreading without clogging.

Improving the biological side of soil fertility is the main focus. Organic matter content and soil water holding capacity have been greatly improved since using dietary clinoptilolite in pig diets. A process of soil-building has occurred where historically poorer fields have been rejuvenated to be equivalent now to the best fields.

Plate 5: Piggery layout and effluent storage ponds (photo source: Ken Crawford, 2003).

The breeding herd consists of 70 sows and three boars and all herd introductions are through artificial insemination. In this way the bio-security of the herd is maintained. 1200 medium to heavy pork (45kg DW – 60 kg DW) pa is the productivity goal. From an Environmental Management Systems (EMS) point of view, this is equivalent to approximately 1000 Standard Pig Units (SPU). One SPU is the amount of excreta produced by a pig weighing 45 Kg LW.

Gowrie EcoFarm has its own feed milling system so that the highly nutritious cereal grains, grown on the zeolite treated slurry fertiliser, can be processed on-farm. The farm has a balance of 90 ha of raised bed irrigation fields and 30 ha of dryland. This is sufficient to recycle all the waste nutrients from the piggery without over-fertilising any fields. One of the advantages of irrigation is that whenever excess nutrients and water are available an ‘opportunity’ or double crop may be considered.

Dietary clinoptilolite powder has played a central role in nutrient management on Gowrie EcoFarm during the last decade. Pig diets are formulated with clinoptilolite to increase daily weight gain, to reduce mortality, to reduce odour and to manage effluent usage as fertiliser. Treated effluent is spread on cropping land during the fallow period. Spreading occurs only when the land is dry and able to receive it without causing compaction to the soil. Each field is fertilised with the correct amount of evenly spread slurry. The correct amount is the amount the next crop will require for optimal yield without causing an adverse environmental impact.

5.5 Crop nutrient uptake

A simple nutrient balance estimating nutrient uptake of the next crop at an estimated optimal yield is possible if the slurry fertiliser analysis is available. These nutrients are retained in zeolite treated piggery effluent until the Black Earth soil also adsorbs them. Dietary clinoptilolite acts as an insurance policy for potential nutrient loss during storage and spreading. Plate 6 shows an irrigated crop of the wheat variety Sunlin, grown with treated piggery slurry and no artificial fertiliser. The crop was given two irrigations and yielded 8.68 t/ha (prime hard 2nd grade (PH2), which is very high quality by Australian standards).

Plate 6: High yielding nutritious crops can be grown with treated pig manure without artificial fertiliser (photo source: Ken Crawford 2003).

5.6 Clinoptilolite treated effluent; laboratory analysis

Typical effluent analysis of treated piggery slurry from Gowrie EcoFarm is provided in Table 3. Consistent results over time demonstrate that N losses are reduced using dietary clinoptilolite and soluble nitrate formation is minimal. It should be noted that this is anecdotal evidence as there was no control with which to compare values, however, when compared to base values of effluent analysis for the Australian pork industry, there is a trend towards NH_4^+ levels being higher and NO_3^- levels being lower. This results in maximising the fertiliser value.

Table 3: Summary of effluent samples at Gowrie EcoFarm 2003 – 2005. Feed rations included 5% clinoptilolite. Sample 14: an anaerobic pond; 15A is 1st pond and anaerobic; 15B is 2nd pond and partly oxygenated (facultative); 16A is 1st pond and anaerobic; 16B is 2nd pond and facultative.

Date	**30/09/03**	**Comments**	**22/10/03**	**Comments**	**22/10/03**	**Comments**	**2/08/04**	**Comments**	**2/08/04**	**2/09/05**
Sample	14		15A		15B		16A		16B	Effluent
pH	7.5		8.1		7.1		6.9		7.7	7.1
EC (mS/cm)	8.33		13.82		13.69		6.45		7.89	7.8
Total dissolved salts (mg/L)	5331.2		8844.8		8761.6		4128		5049.6	4992
Cations (mg/L)										
Na	264.5	high	340.4	high	476.1	high	305.9		280.6	310.5
K	351	high	674.7	high	741	high	184.9		432.9	401.7
Ca	240	high	129.6	high	268.8	high	253.2		184	228.8
Mg	109.9	high	126.2	high	139.7	high	100.1		79.9	56.2
NH_4	980	very high	1855	high	2023	very high	847	very high	784	1274
Anions (mg/L)										
Cl	321.3	high	556.5	high	770	high	479.5		416.5	423.5
SO_4	213	high	849.6	high	1622	very high	124.8		65.3	71
NO_3	< 5.0	low	< 5.0	low	< 5.0	low	< 5.0	low	< 5.0	< 5.0
PO_4	84.6	high	33.3	low	138.7	high	171	high	5402	73.2
Derived values										
Na adsorption ratio ($mmol^{1/2}.L^{1/2}$)	3.54	low	5.08	low	5.85	low	4.1		4.33	4.33
Anion/Cation balance meq/L	96.2		147.3		150.56		79.64		80.76	115.8
Total P			58		630		1010		34	2500
Total N			2200		4100		4020		930	4700
Total organic Carbon							23000mg/kg			27000

5.7 Dietary clinoptilolite recommended inclusion rates in pig diets

Typical values for annual excretion of N expressed as a percentage of bodyweight of pigs is shown in Table 4. The older and heavier the pig the lower the annual excretion rate of N.

Table 4: Annual excretion of N by various classes of pig expressed as % body weight (after Koelsh & Shapiro 1998 in Rotz 2004).

Pig class	Annual N excretion as % of body weight
Weaner	22
Grower	15
Finisher	15
Sows and litter	17
Dry Sows	7
Gilts	9
Boars	6

Table 4 shows that as pigs mature the percentage of N excreted, in relation to body weight, also decreases. This is also reflected in the lowered inclusion rates of clinoptilolite required to adsorb NH_4^+ as the pigs mature.

Based on a decade of experience under veterinary supervision on Gowrie EcoFarm using powdered clinoptilolite, as a feed additive (Castle Mountain deposit), the following maximum inclusion rates (by weight) for various classes of pig are recommended in Table 5.

Table 5: Recommended inclusion rates of powdered clinoptilolite in pig rations (case study Gowrie EcoFarm).

Pig class	Inclusion rate of powdered clinoptilolite (by weight)
Weaners and creep-feed	5
Growers	2.5
Breeders	1

Chapter 6: Discussion

There is no doubt that the intensification of the pork industry globally has brought with it many environmental risks (Tiwari, 2007). There are over a billion pigs world-wide and this inevitably leads to a concentration of waste nutrients in piggery effluent slurry (Monteny, 2007). Normally, these waste nutrients are stored in ponds where they may pose a threat to the environment through volatilisation to the atmosphere or leaching to the groundwater. However, if the same slurry has been treated by using dietary clinoptilolite to formulate pig rations the main problem of preventing or at least reducing volatile N and soluble N can be achieved (Tiwari et al., 2009). Laboratory tests on clinoptilolite powder show the efficacy of the zeolite in adsorbing NH_4^+. The high CEC of clinoptilolite also accommodates K^+, Cu^{2+} and Zn^{2+} (Appendix 1) and carries them in the effluent stream. In this respect dietary clinoptilolite has proven to be a suitable absorber and carrier of waste nutrients in piggery effluent slurry. Tiwari reported that in his trial work can have some positive impact on the physico-chemical properties of the manure. Clinoptilolite formulated pig diets produced manure that flowed better and had less odour than the control diet (Tiwari, 2007). Dietary clinoptilolite treated piggery slurry has been spread for many years on Gowrie EcoFarm with positive benefits of odour reduction, retention of nutrients and flow ability of the slurry. The ease of effluent handling is thought to be due to the anti caking properties of the clinoptilolite.

Diet manipulation is the most efficient way to reduce the amount of nutrients excreted, in the first instance, and avoid environmental problems. Lowering the crude protein and phosphorous content of pig diets, using additives like phytase, has been well researched and is a common feature of modern pig diets (Rotz, 2004). Dietary measures may be the most economic and can have an effect on reducing gaseous emissions like NH_3. Feed additives like benzoic acid can lower the urinary acidity (pH) and therefore, ammonia NH_3 emissions. The challenge for the pig feed industries will be to embrace these developments in order to assure successful market penetration of sustainable pork production (Monteny, 2007).

Dietary clinoptilolite has been shown to improve daily gain in weaner pigs (Giles, 2004; Giles, 2005). Investigations conducted at the Clay centre Nebraska indicated that daily gain of weaner pigs increased by 14 % when fed 20 g/kg and that geographic source and particle size of clinoptilolite affected the growth response. Other investigations showed that growth was unaffected by dietary clinoptilolite (Pearson et al; 1985: Poulsen and Oksbjerg, 1995; Magagutti et al, 2002). There are a number of reasons why the results of growth response may vary. Two factors have already been mentioned: geographic source of clinoptilolite and particle size. The study at the Elisabeth Macarthur Agricultural Institute highlighted the need to reformulate diets when feeding dietary clinoptilolite (Giles, 2004). In this trial dietary DE level was maintained at 15 MJ with additions of feed oil and full-fat soybean meal. In addition amino acid levels were maintained relative to lysine at 0.82 g/MJ DE with additions of free amino acids and protein such as blood and soybean meal. This method differed to other investigators who diluted the ration by simply adding clinoptilolite without reformulating the diet. This appears to have compromised any growth improvement associated with the clinoptilolite. It is important to note that despite an increase in diet cost when reformulating diets with clinoptilolite, the EMAI study found that the improvement in daily gain was achieved at no increase in cost per kg of weight gain (Giles, 2004). Dietary clinoptilolite, therefore provides a cost effective means of improving growth in weaner pigs. How dietary clinoptilolite works remains unclear: it may be that pigs are prevented from scouring or that it enables increased uptake of nutrients, particularly energy. The absorbent property alone is not sufficient to explain the improvement in growth as other studies on absorbent feed additives, such as bentonite, have shown no effect on pig growth (Tavener et al, 1984). A recent study from Yugoslavia (Stojic et al, 2003) may provide an explanation for the growth promoting effect of dietary clinoptilolite. According to Giles, (Giles, 2004) these authors investigated serum levels of insulin and insulin-like growth factor1 (IGF-1) with newborn piglets treated orally with a 10 ml suspension containing 15 % clinoptilolite. Serum IGF-1 increased significantly following clinoptilolite treatment and there was a non-significant 20 % increase in serum insulin with a high variation in insulin levels between piglets. These findings suggest that dietary clinoptilolite may be associated with an increase in endogenous growth hormone production in young piglets (Stojic et al, 2003).

The place dietary clinoptilolite will play in the Australian pork industry will be in combination with other ‘environmental nutrition’ tools to reformulate pig diets in an attempt to reduce the amount of nutrients excreted and also in preventing nutrient loss from piggery effluent slurry. More research is required in Australia to quantify the reduction of the amount of nutrients excreted with the same amount of scientific rigor in which the EMAI trial on growth-rate was conducted. Researches should be very specific about where the zeolite comes from, the percentage of zeolite, the particle size analysis, the CEC and NH_4^+adsorption capacity of the sample and the class of pig in the trial as well as the way in which the diets were formulated. In the past, results have not been able to be compared properly because some of these elements have been lacking.

Preventing or at least reducing NH_3 and other nutrients from escaping from the slurry until it is used as a fertiliser for crop production is another approach which works well in combination. Dietary clinoptilolite also fits in this category as part of the solution to reducing volatile N and soluble N. As most of the NH_3 originates from slurry below the floor; the faster it is removed by flushing drains, the better. A small surface area of the pit provides a better environment for reduced emissions. Slurry cooling and acidification are two methods to reduce gaseous emissions and odour problems (Nicks, 2006). Once NH_3 is kept in the slurry, by using all these methods, including dietary clinoptilolite, it will remain there during storage and spreading. In this way a balanced natural liquid fertiliser, that has no equal, is ready to be used in INM on cropping land on a diversified farm.

Chapter 7: Conclusion and recommendations

Formulating pig rations with dietary clinoptilolite is a tested way of increasing daily gain in young pigs and a safe and effective way of recycling waste nutrients in piggery effluent slurry. Dietary clinoptilolite is particularly useful in managing the N cycle in Integrated Nutrient Management (INM) for sustainable cropping. Effluent N losses can be prevented or at least reduced if dietary clinoptilolite is used in combination with other recognised methods such as lowering slurry temperature and reducing pH as well as the principles involved in environmental nutrition. Therefore, dietary clinoptilolite is a very suitable absorber and carrier of nutrients and has the unique properties of; (1) being able to reduce the amount of nutrients excreted (2) retain those nutrients in the effluent stream without nutrient loss and (3) to release those nutrients to crops after land application.

Holistic planning of diversified farms where most of the resources come from within the farm will create resilience for pork producers of the future. Recycling waste nutrients in piggery effluent slurry using all available techniques, including dietary clinoptilolite, is providing an opportunity for Australian pork producers to limit their need for artificial fertiliser on their cropping land. Natural zeolites from Australian deposits are readily available, and if used in the powdered form, clinoptilolite will give useful results in a cost effective manner.

Vacuum slurry tankers are the preferred method of spreading piggery slurry from conventional housing systems. The ability to irrigate cropping land, after spreading in the fallow, enables the crop to take up large quantities of crop nutrients and limit build-up or concentrations in the soil. With irrigation a smaller area is required to spread the slurry and nutrient balances can be more reliably achieved. If irrigation is not available, a larger area of land for slurry spreading is required.

Soil fertility, including chemical, physical and biological aspects, will be improved if the recommendations in this dissertation are adopted. Dietary clinoptilolite creates a slow release fertiliser in the piggery slurry. Slurry spreading in the early years should be supplemented with urea. By year three the beneficial effects to crop health and yields are maximised. This beneficial result will continue long after slurry application ceases.

Based on overseas experience and pig trials at EMAI and Gowrie EcoFarm
maximum inclusion rates for formulating pig diets with dietary clinoptilolite are
weaners and
creep-feed 5 % by weight; growers 2 .5 % by weight; and breeders 1 % by weight.

Further investigation needs to be done on quantifying the reduction in nutrients excreted by using dietary clinoptilolite compared to a control ration. A pig weaner trial of this type is planned for 2009 in the commercial piggery complex of Gowrie EcoFarm. In the meantime, there is potential for the widespread adoption of dietary clinoptilolite technology in the Australian pork industry as fertiliser prices are rising, land is usually available for slurry spreading, and soils are often infertile and require building up, in terms of chemical, physical and biological fertility.

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Appendix

Appendix 1: Laboratory sample analysis of a clinoptilolite for CEC and NH4+ adsorption.

General Soil Chemistry Profile

CLIENT: **Castle Mountain Zeolites**
PO Box 54
Quirindi NSW 2343
Attn: Erik ten Brink

PROJECT: Name: **Sample received 21/8/08**
Location:
SESL Quote N°: Client Job N°: Order N°: **639**
Date Received: **21/08/2008**

Quality System
Quality Endorsed Company
AS/NZS ISO 9001: 2000
QEC 21650

Sydney Environmental and Soil Laboratory
Specialists in Soil Chemistry, Agronomy and Contamination Assessments

Sydney Environmental & Soil Laboratory Pty Ltd
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16 Chilvers Road
Thornleigh NSW 2120
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Address mail to:
PO Box 357
Pennant Hills NSW 1715
Tel: 02 9980 6554
Fax: 02 9484 2427
Em: info@sesl.com.au
Web: www.sesl.com.au

SAMPLE: Batch N°: **7589** Sample N°: **4**
Name: **4 - CMZ ANZ38 ground down sample**
Test Type: **NH4 CEC + ECEC (90min extract)**

SUMMARY AND RECOMMENDATIONS

Ammonium Exchange Capacity: 80.7 meq%
[Calculated NH4 Abs meq% = (NH4blank - NH4extract) x 0.5 where NH4blank and extract is measured in mmol/l]

pH & ELECTRICAL CONDUCTIVITY

TEST	RESULT	COMMENTS
pH in water 1:5		
pH in $CaCl_2$ 1:5		
EC mS/cm 1:5		
Chlorides (mg/kg)		

CATION ANALYSIS

TEST	SOLUBLE	EXCHANGEABLE		
Unit	meq%	meq%	% of ECEC	COMMENTS
Aluminium				
Calcium		41.4	43.00	
Magnesium		6.1	6.30	
Potassium		1.55	1.60	
Sodium		47.1	49.00	

Cation Exchange Capacity	96.2	
Ca:Mg Ratio	6.80	
Sodium Absorbtion Ratio (SAR)		ND

AVAILABLE NUTRIENT PROFILE

TEST	mg/kg	COMMENTS
Ammonium as N	ND	
Nitrate as N		
Phosphate as P	ND	
Potassium	606	
Sulphate as S	N.D.	
Calcium	8297	
Magnesium	741	

AVAILABLE MICRONUTRIENT PROFILE

TEST	mg/kg	COMMENTS
Boron		
Copper	ND	
Iron	ND	
Manganese	ND	
Zinc	ND	

Explanation of the Methods:
pH, EC, Soluble Cations, Nitrate: Bradley et al (1983). **Exchangeable Cations, ECEC:** Method 15A1 Rayment & Higginson (1992)
Chloride: Vogel (1961). **Aluminium:** Method 3500 APHA (1992). **Phosphate:** Method 9E1 Rayment & Higginson (1992). **Ammonium, Sulphate, Iron, Copper, Manganese + Zinc:** Method 83-1 to 83-5 Black (1983). **Boron:** Method 12C2 Rayment & Higginson (1992).

Consultant
Simon Leake

Authorised Signatory
Simon Leake

Date of Report
15/09/2008