The beneficial and detrimental effects of sewage sludge applications in South Australia

by

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Summary

There is little information regarding the fertiliser value of low sewage sludge (sludge) application rates in comparison to inorganic fertiliser in an arid environment such as South Australia or on micronutrient deficient (calcareous) soils. Furthermore, the locally produced sludge is an air dried product with a comparatively high content of water-soluble salts, quite different from the majority of sludges used in studies in Europe and Northern America.

The main aim of the field studies reported in this thesis was to establish the replacement value of sludge applications for inorganic N and P fertiliser at a rate commonly applied by farmers on the sandy, low fertility soils in the cereal cropping area of South Australia. In field studies over 2 years sludge applications of 2t ha^{-1} with varying additions of inorganic N and P were compared with a standard inorganic fertiliser application rate of 20 kg N ha^{-1}, 20 kg P ha^{-1} either with or without micronutrient addition (Zn, Cu, Mn). Shoot dry matter production at different stages of plant development (9 and 15 weeks after sowing) and grain production, as well as nutrient concentration in shoots and grain were taken as indicators for the comparison of nutrient availability of the two sources. Field experiments determining crop response to increasing sludge rates (0 - 10t ha^{-1}) were conducted in 1993.

Sludge applications increased yield considerably in both years, using wheat (*T. durum*) and barley (*H. vulgare*) as a test crop, compared to the nil treatment. The yield of plants receiving 2t sludge or 2t plus some inorganic N, was in general equal to yields obtained from inorganically fertilised plants. The field experiment with increasing sludge application rates (2 to 10 t ha^{-1}) determined a response curve of shoot dry matter production and grain yield to increasing sludge additions. When productivity of inorganically fertilised plants was compared with the corresponding response curves it confirmed previous findings that 2t

sludge plus additional N (12-15 kg N ha^{-1}) was equivalent to the inorganic fertiliser in terms of enhancing shoot and grain yield.

However, considerable differences in shoot dry matter production between sludge and inorganic P fertilised plants were observed with wheat in 1992. Concentration of P in shoots differed between plants amended with sludge or inorganic fertiliser in wheat in 1992 and barley in 1993. Hence it was concluded that 2t sludge had a lower plant P availability in the earlier part of the season until at least 15 weeks after sowing (late booting stage) compared to 20 kg P (DAP), despite equal grain yield in the tested environments. Shoot uptake of P showed a linear (late booting) and grain uptake of P a logarithmic response to increasing sludge rates. The comparison of the P uptake of inorganic fertiliser amended plants (20 kg N ha^{-1}, 20 kg P ha^{-1}, TE) with the corresponding response curves of the sludge treated plants showed that sludge rates of approximately 4t was the equivalent in terms of P supply of the two sources. Hence sludge P availability was estimated to be 36 % of that of inorganic fertiliser P.

An estimation of the availability of sludge N was possible, when shoot and grain yield of sludge amended plants were compared with the inorganic fertiliser treatment containing 20 kg N ha^{-1}. The yield of sludge only fertilised plants was generally lower, but the yield of sludge plus N fertilised plants was generally similar to the inorganic fertiliser comparison. However, differences between sludge fertilisation and the inorganic comparison were small and not significant at every site in the two years. The percentage of sludge N mineralised in one season could be narrowed down to a range of 10 - 42 %, but combining the information of all sites it seemed more likely to be at the higher end of this range.

A second aim of the study was to establish if sludge could replace an inorganic micronutrient fertiliser application on calcareous or sandy, low fertility soils, frequently deficient in Zn, Cu or Mn. At a Zn-deficient site low sludge application rates, which contained the same amount of total Zn (Cu and Mn) as the inorganic fertiliser, enhanced plant growth and Zn uptake of plants to a similar extent as the inorganic Zn fertiliser. At the sites without obvious micronutrient deficiency the Zn concentration and/or Zn uptake of sludge-amended plants were equivalent to values obtained from inorganically fertilised plants, and higher than the inorganic fertiliser without TE. The Zn uptake of plant shoots and grain increased linearly with sludge application rates up to 10t ha^{-1}. Comparison of the response curve to sludge Zn with the Zn uptake value of inorganically fertilised plants confirmed the finding that a 2t sludge provided a similar amount of Zn as the same amount given in an inorganic form.

The sludge did not have a high concentration of Mn and hence cannot be a Mn fertiliser as such. Sludge amended with Mn sulphate supplied an equivalent amount of plant available Mn as the inorganic Mn fertiliser, at sludge rates of 2t ha^{-1}.

The residual value of sludge in the year after sludge application in comparison to the inorganic fertiliser application (20 kg N, 20 kg P ha^{-1}, Zn, Cu, Mn) was tested at two sites and in two years. After applying a base fertiliser to the plants no differences in terms of shoot and grain yield between the treatments was measured. The effectiveness of both fertiliser sources, sludge and inorganic fertiliser, in terms of P and Zn supply were ranked as in the year of application, according to differences in P and Zn concentration of plants, but effects were low in absolute terms.

The analysis of Cd in shoot and grain of one field experiment showed that even sludge application rates of 10t ha^{-1} can significantly increase the Cd concentration in plants compared to inorganic fertiliser applications, although soil pH was close to neutral. Recent research has shown that high chloride (Cl) levels in soils can enhance plant availability of Cd considerably. In view of the transport costs of sludge it is most likely that sludge will be applied in a restricted radius (90-150 km) around Adelaide, which includes areas with salinity problems and irrigated land. Hence the question arose if an increase in concentration

of Cl in soil solution influences the phyto-availability of sludge-Cd in the same way as fertiliser borne Cd.

In pot experiments wheat (*T. aestivum*) and Swiss chard (*B. vulgaris*) were grown for approximately 30 days in sludge-amended soil (sludge rate equivalent to 50t ha^{-1}). The sludge was preleached and NaCl (Cl) treatments were imposed in the irrigation water, resulting in Cl concentrations of 0 - 120 mM in soil solution. Soil solution was displaced after shoot harvest and chemical speciation of Cd in soil solution was calculated using GEOCHEM-PC. The concentrations of Cd in soil solution and shoots of plants were positively correlated with the concentration of Cl in soil solution for both plant species. The activity of $CdCl^+$ explained most of the variation in Cd concentration in plant shoots, whereas Cd^{2+} activity showed only a weak or no correlation to Cd concentration in shoots.

In a factorial experiment using increasing sludge rates equivalent to 0, 25, 50 and 100t ha^{-1} and NaCl treatments similar to previous experiments (resulting in 0-145 mM Cl in soil solution), the mobilising effect of chloro ligands on sludge-Cd in contrast to the effect on soil-Cd could be distinguished. The increase in sludge application rate increased Cd concentration in soil solution and plant shoots up to sludge rates of 50t ha^{-1}. A positive correlation of NaCl (Cl) concentration in soil solution and Cd concentration in soil solution and plant shoots was measured for each sludge rate. However, the mobilising effect of Cl ligands on sludge-Cd seemed to be less than on soil (fertiliser) Cd, as the comparison of relative increase in available Cd as a percentage of the total Cd in soil suggested.

The highest sludge treatments (100t) showed some exceptions in that Cd concentrations in soil solution and shoots were similar or lower than in the medium (50t) sludge treatments. Increased alkalinity was observed in the high (100t) compared to low sludge treatments. Hypotheses for the reduced Cd availability in the high sludge treatments, such as precipitation of $CaCO_3$ and $MgCO_3$ and adsorption of Cd on those surfaces are discussed.

Declaration

This thesis contains no material which has been accepted for the award of any other degree or diploma in any University or other tertiary institution, and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text.

I give consent to this copy of my thesis, when deposited in the University Library, being available for photocopying and loan.

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Chapter 1

General Introduction

Ocean disposal of sludge was a common practice throughout the world for some time, but it is being banned world-wide owing to concern over the possible adverse effects of sludge on the marine environment. The decision to cease sludge discharge to the ocean has been endorsed by the Australian government and a fully land-based disposal scheme was required by the end of 1993 (Gobbie, 1990). Since 1993 when sludge dumping into the sea was officially terminated in Australia, the cities and states had to find other means for sludge deposition or usage.

The environmental impact and cost of disposal of sludges resulting from sewage treatment are major problems facing water authorities. It has been estimated that more than 220 000 tonnes of dry sludge are produced annually in Australia, at a disposal cost of $35 million. Adelaide produces about 22 000 tonnes or 10% of the national total. Annual disposal costs therefore would be expected to be around $3.5 million in South Australia (EWS, 1992).

The Bolivar works is Adelaide's largest sewage treatment plant and includes primary sedimentation followed by a trickle-filter process and a series of stabilisation lagoons. Primary and secondary sludges are fed to an anaerobic digester to undergo mesophilic digestion for about 18 days prior to lagooning. Dewatered sludge is removed from the lagoons and stockpiled on site for further drying before removal for final disposal (Gobbie, 1990).

The application of digested waste water sludge to agricultural land has been recognised both environmentally and economically as a desirable means of sludge disposal. In addition to being inexpensive, land application results in recycling of nutrients essential for plant growth and organic matter important for soil structure (Stover *et al.*, 1976).

Agricultural application of sludge has become a common practice for both practical and economical reasons (Lamy *et al.*, 1993) in various countries and has been practised widely (Schalscha *et al.*, 1980). The agricultural application of sewage products was already practised by Greek and Roman farmers as indicated by writings of Theophrastus (327-287 BC).

The use of sludge in Australian agriculture would not only serve the purpose of recycling nutrients back to the food producing areas, it would also allow use of some metals in the sludge, such as Zn or Cu, in a beneficial way. These metals, deficient in Australian soils, are considered a toxic risk factor in sludge application in other countries. There is an extensive literature on heavy metal chemistry and plant availability of sludge-borne metals (Leschber *et al.*, 1984; Hornick *et al.*, 1984; Chaney 1985; Sauerbeck and Stypereck, 1987a,b; Page *et al.*, 1987; Alloway, 1990; Osborne et al, 1992) and different aspects of sludge nitrogen (N) and phosphate (P) availability (Kirkham, 1982; Coker, 1983; Hornick *et al.*, 1984; Osborne *et al.*, 1992). However, most of the published research has been conducted in temperate regions with abundant rainfall, eg. northern Europe and northern USA. Also there is little literature regarding the use of sludge as a trace element fertiliser and that is focussed mainly on iron (McCaslin and O'Conner, 1982; McCaslin *et al.*, 1987; Cripps and Matocha, 1991). There was a need to establish if sludge could be used as a valuable fertiliser replacement for micronutrients, zinc particularly, in sandy soils of South Australia. The availability of trace elements can vary considerably among fertiliser products and the soils treated. Also, air-dry sludges are characteristic of drier climates and have been less studied, but drying affects the availability of N and P especially, and needed to be quantified

Sludge is also generally a source of heavy metals other than Zn, uch as Cd, which can potentially be toxic to animals and humans. Before recommending sludge as a fertiliser replacement, potential adverse effects of sludge have to be investigated. The availability of sludge Cd has been the focus of many studies. Recent work has shown that NaCl has a major impact on the phytoavailability of fertiliser Cd (McLaughlin *et al.*, 1994). The air dried sewage sludge of the Bolivar treatment plant contains a considerable amount of NaCl. Also it is possible that sludge will be applied in saline soils or irrigated land and thus exposed to elevated NaCl levels. Hence there was a need to clarify the effects of NaCl on the phytoavailability of sludge Cd.

Chapter 2

Literature Review

2.1 Adelaide sewage treatment works

The Adelaide (Bolivar) sewage treatment works is the largest of the four treatment works of Adelaide. Average daily inflow of waste water to the plant is currently 135 ML. The waste water receives a primary and secondary treatment which consists of a selected combination of physical and biological processes. The physical processes include the screening of sewage to remove larger solids, aerating the sewage under controlled conditions to precipitate grit and promote settling in the primary sedimentation tanks. The biological processes or secondary treatments employ living organisms (bacteria, fungi, algae) to convert finely divided suspended particles and dissolved organic material into more stable chemical constituents. The solid components accumulated from primary and secondary treatment are concentrated to a slurry known as sludge. This material is stabilised by digestion in closed, anaerobic digester tanks maintained at body temperature, followed by discharge to drying pans for air drying (EWS, 1992). It is estimated that more than 1.1 million m^3 of sludge are contained in the stabilisation lagoons at Bolivar. Newly constructed pipelines transport digested sludge from two other treatment works (Glenelg and Port Adelaide) to the lagoons at Bolivar for air drying and disposal. The Bolivar treatment plant currently produces 14000 t sludge solids per year while Port Adelaide and Glenelg produce 2400t and 2700t sludge solids per year respectively (EWS, 1992).

The disposal of sludge is costly. The sludge-handling costs of the accumulated solids after removal from the lagoons were estimated as follows: a) cost of trucking dewatered sludge to the abandoned Brukunga mines in the Adelaide Hills: $1.4 m b) disposal of dried sludge at the ACC Wingfield landfill allowing for cartage and tip fee: in the order of $1.4 m (Gobbie *et al.*, 1993). The same amount of expenditure would allow a trucking radius of around 100 to 200 km to agricultural areas around Adelaide (R. Scott Young&Co., 1995). This makes sludge application in agriculture a feasible option.

2.2 Sludge use in Australia

Since sludge dumping into the sea is no longer an option in Australia, cities and states have had to find other means for sludge disposal or reuse. Sludge is used in various ways in the other states of Australia, for example incineration, co-composting with other material, mine site rehabilitation, as a component of soil mix, cover of municipal refuse tips or application on agricultural land (AWWA, 1990). In South Australia, air-dried sludge from the Bolivar treatment works was mainly used by Pivot Pty Ltd as an organic fertiliser, frequently amended with inorganic nutrients. Health regulations demand that the sludge is rotary kilned (minimum temperature of 120°C for 1 hour) to kill pathogens before sale (Gobbie, 1990), which adds considerable cost to the sludge handling. In recent years the tonnages of sludge processed have declined from more than 21000 tonnes in 1988/89 to less than 10000 tonnes in 1992/93 (Desmier, 1994) and sludge processing by Pivot Pty Ltd ceased in 1996. Thus there is a need for additional recycling options for sludge, because landfill only offers a finite solution to the sludge problem.

Sludge use in agriculture is always mentioned as a potential reuse option, but the local research into effects of sludge applications is quite limited so far. There is a vast amount of dry-land agricultural land, which is in constant demand of nutrient replacement for their nutrient exported in agricultural products. Cereal production in particular is demanding in terms of fertiliser input. Recent statistical data indicate that there is more than 50 000 ha of cereal crops within a 50 km distance from the Bolivar plant. If all the metropolitan sludge (21000t year^{-1}) were to be applied to cereals at a rate of 2.5t ha^{-1} year^{-1} then an area of about 8400 ha would be needed annually (Desmier, 1994).

Some research about the use of sludge in broad-acre agriculture was conducted in NSW, where guidelines for sludge use in agriculture were published (Lawrie *et al.*, 1990; Ross *et* *al.*, 1991). However, most studies deal with high sludge application rates (Lawrie *et al.*, 1990) to establish the potential risk of heavy metal accumulation by plants in the Australian environment. Only few studies address the fertiliser value of sewage sludge under Australian conditions. DeVries *et al.* (DeVries and Tiller, 1978a and b; DeVries 1979; DeVries and Merry, 1980) carried out a number of experiments using Bolivar sludge with the main emphasis to establish the heavy metal uptake by horticultural crops and partly to assess the fertiliser value of the material. DeVries and Tiller (1978b) found that higher rates (24 and 72t ha^{-1}) of dried Bolivar sludge could be used as a fertiliser for some, but not for all horticultural crops tested. However DeVries and Tiller tested only horticultural crops, for which higher fertiliser applications are common practice. Horticultural soils may, through past practice, have an elevated nutrient level compared to soils in the cereal belt of South Australia. Also horticultural crops have in general a higher nutrient demand than cereal plants.

Willett *et al.* (1986) used sludge application rates of up to 25t ha^{-1} on a strongly acidic soil with lucerne as a test crop. The significant yield responses to the sludge applications were equivalent to a number of combinations of N and P fertilisers and lime. For example a 5t sludge application was equivalent to a P rate of between 20 to 40 kg P ha^{-1} plus a N rate of between 18 to 68 kg ha^{-1} (low P rates combined with high N rates or vice versa) in the first 6 months. Five tonnes of the sludge used by Willett *et al.* (1986) contained 54.5 kg N and 51 kg P. These results imply a high sludge N and P availability under field conditions. However, those experiments were performed on an acidic soil. No comparable study using low sludge application rates on calcareous soils and cropped to cereals has been conducted in Australia prior to the study reported here.

2.3 Fertiliser requirement of cereal crops in South Australia

2.3.1 Nitrogen (N)

Legume-derived N in cereal/pasture rotations is still the major source of N for wheat crops in southern Australia. However, applications of nitrogenous fertiliser are becoming more important to maintain yields and grain protein levels, particularly in more intensive cropping systems. The rates of N used vary depending on the previous crop rotation, soil type, rainfall and expected yield, but generally in South Australia application rates are low and commonly less than 25 kg ha^{-1} (McDonald, 1992).

Because of the relatively small and infrequent responses of wheat to fertiliser N in southern Australia (Russell, 1967; Taylor *et al.*, 1978) it is generally believed that the efficiency of N fertilisers for increasing wheat yield is low under the dry-land conditions of the Australian wheat belt (Angus and Fischer, 1991). Grain yield responses to additional N are variable because of the effects of residual soil N as well as the influence of moisture availability and temperature in spring (Russell, 1968a, b). Changes in the management of wheat crops may warrant a re-evaluation of the efficiency of N fertiliser inputs. Increasing intensity of cropping presumably has led to a reduction in levels of available soil N and the semi-dwarf wheat varieties now available are more N responsive than their predecessors (Syme *et al.*, 1976). McDonald (1992) examined the wheat response to applications of nitrogenous fertiliser in South Australia in 3 years at 10 sites. Nitrogen often increased early crop vigour and subsequent growth but significant increases in grain yield occurred at only three of the 10 sites. At the N responsive sites the N utilisation efficiency, the average grain yield per unit of N in the crop at maturity, was 33.5 kg grain kg N^{-1}. Studies in dry-land wheat crops in southern NSW showed a more consistent response to N fertilisers (Angus and Fischer, 1991), with larger responses obtained in wetter than average seasons and smaller responses during drought.

2.3.2 Phosphorus (P)

Phosphorus fertiliser application rates in Australia are currently in the range of 0 -30 kg ha^{-1} for cereal crops (Incitec, 1994). Applications of fertiliser P to wheat in Australia have declined in recent years because of a high ratio of fertiliser cost to price of wheat (Holford and Cullis, 1985). Crop responses to P fertiliser are generally quite dependent on soil P status, soil type, crop yield potential and moisture conditions.

In 37 out of 59 wheat nutrition experiments in the wheat belt of NSW, Holford and Doyle (1992) found significant yield responses with P application rates of up to 38 kg P ha^{-1} compared to the control. Average responsiveness to P seemed to be greater in dry years compared to wet years (Holford and Doyle, 1993). The critical value of the lactate-extractable soil P was lower in dry years (14 mg kg^{-1}) than in normal to humid years (17 mg kg^{-1}) (rain 500-650 mm). However, P uptake, P fertiliser recovery, agronomic efficiency and P fertiliser requirement were higher in the wettest year (Holford and Doyle, 1993). In general the values of those parameters (except lactate-extractable P) in the dry year were about half the values in the wetter years. The yield response relationships to P fertiliser were curvilinear as were the soil P uptake relationships (Holford and Doyle, 1992). Accordingly there was a general decline in the agronomic efficiency of P at each successive increment of fertiliser (Holford and Doyle, 1993). The agronomic efficiency of a P rate of 20 kg ha^{-1} was 10.6; 11.3; 12.9; 7.7 (kg grain kg P^{-1}) in the 4 years respectively, with the lowest efficiency occurring in a drier year. Judging the P fertiliser value by tissue P concentration rather than yield, it was found that the relationship for P uptake in tops was significant in each individual year, but for grain it was significant only in 2 years. Fertiliser recovery in grain was low and declined at increasing levels of soil P (Holford and Doyle, 1993).

2.3.3 Zinc (Zn)

Zinc-deficient soils are common all over the world in both tropical and temperate lands, but are most widespread in the Mediterranean region, including the cropping areas of Western and South Australia (Sillanpää and Vlek, 1985). Zn deficiency can occur because of low total Zn content of the soil or a low soil Zn availability, most likely in high pH soils. Soils with chronic micronutrient deficiency are often high pH calcareous and alkaline soils in seasonally dry climates, but may include deep sands in any climate (Graham, 1990; Takkar and Walker, 1993). In Western and South Australia widespread Zn deficiency occurs in several million hectares of clover-grass pastures growing on calcareous soils or siliceous sands and loams (Takkar and Walker, 1993). Widespread Zn deficiency is found in the famous Ninety Mile Desert on the border of Victoria and South Australia.

Field experiments have indicated that 2.5 to 25 kg Zn ha^{-1} applied as $ZnSO_4$ or 0.3 to 6 kg Zn ha^{-1} applied as chelates and broadcast and mixed or banded below the seed proved most effective in correcting Zn deficiency in field and vegetable crops. In Australia the rates of Zn application to cereals and pasture on light soils were lower at 0.6-2.4 kg Zn ha^{-1} (Takkar and Walker, 1993). The relative effectiveness of Zn fertilisers varies markedly with Zn rate. Often the chelate, Zn-EDTA, is more effective than ZnO at low Zn rates, whereas all sources are equally effective at the highest Zn rate (Takkar and Walker, 1993). Particle size is also important for the relative agronomic effectiveness of $ZnSO_4$ and ZnO fertilisers. Mortvedt (1992) showed that at least 40% of the total Zn in granular Zn fertiliser should be in a water-soluble form to be fully effective for maize. In treatments with finely ground Zn fertiliser, no difference in dry matter production or Zn uptake was detectable.

Zinc fertiliser has a residual benefit to subsequent crops; however, the duration of this effect varies with the nature of the soil and cropping system. Depending on the rate, a Zn application usually ameliorates Zn deficiency for around 7 subsequent crops (Takkar and Walker, 1993). Similarly, Mortvedt and Gilkes (1993) cited reports demonstrating a crop response to applied Zn at least 5 years after application.

Zinc deficiency: Zinc is a micronutrient that is essential for a number of different aspects of plant physiology and biochemistry, including hormone biosynthesis, structure; stability of organelles, cytochrome c synthesis, activation and proper function of a number of enzymes, protein synthesis, and stability and integrity of the cell plasma membrane (Kochian, 1993 and citations therein). In Zn-deficient plants metabolic changes are numerous, quite complex and include changes in metabolism of carbohydrates, proteins, auxins and impaired membrane integrity (Römheld and Marschner, 1991). Zn deficiency stress usually involves peroxidative damage of crucial components of biomembranes, enzymes and thylakoids, which are the major targets of toxic O_2 radicals . By binding sulfhydryl groups and phospholipids, Zn ions stabilise and protect cell membranes and enzyme proteins against oxidative attack by toxic O_2 species (Cakmak and Marschner, 1993 and citations therein).

Generally, the first symptoms of Zn-deficiency in cereals are a change in colour from healthy green to a muddy grey-green in the central regions of middle aged leaves. Necrotic areas soon develop. As the Zn-deficiency becomes more severe, many leaves take on an oily appearance. The necrotic patches become larger and are surrounded by mottled yellow-green areas. At this stage Zn-deficient leaves tend to collapse in the middle regions (Snowball and Robson, 1991). In the shoots plant Zn concentration indicative of Zn deficiency are in general in the range of 10 to 15 mg and 20 to 30 mg Zn kg^{-1} dry weight in gramineous and dicotyledonous species, respectively.

Alkaline soils are prone to Zn deficiency. From physiological evidence reported elsewhere, it would appear that a critical level for Zn is required in the soil before roots will either grow in it or function effectively. It is likely the requirement is frequently not met in deep sandy infertile soil profiles widespread in southern Australia (Graham *et al.*, 1993). This inhibits the development of the root system and thus restricts nutrient and water uptake, which can be crucial in dry conditions. Because Zn nutrition is crucial for penetration of roots into the subsoil, it also appears to be strongly linked to disease resistance and tolerance to environmental stresses. Zn deficiency decreased the resistance of wheat to *Fusarium graminearum*, the crown rot fungus and to *Rhizoctonia solani*, the causal agent of bare patch (Graham, 1990).

Zn deficiency in the field is typically patchy, even within a single paddock (Kubota and Alloway, 1972). It is now also evident that foliar symptoms are not exhibited by plants suffering moderate to mild Zn stress. Indeed, in some studies dry matter production has been reduced by 40% or more by Zn deficiency in plants which show no visible symptoms (Brennan *et al.*, 1993 and citations therein). Durum wheats are generally more sensitive to micronutrient deficiency than bread wheats (Graham, 1990).

2.4 Sludge use as fertiliser

The idea of recycling nutrients such as N, P, K, Mg back to the land by using sludge in agriculture has been investigated in many countries. Sludge was mainly valued for its N content and only secondarily for P and organic matter content. Accordingly, sludge application rates are often estimated according to the N needs of the crop (Pierszynski, 1994) which usually results in P being added to soils in luxury amounts. Studies assessing the fertiliser values of sludge often concentrate on N or P or just the overall value of the sludge without comparing it to an inorganic fertiliser source. Studies dealing with sludge N or P or micronutrients (TE) plant availability will be addressed in the following separate sections.

2.4.1 Nitrogen (N)

Total N in sludge is quite variable and may range from <0.1 to 18 % with a median of 3.3% (Sommers, 1977). Nitrate N in sludges is usually low (<0.5%) and NH_4-N is usually below 1 %, but levels may reach 6.7% (Sommers, 1977). The level of NH_4^+ will depend on the process of waste water treatment. Secondary aeration, aerobic or anaerobic digestion and lime additions generally reduce the level of soluble N and total N. In addition, sludge composition can vary considerably over time from a given treatment facility. Because most of the N in sludge is organic (Sommers, 1977; Magdoff and Chromec, 1977) more information about the rate of N mineralisation is required to predict N availability during a cropping season (Serna and Pomares, 1992). Difficulties in judging the potential N mineralisation of organic sludge N may arise from the fact that mineralisation of organic N is dependent on 1) type of organic material (pre-treatment of the sludge) 2) rate of application 3) soil type 4) soil water content 5) soil temperature (Epstein *et al.*, 1978; Parker and Sommers, 1983; Clark and Gilmour, 1983; Barbarika *et al.*, 1985).

Serna and Pomares (1992) found that aerobically treated sludge showed generally higher mineralisation rates than the anaerobically treated sludge. Chae and Tabatabai (1986) also found that the total N mineralised from the organic waste material varied considerably according to the composition of the waste material, but also that soil type has some influence. Garau *et al.* (1986) reported that soil type had a bigger effect on mineralisation processes than the rate and kind of sludge applied. These results were gained in laboratory incubation studies. Beside the relative uniformity of environmental conditions in laboratory studies compared to field studies Parker and Sommers (1983) mentioned, that various laboratory techniques gave quite different results for mineralisation rate and potential. Rajimakers and Janssen (1993) mentioned that for processed organic materials with a high content of inorganic N, the assessment of the fraction of organic N mineralised could be improved by leaching inorganic N before use. The same phenomena was observed by Garau *et al.* (1986) who found the potentially mineralisable N versus organic N in an incubation study of dried sludge was 43 % for leached and 28% for the non leached procedure.

Even though incubation studies have their shortcomings, they can indicate a range in which N mineralisation is likely to occur. Therefore the percentage of organic N mineralisation found by various studies will be listed.

[%] mineralised	Material	Reference
2-48 %	anaerobically digested sludge	(several studies summarised by Parker and Sommers, 1983)
4-48 %	anaerobically digested sludge	(Ryan *et al.*, 1973)
15 %	anaerobically digested sludge	(Parker and Sommers, 1983)
14-25 %	anaerobically digested sludge	(Magdoff and Chromec, 1977)
36-61 %	aerobically digested sludge	(Magdoff and Chromec, 1977)
1-58 %	4 sludges in 5 soils	(Chae and Tabatabai, 1986)
4 %	of added organic N	(Premi and Cornfield, 1971)
41 %	digested sludge	(Epstein *et al.*, 1978)
42 %	raw sludge	(Epstein *et al.*, 1978)
25 %	raw and primary sludge	(Parker and Sommers, 1983)
9 %	digested sludge compost	(Epstein *et al.*, 1978)
8 %	sludge compost	(Parker and Sommers, 1983)
13-67 %	animal manures	(Chae and Tabatabai, 1986)

Epstein *et al.*, (1978) claimed that the N mineralisation patterns from previously stabilised amendments (digested sludge) give mineralisation patterns similar to native soil organic-N, although larger amounts of N are released. According to Chae and Tabatabai (1986) the mineralisation of sludge N generally exhibits a slow initial rate, which was indicative of a lag period, followed by a rapid increase in rate and subsequent slow rate of N release. They added that the patterns of N mineralisation in animal manure treated soils were generally similar to those of sludge-treated soils. Poletschny (1987) mentioned a late N release after application of sludge or other organic material. Smith and Hadley (1989) found similarities in the N release characteristics of the organic material (dried blood, Protox-sludge) which matched the requirement of lettuce more closely than the inorganic fertiliser. (Protox=activated sludge, processed to reduce heavy metals content). However N was rapidly released from the protein based materials such that the processed sludge was depleted of available fertiliser N at the same time irrespective of the form supplied. Approximately 20% of the N in Protox appeared to be resistant to microbial degradation and was unavailable to plants.

Field studies: In field work, similarly as in incubation studies, the mineralisation of sludge organic N was rated quite differently in the various studies, probably because of the many aspects that can vary (soil type, sludge type and rate, temperature, moisture content and others). In particular sludge type and rate have to be considered when comparing results from field studies.

Estimates of mineralisation of organic N from sludge applied to corn and hay crops averaged 55% for the first year of application in a study by Magdoff and Amadon (1980), with 44 % and 63% for the high and low sludge rates, respectively. Aerobically-treated liquid sludge at four sludge levels chosen to supply about 50 to 200 kg N ha^{-1} $year^{-1}$ in a sandy loam were used. Kelling *et al.* (1977), using liquid digested sludge at rates from 3.75 to 60 metric tonnes dry solids ha^{-1} (~350 to 5500 kg total N) on a silt loam and a sandy loam, found a similar mineralisation of organic N of up to 50 % within three weeks.

The higher percentage of mineralisation occurred at lower sludge application rates. Boguslawski (1987), using much lower sludge application rates, which are considered more representative of agronomic practice in European agriculture, found that 3 t ha^{-1} sludge could replace a 20-30 kg N application. Assuming 2% total N for the sludge used (the total N content of the sludge is not mentioned), the total N applied with 3t sludge would be 60 kg ha^{-1}, and therefore 50 % of the total N was available to the crop (not considering organic and inorganic fractions). The N mineralisation rate in a dry product like sludge compost was found to be much lower and equal to 10% of the total N content (McCoy *et al.*, 1983 unpub. in Hornick *et al.*, 1984). On the basis of data from several independent field studies, Poletschny (1987) claimed that the total N, as well as the percentage of NH_4^+-N, may influence N availability in the first year. On that basis, he distinguished the different sludges into two main categories depending on their total N and NH_4^+ content. Sludges with a high total N content and a high percentage NH_4^+ (about 30 %), which are generally little dewatered sludges, had a N availability of 50 % in the first year. The N availability for sludges with low total N and a low percentage NH_4^+ (about 10%), generally heavily dewatered sludges, was lower and about 20 to 25 % in the first year.

In cases when it is impractical to analyse NH_4^+ as well as sludge organic N (for example commercial sludge application) sludge organic N is still a reasonable predictor of mineralisation of sludge N added to soil, as sludges high in total N also generally have a high inorganic N content. A formula, taking sludge organic N content into account, was established by Parker and Sommers (1983) to predict N mineralisation.

$$\% \text{ of sludge N mineralised} = 6.37 * \% \text{ sludge org.N} + 4.63 \qquad (R^2=0.77)$$

For a sludge with 2% organic N the N mineralisation would be estimated to be 17.4% of the added N. This figure is quite close to the gross factor used in guidelines in the U.S. of 20 to 25% of organic N mineralised during the first year after application.(Keeney *et al.*, 1975).

Most of the above mentioned studies have been conducted in temperate regions. It is possible that sludge mineralisation is somewhat different under dry land conditions. Day *et al.* (1990a) applied liquid sludge to a sandy loam in a field experiment in Arizona with durum wheat as the test crop. The low sludge rate, which was assumed to provide as much N as the inorganic fertiliser (112 kg N ha^{-1}), produced yields of hay, grain and straw similar to the inorganic N fertiliser. The availability of sludge N was considered 75% of the total N. However, the high sludge N content suggests that a high percentage of inorganic N was in the sludge. Also, it was not explicitly mentioned if the crop was irrigated. Therefore it does not seem advisable to take such a high N mineralisation rate as an indicator for dry-land farming. Even though the mineralisation rate as suchwas not directly measured in the study of Day *et al.* (1990) the sludge and inorganic fertiliser N contributed similar amounts of N to the crop as verified by plant growth. The calculation of the inorganic N equivalent to the sludge application was based on models by Gilmour *et al.* (1985). Gilmour and Gilmour (1980) developed a computer simulation model which describes the rate of sludge decomposition in soils. Besides other assumptions, it is assumed that the N mineralisation rate is quite closely related to the C mineralisation in organic material. The output of the model showed that half of the sludge was decomposed over a 32 to 57 month period, for the soil temperature and moisture regimes considered. When "optimum" soil temperature and water content were used in the model the half life of sludge was reduced by 37% to 66%. One of the sites, where Gilmour and Gilmour (1980) measured decomposition data had a climate generally comparable to South Australia, with hot dry summers and warm moist winters. This site showed a 50% sludge decomposition after 43 months and a 20 % decomposition after approximately 1.75 months. A logarithmic curve based on the observed sludge decomposition at this site would be: $y = 9.37 * \ln(x) + 14.76$ ($y = \%$ decomposition, x=months). According to this formula after 6 months about 32 % of the sludge material would be decomposed. (For example Bolivar sludge: 32 % decomposition of 2t sludge containing 1.9% organic N would provide 12.2 kg N in the first 6 months, plus 0.2 % inorganic N (= 4 kg)).

As well as the plant N availability in the immediate cropping season, the models predicted a slow sludge mineralisation, beyond the initial 6 months. This could benefit the following crop as a so called residual value of the initial sludge application. However, contrary to this predictions, Poletschny (1987) found in field experiments in Germany (probably on well fertilised soils), that the residual N effect of sludge in the years after application is only noticeable after frequent sludge applications and also then rarely exceeds 20 to 30 kg N ha^{-1} $year^{-1}$.

2.4.2 Phosphorus (P)

Beside being an important source of N, sludge also contains a considerable amount of P. With natural resources of inorganic P being limited, the recycling of sludge P may become even more important in the future.

Sludge P concentration is quite variable. The total P content of sludge may vary from less than 0.1% to over 14 % on a dry weight basis (Sommers, 1977) depending on the nature of the raw sludge being treated and the treatment process under consideration. The increasing or decreasing use of P-based detergents, amount of industrial waste and use of P-removal techniques will determine the changes in P content of sludge in the future (McLaughlin, 1984). The plant availability of sludge P can vary according to a) treatment process b) method of chemical P precipitation (Al, Fe, Ca) c) pH of soil sludge mixture d) P status of the soil (and P fixation capacity of the soil (Pastene, 1981)) and e) amount of P applied (Fritsch and Werner, 1988).

2.4.2.1 Chemical forms of P in sludge

The forms of P in sludge are dependent on the composition of the raw sludge and the type of treatment which the sewage is subjected to (McLaughlin, 1984). In conventional treatment plants about one half of the P removed is settled out during primary sedimentation and one half in the activated sludge process (Harkness and Jenkins, 1958). Phosphate removal during the primary sedimentation is mostly by the settling of insoluble precipitates and therefore these sludges contain mostly inorganic P forms (Pastene, 1981).

Biological treatment of the waste water in the activated sludge process removes soluble P forms from the water by incorporating them into microbial cellular protoplasm. This P is mainly organically bound P, while some P may also be incorporated as inorganic P into the micro-organisms in the form of polyphosphates (McLaughlin, 1984).

2.4.2.2 Influence of iron (Fe) and aluminium (Al) on sludge chemistry

Increasingly stringent standards for sewage effluent P levels in various countries have led to additional P-removal technologies. At present the chemical precipitation of P is by far the most common method with Ca, Fe and Al salts being the principal precipitants employed (McLaughlin, 1984). Removal of P by the metal salts is probably a combination of surface adsorption onto the metal hydroxide combined with a chemical precipitation of the metal phosphate. The "mixed hydroxyphosphate" is therefore neither a pure metal hydroxide nor a pure crystalline phosphate but probably exists as an amorphous mixture (Pastene, 1981). Lime induced phosphate removal is probably a similar combination of precipitation and adsorption reactions (McLaughlin, 1984). Even where no chemical precipitants are added, much of the P may still be associated with Al (Hanotiaux *et al.*, 1981), Fe or Ca as these are usually the major components of raw sewage and form insoluble precipitates readily (McLaughlin, 1984).

Sludge generally gets subjected to a tertiary digestion treatment for stabilisation purposes. Digestion may be either anaerobic or aerobic and may alter the forms of phosphorus in sludge considerably. Any form of digestion, because it involves the breakdown of organic material, will tend to decrease the organically bound P component of the sludge (McLaughlin, 1984). Sludges which have undergone tertiary treatment therefore contain P predominantly in an inorganic form (Sommers *et al.*, 1976).

2.4.2.3 Sludge-P behaviour in soil

Both P status and P fixation capacity of the soil are important influences on plant availability of sludge P. Most soils display the characteristic of being able to retain large amounts of applied P, transforming a part of the mobile forms of P into immobile forms.

Physical, chemical and biological processes can be involved in the transformation of mobile into immobile forms of P. Aluminium and iron oxides, hydroxides and hydrous oxides, clay minerals and solid calcium carbonate are the most active soil components with regard to sorption of both dissolved inorganic and organic P species (McLaughlin, 1984). Also sludge organic matter applications to soils could affect P sorption characteristics. Organic matter may interfere with adsorption and precipitation processes by inhibiting P adsorption through either blocking active exchange sites or by solubilising soil components active in P fixation (Earl *et al.*, 1979). Decreased adsorption of P in soils treated with animal wastes have been attributed to such organic matter effects (Reddy *et al.*, 1980).

2.4.2.4 Plant uptake of P from sludge

The plant availability of sludge P is rated differently in various studies, probably due to the modifying influences mentioned above. Sikora *et al.* (1982) found sludge P availability in the range of 25 to 40% compared to inorganic P. According to Werner (1976) and Gestring and Jarrell (1982) sludge-P fertilisation is about similar to a mineral P fertilisation on a long term basis. McLaughlin and Champion (1987) found sludge showed the characteristics of a slow release P fertiliser in the sesquioxic P-deficient soils studied. The relative efficiency of sludge P compared with mono calcium phosphate (MCP) increased from 44 and 64% to 90% and 100% with time on the 2 soils used. The increase in relative efficiency values from sludge in this study was similar to that noted by Pommel (1981). He found P availability in a sludge-amended sand to increase from 17% (day 7) to 66% (day 300). The P supply to plants itself remained lower than from MCP.

Several authors also reported a lower agronomic efficiency of P in sludge compared to inorganic P fertiliser (DeHaan, 1980; McCoy *et al.*, 1986; O'Riordan *et al.*, 1987). DeHaan (1980) was comparing P uptake from sludge-amended soil with a soil receiving a fertiliser containing the same elements in mineral form and found sludge to be effective in supplying N, P, K, Mg and TE. He found that availability of P in 15 different sludges from Holland, Germany and Sweden varied from 20 to 100 % in comparison with P in

MCP. Sludges from waste water treatment plants without specific P-removal systems (ie. without Al, Fe additions) had P availabilities of 36 % to 90 % of MCP.

Pastene (1981) examined sludge P availability from various sludges. He found that the solubility of sludge-borne P is controlled predominantely by sludge Fe and Al and that a decrease of Al and Fe in sludge will cause a large increase in sludge-P availability. Similarly Fritsch and Werner (1988) found that the use of sludge from plants with chemical P precipitation (tertiary treatment) lead to decreased P uptake by plants in comparison to mineral and manure fertilisation in a long term fertilisation study. The important influence of Al and Fe on P solubility was also recently demonstrated by Moore and Miller (1994) who found greatly reduced levels of water soluble P levels in poultry litter with the addition of alum, ferric chloride, ferrous sulfate and ferric sulfate. To judge P availability in terms of Al content of sludge Pastene (1981) suggested the molar ratio of total Al plus Fe to P in the sludge as a reasonable measure of the relationship of the metals in terms of controlling P solubility. If this value is considerably less than one, the potential exists for large quantities of soluble P to be unavailable for plant uptake.

O'Conner *et al.* (1986) found in field and greenhouse studies that sludge can serve as an excellent amendment to increase water-extractable P-levels in calcareous soils. The P in sludge increased waterextractable P-levels in soil almost immediately and the P status was maintained for 1-2 years. Additions of inorganic P fertilisers to the same soils however had only temporary effects on waterextractable P. They found sludge to be more effective than inorganic fertiliser on those calcareous soils and explained that by a slight pH decrease caused by the sludge. (O'Conner *et al.*, 1986). O'Conner *et al.*, (1986) found that the solubility behaviour of sludge P suggests a complex equilibrium balance between DCPA (di calcium phosphate anhydrous) and Fe and Al compounds similar to variscite and strengite , which would be expected to be good sources of P for high pH soils. However variscite and strengite show a low solubility in low pH soils. Sludge with a Fe and Al compounds therefore could be different in their potential P supply depending on the soil type.

Care must be taken to use soil extractants as a measure to compare P availability of sludge and mineral P fertilisers. Additions of municipal sludge to calcareous soils of New Mexico increased $NaHCO_3$-extractable and water-soluble P levels and increased P tissue concentration (Sanchez, 1982) in comparison to plants fertilised with inorganic P. Inorganic P fertiliser increased the $NaHCO_3$ extractable P, but water soluble P increased only slightly and plants failed to reflect increases in either P uptake or tissue concentration. The problem of increased plant available P levels in soils but plants not responding in terms of uptake has been also noticed for sludge additions. While soil extractable P levels have always increased following sludge addition, the same cannot be said of crop uptake (McLaughlin, 1984). McLaughlin (1988) compared 5 chemical tests assessing P availability with a short term bioassay procedure in two acid soils. All the chemical tests greatly underestimated the effectiveness of sludge P as a source of fertiliser P. According to these findings plant or even field experiments can not be replaced with soil chemical extraction methods until the effect of sludge P on soil solution P and plant uptake of P in a particular soil is established.

2.4.3 Sludge use for amelioration of micronutrient deficiencies

2.4.3.1 Iron (Fe) and zinc (Zn)

The idea of recycling sludge nutrients like N, P, K, Mg in agriculture is not new but rarely has the idea been applied to micronutrients like Zn, Cu, Fe, Mn and others. The emphasis has been mainly on toxic effects of heavy metals, i.e. micronutrients and metals without biological function. One reason for this different perspective might be that trace element deficient land is not concentrated around big cities in northern Europe and USA, where the bulk of research on sludge effects on soil and plants has been conducted. Experiments considering sludge as a trace element fertiliser have mainly been undertaken in arid regions and on alkaline soils developed from calcareous material where Zn, Cu and Fe deficiencies can occur. A common problem in these trace element deficient alkaline soils is that micronutrients applied in mineral form do not remain plant available for a extended period of time. Adsorption and precipitation processes decrease plant availability over time. Synthetic chelates generally are the most effective micronutrient sources, but they usually are the most costly per unit of micronutrient (Mortvedt and Gilkes, 1993). Therefore agronomic considerations often prohibit their use. The idea to use natural organic complexes from sewage sludge to ameliorate micronutrient deficiencies, particularly iron (Fe) deficiency, was examined by McCaslin and O'Conner (1982). Sludge improved sorghum (*Sorghum bicolor*) yield in an Fe-deficient (calcareous) soil beyond yield of plants fertilised with Sequestren (chelated Fe). The application of 30-90t ha^{-1} sludge to a calcareous soil in a field study decreased Fe deficiency in *Sorghum bicolor* (McCaslin *et al.*, 1987). However the addition of a sludge water extract with or without inorganic Fe, and Fe alone, were found to be ineffective (McCaslin and O'Conner, 1982). In the field study, sludge improved yields and soil test Fe levels in following years which mineral fertiliser and manure failed to achieve. Sludge also significantly increased yields on a Zn deficient soil. However Cripps and Matocha (1991) could not completely ameliorate grain sorghum Fe deficiency with sludge amendments, compared to using Fe-EDDHA. Therefore no clear conclusion can be drawn on whether sludge trace metals are as efficient or are a superior metal source to synthetic chelates or the inorganic form of the metal.

2.4.3.2 Manganese (Mn)

Sludge applications can also have an influence on Mn uptake of plants. Both increases and decreases in plant Mn concentrations of plants after sludge additions have been observed. The use of one sludge type (liquid, anaerobic, digested, low metal) drastically increased the Mn content of maize compared to the Mn content of the maize growing in the control plots (Juste and Solda, 1984). However another sludge type (solid, anaerobic digested sludge, high metal) decreased Mn content of maize below the level measured in control plots.

2.4.4 Sludge as a source of organic matter

Besides its quality as a nutrient provider sludge also contains organic C, at concentrations ranging from 18-39 % (median 27) for anaerobic sludges (Sommers, 1977). The use of sludge to increase soil organic matter content or improve soil structure has been judged differently by various authors. Poletschny (1987) claimed that sludges are mainly nutrient contributors and benefits from addition of organic matter are only of minor importance. He argued that 5t of sludge (maximum permitted application rate in three years in Germany) contain usually at most 2.5t organic material, which is a comparatively low amount and easily exceeded by the crop residues normally returned to the soil. Boguslawski (1987) mentioned that the two parameters, carbon (C) and N content of soil treated 16 years with sludge (sludge application rate 2.5 t year^{-1}) or inorganic fertiliser were not considerably different.

2.5 Metals in sludge

There is a vast amount of literature about heavy metals in sludge covering different aspects like sludge chemistry, heavy metal mobility in sludge-amended soils, heavy metal adsorption and precipitation in sludge and soil and plant uptake of metals (Sterritt and Lester, 1980; Beckett *et al.*, 1983; Chaney, 1985; Sauerbeck and Styереck, 1987a,b; Sauerbeck, 1991). A complete review of the various studies is very extensive and would go beyond the scope of this work. Only certain issues will be raised, which address the influence of organic matter on plant availability of metals and a brief summary of methods used to assess this.

2.5.1 Form of metals in sludge

The chemistry of metals in sludge is complex and a range of chemical forms of metals can be expected. The chemical form of a metal is important because it determines to a certain extent the availability of the metal in a sludge-soil mixture (Lake *et al.*, 1984). If metals such as Cd or Zn enter the treatment plant in aqueous form, co-precipitation with phosphates, hydrous oxides or sulphides of Fe, Al and with phosphates and carbonates of Ca would be expected (Logan and Chaney, 1983). Metals associated with organic matter are probably bound strongly to complexing sites. Soon (1981) suggested that metals in sludges are often associated with the insoluble inorganic components and are not readily plant available. However the maximum concentration of Cu, Ni, Zn, Pb and Cd found in saturation extracts of sludges exceeded the solubility products of the hydroxides and carbonates of those elements. This suggests that the chemical form of these elements which occurs in solution is in part organic (US-EPA, 1974).

Sludges contain a wide variety of sites capable of metal retention. Retention mechanisms include ion exchange, sorption, chelation and precipitation. Numerous chemical and physical fractionation methods have been used to characterise metal forms in sludge and to estimate metal bio-availability (Leschber *et al.*, 1984; Lake *et al.*, 1984). A number of studies have attempted to examine the chemical form of heavy metals in extracts of sludge-amended soils (Dudley *et al.*, 1987). Dudley *et al.* incubated a soil sludge mix for up to 30 weeks and separated metal species in the saturation paste by gel filtration chromathography. They found Cu mainly associated with soluble organic compounds throughout the 30 week period. Zinc generally eluded in a region suggesting Zn inorganic complexes. Dudka and Chlopecka (1990) used a sequential extraction to partition Cd, Cr, Ni, Zn in soil and sludge into five operationally defined fractions: exchangeable, bound to carbonates, bound to Fe, Mn oxides, bound to organic matter and residual metals. They found an agreement between metal speciation of Cd, Cr, Ni, Zn in the soils and uptake of the metals by plants and their capacity for leaching. However, the exchangeable fraction of Zn and Ni in the sludge amended soil increased by the factor of 57 and 2 after sludge application, but plant uptake increased by the factor of 7.5 and 3, which shows some problems in quantitative predictions of plant metal uptake based on chemical fractionation.

The diversity of reagents used to extract specific metal forms in (sludge amended) soils make comparisons of such studies difficult. Even if the reagent used is the same, the amount of extractable metals will be a function of the sample size, duration of extraction, temperature and other factors (Sterrit and Lester, 1984).

2.5.2 Influence of soil properties on sludge heavy metal availability

The uptake of heavy metals by plants is dependent on plant species, metal source and soil properties. The accumulation of TE, or heavy metals, by plants is a reflection of the influence of soil physical properties, plant growth, soil hydraulic properties and chemical properties. Important soil properties are soil pH, soil organic matter, clay minerals and oxidation and reduction status of the soil (Sommers *et al.*, 1987). The most important chemical processes affecting the behaviour and bio-availability of metals in soils are those concerned with the adsorption of metals from the liquid phase on to the solid phase. The CEC is often seen as a measurement summarising the adsorption capacities of clay, various oxides and organic matter in the soil. But the relationship between CEC and plant uptake remains unclear (Logan and Chaney, 1983). Cation exchange capacity is a soil parameter, in which specific sorption of particular elements cannot be expressed. Mineral soil components such as Fe and Mn oxides have, like organic substances, a considerable but pH dependent sorption capacity for heavy metals (Herms and Brümmer, 1984). Herms and Brümmer (1984) considered the adsorption capacity of Mn, Fe, Al oxides as high at neutral reaction of the soil. Although hydrous oxides do not contribute much to the CEC of a soil below pH 8, they specifically adsorb considerable amounts of Cd (Alloway, 1990).

In the case of metal activity in sludge, the major influences controlling metal availability could be application rate dependent, because the sludge itself contains adsorption capacity. If the trace element adsorption capacity of the applied sludge is small compared to the adsorption capacity of the soil, the soil properties will be very important in determining the equilibrium solution activity. However if the trace element adsorption capacity of the sludge is high compared to that of the soil (usually associated with high sludge rates) the sludge properties will dominate (Corey *et al.*, 1987).

2.5.3 Influence of organic matter of sludge on mobility and plant uptake of metals

Metal complexation by dissolved humic materials affects metal solubility and thus has been the subject of much research (Hesterberg *et al.*, 1993). Information about the importance of organic matter on TE and/or heavy metal availability is still equivocal.

In the literature dealing with application of sludge to land, it is generally accepted that sludge metals are less plant available than the comparable amount of metal applied as a inorganic salt (Chaney, 1985; Logan and Chaney, 1983). Considerable research on trace element (heavy metal) uptake by plants revealed that metals applied as salt accumulate in plants more readily than the same quantity of metal added in sludge. Similarly van der Watt *et al.* (1994) found that the Zn content of Sudan grass was higher when Zn was given as Zn sulfate in comparison to Zn in poultry litter. However, Singhania *et al.* (1983) found in a pot study that plant availability of Zn from Zn-enriched manure was less than equal amounts of $ZnSO_4$, while Zn availability from Zn-enriched cow dung slurry was greater.

The literature dealing with Zn, Cu and Fe as micronutrients claim that their availability is increased in the presence of organic complexing agents. For example soil organic matter may increase the diffusion of zinc in soils (Sharma and Deb, 1988) by desorption of zinc and formation of soluble complexes, thereby increasing release, concentration and thus supply rate to the root surface (Marschner, 1993). Complexed cations are less prone to adsorption and thus remain available for plant uptake. Zinc chelates were reported by a large number of workers to be more effective in counteracting deficiency symptoms in crop plants than treatments with equivalent amounts of $ZnSO_4$ (Wallace and Romney, 1970; Rehm *et al.*, 1980). Addition of chelating agents to soils also increased plant uptake of Cd by beans (Wallace *et al.*, 1977). The added chelator forms a soluble chelate with part of the Cd which is normally strongly adsorbed to soil. McCaslin and O'Conner (1982) concluded from their experiments that long term benefits of sludge additions may include effects of natural chelates, but that the dominant benefit of sludge is in being a source of readily available metals.

The fact that influences of organic material on trace element availability are assessed differently in the above mentioned studies may be based on several points. The application of organic material involves several changes to the soil environment, which poses an experimental problem. The pH is likely to be influenced and that in turn affects metal solubility and metal complexation. Barnard *et al.* (1992) found that at high pH the uptake of Fe and Zn is significantly enhanced by coal-derived fulvic (FA) and humic acids (HA). Van der Watt *et al.* (1994) also found that at high pH the FA increased the uptake of Mn and Zn from one soil and quartz sand, while it had no effect in another soil. However, at low pH the FA additions decreased the uptake of metals significantly in five out of 18 cases, while in the remainder no significant effect was observed.

Also the quality of organic material seems to be of importance. Organic matter can be variable in terms of size and other characteristics such as attached chemical groups, differing considerably in metal binding ability. Therefore, the kind of organic matter can have an impact on metal solubility. Herms and Brümmer (1984) found that an addition of high molecular weight organic substances (peat) caused a decrease of the Cu, Cd (pH 3 to 8) and to a lesser extent the Zn (pH 3 to 7) concentrations in the soil solution, in comparison to soil samples without peat addition. With the addition of low molecular weight soluble complexing agents (hay), a mobilisation of Cu, Cd and Zn (Zn from pH 4) resulted. The resulting net effect for the solubility of heavy metals can be quite variable, because in different soils, various concentrations of organic substances with mobilising and immobilising effects as well as competing mineral substances can be present (Herms and Brümmer, 1984).

Some other differences between studies examining the availability of micronutrients or the availability or toxicity of heavy metals are also worth considering.

-the sludge/organic manure addition comprises the addition of not only water-soluble FA and HA but water insoluble organic adsorption sites as well, whereas the addition of synthetic chelators only include the water soluble part of organic matter.

-the sludge is considered to be a source of organic complexing agents and a source of metals. Both influence metal availability but can hardly be studied separately.

-sludges could provide a proportion of very specific sorption sites for some metals and thus could adsorb a proportion of metals strongly. Plants have specific sulphur-rich proteins to trap metals in the root and avoid damage to the shoot (Reddy and Prasad, 1990) . Sludge is often is rich in sulphur and could possibly also have special sulphur metal bonds which strongly adsorb metals (possibly stronger than other organic materials).

-studies dealing with metals as micronutrients are generally performed at a much lower soil or soil solution concentrations of metals than studies dealing with metals in terms of potential toxicity. Different soil chemical processes operate at low and high concentrations in solution and therefore are not directly comparable.

- soil pH values are often different. Studies dealing with sludge as a source of potentially hazardous heavy metals are often performed under low pH conditions, to establish a worst case scenario. Studies ameliorating TE deficiency are often done under high pH conditions.

Although the effects of organic complexation of metals on their plant availability are not yet completely known, some effects on the soil chemistry of metals are known. Water soluble organic material is known to affect cation concentration, speciation and replenishment of cations in soil solution by (Kuiters and Mulder, 1993b) :

a) maintaining cations in a soluble state at higher concentration than expected on the basis of their solubility products

b) by lowering free cationic concentrations in the equilibrium solution due to complexation

c) by mobilising cations from the solid phase at a higher rate than by solubilisation from (hydro) oxides (a process which normally proceeds very slowly)

d) by facilitating their transport, especially at higher soil pH.

For Zn, Cd and Mn, the pH and electrolyte-concentration dependent sorption at the surface of particles determines the concentration of metals in solution (König *et al.*, 1986), because at low concentrations of metals, adsorption processes maintain solubility at a level too low for precipitation to occur (Herms and Brümmer, 1984). Hodgson *et al.* (1966) found that soluble metal concentrations in systems containing naturally occurring complexing agents are normally several orders of magnitude above those in comparable systems devoid of complexing agents. Maintaining cations in a soluble state in solution implies that they are not adsorbed as readily as would be expected from experiments with free cations. Low molecular weight organic ligands can form soluble complexes with metals and prevent them from being adsorbed or precipitated (Alloway, 1990). Chairidchai and Ritchie (1990) found that 6 organic ligands all decreased sorption of Zn by a lateritic soil. For Cd, Neal and Sposito (1986) found only at low Cd concentrations that soluble organic material can inhibit Cd sorption due to formation of Cd organo complexes in solution. In contrast, Haas and Horowitz (1986) found that in a few cases Cd complexation with organic matter enhanced adsorption to kaolinite and suggested that this is due to formation of an adsorbed organic layer on the clay surface.

There are a number of studies to determine the extent of complexation of metals in soils, but given the complexity of various systems the results are quite variable. Quantitative data about soluble organic substances as carriers of micronutrient cations in the soil solution are limited (Stevenson, 1991). Predictions based on computer modelling (GEOCHEM) have shown that metals that form weak complexes (Cd^{2+}) are found mostly in free ionic forms. Sposito and Bingham (1981) found less than 5 % of the Cd in solution to be bound to organic ligands in a study with sludge-amended soil.

However several difficulties are encountered in determining stability constants of metal/soil organic matter complexes (Stevenson, 1991). The stability constant of an organic metal complex determines the extent of complexation in the soil solution where cations such as Ca and Mg are abundant in orders of magnitude higher than the metals. Iron, Al, Pb and Cu form considerably more stable complexes with fulvic or humic acids than Cd, Zn, Mn, Ca and Mg (König *et al.*, 1986; Kuiters and Mulder, 1993a). Pohlmann and McColl (1988) found a direct relationship between organic compounds released from litters and Al and Fe dissolved from soil, but not for Mn, Mg. At low pH, metal ions showed the following order of stabilities Fe>Al>Cu>Ni>Pb>Ca>Zn>Mn (Krishnamurthy, 1992). König *et al.* (1986) argues that for Zn, Cd and Mn possible humic complexes have only a low stability or do not form at all. Also Kabata-Pendias and Pendias (1992) reported that the stability constants of Zn organic matter in soils are relatively low, but a high proportion of Zn is bound to organic matter in mineral soils. Formation constants have been determined but the reported values vary over as many as eight orders of magnitude depending on pH, type of humic substance and other variables (Barak and Helmke, 1993). In general the stability of the complexes increases with increasing soil pH due to increased ionisation of functional groups (Jones and Jarvis, 1981) . Also, with increasing pH an increased solubility of organic complexing agents is noticeable (Herms and Brümmer, 1984; Kabata-Pendias and Pendias, 1992). Also the ionic strength can influence metal organic complexes. The values of the stability constants of FA-metal complexes decreases linearly as the ionic strength increases from 0 to 0.15 (Krishnamurthy, 1992). Additionally under high ionic strength, dissolved organic substances can change their molecular shape or may flocculate. On addition of salt, the cations attach themselves to the negative groups (of polyelectrolyte- humic substances) causing a reduction in the mutual repulsion and thus favouring coiling of the chains (Krishnamurthy, 1992). Another important factor in the binding of divalent cations is the extent to which binding sites on organic surfaces are occupied by trivalent cations, notably Fe and Al (Stevenson, 1991).

Hendrickson and Corey (1983) characterised soluble complexing agents from a sludge-amended soil. The results indicate that a portion of the ligands had approximately $10^{5.5}$ times greater affinity for Cd and Zn than for Ca. This marked selectivity for Cd and Zn, determined by the chelating resin method, is much greater than existing selectivity data from similar systems.

Plants only take up dissolved substances out of the soil solution. Complexed metals which are protected to some degree from adsorption could therefore be assumed to be good sources for plant uptake. However, which complexes and to what extent soluble heavy metal complexes (with organic substances) are plant available is not completely known. Checkai *et al.* (1987) argued that the accumulation of Cd, Zn, Mn and Cu in plant shoots appears to be related to their respective ionic activities rather than their concentrations in hydroponic solution. However recent studies with chloro complexed Cd ions suggest that uptake of complexed Cd by plants may be possible (Smolders and McLaughlin, 1996a,b). The ionic radius of chloro complexed Cd is presumably smaller than for organically complexed Cd and thus those findings may not have any implications for organically-complexed ions.

Organic complexation of metals may alter the phyto-availability of some metals but a substantial increase of metal movement in the soil profile seems to be unlikely in most cases after sludge additions. A substantial metal movement in the soil profile due to sludge application was only noticed when very high amounts of liquid sludge were applied (Dowdy *et al.*, 1991; McLaren and Smith, 1996). In sludge-amended soils it is often found that the majority of the Cd and other heavy metals remain in the top 15 cm (Alloway, 1990; Guisquiani *et al.*, 1992). Emmerich *et al.* (1982) added anaerobically digested sludge to a soil column and leached it for 25 months. The concentration of the metals in the soil solution were very low, so that their contribution to metal movement was considered negligible. The changes in metal concentration across the sludge soil interface in most columns was dramatic indicating that the metals had not moved out of the sludge soil layers (Emmerich *et al.*, 1982).

The extent and the importance of organic chelation of metal cations on metal concentration in solution and phyto-availability is difficult to quantify and will vary from soil to soil. However, sludge additions can alter the soil environment in many ways, and the addition of organic complexing agents is only one factor. The possible significance of inorganic complexing agents (for example Cl) will be discussed in a following section.

2.5.4 Methods to assess bio-availability of metals

Various approaches to assess the potential bio-availability of metals have been used. Firstly the total content of a particular element in the soil can be measured, or EDTA- (ethylene-diamine-tetra-acetate) , $CaCl_2$ extractable or other chemical fractionation techniques may be used. The correlation of the different methods with plant metal uptake varies between studies, depending on test plant, soil type, metal considered and source of metal. Sequential extraction procedures have recently been reviewed by Beckett (1989. Jing and Logan (1992) used a chelating resin to estimate metal bio-availability in 17 different sludges. The resin extracted about 0-5.3% of total sludge Cd, and correlation to Cd uptake by Sudax grass (*Sorghum bicolor*) was R^2=0.57. Jing and Logan (1992) also extracted a number of sludges with different extractants ($Ca(N0_3)_2$ 0.05 M, $Ca(NO_3)_2$ + 50 uM NaEDTA, water) and found a very good positive correlation with the Cd uptake by Sudax grass. However, Beckett *et al.* (1983) analysed EDTA-extractable and acetic acid soluble Cu and Zn in sludge amended soil and plant uptake of those elements, but increased extractability did not necessarily lead to increased plant uptake and in some cases uptake increased even when extractability did not.

Evaluating the Cd uptake by plants is often done in pot experiments. However, the uptake of metals by plants grown on sludge-treated soils in the field can neither be simulated by the uptake of plants grown in hydroponic or pot cultures, nor represented by the uptake of plants grown on media spiked with soluble inorganic metal salts (Chang, 1992). These conditions do not simulate metal uptake by crops grown on sludge-amended soils in the field. Plants under such conditions tend to accumulate greater amounts of metals than when they are grown in the field receiving similar sludge treatments. DeVries and Tiller (1978a) have shown that a sludge application brought about a sharp increase in metal concentration in plants grown under glasshouse conditions, but there was generally little increase in the concentration in the field-grown plants.

Soil extraction methods or pot studies are an easier and quicker method to assess metal availability in sludge-amended soil, but some uncertainty remains. Field experiments are still required, until extraction methods have been calibrated for various soils in a particular region.

2.5.5 Metal uptake of plants after sludge applications

The relationship between sludge application rate and metal uptake by plants has been investigated by many researchers (Gestring and Jarrell, 1982; Chaney, 1985; Chang *et al.*, 1987a,b; Sauerbeck 1991). In general experiments have to be distinguished on the basis of their application rates. The factors controlling heavy metal transfer from soil to plants do not just depend on the soil and plant attributes, but as well on the specific contamination level (Sauerbeck and Styperek, 1987b). A number of experiments have used high application rates to establish soil metal levels causing phyto-toxicity or a risk for animal or human nutrition when consuming plant parts (Soon *et al.*, 1980). For Cd and Zn the metal concentration in tissue approaches in general a maximum and has shown a logarithmic or Langmuir type relationship with sludge rate (plateau effect) (Corey *et al.*, 1987).

In agricultural practice, lower sludge application rates are more likely to be used. Field experiments where sludge was applied annually for three consecutive years at agronomic nitrogen rates showed that Cd and Zn concentrations in leaves, stover and grain of corn were increased significantly by the sludge additions. After sludge applications were terminated, concentrations of these metals in aerial parts of corn plants, although still higher than the control, decreased with each successive corn crop (Hinesly *et al.*, 1984).

The hypothesis that sludges with low Cd content contribute less to Cd uptake of plants than high Cd sludges is generally accepted. However Jing and Logan (1992) could not prove this hypothesis in their study using different sludges and applying similar amounts of Cd per pot. The weak correlation of Cd uptake with sludge content vs the much higher correlation with the various estimates of Cd bio-availability indicate that there are factors other than Cd content alone that determine the potential for sludge Cd to be transferred to the food chain.

Corey *et al.* (1987) suggested that some low metal sludges might even reduce metal uptake compared to that from unamended soil. They suggest that sludge P may reduce the solubility of sludge Cd by co-precipitating Cd as various phosphates. Bates (1986) cited by Corey *et al.* (1987) found a measurable though not statistically significant decrease in plant Cd concentration compared to the control treatment with a sludge in which the Fe and P contents were 8% and 5% respectively, even though the total sludge-applied Cd was 1.63 kg ha^{-1}. Also Hooda and Alloway (1993) found a lower Cd accumulation of plants grown in soil treated with high sludge rates (150 t ha^{-1}) than in soil treated with low sludge rates (50 t ha^{-1}).

These above mentioned studies describe the effect of a single sludge application on the metal uptake of plants. The question of whether a single large sludge application has a similar effect to a number of smaller applications over years has often been posed. Response curves (ie. metal input from sludge application vs. metal levels in plants) generated from single sludge additions usually have steeper slopes than response curves generated from multiple sludge additions which have the same total input spanned over a period of time (Chang *et al.*, 1987a). The comparison of a single large application of sludge to annual low (20t ha^{-1}) applications performed at 15 sites in USA revealed that by the time when inputs from the multiple applications had reached the same amounts as with the single application, plant tissue metal concentrations of the single sludge application were not significantly different from incremental additions (Chang *et al.*, 1987a) .

The resulting cumulative effects from annual sludge applications (mainly field experiments) in terms of metal uptake may also be broken into 2 categories as was apparent from data of several researchers (Chang *et al.*, 1987a), namely:

-high levels of Zn and Cd (>100 kg Zn ha^{-1} $year^{-1}$, >1 kg Cd ha^{-1} $year^{-1}$) resulted in increases in plant tissue metal concentration over the years of sludge application , but the rate of increase decreased over time.

-sludge application applied at agronomic rates to satisfy N requirements for crop growth cause Cd and Zn concentration in plants to become greater than those of the control, but Cd and Zn contents of plant tissue remained at a low, nearly constant level with each successive sludge application.

In the long term, plant uptake of sludge applied Cd and Zn is a curvilinear (plateauing) response to the cumulative application rate of applied constituent in sludge. Further, the plateau reached is a function of the concentration of the constituent in sludge and other sludge properties such as Fe added during sludge processing (Chaney *et al.*, 1987).

The availability of metals after cessation of sludge applications has also been studied by a number of workers. In an incubation study Goto *et al.* (1993) found the Zn concentrations in plants decreased with increasing time of incubation of the sludges with the soil. The long-term observations made in field experiments showed that the plant availability of metals in sludge-treated soils either remained unchanged or was reduced with time after cessation of sludge applications (Chang *et al.*, 1987a). Heckman *et al.* (1987) examined the residual effect from sludge application on heavy metal uptake by soybean with respect to different sludge processing technologies, metal concentrations, application rates and soil pH (7-8 years after sludge application). The results indicated that sludge composition and soil pH can have a substantial influence on soybean metal uptake for at least nine years after the initial sludge application. Similarly McGrath (1987) found in a review of other work that metal uptake by crops in the years after sludge application remained constant in 9 out of 11 studies considered. (Lloyd *et al.*, 1981) indicated that sludge Cd remained nearly 100% labile many years after application.

2.5.6 Effect of liming on metal uptake of sludge-amended soil

With pH being a crucial factor in metal availability, liming was and is often used as a treatment to decrease plant metal, in particular Cd, uptake. Metal availability except for Mo and Se, tends to decrease with liming (Sommers *et al.*, 1987). However, it was found that an increase in soil pH may not necessarily reduce markedly the uptake of trace elements from sludge treated soils (Sommers *et al.*, 1987). In general, lime applications reduce uptake of Zn and Ni more than Cd (Singh and Narwal, 1984). Also the impact of reducing pH is more marked with high metal sludges (Sommers *et al.*, 1987). Hence lime application or a high pH soil might not in all cases assure a low metal uptake by plants.

Increases in Ca^{2+} concentrations in soil solution, which can arise after liming of soils, can lead to an increase of the solution concentration of Cd (Christensen, 1984), because with increased concentration of cations in solution (and ionic strength) a desorption of heavy metals from the non-specifically adsorbed fraction can take place (Herms and Brümmer, 1984). Christensen (1984) found that increasing the solution Ca concentration by a factor of 10 (10^{-3} to 10^{-2}) reduced the adsorption capacity of a sandy loam by 67%. Salardini *et al.* (1993) observed an increase in poppy seed Cd concentration with gypsum. This may be the result of an increase in Cd ion availability due to the influence of both Ca ion concentration and the ionic strength of the soil solution.

2.5.7 Guidelines for the use of sludge in agriculture

In a number of countries there are sludge guidelines in place restricting the application of metals, organic toxicants and potential pathogens to the soil (Lübben and Sauerbeck, 1990; US-EPA, 1992). So far there are no national guidelines regulating sludge applications for Australia. There are specific guidelines (but no regulations) for the use of sludge on agricultural land for New South Wales (Ross *et al.*, 1991) and for South Australia regulations are in preparation.

The US guidelines are based on a risk assessment approach, which considered 13 pollutant transport routes and exposure scenarios for land application of sludge, which in turn determined maximum permissible metal concentrations in sludge and maximum annual or cumulative loading rates of metals with sludge to soils (McGrath *et al.,* 1994). The soil-plant-human pathway, that means the risk of metal uptake by humans via their plant based nutrition, is especially critical for Cd in comparison to Cu, Cr, Ni, Pb, Zn and Hg (McGrath *et al.,* 1994).

Although acute Cd toxicity caused by food consumption is rare, chronic exposure to Cd in food significantly increases the accumulation of this trace element in body organs like kidneys and liver. Renal tubular dysfunction and consequently proteinuria is generally accepted as the main effect following long term low level exposure to Cd, that may continue even after cessation of the exposure. Long term renal tubular dysfunction may lead to abnormalities of calcium metabolism and osteomalacia (Hallenbeck, 1984). The Acceptable Daily Intake (ADI) standard given by the WHO/EPA for Cd uptake by humans is 7 ug kg^{-1} body weight $week^{-1}$.

The Cd content of Australian food products is very low as indicated in a recent survey by the Food and Agricultural Organisation/World Health Organisation (FAO/WHO, 1990) which also showed Australians have one of the lowest dietary intakes of Cd of those countries surveyed. However, the Cd concentration in food has recently been of concern in Australia because of the strict maximum permissible limits set by the Australian authorities (0.05 mg kg-1) for some items, including all cereal products except bran (Oliver *et al.*, 1995).

The potential risk posed by sludge-Cd in terms of possible contamination of the human food chain or devaluation of food products such as cereals if trade restrictions are not met, illustrates the importance of evaluating sludge-Cd availability under local conditions.

2.6 Cadmium (Cd)

Cadmium is a relatively rare metal, being 67 th in order of elemental abundance. It has no known biological function and is highly toxic to plants and animals in elevated concentration (Alloway, 1990). In general most soils can be expected to contain <1 mg kg^{-1} Cd, except those contaminated from discrete sources (Alloway, 1990). Williams and David (1973) analysed 19 Australian soils and found that the Cd concentrations ranged from 0.02-0.38 mg kg^{-1}.

All plants contain detectable concentrations of this biologically non-essential element (Florijn, 1993). The background levels of Cd in cereal grains as well as in common feed plants that are reported for various countries are fairly low and surprisingly similar. The grand mean values for all cereal grains range from 0.013-0.22 mg kg^{-1} dry weight. (grasses: 0.07-0.27 mg kg^{-1}, legumes: 0.08-0.28 mg kg^{-1}) (Kabata-Pendias and Pendias, 1992).

2.6.1 Cadmium behaviour in soils

Field or controlled column studies generally show that Cd does not accumulate in subsoil horizons, which suggests that Cd is relatively immobile in terms of movement in the soil profile (Emmerich *et al.*, 1982). Cadmium may be retained by soil through both precipitation and sorption processes. However, at low concentration of most metals in soil solutions, concentrations are likely to be controlled by adsorption-desorption, whereas precipitation-dissolution reactions become important at higher metal concentrations (Herms and Brümmer, 1984). Sorption processes can be separated broadly into two groups, depending on the affinity of the adsorbent for the adsorbates. Part of the binding sites in soil are not especially selective; they bind Cd as strongly as Ca. These include the clay cation exchange sites and carboxylate sites on organic matter. Other sites bind Cd much more strongly than they bind Ca, such as particles of Al, Mn or Fe oxides and some sorption sites of organic matter and are called selective adsorption sites (Chaney, 1988).

The sorption potential for divalent metals is determined primarily by the quantities of soil organic matter and oxides of iron and manganese present in the soil (Jenne, 1968).

Factors such as pH, ionic strength, competing effects of other cations, inorganic and organic ligands further influence sorption-desorption processes in the soil. Soil pH affects Cd adsorption by influencing Cd speciation and surface charge on the adsorbing surfaces. Hydrolysis is favoured by increasing the pH and is characterised by a sigmoidal adsorption vs solution pH curve (Forbes *et al.*, 1976). The metal hydrolysis products are more strongly adsorbed than the divalent free metal cations. Moreover, for variably charged surfaces in soils it was found that the magnitude of charge and thus the adsorption capacity of soils increases with soil pH (Van Raij and Peech, 1972). Increasing soil pH therefore causes stronger adsorption of Cd by soil (Christensen, 1984). Soil pH is often regarded as the major variable controlling plant uptake of Cd from soils (Chaney and Hornick, 1978), which is largely ascribed to the large effect of pH on the retention of Cd^{2+} by soil surfaces.

2.6.2 Cadmium uptake from sludge-amended soil

Plant Cd uptake is dependent on soil factors and plant species and varieties. It is well established that plant species can differ considerably in their metal uptake and transfer-coefficient, which is the ratio of metal concentration in the plant to metal concentration in the soil. Cereals show a comparatively low uptake of heavy metals in comparison to many vegetables in particular leafy vegetables (Sauerbeck and Stypereck, 1987b). Additionally cultivars (varieties, genotypes) within a crop species vary significantly in uptake of sludge applied trace elements. As a general rule, cultivars have been found to vary by at least 2-5 fold from lowest to highest uptake response (Florijn, 1993). However a 30-fold variation was found in corn inbreeds (Chaney *et al.*, 1987). Chaney (1985) found substantial differences among wheat types grown on U.S. soils containing background Cd levels. Durum type cultivars contained 0.140 mg Cd kg^{-1} dry grain, while soft red winter, hard red spring and white wheat cultivars contained only 0.044 mg Cd kg^{-1}. In field trials in Australia Oliver and Tiller (1993) found Cd in grain (*T. aestivum*) in the range of 0.04 to 0.1 mg kg^{-1} Cd.

2.6.3 Cadmium and zinc interactions

Geochemically, Cd is closely related to Zn and is found in association with this element in Zn ores (Florijn, 1993). Both metals belong to the group of oxyphilic and sulphophilic elements (Hahne and Kroontje, 1973). There are extensive similarities in the solubility behaviour of Cd and Zn (Herms and Brümmer, 1984), but Zn concentrations in the environment are usually much higher than Cd concentrations (100 to 1000 fold) (Christensen, 1987a). Cadmium and Zn have similar ionic structures and electronegativities. However, they have different ionic radii (Zn^{2+}=0.074 nm, Cd^{2+}=0.097 nm); this difference could be related to the plant selectivity (Abdel-Sabour *et al.*, 1988).

Initially the Cd to Zn ratio limitations for metals in sludge was meant to add additional protection under the conditions where soil pH was poorly managed Chaney (1974). It was based on the parallel increase of Cd and Zn in crops as sludge rates increases or soil pH declines. Chaney (1974) advocated that the Cd content of sludges should not exceed 1% of the Zn content. Where Zn concentrations were high, Zn toxicity to plants would reduce the chances of crops with high contents of Cd being consumed (Chaney, 1974). Compared to Cd only pollution, Zn-Cd combined pollution may or may not decrease Cd concentration in edible tissue, but because it increases their Zn concentration it also lowers plant Cd bioavailability to humans or animals (Chaney, 1988).

Cadmium and Zn competition can potentially occur as competition for adsorption sites in the soil and for the uptake by plants. These processes should be distinguished. Tiller *et al.* (1979) looked at the specific and non-specific sorption of Cd and found that the addition of Zn decreased the specific adsorption of Cd in 3 of 4 clays studied. Christensen (1987a) also showed Zn competition for Cd soil sorption sites. This may be significant at a Zn solute concentration above 100 μg Zn l^{-1}. Christensen (1987b) showed that a mixture of Ni, Co and Zn or Cr, Cu and Pb effectively reduced the sorption of Cd onto the soils. The mixture of heavy metals was to resemble a moderately polluted soil. Zinc which is present in relatively higher concentration than Ni and Co, accounted for most of the observed competition with Cd (Christensen, 1987b).

However, when considering the plant uptake there appears to be no consensus in the literature about the effect of Zn in soil on Cd uptake by plants (Oliver, 1994). It is not clear yet if Zn and Cd get taken up by the same mechanism at the plant cellular level. This makes the interaction of Cd and Zn even more complex. Cadmium uptake at low external concentrations (below 0.5 µM) appears to be under metabolic regulation with a passive component at higher concentrations (Florijn, 1993).

Smilde *et al.* (1992) showed that (comparatively high) Zn additions reduced plant Cd uptake in a number of different plant species. Abdel-Sabour *et al.* (1988) noted that increasing Zn concentration in soil inhibited Cd uptake by Swiss chard and maize. Addition of $ZnSO_4$ and $ZnCl_2$ decreased the seed Cd concentration of poppies (Salardini *et al.*, 1993). Similar results have been found in field grown wheat in South Australia when soils were Zn deficient (Oliver, 1994; Oliver *et al.*, 1994). The partly South Australian field-based study has shown that the Cd concentration in wheat grain can be decreased by up to 50 % by the addition of 2.5 to 5 kg Zn ha^{-1} to soils that are marginally or severely Zn deficient. For potatoes, McLaughlin *et al.* (1994) found only a small but significant negative correlation between tuber Cd concentration and EDTA extractable Zn concentration in soils and added Zn.

McKenna *et al.* (1993) and Gerritse *et al.* (1983) found that the antagonistic effect of Zn on the accumulation of Cd depended upon the level of Cd in solution. The antagonistic effect of Zn on plant Cd uptake was stronger at low than at high Cd concentrations. According to Chaney (1988) the Zn/Cd ratio in the soil is probably decisive for Zn behaving synergistic or competitive to Cd uptake.

Another aspect of TE deficient soils is the fact that graminae can excrete an organic chelating agent under iron (Römheld, 1987) and possibly Zn deficiency which facilitates diffusion to the root and Fe uptake. Root exudates from Fe deficient barley increased the concentrations of Fe, Mn, Zn, Cu in solution (factor 20) and in shoots of Fe deficient barley. This suggests a limited selectivity of the Fe-phytosiderophore carrier (Treeby *et al.*, 1989). An increased Cd uptake due to phytosiderophore production is not impossible. Further research in this area is still needed, but it seems that Zn additions to a Zn deficient soil could be a safeguard in this respect.

These aspects may be quite important when sludge instead of mineral fertiliser as a source of Cd is applied on Zn deficient soils, which are common in South Australia. Under those circumstances a Cd plus Zn application from sludge could then be more desirable than a Cd only source (for example inorganic P fertiliser).

Concentrations of Zn and Cd in sludge can vary widely, but frequently the concentration ratio of Zn to Cd is in the order of >100 to 1 (Zn/Cd ratio of medians of heavy metal concentrations in sewage sludges from Australia, USA and Sweden were 73, 183 and 228 respectively (DeVries, 1983b)). In comparison the Cd concentrations in the main rock phosphate sources for manufacture of phosphatic fertilisers in Australia, until recently, were ranging from 42-99 mg kg^{-1} (McLaughlin, *et al.* 1996). Average concentration of Cd in the most commonly used phosphate fertiliser in Victoria were 17, 19 and 6 mg Cd kg^{-1} for single, double and triple-superphosphate respectively (North -Coombes and Berg, 1990) and lower than the average levels of 38-48 mg kg^{-1} Cd in an earlier Australian study (Williams and David, 1973). Single superphosphate commonly contained approximately 400 mg Zn kg^{-1}, however more recently introduced P sources to Australia can have Zn concentrations as low as 70 mg kg^{-1} (Riley *et al.*, 1992). The ratio of Zn to Cd in P fertilisers is thus in the range of 10 to 1 and considerably lower than in most sludges.

As long as the interaction between the two metals have not been clarified, the addition of Zn with Cd at least still allows a safeguard in terms of human nutrition, because increases in Zn concentrations in plants lowers the Cd bio-availability to humans or animals (Chaney, 1988).

2.7 Influence of chloride (Cl) on Cd and Zn uptake by plants

2.7.1 Cadmium

Chlorides occur in all natural soils and waters and may be regarded as one of the most mobile and persistent complexing agents with regard to heavy metals. Chlorides may also be regarded as being more selective than many organic complexing agents in that they do not complex strongly with Al (III), Ca^{2+} and Mg^{2+} Na^+ and K^+, all of which are in concentration of several orders of magnitude higher than Cd in natural waters and soil solutions (Hahne and Krontje, 1973). Formation of $CdCl^+$ begins at chloride concentrations 10^{-3}M (35 mg l^{-1}) and peaks at $10^{-1.2}$M (2200 mg l^{-1}). Calculations to evaluate the significance of Cl complexation in natural systems showed that at pH 8.5 and a chloride concentration range of 350 to 60000 mg kg^{-1}, Hg (II) and Cd (II) are complexed strongly by chlorides. Zinc (II) and Pb (II) under these conditions are predominantly in the form of hydroxy complexes (Hahne and Krontje, 1973). Chloride forms relatively strong complexes with Cd, with stability constants for the mono and dichloro complexes being 10^{-2} and $10^{-2.6}$ respectively (Smith and Martell, 1981). Depending on the chloride concentration, a range of chloro-Cd complexes form ($CdCl^+$, $CdCl_2$, $CdCl_3^-$, $CdCl_4{}^{2-}$). Soil pH is also known to have a significant influence on Cd sorption/desorption mechanisms and speciation of Cd in soil solution and thus alters the plant availability of Cd. In general Cd sorption decreases with decreasing soil pH.

Garcia-Miragaya and Page (1976) and Hirsch *et al.*, (1989) showed that the amounts of Cd sorbed by montmorillonite were appreciably smaller when the equilibrating solution contained NaCl (0.03 to 0.05 M Cl) compared to ClO_4, which does not form stable complexes with Cd. Similarly O'Conner *et al.* (1984) found that Cd sorption in Ca saturated calcareous soils was reduced in soils equilibrated with solutions containing increased levels of Cl (0.05 M $CaCl_2$) compared to solutions with low Cl concentrations or ClO_4 as a ligand. Decreased adsorption was partly attributed to an increase in ionic strength in the equilibrating solution and partly to the effect of Cl complexing the free Cd^{2+} and thus reducing adsorption.

Elevated levels of Cl concentration in soils are normally combined with enhanced cation concentrations and increased ionic strength, which also potentially could decrease adsorption of Cd to soil. The influence of enhanced cation concentrations and ionic strength can be attributed to three main effects:

1) competition of Cd^{2+} with increasing amounts of the electrolyte cation for available clay surfaces;
2) decrease in the initial activity of Cd^{2+} in solution (before sorption takes place);
3) formation of uncharged ion pairs and/or uncharged and negatively charged complexes of Cd with the anion (ligand) of the electrolyte (Garcia-Miragaya and Page, 1976).

Nevertheless, Gerth *et al.* (1981) found that the adsorption of Cd to different soil types was decreased, when the ionic strength was kept similar to a a comparable equilibrating solution contaning $NaNO_3$ instead of NaCl (10^{-2} to 10^{-1} M Cl). That reduced adsorption of Cd-Cl-complexes can lead to increased mobility in the soil profile was shown by Doner (1978). However, the Cd additions in those experiments were some orders of magnitude higher (0.01-1000 mg Cd l^{-1} in O'Conner *et al.*, 1984; 0.5-50 mM kg^{-1} in Gerth *et al.*, 1981) than Cd concentrations representative of agricultural soils, which are most often in the range of 0.05-0.5 mg kg^{-1} for total Cd in soils (Smolders *et al.*, 1996) and in soil solution values of < 6 µg l^{-1} were found (Gerritse *et al.*, 1983). However, Boekhold *et al.* (1993) also found a decreased adsorption of Cd in an acid sandy soil in the presence of Cl in solution, when using a lower Cd concentration of 0-1.2 µM.

In pot studies Giordano *et al.* (1983) and Bingham *et al.* (1983, 1984) found an increase in Cd concentration of plants when grown in soils with a high salt concentration containing Cl as a major ligand. These studies were conducted in soils with high Cd additions, where Cd can be expected to be weakly bound and thus ion exchange reactions with the accompanying cation could also have influenced Cd availability. However, in a field study by McLaughlin *et al.* (1994) on agricultural soils they found that Cd concentration in potato plants (tubers) best correlated with water-extractable chloride (Cl) concentrations in soils than any other soil factor, even soil pH. Also elevated Cd concentrations in field grown sunflowers (Li *et al.*, 1994) and poppy plants (Salardini *et al.*, 1993) were suggested to be due to high Cl concentrations. These findings suggest that Cl concentrations in soils are also enhancing Cd availability in soils with Cd concentrations normally encountered in agricultural soils. These suggestions were confirmed by a pot experiment of Smolders *et al.* (1996) in agricultural soil (0.02-0.31 mg Cd kg^{-1} EDTA extractable), who showed that increasing concentrations of NaCl in the soil solution increased Cd uptake of plants, whereas increasing ionic strength in the soil solution based on $NaNO_3$ additions were shown to have no effect.

The 'free metal ion' hypothesis has gained credence in recent years, where the bio-availability of metal ions is assumed to be directly related to the activity in solution of the uncomplexed aquo species (Lund, 1990). However, Smolders *et al.*, (1995, 1996) using increasing levels of NaCl or $NaNO_3$ found that with increasing Cl concentration in the soil solution the Cd concentration in solution increased, whereas the Cd^{2+} activity remained constant. Regression analysis showed that $CdCl^+$ was the variable explaining most of the variation in Cd concentration in the shoots of Swiss chard. Although the mobility of Cd is increased at higher Cl levels due to increased Cd concentration in solution, the authors suggested that an uptake of $CdCl_n^{2-n}$ species was more likely to explain the increase in Cd uptake of plants. The increased Cd uptake (due to increased Cl levels in solution) was also demonstrated in solution culture experiments (Smolders and McLaughlin, 1996a,b) and two possible mechanisms were postulated a) $CdCl_n^{2-n}$ species in solution were also plant available (in addition to Cd^{2+}) or b) Cl enhanced diffusion of Cd^{2+} through the unstirred liquid layer adjacent to the root surface or through the apoplast to sites of Cd uptake within the root itself (Smolders *et al.*, 1995 and 1996). However, it appeared that the most likely explanation for the Cl induced in Cd uptake by plants is through uptake of $CdCl_n^{2-n}$ species by plant roots, but that the efficiency of $CdCl^+$ uptake compared to Cd^{2+} was 20%.

These recent findings are in contrast to earlier findings of Bingham *et al.* (1983 and 1984), which investigated the influence of salinity on Cd uptake by Swiss chard. In those studies Cd^{2+} activity in solution was increased due to the Cl treatment; plant Cd concentrations were positively correlated with Cd^{2+} activities. However, in both studies the soil was amended with high rates of inorganic Cd prior to the experiment. In soils with high Cd concentrations ion exchange mechanisms of the weakly bound Cd (at high soil Cd levels) may be more important in determining Cd concentration in solution than at soil Cd concentrations normally encountered in soils.

2.7.2 Zinc

As mentioned earlier, there are extensive similarities in the solubility behaviour of Cd and Zn (Herms and Brümmer, 1984). Speciation of Zn with inorganic ligands such as chloride, which could influence Zn adsorption, is usually of lesser importance because of weak complexing strength (Barak and Helmke, 1993). The formation of $ZnCl^+$ was found to begin at chloride concentrations of 10^{-2} M (354 mg l^{-1}) and peaks at $10^{-0.5}$ M (10000 mg l^{-1}), where plant growth is hardly possible any more. At Cl concentrations less than $10^{-0.4}$ M (89000 mg l^{-1}) pH 8.5 $Zn(OH)_2$ predominates over the Zn (II)-Cl complexes (Hahne and Kroontje, 1973).

2.8 Conclusions

In this literature review only selected areas of the vast amount of literature about different aspects of sludge application to land have been mentioned. However, a significant conclusion is that the number of studies using low sludge application rates in comparison with inorganic fertiliser applications are very few. Even less information is available about the fertiliser value of low sludge application rates in an arid environment or with lagooned and air dried sludge.

Additionally, a unique opportunity existed to assess the use of sludge in comparison to inorganic TE fertiliser as a means to ameliorate Zn or Mn (or Cu, Fe) deficiency on calcareous or sandy, low fertility soils, which are widespread in the cereal belt of South Australia. On soils in Europe and major parts of the USA, the application of heavy metals such as Zn and Cu with sewage sludge is generally considered a potential risk for sludge applications, because soils in those countries contain a higher amount of micronutrients.

However, the potential plant availability of sludge-Cd also needs some consideration, before sludge can be recommended as a inorganic fertiliser replacement. Recent research has shown that high Cl levels in soils can considerably enhance Cd availability in soils. In an arid state such as South Australia this is of importance, because Adelaide sludge contains a comparatively high amount of soluble salts and sludge could potentially be applied on saline soils or irrigated land with possibly low quality irrigation water. Detailed research has been conducted about the influence of Cl on the mobility of soil-(or fertiliser-) Cd. However, the question of whether Cl ligands influence the plant availability of sludge borne-Cd or the Cd in a sludge-amended soil has not yet been addressed.

Objectives of the study:

- Firstly to establish if sludge applications are a beneficial source of N and P to replace a commonly used inorganic fertiliser application on sandy or calcareous soils with low organic matter content.
- Secondly to assess the use of sludge as a means to ameliorate Zn or Mn (or Cu) deficiency on calcareous or sandy, low fertility soils.
- Thirdly to assess the influence of Cl concentrations in soils or soil solutions on the Cd uptake of plants grown in sludge-amended soils.

Chapter 3

Field experiments 1992
Replacement value of sludge for inorganic fertiliser

3.1 Introduction

The N and P fertiliser value of sewage sludge has been the focus of many studies, mainly in Northern USA and Europe (Sabey *et al.*, 1977; Kirkham 1982; Gestring and Jarrell, 1982; Coker, 1983; Parker and Sommers, 1983). The availability of sludge N seems to depend on the sludge type, percentage of total N and the percentage of inorganic N in the sludge as well as application rate and environmental factors. Generally sludge N availability was shown to vary within a broad range of 2-60% of the total N depending on the sludge type and the environment (Chapter 2). For a sludge with a low concentration of inorganic N the gross figure of 10-25 % N availability of the total N was found in a number of studies (Poletschny, 1987; Parker and Sommers, 1983; Pierzynski, 1994). Similarly the P availability of sludge can vary to a great extent. Sludge P availability was judged to be between 20-100 % of that of inorganic P (MCP, DAP) (DeHaan, 1980; Kirkham, 1982; O'Riordan *et al.*, 1987; McLaughlin and Champion, 1987). Sludge type and content of Ca, Al and Fe in sludge were mentioned to have an influence on sludge P availability (Pastene, 1981).

The considerable differences in availability of sludge N and P between the various sludge types makes it difficult to predict the nutrient availability of an untested sludge. Furthermore, few studies of the nutrient value of sludge have been conducted in Australia or on similar soil types and climatic conditions. Willett *et al.* (1986), found in a study conducted under dryland conditions in Australia that sludge was 49 % as effective as the P of superphosphate fertiliser in raising extractable P levels in soils. The sludge proved to be a valuable source of N and P with yields of 5t sludge-treated plants being equivalent to fertiliser rates of 20-40 kg P ha^{-1} and 18-68 kg N ha^{-1} (high P rates combined with low N rates and vice versa). However, this study was conducted on a strongly acidic soil with a legume as the test plant. Furthermore the undigested, lime-treated sludge used in the study of Willett *et al.* (1986) probably had different mineralisation features than the anaerobically digested, air dried sludge produced in Adelaide (Bolivar). Nutrient availability of undigested sludges is generally higher than in digested sludges (Epstein *et al.*, 1978; Parker and Sommers, 1983). The Adelaide (Bolivar) sludge was used in a number of studies by De Vries (De Vries, 1979, 1981, 1983a,b). Low sludge application rates (< 9t ha^{-1}) were found to have little fertiliser value for vegetable crops (De Vries, 1979). However, in the experiments by De Vries (1979) varying amounts of base fertiliser were applied (partly by the farmer) and in most of the experiments no inorganic fertiliser comparison was included. The availability of heavy metals in the sludge was the main emphasis of the experiments by De Vries and hence the results can only give rough indications about the fertiliser value (N and P) of the sludge material. Moreover, nutrient applications to vegetable crops are generally high and an extrapolation of results to cereal crops produced under dryland conditions with low nutrient input is hardly possible. Sandy soils with a low content of organic matter and low N, P and TE content are widespread in Australia and plant response to sludge additions under those conditions is likely to be different than in highly fertilised vegetable crops.

With the field experiments in 1992 it was intended to establish the replacement value of air-dry (unkilned) sludge for inorganic fertiliser in cereal crops at application rates commonly used by farmers in South Australia. Five sites at varying distances from Adelaide and with different soil fertility levels were chosen for the experiment. According to assumptions based on information in the literature a 2t sludge application could be close in nutritional P, Cu and Zn value to the conventional inorganic fertiliser rates used in South Australia. Hence a sludge application rate of 2t ha^{-1} was chosen as a base rate to be compared with the inorganic fertiliser treatment. Sludge treatments with additional inorganic fertiliser amendments were included to supply the (expected) shortfall of N compared to the inorganic fertiliser comparison and to establish if plants were responsive to certain nutrients (N or P) at each particular site. Plant growth at three development stages and shoot or grain concentration of various elements in sludge or inorganic fertiliser treated plants were compared.

Micronutrient deficiencies, such as Zn, Cu and Mn deficiency, are widespread in South Australia and can reduce cereal grain yield to a considerable extent (Graham *et al.*, 1993). Sludge contains heavy metals, of which some are so called 'micronutrients' (TE) essential for plant development. Hence sludge could potentially be a source of both macronutrients and micronutrients. In soils where plants show Zn, Cu or Mn deficiency the availability rather than the total amount of TE is the factor limiting the TE uptake of plants. Sludge borne heavy metals, for example Zn, are generally less plant available than the same metal added as soluble salts (Chaney, 1985). However, chelated micronutrients can be a superior source of nutrients than the metal salts when applied to TE deficient soils (Mortvedt and Gilkes, 1993). The field experiments in 1992 examined whether sludge borne micronutrients (particularly Zn) would be equal to the commonly used inorganic TE fertilisers in alleviating TE deficiency in cereal crops.

The Adelaide (Bolivar) sludge does not contain a high concentration of Mn. Sludge would have to be amended with Mn to be a sufficient source of Mn for plants grown in deficient soil. However, in several studies it was reported that sludge applications reduced the uptake of Mn by plants (Juste and Solda, 1984; Hernandez *et al.*, 1991). The third aim of the field experiments was to determine if Mn treated sludge could be an equal source of Mn when compared to Mn sulphate at a severely Mn deficient site.

3.2 Materials and methods

3.2.1 Sewage sludge chemical properties

The sewage sludge (sludge) from the Adelaide (Bolivar) sewage treatment works used in the field experiments in 1992 and 1993 originated from a single batch, sampled in April 1992. Sludge at this plant is anaerobically digested, lagooned and air dried in the lagoon ponds. Prior to application in the field experiments the sludge was crushed by Pivot Pty Ltd, Wingfield plant, to a particle size of < 1 cm. The air dried product with a water content of around 13 % was used unkilned for the experiments. The rotary kiln process reduces potential pathogens in the sludge and is normally used to treat commercially sold sludge from the Bolivar treatment plant for horticultural crops or private gardens. The kilning of the material is energy demanding and therefore adds considerable cost to sludge handling. When sludge is used in broad-acre farming and incorporated into the soil, it poses a low risk of pathogenic infection to humans or animals; thus a sludge heat treatment was deemed not necessary. A portion of the sludge collected in 1992 was stored for one year in the air-dry state until applied in 1993. Selected properties of the sludge are given in Tables 3.1, 3.2 and 3.3.

Table 3.1 Chemical analysis of the batch of sludge used in the field experiments in 1992 and 1993: general data.

Sludge properties		
Organic carbon	185	[g kg^{-1}]
Ratio C:N	8.8	[g g^{-1}]
Ratio C:P	10.3	[g g^{-1}]
pH (H_20) (soil:water = 1:5)	8.1	
Electrical conductivity	18.2	[mS cm^{-1}]
Water content	13.0	[%]
Bulk density	885	[g l^{-1}]

Table 3.2 Chemical analysis of the sludge used in the field experiments 1992 and 1993: Total content of selected macronutrients and boron, sodium and chloride and potential plant available fractions of sludge N and P

Element		[mg kg^{-1}]	[kg in 2t sludge]
Nitrogen	N	21000	42
	NH_4^+	1800	3.6
	NO_3^-	133	0.26
Phosphorus	P-total	17971	36
	P-citrate	13233	26
	P-HCO_3^{-a}	6333	12.6
Potassium	K	10397	20.8
Calcium	Ca	56502	113
Magnesium	Mg	10176	20.3
Boron	B	86	0.17
Sodium	Na	19598	39
Chloride	Cl	22000	44

[a] bicarbonate soluble P (Rayment and Higginson, 1992)

Table 3.3 Chemical analyses of the sludge used in the field experiments 1992 and 1993: Total content of metals and heavy metals.

Element			[mg kg^{-1}]	[kg in 2t sludge]
Cadmium	*	Cd	3	0.006
Chromium	*	Cr	1623	3.3
Mercury	*	Hg	0.5	0.001
Nickel	*	Ni	80	0.16
Lead	*	Pb	340	0.7
Zinc		Zn	939	1.9
Copper		Cu	723	1.5
Manganese		Mn	220	0.4
Cobalt		Co	10	0.02
Molybdenum		Mo	6	0.012
Aluminium		Al	58225	116
Iron		Fe	18324	36

* analysed by State Water Laboratory (Bolivar)

3.2.1.1 Chemical analyses of sludge

The elements Zn, Cu, Mn, Co, Mo, Al, Fe, as well as total-P and the alkali and alkali-earth cations were analysed by inductively coupled plasma optical-emissions spectrometer (ICP) after a nitric acid digestion (Christensen *et al.*, 1982) (p. 255a, 255b). The results for the heavy metals Cd, Cr, Hg, Ni and Pb analyses were obtained by the State Water Laboratory. Inorganic N (NH_4^+ and NO_3^-) was analysed by autoanalyzer according to Rayment and Higginson (1992). Total N was analysed with a Leco N analyser FP 288 and a N Analyser 1500 series 2 (Carlo Erba Instruments). Bicarbonate-extractable P (P-HCO_3^-) and chloride were analysed according to Rayment and Higginson (1992). The citrate soluble P was analysed by Pivot Pty Ltd. Organic carbon was analysed by the Heanes wet-oxidation method (Heanes, 1984).

3.2.2 Sludge application rates

The purpose of the field experiments was to determine the value of Bolivar sludge as a replacement for inorganic fertiliser and in particular for micronutrients, such as Zn, Cu and Mn (TE), at application rates generally applied by farmers in South Australia. Two tonnes of Bolivar sludge contain Zn and Cu in an amount close to conventional TE fertiliser application rates (Section 3.2.2.3). Also it could contain a comparable amount of plant available P as the conventional P fertiliser rates for South Australia (Section 3.2.2.2). Hence this sludge application rate was chosen as a basic rate for the field studies. The effectiveness of a sludge application or a mix of sludge and inorganic fertilisation can be judged in comparison to a conventional inorganic fertiliser application using plant growth as a criterion. Conventional fertiliser rates for the average cropping area on the sandier soils of South Australia are approximately 20 kg N ha^{-1}, 20 kg P ha^{-1}, 4 kg Mn ha^{-1}, 2-3 kg Zn ha^{-1}, 2 kg Cu ha^{-1} (McDonald, 1992; Batten *et al.*, 1993, Takkar and Walker , 1993).

Single nutrient comparisons between inorganic and mixed organic fertilisers such as sludge are beset with a number of problems. Not only are various amounts of N, P, Ca, Mg, K and trace elements present in sludges, they are also present in organically bound forms not immediately available for plant uptake (Cooke, 1967) . Both the mineralisation rate of sludge N and P and the availability of sludge micronutrients (TE's), particularly Zn in neutral or alkaline soils under South Australian climatic conditions, are unknown. Ideally, one needs to estimate the replacement value for one element at a time for which it is necessary that no other element is deficient or cause a nutritional imbalance to the plants. To compare sludge with inorganic fertiliser two of the three locally important nutritional components (N, P, TE) had to be sufficiently available to plants. Therefore in some sludge treatments additional inorganic nutrients were applied to ensure sufficient supply of these components. Plant growth responses to fertiliser additions generally follow a Mitscherlich type response curve. However, the farmers aim is to ensure optimal agronomic efficiency (highest monetary return rather than highest yield) and, hence, it is in comparison to this target that the sludge will be evaluated. Accordingly, the inorganic fertiliser additions, as chosen in the present study were not meant to ensure maximum plant growth, but rather to match commercial fertiliser rates which are likely to aim at optimal agronomic efficiency.

Because the three unknown factors (N, P, TE) result in a number of possible treatment combinations, some assumptions had to be made to restrict the field experiments to a workable size. Information about potential availability of N, P and TE in sludge is summarised in the following three sections (3.2.2.1, 3.2.2.2 and 3.2.2.3). The applied treatments, which were based on assumptions described in these sections are listed in Section 3.2.4 and Table 3.5.

3.2.2.1 Nitrogen (N)

The literature gives varying figures for potential mineralisation of sludge organic N within a growing season. The mineralisation is dependent on environmental conditions such as weather patterns and soil type, as well as on the kind of organic material itself.

For anaerobically digested sludge, Ryan *et al.* (1973) reported that 4 to 48 % of the organic N was mineralised during a 16 week incubation study. Epstein *et al.* (1978) mentioned that sludge and sludge compost differ markedly in their initial net mineralisation patterns.

Tester *et al.* (1982) found that 10 % of the total N in compost is available as inorganic N for the first crop. Further work in this area is mentioned in the Literature Review (Chapter 2).

The sludge production process used at the Bolivar sewage treatment works makes it difficult to predict whether the mineralisation pattern of the Bolivar material is likely to resemble the mineralisation of digested liquid sludge (dried only for experimental purposes) or a sludge compost. For both materials figures are given in the literature. The comparatively long storage of the Bolivar sludge, in lagoons or stockpiles, is also likely to have an influence on the chemistry and rate of mineralisation of the material.

Another difference to overseas studies is the timing of cereal production, with the majority of the growth period in the cool winter months. Because of all these uncertainties a cautious assumption of 10% mineralisation of the organic N within one growth period was taken. The inorganic N (NH_4^+ and NO_3^-) was considered fully available to the crop.

***Sludge N mineralisation assumptions in 1992*:** At the start of the cropping season 1992 the analysis of the batch of sludge used was incomplete. Average data (#) of the Bolivar sludge provided by Pivot Pty Ltd and State Water Laboratory were therefore used for the calculation (Table 3.4). According to above mentioned assumptions 2t sludge would provide:

$$\begin{aligned} \text{N-available } [\text{kg N } 2t^{-1}] &= (NH_4^+ + NO_3^-) + 0.1 * \text{N-organic } [\text{kg N } 2t^{-1}] \\ &= 2 \;+\; 0.1 * 32 \quad = 5.2 \qquad [\text{kg N } 2t^{-1}] \;\# \end{aligned}$$

Based on these assumptions the available N from 2t sludge would not match the target of 20 kg N ha^{-1}. Thus some sludge amended plots received additional inorganic nitrogen to make up the shortfall between assumed available N from the sludge (5.2 kg N $2t^{-1}$) and 20 kg N ha^{-1}, see Table 3.5.

Table 3.4 Average *# composition of Bolivar sludge and composition of the sludge used in the field experiments 1992 and 1993.

Element	Average sludge		Sludge used	
	concentration	amount in 2t sludge	concentration	amount in 2t sludge
	[g kg^{-1}]	[kg]	[g kg^{-1}]	[kg $2t^{-1}$ sludge]
Mn	0.2 *	0.4	0.22	0.4
Zn	1.4 *	2.8	0.94	1.9
Cu	0.9 *	1.8	0.72	1.5
	[%]		[%]	
N	1.6 #	32	2.1	42
NH_4^+	0.1 #	2	0.18	3.6
NO_3^-			0.013	0.3
P	1.4 #	28	1.8	36
P citrate soluble	1.1 #	22	1.3	26
P HCO_3^- soluble			0.63	12.6

[(*) data from liquid sludge ex anaerobic digester, averaged over the period of 1987 to 1991, State Water Laboratory ; (#) data from Pivot Pty Ltd]

3.2.2.2 Phosphorus (P)

Similar to N, there was an uncertainty about the potential sludge P mineralisation rate and P availability to the crop under South Australian conditions. Therefore some assumptions concerning P availability were necessary to ensure sufficient plant P nutrition in some treatments.

Citrate-soluble phosphorus is a method to determine available P in fertilisers. Bicarbonate-extractable P (HCO_3^- -P) is a method to determine available P in soils. The former uses an acid to dissolve the phosphorus. Sludge as a material is neither similar to soils nor to inorganic fertiliser. Even though sludge P is suggested to be mainly in inorganic form, it is most likely not a crystalline Ca-phosphate or Al-phosphate but is in a organo-mineral-P structure (see Literature Review). Therefore, neither of the two tests is fully appropriate to assess the potentially plant available P from the sludge.

Sludge P availability assumptions in 1992: At the start of the cropping season 1992 the analysis of the batch of sludge used was incomplete. Average data (#) of the Bolivar sludge provided by Pivot Pty Ltd and State Water Laboratory were therefore used for the calculation (Table 3.4). Two tonnes of sludge contained:

P total	28	kg $2t^{-1}$ sludge	#
P as citrate-soluble P	22	kg $2t^{-1}$ sludge	#

Although the citrate soluble P test may not be fully appropriate to be used for sludge, the measured value indicated that a sludge rate of 2t ha^{-1} could provide plant available P in the range considered sufficient for the current study. Additional P therefore would not be needed for the crop. However, sludges high in Al or Fe can have a considerably lower plant P availability than other sludges (Pastene, 1981). The Bolivar sewage treatment works does not have a third, chemical, water treatment step using Fe, Al or Ca for chemical P flocculation. However, the sludge used had a comparatively high concentrations of Al and Fe. An Al-rich byproduct of the drinking-water filtration plant may have been added to the sludge in the anaerobic digester (P. Thomas, pers. commun.). Because of this potential influence of Al and Fe on sludge P availability a sludge treatment with additional inorganic P fertiliser was included. (For details see Table 3.5.)

3.2.2.3 Micronutrients (TE)

a) Zinc (Zn) and copper (Cu) applications in 1992

Based on general data from Bolivar sludge, 2t sludge ha^{-1} would provide: 0.4 kg Mn, 2.8 kg Zn, 1.8 kg Cu (see Table 3.4). The normal application rates for trace element (TE) fertilisers in South Australia are 4-6 kg Mn ha^{-1}, 2-3 kg Zn ha^{-1} and 2 kg Cu ha^{-1} as mentioned above. Therefore a 2t sludge application would contain about the amount of Zn and Cu needed, provided the metals have at least equal or better plant availability compared to inorganic fertiliser trace metals. The use of sludge as a Mn fertiliser and Mn fertiliser rates are discussed in the following section.

In order to compare availability of sludge-borne and inorganic fertiliser TE, the same amounts of Zn and Cu as in 2t sludge were applied in inorganic form to conventionally fertilised plots. Half the amount of the TE was incorporated into the N and P granules and the remaining half was sprayed onto the plots prior to the three workings of the plots. This split TE application meant that part of the TE's were banded with the seeds, similar to conventional TE fertiliser and a part was incorporated into the plowed soil volume similar to sludge TE's. For application rate details see Table 3.5.

A hand-held spraying unit with a boom width of 1.5 m was used to apply the liquid trace element fertiliser mix. The spraying unit applied 0.4 l of liquid TE-Mix on each 30 m^2 plot.

b) Manganese (Mn) applications in 1992

The total amount of Mn in 2t of the sludge was 0.4 kg. This was too low an application rate for most soils in South Australia. The recommended Mn fertiliser rate in South Australia is around 4-6 kg ha^{-1}. On the Mn deficient calcareous sand at the Marion Bay experimental site, a low addition of Mn would probably result in restricted plant growth. Additional Mn therefore had to be given to some inorganic and all sludge amended plots, up to the total of 4 kg Mn ha^{-1}. The (nil) and (nil+N+P) treatment did not receive any Mn or other micronutrients.

To transform the sludge into a potential Mn fertiliser the Mn was applied to the sludge prior to application. Sludge was spread out in thin layers (batches of 6 kg sludge were spread in 8 trays, each with a surface area of 1120 cm^2). Forty ml of a dilute Mangasol solution (13.7 % Mn as $MnSO_4$) was sprayed on the sludge surface, mixed and another 40 ml were applied the same way. The Mn for the inorganic fertiliser plots was partly incorporated into the base fertiliser granules and partly applied as a spray prior to seeding, similar to the other trace elements Cu and Zn (see description above).

3.2.3 Fertiliser and sludge treatments applied in the field experiments 1992

The composition of the various fertiliser and sludge treatments are shown in Table 3.5. The addition of only one growth limiting macronutrient (for example N or P) is of restricted use for balanced plant nutrition, and accordingly the growth response will be limited. Therefore (nil+N) and a (nil+P) treatments were not included in the study. The inorganic fertiliser comparisons at the five sites were (nil), (nil+N+P) and (nil+N+P+TE) treatments. In the sludge treatments, additional N was added to supplement the available N in the sludge and to give N rates of approximately 20 kg ha^{-1}. Consequently the amount of extra N varied with the sludge treatment and the amounts were less than in the inorganic fertiliser. Therefore, this has been designated N* in the sludge treatments to indicate that the rates differ between treatments. The (1t+N^*+P/2+TE/2) treatment was included as a variat of 'optional farmer practice', in case they do not want to rely on sludge fertilisation only. Based on the previous assumptions, the following treatments were applied at the five experimental sites in 1992. For a field plan see Plate 1 in the Appendices for Chapter 3.

nil
nil+N+P
nil+N+P+TE

2t
2t+N^*
2t+N^*+P/2

1t+N^*+P/2+TE/2

Inorganic fertiliser used: The fertiliser used in the inorganic fertiliser comparison and for the additions to sludge amendments were as followed:

$(NH_4)_2SO_4$ (Sulphate of Ammonia (granular))
NP 18/20 (DAP (N/P/K 18/20/0) $P_{available}$ =20 %, P_{total}=20 %)
N,P,TE Mix, 1992: DAP based granular fertiliser with TE
Zincsol (Zinc sulphate, Zn 16.7 %, S 8.2 % w/v)
Coppersol (Copper sulphate, Cu 6.7 %, S 3.4 % w/v)
Mangasol (Manganese sulphate, Mn 17.3 %, S 10 % w/v)

Table 3.5 Inorganic fertiliser (N, P, Zn, Cu, Mn) and calculated sludge nutrients (N_s, P_s, Zn_s, Cu_s, Mn_s) applied in the different treatments in 1992. The calculated plant available fractions of sludge borne N and P listed here, are based on assumptions described in section 3.2.2.1-3. Sludge Zn, Cu and Mn values are the total content of the elements in the sludge used.

Treatments [a]	N	N_s	P	P_s	Zn	Zn_s	Cu	Cu_s	Mn	Mn_s
					[kg ha^{-1}]					
nil										
nil+N+P	20		20							
nil+N+P+TE	20		20		2.8[b]		1.9[b]		4.0[b]	
2t +Mn		*5.2*		*20*		*1.9*		*1.5*	3.6	*0.4*
2t+N* +Mn	15	*5.2*		*20*		*1.9*		*1.5*	3.6	*0.4*
2t+N*+P/2 +Mn	15	*5.2*	10	*20*		*1.9*		*1.5*	3.6	*0.4*
1t+N*+P/2+TE/2+Mn	17.5	*2.6*	10	*10*	1.4[c]	*0.9*	1.0[c]	*0.8*	3.8	*0.2*

[a] commercial grade inorganic fertiliser was used (see Section 3.2.3)

[b] TE fertiliser applied half with the NP fertiliser base granules and the remaining half sprayed onto the plots prior to seeding

[c] applied as liquid fertiliser spray onto the plots prior to seeding

3.2.4 Method of inorganic fertiliser and sludge application in the field

The treatments were arranged in a completely randomised block design with 5 replicates per treatment. The air dry sludge was applied just prior to sowing. A 10 row, tyned cone seeder was used to apply the sludge 2 to 5 cm below the seeding depth of 2 cm. Plot size was 30 m^2 (20 long, 1.5 m wide). Two seeder runs were necessary to apply 6 kg of sludge, which together were equivalent to 2t sludge ha^{-1}.

The inorganic and control plots were worked similarly to the sludge-amended plots. The inorganic fertiliser as well as the nutrient additions to the sludge-amended plots were applied together with the seed in the third working of the plots, using the same cone seeder. Seeding rates are recorded in Table 3.6. Field preparation and herbicide treatment were according to farmer's practice.

3.2.5 Field crops and plant analysis

In 1992 five sites, representing different soil types and located at various distances from Adelaide, were chosen for the field experiments. The test crop in 1992 was the durum wheat variety Yallaroi (*Triticum durum* L.) except at Marion Bay where barley (*Hordeum vulgare* L.) variety Galleon was seeded. Seeds were pickled with Baytan at the rate 100g Baytan 100 kg^{-1} seed. Crop rotations, seeding rates, harvest dates and harvested areas are listed in Tables 3.6 and 3.7.

Two mid-season harvests and a final grain harvest were taken at all sites in both years, to measure the influence of nutrients at different growth stages and to establish if there are any differences in nutrient availability of the two sources (sludge and inorganic fertiliser) over time. Harvest 1, which showed the early establishment of plants, was taken about 9 weeks after planting,when plants were generally in late tillering stage. The second harvest was taken about 16 weeks after planting and plants were in late booting stage. Harvest 2 shows the biological yield enhancement due to nutrient availability, a measure that in some cases may not lead to grain yield increases in South Australia, due to differences in late season rainfall and availability of soil moisture. For details about exact harvest dates and sub-sampled area at the five sites see Tables 3.6 and 3.7. For each sample plants were harvested at two seperate locations along a central row.

Plants were cut approximately 2 cm above ground and dry weight of shoots in Harvest 1 and 2 and grain yield in the final harvest were recorded. Shoots and grain were dried in a forced-air oven at 70°C for at least 24 hours, digested in concentrated HNO_3 and analysed for Ca, K, Mg, Mn, Cu, Zn, P, S and Mo concentrations using an inductively coupled plasma emission spectrometer (ICP) (p. 255a, 255b).

Dry matter and grain yield were transformed to relativ yield by dividing all the values, including the values for the nil treatment, by a common factor, the site average for the nil treatment. The Anova was calculated for the transformed data.

Table 3.6 Crop rotation, seeding rate and seeding and harvesting dates on the five experimental sites in 1992.

	Callington	Strathalbyn	Lameroo	Freeling	Marion Bay
			Crop rotation		
1990	pasture	pasture	wheat	wheat	oat
1991	pasture	pasture	barley	vetch	pasture
Seeding rate	70 kg ha^{-1}	80 kg ha^{-1}	65 kg ha^{-1}	70 kg ha^{-1}	55 kg ha^{-1}
1992			***Seeding and harvest dates***		
Sown	2.6.92	12.6.92	25.6.92	15.6.92	18.6.92
Harvest 1	17.8.92	4.8.92	26.8.92	24.8.92	21.8.92
Harvest 2	23.9.92	1.10.92	16.10.92	6.10.92	13.10.92
Grain harvest	13.1.93	12.1.93	18.1.93	24.12.92	22.12.92

Table 3.7 Area sub-sampled at the five sites in 1992

Sub-sampled area [a]	Callington	Strathalbyn	Lameroo	Freeling	Marion Bay
Harvest 1	0.075 m^2	0.15 m^2	0.15 m^2	0.113 m^2	0.15 m^2
Harvest 2	0.113 m^2	0.12 m^2	0.15 m^2	0.12 m^2	0.12 m^2
Grain	28.5 m^2	30 m^2	30 m^2	28.5 m^2	26 m^2

[a] Sub-samples in Harvest 1 and 2 were taken along one central row in the plot

3.2.6 Soil characteristics and climate

The soil classifications are presented in Table 3.8 and selected properties of the soils are given in Table 3.9 and 3.10. Rainfall and temperature data in comparison to site averages are listed in Tables 3.11 and 3.12. Previous TE fertilisation experiments at the sites revealed that Zn deficiency was likely at Lameroo, Callington and to a lesser extent at Freeling. Marion Bay was chosen as a severely Mn-deficient site. All sites are deemed deficient in N and P.

Table 3.8 Soil classification of the experimental sites used in 1992.

Callington	Strathalbyn	Lameroo	Freeling	Marion Bay
		Australian classification[a]		
Sodic Brown Kandosol-Dermosol	Sodic Brown Kandosol-Dermosol	Endohypersodic Hypercalcic Calcarosol	Epicalcareous Vertosol	Shelly Calcarosol
		U.S. classification[b]		
Palexeralf	Palexeralf	Haploxeralf	Chromoxerert	Xeropsamments

[a] Isbell (1995)

[b] Soil Survey Staff (1990)

3.2.6.1 Methods of soil analysis

$CaCO_3$ was analysed according to the method of Loveday and Reeve (1974). Bicarbonate extractable P, cation exchange capacity (CEC) and pH (soil:water ratio of 1:5) were analysed according to Rayment and Higginson (1992). Organic matter content was analysed according to Heanes wet oxidation procedure (Heanes, 1984). Particle size distribution was analysed according to USDA-Soil Conservation Service (1982). Total contents of metals in soils were determined by the State Water Laboratory.

Table 3.9 Selected soil properites at the field sites

	pH	pH	E C	Org. C	$CaCO_3$	P*	K*	Clay	Silt	Sand	Sand	CEC	exchangeable cations			
	(H_20)	($CaCl_2$)				(HCO_3^-)				(fine)	(coarse)		Ca	Mg	K	Na
			[mS cm^{-1}]	[mg kg^{-1}]	[%]	[mg kg^{-1}]	[mg kg^{-1}]	————	[%] #		———	[$cmol^+$ kg^{-1}]	[cmol(+) kg^{-1}]			
Callington																
0-10 cm	8.4	7.9	0.14	13	1	12.3	469	22	4	31	40	16	12	2.8	1.1	0.3
10-20 cm	8.7	8.2	0.16	9	1	4.4	341	25	4	43	30	15	12	3.5	0.8	0.5
20-30 cm	9.0	8.3	0.19	6	1	4.4	302	32	4	35	30	19	13	5.3	0.8	1.1
Strathalbyn																
0-10 cm	6.5	6.1	0.16	19	0.1	18.1	349	21	15	47	17	13	8	2.8	0.7	0.4
10-20 cm	7.4	6.8	0.18	13	0.1	6.3	272	29	18	42	12	17	9	4.6	0.6	1.1
20-30 cm	7.9	7.1	0.19	9	0.1	5.0	259	46	18	34	7	21	9	6.3	0.6	1.9
Lameroo																
0-10 cm	6.8	6.3	0.07	5	1	30.2	207	6	1	37	59	5	3	0.8	0.4	0.1
10-20 cm	6.8	6.2	0.06	3	5	16.1	257	5	1	31	68	6	4	1.6	0.5	0.1
20-30 cm	7.5	6.9	0.08	2	20	7.6	298	10	1	34	57	9	5	2.7	0.8	0.6
Freeling																
0-10 cm	8.4	8.0	0.14	13	6	18.1	547	47	9	31	13	31	24	3.9	1.7	0.3
10-20 cm	8.5	8.0	0.14	11	11	5.8	318	49	9	28	14	31	24	5.0	1.1	0.5
20-30 cm	8.6	8.0	0.15	9	19	3.1	244	50	9	28	15	31	23	5.5	0.8	0.7
Marion Bay																
0-10 cm	8.4	7.9	0.26	41	85.0	56.7	198	24	9	16	46	13	15	1.2	0.3	0.2
10-20 cm	8.3	7.9	2.88	28	90	25.1	142	24	8	16	46	11	13	1.1	0.2	0.2
20-30 cm	8.4	8.0	2.76	20	88	13.7	105	32	6	19	40	9	11	1.0	0.1	0.2

Particle size analysis: $CaCO_3$ not destroyed before the measurement
* Bicarbonate extractable P

Table 3.10 Total content of selected heavy metals in soils from the five field sites.

Depth	Cd	Cr	Cu	Pb	Mn	Ni	Zn
				[mg kg^{-1}]			
Callington							
0-10 cm	<0.1	12	7.0	6.7	63	7.7	7.8
10-20 cm	<0.1	10	<5	6.3	61	7.5	5.0
20-30 cm	0.1	13	<5	7.3	99	23	6.3
Strathalbyn							
0-10 cm	0.14	12	9.0	13.6	99	9.5	14
10-20 cm	0.17	14	8.6	16.5	113	10.9	9
20-30 cm	0.20	15	8.9	18.5	112	10.1	8
Lameroo							
0-10 cm	0.13	<0.5	<0.5	3.7	11	4.5	<0.5
10-20 cm	0.14	<0.5	<0.5	3.6	13	3.7	<0.5
20-30 cm	0.15	6.0	<0.5	4.2	18	7.4	<0.5
Freeling							
0-10 cm	0.17	13	11.0	11	153	12.0	13
10-20 cm	0.11	13	9.7	11	134	12.0	11
20-30 cm	0.11	13	9.6	10	155	12.0	12
Marion Bay							
0-10 cm	0.17	30	8.0	3.4	87	7.0	10
10-20 cm	0.13	25	5.0	1.9	44	5.3	6
20-30 cm	0.13	26	5.0	1.5	26	6.5	8

Table 3.11 Monthly rainfall data at the various sites in the experimental years. Long term site averages are listed for comparison.

Rainfall	Callington				Strathalbyn		Freeling				Lameroo			Marion Bay[e]	
[mm]	1992	1993	1994	av.[a]	1992	av.[b]	1992	1993	1994	av.[c]	1992	1993	av.[d]	1992	av.[b]
January	3	28	10	20	4	20	2	48	23	19	13	18	19	13	14
February	42	14	19	18	44	21	11	11	20	18	17	9	22	10	17
March	61	3	0	20	57	24	70	9	0	20	30	3	19	76	16
April	38	1	0	30	58	39	48	3	6	39	61	1	28	83	34
May	43	18	37	39	39	55	66	23	26	52	49	23	42	62	55
June	29	36	76	42	44	59	50	43	81	55	37	23	41	56	63
July	49	84	16	43	55	64	35	61	34	62	25	48	42	41	66
August	92	38		45	117	62	124	32	18	62	85	42	45	114	61
September	87	66	28	41	128	53	148	64	16	60	109	70	43	111	46
October	30	52	27	35	84	45	96	62	37	45	58	49	38	79	36
November	69	25	25	25	78	29	95	34	55	31	67	35	27	71	22
December	207	20	17	23	171	25	90	47	6	24	58	31	24	82	17
Sum	751	385	255	379	879	498	834	436	322	490	609	352	391	798	447
Jan.-Mar.	106	45	29	58	105	66	83	68	43	57	60	30	60	99	46
Apr.-Oct.	368	295	184	275	525	376	566	288	218	374	424	257	279	546	360
Nov.-Dec.	276	45	42	47	249	54	185	81	61	55	125	66	51	153	40

[a] average of 110 years of available data

[b] average of 132 years of available data

[c] average of 30 years

[d] average 94 years of available data

[e] climatic data from Warooka, which is 30 km north-east of Marion Bay

Table 3.12 Average monthly temperatures at the various sites in the experimental years. ([a] Average of daily maximum and minimum temperatures)

Average temperatures [°C] [a]	Callington			Strathalbyn	Freeling			Lameroo		Marion Bay[b]
	1992	1993	1994	1992	1992	1993	1994	1992	1993	1992
January	19	22	20	18	18	21	19	20	23	19
February	22	22	21	21	22	21	21	23	22	21
March	20	20	19	19	20	19	18	21	20	20
April	17	18	18	17	16	16	16	17	17	17
May	13	14	14	13	11	13	12	13	14	14
June	12	11	12	12	9	9	11	11	11	13
July	11	12	11	12	9	10	9	11	11	12
August	11	13	11	11	9	11	9	10	12	11
September	12	14	13	11	10	*	11	11	13	12
October	16	15	17	15	14	14	16	16	15	16
November	16	18	17	16	15	18	17	16	18	16
December	20	20	21	19	19	19	21	21	20	19
Average	16	17	16	15	14	16	15	16	16	16
Jan.-Mar.	20	21	20	20	20	20	20	21	22	20
Apr.-Oct.	13	14	14	13	11	12	12	13	13	14
Nov.-Dec.	18	19	19	18	17	18	19	18	19	18

[b] climatic data from Warooka, which is 30 km north-east of Marion Bay

Location of the five field sites in South Australia

1) Callington
2) Strathalbyn
3) Freeling
4) Lameroo
5) Marion Bay

3.3 Results of field experiments 1992

The results will be divided into three sections, because the plant response to the various treatments showed distinct features at some of the sites. This was mainly due to observed micronutrient (TE) deficiency at some sites. At the three sites Callington, Strathalbyn and Freeling no additional grain yield responses due to TE additions were observed (comparison of treatment (nil+N+P) with (nil+N+P+TE)). At those three sites plant growth was mainly enhanced by N and P addition and therefore the sites will be discussed together in Section 3.4. At Lameroo plant growth was considerably enhanced by applications of TE, in particular Zn. This site will be discussed on its own (see Section 3.5). The experimental site Marion Bay is unique in that it shows severe Mn deficiency, which seemed to have been the overriding growth factor in the experiment in 1992. This site will be discussed separately in Section 3.6. (All treatments will be mentioned in parenthesis, for example (nil+N+P).)

3.4 Results at Callington, Strathalbyn and Freeling

3.4.1 Nitrogen and phosphorus replacement potential of sludge

To keep the field experiment to a manageable size, (nil+N) and (nil+P) treatments have not been included in the study (see Section 3.2). The growth response to the macronutrients can be assessed comparing the (nil) treatment with the (nil+N+P) treatment. Likewise, the micronutrients Zn and Cu are treated together.

The general pattern of growth response of durum wheat to the various treatments at Callington, Freeling and Strathalbyn was quite similar during all the three harvests, varying only in the degree of response. A significant Treatment∗Site interaction for dry weight occurred at Harvest 1 (Table 3.14). This interaction was probably caused by a weaker plant response to one or two treatments at Callington only. Otherwise the plant responses to the various treatments were quite similar at the three sites. Figure 3.4 shows the plant growth results calculated across the three sites, whereas Figures 3.1, 3.2 and 3.3 show the results of the sites singly.

The growth response data expressed as a percentage of the nil treatment may sometimes be misleading in terms of absolute growth response at certain sites, particularly for the grain harvest. The relative yield increase at Strathalbyn seems to be small compared to the response in Callington, but the absolute grain yield increase measured in kg ha^{-1} in Strathalbyn was of the same order as in Callington. Table 3.13 gives the absolute yield of the nil treatment in g m^{-2} or kg m^{-2} for the different sites and harvests. However, expressing the data as percentage allows comparisons of the plant responses of the differing sites on a common relative scale.

Harvest 1: An addition of inorganic N and P fertiliser increased yield between 48 and 62 % depending on the site (Figure 3.1-3.3). Calculated across the three sites the sludge treatments ((2t), (2t+N*) and (2t+N*+P/2)) enhanced growth by 12 %, 14 %, 43 %, respectively, compared to the nil treatment. The plants fertilised with (2t) or (2t+N*) showed a significantly reduced growth compared to the other fertilised plants at two of the three sites (Figure 3.2 and 3.3.). In Callington those differences were not significant but the trend was similar (Figure 3.1). At Freeling the (2t) and (2t+N*) amended plots showed a productivity significantly different from the nil control plots. Plants amended with sludge and additional inorganic P ((2t+N*+P/2) and (1t+N*+P/2+TE/2)) showed in almost all cases a similar growth compared to the inorganic fertilised plants.

Harvest 2: At Strathalbyn and Freeling, the growth response to the various treatments in Harvest 2 was similar to the response in Harvest 1. The inorganic fertilised plants and the sludge plus inorganic P amended plants show a significantly increased growth compared to the nil treatment. The shoot dry matter production of (2t) and (2t+N*) treated plants was similar to the nil treatment at Strathalbyn and between the nil and (2t+N*+P/2) treated plants at Freeling. At Callington growth of (2t) and (2t+N*) treated plants was generally not different from the other fertiliser/sludge amended plants, which received inorganic P.

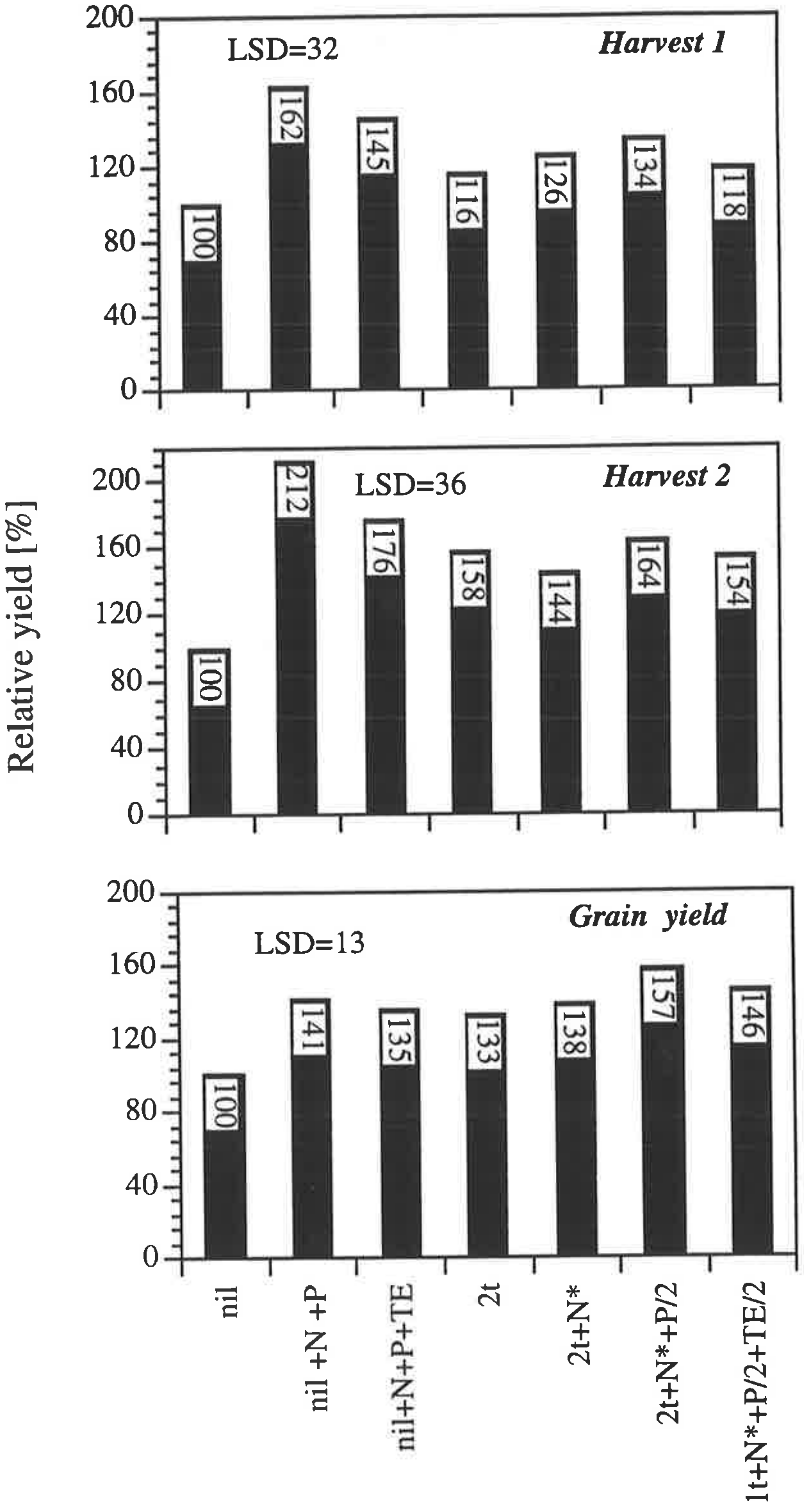

Figure 3.1 Callington, 1992: Dry weight of shoots at harvests 1 and 2 and grain yield relative to the nil treatment (100%). Harvest 1: 76 days , Harvest 2: 113 days after sowing.(LSD, P=0.05) (value in the bar represents relative yield expressed as percentage of the nil treatment)

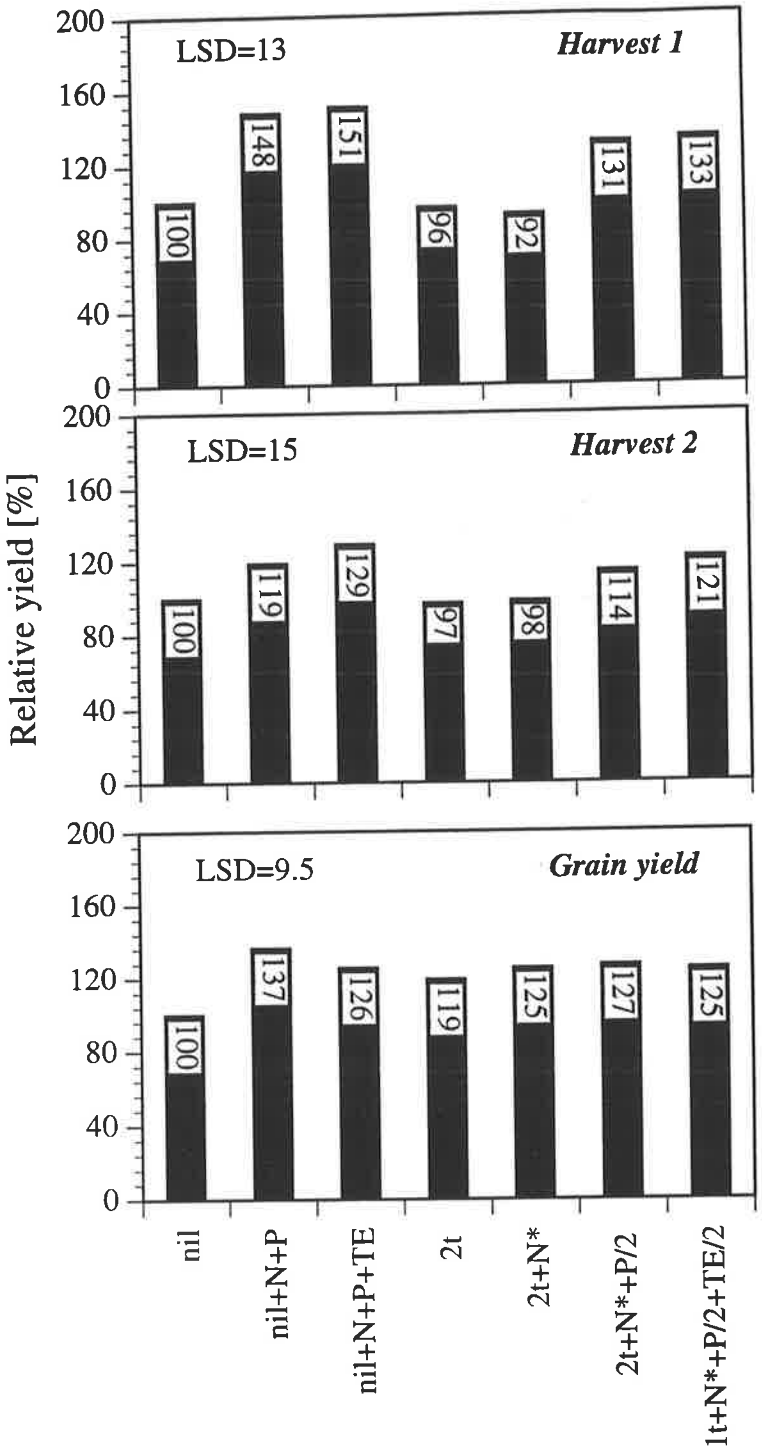

Figure 3.2 Strathalbyn, 1992: Dry weight of shoots at harvest 1 and 2 and grain yield relative to the nil treatment (100%). Harvest 1: 53 days, Harvest 2: 112 days after sowing. (LSD, P=0.05) (value in the bar represents relative yield expressed as percentage of the nil treatment)

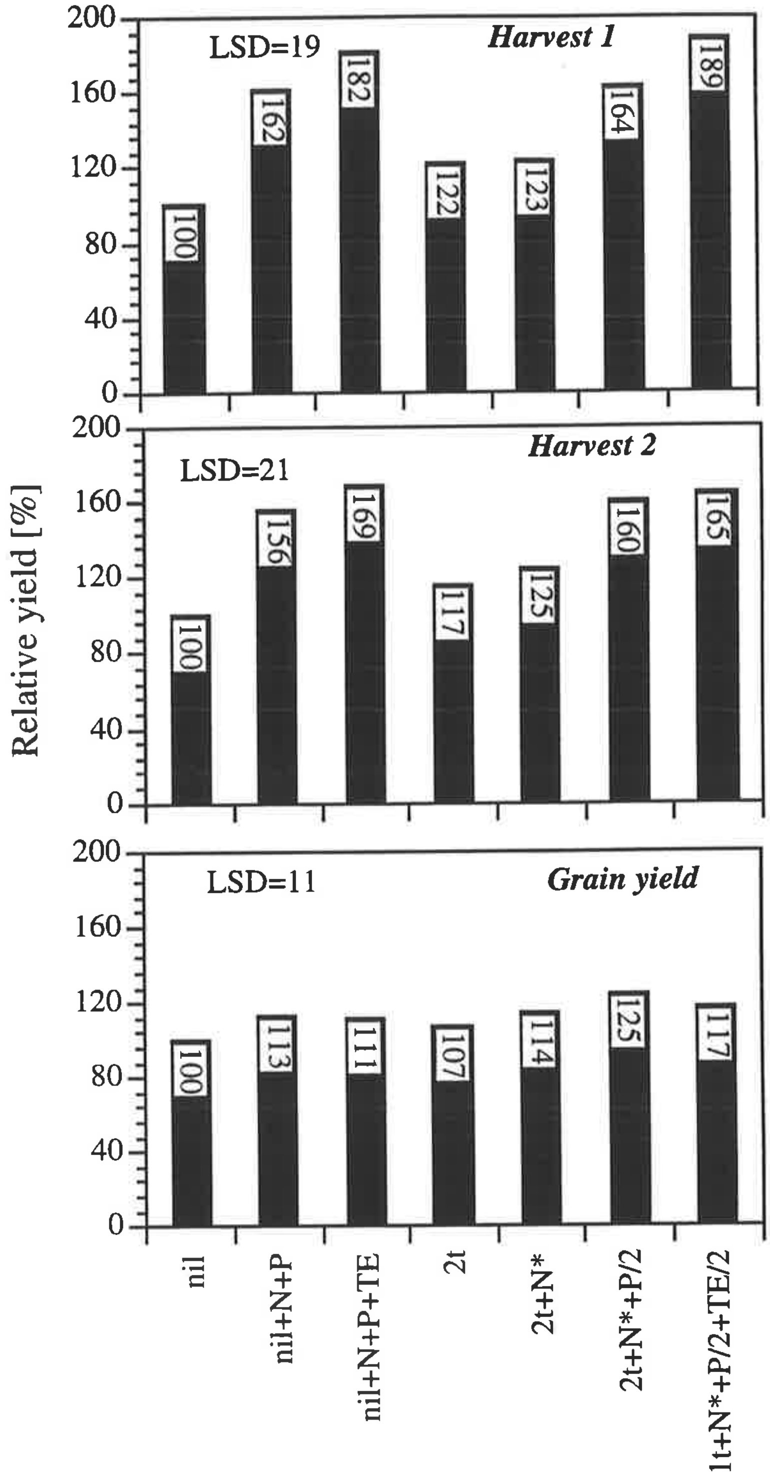

Figure 3.3 Freeling, 1992: Dry weight of shoots at harvests 1 and 2 and grain yield relative to the nil treatment (100%). Harvest 1: 70 days , Harvest 2: 113 days after sowing. (LSD, P=0.05) (value in the bar represents relative yield expressed as percentage of the nil treatment)

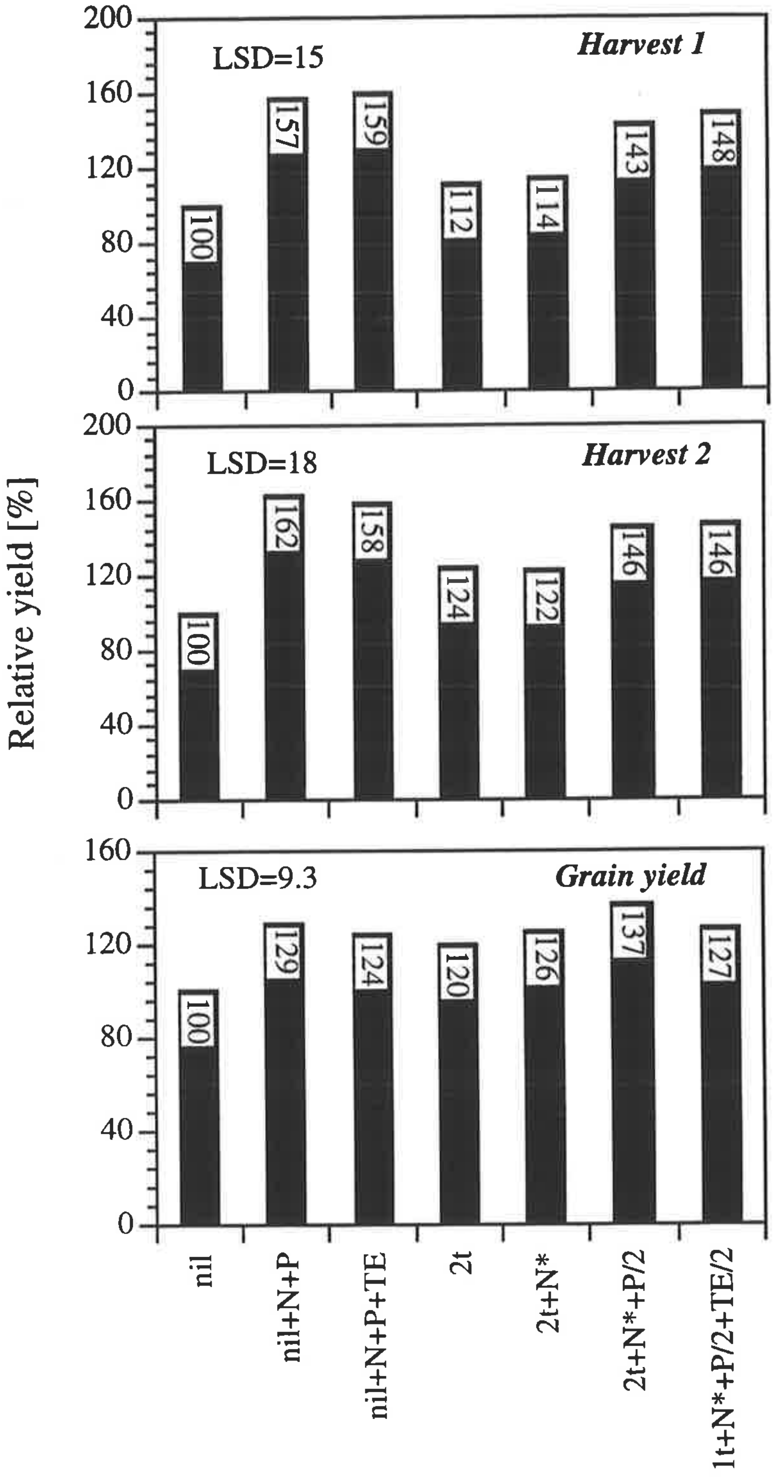

Figure 3.4 Averaged over the three sites Callington, Strathalbyn, Freeling 1992: Dry weight of shoots in harvests 1 and 2 and grain yield relative to the nil treatment (100%). Harvest 1: about 66 days, Harvest 2: about 113 days after sowing. (LSD, P=0.05) (value in the bar represents relative yield expressed as a percentage of the nil treatment)

Grain yield: Generally all inorganic fertilised or sludge amended plots produced a significantly higher grain yield than the nil control plots, except the (2t) treatment at Freeling. The average grain yield increase of all the sludge amended plots over the nil treatment was 0.69, 0.77 and 0.55 t ha^{-1} for Callington, Strathalbyn, and Freeling respectively compared to a 0.63, 1.01 and 0.43 t ha^{-1} grain yield increase by the inorganic fertiliser treated plants.

The differences in plant growth between the fertilised or sludged plants encountered in the previous harvests were not as distinct in the final grain yield. The (2t+N*+P/2) treatment yielded significantly higher than both inorganic fertiliser treatments at two of the three sites. The (2t) treatment tended to have a lower yield than both inorganic fertilised treatments, but this was only significant at Strathalbyn when compared with either one of the two fertiliser treatments. At this site the two inorganic fertiliser treatments were significantly different, with (nil+N+P) producing superior yields than (nil+N+P+TE). This might be an artefact, because it is not likely that the difference in yield between (nil+N+P) and (nil+N+P+TE) is based on a detrimental effect of TE.

The (2t+N*) treatment yields were similar to the (2t) and (2t+N*+P/2) treatments. The higher yield of the (2t+N*+P/2) compared to the (nil+N+P+TE), (2t) and (2t+N*) treatments is significant, when an Anova is calculated using site as a blocking factor.

Table 3.13 Dry weight [g m^{-2}] and grain yield [t ha^{-1}] of the nil treatment for the two vegetative and the average grain yield* [t ha^{-1}] of all fertiliser or sludge treated plants (fert./sl.).

	Callington	Strathalbyn	Freeling	Lameroo	Marion Bay
			Dry matter [g m^{-2}]		
Harvest 1	71	36	44	18	7
Harvest 2	190	470	250	130	52
			Grain yield [t ha^{-1}]		
Nil treatm.	1.65	3.2	3.6	0.9	0.05
Fert./sl.*	2.34	4.1	4.1	1.4	1.4

Table 3.14 F-Probability of Treatment$*$Site interactions for dry weight, P concentration and uptake values, Zn concentration and uptake values for the three harvests and the sites Callington, Strathalbyn and Freeling.

F-Prob.	Dry weight	P concentration	P uptake	Zn concentration	Zn uptake
Harvest 1	0.014	0.002	0.001	n.s.	0.001
Harvest 2	n.s.	0.002	n.s.	0.010	n.s.
Grain	n.s.	0.001	n.s.	n.s.	n.s.

3.4.2 Results of chemical analysis of shoots and grain

3.4.2.1 Phosphorus concentrations in shoots and grain

Phosphorus concentration of plants did not differ appreciably among the three sites. The average P concentrations for the sites were 3038, 4405 and 3074 mg kg^{-1} at Harvest 1, 2258, 1954 and 1748 mg kg^{-1} at Harvest 2 and 4013, 3844 and 3678 mg kg^{-1} in the grain at Callington, Strathalbyn and Freeling respectively.The results for each site separately are given in the Appendices Table A 3.1 to A 3.6. The data for P concentrations in shoot and grain and P uptake values per m^2 or per hectare calculated across the three sites are given in Table 3.15. The P uptake values are useful in conjunction with the concentration data to identify P concentration or growth-dilution effects due to changes in dry matter production resulting from other factors.

The average P concentration and P uptake of the treatments were calculated across the three sites because certain trends were quite consistent across the sites. However, a Treatment$*$Site interaction for P concentration values was observed at all harvests. For P uptake an interaction was noticed only at Harvest 1. This suggests that a dilution effect existed at Harvest 2 and for grain yield. In experiments where several factors (such as N, P and TE) can have an influence on plant growth and dilution effects, the values for nutrient uptake are more reliable than the concentration values in terms of judging plant availability of a single nutrient. Treatment$*$Site interactions for P concentration and uptake are given in Table 3.14. Although some interactions (mainly in concentration values) existed, the results averaged across the sites are presented to describe the strong common trends in the data. The cause of Treatment∗Site interactions will be described, when necessary.

Table 3.15 Plant P concentration in shoot and grain and P uptake of shoot or grain per harvested area at the three harvests in 1992, as an average across the three sites Callington, Strathalbyn and Freeling.

	nil	nil +N+P	nil +N+P +TE	2t	2t +N*	2t +N*+P/2	1t +N*+P/2 +TE/2	LSD (P=0.05)
			P concentration [mg kg^{-1}]					
H1 shoot	2847[a]	4139	4166	3025	2987	3707	3774	267
H2 shoot	1818[a]	1947	2066	2009	1927	2131	2005	129
Grain	3774[a]	3831	3807	3911	3731	3844	4019	136
			P uptake [mg m^{-2}]					
H1 shoot	132	303	302	153	154	242	253	34
H2 shoot	530	877	942	702	668	886	839	100
Grain	1059	1379	1314	1307	1297	1434	1383	93

[a] approximate critical values for *T. aestivum* : Harvest 1 (shoot) 3500 mg P kg^{-1}, Harvest 2 (shoot) 2000 mg P kg^{-1}; Grain 2-3000 mg P kg^{-1} , (Reuter and Robinson, 1986).

Harvest 1: The plants treated with (2t) or (2t+N*) had a P concentration similar to the nil treated plants and lower than plants treated with inorganic P. The sludge treated plants with additional inorganic P did have a higher P concentration than the (2t) and (2t+N*) treatments, but still lower than from the inorganic fertiliser treated plants. Data for the P uptake per harvested area reflect similar trends. *(The Treatment∗Site interactions for plant P concentration and uptake data were based on a more pronounced uptake of inorganic P compared to sludge-P at Strathalbyn, but the general trend was similar to the other sites).*

Harvest 2: The differences in plant P concentration encountered in Harvest 1 were not apparent at Harvest 2. The nil treated plants still had a significantly lower P concentration compared to most of the treatments (except the (2t+N*) treatment), but there were no differences in P concentration between differently fertilised plants. However, the P uptake

data show that there was still a difference in P nutrition between treatments. As in Harvest 1, the P uptake of the nil treated plants was lowest, followed by the (2t) and (2t+N*) treated plants, and their plant P uptake was significantly lower than the P uptake by plants that received inorganic P fertiliser. The P uptake of (2t+N*+P/2) and solely inorganic fertilised plants was similar.
*(The Treatment*Site interaction for P concentration values are based on similar plant P concentrations irrespective of the P fertiliser treatment at Freeling. This probably reflects a dilution effect due to enhanced growth differences at this site.)*

Grain yield: The P concentration in the grain was quite uniform across the treatments. The P uptake values differed considerably between treatments, suggesting that differences in P concentration were related to growth dilution effects. Nil treated plants showed a low P uptake, but the remaining treatments had similar P uptakes. *(The significant interactions in grain P level is based on a higher P concentration of treatment (1t+N+P/2+TE/2) at Callington.)*

3.4.2.2 Zinc concentrations in shoots and grain

Replacement potential of sludge for Zn inorganic fertiliser: The extent of TE deficiency, mostly Zn deficiency in this case, is dependent on the soil type, plant species and variety and as well the climatic conditions of the particular year. The extent of Zn deficiency and the resulting Zn response of a crop cannot be forecast accurately. However the fertiliser value of any element can only be measured reliably on a site responsive to, or deficient in, the particular element. Significant growth differences between the (nil+N+P) and the (nil+N+P+TE) treatments were generally not noticeable at Callington, Strathalbyn, and Freeling (Figure 3.1-3.4). A comparison of the Zn concentrations (mg Zn kg^{-1}) or Zn contents (mg Zn $plant^{-1}$) of plants receiving a common rate of different fertilisers provides a more sensitive measure of the relative agronomic effectiveness of a fertiliser compared to the comparison of growth responses alone. This is because the Zn concentration and Zn content versus rate of applied Zn response functions do not reach a constant value (plateau) when Zn sufficiency is achieved, as does yield (Mortvedt and Gilkes, 1993). Therefore Zn concentration and uptake data of the three harvests averaged across the 3 sites are presented in Table 3.16, even though they were not growth limiting in 1992. The three sites differed in their level of Zn concentration in shoots and grain with lowest levels measured at Callington. The Zn concentration as an average across the treatments at the three sites were 15.5, 38.8 and 18.2 mg kg^{-1} Zn at Harvest 1; 10.9, 14.3 and 9.0 mg kg^{-1} Zn at Harvest 2; 23.5, 31.3 and 22.3 mg kg^{-1} Zn in the grain, for Callington, Strathalbyn and Freeling respectively.

Although significant Treatment∗Site interactions occurred twice (see Table 3.14), it was appropriate to combine the data of the three sites to describe the common trends. The cause of interactions will be described, when necessary. The results for each site are listed in the Appendix, Table A.3.4-6.

Harvest 1: There was no significant difference in Zn concentration between inorganic fertilised plants with or without TE amendment. All the sludge-treated plants showed a higher Zn concentration than inorganic fertilised plants at Harvest 1 and values were similar to the nil treated plants. The Zn uptake values reflect the general growth differences at this Harvest, with higher Zn uptake by plants that received inorganic P. Hence these values are probably of little value for judging the Zn nutritional status at this early point in development.

Harvest 2: The sludge-treated plants showed a higher shoot Zn concentration compared to the inorganic fertilised plants. There was no difference in shoot Zn concentration between (nil+N+P) and (nil+N+P+TE) treated plants. In general the sludge treated plants had Zn uptake values similar to those of the inorganic fertilised plants, which were significantly higher than from the nil treated plants. *(Treatment∗Site interactions were probably based on differences in Zn concentration of (nil+N+P+TE) treated plants which were somewhat lower compared to the (nil+N+P) treated plants in Freeling only. This was likely due to growth dilution effects)*

Zinc concentrations in plants at Harvest 2 were quite low. A 'marginal' value for bread wheat (*T.aestivum*) given by Reuter and Robinson (1986) is <15 mg kg^{-1} for whole shoots at heading. The shoot Zn concentrations were well below this level for whole shoots, but a significant growth response to TE fertiliser was not observed at any of the sites in Harvest 2. The lack of crop response to Zn nutrition in terms of dry matter production may indicate that other factors were limiting plant production.

Grain: The (nil+N+P) treated plants show a lower grain Zn concentration than the (nil+N+P+TE) treated plants. However, the values for Zn uptake of both treatments were similar. Sludge-amended plants showed a similar or slightly higher Zn concentration in grain compared to (nil+N+P+TE) treated plants, in two of the four sludge treatments. Zinc uptake values of sludge or inorganic fertiliser treated plants were similar and higher than from (nil) treated plants. *(No Treatment*Site interactions occurred)*

Table 3.16 Plant Zn concentration in shoot and grain and Zn uptake values at the three harvests in 1992, as an average across the three sites Callington, Strathalbyn and Freeling.

	nil	nil +N+P	nil +N+P +TE	2t	2t +N*	2t +N*+P/2	1t +N*+P/2 +TE/2	LSD (P=0.05)
				Zn concentration [mg kg^{-1}]				
H1 shoot	24.9[a]	20.8	20.8	25.4	27.5	24.5	25.3	1.90
H2 shoot	11.7[a]	9.8	10.4	12.4	12.0	11.6	11.9	0.89
Grain	27.6[a]	23.5	24.9	27.1	26.0	24.6	26.7	1.42
				Zn uptake [mg m^{-2}]				
H1 shoot	1.15	1.49	1.51	1.26	1.38	1.59	1.70	0.21
H2 shoot	3.75	4.57	5.04	4.55	4.39	4.97	5.24	0.65
Grain	7.79	8.69	8.79	9.21	9.21	9.34	9.41	0.61

[a] approximate critical values for *T. aestivum* : Harvest 1 (shoot) 20 mg Zn kg^{-1}, Harvest 2 (shoot) <15 mg Zn kg^{-1}; Grain 5-10 mg Zn kg^{-1} , (Reuter and Robinson, 1986).

3.5 Results for the micronutrient responsive site, Lameroo

Lameroo is situated in a part of South Australia, the so-called Mallee, where TE deficiencies, particularly Zn deficiency, are quite common. The plant response to treatments at this site differed from the previous three sites in that TE deficiency limited growth and yield in 1992.

3.5.1 Value of sludge as a TE fertiliser

The dominant influence of TE nutrition at this site was shown by the 44 % grain yield increase caused by the addition of TE to inorganic fertiliser (Figure 3.5). This productivity difference was noticeable at Harvest 2 (69 % dry matter increase), and the grain Harvest, but not at the first Harvest. Early plant development seemed to be influenced by N and P nutrition mainly and will be discussed in the following Section.

The plots amended with sludge only (2t) showed a 51% enhancement of dry matter production compared to the (nil+N+P) treatment at Harvest 2, and grain yield was increased by 39%. The dry matter production and grain yield were similar to plants treated with inorganic fertiliser plus TE. The other sludge treatments, namely (2t+N*), (2t+N*+P/2) and (1t+N*+P/2+TE/2) increased plant growth and grain yield even more than inorganic fertiliser and the (2t) treatment. The TE addition in those treatments was similar to the (2t) treatment, suggesting that N and P nutrition improved production, once the Zn requirements were met.

3.5.2 Nitrogen and phosphorus replacement potential of sludge at Lameroo

The results of the N and P replacement value of a sludge treatment (2t) in Lameroo were quite similar to results achieved at the other three sites in 1992. The (2t) treated plants lagged behind in their early development (Harvest 1) but had a 53 % yield increase at the final harvest, which is similar to the 58 % yield increase achieved by the inorganic

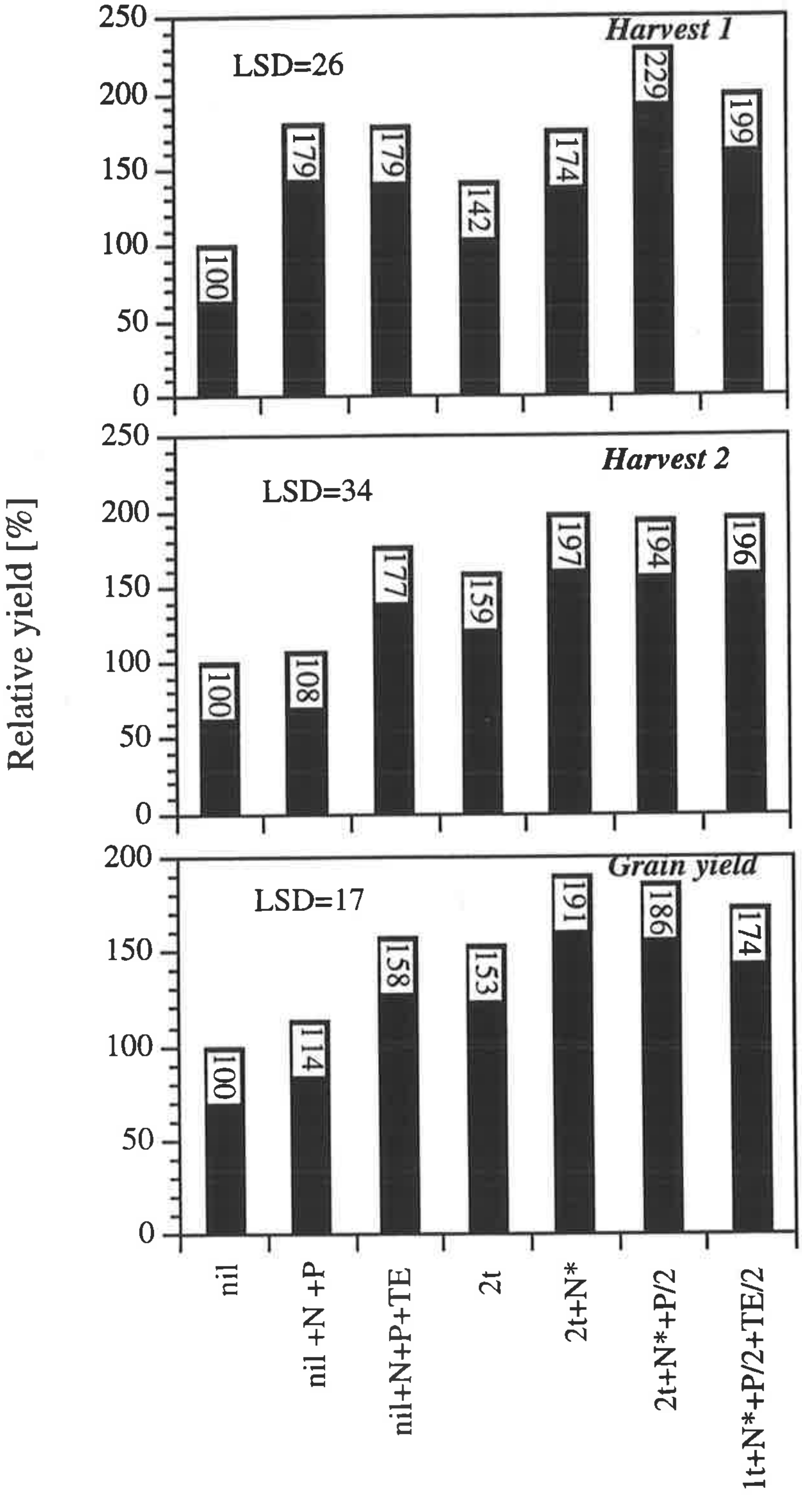

Figure 3.5 Lameroo, 1992: Dry weight of shoots at harvests 1 and 2 and grain yield relative to the nil treatment (100%). Harvest 1: 62 days, Harvest 2: 113 days after sowing. (LSD, P=0.05) (value in the bar represents relative yield expressed as percentage of the nil treatment)

fertiliser (nil+N+P+TE) treatment. Applying additional inorganic N to the sludge amended plots further enhanced plant dry matter production, beyond the level achieved by a sludge only application (2t) or an inorganic fertiliser application (nil+N+P+TE). The further addition of inorganic P to the sludge in the (2t+N*+P/2) further increased the early plant growth (Harvest 1). The (2t+N*), (2t+N*+P/2) and the (1t+N*+P/2+TE/2) caused a significantly higher yield than inorganic fertilised plants (nil+N+P+TE).

3.5.3 Chemical analysis of shoot and grain from Lameroo

3.5.3.1 Zinc concentration and uptake in shoot and grain

Harvest 1: There was a significant increase in Zn concentrations of shoots as well as in Zn uptake in the (nil+N+P+TE) compared to (nil+N+P) inorganic fertiliser treated plants (Table 3.17). The Zn concentrations and uptake values of sludge amended plants were generally similar to the values of (nil+N+P+TE) treated plants.

Harvest 2: At late booting (Harvest 2) no significant differences in Zn concentration between the treatments were noticed, but differences in Zn uptake values were apparent. Plant Zn concentrations of between 6.2 and 7.1 mg Zn kg^{-1} were quite low and below the critical value mentioned by Reuter and Robinson (1986) for bread wheat (marginal: whole shoot at heading 15 mg Zn kg^{-1}). The Zn uptake of the (nil) and (nil+N+P) treatments were similarly low and significantly different from the Zn uptake of the (nil+N+P+TE) treatment. Zinc uptake by the various sludge treated plots tended to be higher than that in inorganic TE (nil+N+P+TE) treated plants, but the differences were not significant at the P=0.05 level.

Grain: There was a significant increase in Zn concentrations in the grain as well as in Zn content in the (nil+N+P+TE) compared to (nil+N+P) inorganic fertiliser treated plants (Table 3.17). The grain Zn concentrations of (nil) and (nil+N+P) treated plants differed, but the Zn uptake values were similar, indicating that N and P enhanced plant growth to some extent, although TE deficiency seemed to be the major limiting factor. In the sludge treatments, the Zn concentrations and uptake values of shoot and grain were generally similar to the values of (nil+N+P+TE) treated plants. The (2t+N*) treated plants show some exceptions in that the grain Zn concentration and uptake were significantly higher than values from (nil+N+P+TE) treated plants.

Table 3.17 Plant Zn concentrations in shoot and grain and Zn uptake values for the three harvests at Lameroo 1992.

	nil	nil +N+P	nil +N+P +TE	2t	2t +N*	2t +N*+P/2	1t +N*+P/2 +TE/2	LSD (P=0.05)
				Zn concentration [mg kg^{-1}]				
H1 shoot	14.2[a]	10.9	17.6	19.5	20.9	17.7	18.2	2.33
H2 shoot	6.2[a]	6.2	6.3	7.1	6.2	6.2	6.8	-
Grain	17.7[a]	14.6	17.3	18.5	17.0	15.7	16.1	2.25
				Zn uptake [mg m^{-2}]				
H1 shoot	0.25	0.35	0.58	0.50	0.66	0.73	0.65	0.09
H2 shoot	0.81	0.87	1.43	1.47	1.58	1.58	1.74	0.36
Grain	1.61	1.47	2.47	2.60	2.95	2.63	2.55	0.42

[a] approximate critical values for *T. aestivum* : Harvest 1 (shoot) 20 mg Zn kg^{-1}, Harvest 2 (shoot) <15 mg Zn kg^{-1}; Grain 5-10 mg Zn kg^{-1} , (Reuter and Robinson, 1986).

3.5.3.2.Phosphorus concentration and uptake of shoot and grain

Harvest 1: P concentration and uptake values are listed in Table 3.18. The P concentration of plants indicate P nutrition was sufficient for all growth stages. The P concentrations of sludge-treated plants without additional inorganic P were significantly lower than the P concentration of plants receiving inorganic P such as treatments (nil+N+P+TE), (2t+N*+P/2) and (1t+N*+P/2+TE/2) (see Table 3.18). The P uptake values of the (2t) and (2t+N*) treated plants were also significantly lower than in (nil+N+P+TE) treated plants. The lower P concentration or uptake values of plants receiving sludge without inorganic P was similar to the results encountered at the sites previously discussed.

Harvest 2: At the late boot stage (Harvest 2) the P concentration of plants and the P uptake of all fertilised plants were similar, with P concentrations between 2315 and 2493 mg P kg^{-1}, except for the (nil+N+P) treated plants, which had a significantly higher P concentration of 3690 mg P kg^{-1}, due to restricted plant dry matter production (Figure 3.5).

Grain : The P concentrations in grain were comparatively high (4104 to 4738 mg P kg^{-1}) with the (2t+N*) treatment showing the lowest P concentration and the (nil+N+P) treatment the highest (Table 3.18). The remaining treatments had similar P concentrations, which were between these two values. Grain yield was not significantly different for these treatments.

The grain content of P for (nil+N+P+TE), (2t) and (1t+N*+P/2+TE/2) were similar and significantly lower than the P uptake values of (2t+N*) and (2t+N*+P/2) treated plants. The higher P uptake for (2t+N*) treated plots was caused by increased grain yield and that for (2t+N*+P/2) by both crop yield and increased grain P concentration. These fertilisation methods seem to be similar and interchangeable at this site. It has to be kept in mind though that this site had a comparatively high bicarbonate-soluble P level prior to the experiment. Therefore P nutrition is not likely to be a growth restricting factor at this site.

Table 3.18 Plant P concentration in shoot and grain and uptake values for the three harvests at Lameroo 1992.

	nil	nil +N+P	nil +N+P +TE	2t	2t +N*	2t +N*+P/2	1t +N*+P/2 +TE/2	LSD (P=0.05)
				P concentration [mg kg^{-1}]				
H1 shoot	5348[a]	7854	6486	5240	4600	5861	6105	699
H2 shoot	2492[a]	3690	2390	2494	2315	2493	2403	301
Grain	4544[a]	4738	4420	4443	4104	4419	4312	186
				P uptake [mg m^{-2}]				
H1 shoot	96	254	212	135	146	242	219	35
H2 shoot	329	517	543	513	589	630	613	125
Grain	390	463	603	590	677	707	647	63

[a] approximate critical values for *T. aestivum* : Harvest 1 (shoot) 3500 mg P kg^{-1}, Harvest 2 (shoot) 2000 mg P kg^{-1}; Grain 2-3000 mg P kg^{-1} , (Reuter and Robinson, 1986).

3.6 Results for the manganese (Mn) responsive site, Marion Bay

3.6.1 Plant productivity

Harvest 1: Manganese deficiency at the Marion Bay site was severe and Mn nutrition having a major influence on plant growth. At Harvest 1, the influence of TE nutrition on plant productivity was obvious from growth differences between the (nil+N+P) and (nil+N+P+TE) treated plants (Figure 3.6). Nitrogen and P nutrition were also enhancing plant growth considerably as can be seen from the yield differences between (nil) and (nil+N+P) treated plants. However, acidity from the NP fertiliser could also have released Mn and contributed in this way to enhanced growth. The lower growth responses of the (2t) and (2t+N*) treated plants compared to (nil+N+P+TE) and (2t+N+P/2) treatments is likely to be due to limited P rather than Mn nutrition, because they both had Mn applied, but did not have inorganic P added.

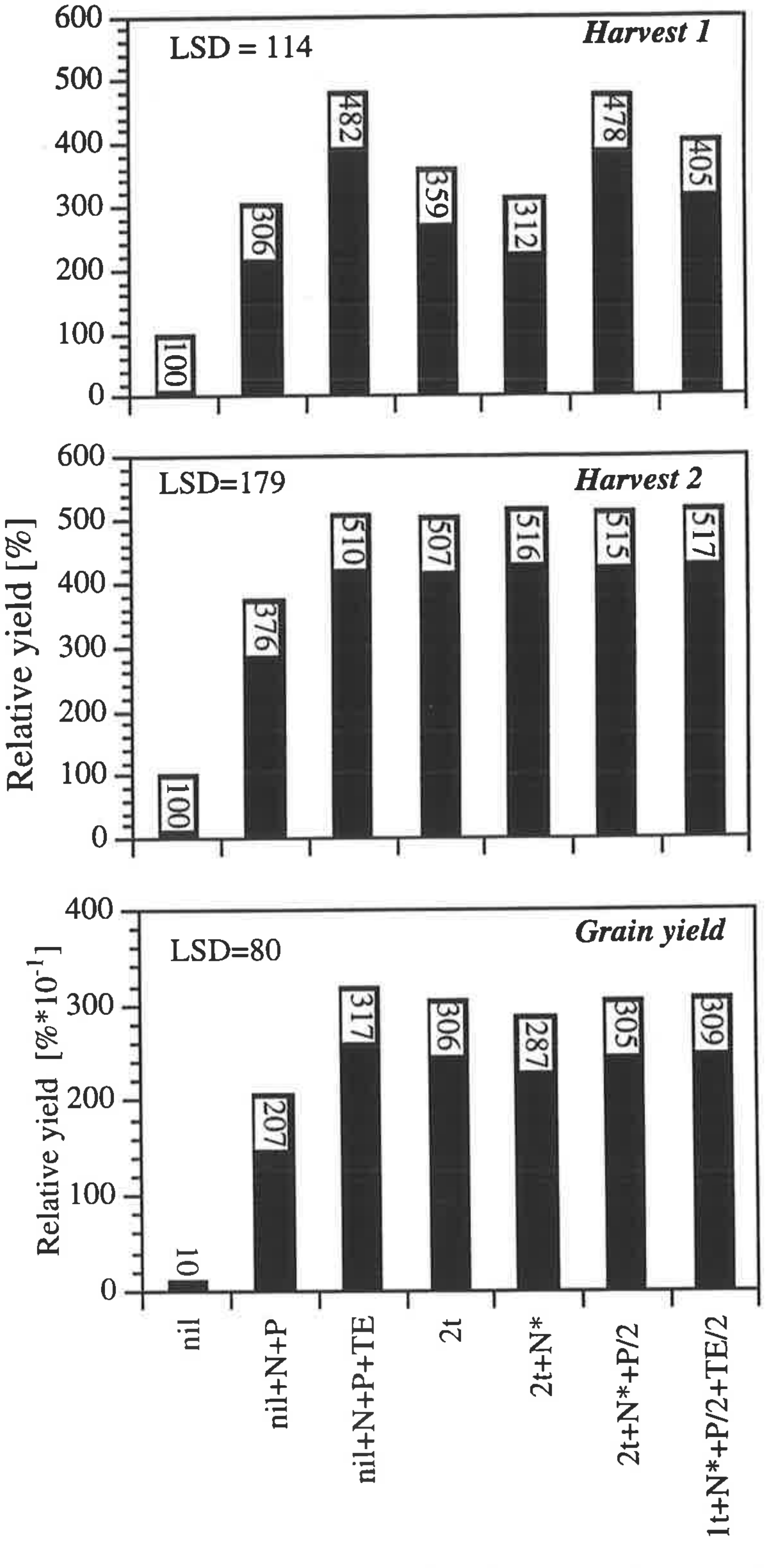

Figure 3.6 Marion Bay, 1992: Dry weight of shoots at harvests 1 and 2 and grain yield relative to the nil treatment (100%). Harvest 1: 64 days, Harvest 2: 118 days after sowing. (LSD, P=0.05) (Treatment (nil) and (nil+N+P) did not receive Mn fertiliser) (value in the bar represents relative yield expressed as percentage of the nil treatment)

Harvest 2 and grain: The growth responses at Harvest 2 and the final Harvest were similar (Figure 3.6) with a very restricted plant development in the (nil) plots, an intermediate growth in the (nil+N+P) plots, and similar yields in the plots that received either sludge or inorganic TE. The Mn nutrition in TE treated plots was improved but probably not sufficiently, because the Mn concentration values were still considered to be deficient, or just marginal to sustain plant growth (Reuter and Robinson, 1986) (Table 3.19, see Section 3.5.2). Therefore grain yield data may not have shown the response to enhanced N and P nutrition, but may have been a reflection of the supply of the major growth limiting nutrient: Mn.

3.6.2 Chemical analysis of shoot and grain

3.6.2.1 Manganese concentration and uptake

Mn concentrations were quite low in all harvests, and considered to be in the acutely deficient range for barley plant growth, according to Reuter and Robinson (1986) (Table 3.19).

Harvest 1: An increase in Mn concentration and uptake values of (nil+N+P+TE) compared to (nil+N+P) treated plants was apparent. The Mn concentration in the TE or sludge treated plants were quite similar and uptake values reflect the overall plant growth being lower for the (2t) and (2t+N*) treatments compared to (nil+N+P+TE) treatment. Shoots have partly drawn from seed Mn as a source for their development and this may have offset growth dilution effects in high yielding treatments.

Harvest 2 : The Mn concentrations of plants were similar in all the treatments, except for the nil treatment. Manganese uptake values were also significantly lower in the nil treated plants.

Grain: The Mn concentration and grain content of plants fertilised with TE or sludge (plus Mn) were similar and increased compared to concentration and uptake values of non TE treated plants. The Mn availability in the TE and sludge treated plots therefore seemed to be quite similar.

Table 3.19 Plant Mn concentration in shoot and grain and Mn uptake values for the three harvests at Marion Bay 1992 .

	nil	nil +N+P	nil +N+P +TE	2t	2t +N*	2t +N*+P/2	1t +N*+P/2 +TE/2	LSD (P=0.05)
				Mn concentration [mg kg^{-1}]				
H1 shoot	14.4[a]	12.0	13.5	13.6	12.7	12.7	13.1	1.38
H2 shoot	7.7[a]	4.9	4.7	4.7	5.0	5.0	4.6	0.63
Grain	2.3[a]	2.5	2.9	3.0	2.7	2.9	2.8	0.31
				Mn uptake [mg m^{-2}]				
H1 shoot	0.09	0.25	0.44	0.34	0.27	0.41	0.36	0.113
H2 shoot	0.39	0.93	1.23	1.23	1.35	1.32	1.21	0.46
Grain	0.01	0.25	0.44	0.44	0.38	0.42	0.42	0.13

[a] approximate critical values for *T. aestivum* : Harvest 1 (shoot) 13-16 mg Mn kg^{-1}, Harvest 2 (shoot) 5-24 mg Mn kg^{-1}; Grain not given , (Reuter and Robinson, 1986).

3.6.2.2 Zinc concentration

In Harvest 2 and the grain Harvest plant growth of (nil+N+P+TE) or sludge treated plants were uniformly restricted by Mn nutrition. The accumulation of Zn in the tissue of those treatments therefore should reflect the Zn availability in those plots. Zinc concentration in shoot and grain and Zn uptake values are given in Table 3.20.

Harvest 2 and grain : Shoot and grain Zn uptake values of (nil+N+P+TE) and sludge treated plants were generally similar. The concentration of Zn in shoot and grain of (nil+N+P+TE) treated plants tended to be lower than from sludge treated plants.

The similar Zn uptake values of sludge or inorganic TE treated plants indicate that the Zn availability of both sources may have been equal. However, this has to remain a hypothesis, because a clear response to Zn additions can not be proven, because the (nil+N+P) comparison was restriced in growth by Mn nutrition.

Table 3.20 Plant Zn concentration in shoot and grain and uptake values for the three harvests at Marion Bay 1992.

	nil	nil +N+P	nil +N+P +TE	2t	2t +N*	2t +N*+P/2	1t +N*+P/2 +TE/2	LSD (P=0.05)
				Zn concentration [mg kg^{-1}]				
H1 shoot	43[a]	28	32	41	44	38	37	3.9
H2 shoot	42[a]	23	18	22	22	20	20	4.1
Grain	37[a]	27	24	27	27	26	27	2.5
				Zn uptake [mg m^{-2}]				
H1 shoot	0.29	0.59	1.03	0.99	0.93	1.23	1.02	0.34
H2 shoot	2.16	4.36	4.63	5.15	5.83	5.08	5.18	1.48
Grain	0.18	2.69	3.65	3.85	3.65	3.81	3.92	0.87

[a] approximate critical values for *T. aestivum* : Harvest 1 (shoot) not given, Harvest 2 (shoot) 5-24 mg Zn kg^{-1}; Grain not given , (Reuter and Robinson, 1986).

3.6.2.3 Phosphorus concentration and uptake

The Mn nutrition was the overriding growth factor at this site, particularly at Harvest 2 and the grain harvest. Therefore only TE or sludge treated plots can be compared sensibly in terms of P nutrition. Plant P concentration and uptake values are listed in Table 3.21.

Harvest 1, 2 and grain: The P concentration and uptake of (2t) and (2t+N*) treated plants were significantly lower compared to inorganic P amended plants (Table 3.21) at Harvest 1, but not at later harvests. This suggests that sludge P availability was lower compared to inorganic P in the early part of the growth period, but this did not affect grain yield. However, plant P nutrition seemed to be quite sufficient at this site as can be judged from the P concentrations in tissues and hence a major increase in yield due to additional P amendment is less likely.

Table 3.21 Plant P concentration in shoot and grain and P uptake values at the three harvests at Marion Bay 1992.

	nil	nil +N+P	nil +N+P +TE	2t	2t +N*	2t +N*+P/2	1t +N*+P/2 +TE/2	LSD (P=0.05)
				P concentration [mg kg^{-1}]				
H1 shoot	5825[a]	6415	6123	5194	5493	5825	6009	384
H2 shoot	5511[a]	3641	3042	3168	3523	3330	3165	449
Grain	3467[a]	3592	3384	3620	3561	3602	3565	-
				P uptake [mg m^{-2}]				
H1 shoot	39	131	197	125	114	186	161	41
H2 shoot	283	700	800	792	917	858	817	221
Grain	15	358	515	527	488	523	527	131

[a] approximate critical values for *T. aestivum* : Harvest 1 (shoot) 3100 mg P kg^{-1}, Harvest 2 (shoot) 1700 mg P kg^{-1}; Grain not given , (Reuter and Robinson, 1986).

3.7 Discussion

Only in field trials it is possible to establish a realistic picture of the fertiliser value of sludge or the sludge potential to replace inorganic fertiliser. Certain aspects of fertiliser/sludge availability, such as mineralisation, could be more precisely analysed under controlled conditions in the laboratory, but numerous environmental influences, such as temperature, moisture fluctuation and microbial activity, which are influenced by weather, soil type, crop rotation and other factors, make interactions more complex in the field. Consequently, field experiments are indispensable to get a realistic picture of the relative value of different treatments. Field experiments however, have the disadvantage that variability is generally higher than in pot experiments. In a field trial it is possible to establish a sludge or fertiliser-sludge combination which enhances growth to the same extent as conventionally-used fertiliser additions, but mechanisms of fertiliser/sludge mineralisation or transformation in the soil are often difficult to establish.

All the sites proved to be responsive to macronutrients, as can be seen by significantly higher shoot and grain yields from plots treated with inorganic fertiliser compared to the control plots. The various sewage sludge treatments improved yield to approximately the same degree. The grain yield increases of 600, 813, 473 and 819 kg ha^{-1} at Callington, Strathalbyn, Freeling and Lameroo respectively for the (2t+N*) treatment, compared to the nil treatment were more extensive than in N fertilisation experiments conducted in South Australia (McDonald, 1992). McDonald (1992) reported a yield increase of between 160 to 280 kg grain ha^{-1} for the N addition of 20 to 25 kg N ha^{-1} at the three N responsive sites of the ten sites tested. Doyle and Holford (1993) in a more humid environment (NSW) reported a more consistent growth response to N fertiliser of on average 266 kg ha^{-1} from the first 15 kg N given and decreased efficiency at the higher N fertiliser increments. However, the yield response to sludge is probably a response to N and P fertilisation. (The addition of Ca, Mg, K and TE with sludge was likely to have had a small influence on yield at these sites). Holford and Doyle (1992) found yield responses to 20 kg P ha^{-1} ranging from 310 to 400 kg grain ha^{-1} in the four years considered. The yield increase in the current study were higher than in other N or P fertiliser studies in Australia. Yield increases for (nil+N+P) and (2t) treatments are most likely caused by both factors, N and P nutrition. The N and P potential for yield increase is not additive, but usually positively interactive, and thus higher yield increases than from N or P fertilisation experiments are possible. Also the favourable moisture conditions in 1992 explain to some extent the considerable yield increases.

There have been a number of studies on the fertiliser value of sludge, but direct comparison is difficult, because some studies did not include an inorganic fertiliser comparison (Sabey *et al.*, 1975; Kelling *et al.*, 1977; Hernandez *et al.*, 1991), or sludge nutrient/application rates were considerably higher (Sabey *et al.*, 1977; Sims and Boswell, 1980; Stark and Clapp, 1980; Amundson and Jarrell, 1983; Warmann, 1986) than in the current study. In field studies liquid sludge rather than air dried sludge was often applied (Sabey and Hart, 1975; Kelling *et al.*, 1977). Many studies concentrated on the plant availability of just one of the sludge nutrients, mainly N or P (Sabey *et al.*, 1977; O'Conner *et al.*, 1986; O'Riordan *et al.*, 1987; Sims and Boswell, 1980; Parker and Sommers, 1983) and its inorganic fertiliser equivalent and not on the sum of nutrients in sludge. This may be because N and P contents in sludge are generally not in the proportion normally added to agricultural crops (Pierzynski, 1994).

A few studies compared sludge with inorganic N and P fertilisation at the same time. In the a comparison of sludge with a N and P fertiliser, in a pot study, the applications of air dried sludge at rates of 67-84t ha^{-1} resulted in a similar yield increase as a 56 kg N ha^{-1} and 56 kg P ha^{-1} inorganic fertiliser (Milne and Graveland, 1972). Accordingly, sludge N and P availability can be calculated and were 6 % and 8.8 % respectively, compared to inorganic fertiliser. However, the study by Milne and Graveland (1972) used a range of comparatively high sludge application rates including rates up to 101t ha^{-1}, which is the case in a number of studies. Willett *et al.* (1986) used lower sludge applications (5-25t ha^{-1}) and compared the effect on yield of lucerne with varying combinations of N and P inorganic fertiliser. A 5t sludge application (55 kg total N, 51 kg total P) was equal to an inorganic fertiliser application containing N and P at rates of between 18-68 kg P and 20-40 kg N ha^{-1} (lower N rates plus high P rates and vice versa). The N and P efficiency of sludge compared to inorganic fertiliser was thus in the range of 35-133 % for P and 36-73% for N. However in their study lime-treated undigested sludge was used. Undigested sludge is generally more easily mineralised than digested sludge. The N and P availability in the current study (see following sections) was at the lower end of the range measured by Willett *et al.* under Australian conditions.

The results of the factorial experiment by Willett *et al.* (1986) also show that N and P fertilisers are to some degree interchangeable in terms of their effect on yield. This renders the quantification of the N and P supply of sludge based on plant yield response more difficult, because both nutrients cannot be dosed independently in sludge. In the current experiment treatments having additions of N or P to the sludge were given to assess if plants were responsive to either nutrient and thus yield response to sludge could partly be ascribed to that nutrient. However, the field design had to be kept to a reasonable size, so it could not offer various N and P rates factorially combined to quantify the response profile of plants more precisely. For the nutrients P and Zn shoot and grain analysis was an additional tool, which to a certain degree overcame the problems, because nutrient concentration or dilution effects due to plant growth based on other nutritional factors can be measured. However, for nitrogen information was solely based on plant growth and yield.

The interaction of various nutrients on plant growth and yield is complex. Using sludge as a nutrient source N, P and TE are applied together and hence interactions can be expected. However, the potential N, P or TE supply of sludge will be discussed in separate sections, to keep the complexity within bounds and have some judgement about the nutritional value of sludge. Also in the literature more information is available for one nutrient only.

3.7.1 Phosphorus replacement value of sludge

Assessing both shoot dry matter production at different growth stages and chemical content of shoots and grain allows a somewhat more precise judgement of nutritional value of sludge during the growth period than just grain yield data. At all sites yield or grain P concentration of (2t+N*) treated plants and the inorganic fertilised plants were similar (or higher at Lameroo), although plants fertilised with sludge lagged behind in shoot growth in the early part of the season at some sites. Hence the results suggest that the sludge treatment without additional P was equivalent to the inorganic P treatment (ie 20 kg ha^{-1}), when grain yield is used as a indicator. This would agree with the postulated hypothesis about sludge P availability prior to the field experiment (see Section 3.1.2). However, when shoot dry matter production or shoot P uptake is taken as an indicator, 2t sludge seemed to be lower source of plant available P than the inorganic fertiliser containing 20 kg P ha^{-1}.

The importance of shoot dry matter production in comparison to grain yield in this experiment is somewhat different to fertiliser experiments which establish the agronomic efficiency of a fertiliser source (yield increase caused by 1 kg of applied nutrient). Grain yield increases by inorganic fertiliser are far from certain under South Australian conditions and are dependent on environmental circumstances in each case. Therefore the shoot data (more reflective of the nutrient uptake) at different development stages is as important in interpreting the sludge nutrient potential as the grain yield data. The elemental constitution of grain reflects both the nutrient availability late in the season as well as nutrient transfer from shoot to grain. Also the nutrient uptake of grain compared to shoots can depend on climatic conditions (Holford and Doyle, 1993; Doyle and Holford, 1993). Shoot elemental composition therefore can be a more reliable guide to soil nutrient availability.

Sludge-amended plants without inorganic P showed weaker plant development throughout the season at Freeling and Strathalbyn. These treatments also had lower shoot P concentrations and/or P uptake values (Table 3.15), which suggest a somewhat reduced sludge P availability compared to the inorganic fertiliser. Reduced growth of plants which were not fertilised with inorganic P occurred even though the grain P concentrations were above critical values for bread wheat varieties at those sites (Reuter and Robinson, 1986).

Batten (1986) has shown that the change from diploid to tetraploid (for example *T. durum*) and hexaploid wheat (*T.aestivum*) was associated with a reduction in the concentration of phosphorus in the grain in both sufficient and low P fertilised plants. Also the efficiency of utilisation of phosphorus (P taken up by plants) increased in the order diploids<tetraploids<hexaploids and was highly correlated with the harvest index, but there was considerable variation between lines within each ploidy group (Batten, 1986). This may indicate that durum wheat varieties have a higher nutrient demand than bread wheats and may partly explain why durum wheat varieties do have a similar yield potential as bread wheats on the more fertile soils, but not on sandy or low fertility soils (Brooks *et al.*, 1994).

The results imply a lower P availability from the sludge in the first part of the season, but this increases with time compared to the inorganic fertiliser, because differences in grain yields were not observed. A late mineralisation of sludge P and increased P supply in the warmer months of spring could have improved the plant availability of sludge P. Chang *et al.* (1992) claimed that plants are frequently able to overcome deficiency symptoms that are developed in the early stage of growth, particularly if such symptoms are not severe. Other authors found an increase in relative efficiency of sludge P compared to inorganic P over time (McLaughlin and Champion, 1987). It is known that P mineralisation can be slow in cooler parts of the year. However, in the current experiments, the limitation of P availability on shoot growth were noticeable until late booting stage (Harvest 2). This long period of reduced P nutrition suggests a lower plant availability of sludge P compared to fertiliser P, which still may slowly increase over time. Pastene (1981) noticed that sludge P availability is lower in sludges with a high content of Al and Fe. The sludge used in the current experiment had a high total content of these elements (Al 58 g kg^{-1}, Fe 1.8 g kg^{-1}) and a similar influence of those compounds on sludge P availability is quite likely. The grain P concentrations and P contents were similar across all the fertiliser or sludge amended plots (except nil) at Callington, Freeling and Strathalbyn. However, it was found that in wet years fertiliser P has a larger effect on P uptake in the shoots than in the grain (Holford and Doyle, 1993). Hence the shoot P concentration and uptake results may be more reliable for assessing the P supply of the two sources.

At Callington plant responses to inorganic P compared to sludge P were not as varied as at the other two sites (Freeling and Strathalbyn), although the bicarbonate-extractable soil P at this site was lower. The lower yield potential of the site at Callington may partly explain why the sludge seemed to be an equivalent source of plant available P compared to the fertiliser treatments. Different mineralisation patterns in the soil could have also caused a quicker mineralisation of the sludge compared to the other sites. Callington has a lighter and sandier soil than Freeling and Strathalbyn, with the highest percentage of coarse sand in the sand fraction. Sandy soil can dry and warm up faster after rain. In the moist, cool year of 1992 a slight difference in soil temperature may have influenced mineralisation patterns.

At Lameroo there was only a small plant response to increased P additions (treatment (2t+N*+P/2)). The bicarbonate-extractable P level and plant P concentrations at this site were higher than at the previously mentioned sites, indicating sufficiency in P nutrition. However, differences in P nutrition between the two sources could be observed in P concentration and P uptake values at Harvest 1, being higher for the (nil+N+P+TE) treated plants, compared sludge treated plants without inorganic P((2t), (2t+N*). This also indicates a low sludge P availability early in the season and supports the findings at the other sites.

Replacement calculation: The general response in growth to increasing rates of fertiliser is curvilinear: initially there is a large increase in growth, but as the fertiliser rate increases, the responses diminish. When comparing the efficiency of different fertilisers, it is preferable to be working in the responsive part of the curve so that differences in efficiency can be established. Adding inorganic P to the sludge-treated plots (treatment

(2t+N*+P/2)) increased yield beyond the comparable inorganic fertilised plots at three of the sites. Although no N and P response curves were established at the sites, the significantly enhanced grain yield of the (2t+N*+P/2) treatment compared to most of the other treatments shows that grain yield increases with higher fertiliser additions were still possible, and that the optimum level of nutrient in terms of maximum yield had not been achieved.

The current results suggest that the plant available P from 2t sludge can be up to 20 kg P, as the grain yield suggest, but may be somewhat below that margin as the shoot P concentration and uptake values at the various sites suggest.

Based on the assumption that a (2t+N*) sludge application provided plant available P up to the amount of the inorganic comparison (nil+N+P), the percentage of available P in the sludge can be calculated:

Total P applied in sludge: 36 kg P ha^{-1}
Inorganic P equivalent based on grain yield responses: 20 kg P ha^{-1}
Available P in sludge: ≤ 55 %

The calculated value of up to 55 % plant available P is at the lower end of the broad range of values given in the literature. The approximate value of 55 % effectiveness (of total sludge P) is in agreement with Willett et al (1986) who found in field experiments that sludge P was 49% as effective as the P of superphosphate in raising extractable soil P levels on an P-deficient soil. The relative efficiency of sludge P compared with inorganic fertiliser P in other studies was estimated to be 100 % (Gestring and Jarrell, 1982), 44-100 % (McLaughlin and Champion, 1987) and 20-80 % (DeHaan, 1980). Coker (1983) summarised a range of studies and concluded that sludge P availability is approximately 65 % of superphosphate, when the values for sludges with chemical precipitants, such as Al, Fe or Ca which are used for P precipitation in a number of waste water plants, were excluded. O'Riordan *et al.* (1987) found sludge-P to have an efficiency of 79 and 74 % relative to superphosphate on a silty and a clay loam respectively. On the addition of Al and ferrous salts, DeHaan (1980) noticed a sludge phosphorus uptake of only 10% relative to monocalcium phosphate. The high Al and Fe contents of the sludge used may have reduced P availability (Pastene, 1981) (see Literature Review, Section 2.4.2). It probably would be advisable to monitor the Al and Fe level of the sludge to see if this is a general feature of the Bolivar sludge or if the Al and Fe level could be decreased by mixing several batches of sludge.

Summarising the results of shoot and grain yield and their P content it seems that sludge P availability is somewhat below 55 % compared to inorganic P when applied to a cereal crop. The release of sludge P over time is not similar to the features of inorganic fertiliser, but lower in the earlier part of the season.

These results cannot be taken as an indication of the potential fertiliser value of rotary kilned sludge, the treatment process generally used to date for marketing Bolivar sludge. Häni and Gupta (1978) observed that due to a sludge drying process at 105 °C the citric-acid-soluble P was reduced by 10 to 40 %. Van Erp and van Dijk (1992) found the relative P efficiency in ground air-dried pig slurry to vary from 81% to 100% but the pelletised product (heat treatment 120°C) had a reduced relative efficiency index of 41 to 62 %.

3.7.2 Nitrogen replacement value of sludge

The fertiliser value of sludge N can be best assessed with the results from Lameroo, where plants were clearly responsive to N fertilisation, as can be judged from growth and yield differences between the (2t) and (2t+N*) treatments.

(At the TE deficient site Lameroo the inorganic TE and sludge treated plants can be compared in terms of N and P availability, because TE or at least Zn nutrition was elevated in a similar way in those treatments: (nil+N+P+TE), (2t), (2t+N*), (2t+N*+P/2) and (1t+N*+P/2+TE/2)).

The similar yield of sludge only (2t) and inorganic fertiliser treated plants suggests that the N availability of the two sources were equal in the sandy type soils at Lameroo and that 2t of sludge has an N replacement value of 20 kg N ha^{-1}.

Sludge N mineralisation calculation: Some sludge N must have been mineralised during the growth period, because initially only a small amount of NO_3^- and NH_4^+, the plant-available forms of N, were in the sludge. Sludge analysis prior to application gave the following fractions of sludge N (Table 3.2): Total N = 42.0 kg $2t^{-1}$, Organic N = 38.1 kg $2t^{-1}$, NH_4^+-N, NO_3^--N= 3.9 kg $2t^{-1}$. As mentioned above a 2t sludge application may substitute for approximately 20 kg N. The amount of N mineralised from sludge organic material can then be calculated as the difference between the replacement value (= plant available N) and the amount of inorganic N in the sludge prior to application, if the N loss by volatilisation is considered negligible.

Substitution value of sludge	20	kg N ha^{-1}
Total organic N applied in sludge	38	kg N ha^{-1}
Inorganic N applied in sludge	3.9	kg N ha^{-1}
Amount of sludge organic N mineralised	16.1	kg N ha^{-1}
Sludge organic N mineralised	42	%

At Callington, Freeling and Strathalbyn plant response to N was not as marked as in Lamero as can be seen by the similarity in growth and grain yield of sludge amendments alone (2t) or sludge plus inorganic N fertilisation (2t+N*). Lameroo has a sandy soil with a lower organic matter content than Callington, Freeling and Strathalbyn and thus lower soil N reserves are likely to be low, which may have caused the difference in response. Also at Callington, Freeling and Strathalbyn plants were grown in rotation after pasture or vetch as opposed to Lameroo, where plants were grown after two years of cereals and thus a lower soil N content can be expected.

However, it seems unlikely that plants at Callington, Freeling and Strathalbyn would not show any response to additional N fertiliser applications in a wet year such as 1992, because grain yield potential was shown to increase linearly with seasonal rainfall and with total N in the top soil (Xu and Elliott, 1993). Dry matter production, particularly 10 weeks after sowing and to a lesser extent at anthesis, were shown to be more responsive to N additions than the grain yield (McDonald, 1992). Again it seems unusual that N additions did not have any significant influence on growth at Callington, Strathalbyn and Freeling in 1992. The lack of significant growth or grain yield differences to the 15 kg N ha^{-1} addition to sludge amended plots at the three sites could have the following reasons: a) plant response declines as fertiliser rates increase and the resulting plant response differences were too small to be measured in a field experiment; b) wet conditions in 1992 could have leached a considerable amount of (sludge and/or fertiliser) N beyond the root zone.

However, the addition of 15 kg N ha^{-1} to the sludge amended plots had a consistent positive but non-significant effect on grain yield at those three sites, which suggests a positive influence of N fertiliser. If one accepts the assumption that N also had some influence on plant production at the above mentioned three sites, the N supply of sludge can then be narrowed down to a range of between 5 and 20 kg 2t^{-1}, depending on which treatment is considered equivalent to the inorganic comparison ((2t) or (2t+N*)). The sludge N replacement value of 5 or 20 kg N ha^{-1} represents the upper and lower limits of the range of possible sludge N availability in the given environment.

The calculated mineralisation of organic N from the sludge based on the results of Lameroo of 42 % is at the upper end of the broad range of values given in the literature about this topic (see Literature Review, Section 2.4.1). The sludge N availability, calculated as a percentage of the total N, was approximately 48 %. Coker (1983) found on average 15% of sludge organic N mineralised (digested sludge), when he summarised a number of reports and excluded incubation and glasshouse experiments. Amundson and Jarrell (1983) found 1t of sludge (22 kg total N) as effective as 7-13 kg N in the form of inorganic fertiliser, even when using high sludge application rates. Sabey *et al.* (1977)

found a sludge application of 22t ha^{-1} with a total N of 814 kg equivalent to a 200 kg N ha^{-1} fertiliser application. The calculated N availability of sludge was higher than in the study of Poletschny (1987) who found for temperate regions a 20-25 % sludge N availability in the first year for heavily dewatered sludges with a low amount of total N and inorganic N. This figure is quite similar to the general assumptions used in the U.S. of 20 to 25% of organic N mineralisation in the first year. Day *et al.* (1990a) did a study with durum wheat in a hotter and drier climate (Arizona), but under irrigated conditions (not mentioned explicitly). Day *et al.* (1990a) found 75% of the total sludge N content to be available to the crop. The N availability is considerably higher than in the current study, which is probably due to the different quality of the liquid sludge with a higher total N content of 9 % (and probably higher inorganic N) content compared to 2.1% for the Bolivar sludge. Also high temperature and possibly irrigation, keeping the soil moist, may have supported sludge mineralisation.

3.7.3 Micronutrient (Zinc) replacement value of sludge

At Lameroo, the addition of TE had a significant influence on shoot production at Harvest 2 and the grain yield. The addition of TE increased yield by about 0.38t ha^{-1}. Graham *et al.* (1993) observed yield increases due to Zn additions of about 0.67-0.84 t ha^{-1} with Durum wheat varieties in this 'Mallee' region. The grain yield of TE (Zn) treated plants (nil+N+P+Te) in the current experiment of 1.36 t ha^{-1} was comparable to the yield of Durum wheat varieties of 1.12-1.29 t ha^{-1} after a high application of Zn observed by Graham *et al.* (1993). Plants receiving sludge or inorganic TE had a higher Zn concentration and uptake than (nil+N+P) fertilised plants. The Zn concentration and Zn uptake of plants treated with sludge or inorganic TE fertiliser were generally similar in all three harvests. Hence a 2t sludge application seemed to provide a similar amount of plant available Zn as the inorganic TE fertiliser application.

At Callington, Freeling and Strathalbyn TE or Zn additions did not influence shoot or grain yield, but grain Zn concentrations differed between the (nil+N+P) and (nil+N+P+TE) treatments, indicating some response to applied Zn. Also at those sites the sludge treated plants showed in general similar grain Zn concentrations and contents to the inorganic fertiliser comparison (nil+N+P+TE), supporting the findings of similar phyto-availability of Zn of the two sources.

After sludge application a number of authors reported increased Zn concentration in shoot or grain of plants (Hernandez *et al.*, 1991). Goto *et al.* (1993) also suggested that Zn in sludges is readily available to plants, with increases in plant Zn concentration closely correlated with the amount of Zn added with sludge. However, no inorganic fertiliser comparison was included in that work. Chang *et al.* (1983) found that Zn concentration in plants increased with the rate of sludge application.

A number of studies have shown that metals applied to soil as a salt accumulate in plants more readily than the same quantity of metal added in sewage sludge (Giordano *et al.*, 1975; Logan and Chaney, 1983). These studies were often done with comparatively high Zn application rates (Giordano *et al.*, 1975; Dijkshoorn *et al.*, 1981), or on low pH soils (Mortvedt and Giordano, 1975). The study of van der Watt *et al.* (1994), using soils with low and high pH has shown that the Zn uptake by Sudax (*Sorghum bicolor*) grown in soil was decreased in a low pH soil but similar or increased in a high pH soil (pH 6.4-7.4), when coal derived fulvic acid was applied. Sludge application was shown to increase the DTPA extractable Zn in calcareous soils (McCaslin *et al.*, 1987) and Zn concentration of plants (Fresquez *et al.*, 1990). Singhania *et al.* (1983) found that Zn applied in the form of slurry (cow dung, anaerobically decomposed) increased total Zn uptake by the crop to the same degree as Zn applied as Zn-sulfate to a calcareous growth medium. In fertiliser studies often the chelated form of Zn, Zn EDTA, was found to be more effective than ZnO in ameliorating deficiency at low Zn rates while all sources are equally effective at a high Zn rate (Takkar and Walker, 1993). In the current experiment the inorganic Zn and sludge borne Zn increased plant Zn concentration and uptake to a similar extent and thus seemed to be an equal source of Zn in the year of application.

At Lameroo the shoot Zn concentrations in all treatments at Harvest 2 were well below the critical values for wheat, but the grain Zn concentrations indicated no deficiency according to values established for bread wheat varieties (Reuter and Robinson, 1986). However, these values may not apply for Durum wheat varieties. Durum wheats are poorly adapted to TE deficient soils and the range in Zn efficiency (or lack of it) was found to be much greater in durum wheat than in bread wheat varieties (Graham and Rengel, 1993). Saberi Hossein (pers. commun.) observed growth responses of durum wheat (*T. durum*) to Zn fertilisers, at Zn tissue concentrations considered sufficient for bread wheat varieties (*T. aestivum*). The responsiveness of durum wheat varieties to Zn fertilisation (calculated as 100*-Zn/+Zn) was found to be considerably higher compared to most bread wheat varieties when Zn concentration in shoot and grain of the minus and plus Zn treated plants were similar (Graham *et al.*, 1993). Day *et al.* (1990 a,b) reported that durum wheat varieties accumulated more Zn in the grain than in the straw, which is generally not reported for bread wheat varieties. It seems that critical values for crop production for durum wheat and bread wheat varieties may have to be evaluated separately.

Zinc was a growth limiting nutrient at Lameroo, but the growth response to TE cannot conclusively be pinpointed to this nutrient alone, because the TE mix did contain Mn and Cu as well to match the TE application given by 2t of sludge. However, plant Mn concentration were not deficient and there were no significant differences in Mn concentration in shoots at any of the harvests (Appendices, Table A.3.8). The concentrations of Cu in shoots were fairly low, with an average of 1.2 mg kg^{-1} Cu at Harvest 2 and 2.3 mg kg^{-1} Cu in the grain (Appendices, Table A.3.7). Copper concentrations of <1.6 mg kg^{-1} in the YEB (youngest emerging blade) in bread wheat at heading stage indicate deficiency (Reuter and Robinson, 1986). However, shoot tissue concentrations of TE are in general lower than concentrations in the YEB. King and Alston (1975) found in field experiments in South Australia that Cu responsive and unresponsive sites are largely separated by a critical concentration of 2.5 mg kg^{-1} Cu in the grain. Thus it could be possible that Cu in the TE mix enhanced plant growth. Differences in shoot Cu concentrations between treatments were only observed at Harvest 1, when plants not treated with TE showed lower Cu concentrations. Marginal Cu nutrition of plants cannot be excluded, but again sludge and inorganic Cu seem to be similar sources of plant available Cu.

It could be argued that results achieved with a TE responsive durum wheat variety are of limited use for the more TE efficient bread wheat varieties. However, in this experiment, the purpose was to establish if and to what extent sludge can replace a TE fertiliser addition. For experimental reasons this is easier to examine with a TE inefficient variety. When the fertiliser value is established, it remains to the judgement of the farmer if yield increases from TE additions with a particular species or variety at the given site can be expected. However, marginal TE nutrition is widespread in wheat and barley in South Australia (Hannam, 1991). Also seasonal differences can be more important than the varietal differences between bread and durum wheats.

3.7.4 Manganese deficient site, Marion Bay

On calcareous sands Mn deficiency is often both chronic and severe with yields without Mn fertiliser ranging from 40-75% of those with Mn (Graham *et al.*, 1983). The barley variety 'Galleon' sown is a relatively Mn inefficient variety (Graham *et al.*, 1983). The addition of TE in the current experiment had a considerable influence on plant growth and grain yield, with the latter being increased by about 35% due to TE additions. It is likely that Mn was the most important element in the TE mix, because Mn concentrations in the shoots were marginal during the whole growth period, whereas Zn and Cu concentrations were in the sufficient range (Reuter and Robinson, 1986). Manganese uptake values also showed clear differences between plants treated with or without Mn fertiliser. The sludge-treated plants showed similar yields and Mn uptake values compared to inorganically fertilised plants plus TE, suggesting that Mn applied with sludge has a similar plant availability to fertiliser Mn. A decreased Mn uptake by plants after sludge application, as observed by Hernandez *et al.* (1991), Juste and Solda (1984), Willett *et al.* (1984) and Soon *et al.* (1980) was not noticed in the current study. A difference in sludge application rate could be the reason for the discrepancy. Two unreplicated plots in the current study, which received higher sludge applications showed a lower shoot and grain yield and lower shoot Mn concentrations at booting (data not shown) compared to plants treated with low sludge rates.

Nitrogen and P fertiliser enhanced shoot growth and grain yield considerably at the site. Sludge-treated plants enhanced growth similarly to the inorganic N, P and TE comparison. However, a lower sludge P availability compared to inorganic P in the early part of the growth season was also noticed at this site. It cannot be distinguished if the similarity in grain yield response was due to: a) similar N and P supply of the two sources b) limited growth due to low Mn nutrition or c) the plateau part of the growth response curve was reached. However, given the widespread Mn deficiency in the region, it is most likely that Mn nutrition was still limiting. Although the N and P supply cannot be exactly quantified, it was shown that a 2t ha^{-1} sludge application enhanced growth considerably and similarly to a conventional fertiliser application of 20 kg N, 20 kg P and 4 kg Mn ha^{-1} (plus Zn and Cu).

3.8 Conclusions

- A 2t sludge application caused a grain yield increase similar to an inorganic fertiliser application of 20 kg N and 20 kg P, 1.9 kg Zn 1.5 kg Cu, 4 kg Mn per hectare at all sites.

- The N nutritional value of 2t sludge was estimated to be approximately 20 kg N. However, the combined grain yield data from three sites (Callington, Strathalbyn and Freeling) suggested that the N value may be somewhat below that value.

- The plants treated with sludge (without inorganic P) showed reduced shoot growth in the early part of the season compared to plants amended with inorganic P fertiliser (or sludge plus inorganic P). However, grain yield was similar for the sludge or inorganic P fertilised plants. The availability of sludge P was estimated to be up to 55 % of the total P.

- Sludge or inorganic TE additions enhanced plant growth and tissue Zn concentrations to a similar extent. Hence, supply of plant available Zn was similar from sludge and inorganic fertiliser in the year of application.

- Manganese applied with a low application rate of sludge enhanced growth and grain yield similarly to an inorganic Mn application of 4 kg ha^{-1} at a Mn deficient site.

Chapter 4

Field experiments 1993
Comparison of sludge and inorganic fertiliser

4.1 Introduction

Sludge is a significant source of plant nutrients and can replace inorganic fertilisers to some extent. In the field experiments in 1992 sludge proved to be a valuable source of N, P and Zn (Chapter 3). A sludge application of 2t ha^{-1} was equal to an inorganic fertiliser application of 20 kg N ha^{-1} and 20 kg P ha^{-1}, when grain yield was compared. The sludge N availability of 2t was rated between 5 and 20 kg N ha^{-1}, but most likely closer to the upper margin of 20 kg. Also it was found that the availability of sludge-borne Zn is equal to Zn sulphate under field conditions, including a Zn deficient site. However, field results vary with seasonal conditions. A repetition over a number of years is generally advisable. Moreover, in 1992 the crop received above average rainfall and plants neither experienced severe water shortage during growth nor were forced into maturing early as can be the case in South Australia. It was intended to repeat the field experiments of 1992 in an another year, which may have climatic conditions closer to the average growth period for South Australia. Two of the sites planted in 1992 were used again to have the same soil types as in the previous year.

4.2 Material and Methods

4.2.1 Sludge application rates

For general assumptions about the sludge application rates and choice of the selected treatments see Section 3.2.2. A short summary of the assumptions will be given in the following Sections 4.2.1.1 - 4.2.1.4. The plant availability of nutrients in Adelaide (Bolivar) sludge and for South Australian soils and climates was not known. A 2t sludge application was chosen as a base treatment under the assumptions, because it contained TE and P in concentrations approximately in the range of commonly used fertiliser application rates in South Australia.

4.2.1.1 Nitrogen (N)

As in 1992, sludge inorganic N and 10% of the organic N was assumed to be available to the plant in the year of application. In 1993 data for inorganic N and total N of the batch of sludge used were available prior to seeding and were used to calculate necessary fertiliser N additions.

Accordingly, 2t Bolivar sludge was assumed to provide:

$$\text{N-available} = (NH_4^+ + NO_3^-)\ N + 0.1 * \text{organic N}$$

According to this equation the sludge from the Bolivar treatment works (N_{total} =21 kg t^{-1}, $N_{inorg.}$ = 2 kg t^{-1}; $N_{org.}$ = 21-2 =19 kg t^{-1}) would supply the following amount of plant available N:

$$= 2 + 0.1 * 19 = 3.9 \quad [\text{kg N } t^{-1}]$$
$$7.8 \quad [\text{kg N } 2\,t^{-1}]$$

Based on these assumptions the N nutrition would be insufficient for a 2t sludge application rate compared to the target of 20 kg N ha^{-1}. Therefore some sludge amended plots received additional inorganic nitrogen to supply the shortfall between assumed available N from the sludge and 20 kg N ha^{-1}. The results from the field experiments in 1992 indicated a higher sludge N availability to plants than the assumption of 10 % sludge organic N availability. However 1992 was a comparatively humid year, with abundant rainfall allowing a fairly long growth period for the plants. Some sludge fertilised plants lagged behind in their early development in 1992 and hence it remained unclear, if availability of the sludge nutrients to the plants would also match the need of plants in a shorter growth season. Therefore the cautious assumptions used for the field planning in 1992 were again used in 1993, but with updated N data. Inorganic fertiliser additions to the various treatments are listed in Table 4.1.

4.2.1.2. Phosphorus (P)

In 1993 data for total P of the batch of sludge used were available prior to seeding. The same assumptions as in 1992 about the potential plant availability of sludge P were applied, based on updated data for total P (for assumptions see Chapter 3). Plant available P of 2t sludge in one season was assumed to be between the values indicated by citrate soluble P and HCO_3^- soluble P and therefore around 20 kg ha^{-1} available P. Sludge from the Bolivar treatment works contained:

P as total phosphorus	36	kg $2t^{-1}$ sludge
P as citrate soluble P	26	kg $2t^{-1}$ sludge
P as HCO_3^- soluble P	12.6	kg $2t^{-1}$ sludge

Results from the field experiments in 1992 suggested that a 2t ha^{-1} sludge addition may be a sufficient P source for cereal plants in some but perhaps not all stages of their development. The results from the field experiments in 1992 were obtained from a long season with sufficient time for the mineralisation processes to take place. It remained unclear if the P mineralisation, like N, takes place early enough to support plant growth efficiently. Therefore it was again assumed that 2t sludge provides P equivalent to the inorganic treatment of 20 kg P ha^{-1}, but also a sludge treatment with additional inorganic P was retained in the experiment. For treatment details see Table 4.1.

4.2.1.3 Micronutrients zinc (Zn) and copper (Cu)

The TE additions in the inorganic fertilised plots were equivalent to the total content of Zn, Cu or Mn in 2t sludge. For details of inorganic TE application rates see Table 4.1.

4.2.1.4 Micronutrient manganese (Mn)

In 1993 the sludge was not amended with inorganic Mn, because the Mn deficient site, Marion Bay, was not used again in 1993. The micronutrient-mix for the inorganic fertiliser treatment therefore contained only a Mn content equivalent to the total Mn of 2t sludge.

Table 4.1 Inorganic fertiliser (Roman) and calculated sludge nutrients (italic) applied in the different treatments in 1993. The assumed plant available fraction of sludge borne N and P which are listed here is based on assumptions described in section 4.1.

Inorganic fertiliser #	N	N_S	P	P_S	Zn	Zn_S	Cu	Cu_S	Mn	Mn_S
					[kg ha^{-1}]					
nil										
nil+N+P	20.0		20							
nil+N+P+TE	20.0		20		1.8*		1.4*		0.5*	
2t		*7.8*		*20*		*1.8*		*1.4*		*0.44*
2t+N	12.2	*7.8*		*20*		*1.8*		*1.4*		*0.44*
2t+N+P/2	12.2	*7.8*	10	*20*		*1.8*		*1.4*		*0.44*
2t+ P/2		*7.8*	10	*20*		*1.8*		*1.4*		*0.44*
1t+N+P/2+TE/2	16.1	*3.9*	10	*10*	1.0**	*0.9*	0.7**	*0.7*	0.3**	*0.22*

commercial grade inorganic fertiliser

* Te application was split, half of the amount was incorporated into the N/P-base granules, the other half was applied as liquid TE fertiliser prior seeding,

**applied as liquid TE fertiliser sprayed onto the plots prior to seeding

4.2.2 Sludge treatments

In 1993 the same treatments as in 1992 were applied at the two sites, Freeling and Callington. However the treatments in Callington were applied on previously conventionally worked soil (inorganic fertiliser: 20 kg N ha^{-1}, 20 kg P ha^{-1}), whereas at Freeling the treatments were superimposed. Hence only the experiment at Callington was a real repetition of the experiments in 1992, where all treatments were applied on conventionally worked soil. In Callington the experimental plots of 1992 were subdivided and newly applied treatments were located on formerly (nil+N+P) treated plots. The treatment (2t+P/2) was added in 1993.

The nil treatment was applied on the nil treated plots of the previous year. At Freeling treatments as in 1992 were reapplied on the same plots in 1993 to compare the effects of repeated sludge application compared to inorganic fertiliser amelioration of soils and crop growth. For the field plan see Plate 2 and 3 in the Apendices for Chapter 4.

Treatments:

nil
nil+N+P
nil+N+P+TE

2t
2t+N^*
2t+N^*+P/2
2t+ P/2 (#)
1t+N^*+P/2+TE/2 (##)

(# applied in Callington only; ## applied in Freeling only)

4.2.3 Method of inorganic fertiliser and sludge application in the field

The treatments were arranged in a completely randomised block design with 5 replicates per treatment. The air dry sludge was applied on the date of seeding, but prior to the seeding operation. In 1993 a modified 10 row, tyned cone seeder was used, where two parallel cones fed sludge into the seeder shafts. With this set up a maximum of 4t sludge ha^{-1} could be applied in two workings. The sludge was applied 2-5 cm below the seeding depth of 5 cm similarly to the application process in 1992. Plot size was 30 m^2 (20 m long, 1.5 m wide) at Freeling and 15 m^2 (10 m long, 1.5 m wide) at Callington. The inorganic fertiliser and control plots were worked the same way as the sludge amended plots. The inorganic fertiliser as well as the inorganic additions to the sludge-amended plots were applied together with the seed in the third working of the plots, using the cone seeder. Seeding rates are recorded in Table 4.19.

4.2.4 Field crop and plant analysis

The barley (*Hordeum vulgare* L.) variety 'Galleon' was seeded at a rate of 70 kg ha^{-1} (seed treated with Baytan). Because the experimental sites of 1992 (Callington, Freeling) were replanted with a cereal crop in 1993 the crop was changed to a cereal cyst nematode (CCN) resistant barley variety to avoid possible influences by nematodes. Crop rotation at the two sites is detailed in Table 4.2. Apart from the fertiliser treatments, crop husbandry was undertaken by the farmer as part of his normal management practices.

Two mid season harvests and a final grain harvest were taken at both sites. Plant samples in Harvest 1 and 2 were taken at two independent positions along a central row in the plots. Plants were cut 2 cm above ground. Harvest 1 was taken about 10 weeks after planting, when plants were generally in stem extension stage. The second harvest was taken about 15 weeks after planting, when plants were flowering. For details about exact harvest dates and subsampled area, at the three harvests see Table 4.2. Dry weight of shoots in Harvest 1 and 2 and grain yield was recorded. The shoots were dried in a forced air oven at 70°C for at least 24 hours, digested in concentrated HNO_3 and analysed for Ca, K, Mg, Mn, Cu, Zn, P, S, Mo concentrations using an inductively coupled plasma emission spectrometer (ICP) (p. 255a, 255b). Nitrogen content of shoots was analysed with a N analyser 1500 series 2 (Carlo Erba Instruments). Grain was analysed for N content using a Kjeldahl technique.

Dry matter and grain yield were transformed into relative yield by dividing all the values, including the values for the nil treatment, by a common factor, the site average for the nil treatment. The Anova was calculated for the transformed data.

Due to widespread mice damage in 1993 in South Australia the plant densities at both sites were reduced by approximately 35%. The plots were scored for mice damage to assess the damage, which was even across the treatments. In Callington only a part of the initial plot (two centre rows) was harvested for grain yield to insure that mice damaged areas at outer parts of the plots were not included in the harvest. In Freeling the plant density was evenly reduced in all rows of the plots.

Table 4.2 Crop rotation, seeding and harvesting dates of the experimental sites in 1993.

	Callington		Freeling	
	Crop rotation			
1991	pasture		vetch	
1992	wheat		wheat	
	Seeding and harvest dates	Harvested area [m^2]	Seeding and harvest dates	Harvested area [m^2]
Seeded	22. 7.93		6.7.93	
Harvest 1	27. 9.93	0.09	15. 9.93	0.09
Harvest 2	29.10.93	0.12	25.10.93	0.12
Grain harvest	9.12.93	2.40*	17.12.93	27

* Due to partial mice damage only a portion of the plot was harvested for grain yield.

4.2.5 Soil characteristics and weather

The soil type in Callington was a sodic brown Kandosol-Dermosol and Freeling soil can be classified as a epicalcareous Vertosol (Isbell, 1995). For a more detailed soil description of the sites and their location in South Australia see Chapter 3, Table 3.9 and 3.10. Climatic data such as rainfall and temperature in the experimental year are listed in Table 3.11 and 3.12 in Chapter 3.

4.3 Results

The results from Callington and Freeling will be discussed together although Freeling had two consecutive years of treatment applications whereas at Callington the 1993 treatments were applied on plots that were conventionally fertilised in 1992 (except for the nil treatment). However, the residual value of a the sludge or inorganic fertiliser application used was found to be quite low and similar for the two sources (Chapter 6). The shoot and grain yield therefore seems to be dominated by the current year's fertiliser/sludge application.

The nil treatment at Callington was superimposed, as it was also in Freeling. Therefore absolute growth and yield increase at the sites, which is based on a comparison of the nil treatment with other treatments, may be slightly overestimated, because the nil treatment receiving no fertilisation for two years. However, comparisons between the sites Callington and Freeling are possible, because a superimposed nil treatment existed at both sites.

4.3.1 Nitrogen (N) and phosphorus (P) replacement potential of sludge

At both sites considerable responses to fertiliser/sludge additions in both shoot dry matter and grain yield occurred (Figure 4.1 and 4.2). Responses, expressed as a percentage of the nil treatment, were more pronounced in terms of shoot dry matter production than grain yield. The absolute yields of the nil treatment and an average of the fertilised/sludged treatments are listed in Table 4.3.

Shoot harvests: Callington: Shoot dry matter of fertiliser or sludge treated plants were significantly higher than in the nil treatment (Figure 4.1). Sludge amended plants showed a dry matter production similar to the inorganic fertiliser treatments.

Freeling: Sludge amended with additional N (2t+N*) allowed a dry matter production similar to the inorganic fertiliser (Figure 4.2). Shoot dry matter of (2t) treated plants was lower than the inorganic fertiliser comparison, with differences being significant when compared to one of the inorganic fertiliser treatments. The addition of inorganic P to a sludge application (2t+N*+P/2) tended to enhance plant growth at both shoot harvests beyond the inorganic fertiliser comparison, with differences being significant compared to one of the two fertiliser treatments (nil+N+P+TE). The productivity of (1t+N*+P/2+TE/2) was similar to the (2t+N*+P/2) treatment at Harvest 2 whereas at Harvest 1 it was clearly lower.

Grain yield: Callington: All sludge or fertiliser amended plants yielded in the same range, between 36 % and 45 % higher than the nil treatment, reflecting the results of the shoot dry matter harvests. The high variability at Callington may have prevented a better judgement of possible growth differences.

The absolute grain yields for Callington are probably overestimated owing to the area which was harvested. The central rows of the plots, which were harvested, did not have a direct bordering row due to the mice damage. Only rows further away remained. The central rows therefore did have a space advantage, which could be used for enhanced tillering and dry matter production.

Freeling : There was a significant yield increase due to fertiliser or sludge addition. The (2t+N*) treatment produced equivalent yield to the inorganic fertiliser comparison. Plants in the the sludge only treatment yielded higher than the nil treatment, but significantly lower than the other fertiliser/sludge treatments. The plants amended with sludge and additional inorganic P ((2t+N*+P/2) and (1t+N*+P/2+TE/2)) tended to yield higher than the comparable inorganic fertiliser treatment, but differences were insignificant.

4.3.2 Micronutrients (TE) replacement potential of sludge

In all three harvests at both of the sites plants treated with or without inorganic TE ((nil+N+P) or(nil+N+P+TE)) yielded similarly (Figure 4.1 and 4.2). TE deficiency was not a yield restricting factor at the two experimental sites in 1993.

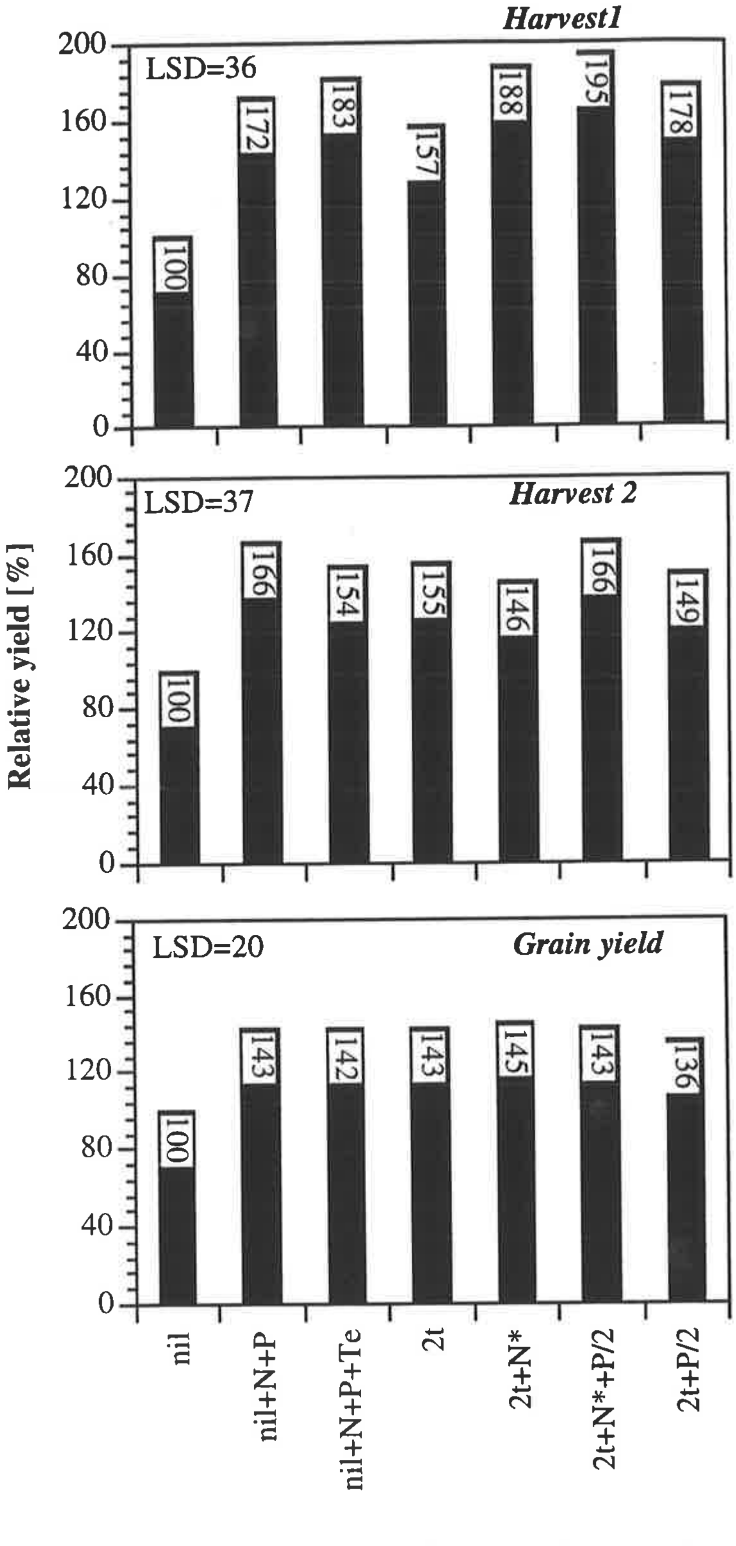

Figure 4.1 Callington 1993: Dry weight of shoots at harvests 1 and 2 and grain yield relative to the nil treatment (100%). Harvest 1: 67 days, Harvest 2: 99 days after sowing. (LSD, P=0.05) (Value in the bar represents relative yield expressed as percentage of the nil treatment.)

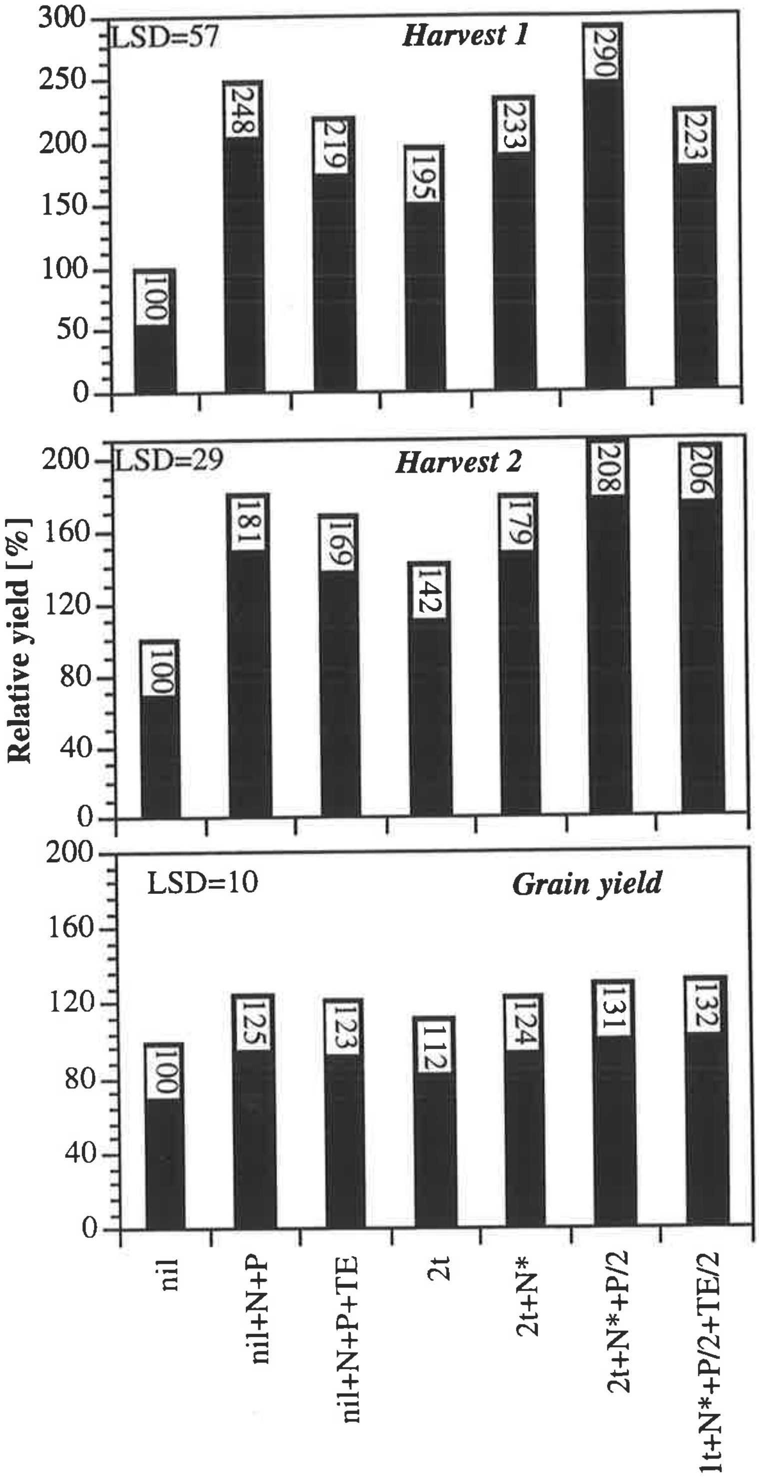

Figure 4.2 Freeling, 1993: Dry weight of shoots at harvests 1 and 2 and grain yield relative to the nil treatment (100%). Harvest 1: 70 days, Harvest 2: 110 days after sowing. (LSD, P=0.05) (Value in the bar represents relative yield expressed as percentage of the nil treatment.)

Table 4.3 Dry weight of the nil treatment and an average of the sludge or fertiliser treatments for the sites in 1993.

	Callington		Freeling	
	nil	**sludge/fertiliser**	**nil**	**sludge/fertiliser**
		[g m^{-2}]		
Harvest 1	132	236	53	124
Harvest 2	498	777	474	857
Grain	363	515	209	260
		[t ha^{-1}]		
Grain	3.6#	5.2#	2.1	2.6

overestimated grain yield, see section 4.3.1 for explanation

4.3.3 Chemical analysis of shoot and grain

4.3.3.1 Phosphorus

Phosphorus concentration and uptake values for the three harvests at the two sites are listed in Tables 4.4 and 4.5.

Callington: At Callington application of inorganic fertiliser or sludge resulted in a higher P concentration and P uptake value compared to the nil treatment, except at Harvest 2. Also the P uptake values of fertiliser or sludge treated plants compared to the nil treated plants were always significantly greater. Shoot P concentrations were quite low. The shoot P concentrations in the nil treatment were below the critical value for barley in Harvest 1 and 2 with 3062 mg kg^{-1} and 1418 mg kg^{-1} P respectively. The values for fertiliser or sludge amended plants at Harvest 1 were higher, but particularly at Harvest 2 still within the range considered marginal for barley (Harvest 2: 1500 to 1900 mg kg^{-1} P indicative for marginal P nutrition; Reuter and Robinson, 1986).

The sludge treated plants did have a lower P concentration than the comparable inorganic fertiliser treated plants at Harvest 1 and in the grain (except for treatment (2t+P/2)). However, the P uptake values of sludge treated plants (Harvest 1 and grain) were generally similar to the uptake values of the inorganic fertiliser treatments. However, the grain P content of sludge treated plants tended to be lower. It is possible that the high variability in the grain harvest may have masked differences in terms of grain content at this site.

Freeling: The P concentration values of plants in Freeling were somewhat higher than those at Callington. The bicarbonate extractable P level in the Freeling soil was higher than in Callington (18 mg kg^{-1} compared to 12 mg kg^{-1} in the top 10 cm), but still below the desirable level for cereal growing areas in medium rainfall country (calc. sand: 26 mg kg^{-1}; calc. loam 38 mg kg^{-1}; Dept. Agric., 1975). The addition of fertiliser or sludge in general increased plant P concentration and/or uptake. A lower level of plant available P was noticeable in the sludge treatments without additional inorganic P ((2t) and (2t+N*)). Lower P concentration or lower P uptake values compared to the inorganic fertiliser treated plants were generally measured in all three harvests. Plants amended with sludge and additional inorganic P (2t+N*+P/2) had similar P concentration and uptake values compared to the fertiliser treated plants.

Table 4.4 Callington 1993: Concentration of P in plant shoots and grain and P uptake at the three harvests.

	nil	nil +N+P	nil +N+P +TE	2t	2t +N*	2t +N*+P/2	2t +P/2	LSD (P=0.05)
				Concentration [mg kg^{-1}]				
H1 shoot	3062[a]	4503	4347	3854	3938	3839	4201	423
H2 shoot	1418[a]	1633	1725	1638	1570	1516	1631	277
Grain	2669[a]	3295	3365	3067	3060	3088	3369	195
				Uptake [g m^{-2}]				
H1 shoot	0.40	1.02	1.05	0.80	0.97	1.00	1.00	0.190
H2 shoot	0.71	1.34	1.33	1.27	1.16	1.38	1.22	0.407
Grain	1.00	1.77	1.80	1.66	1.67	1.65	1.73	0.254

[a] approximate critical values for *H. vulgare* : Harvest 1 (shoot) 3100 mg P kg^{-1}, Harvest 2 (shoot) 1700 mg P kg^{-1}; Grain value not given , (Reuter and Robinson, 1986).

Table 4.5 Freeling 1993: Concentration of P in plant shoots and grain and P uptake at the three harvests.

	nil	nil +N+P	nil +N+P +TE	2t	2t +N*	2t +N*+P/2	1t +N*+P/2 +TE/2	LSD (P=0.05)
				Concentration [mg kg^{-1}]				
H1 shoot	3255[a]	3783	4036	3900	3422	3748	3887	357
H2 shoot	1969[a]	1365	1776	2027	1439	1530	1623	288
Grain	3301[a]	3496	3386	3402	3281	3412	3285	136
				Uptake [g m^{-2}]				
H1 shoot	0.17	0.50	0.47	0.40	0.43	0.58	0.46	0.109
H2 shoot	0.93	1.18	1.41	1.33	1.21	1.50	1.58	0.248
Grain	0.69	0.91	0.87	0.79	0.85	0.93	0.91	0.068

[a] approximate critical values for *H. vulgare* : Harvest 1 (shoot) 3100 mg P kg^{-1}, Harvest 2 (shoot) 1700 mg P kg^{-1}; Grain value not given , (Reuter and Robinson, 1986).

4.3.3.2 Zinc

Concentration of Zn in shoots and grain and Zn uptake values are listed in Tables 4.6 and 4.7. At Callington, concentrations of Zn in plants were lower than at Freeling with 19, 8.5 and 16 mg kg^{-1} Zn for the nil treatment at the three harvests, compared to Freeling of 24, 12 and 25 mg Zn kg^{-1}. Soil Zn levels of the two soils confirm the difference in Zn status of the soil (see Table 3.10, Chapter 3) The shoot Zn values at Harvest 2 at Callington and to a lesser extent at Freeling were in a concentration range considered marginal for barley at this growth stage (Reuter and Robinson, 1986).

Callington: A significant difference in Zn concentration and uptake beween plus and minus inorganic TE treated plants was measured at Harvest 1 and in the grain. At Harvest 2, a similar trend was evident but differences were insignificant. The Zn concentration and uptake values of the inorganic TE or sludge treated plants were in general similar.

Freeling: Significantly higher concentrations of Zn in tissues of inorganic TE treated plants compared to plants receiving N and P only were measured at all three harvests. However, the Zn uptake values were similar. Sludge treated plants did in general show tissue Zn concentrations similar to the (nil+N+P+TE) treated plants, with a tendency to slightly higher values.The (2t+N*) treated plants, which showed a similar growth pattern to the inorganic fertiliser treated plants, had a significantly higher concentrations of Zn in Harvest 1 and the grain compared to the (nil+N+P+TE) treatment and uptake values also increased.

Table 4.6 Callington 1993: Concentration of Zn in plant shoots and grain and Zn uptake at the three harvests.

	nil	nil +N+P	nil +N+P +TE	2t	2t +N*	2t +N*+P/2	2t +P/2	LSD (P=0.05)
				Concentration [mg kg^{-1}]				
H1 shoot	18.6[a]	15.3	18.6	17.9	19.3	19.4	17.5	2.8
H2 shoot	8.5[a]	6.3	6.9	7.2	7.4	8.4	7.3	2.0
Grain	16.2[a]	12.3	15.8	15.7	16.3	15.0	17.4	2.0
				Uptake [mg m^{-2}]				
H1 shoot	2.4	3.4	4.5	3.7	4.8	4.8	4.1	0.82
H2 shoot	4.2	5.2	5.3	5.5	5.4	7.5	5.4	1.87
Grain	6.3	6.7	8.3	8.3	8.8	7.9	8.8	1.17

[a] approximate critical values for *H. vulgare* : Harvest 1 (shoot) value not given, Harvest 2 (shoot) 5-24 mg Zn kg^{-1}; Grain value not given , (Reuter and Robinson, 1986).

Table 4.7 Freeling 1993: Concentration of Zn in plant shoots and grain and Zn uptake at the three harvests .

	nil	nil +N+P	nil +N+P +TE	2t	2t +N*	2t +N*+P/2	1t +N*+P/2 +TE/2	LSD (P=0.05)
				Concentration [mg kg^{-1}]				
H1 shoot	24.2[a]	18.2	22.5	24.8	26.8	22.4	23.4	2.4
H2 shoot	12.3[a]	7.6	9.0	11.4	10.0	9.5	9.8	1.3
Grain	25.3[a]	22.2	23.7	26.4	25.4	24.9	23.8	1.8
				Uptake [mg m^{-2}]				
H1 shoot	1.3	2.4	2.4	2.6	3.4	3.5	2.8	0.67
H2 shoot	5.9	6.6	7.1	7.7	8.4	9.3	9.4	1.73
Grain	5.3	5.8	6.1	6.2	6.6	6.8	6.6	0.50

[a] approximate critical values for *H. vulgare* : Harvest 1 (shoot)value not given, Harvest 2 (shoot) 5-24 mg Zn kg^{-1}; Grain value not given , (Reuter and Robinson, 1986).

4.3.3.3 Nitrogen (N)

The concentration of N in plant shoots and the concentration of protein in the grain as well as total protein (gm^{-2}) are listed in Table 4.8 for Freeling and Callington. The N or protein concentrations were quite low at both sites. The (nil) treatment showed higher (Freeling) or similar (Callington) grain protein concentrations but lower protein content than the sludge/fertiliser amended plants. There was in general no difference in N concentration or N uptake between the inorganically fertilised or sludge treated plants. Lower N uptake values for the (2t) treatment were measured at Freeling only.

Table 4.8 Concentration of nitrogen (N) and N uptake of shoots (Harvest 2, Freeling) and concentration of protein and protein content of grain at Freeling and Callington.

		nil	nil +N+P	nil +N+P +TE	2t	2t +N*	2t +N*+P/2	1t +N*+P/2 +TE/2	LSD (P= 0.05)
Freeling, Shoots-Harvest 2									
N	[%]	1.01	0.64	0.72	0.80	0.74	0.70	0.70	0.14
N uptake	[mg m^{-2}]	5.00	5.50	5.80	5.30	6.30	7.00	7.00	1.70
Freeling, Grain									
Protein	[%]	8.4	7.7	7.7	7.8	7.5	7.9	7.8	0.43
Protein Content	[g m^{-2}]	2.8	3.2	3.2	2.9	3.1	3.5	3.6	0.33
Callington, Grain									
Protein	[%]	7.2	7.3	6.9	7.4	7.4	7.3	-	n.s.
Protein Content	[g m^{-2}]	4.3	6.4	6.0	6.4	6.5	6.3	-	1.21

4.4 Discussion

In the field experiments in 1993, as in 1992, the aim was to determine if a sludge application would result in a similar yield response as a conventional inorganic fertiliser application. The sites Callington and Freeling will be discussed together, although the former received treatments for one year and the latter for two years, because the residual value in the year after application of low sludge application rates were similar to the inorganic comparison, when low amounts of fertiliser are applied in the current year (Chapter 6).

At both experimental sites in 1993 considerable grain yield increases due to sludge or inorganic fertiliser additions were measured. This is a prerequisite for a fertiliser assessement based on growth or yield comparison, because responses to fertiliser can only be compared when responses occur (Barrow, 1985). Grain yield increases to inorganic fertiliser additions (20 kg N ha^{-1}, 20 kg P ha^{-1}, TE) of 1.5t ha^{-1} and 0.50 t ha^{-1} at Callington and Freeling respectively were obtained. Yield responses to the different sludge treatments were approximately the same as the inorganic fertiliser treatments at the two sites. Yield increases of wheat in Australia due to N fertiliser additions were shown to be in the range of 0.16-0.28 t grain ha^{-1} for N additions of between 15-25 kg N ha^{-1} (McDonald, 1992, Doyle and Holford, 1992) and between 0.3 to 0.4 t grain ha^{-1} for 20 kg P ha^{-1} (Holford and Doyle, 1992) as has been mentioned in Chapter 3. For barley Fahti (1994) found a mean response of 0.27 t ha^{-1} to a N application rate of 20 kg ha^{-1} for the variety Chebec. Wheeler *et al.* (1989) found an average grain yield increase of 12 barley varieties of 2.35t ha^{-1} with a P application of 60 kg P ha^{-1} on a P deficient soil. The grain yield responses measured in the current experiment were above the values measured in N fertilisation experiments and P fertilisation experiments (wheat) just mentioned and below the maximum responses gained in barley P fertilisation experiments. This is in spite of plant density being lower than general practice at Freeling owing to mice damage after seeding. Grain yield at Callington probably was slightly overestimated because unbordered plants were harvested for grain yield. Also, at both sites the control treatment (1993) was unfertilised for two consecutive years instead of one year.

4.4.1 Nitrogen replacement potential of sludge

The sludge only treatment (2t) caused significant yield increases at both sites compared to the nil treatment. At Callington this sludge treatment enhanced plant growth and grain yield similarly to the inorganic fertiliser comparison. At Freeling the performance was weaker than the inorganic fertiliser treatment. The application of additional N with the sludge proved to be beneficial in Freeling for the grain yield and at Callington at Harvest 1. At both sites barley was planted after a cereal crop, thus available soil N reserves can expected to be low and plants increasingly dependent on N additions.

To establish response curves for two nutrients such as N and P at the same time requires a factorial experiment, because the level of one nutrient influences the response curve to the second nutrient. However, a response curve to increasing sludge rates was established at Freeling and Callington in 1993 and results are described in Chapter 5. At both sites plant productivity was not on the plateau part of the Mitscherlich type yield response curve, as the significant yield responses to N additions to the sludge (Freeling) or to increased sludge-nutrient applications (Freeling, Callington, Chapter 5) showed. At Callington the (2t) treatment was equivalent to the inorganic fertiliser comparison and at Freeling the (2t+N*) sludge treatment was equivalent in terms of yield to the inorganic fertiliser comparison of 20 kg N ha^{-1}. The (2t) treatment contained sludge N and the (2t+N*) contained contained sludge N plus 12.2 kg inorganic N. Hence the sludge N replacement value can be narrowed down to a range of between 7.8 to 20 kg N ha^{-1}, depending on the site.

The amount of N mineralised from sludge organic material can be calculated (as in Chapter 3) as the difference between the replacement value (7.8 to 20 kg) and the amount of inorganic N in the sludge prior to application, if the N loss by volatilisation is considered negligible.

Substitution value of sludge	7.8	20	kg N ha^{-1}
Total organic N applied in sludge	38	38	kg N ha^{-1}
Inorganic N applied in sludge	3.9	3.9	kg N ha^{-1}
Amount of sludge organic N mineralised	3.9	16.1	kg N ha^{-1}
Sludge organic N mineralised	10	42	%

According to this, 3.9 to 16.1 kg N must have been mineralised from sludge organic material during the growth period, which is in the range of 10-42% . This range of potential N mineralisation is similar to the range suspected for the field results in 1992 (Section 3.6). The percentage of sludge N mineralised or the percentage of total sludge N available in one growth period is within the broad range of values given in the literature about sludge mineralisation and sludge-N availability (see Section 3.7).

The difference in sludge N replacement potential and probably sludge N availability between the two sites Callington and Freeling could be based on soil type, rainfall or yield potential of the sites. Enhanced mineralisation of the sludge in the light sandy soil at Callington which had a higher average temperature (1°C) than Freeling, could have allowed a higher rate of sludge N mineralisation than at Freeling. This remains a hypothesis, because in the experiment at Callington the plant response cannot be conclusively proven to be due to N fertiliser. It could be objected that with the reduced plant density (see Section 4.2) the nutrient demand of plants was met and thus all sludge or inorganic fertiliser treatments yielded as well. However, a general potential for enhanced plant growth and grain yield at this site and year was demonstrated with higher sludge rates (Chapter 5). Hence it seems more likely that a difference in mineralisation patterns at the two sites caused the difference in sludge N availability.

4.4.2 Phosphorus replacement potential of sludge

At both sites a 2t sludge application appeared to be equivalent to inorganic fertiliser at 20 kg P ha^{-1} in its ability to enhance plant productivity, because the responses in dry matter and grain yield of (2t+N*) and inorganic fertiliser treated plants were similar.

Plants were responsive to P fertilisation, as can be seen at the enhanced early growth beyond the inorganic fertiliser comparison (nil+N+P+TE) of plants treated with sludge plus additional inorganic P at Freeling. The growth differences remained noticeable in the later harvests, but were just below the significance level. (A generally lower agronomic efficiency with increasing rates of fertiliser applied makes a significant grain yield increase at a elevated level of nutrition less likely.) At Callington a plant response to additional inorganic P added to sludge was not measured. However, increased plant growth beyond the inorganic fertiliser comparison was potentially possible at this site as the results in Chapter 5 with increased sludge rates show. The result of shoot and grain yield of the (2t+N*) treatment suggest that a sludge treatment without additional P provided an equivalent amount of plant available P to the inorganic fertiliser treatment (ie. 20 kg ha^{-1}) throughout the whole growth season 1993.

As has been mentioned in Section 3.6, the nutrients N and P are to a certain degree interchangeable in their ability to enhance plant growth and plant yield, at sites where both nutrients are in low supply. However, the uptake of nutrients can be a more sensitive measure than the production of dry matter to compare fertiliser sources (Van Burg, 1963). The P uptake values of sludge and inorganic fertiliser treated plants were similar. However, at Callington lower shoot (Harvest 1) and grain P concentrations of sludge treated plants were noticed. At Freeling the P concentration in shoot and the grain of (2t+N*) treated plants and the P uptake values of (2t) treated plants were generally lower than the comparable values of the inorganic fertiliser treatments. The consistent tendency of the (2t) and (2t+N*) treatments to lower P concentration or uptake values, compared to the other treatments, suggests that the sludge supplies a somewhat lower amount of plant available P than 20 kg inorganic P, which was the equivalence using grain yield as the indicator. However, the differences between sludge and inorganic fertiliser treated plants in terms of plant P concentration and uptake were small. Even though a variation in P nutrition between inorganic and sludge treatments did not cause yield variations, differences could become obvious in a more P-demanding situation.

Replacement calculation: As in 1992, the sludge available P can be estimated, based on the assumption that a (2t+N*) sludge application (P total =36 kg $2t^{-1}$) provided plant available P up to the amount of the inorganic fertiliser containing of 20 kg P, in terms of enhancing shoot and grain yield. This can be considered the upper margin of potential P supply of sludge, because the N supplement to sludge may also to some degree contributed to the yield, as the plant tissue analysis for P suggests. The percentage of sludge available P can be calculated as follows:

Total P applied in sludge:	36 kg P ha^{-1}
Inorganic P equivalent based on yield responses:	20 kg P ha^{-1}
Available P in sludge *:	$\leq$ 55 %

This indicates that sludge P availability can be up to 55% compared to inorganic fertiliser P in the year of application. The estimated plant availability of sludge P in 1993 was the same as calculated for the field results in 1992. This value of plant available P is at the lower range of values reported in the literature (see Chapter 3).

(* The results of these experiments can not be taken as a indicator for nutrient availability of kilned sludge, the treatment process generally used to date for marketing Bolivar sludge (see Chapter 3).)

The (2t+N*) treated plants showed the same development as inorganically fertilised plants through the whole growth period. No reduction in early plant growth in the sludge treatments without inorganic P, as experienced in 1992 (Chapter 3), were observed in 1993. The later harvest dates of Harvest 1 and 2 (with more advanced plant phenology in 1993) could be partly a reason for this. However, in 1992 differences in growth due to inorganic P fertilisation were noticeable until approximately booting stage. More likely, different crops used in 1992 and 1993 (durum wheat and barley respectively) may have caused the differences in crop responses in the two years. Wheeler *et al.* (1989) found that barley was more responsive to applied P than wheat, measured as a higher yield increase per kg P applied. Wheeler *et al.* (1989) also noticed a lower external P requirement of barley compared to wheat, which estimates the P rate necessary for 90% of the yield maximum. Therefore it seems that barley may be more effective in acquiring soil P in a moderately fertile soil than wheat, which was likely the case in the sludged plots.

Besides a difference in plant species used in the field experiments in 1992 and 1993, there was also a considerable difference in weather patterns in those years. 1992 was a cooler and wetter year than 1993, which was closer to average rainfall at the two sites (rainfall in 1992 for the period of April to October: 368 and 566 mm, 1993: 295 and 288 mm for Callington and Freeling respectively). It can be hypothesised that the presumably lower soil water content in 1993 and higher temperatures might have favoured sludge P transformation in the soil moreso than in 1992. Further experiments are needed to clarify if crop species, or annual influences were the major factors causing a different growth response of plants in 1992 and 1993 to sludge as a source of P.

4.4.3 Zinc replacement value of sludge

At both sites, Freeling and Callington, there was a significant plant response to TE (Zn) fertiliser as can be seen from elevated Zn concentrations of shoots and grain of the (nil+N+P+TE) compared to the (nil+N+P) treatment. Also the Zn uptake values of TE or sludge treated plants were increased compared to the (nil+N+P) treatment at one of the two sites (Callington), where the overall plant Zn level was lower than at the other site (Freeling). However, micronutrient fertilisation did not increase plant growth.

In the year of treatment application the Zn availability of inorganic Zn and sludge borne Zn was equal, as demonstrated by similar Zn concentration and uptake values of sludge or (nil+N+P+Te) treated plants at Callington and at Freeling. This confirms the findings of the field experiments in 1992 when it was similarly concluded that sludge Zn and inorganic Zn were equal in their plant availability (Chapter 3.6.1.4 and 3.7). For comparable literature see Chapter 3.7.

Sludge and inorganic Zn additions were also equal after 2 years of treatment application, as the results from Freeling indicate. Consecutive applications of sludge were found to increase the Zinc content of barley plants from year to year (Vlamis *et al.*, 1985). This effect was only noticeable when sludge with a high Zn concentration (2800-4800 mg Zn kg^{-1}) was used. Application of sludge with low Zn concentration (440-720 mg Zn kg^{-1}) did generally not increase the Zn concentration of plants over the years. However, the low Zn sludge used by Vlamis *et al.* (1985) increased soil pH and thus may have reduced the plant availability of Zn.

At Freeling, after 2 years of sludge application, some vague indications of an increased sludge Zn availability compared to inorganic Zn fertiliser were noticeable, because some sludge treatments showed increased Zn concentration or uptake values beyond the mineral TE fertiliser comparison. This was not observed at Callington 1993 or at Freeling in 1992 after 1 year of sludge application. It could be hypothesized that Zn availability to the plant after consecutive years of sludge application may be slightly higher than that of Zn applied over consecutive years as inorganic fertiliser. However on a short term basis the two Zn sources, sludge or inorganic fertiliser, were equal in terms of Zn nutritional value and can be treated as equal in terms of fertiliser application rate recommendations. Additional experiments or long term trials would be needed to explore sludge Zn availability over consecutive years of sludge application in comparison to inorganic fertiliser on calcareous soils in South Australia. Variations due to possible pH changes after sludge application then have to be considered.

4.5 Conclusions

- A (2t+N*) sludge treatment incorporated into the soil sustained yield increases similar to a inorganic fertiliser addition of 20 kg N ha^{-1}, 20 kg P ha^{-1}, 4 kg Zn ha^{-1}, 2 kg Cu ha^{-1}, 0.6 kg Mn ha^{-1} in a year of lower rainfall than 1992, and closer to the long term average.

- A (2t) sludge application provided sufficient N at one of the two sites (Callington) to sustain a yield equivalent to a inorganic fertiliser addition containing (20 kg N ha^{-1}). At the second site (Freeling) inorganic N additions of 12.2 kg ha^{-1} to the sludge were necessary to achieve yields similar to the inorganic fertiliser comparison. Based on the replacement value of sewage sludge (7.8 - 20 kg N $2t^{-1}$) the mineralisation of sludge organic N was calculated to be in the range of 10 to 42% .

- Additional N applications with 2t sludge ha^{-1} will be necessary in some crop rotations and on sites with a high yield potential, to achieve yields equivalent to inorganic fertiliser containing 20 kg N ha^{-1} and P.

- A (2t) sludge application provided an equivalent level of P nutrition throughout the whole growth period compared to an inorganic P fertiliser containing 20 kg P ha^{-1} , when shoot dry matter and grain yield were used as indicators. According to grain yield results the total P in sludge was calculated to have an availability of 55 % compared to P in inorganic fertiliser. However, the P availability seemed to be somewhat below this margin, when P content of plants was used as an indicator.

- Shoot Zn concentrations of plants receiving sludge or inorganic TE were equally increased at the two sites compared to plants fertilised with N and P only. This indicated a similar plant availability of sludge borne Zn or inorganic Zn.

Chapter 5

Field experiments 1993
Sewage sludge application rate experiment

5.1 Introduction

In previous experiments it was shown that sludge is of considerable nutritional value for cereal crops in South Australia (Chapter 3 and 4). In those experiments an estimate of the fertiliser value of sludge and inorganic fertiliser was made. Although the equivalence of sludge N and P to inorganic fertiliser could be narrowed down to a range of values, which varied with the environment and the N :P availability ratio of the soil, it is appropriate to establish a response profile to a particular nutrient source before comparing yield data. The objective of the current study was to establish a response curve of plant growth and plant nutrient uptake to increasing rates of sludge. The comparison of these response curves with the yield increases and nutrient uptake obtained by a conventional inorganic fertiliser application in the same year and at the same site, may lead to a more refined judgement of the nutritional value of sludge.

5.2 Material and Methods

5.2.1 General considerations about sludge application rates

General assumptions about sludge application rates are discussed in Section 3.2.2 and Section 4.2. In brief the assumptions were as follows: Sludge inorganic N and 10% of the organic N were assumed to be available to plants in the year of application. Additional inorganic N was supplied to make up the difference between assumed available N from the sludge and 20 kg N ha^{-1}. Plant available P in 2t sludge was assumed to be between the values for citrate soluble P and HCO_3^- soluble P and around 20 kg P in the year of application (Chapter 3, Section 3.2.2). Sludge applications were compared with a conventional inorganic fertiliser application of 20 kg N, 20 kg P, 1.8 kg Zn, 1.4 kg Cu and 0.5 kg Mn applied per hectare. The TE additions in the inorganically fertilised plots were equivalent to the total content of Zn, Cu and Mn in 2t sludge.

5.2.2 Sludge treatments

Sludge rates of 2t to 10t ha^{-1} were applied at the two sites, Callington and Freeling, where field experiments in 1992 and 1993 were located (Chapter 3 and 4). The experiments conducted were spatially included in the field trials described in Chapter 4 (for a field plan see Plate 2 and 3 in Appendices for Chapter 4). The high sludge application rates (4t and 10t ha^{-1}) were applied on completely randomised plots which were included in the original trial layout in 1992, but not in the experiment itself. At Callington all treatments were applied on plots which received conventional fertiliser (20 kg N ha^{-1}, 20 kg P ha^{-1} = (nil+N+P)) in the previous year; except the (nil) treatment, which was superimposed on the (nil) treatment. At Freeling the previous treatment history of the plots varied slightly (see list below). However, the residual value of low sludge applications (applied in the previous year) were equivalent to the residual value of the inorganic fertiliser treatment used (see Chapter 6.). Therefore the influence of this difference in soil history in the previous year, can expected to be minor or negligible. At both sites the (nil) treatment was superimposed on the (nil) treatment.

Treatments	***Soil amendments in the previous year***	
applied 1993	***Callington 1992***	***Freeling 1992***
nil	*nil*	*nil*
nil+N+P+TE	*nil+N+P*	*nil+N+P+TE*
2t+N*	*nil+N+P*	*2t+N*
4t+N*	*nil+N+P*	*nil+N+P*
10t	*nil+N+P*	*nil+N+P*

Additional inorganic N was applied to the sludge treatments, when necessary, to make up the difference between assumed available N from the sludge (see Section 5.2.1.) and 20 kg N ha^{-1}. The plant nutrients applied with each treatment are listed in Table 5.1.

Table 5.1 Inorganic fertiliser (N, P, Zn, Cu, Mn) and calculated sludge nutrients (N_S, P_S, Zn_S, Cu_S, Mn_S) applied in the different treatments in 1993. The calculated plant available fractions of sludge borne N and P listed here, are based on assumptions described in Chapter 4.1. Sludge Zn, Cu and Mn values are the total content of the elements in the sludge used.

Inorganic fertiliser [a]	N	N_S	P	P_S	Zn	Zn_S	Cu	Cu_S	Mn	Mn_S
						[kg ha^{-1}]				
nil										
nil+N+P+TE	20.0		20		1.8[b]		1.4[b]		0.5[b]	
2t+N*	12.2	*7.8*		*20*		*1.8*		*1.4*		*0.4*
4t+N*	4.4	*15.6*		*40*		*3.6*		2.8		*0.9*
10t		*39.0*		*100*		*9.0*		*7.0*		2.2

[a] commercial grade inorganic fertiliser

[b] TE fertiliser applied half with the NP fertiliser base granules and the remaining half sprayed onto the plots prior to seeding

5.2.3 Method of inorganic fertiliser and sludge application in the field

The treatments were arranged in a completely randomised block design with 5 replicates per treatment. The air dry sludge was applied on the date of seeding, prior to the seeding operation. In 1993 a modified 10 row tyned cone seeder was used, where 2 parallel cones fed sludge into the seeder shafts. With this set up a maximum of 4t sludge ha^{-1} could be applied in two workings. The sludge was applied just below the seeding depth of approximately 3 cm. Plot size was 30 m^2 (20 m long, 1.5 m wide) at Freeling and 15 m^2 (10 m long, 1.5 m wide) at Callington. For the application rate of 10t sludge ha^{-1} the sludge application had to be split. The equivalent of 6t sludge ha^{-1} was surface applied and subsequently worked into the soil by the following three workings of the soil by the seeder. The remaining 4t sludge ha^{-1} was applied with the seeder like the lower sludge treatments. The nil and inorganic fertiliser treatments were worked three times as were the sludge amended plots. The inorganic fertiliser as well as the inorganic additions to the sludge amended plots were applied together with the seed in the third working of the plots, using the same cone seeder.

5.2.4 Field crop and plant analysis

In 1993 barley (*Hordeum vulgare* L.) cv Galleon, a cereal cyst nematode (CCN) resistant variety, was used as the test crop and sown at a rate of 70 kg ha^{-1} (seed treatment: Baytan). The crop rotation prior to the field experiment in 1993 was pasture followed by wheat at Callington and vetch followed by wheat at Freeling. Apart from the fertiliser treatments, the crop husbandry was undertaken by the farmer as part of his normal management practice.

Two mid season harvests and a final grain harvest were taken at both sites. Harvest 1 was taken about 10 weeks after planting, when plants were in the late booting stage. Harvest 2 was taken about 15 weeks after planting, when plants were flowering. At Harvest 1 and 2 an area of 0.09 m^2 and 0.12 m^2 respectively was harvested. The grain yield was taken from 2.4 m^2 and 27 m^2 respectively for Callington and Freeling. For details about exact harvest dates see Table 4.2 Chapter 4. Plant samples in Harvest 1 and 2 were taken at two independent positions along a central row in the plots. Plants were cut 2 cm above ground and dried in a forced air oven at 70°C for at least 24 hours. Dry weight of shoots in Harvest 1 and 2 and grain yield in the final harvest were recorded. At Freeling (Harvest 2) the number of heads were counted, separated and weighed individually. Shoots (heads plus shoot) and grain were digested in concentrated HNO_3 and analysed for Mn, Cu, Zn, and P concentrations by ICP (p. 255a, 255b). Nitrogen content of shoots was analysed with a N analyser 1500 series 2 (Carlo Erba Instruments). Grain was analysed for N content using a Kjeldahl technique.

Due to widespread mice damage in 1993 in South Australia the plant density at Freeling and Callington was reduced by approximately 35%. The plots were scored for mice damage to assess the damage, which was evenly spread across the treatments. In Callington only a part of the plot (two central rows) were harvested for grain yield to ensure that mice damaged areas were not included in the harvest.

Dry matter and grain yield were transformed into relative yield by dividing all the values, including the values for the nil treatment, by the site average for the nil treatment. The Anova was calculated for the transformed data.

5.2.5 Soil characteristics and weather

The soil type in Callington was a sodic brown Kandosol-Dermosol and the Freeling soil can be classified as an epicalcareous Vertosol (Isbell, 1995). For a more detailed soil description of the sites and their location in South Australia see Table 3.9 and 3.10, Chapter 3. Also climatic data such as rainfall and temperature in the experimental year are listed in Tables 3.11 and 3.12, Chapter 3.

5.3 Results

5.3.1 Dry weight of shoot and grain

At both experimental sites an increase in sludge rate caused an increase in shoot dry matter production and grain yield. The relative yield increases expressed as a percentage of the nil treatment (100%) are described in Figures 5.1 , 5.2 and 5.3. Sludge application rates of 2 and 4 t ha^{-1} received additional inorganic N to ensure a N supply of approximately 20 kg ha^{-1} in both treatments within the current season, comparable to the inorganic fertiliser comparison. However, the 10t treatment, according to assumptions (Sections 5.2.1 and 5.2.2), would on its own have supplied around 39 kg ha^{-1}. Hence for the corelation between sludge application rate and dry weight production only sludge rates up to 4t ha^{-1} have been included, where P and TE supply increased with sludge rates but N supply has been kept similar. However, the results for the 10t ha^{-1} treatment have been included in the graph (Figure 5.3). Similar arguments apply to the following response curves for P,though N is less likely to affect P uptake. The absolute yields of the (nil) treatment are listed in Table 5.2. At both sites and all three harvests, plants showed a logarithmic response in shoot dry matter production and grain yield to sludge additions, although at Freeling the grain yield response was equally well described by a linear relation (for comparisons of R^2 values for a linear or logarithmic correlation, see

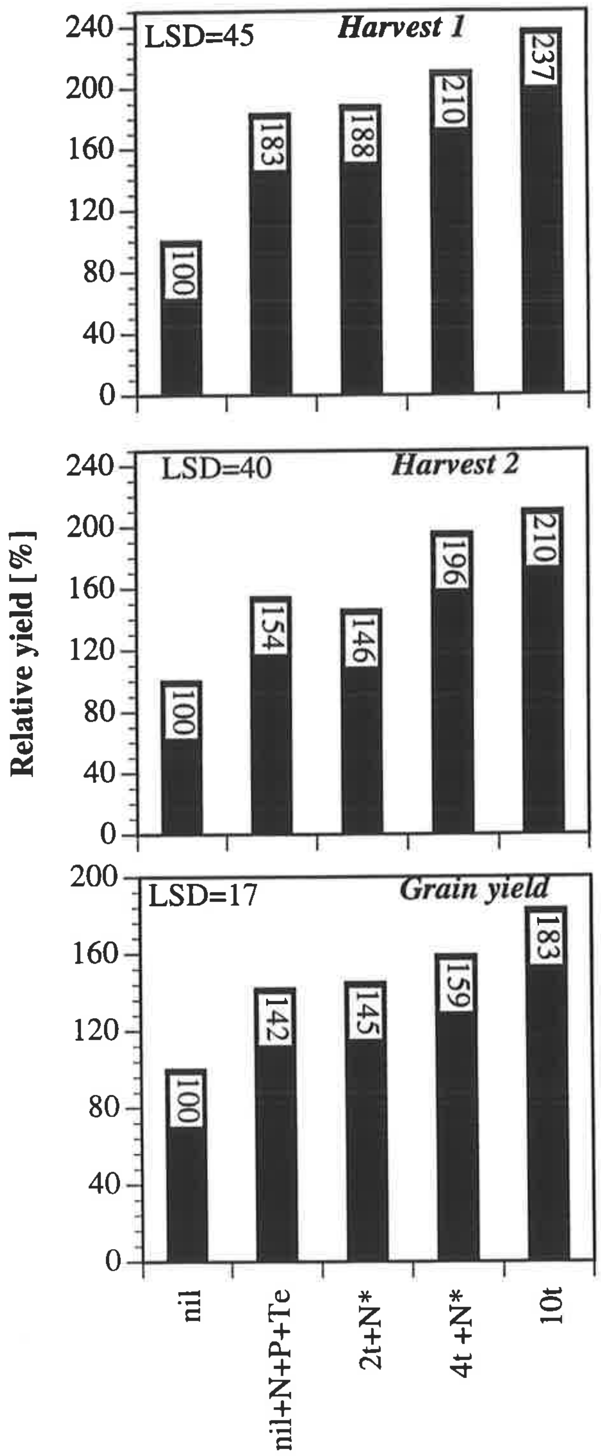

Figure 5.1 Callington, 1993: Dry weight of shoots at harvests 1 and 2 and grain yield relative to the nil treatment (100%). Harvest 1: 67 days, Harvest 2: 99 days after sowing. (LSD, P=0.05) (Value in the bar represents relative yield expressed as percentage of the nil treatment.)

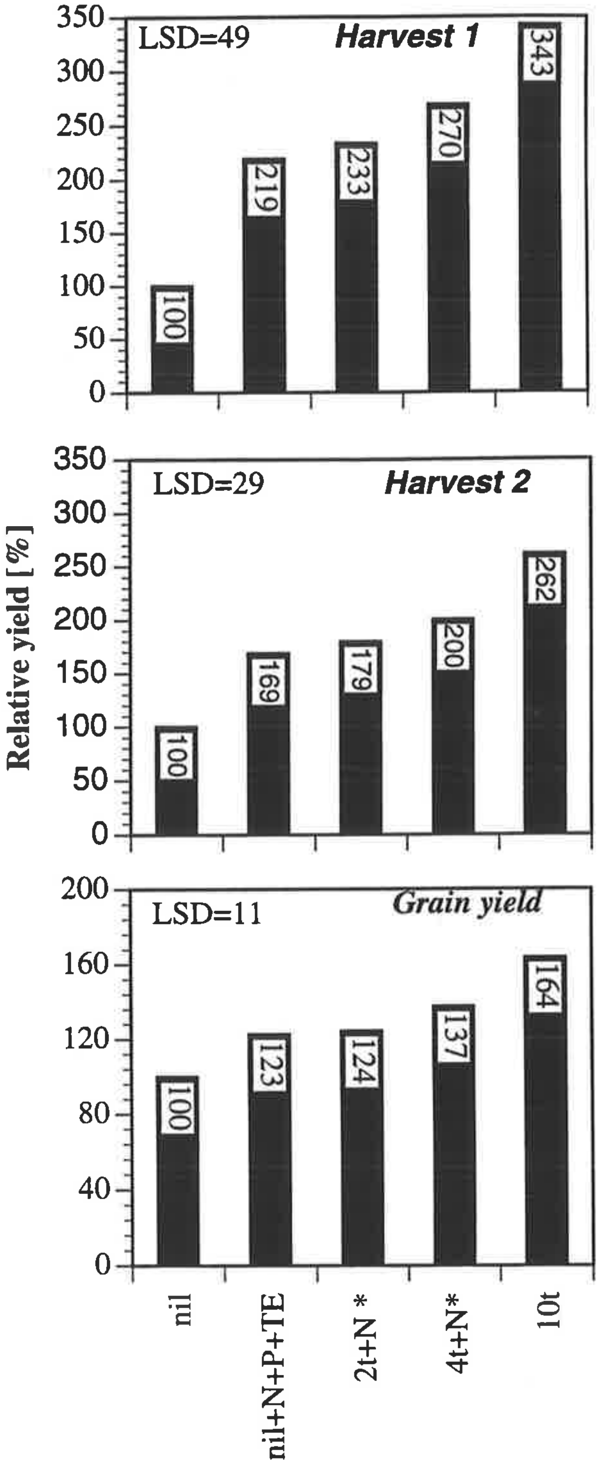

Figure 5.2 Freeling, 1993: Dry weight of shoots at harvest 1,2 and grain yield relative to the nil treatment (100%). Harvest 1: 70 days, Harvest 2: 110 days after sowing. (LSD, P=0.05) (values in the bar tops represent relative yield expressed as percentage of the nil treatments)

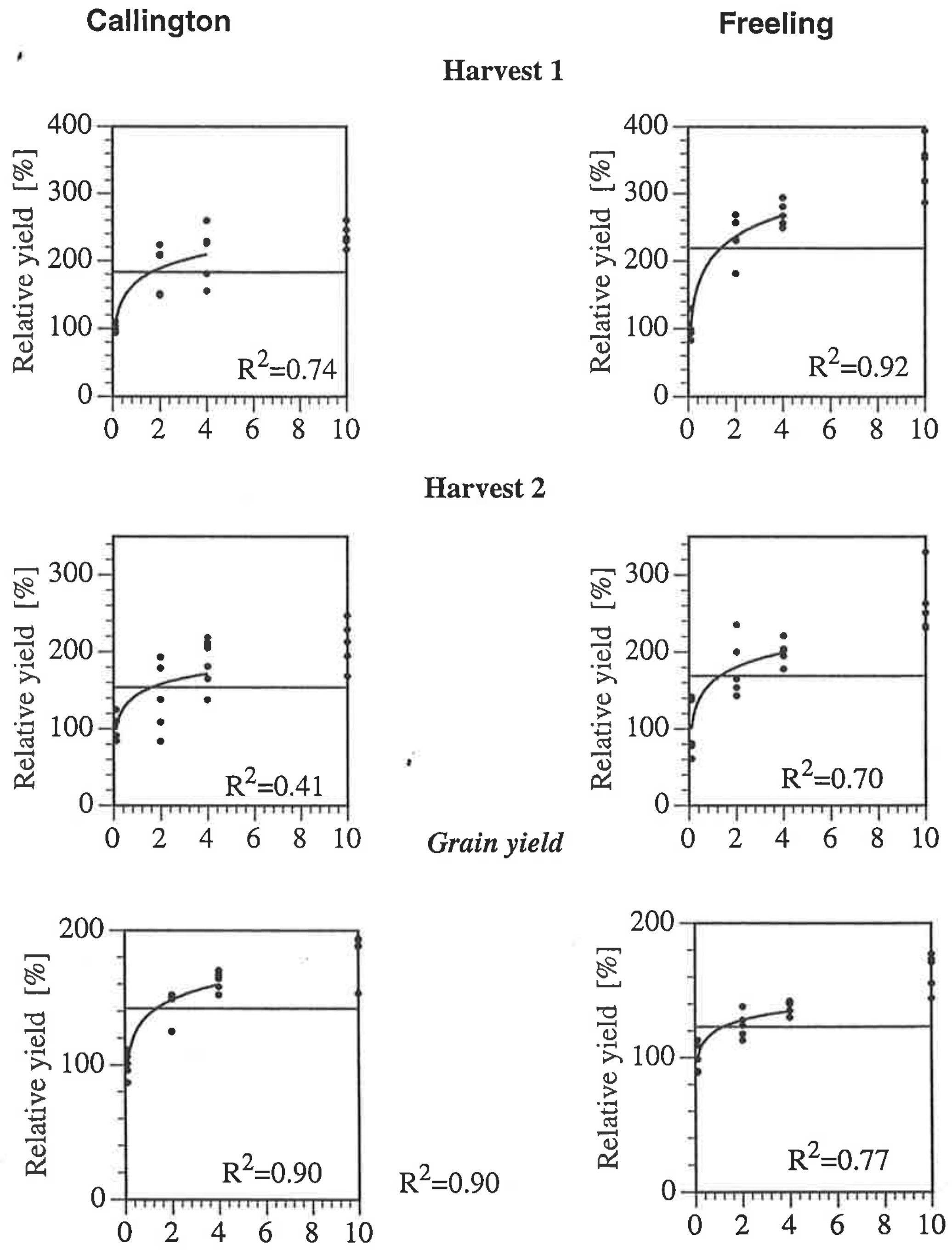

Figure 5.3 The effect of sludge application rate on the dry weight production of plants at late tillering (Harvest 1), flowering (Harvest 2) and grain yield at Callington and Freeling in 1993 in comparison with the dry weight production of the inorganic fertilised plants (nil+N+P+Te), represented by the horizontal line.

(Only sludge rates of 0 to 4t ha^{-1} have been included in the curve fitting.)

Appendix, Table A.5.1). The response diminished over the three harvests. Shoot dry matter production in Harvest 1 and 2 was relatively more enhanced by increasing sludge application rate than the grain yield. The inorganic fertilised plants showed a dry matter production and grain yield equal to the (2t+N*) sludge treatment. The relative growth response to increasing sludge amendments was similar at the two sites. The absolute yield increases were higher at Callington than at Freeling, but grain yields at Callington were probably overestimated because unbordered plots were harvested (see Section 5.2.4 and Chapter 4).

Table 5.2 Dry weight of the (nil) treatment for the sites in 1993

	Callington	Freeling
	$[g\ m^{-2}]$	
Harvest 1	132	53
Harvest 2	498	474
Grain	363[a]	209

[a] overestimated grain yield, because unbordered plants were harvested (see 5.3.1).

5.3.2 Chemical analysis of shoot and grain

5.3.2.1 Phosphorus

Plant P concentration and uptake values for the two sites are listed in Tables 5.3, 5.4 and Figure 5.4. All sludge treatments have been included in the correlation calculation, although the N supply to plants probably has differed for the treatments, particularly for the 10t ha^{-1} treated plants. However, P uptake (and later zinc uptake) values rather than P concentration were used for the correlation to minimise any dilution effect of a response to N. An increase in sludge application rate resulted in an increase in P uptake values of plants at both sites. At Freeling P uptake increased with each increment of sludge application rate up to 10t, but at Callington P uptake values of the intermediate sludge application rates of (2t+N*) and (4t+N*) were similar. At both sites plants showed a logarithmic type response curve in P uptake values at Harvest 1 and the grain harvest to increasing sludge application rates. The relationships between plant P uptake and sludge rates at Harvest 2 was more closely described by a linear relation (For a comparison of R^2 values for a linear or logarithmic correlation model see Appendix, Table A.5.1) The inorganic fertiliser treated plants showed P uptake values which were matched by sludge application rates of beween 2t to 6t sludge ha^{-1} depending on the harvest and site. However a sludge application rate of (4t+N*) matched the P uptake of the inorganic fertiliser comparison in most of the cases. In Freeling the P uptake values of 2 inorganic fertilisers were included (see Chapter 4), because there was a certain discrepancy in growth response between the fertiliser treatments (nil+N+P) and (nil+N+P+TE), which was probably not based on TE nutrition, but rather on a slight difference in the source of N and P fertiliser.

The increase in sludge application rates did not result in increased shoot or grain P concentrations at either of the sites (Tables 5.3 and 5.4). At Callington the concentration of P in shoots and the grain remained lower than the concentration in the inorganic comparison for sludge application rates up to 4t. Only plants amended with 10t had a similar concentration of P in shoot and grain as the inorganic fertiliser comparison. At Freeling concentration of P in shoots of all sludge amended plants at Harvest 1 were significantly lower than from inorganic fertilised plants. The same trend was noticeable at Harvest 2. Concentration of P in grain were similar for all treatments at this site.

Table 5.3 Callington, 1993: Concentration of P in plant shoots and grain and P uptake at the three harvests .

	nil	nil +N+P +TE	2t +N*	4t +N*	10t	LSD (P=0.05).	Critical values[a]
			Concentration [mg kg^{-1}]				
H1 shoot	3062	4350	3940	3740	4130	375	3100
H2 shoot	1418	1730	1570	1180	1630	239	1700
Grain	2669	3360	3030	2990	3070	196	n.a.
			Uptake [g m^{-2}]				
H1 shoot	0.4	1.1	1.0	1.0	1.3	0.240	
H2 shoot	0.7	1.3	1.2	1.2	1.7	0.368	
Grain	1.0	1.8	1.7	1.8	2.1	0.208	

[a] approximate critical values for *H. vulgare* (Reuter and Robinson, 1986)

Table 5.4 Freeling, 1993: Concentration of P in plant shoots and grain and P uptake at the three harvests.

	nil	nil +N+P +TE	2t +N*	4t +N*	10t	LSD (P=0.05)	Critical values[a]
			Concentration [mg kg^{-1}]				
H1 shoot	3255	4036	3422	3710	3585	324	3100
H2 shoot	1969	1776	1439	1546	1438	384	1700
Grain	3301	3386	3281	3372	3283	n.s.	n.a.
			Uptake [g m^{-2}]				
H1 shoot	0.2	0.5	0.4	0.5	0.6	0.09	
H2 shoot	0.9	1.4	1.2	1.5	1.8	0.26	
Grain	0.7	0.9	0.9	1.0	1.1	0.07	

[a] approximate critical values for *H. vulgare* (Reuter and Robinson, 1986)

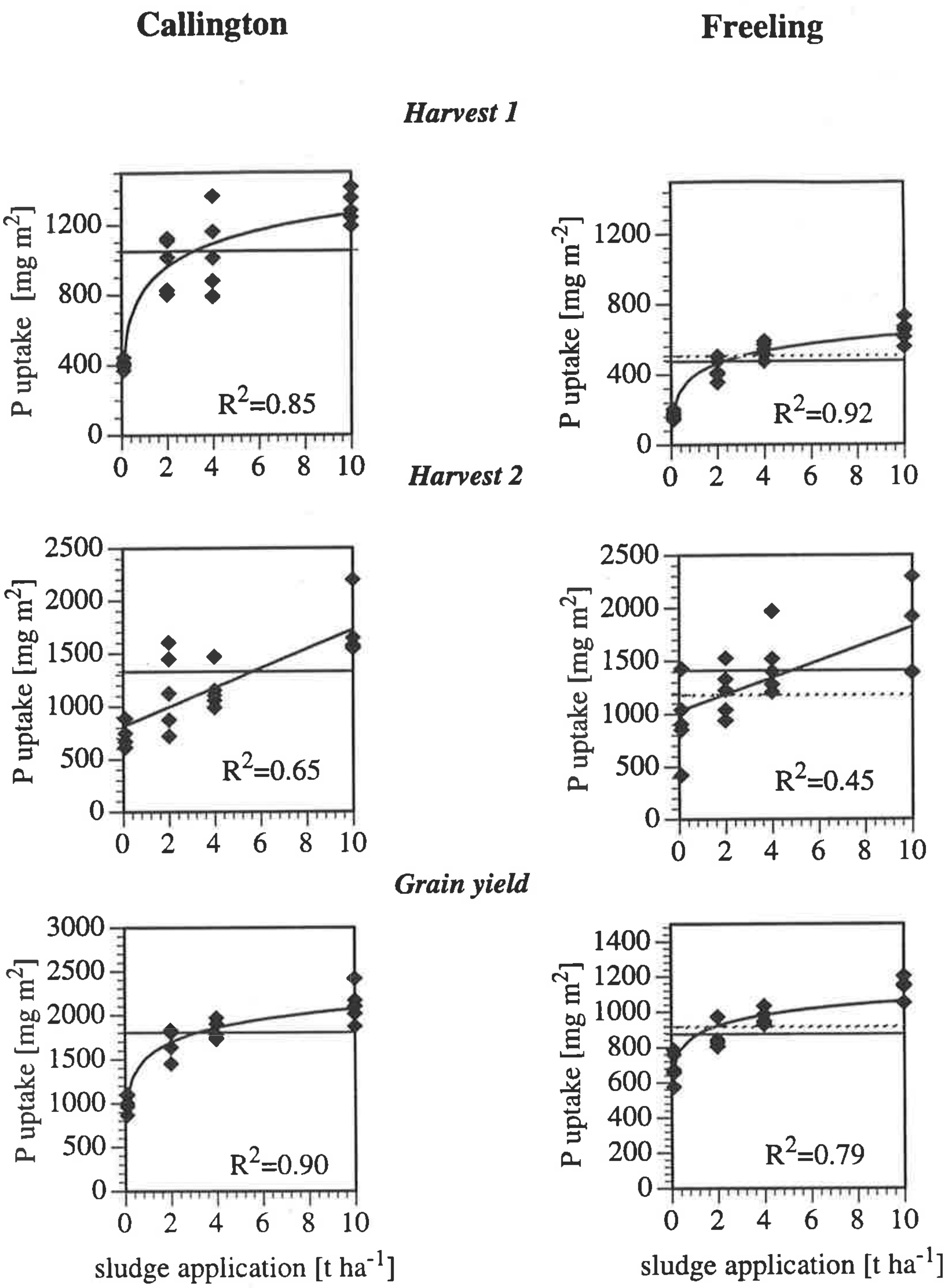

Figure 5.4 The effect of sludge application rate on the P uptake of of plants at late tillering (Harvest 1), flowering (Harvest 2) and grain yield at Callington and Freeling in 1993 in comparison with theP uptake of the inorganic fertilised plants (nil+N+P+Te) —— or (nil+N+P) ...., represented by horizontal lines.

5.3.2.2 Zinc

The values of Zn concentration and Zn uptake of the various treatments at the two sites are listed in Tables 5.5, 5.6 and Figure 5.5. An increase in sludge application rates resulted in an increase in both concentration of Zn in shoots and grain and Zn uptake of plants grown at Callington and Freeling. Differences were more pronounced at Callington, the site with a lower total Zn content in the soil (Table 3.10, Chapter 3). Plant Zn uptake increased linearly with sludge application rates in all three harvests and at both sites. At Harvest 1 and the grain harvest a logarithmic curve would equally fit the data (see Appendix, Table A.5.1). Plants which received an equivalent amount of Zn (treatments (2t+N*) or (nil+N+P+TE)) had similar Zn concentration and Zn uptake values at Callington and differences at Freeling were minor. The increase in Zn uptake caused by the various treatments was more pronounced than the increase in shoot Zn concentration.

Table 5.5 Callington, 1993: Concentration of Zn in plant shoots and grain and Zn uptake at the three harvests.

	nil	nil +N+P +TE	2t +N*	4t +N*	10t	LSD (P=0.05)	Critical values[a]
			Concentration [mg kg^{-1}]				
H1 shoot	19.0	18.6	19.3	23.6	28.4	2.80	n.a.
H2 shoot	8.5	6.9	7.4	7.8	10.9	1.45	5-24
Grain	16.0	15.9	16.2	19.5	20.6	1.84	n.a.
			Uptake [mg m^{-2}]				
H1 shoot	2.4	4.5	4.8	6.5	8.9	1.37	
H2 shoot	4.2	5.3	5.4	7.6	11.5	2.28	
Grain	6.3	8.4	8.9	11.9	14.2	1.33	

[a] approximate critical values for *H. vulgare* (Reuter and Robinson, 1986)

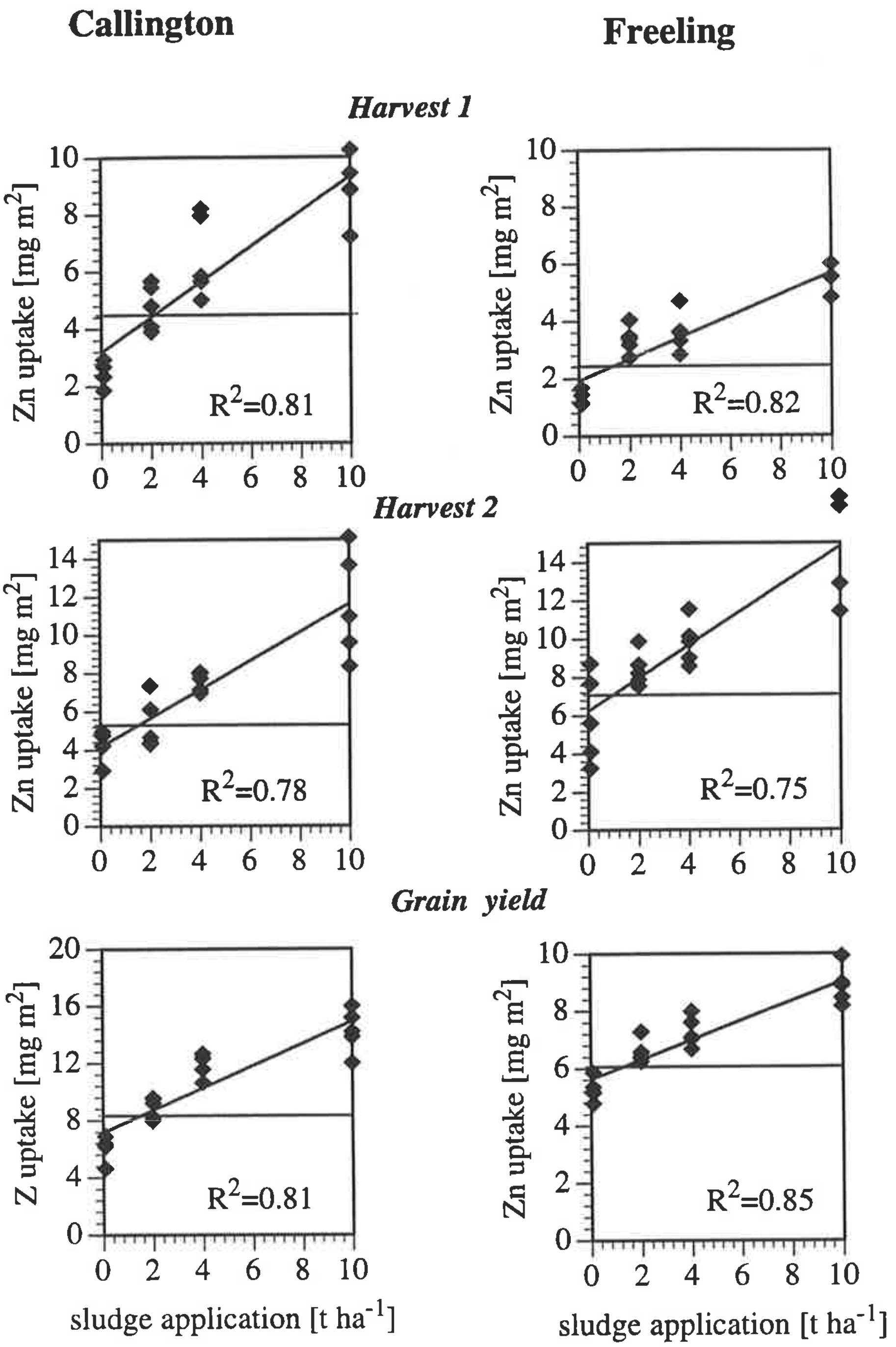

Figure 5.5 The effect of sludge application rate on the Zn uptake of plants at late tillering (Harvest 1), flowering (Harvest 2) and grain yield at Callington and Freeling in 1993 in comparison with the Zn uptake of the inorganic fertilised plants (nil+N+P+Te), represented by the horizontal line.

Table 5.6 Freeling, 1993: Concentration of Zn in plant shoots and grain and Zn uptake at the three harvests.

	nil	nil +N+P +TE	2t +N*	4t +N*	10t	LSD (P=0.05)	Critical values[a]
			Concentration [mg kg^{-1}]				
H1 shoot	24.2	22.5	26.8	24.8	29.8	3.3	n.a.
H2 shoot	12.3	8.9	10.0	10.3	11.8	1.6	5-24
Grain	25.3	23.7	25.4	25.3	26.0	1.6	n.a.
			Uptake [mg m^{-2}]				
H1 shoot	1.3	2.4	3.3	3.6	5.4	0.43	
H2 shoot	5.9	7.1	8.4	9.8	14.6	1.82	
Grain	5.3	6.1	6.6	7.3	8.9	0.59	

[a] approximate critical values for *H. vulgare* (Reuter and Robinson, 1986)

5.3.2.3 Nitrogen

Grain protein concentrations, total grain protein and N concentration and uptake of shoots at Harvest 2 at Freeling are listed in Table 5.7. The grain protein concentration as well as the grain protein content of the (10t) treated plants were significantly increased at both sites compared to low sludge or inorganic fertiliser treated plants. The (4t+N*) treated plants had grain protein concentrations between the high sludge and low sludge or inorganically treated plants. The shoot N concentrations in the high sludge treated plants were decreased compared to (2t+N*) or inorganic fertiliser treated plants, but uptake values were on the same level.

Table 5.7 Concentration of N in plant shoots (Harvest 2), N uptake, concentration of protein in grain and protein content in grain at the three harvests.

		nil	nil +N+P +TE	2t +N*	4t +N*	10t	LSD (P=0.05)
				Freeling, Harvest 2			
N	N in [%]	1.0	0.7	0.7	0.5	0.4	0.14
N uptake	[mg m^{-2}]	5.0	5.8	6.3	4.7	5.2	1.70
				Freeling, Grain			
Protein	[%]	8.4	7.7	7.5	7.8	8.2	0.43
Protein content	[g m^{-2}]	2.8	3.2	3.1	3.6	4.5	0.33
				Callington, Grain			
Protein	[%]	7.2	6.9	7.4	7.4	8.9	0.69
Protein content	[g m^{-2}]	4.3	6.0	6.5	7.2	9.9	1.21

5.3.2.4 Head to shoot ratio

The head to shoot ratios [g g^{-1}] of plants taken at Harvest 2 at Callington and Freeling are listed in Table 5.8. The head to shoot ratio gives an indication of how much the vegetative growth relative to the reproductive growth was enhanced by a particular fertiliser treatment. The head to shoot ratio was lower for plants grown on (10t) treated plots compared to the other treatments. The (10t) sludge application obviously allowed strong vegetative growth, with an increased number of tillers and heads as shown by the number of heads counted per harvested area at Freeling (see Table 5.8). (At Callington the number of heads per m^2 were not counted.)

Table 5.8 Head : shoot ratio of cereal plants (Harvest 2) at Callington and Freeling and number of heads in the harvested area at Freeling.

	nil	nil +N+P +TE	2t +N*	4t +N*	10t	LSD (P=0.05)
			Ratio head to shoot [g g^{-1}]			
Callington	0.47	0.49	0.50	0.47	0.39	0.050
Freeling	0.43	0.65	0.62	0.66	0.55	0.068
			Number of heads m^{-2}			
Freeling	467	750	742	808	942	121

5.4 Discussion

Sludge applications up to a rate of 10t ha^{-1} caused a logarithmic or Mitscherlich type response curve in shoot dry matter production and grain yield at two different sites. When shoot or grain yield of the inorganic fertiliser treatment (nil+N+P+TE) is set against the appropriate response curve, it shows that sludge rates of less than (2t+N*) are equivalent in enhancing plant productivity at the two sites. This supports the findings in Chapter 4 that a sludge rate of (2t+N*) is a close equivalent to the chosen fertiliser rate in terms of yield in 1993.

5.4.1 Phosphorus replacement value of sludge

To estimate the P fertiliser value of sludge in comparison to inorganic fertiliser more closely, the P uptake values of the (nil+N+P+TE) treated plants can be compared to P uptake values of sludge treated plants and the established response profile. At Harvest 1 and at grain harvest a logarithmic or Mitscherlich type response curve of P uptake values to sludge rate (and hence P addition) was noticeable at both sites. At Harvest 2 the relationship was linear. The horizontal line, representing the P uptake of inorganic fertilised plants, intersects the P uptake response curves to sludge at application rates of between 2- 6t ha^{-1}, and most often at 4t ha^{-1}, depending on harvest and site. A 4t sludge application being equivalent to an inorganic fertiliser addition of 20 kg P would translate into a sludge P availability of 36 % compared to that of inorganic P fertiliser (2t-6t would translate into a sludge P availability of between 5-55 %). However, the yield response curves of shoot and grain yield to sludge additions intersect the value for inorganic fertilised plants at sludge application rates less than (2t+N*). The P uptake values, particularly of shoots, may judge the P availability of sludge more validly than shoot or grain yield, because yield is influenced by other nutritional factors as well as P uptake of plants. Hence in terms of P nutritional value, it seems that a sludge application of 4t is closer to the inorganic fertiliser equivalent of 20 kg ha^{-1} than a 2t sludge application, particularly in the early part of the season.

Phosphorus nutrition quite likely contributed to growth, because the shoot P concentrations at both sites were not very high and close to the critical values of approximately 3100 mg P kg^{-1} (Harvest 1) and 1500-1900 mg P kg^{-1} (Harvest 2) considered marginal for shoots (Reuter and Robinson, 1986). However, P nutrition may not be the only factor enhancing plant growth in the given environment. Willett *et al.* (1986) found that similar yield increases can be obtained with varying combinations of N and P fertiliser. In their study no unique combination of N and P fertiliser resulted in the yields equivalent to sludge applications. Hence an influence of both P and N and maybe other sludge factors may have contributed to increased plant productivity in the current study.

5.4.2 Effects of high sludge application rates (10t ha^{-1})

Growth increases after sludge application are likely to be due to improved N and P supply, but particularly after high sludge application rates other beneficial aspects of sludge such as the addition of organic matter could also be of importance. Willett *et al.* (1986) found the higher yields obtained with a 25 t sludge ha^{-1} could not be achieved from the highest combinations of inorganic fertiliser amendments. He suspected sludge effects on soil physical properties were the decisive factor because a decreased soil bulk density and increased moisture content of 25t sludge amended soil was measured. The effect of sludge application rates of between 5 and 50t sludge ha^{-1} on soil organic matter content, and consequently on soil physical properties, is judged differently by various authors. Fresquez *et al.* (1990) found in a sludge application study in grassland in the semiarid southwest of USA that organic matter levels did not significantly change with sludge amendments (0-90t ha^{-1}) after only one growing season. Moreover it was mentioned by Haghiri *et al.* (1978) that at low loading rates (15.5t of C ha^{-1}) a greater proportion of all the decomposition that took place occurred during the first year compared to higher loading rates (49-100 metric t of C ha^{-1}). However, Khaleel *et al.* (1981) summarised a number of studies using organic waste application under a range of climatic conditions and found a linear relationship between increases in soil organic carbon as a result of waste applications and percent reduction in soil bulk density. However, the increase in water holding capacity showed an exponential relationship to the increase in organic carbon percentage and soil texture. From these reports it appears that an influence of medium sludge rates (~10t) on soil organic matter content, bulk density and waterholding capacity is possible, but maybe relatively lower for those application rates than for high application rates. However, sandy soils with a low waterholding capacity, such as some of the experimental sites, used may still benefit from the small organic matter additions. For the current study, the low residual value of a 10t sludge application when the current crop receives some fertiliser suggests that the influence of low sludge rates on soil structure might be short term or of lower importance than the applied plant nutrients at the sites used. Further research is needed to quantify the impact of sludge organic matter on soil structure, water holding capacity and thus plant growth in the South Australian environment.

The additional plant growth due to high sludge application rate was mainly due to increased tillering and increased number of heads per m^2 (Table 5.8). The lower head to shoot ratio and the higher number of heads per m^2 of (10t) treated plants compared to plants treated with inorganic fertiliser or lower sludge rates indicates that increasingly secondary and higher order tillers were produced and their grain filling was generally reduced. However, the relatively enhanced shoot growth compared to grain production still resulted in an overall yield increase for the high sludge treatment. The (2t+N*) treated plants had a similar number of heads per m^{-2} as inorganically fertilised plants. This is in agreement with the study of Day *et al.* (1983) who found that barley genotypes responded equally in vegetative growth and grain yield when fertilized with equivalent quantities of N whether as dried sludge or commercial inorganic fertiliser. Day *et al.* (1988, 1990a) found that all the measured growth parameters of wheat (days from planting to flowering, plant height, lodging, heads per m^2, seeds per head, 1000 seed weight, grain yield and grain/straw ratio) were similar between the fertiliser and sludge treatments. In pot and field studies with durum wheat (*Triticum durum* Desf.) Day *et al.* (1990a,b) gained similar results. However, sludge rates higher than the rate considered equivalent to the inorganic fertiliser comparison in terms of N supply produced the most hay or straw (Day *et al.*, 1990a), which is in agreement with the current study. Those higher sludge rates resulted in a significant yield increase in the greenhouse (Day *et al.*, 1990b), but not in the field (Day *et al.*, 1990a).

The possibility of a yield depression after high N applications in dry seasons (McDonald, 1992) did not negatively affect yield in the current experiment. The rainfall in 1993 was close to the site averages (see Table 3.11), but plant density was lower than what is generally desired and water competition presumably was not as severe as normally expected. Fahti (1994) found significant responses in barley grain yield to N rates of between 45 and 90 kg N ha^{-1} at sites in South Australia, in years with rainfall close to site averages. Elliott *et al.* (1993) found that the external N requirement of the barley variety 'Galleon' for maximum yield was 85 kg ha-1 and lower than for the common malting variety 'Schooner' of 150 kg ha^{-1}. If the sludge N contribution of 2t is considered to be below 20 and around 15 kg N ha^{-1} (for details see Chapter 4) the N contribution of a 10t sludge application would then be around 75 kg N ha^{-1} and thus still in the range where growth enhancement rather than depression can be expected in an average year. Hence, yield depression or severe haying off of plants after a 10t sludge addition is unlikely to be a problem in average rainfall years such as 1993.

5.4.3 Micronutrient (Zn) value of sludge applications

Micronutrient (or Zn) nutrition of plants was not a yield enhancing factor in 1993 (Chapter 5) at the two sites, although concentrations of Zn in shoots (Harvest 2) at Callington were at the lower end of the 5-24 mg Zn kg^{-1} range considered marginal for barley shoot concentration (Reuter and Robinson, 1986). However, the effectiveness of the two sources of Zn still can be compared, because Zn concentration and Zn content versus rate of applied Zn response functions do not reach a constant value (plateau) when Zn sufficiency is achieved (Mortvedt and Gilkes, 1993).

Increases in sludge application rates strongly influenced Zn uptake values with a linear relationship between shoot and grain Zn uptake and sludge application rates at both sites. Also the concentration of Zn in shoots and grain increased with sludge rate. The clear relation between sludge application rate and Zn uptake by plants shows that sludge borne Zn is plant available as the sludge application rates increase. This is in agreement with the study of Goto *et al.* (1993) who found that the increase in concentration of Zn in shoots of *Brassica rapa* L. correlated closely with the amount of Zn in sludges added to the soil. McCaslin and O'Conner (1982) similarly observed in a pot study that Zn concentration in sorghum plants increased with increasing sludge rates applied to a calcareous soil. Also Fresquez *et al.* (1990) noted that the levels of micronutrients such as Cu, Mn and Zn in grassland on a calcareous and TE deficient soil in the semiarid southwest of USA increased linearly after sludge application rates of 0 to 90t ha^{-1}. Corey *et al.* (1987 and studies cited there) stated that in general for Cd and Zn the metal concentration in tissue approaches a maximum and has shown a logarithmic relationship with sludge rate. However, in studies when the sludge addition was not high enough to approach a constant metal activity in solution, the relationship between sludge rate and tissue concentration often approached linearity (Pietz *et al.*, 1983; Vlamis *et al.*, 1985; Corey *et al.*, 1987). In the current study a maximum (plateau) level in plant Zn concentration was most likely not reached yet with the comparatively low sludge application rates used in this experiment, because shoot tissue concentrations between 4t and 10t treated plants still increased significantly.

Generally, no inorganic Zn fertiliser comparison was included in the above mentioned studies. When comparing the Zn uptake of the inorganic fertiliser comparison (nil+N+P+TE) with the response curve of sludge treated plants it appears that sludge application rates of approximately 2t are equivalent to the inorganic fertiliser comparsison. These findings confirm the results in Chapters 3 and 4, where it was concluded that the total Zn of a 2t sludge application was equivalent to the Zn application in inorganic form. The fact that sludge and the TE mix in the inorganic comparison contained Cu and Mn as well as Zn have been discussed in Chapter 3. The Cu and Mn tissue concentrations in the 1993 experiments were in the range considered sufficient for barley growth and therefore not discussed in detail (See Appendices, Table A.5.2 - A.5.5).

5.5 Conclusions

- An increase in shoot dry matter production and grain yield is achievable with sludge application rates of up to 10t ha^{-1} in a year with average rainfall.

- A (2t+N*) sludge application produced a grain yield equal to an inorganic fertiliser application of 20 kg N ha^{-1} and 20 kg P ha^{-1}.

- A (4t+N*) sludge application seemed to be the equivalent to an inorganic P application of 20 kg ha^{-1}, when P uptake values were taken as an indicator.

- Plants treated with 10t ha^{-1} sludge had a lower head to shoot ratio than inorganic fertilised plants or plants receiving lower rates of sludge, suggesting that additions approaching the 10t rate are probably giving only relatively low increments in yield.

- The Zn uptake in shoots and grain was positively correlated with sludge application rates, showing a linear relationship. The sludge application rate of 2t provided an equivalent amount of phyto-available Zn to the inorganic comparison containing the same amount of total Zn.

Chapter 6

Residual value of sludge applications in comparison to inorganic fertiliser

6.1 Introduction

Sludge amendments have a considerable agronomic value in the year of application. Sludge P availability was about 18 to 55 % compared to inorganic P and 10 to 42 % of the organic N in sludge were shown to be plant available in the year of application (Chapter 3, 4 and 5). However, most of the nutrients that were applied with sludge were not taken up by plants and may have remained in the soil. The same applies to inorganic fertilisers. In terms of P availability sludge is considered a slow release fertiliser. It has been shown that the relative efficiency of sludge-P can increase over time (Pommel, 1981; McLaughlin and Champion, 1987). Hence it could be possible that sludge is a relatively better source of P in the following year after application compared to inorganic fertiliser than in the year of application. This is important to determine, because it would add further value to the sludge as a fertiliser product.

The availability of inorganic Zn fertiliser decreases over time (Brennan, 1990). It is possible that the application of both Zn and organic matter with the sludge may inhibit or slow down the adsorption or precipitation processes that decrease the Zn availability over time. The aim of the field experiments was to determine the residual value of a sludge application in comparison to an inorganic fertiliser amendment. Similar to the previous field experiments shoot dry matter at different developmental stages, grain yield and tissue concentration of selected elements were taken as indicators for nutrient availability. A low basal nutrient application was given to enhance plant establishment and early growth. A high number of tillers and shoot dry matter presumably poses an elevated nutrient demand later on in the season and may enhance possible differences between the two nutrient sources, sludge and inorganic fertiliser.

6.2 Material and methods

6.2.1 Sludge treatments

The residual value of low sewage sludge application rates in comparison to inorganic fertiliser was assessed at Callington in 1993 and 1994 and Freeling in 1994. At Callington the plots from the field experiment in 1992 (Chapter 3) were used in 1993 to determine the residual value of the treaments applied in the previous year. (The initial plots at Callington in 1992 were subdivided into plots: 10 m long, 1.5 m wide. One half of the plots was used in the experiment described in Chapter 4 and the other half of the plot was used for the current experiment determining the residual value of a sludge or fertiliser amendment.) The experiments at Callington and Freeling in 1993 and 1994 determined the residual value of the following treatments applied in 1992 or 1993 respectively. (For treatment details see Chapter 3 and 4). Generally the treatments were applied for one year (in the previous season), except at Freeling 1993 (residual value experiment in 1994) where treatments were applied over two consecutive years.

Two years prior to experiment Freeling	***Two years prior to experiment Callington*** ***(both years)***	**One year prior to experiment**	**Experimental year**
nil	*nil+N+P*	nil	basal fertiliser
nil+N+P	*nil+N+P*	nil+N+P	basal fertiliser
nil+N+P+TE	*nil+N+P*	nil+N+P+TE	basal fertiliser
2t	*nil+N+P*	2t	basal fertiliser
*2t+N**	*nil+N+P*	2t+N*	basal fertiliser
2t+N+P/2*	*nil+N+P*	2t+N*+P/2	basal fertiliser

Increasing sludge rates (0-10t ha^{-1}) were applied at Freeling and Callington in 1993 (Chapter 5), including the following treatments (for treatment details see Chapter 5). Treatments were applied for one season only (previous year).

Two years prior to experiment ***Freeling***	***Two years prior to experiment*** ***Callington***	**One year prior to experiment**	**Experimental year**
nil+N+P	*nil+N+P*	nil	basal fertiliser
nil+N+P+TE	*nil+N+P*	nil+N+P+TE	basal fertiliser
*2t+N**	*nil+N+P*	2t+N*	basal fertiliser
nil+N+P	*nil+N+P*	4t+N*	basal fertiliser
nil+N+P	*nil+N+P*	10t	basal fertiliser

The residual value of those treatments was determined in 1994 at the two mentioned sites. In both years the plots were amended with a basal fertiliser rate of N (7 kg ha^{-1}) and P (7.7 kg ha^{-1}), applied at seeding. Commercial grade fertiliser (DAP) was used. The treatments were arranged in a completely randomised block design with 5 replicates per treatment.

6.2.2 Field crop, crop rotation and plant analysis

Galleon barley (*Hordeum vulgare* L.) was seeded at a rate of 70 kg ha^{-1}. A 10 row tyned cone seeder was used for seeding and fertiliser application. The crop rotation at the sites were as follows:

	Callington	**Freeling**
1991	pasture	vetch
1992	wheat	wheat
1993	barley	barley
1994	barley	barley

Apart from the fertiliser treatments, the husbandry of the crop was undertaken by the farmer as part of his normal management practice. At Callington one mid season harvest on the 2 November (late flowering) was taken and also the grain harvest. At the mid season harvest, plant samples were taken at two independent positions, 40 cm along a central row in the plots. The shoots were cut 2 cm above ground (harvested area: 0.12 m^2). In 1994 only grain harvest was taken at both sites. Shoot and grain chemical analysis were as described in Chapter 3.

Dry matter and grain yield were transformed into relative yield by dividing all the values, including the values for the nil treatment, by a common factor, the site average for the nil treatment. The Anova was calculated for the transformed data.

6.2.3 Soil characteristics and weather

The soil classification and selected soil properties are listed in Tables 3.8, 3.9 and 3.10 and climatic data are given in Tables 3.11 and 3.12 (Chapter 3).

6.3 Results

6.3.1 Shoot and grain yield

The shoot and grain yields relative to the nil treatment of plants treated with low sludge application rates or inorganic fertiliser are listed in Table 6.1. The absolute yield for the nil treatment was 626 g m^{-2} and 410 g m^{-2} for Callington 1993 shoot and grain harvest respectively and 153 g m^{-2} and 128 g m^{-2} grain yield for Callington 1994 and Freeling 1994 respectively. The (2t+N*) treatment showed increased shoot dry matter production compared to the remaining treatments at Callington1993. However, there was no statistical difference in grain yield between the different treatments at Callington or Freeling in any of the years. Even when low sludge rates were applied over two consecutive years (Freeling 1994) or higher sludge applications up to 10t ha^{-1} were used (Table 6.2) no significant increase in grain yield were noticeable due to a former sludge or inorganic fertiliser application.

Table 6.1 Dry weight of shoots at the mid season harvest (flowering) and grain yield relative to the nil treatments (100%) when sludge or inorganic fertiliser were applied in the previous year at Callington (Call.) and Freeling (Freel.): Low sludge application rates .

		nil	nil +N+P	nil +N+P +TE	2t	2t +N*	2t +N*+P/2	LSD (P=0.05)
Call. 1993	shoot	100	98	89	100	127	108	18
Call. 1993	grain	100	110	102	112	126	113	n.s.
Call. 1994	grain	100	95	97	103	93	95	n.s.
Freel. 1994	grain	100	104	99	110	99	104	n.s.

Table 6.2 Grain yield relative to the nil treatment (100%) when sludge or inorganic fertiliser were applied in the previous year at Callington (Call.) and Freeling (Freel.): high sludge application rates.

		nil	nil +N+P +TE	2t +N*	4t +N*	10t	LSD (P=0.05)
Call. 1994	Grain	100	97	93	82	106	n.s.
Freel. 1994	Grain	100	99	99	109	103	n.s.

6.3.2 Chemical analysis of shoot and grain

6.3.2.1 Phosphorus

Plant P shoot and grain concentration of plants amended with low sludge or inorganic fertiliser applications in the previous year are shown in Table 6.3 and of increased sludge application rates in Table 6.4. Generally the sludge or fertiliser treated plants showed a higher shoot or grain P concentration than control plants. At Callington1993 the shoot and grain P concentrations showed the same trend in that plants amended with sludge without inorganic P ((2t), (2t+N*)) had a lower P concentration compared to the (nil+N+P+TE) treated plants, but similar compared to (nil+N+P) treated plants. Plants amended with sludge and additional P (2t+N*+P/2) showed P concentrations in the range of the (nil+N+P+TE) treatment in both harvests. At the same site in 1994 the two inorganic fertiliser treatments had similar grain P concentrations, which was higher than grain P concentration of all the different sludge treatments. At Freeling differences between sludge and inorganic fertilisation in terms of grain P concentration were not noticeable and all were significantly greater than the nil treatment.

Elevated grain P concentrations were noticeable when sludge application rates were increased from 2 to 10t ha^{-1} (Table 6.4). The intermediate rate of 4t ha^{-1} did not show an increase in P concentration compared to a sludge application rate of 2t. The grain P concentration of 10t ha^{-1} sludge amended plants increased to the level of inorganic fertilised plants.

Table 6.3 Concentration of P in shoot and grain, when sludge or inorganic fertiliser were applied in the previous year at Callington and Freeling: low sludge application rates.

		nil	nil +N+P	nil +N+P +TE	2t	2t +N*	2t +N*+P/2	LSD (P=0.05)
		Concentration [mg kg^{-1}]						
Call.93	shoot[a]	1040	1380	1610	1300	1300	1500	200
Call.93	grain	2900	3060	3300	3090	3150	3380	190
Call.94	grain	2565	3175	3222	2918	3098	3037	218
Freel.94	grain	2652	3001	3104	3087	3009	3014	211

[a] 1700 mg P kg^{-1} approximate critical value for *H. vulgare* (Reuter and Robinson, 1986)

Table 6.4 Concentration of P in shoot and grain, when sludge or inorganic fertiliser were applied in the previous year at Callington and Freeling: high sludge application rates.

		nil +N+P +TE	2t +N*	4t +N*	10t	LSD (P=0.05)
Call. 1994	grain	3222	3098	3062	3307	218
Freel. 1994	grain	3104	3009	3099	3282	211

6.3.2.2 Zinc

Grain Zn concentrations at Callington were lower than at Freeling. Plants treated with (nil+N+P+TE) showed a significantly increased concentration of Zn in shoot and grain when compared with the (nil+N+P) treatment at all the sites. The concentrations of Zn in shoots and grain for plants treated with low sludge rates or the (nil+N+P+TE) treatment were generally similar at both sites and years (Table 6.5).

Increasing sludge applications had a significant influence on the grain Zn concentration, with 10t ha^{-1} treated plants having a 4 mg kg^{-1} and 3.4 mg kg^{-1} higher grain Zn concentrations compared to (nil+N+P+TE) treated plants at Callington and Freeling (1994) respectively (Table 6.6). The (4t+N*) treated plants showed values between the (2t+N*) and (10t) treated plants.

Table 6.5 Concentration of Zn in shoot and grain, when sludge or inorganic fertiliser were applied in the previous year at Callington and Freeling: inorganic fertiliser and low sludge application rates.

		nil	nil +N+P	nil +N+P +TE	2t	2t +N*	2t +N*+P/2	1t +N*+P/2 +TE/2	LSD (P=0.05)
					Zn [mg kg^{-1}]				
Call.93	shoot[a]	5.2	4.7	6.5	5.8	6.5	6.6	6.2	1.1
Call.93	grain	14.2	12.3	17.3	16.7	17.4	17.1	15.9	1.7
Call.94	grain	13.7	13.8	17.3	14.1	17.4	16.1	-	1.95
Freel.94	grain	21.6	20.2	23.1	25.2	24.4	23.8	-	2.06

[a] 5-24 mg Zn kg^{-1} appproximate critical value for *H. vulgare* (Reuter and Robinson, 1986)

Table 6.6 Concentration of Zn in shoot and grain, when sludge or inorganic fertiliser were applied in the previous year at Callington and Freeling: high sludge application rates.

		nil +N+P +TE	2t +N*	4t +N*	10t	LSD (P=0.05)
Call. 94	Grain	17.3	17.4	18.8	21.3	1.95
Freel. 94	Grain	23.1	24.4	25.1	26.5	2.06

6.4 Discussion

6.4.1 Residual effect of sludge and inorganic fertiliser applications on grain yield and phosphorus content of plants

In terms of grain yield no beneficial residual value of low sludge application rates (2t ha^{-1}) or inorganic fertiliser amendments was measured at any of the sites in 1993 and 1994. (1994 was an exceptionally dry year and plants may not have been very responsive to nutrient supply; see below.) A cereal after cereal rotation was used in both years, which is quite demanding on the nutrient and particularly N supply. Any remaining plant available nutrients thus would be expected to increase plant growth. The lack of growth response suggests that either N or P or both nutrients were insufficient for growth enhancement beyond that produced by the base fertiliser, which may have been sufficient to meet the nutrient demand of the crop.

The residual value of high sludge application rates (4t ha^{-1}, 10t ha^{-1}) was only assessed in 1994. This growing season was exceptionally dry and plant growth and grain yield, particularly at Freeling, was lower than usually expected. The dry conditions limited plant growth and hence may have reduced the nutrient demand of the crop. The absolute crop response to fertiliser is generally lower in drier years (Holford *et al.*, 1985; Angus and Fischer, 1991), whereas relative responses to P fertilisers (low rates) can be higher in dry years than humid years (Holford and Doyle, 1992 and 1993). Hence it is likely that the plant growth in 1994 was dominated by the basal nutrient application at seeding rather than the possible residual value of the sludge application. A conclusion on the residual value of high sludge application rates cannot be drawn from the grain yield data in 1994.

Although the lack in crop response may be due to several reasons, it is likely that the residual N value of both sources was rather low. Milne and Graveland (1972) found that most of the available N from sludge had been used by the first crop and N supply of sludge was rather low for the second crop. Keeney *et al.* (1975) suggested that the N mineralisation of sludge organic N is rather low in the years after application and around 6 % in the second year compared to 15 % in the year of application. Also low N nutrition could have prevented a plant response to P nutrition. Milne and Graveland (1972) found yield increases to be higher with N plus P fertiliser than with N alone, even where no response to P alone was noted.

The concentration of P in shoot and grain differed between treatments in both experimental years, although yield differences did not occur. At Callington 1993 the (2t) treated plants showed in general lower shoot and grain P tissue concentration than one of the two inorganic fertiliser comparison, but considerably higher than the control. Because P concentrations of the two inorganic fertiliser comparison were different, conclusions in terms of sludge P availability of a (2t) treatment are difficult. However, in 1994 the (2t) treated plants again showed lower grain P concentrations than inorganic P treated plants. The (2t+N*) treated plants showed a similar trend, but P levels were generally higher than from (2t) treated plants. At Freeling grain P concentrations of plants amended with low sludge rates or inorganic fertiliser were similar, and higher than the control. Hence it seems that the residual P value of a sludge application was somewhat lower at Callington compared to an inorganic fertiliser application, but similar at Freeling. If differences between Callington and Freeling are based on site differences or on the fact that Callington had one year and Freeling two consecutive years of sludge applications cannot be clarified. However, the results indicate that relative availability of sludge P compared to inorganic P remains about the same, because also in the year of application it was suggested that sludge P availability of a 2t application may be somewhat below a 20 kg ha^{-1} fertiliser application. Coker (1983) found that availability of sludge P did not substantially decline compared to P from superphosphate. McCoy *et al.* (1983) estimated that the availability of sludge compost P was 70-90 % of the first year levels. Willett *et al.* (1986) found, using low sludge application rates (0-25t), that the sludge had a greater residual value as a source of P than the phosphorus fertiliser. However, these experiments were done on an acid soil using a legume (lucerne) as a test crop and thus N nutrition was less crucial. For a calcareous soil O'Conner *et al.* (1986) showed that sludge increased the P levels in calcareous soils and this status was maintained for 1-2 years, whereas the inorganic P fertilisers had only a temporary effect on soluble P levels. He suggested that a slight decrease in soil pH was mainly responsible for the improved P solubility of sludge P. However, P availability was measured in soil extractions rather than using plant uptake as a indicator. Nevertheless it indicates that sludge P may be a similar or superior source of residual P in those types of soil.

Increased sludge applications (10t) resulted in higher grain P concentrations compared to low sludge treated plants (2-4t ha^{-1}). The grain P concentrations of inorganic fertilised plants were between the low and the high (10t) sludge treated plants. This would suggest that a sludge application rate between 2 and 10t, probably close to 4t - 6t, has a residual value equivalent to the inorganic fertiliser comparison (20 kg P ha^{-1}). These results in terms of P nutrition of sludge and inorganic fertiliser are corresponding to the results obtained in the year of treatment application (Chapter 5). Hence it seems that the relative availability of sludge P compared to inorganic P remains the same in the second year after application. However, these results are obtained in a dry year and extrapolation to a more humid year has to be treated with caution.

6.4.2 Residual effect of sludge and inorganic fertiliser applications on zinc content of plants

The residual value of sludge and inorganic fertiliser applications was a reflection of the fertiliser value measured in the actual year of application. Shoot and grain Zn concentrations of TE treated plants were increased, but differences between similar Zn application rates in inorganic or sludge form were not detected. This was the case whether previous treatments were applied over one or two years (Callington or Freeling). When Zn application rates were increased (10t sludge ha^{-1}) a increased grain Zn concentration was measurable at the two sites compared to low sludge or inorganic Zn fertilised plants. This suggests that the residual value of a Zn application is similar whether it was applied in sludge or as an inorganic fertiliser and increased application rates result in increased levels of plant available Zn in the soil. A 'reasonable' residual value effect of sludge Zn was also found by McCaslin *et al.* (1987) when applied on calcareous soil. The DTPA extractable Zn did decrease in each year after sludge application, but a considerable residual effect was measurable for at least 5 years after application. No inorganic fertiliser comparison was included in the experiment. Mortvedt and Giordano (1975) applied a similar but high amount of sludge Zn and inorganic Zn and found that for both sources the plant Zn uptake decreased slowly over time. A direct comparison of the two sources was not possible, because the inorganic Zn increased Zn availability much more in the year of application than sludge Zn.

6.5 Conclusions

- The residual value of sludge or inorganic fertiliser applied in the previous year did not influence grain yield in the following year beyond the level of a basal fertiliser.

- The residual value of sludge P compared to inorganic P reflected the P fertiliser value in the year of application. A sludge application of approximately 4 to 6t seems to have a similar residual P value as an inorganic P application of 20 kg P ha^{-1}.

- The residual influence of inorganic or sludge Zn application resulted in increased grain Zn concentrations compared to plants not receiving TE in the previous year. The residual value of the two TE sources was similar.

- Higher sludge applications (with a higher amount of TE compared to the inorganic fertiliser comparison) did increase grain Zn concentration in the year after treatment application beyond the level of inorganic fertiliser treated plants.

Chapter 7

Grain cadmium analysis of sludge or inorganic fertiliser treated plants

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7.1 Introduction

Sludge contains variable amounts of heavy metals which in the case of Zn and Cu can be a valuable resource in terms of plant nutrition. However, sludge also contains heavy metals, such as cadmium (Cd), with no known essential biological function in plants or animals. Chronic exposure to Cd in food can significantly increase the accumulation of this trace element in body organs like kidneys and liver and can cause renal tubular dysfunction (Hallenbeck, 1984). However, a study by the FAO/WHO (1990) indicated that the Australian population has one of the lowest dietary intakes of Cd of those countries surveyed. Australia has a low maximum permissible Cd concentration in unspecified foods, which include cereal grain, set at 0.05 mg kg^{-1} (NHMRC, 1987). The concern that Cd concentrations in grain may exceed the maximum permissible concentration has arisen in Australia from a marketing and trade point of view. Sludge applications have been shown to increase Cd concentrations in plants (Gestring and Jarrell, 1982; Pietz *et al.*, 1983; Sauerbeck and Stypereck, 1987a,b; Page *et al.*, 1987) and hence the input of sludge-Cd to agricultural land has to be monitored. In the current study it was intended to determine if comparatively low sludge application rates (0-10t ha^{-1}) have an effect on Cd concentrations in shoots and grain of cereal plants. Cadmium concentration in plants treated with inorganic fertiliser was compared to sludge treated plants, because phosphate fertilisers are, like sludge, a major source of Cd in agricultural soils.

7.2 Material and Methods

In Lameroo, 1993, the following treatments were applied to conventionally worked soil:

nil	2t+N*
nil+N+P+TE	4t+N*
	10t

The inorganic fertiliser rates and fertiliser type are as described in Chapter 4 and 5. The plot size was 30 m^2 (20*1.5 m). Fertiliser and sludge applications followed those described in Chapter 4 and 5. Galleon barley (*Hordeum vulgare* L.) was seeded at a rate of 65 kg ha^{-1}. A mid season shoot harvest (0.12 m^2) and grain harvest was taken. At the mid season harvest at late flowering (1.11.93), plants were cut 2 cm above ground and taken from central rows of the plot. Shoot and grain dry matter was measured and Cd concentration was analysed by graphite furnace atomic absorption spectrophotometry (GFAAS) (Varian, SpectrAA 400) (p. 255a, 255b). The crop rotation was barley-lupins-barley. The soil classification and selected soil properties are listed in Tables 3.8, 3.9 and 3.10; climatic data are given in Tables 3.11 and 3.12. Apart from the fertiliser treatments, the husbandry of the crop was undertaken by the farmer as part of his normal management practice.

7.3 Results

Shoot and grain dry matter are given in Table 7.1. The shoot dry matter at flowering of the control plants was lower than from the remaining treatments, which showed a similar yield. The grain yield did not differ between the treatments, which simplifies the comparison of grain Cd concentrations.

The Cd analysis for both shoot and grain material (Table 7.2) showed an increased Cd concentration for the 10t treated plants compared to plants treated with low sludge rates or inorganic fertiliser. The plants treated with lower sludge rates or inorganic fertiliser showed a similar Cd concentration. The Cd concentrations in grain were considerably lower than in the shoots.

Table 7.1 Lameroo 1993: shoot dry matter at late flowering and grain yield.

	nil	nil +N+P +Te	2t +N*	4t +N*	10t	LSD (P=0.05)
			[kg m^{-2}]			
Shoot	1.96	2.65	2.55	2.86	2.70	0.33
Grain	0.37	0.35	0.38	0.35	0.36	n.s.

Table 7.2 Lameroo 1993: Cd analysis of shoot and grain

	nil	nil +N+P +Te	2t +N*	4t +N*	10t	LSD (P=0.05)
			[μg kg^{-1}]			
Shoot	94	116	132	137	210	56
Grain	16	18	19	18	26	2.4

7.4 Discussion

Numerous studies have shown that sludge additions to soils increase the concentration of Cd in plant tissue (Soon *et al.* 1980; Pietz *et al.*, 1983, Sauerbeck and Stypereck, 1987a,b) and both linear (Fresquez *et al.*, 1990) and logarithmic (Corey *et al.*, 1987) relationships have been suggested, which depended on the rate of metal applied. At low metal application rates the Cd concentration of plants was found to increase linearly with application rate, whereas at high application rates a plateau in terms of Cd uptake of plants can be reached (Chaney *et al.*, 1987). Cadmium uptake is inversely related to soil pH (Alloway, 1990, Dijkshoorn *et al.*, 1981) and hence Cd uptake is generally lower in high pH soils. The soil pH at Lameroo was close to neutral (pH 6.8), with a calcareous layer below 10 cm depth. The Cd availability in this soil was expected to be low, considering the low Cd application rates up to 30 g ha^{-1}. However, significant increases in Cd concentration in shoot and grain were measured, showing that the sludge Cd added is plant available or that sludge increases the plant availability of soil Cd.

Plant uptake of Cd can also vary with the metal concentration in the sludge. The Cd in low-Cd sludges is generally considered less available than Cd from high-Cd sludges (Chaney, 1985). The sludge used in the field experiment in Lameroo can be considered a low-Cd sludge containing 3 mg kg^{-1} Cd only. Nevertheless, a sludge application rate of just 10t ha^{-1} caused a significant increase in Cd concentration in shoots and grain. For comparison, the Cd input by phosphate fertilisers in Australia can range between 0.6- 3.8 g with 20 kg P applied, according to the average concentrations of Cd of 17.1, 19.2 and 5.7 mg kg^{-1} in single-, double- and triple-superphosphate respectively, measured by North-Combes and Berg (1990).

At the other experimental sites, where sludge rates up to 10t ha^{-1} were applied (Chapter 5) the Cd concentrations in shoots and grain were low and a more refined analytical procedure (back-extraction) would have been necessary to determine the Cd concentration more accurately. At those sites, the soil was around pH$_{(H2O)}$ 8.5 and hence Cd availability was expected to be lower. However, at one of the two sites elevated Cd concentrations in shoots of 10t sludge-treated plants were also measured (Appendices, Table A.7.1).

Recent findings have shown that the chloride (Cl) concentration in soils is an important factor in determining Cd availability to plants (McLaughlin *et al.*, 1994; Smolders *et al.*, 1996). The Adelaide (Bolivar) sludge used contains a comparatively high amount of soluble salts, including Cl. The Na concentration of sludge treated plants increased with sludge rate at Lameroo (Appendices, Table A.7.2) and also at one of the other two sites receiving sludge rates beyond 2t (Appendices, Table A.7.3 and A.7.4). The Cl concentration of plants was not measured, but Na is the major cation balancing Cl in the sludge used. The increase in Na concentration of plants indicates that plants treated with high rates of sludge would have been exposed to elevated Cl concentrations in soil solution some time during their development. This could have enhanced the Cd availability in soils during that time. Elevated Na concentrations in 10t treated plants were measured at two of the three sites where Cd concentrations in plants were enhanced at the high sludge application rate. The influence of Cl on sludge borne Cd will be discussed in more detail in Chapters 8 and 9.

Crop rotation could also have had an influence on Cd uptake by plants. The barley crop in Lameroo 1993 was seeded after lupins, which had developed extensive vegetative growth (W. Haywood, pers. comm.) and thus quite likely also an extensive root system. Oliver *et al.* (1993) have shown that the Cd uptake of cereal plants grown in rotation after lupins had enhanced Cd uptake. Thus, an influence of the previous lupin crop on the Cd availability in soil is likely and may have contributed to the measured increase in Cd uptake of high sludge-treated plants.

At Lameroo, which had a soil pH close to neutral, Cd concentrations in grain were still below the maximum permissible limit of 50 $\mu g\ kg^{-1}$ fresh weight (NHMRC, 1987). However, this indicates that even moderate amounts of Cd applied (10t sludge ha^{-1}) can increase Cd uptake of plants. Sludge additions to soils with a lower soil pH or higher inherent soil Cd concentration could lead to higher Cd concentrations in shoots and grain. However, sludge applications onto calcareous soils (Table A.7.1) seem to be a safer option for low metal sludges, because an increase in Cd uptake could not be measured in the short term.

Chapter 8

The influence of sodium chloride (NaCl) on Cd-phyto-availability in sludge amended soils

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8.1 General introduction

In the field experiments in 1992 and 1993, it was shown that the inorganic fertiliser treatment of 20 kg N, 20 kg P, 2 kg Zn and 1.4 kg Cu can be substituted with a sludge application of 2 to 4t ha^{-1}. The equivalent rate is dependent on crop rotation, soil fertility, field crop and seasonal conditions. The sludge application rate of 4t ha^{-1}, as a sole fertiliser, would be a safe recommendation to farmers as a substitution for inorganic fertiliser (rate as above). However, sludge can be expected to be a less acceptable means of fertilisation than the conventional inorganic fertiliser. Hence the recommended rates for sludge applications should assure under any environmental circumstances a plant yield equivalent to conventional inorganic fertiliser rates and allow for safeguards in terms of nutrient supply as well as crop quality.

The area where sludge potentially will be applied in the near future will mainly be determined by economic considerations. In a benefit and cost analysis on various options for the reuse of sewage sludge by R. Scott Young & Co.(1995) a loading and freight cost of up \$ 12 t^{-1} , the cost to dump stockpiled sludge at the Bruckunga mine, was estimated to be at one's disposition for sludge transport. This is the freight cost equivalent to the cost for dumping the sludge at an existing disposal site. The spreading cost of sludge was estimated to be around \$ 6 t^{-1}.

Depending on who has to bear the cost of transport and the spreading of sludge, the economic calculations result in different possible transport distances from the Waste Water treatment plant. R. Scott Young & Co. (1995) estimated a potential transport distance of 150km, if the transport cost of sludge (up to \$12t^{-1}) was to be borne by the Engineering and Water Supply (EWS, now South Australian Water Corporation) and the sludge spreading cost by the farmers. If both the transport cost as well as the loading and spreading costs were to be borne by the farmer a lower transport distance would be estimated.

Fertiliser type	P_{av}	N	Zn	fertiliser cost for 20 kg P plus N *
		[%]		[$]
NPKS-Mallee	11.6	12	1.5	63
DAP	20	18	-	42
Average				52.5

(* bulk prices for fertilisers used)

The cost of inorganic fertiliser application of 20 kg P ha^{-1} and about 20 kg N ha^{-1} (with or without TE) therefore would include the fertiliser cost of approximately $ 52 and a spreading cost of $ 0.9 (for the inorganic fertiliser amount of about 150 kg ha^{-1}). If a farmer instead pays the same amount for a sludge application the transport radius can be calculated as follows.

Spreading cost of 4t sludge	$ 24
Loading and freight cost for 4t	$ x
Maximum to be paid by farmers (inorganic fertiliser cost)	$ 53
Loading and freight cost for 4t	x = 53 - 24 = $ 29
Loading and freight cost for 1t	$ 7.3

A transport radius of 150 km was estimated to be covered by a loading and freight cost of $ 12. Accordingly the loading and freight cost of $ 7.3 would cover a transport distance of approximately only 91 km. The calculated transport distance suggested by R.Scott Young & Co. (1995) is based on the assumptions that back-loading would be available in 50 % of all return journeys. If this was not the case the outer limits of sludge transportation radius would necessarily be further reduced.

The areas where sludge is most likely to be applied based on economic considerations are different in the two scenarios. A transport distance of 90 km would include the Adelaide plains, the Adelaide hills and a small area beyond the Adelaide hills. The Adelaide hills have a reasonable amount of permanent pasture land, where only surface application of sludge is feasible. New South Wales guidelines recommend withholding periods for paddocks when sludge is surface applied and not incorporated (Ross *et al.*, 1991) and thus the useage of the paddock would be restriced for some time. This is not the case when sludge is incorporated into the soil, which is feasible in broadscale cropping and horticulture. Thus it is most likely that sludge will be used in horticultural crops closer to Adelaide rather than the cereal growing areas at the outer boundaries of the calculated transport radius. Sludge application to horticultural crops has to be monitored, due to the generally higher heavy metal uptake (in particular Cd) of those crops compared to cereal crops. Also the conventional fertiliser application rates and thus the equivalents in sludge application rates are considerably higher in horticultural crops. In South Australia, most horticultural crops are irrigated. Recently it was shown that irrigation water quality and the resulting Cl concentration in soils has a major influence on Cd uptake of plants (McLaughlin *et al.*, 1994; Li *et al.*, 1994). The interaction of sludge-Cd and soil Cl levels has not been determined. Before sludge can be recommended as a valuable fertiliser under irrigation or in saline soils, the potential risks of Cd uptake by plants under those circumstances has to be established.

The second scenario, a potential transport radius for sludge of 150 km, when transport costs are borne by the EWS, includes the former mentioned areas as well as cereal cropping areas beyond the Murray River in the East and the mid North up to around Port Broughton (R. Scott Young & Co., 1995). A vast amount of cereal cropping area would be reached, where due to potential sludge application rates and choice of crops, there is a low risk of heavy metal contamination of the food chain. However, the agricultural areas along the Murray River are also irrigated and intensively cropped. The 150 km radius also includes the eastern Mt Lofty Ranges extending from Keyneton in the north to Waitpinga in the south. There are many areas of soil described as salinised or salt scalded. The report of R. Scott Young & Co. (1995) recommended the use of sludge to amend those degraded agricultural soils. For both areas there is a high probability of elevated Cl concentration in soils. Hence for those areas it would be necessary to establish the potential risk of Cl mobilising sludge-Cd.

Furthermore the Adelaide (Bolivar) sludge contains a high amount of NaCl (2% Na, 2.2 % Cl), when compared with sludges produced at other wastewater treatment plants. Sommers (1977) found a median concentration of Na of 0.2 % in a survey of >250 sludge samples in USA. Sludges produced in the northern hemisphere are generally not air dried due to the climate and are dewatered in a number of ways e.g. drainage, centrifugation or belt press. Centrifugation or filtration as a dewatering process decreases the amount of watersoluble constituents remaining in the sludges (Sommers, 1977). In a comparison of 20 Australian sludges by De Vries (1983b), the sludge from the Bolivar water treatment works contained the highest concentration of Na (1 %), which was well above the median value of 0.07 % in that study. De Vries added that 'young' and 'aged' sludges from the same treatment plants can differ considerably in their Na and Cl contents. Although a variation in Na and Cl content of different batches of Bolivar sludge can be expected, the sludge is a significant source of NaCl when applied to crops. The high content of soluble salt was suspected to influence plant emergence (De Vries, 1983a,b), but it also could enhance Cd availability for plants.

8.2 Introduction to the experiments

A number of studies have shown that Cl concentration in the soil or soil solution decreases Cd sorption to soils (O'Conner *et al.* , 1984) increases the Cd mobility in soils (Doner, 1978) and enhances Cd uptake by plants (Bingham *et al.*, 1983; Bingham *et al.*, 1984; McLaughlin *et al.* 1994; Li *et al.*, 1994; Smolders *et al.*, 1995 and 1996). This was found to be true for several plant species and for a range of soil pH. Chloride forms relatively strong complexes with Cd (Smith and Martell, 1981) and may be regarded as a selective ligand for Cd and other heavy metals (Hahne and Kroontje, 1973). Chloride has been found to signficantly reduce sorption of Cd by soils (Boekhold *et al.*, 1993). The increased concentration of Cd in the liquid phase at higher Cl concentrations enhances the mobility of Cd in soils. This effect can be important when the transport of Cd in soil to the roots limits the rate of uptake from soil. Moreover, recent experiments in solution culture conducted by (Smolders and McLaughlin, 1996b) suggested that chloro-complexed Cd may be taken up by plants, along with the free Cd^{2+} species.

The concentration of Cl in soils can be more important than soil pH in its influence on phyto-availability of Cd (McLaughlin *et al.*, 1994). Experiments examining the influence of Cl on Cd uptake by plants have been carried out with agricultural soils where Cd has been derived from phosphatic fertiliser or where the soils were amended with an inorganic Cd salt. The purpose of the current study was to determine if chloro-complexation of Cd is also important in mobilising sludge-Cd as has been determined for fertiliser Cd. The effect of increasing Cl (NaCl) additions on Cd concentrations in soil solution and plant shoots of two plant species grown in a sludge-amended soil were investigated.

8.3 Material and methods

Four independent pot experiments were conducted to examine the influence of sodium chloride (NaCl) on Cd phyto-availability in two plant species and two sludge-amended soils. The four experiments used the following plant species and soils:

Experiment 1: Lameroo soil	wheat	(*T.aestivum* L.cv. Halberd)
Experiment 3: South -East soil	wheat	(*T.aestivum* L.cv. Halberd)
Experiment 2: Lameroo soil	Swiss chard	(*Beta vulgaris* L.cv. Fordhook Giant)
Experiment 4: South -East soil	Swiss chard	(*Beta vulgaris* L.cv. Fordhook Giant)

8.3.1 Sewage sludge

For the pot experiments a mix of Bolivar and Port Adelaide sludge in the ratio 1:1 was used. The Bolivar sludge was the sludge used in the field experiments (for further details see Chapter 3). The Port Adelaide sludge was taken as liquid sludge, ex anaerobic digester, and air dried in a shallow pond. Both sludges were ground to a fine powder and mixed in the ratio 1:1. The sludge mix then was leached with deionised water to reduce the NaCl content. A plastic grid covered with filter paper was placed halfway into a bucket containing a draining hole. The sludge material was moistened and was placed about 10 cm deep onto the grid. Deionised water was added until the sludge material was covered with a liquid layer and left undrained for 12 hours. Afterwards free drainage was allowed and deionised water was added until the leachate reached a stable EC of around 3.5 dS cm^{-1}. The sludge was air dried (60°C) and ground again. The metal and salt contents of the Bolivar and Port Adelaide sludges and the sludge mix used are listed in Table 8.1.

A preliminary experiment to establish the heavy metal and organic matter losses during the leaching process was conducted. Thirty g of air dry sludge (27 g dry matter) was leached in a syringe with about 450 ml deionised water, until the EC reached a stable point (< 3.5). After the first addition of water the syringe was kept undrained for 12 hours, and then water additions of 10 ml were added, when the syringe had drained. In this experiment a loss of dry matter of ± 26 % sludge was observed. Only a small amount of organic matter was lost ± 1.7 % sludge . There loss of dry matter consisted mainly of soluble salts, ± 17 % of Cl ions and about ± 12 % of other ions (Na, Mg, K, P, S) . The loss of Cd was estimated by sludge analyses before and after leaching. Cadmium concentrations in the leachate were low (mainly < 0.0015 mg Cd l^{-1}, see Section 9.4.1), but analyses were unreliable due to interferences by the high salt content.

The sludge Cd concentration increased from 13.9 to 14.8 mg kg^{-1} after the leaching process. The actual increase in Cd concentration was predominantly due to a loss in dry matter. Taking this concentration effect into account about 4 mg kg^{-1} Cd was lost.

Cd sludge 13.9 mg kg^{-1} prior leaching
(dry matter loss of 26% concentrates unleached elements by a factor of 1.35)
Cd sludge 18.8 mg kg^{-1} concentration expected after leaching if no losses occurred
($13.9*1.35= 18.8$ mg kg^{-1})
Cd sludge 14.8 mg kg^{-1} concentration after leaching

Table 8.1 Metal and salt content of the Bolivar sludge, Port Adelaide sludge and the sludge mix used in the pot experiments.

Element		Bolivar sludge	Port Adelaide sludge	Sludge-mix, leached
			[mg kg^{-1}]	
Cadmium	Cd	3.5	20.8	14.8
Chromium	Cr	1623*	n.d.	n.d.
Nickel	Ni	80*	n.d.	n.d.
Lead	Pb	340*	n.d.	n.d.
Zinc	Zn	939	1468	1530
Copper	Cu	723	1213	1142
Manganese	Mn	220	78	214
Cobalt	Co	10	n.d.	8.1
Molybdenum	Mo	6	22	7.6
Aluminium	Al	58225	6413	24780
Iron	Fe	18324	13742	20708
Phosphorus	P	17971	13124	19132
Calcium	Ca	56502	24959	48456
Magnesium	Mg	10176	19526	11722
Potassium	K	10397	10885	3596
Boron	B	86	110	94
Sodium	Na	19598	114000	2507
Chloride	Cl	22000	-	-

* analysed by the State Water Laboratory, Bolivar

8.3.2 Soils

Two sandy top soils differing in pH were used in the experiment. Selected chemical properties of the two soils are listed in Table 8.2. The soil was air dried prior to the experiment and ground with a soil mill, constructed by CSIRO-Adelaide, which uses rubber bands to crush the soil clods to ensure least possible contamination with metals.

Table 8.2: Selected soil properties and soil classification of the soils used in the pot studies.

Soil	Lameroo Soil	South East Soil
pH ($CaCl_2$) (soil:water=1:5)	6.3	4.6
EC [dS m^{-1}](soil:water=1:5)	0.35	0.45
Organic matter [%] [a]	1.2	2.6
Clay/ silt/ f.sand/c.sand [%][b]	3/ <1/ 37/ 58	5/ 8/ 50/ 33
CEC [cmol kg^{-1}][c]	4.1	2.7
Total Cd [mg kg^{-1}][d]	0.12	0.070
EDTA-soluble Cd [mg kg^{-1}][e]	0.0487	0.0162
Total Zn [mg kg^{-1}][d]	4.8	3.6
EDTA-soluble Zn [mg kg^{-1}][e]	0.59	1.56
Soil classification[f]	Xeralf	Xeralf

[a] Total C analyzer (Leco)
[b] USDA, Soil Conservation Service (1982).
[c] Rayment and Higginson (1992)
[d] Digestion in conc.HNO3, analysed by ICP
[e] Clayton and Tiller (1975)
[f] Soil Survey Staff (1990)

8.3.3 Experimental procedure

Polypropylene pots, 15 cm high and 7 cm in diameter were used. 20 g air dried sludge mix, the equivalent of 50t ha^{-1}, was mixed into 480 g soil. (A soil bulk density of 1.3 t m^3 and 10 cm soil depth was assumed for the conversion of t ha^{-1} to g kg^{-1}; 1 ha = 1300t soil; 50t sludge in 1300t soil = 0.038 kg sludge in 1 kg soil.). Basal nutrients (see Table 8.3.) were applied and undrained pots watered to 70% total water capacity (water saturation), which was 20 and 23 % moisture content (w/w) respectively for the two soils. Pots were covered and incubated in a controlled environment chamber (set on a 20/15 °C day/night cycle) for 2 weeks before planting. Seeds of wheat and Swiss chard were pre-germinated at room temperature in moist petri dishes for 2 days and 4 days respectively. Seedlings were then transplanted, covered with 20 g soil and a layer of black plastic beads. Prior to planting Swiss chard seedlings, the incubated soil sludge mixture was drenched with Fongarid (active ingred.: Furalaxyl; Ciba Geigy Limited). Seedlings were planted one week after drenching. Other plant cultivation was similar to wheat. The remaining basal nutrients (see Table 8.3) were diluted with irrigation water and added after seeding. Initially 7 plants per pot were planted and thinned to 5 plants after 7 days. Additional N fertiliser was given during the growth period. In Experiment 1 and 2 $(NH_4)_2SO_4$ was used as the N fertiliser during the growth period to reduce soil pH, because a side study revealed a high pH of Lameroo soil incubated with sludge. In Experiment 3 and 4, with a soil with lower pH $Ca(NO_3)_2$ fertiliser was used. The experiments were conducted in a growth chamber at a 20/15°C day/night cycle.

Treatments were: five levels of irrigation water salinity with NaCl concentrations of 0, 400, 800, 1200, 1600 mg l^{-1} in Experiment 1 and 2 and four levels of salinity with NaCl concentrations of 0, 800, 1200, 1600 mg l^{-1} in Experiment 3 and 4. This is equivalent to chloride (Cl) concentrations in irrigation water of 6.8, 13.7, 20.5, 27.4 mM. There were 4 replicates per treatment. The saline irrigation water was used to moisten the soil prior to incubation as well as daily watering of plants. The quantity of irrigation water applied was recorded and absolute amounts of NaCl added per pot over time were calculated.

Table 8.3 Basal fertiliser additions in Experiment 1 to 4.

	Exp. 1 Wheat	Exp. 3 Wheat	Exp. 2 S.chard	Exp. 4 S.chard
		[mg kg^{-1}]		
KH_2PO_4	136*	136*	136*	136*
$KHSO_4$	136#	136*	136#	136*
$MgSO_4 * 7H_2O$	148#	148*	148#	148*
$Ca(NO_3)_2 * 4H_2O$	314#	314#	314#	314#
$MnSO_4 * 4H_2O$	3.7*	3.7*	3.7*	3.7*
$ZnSO_4 * 7H_2O$	7*	7*	7*	7*
		applied during the growth period		
$Ca(NO_3)_2 * 4H_2O$		629		629
$(NH_4)_2 SO_4$	176		176	

(* applied prior to soil incubation; # applied after seeding)

8.3.4 Analysis of plants and soil solution

Plants: After approximately 30 days plant shoots were cut above ground and wheat shoots were washed in a solution of 1% Dextran prior to drying. Shoots of wheat and Swiss chard plants were dried in a forced air oven at 70°C for 24 hours, digested in concentrated HNO_3 and analysed for Ca, K, Mg, Mn, Zn, S, Mo using an inductively coupled plasma emission spectrometer (ICP). Shoot Cd concentrations in Swiss chard were analysed by ICP; Cd concentration in wheat shoots were analysed by graphite furnace atomic absorption spectrophotometry (GFAAS) (Varian, SpectrAA 400) (p. 255a, 255b).

Soil Solution: Soil solution was displaced from the soil according to the method of Thibault and Sheppard (1992) by centrifugation at 4000 RCF for 30 min. Extracted solutions were centrifuged at 25000 RCF for 60 min. and filtered through a 0.2 µm filter. The pH, EC and alkalinity of the solutions were determined immediately. Anions in solution (SO_4^{2-}, NO_3^-, Cl^-) were determined by ion chromathoghraphy (Dionex 4000i using a AS4A column) and cations (Ca, K, Mg, Mn, Zn, Cu, Fe) and P by ICP. Organic Carbon was analysed with a Total Organic Carbon Analyser, Dohrmann DC 180 (Rosemount Analytical Inc.) using an ultra-violet-promoted persulphate oxidation. The

DC-180 complies with EPA method 415.1 and standard method 5310C. Cadmium concentrations in solution were determined by GFAAS.

Activities of free Cd^{2+}, and $CdCl^{+}$, $CdCl_2^{o}$ complexes were calculated using the computer program GEOCHEM-PC (Parker *et al.*, 1995). The *mixture model* according to Sposito and Bingham (1981) was used to convert soluble organic carbon concentrations to a form useable by GEOCHEM-PC. This model gives an approximate description of the functional group chemistry of the sewage sludge dissolved organic carbon insofar as it relates to the formation of trace metal complexes.

The *mixture model* consists of a set of organic acids whose reactions with trace metal cations are well characterised and whose functional groups are known to exist also in the soluble organic fraction of treated sewage. The quantitative distribution of organic acids in the model is determined by the organic carbon concentration in the sewage natural water system to be modelled (Sposito and Bingham, 1981) (and by any other available data pertinent to the functional group chemistry of the sewage). The Mattigod and Sposito model, used in the current Experiment, comprises aliphatic, aromatic, and amino acids that were selected on the basis of analytical data to describe the fulvic acid fraction of sewage sludge (Sposito and Bingham, 1981). The model is applied to the experimental data by calculating a ratio between the measured dissolved organic carbon concentration and the total organic carbon concentration of sewage sludge fulvic acid that corresponds to the concentrations of the set of organic acids of the model. The molar concentration of any one of the nine acids in the model, then, is equal to the product of this ratio and the molar concentration of the particular acid established for the model. (Acids in the model (in µM): benzenesulfonic (53.7), citric (72.4), maleic (107.2), phthalic (107.2), salicylic (53.7), arginine (32.4), lysine (43.7), ornithine (43.7), valine (43.7); (Sposito and Bingham, 1981)). The calculated total molar concentration of the nine organic acids are then used in the computer program GEOCHEM along with the analytical data for the inorganic components.

The chemical speciation program GEOCHEM-PC can be run as 'open' or 'closed' system in terms of interaction of CO_2 gas with the atmosphere. Closed systems do not allow for transfer of C into or out of the system. When pH and alkalinity are known, but pCO2 and disolved inorganic carbon (DIC) are unknown, as in the current case, it is recommended to run the model as a closed system, where no gas phase is considered (Suarez, 1995). The approximated value for DIC should be adjusted until the calculated alkalinity is equal to the known analytical value (Suarez, 1995; Parker *et al.* 1995) or the charge error (difference in positive and negative charges in solution) is zero (Parker *et al.*, 1995). The activities of Cd species in solution in the current study were calculated specifying a closed system. When DIC values were adjusted such that the calculated alkalinity was close to the measured alkalinity, the remaining charge error then was calculated to be around ± 15 %. An adjustment of DIC values to minimise charge error and gain the matching alkalinity output at the same time is not possible.

The calculations in a closed system mode do not provide satisfactory results when solid phases are included in the calculations (Suarez, 1995). However, in the current calculations precipitation was disallowed because the displaced soil solutions were clear and no precipitates were noticed. It is possible that the solution was oversaturated for some components, but it was considered more important to describe the solution as analysed even though it may not have been in chemical equilibrium.

8.4 Results

All values shown in Tables 8.4, 8.5, 8.7 and 8.8 on page 184, 185, 187 and 187 respectively are the mean of 4 replicates.

8.4.1 Experiments 1 and 3: Cd concentration in soil solution and shoots of wheat plants

The effect of sodium chloride (NaCl) additions and Cl concentration in soil solution on the Cd concentration in soil solution and shoots of wheat plants is shown in Table 8.4. Plant dry matter production was unaffected by salt treatments (see Table 8.4). The soil pH was similar across the various salt (NaCl) treatments and was 7.7 and 7.4 in Experiments 1 and 3 respectively. Sludge addition increased soil pH from 6.3 to 7.7 and 4.6 to 7.4 for the Lameroo and South East soil, respectively. The soil solution alkalinity was also unaffected by salinity treatments and was 4.4 and 4.8 meq l^{-1} as CO_3^{2-} in Experiments 1 and 3 respectively. Further concentrations of selected elements in soil solution and shoots are listed in the Appendices, Table A.8.1 - A.8.4. With Cl concentrations of between 0 and 120 mM in the soil solution a significant increase of Cd in soil solution and shoots in both sludge-amended soils was noticeable. The increases in solution Cd were similar in both soils (slopes of the regression curve), but the Cd concentrations in shoots grown in Lameroo soil were increased more than in the South East soil. Wheat plants grown in Lameroo soil also showed higher Cd concentrations (intercept) with 0.24 and 0.11 mg Cd kg^{-1} in the nil-NaCl treatments in the Lameroo and South East soil respectively.

Table 8.4 The effect of NaCl addition and Cl concentration in soil solution on shoot dry weight and Cd concentration in soil solution and shoots of wheat plants, grown on two sludge-amended soils (Experiments 1 and 3). (** F significance $P < 0.01$)

Irrigation water [mg NaCl l^{-1}]	NaCl added [mg kg^{-1}]	Cl soil solution [mM]	Cd soil solution [$\mu g\ l^{-1}$]^a	Cd shoot [mg kg^{-1}]	shoot dry weight [g pot^{-1}]
Exp. 1 , wheat, Lameroo soil					
0	0	0	3.4	0.23	1.38
400	472	33	6.3	0.30	1.32
800	944	68	10.9	0.37	1.56
1200	1156	82	12.6	0.35	1.31
1600	1412	117	17.8	0.41	1.22
LSD					*n.s.*
Model			**$0.12(Cl)+2.7$**	**$1.4*10^{-3}(Cl)+0.24$**	
F signif.			**	**	
R^2			0.62	0.75	
Exp. 3, wheat, South East soil					
0	0	3	3.4	0.11	1.03
800	724	52	9.6	0.14	0.99
1200	972	67	10.9	0.15	0.91
1600	1236	87	13.5	0.17	0.87
LSD					*n.s.*
Model			**$0.12(Cl)+3.3$**	**$0.62*10^{-3}(Cl)+0.1$**	
F signif.			**	**	
R^2			0.92	0.81	

[a] Units used for solution Cd are [$\mu g\ l^{-1}$] for comparison with the papers of Smolders *et al.* (1995).

8.4.2 Experiments 2 and 4: Cd concentration in soil solution and shoots of Swiss chard plants

Cadmium concentrations in soil solution and Swiss chard shoots as affected by NaCl additions and Cl concentration in the soil solution are listed in Table 8.5. In both experiments the pH and alkalinity of the soil solution was unaffected by the NaCl treatments with a pH of 7.5 and 7.6 and alkalinity of 4.8 and 4.6 meq l^{-1} as $CO_3{}^{2-}$ respectively for the Lameroo and South East soils. Further concentrations of selected elements in soil solution and shoots are listed in the appendices, Table A.8.1 - A.8.4. Shoot growth was unaffected by the NaCl treatments. Cadmium concentrations in soil solution and in shoots were significantly positively correlated with the soil solution Cl concentrations in both sludge-amended soils.

The increases in Cd concentrations (solution and shoots) were however more pronounced in the Lameroo soil with slopes of the regression curves being higher than in the South East soil. Cadmium concentrations in soil solution were increased to a greater extent by increasing Cl than the shoot Cd concentrations.

Table 8.5 The effect of NaCl addition and Cl concentration in soil solution on shoot dry weight and Cd concentration in soil solution and shoots of Swiss chard plants, grown on two sludge-amended soils (Experiments 2 and 4) (F significance * $P< 0.05$, **$P<0.01$).

Irrigation water [mg NaCl l^{-1}]	NaCl added [mg kg^{-1}]	Cl soil solution [mM]	Cd soil solution [$\mu g\ l^{-1}$]	Cd shoot [mg kg^{-1}]	Shoot dry weight [g]
Exp.1, Swiss chard, Lameroo soil					
0	0	1	4.9	1.95	0.68
400	152	21	8.3	2.12	0.62
800	328	47	9.9	2.68	0.75
1200	480	68	13.4	2.65	0.68
1600	636	96	16.0	2.96	0.69
LSD					***n.s.***
Model			0.11(Cl)+5.3	$11*10^{-3}$ (Cl)+2.0	
F signif.			**	**	
R^2			0.75	0.69	
Exp. 3, Swiss chard, South East Soil					
0	0	5	1.9	1.22	0.80
800	596	30	3.9	1.43	0.72
1200	892	46	3.9	1.60	0.71
1600	1196	71	6.4	1.53	0.77
LSD					***n.s.***
Model			0.067Cl)+1.5	$4.6*10^{-3}$ (Cl)+1.3	
F signif.			**	*	
R^2			0.93	0.34	

8.4.3 Summary of regression models

A summary of calculated regression models for the influence of Cl concentration in soil solution on the Cd concentration in soil solution and plant shoots is given in Table 8.6. Smolders *et al.* (1995) using a similar experimental design as in the current study, also found a significant influence of soil Cl levels on Cd availability in non sludge-amended soils. The comparable models in the study of Smolders *et al.* (1995) were $Y=0.28$ (Cl)+5.1 or

$Y=0.28(Cl)+1.0$ for the models describing the relation of Cl and Cd concentration in soil solution for two soils. The regression models for shoot Cd were $Y=0.01(Cl)+1.3$ or $Y=0.01(Cl)+2.2$ for the two soils. Comparing regression models for soil solution Cd concentration, it is apparent that slopes in the current study are similar in three of the four experiments. Regression models of solution Cl and Swiss chard Cd concentration in one of the current studies (Swiss chard in Lameroo soil, Exp. 2) was similar to the results in the study of of Smolders *et al.* (1995). The model for Experiment 4 shows a somewhat lower slope than the other three experiments.

Table 8.6 Comparison of regression models for the correlation of Cd in soil solution and plant shoots in Experiments 1, 2, 3 and 4. (Lameroo soil = La; South East Soil=SE)

Cd in soil solution	**(soil)**	**Cd in plant shoots**	**(soil)**
Wheat		**Wheat**	
Exp.1: $Y=0.12\ (Cl)+2.7$	(La)	*Exp.1:* $Y=0.0014\ (Cl)+0.24$	(La)
Exp.3: $Y=0.12\ (Cl)+3.3$	(SE)	*Exp.3*: $Y=0.00062\ (Cl)+0.11$	(SE)
Swiss chard		**Swiss chard**	
Exp.2: $Y=0.11\ (Cl)+5.3$	(La)	*Exp.2:* $Y=0.011\ (Cl)+2.0$	(La)
Exp.4: $Y=0.067\ (Cl)+1.5$	(SE)	*Exp.4:* $Y=0.0046\ (Cl)+1.3$	(SE)

8.4.4 Cadmium speciation in soil solution

The free Cd^{2+} activity in soil solution as well as the activity of the major Cd-chloro-complexes as calculated by the computer program GEOCHEM-PC are listed in Table 8.7 and 8.8 for the wheat and Swiss chard Experiments, respectively. The $CdCl^{+}$ activity in soil solution showed the highest correlation with plant Cd uptake in all four Experiments. Cadmium uptake by plants was also significantly correlated with the $CdCl_2^0$ activity in solution, but R^2 values were lower than for the correlation with $CdCl^{+}$ activities. In general there was no (Swiss chard experiments) or only a weak correlation (wheat experiments) between Cd^{2+} activity in soil solution and Cd concentration in plants.

Table 8.7 Total Cd concentration and Cd speciation in soil solution and transfer coefficient (Cd shoot [mg kg^{-1}]/(total Cd in solution [mg l^{-1}])) as affected by NaCl addition to sludge-amended soil. Experiments 1 and 3: Wheat grown in Lameroo soil and South East soil. Treatment effects are calculated using linear regression.

Irrigation water [mg NaCl l^{-1}]	Cd shoot [mg kg^{-1}]	Cd^{2+} activity [nM]	$CdCl^+$ activity [nM]	$CdCl_2^0$ activity [nM]	Transfer coefficient [l kg^{-1}]
Exp. 1, wheat, Lameroo soil					
0	0.23	4.9	0.2	0.0	75
400	0.30	4.9	11.7	1.1	53
800	0.37	7.2	35.2	7.1	39
1200	0.35	7.5	40.7	9.2	29
1600	0.41	7.8	66.6	22.5	26
F signif.		***n.s.***	**	**	***LSD=23.7***
R^2			***0.64***	***0.56***	
Exp. 3, wheat, South East soil					
0	0.11	4.8	1.1	0.0	33
800	0.14	7.5	28.8	4.4	14
1200	0.15	7.2	35.0	7.1	14
1600	0.17	7.5	46.9	11.7	13
F signif.		**	**	**	***LSD=6.7***
R^2		***0.60***	***0.81***	***0.73***	

(**F significance $P<0.01$; LSD $P=0.05$)

Table 8.8 Total Cd concentration and Cd speciation in soil solution and transfer coefficient (Cd shoot [mg kg^{-1}]/(total Cd in solution [mg l^{-1}])) as affected by NaCl addition to sludge-amended soil. Experiments 2 and 4: Swiss chard grown in Lameroo soil and South East soil. Treatment effects are calculated using linear regression.

Irrigation water [mg NaCl l^{-1}]	Cd shoot [mg kg^{-1}]	Cd^{2+} activity [nM]	$CdCl^+$ activity [nM]	$CdCl_2^0$ activity [nM]	Transfer coefficient [l kg^{-1}]
Exp. 2, Swiss chard, Lameroo soil					
0	1.95	7.4	0.3	0.0	411
400	2.12	8.8	13.7	0.9	268
800	2.68	8.1	27.3	3.8	271
1200	2.65	8.3	40.0	7.9	225
1600	2.96	8.7	58.6	15.9	187
F signif.		***n.s.***	**	**	***LSD=111***
R^2			***0.66***	***0.60***	
Exp.4, Swiss chard, South East soil					
0	1.22	2.7	1.1	0.0	655
800	1.43	3.9	8.8	0.8	370
1200	1.60	3.3	11.5	1.6	430
1600	1.53	4.1	21.5	4.5	241
F signif.		***n.s.***	*	***n.s.***	***LSD=153***
R^2			***0.27***		

(*F significance $P<0.05$; ** F significance $P<0.01$; LSD $P=0.05$)

8.5 Discussion

The four experiments using sludge-amended soils have shown that NaCl additions, through increasing Cl concentrations in the soil solution, had a major influence on Cd concentration in shoots of both plant species. Increasing NaCl additions increased Cd concentration in both wheat and Swiss chard shoots. Total Cd in soil solution was likewise considerably increased by salt additions.

In all four experiments a highly significant correlation between Cl concentration and total Cd in solution existed. Other soil solution components remained mainly unchanged or did not show such a strong correlation, except for the Na concentration. An increase in Na and Cl concentration in the soil solution can have various effects on soil chemistry and root function and could influence adsorption/desorption mechanisms or root uptake functions. Cation exchange of Na for Cd could displace Cd from soil adsorption sites and increase Cd concentrations in solution. Also the change of ionic strength in solution could influence the surface charge in soils with variable charge and thus indirectly cause mobilisation of cations. However, Smolders *et al.* (1995) have shown that increasing levels of Na or ionic strength (as $NaNO_3$) in soil solution did not cause significant increases in solution Cd levels in the two soils used. Also in the current experiment there was generally no increases in the activity of free Cd^{2+} cations due to the increase in ionic strength. Hence it is likely that the cation exchange of Na for Cd had a minimal effect on solution Cd^{2+} activities. Also the effects of Na concentration or ionic strength on root function or membrane permeability were shown to have no major influence on Cd uptake of plants at the similar ionic strengths to those used here (Smolders *et al.*, 1995 and 1996). Evidence from those results therefore suggests that chloro-complexation of Cd is the major effect causing elevated Cd levels in soil solutions high in Na.

Regression models describing the influence of solution Cl concentration on soil solution Cd in the current experiments showed similar slopes for three of the four experiments, with the slope for Experiment 4 (Swiss chard grown in South East soil) being somewhat lower. This would suggest that influences of Cl on Cd availability was to some extent independent of the soil used. However, both soils were light sandy soils and chemistry of the soils was likely to be strongly influenced by the sludge amendment of 50t per hectare. Smolders *et al.* (1995), in a pot study using two agricultural soils, also found a significant relation for Cl and Cd concentration in solution with correlation models showing slightly but consistently higher slopes than models in the current experiments. This was the case although the total Cd concentration in the sludge-amended soil used in the current study was higher than in the soils used by Smolders *et al.* (1995 and 1996). This could indicate a stronger mobilizing effect of Cl on Cd in their study on fertiliser Cd than in the current study on sludge-Cd. It is possible that sludge Cd might react differently to complexing ligands such as Cl than fertiliser Cd. Chloride levels and soil type were fairly similar in both this study and the study of Smolders *et al.* (1995 and 1996) except for a lower soil pH of 4.6 in their experiments. The addition of sludge in the current study raised soil pH to 7.4 and 7.7 depending on the experiment. The difference in soil pH could be a factor explaining the more pronounced mobilisation of soil Cd in their study. Soil pH is generally considered a major factor determining Cd uptake by plants (Alloway, 1990). The effect of soil pH or liming on the total Cd concentration in soil solution however is not as clear. Similar or increased solution Cd concentrations after liming (Bingham *et al.*, 1986) as well as reduced Cd concentrations in solution (Bingham *et al.*, 1984) were reported. Lime additions increase soil pH and metal adsorption. However, the increased Ca^{2+} concentration in solution after liming could also compete with Cd^{2+} for soil adsorption sites (Boekhold *et al.*, 1993) and hence decrease Cd adsorption.

A close correlation between Cl concentration in soil solution and Cd concentration in plants was also observed in all four experiments. The Cd uptake of Swiss chard plants was considerably higher than by wheat plants with the slope and intercept of calculated regression curves differing by about a factor of 10. Also the transfer-coefficient for Swiss chard plants was 6 to 20 times higher than for wheat plants. This is in agreement with numerous studies showing that the Cd uptake by leafy vegetables (for example, Swiss chard) is considerably higher than by cereal plants (Sauerbeck and Styperek, 1987b). However, in both plant species, Cd uptake was considerably enhanced by increased Cl levels in the soil solution.

Soil salinity influenced plant Cd uptake more in the Lameroo soil (slope of the regression model) than in the South East soil for both plant species (Experiments 1 and 2 compared to Experiments 3 and 4). In one of the experiments (Swiss chard in South East Soil) the lower slopes in the regression model were in agreement with the change in soil solution Cd. It could be hypothesised that the South East soil with a lower soil Cd content and a lower EDTA-extractable Cd concentration compared to the Lameroo soil could have a smaller fraction of weakly adsorbed Cd likely to be complexed by Cl anions. This hypothesis could explain the lower slopes in the regression curves for soil solution Cd concentration in the South East soil compared to the Lameroo soil. Alloway (1990) found the total amount of Cd present in soil as one of the major factors affecting the Cd content of plants. This would suggest that the plant-available Cd was influenced by the soil Cd level and not by the sludge Cd addition, which was similar in both soils. However the results with wheat plants did not show a clear difference in Cd availability for the two soils. In Experiment 3 (wheat in SE soil-sludge mix), soil solution Cd was enhanced similarly to Experiment 1 (wheat in Lameroo soil) but plant Cd concentrations were increased less. A difference in N nutrition could have caused the discrepancy, because it was shown by Florijn *et al.* (1992) that plants grown on NH_4^+ (in solution culture) have a higher Cd uptake than plants grown on NO_3^-. Various other factors such as plant growth stage, evaporation rate influencing uptake of nutrients by mass flow, or a difference in soil solution composition of cations could have influenced the Cd plant uptake rate. However, for each plant the observed regression curves for Cd uptake as influenced by Cl concentration in solution for the two soils are quite similar, which suggests that soil Cl concentration is the main factor determining Cd availability in the two sludge-amended soils. The dominant role of Cl is also clear in the findings of Smolders *et al.* (1995 and 1996) and McLaughlin *et al.* (1994).

Evidence suggests that bio-availability of metal cations is determined by their speciation in solution rather than the total concentration of the element under consideration (Checkai *et al.*, 1987). The speciation of Cd in soil solution was considerably changed by NaCl, or more precisely, the Cl additions to the soil. Findings up to now are still inconclusive in terms of phyto-availability of Cd species such as $CdCl^+$ or $CdCl_2^o$ compared to the free metal cation Cd^{2+}. Earlier findings suggested that the metabolically active uptake of Cd is related to the ionic activity rather than the concentration in solution (Checkai *et al.*, 1987; VanErp and VanLune, 1989). However, it was shown by Smolders and McLaughlin (1996a,b) that the $CdCl^+$ concentration in solution plays a major role in terms of bioavailability of Cd. Whether this effect is by allowing diffusion of Cd in the root zone to sites of Cd uptake (through the unstirred liquid layer adjacent to the root surface or through the apoplast) or if $CdCl^+$ is a phytoavailable form itself could not be distinguished, but phytoavailability of chloro-complexed Cd species seemed the most likely explanation (Smolders and McLaughlin, 1996b). In the current study the Cd-chloro-complexes were the dominant species in the solution with increasing Cl levels in soil solution. Shoot Cd concentration showed the closest correlation with the $CdCl^+$ concentration in solution. Correlation with the $CdCl_2$ species in solution was also significant in most of the cases, but R^2 values were in general lower. However the free Cd^{2+} activity was not correlated at all with Cd uptake in the Swiss chard experiments. In the wheat experiments a correlation was observed in Experiment 3, where the Cd concentration in wheat shoots were not as strongly enhanced by the NaCl treatment as in Experiment 1. In Experiment 1, where differences in shoot Cd concentration were more pronounced, the $CdCl^+$ activity was more closely correlated to plant Cd concentration than the Cd^{2+} activity. These findings, in agreement with the results of Smolders *et al.* (1995 and

1996), suggest that Cd-chloro species play a dominant role in enhancing Cd uptake by plants. The observed weak correlation of Cd^{2+} species with Cd uptake in wheat, but not in Swiss chard plants is unlikely to be based on differences between plant species, as can be seen from the results in Chapter 9, where Cd^{2+} activity in soil solution did not show any correlation to Cd concentration of wheat plants.

Another major influence of increased NaCl additions to the soil was the increased manganese (Mn) concentration in soil solution and in plant shoots in three of the four experiments (exception: Swiss chard grown in South East soil, Exp. 4). Whether influences of cation concentration or ionic strength on adsorption/desorption mechanism or chloro-complexation of Mn has caused the increase of solution Mn can not be conclusively answered. However, it has been noticed that the main inorganic complexes of Mn^{2+} in soil solution are formed with SO_4^{2-}, HCO_3^- and Cl^- (Lindsay, 1979). Speciation by GEOCHEM for the current study showed that the free Mn^{2+} cation was the most abundant species in solution. Sulfate complexes comprised about 20% and chloro complexes increased from <1% to around 7% with increases in Cl concentration (data not shown). The increasing chloro-complexation of Mn may interfere to some extent with adsorption mechanisms of this element. However, the increasing Na or ionic strength influences on adsorption of Mn may also have contributed to the resulting increase of Mn in solution. Khattak and Jarrell (1989) reported a salt dependent increase in the Mn concentration of soil saturation extracts in four Californian soils treated with a NaCl-$CaCl_2$ solution. Gomez *et al.* (1993) using saline irrigation in a tomato crop found increased Mn concentration in leaves due to NaCl additions but Zn concentration remained unchanged or decreased. A small but significant increase in shoot Zn levels in the wheat experiments was detected. However, the differences in Zn concentration in soil solution with NaCl addition were insignificant.

8.6 Conclusions

•The Cd concentration in soil solution and plant shoots of wheat and Swiss chard plants, grown in sludge-amended soils, increased linearly with increasing Cl concentration in soil solution

-The increase in Cd concentration in solution due to Cl concentration was similar for both sludge-amended soils (slopes of regression models).

-The increase in Cd concentration in shoots due to Cl concentration was more pronounced in the Lameroo soil (slope of regression model).

•$CdCl^+$ activity showed the best correlation with Cd uptake of plants for both plant species. Increases in shoot Cd concentrations were unrelated or only weakly correlated to the activity of the free Cd^{2+} ion in solution.

•Increased NaCl (Cl) additions increased the Mn concentration in soil solution considerably. Manganese concentrations in shoots of wheat plants were also increased, and likewise for Swiss chard in one of the two experiments.

•Zinc concentrations in wheat shoots were increased by the NaCl treatment.

Chapter 9

Influence of sludge rate and sodium chloride (NaCl) addition on Cd phyto-availability in sludge-amended soils

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9.1 Introduction

An increase in Cl concentration in the soil or soil solution was shown to increase Cd concentration in plants (Bingham *et al.*, 1983, Bingham *et al.*, 1984; Li *et al.*, 1994; McLaughlin *et al.* 1994, Smolders *et al.*, 1996, Smolders and Mclaughlin, 1996a,b; Chapter 8). Chloro-complexation of Cd and the resulting improved diffusion of Cd through the soil to plant roots and possibly uptake of Cd-chloro complexes were suspected to be the reasons for the Cl effect on Cd uptake (McLaughlin *et al.*, 1994, Smolders and McLaughlin, 1996b and c). However, none of the studies examined the effect of Cl on sludge-Cd. The experiments described in Chapter 8 have shown that increasing Cl concentration in soil solution enhances the plant uptake of Cd in soils amended with sewage sludge. Although the sludge addition provided 83 % and 89 % of the total Cd in the soil sludge mix of the Lameroo and South East soils respectively, it cannot necessarily be concluded that the plant available Cd was sludge-Cd. The increasing Cl concentration in the soil-sludge mixture could equally have mobilised soil-Cd, as has been shown by the studies cited above. Presumably, sludge-Cd was also mobilised, but the two effects could not be distinguished in the previous study (Chapter 8). The aim of the current experiment was to determine to what extent the sludge-Cd is mobilised by increasing Cl concentrations in soil solution. A factorial experiment with increasing sludge rates (the equivalent of 0-100t ha^{-1}) and increasing NaCl additions (0-1600 mg NaCl l^{-1}) was conducted to differentiate between the influence of chloro-ligands on soil and sludge-Cd.

9.2. Material and methods

A factorial experiment using varying sludge rates and irrigation water qualities was conducted. The experimental protocol was similar to Experiment 1 detailed in Chapter 8.

9.2.1 Sewage sludge

The same sludge mix (leached) as in Chapter 8 (Bolivar and Port Adelaide sludge mixed in the ratio 1:1) was used for the experiment. The sludge was leached as described in Chapter 8. For description of the sludge see Table 8.1 and Tables 3.2 and 3.3 in Chapter 3.

9.2.2 Soil characteristics

A sandy topsoil, described as Lameroo soil was used for the experiment. For selected soil properties see Table 8.2, Chapter 8.

9.2.3 Experimental set-up

Polypropylene pots, 15 cm high and 7 cm in diameter, which hold 500 g dry soil were used. Nil, 10, 20 and 40 g air dried sludge equivalent to 0, 25, 50 and 100 t ha^{-1} respectively , was mixed into 480 g soil. The control pots received a $CaCO_3$ amendment of 0.25 g kg^{-1} to increase soil pH to a level similar to the sludge treatments. Basal nutrients as listed in Table 9.1 were mixed into the soil and pots were incubated at 70% water holding capacity for 2 weeks in a controlled environment chamber, set on a 12h/12h 15/10°C day/night cycle similarly to experiments described in Chapter 8. The control pots received additional N, P and micronutrients as listed in Table 9.1 to compensate for sludge nutrients assumed to have been released during the growth period. Based on results from the field experiments in 1992 and 1993, cautious assumptions in terms of sludge N, P, Zn and Cu availability within a growth period of 30 days were taken. For N and P the equivalent of 5 kg nutrient per tonne sludge per hectare and for Cu and Zn 10 percent of the total content in sludge was assumed to be plant available. The control treatment received the equivalent of N, P, Zn and Cu of a

25t sludge addition plus the basal fertiliser, added to all treatments. Seeding of *T. aestivum* L. cv. Halberd and plant care, watering and environmental conditions were similar as in Experiment 1 and 3 in Chapter 8.

Treatments were: five levels of irrigation water salinity with NaCl concentrations of 0, 400, 800, 1200, 1600 mg l^{-1} equivalent to chloride (Cl^-) concentrations of 6.8, 13.7, 20.5, 27.4 mM. There were 4 replicates per treatment. The saline irrigation water was used to moisten the soil as well as daily watering of plants to 75% field capacity. The quantity of irrigation water applied was recorded and absolute amounts of NaCl added per pot calculated.

Table 9.1 Basal fertiliser additions in Experiment 5.

	Control no sludge	Sludge-amended plots
	mg kg^{-1}	
$CaCO_3$	250*	-
$MgSO_4*7H_2O$	148*	148*
$KHSO_4$	136*	136*
KH_2PO_4	558*	136*
$(NH_4)_2SO_4$	123#	48*
$MnSO_4*4H_2O$	3.7*	3.7*
$ZnSO_4*7H_2O$	14*	3.4*
$CuSO_4*5H_2O$	4.9*	-
$Na_2MoO_4*H_2O$	0.45*	-
$CoSO_4*7H_2O$	0.45*	-
	applied during the growth period	
$Ca(NO_3)_2*4H_2O$	878	378

(* applied prior soil incubation; # applied immediately after seeding)

9.2.4 Analysis of plants and soil solution

Plants: _After 31 days plants shoots were cut, dried in a forced air oven at 70°C for 24 hours, digested in concentrated HNO_3 and analysed for Ca, K, Mg, Mn, Zn, S and Mo by ICP. Shoot Cd concentrations were analysed by GFAAS (Varian SpectrAA 400).

Soil Solution: Soil solution was displaced from the soil according to the method of Thibault and Sheppard (1992) by centrifugation at 4000 RCF for 30 minutes. Extracted solutions were centrifuged at 25000 RCF for 60 minutes and filtered through a 0.2 µm filter. The pH, EC and alkalinity of the solutions were determined immediately. Anions in solution (SO_4^{2-}, NO_3^-, Cl^-) were determined by ion chromathoghraphy (Dionex 4000i using a AS4A column) and cations (Ca, K, Mg, Mn, Zn, Cu, Fe) and P by ICP. Organic Carbon was analysed with a Total Organic Carbon Analyser, Dohrmann DC 180 (Rosemount Analytical Inc.) using a ultra-violet promoted persulphate oxidation. The DC-180 complies with EPA method 415.1 and standard method 5310C. Cadmium concentrations in solution were determined by GFAAS.

The Cd speciation and the activities of free Cd^{2+}, and $CdCl^+$, $CdCl_2^0$ complexes were calculated using the chemical speciation program GEOCHEM-PC (Parker *et al.* 1995). The *mixture model* according to Sposito and Bingham (1981) was used to adapt organic carbon data to a form useable by GEOCHEM-PC. This model gives a description of the functional group chemistry of the sewage sludge dissolved organic carbon in so far as it relates to the formation of trace metal complexes (see Chapter 8 for more detailed information).

The program GEOCHEM-PC can be run as 'open' or 'closed' system in terms of interaction of CO_2 gas with the athmosphere. Closed systems do not allow for transfer of C into or out of the system (see Chapter 8). The activities of Cd species in solution in the current study

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The program GEOCHEM-PC can be run as 'open' or 'closed' system in terms of interaction of CO_2 gas with the athmosphere. Closed systems do not allow for transfer of C into or out of the system (see Chapter 8). The activities of Cd species in solution in the current study were calculated specifying a closed system, with approximated DIC values, such that the predicted alkalinity matched the measured alkalinity of the solutions. The predicted charge error was generally in the range of ± 10 % (See also Chapter 8).

Precipitation was disallowed in the calculations, where Cd speciation was determined, because the displaced soil solutions were clear and no precipitates were noticed. However, some GEOCHEM-PC calculations were done allowing precipitation to determine the most likely precipitates in the solution. As mentioned previously, the closed system mode is not satisfactory when solid phases (such as calcite) are allowed in the system (Suarez, 1995). To use the open system mode pH and pCO2 are necessary inputs, but pCO2 was not determined in the soils. As suggested by Suarez (1995), the pCO2 values predicted to be in equilibrium with the solutions, when the cases were run as a closed system, were used as input values for the runs, where precipitation was allowed. The following compounds were oversaturated in the solutions and predicted to precipitate: $CaCO_3$, $MgCO_3$, $CaHPO_4$, $MnCO_3$, $FeOH_3$, $AlOH_3$. The amounts of $FeOH_3$ and $AlOH_3$ predicted to precipitate were low and did not vary very much between sludge rates and salt rates ($FeOH_3$: 1.2-1.9 µM; $AlOH_3$: 0.5-7 µM). However, predicted oversaturation with $CaCO_3$, $MgCO_3$, $CaHPO_4$, $MnCO_3$ varied with sludge rates, but not with salt rates and is listed in Table 9.9 in Section 9.4 (Discussion). The oversaturation for Ca and Mg was considerable and 50-96% of Ca and 9-88% of Mg in solution was predicted to precipitate. The predicted activity of Cd species in solutions (Cd^{2+}, $CdCl^+$, $CdCl_2$) for cases where precipitation was allowed, was 10-20 % lower than when precipitation was dissallowed. However, activity was similarly decreased for the different Cd species in solution. Hence the ratios of the various Cd species in solution remained unchanged and also the increase of certain Cd species in solution with the increase in Cl concentration in solution was predicted similarly for the two scenarios.

9.3 Results

The influence of NaCl (Cl) addition and sludge application rate on Cd concentration in soil solution and shoots were both significant, but some interactions were observed. Cadmium concentrations in soil solution and shoots of the treatments with the highest rate (100t) of sludge showed a different trend to the lower sludge rates. The results therefore will be discussed in different sections with Section 9.3.1 comparing sludge rates from 0 up to 50t and Section 9.3.2 describing the results of the 100t treated pots in comparison to low rates (25t, 50t) of sludge additions.

(All values shown in Tables 9.2, 9.5 and 9.6 on page 201, 207 and 209 respectively are the means of 4 replicates per treatment.)

9.3.1 Influence of Cl concentration in soil solution on Cd concentration in soil solution and shoots of wheat plants: sludge rates equivalent to 0t, 25t, 50t ha^{-1}

9.3.1.1 Soil solution Cd

Both sewage sludge application rate and salt (NaCl) application rate and the resulting Cl concentration in soil solution influenced Cd concentrations in soil solution and shoots considerably (Table 9.2 and Figure 9.1). The concentrations of further cations and anions in the soil solution are listed in the Appendix, Table A.9.1. The soil solution Cd concentration of sludge-treated soil was significantly higher that in control pots. Also within sludge treatments the 50t treatments compared to 25t treatments had higher Cd concentrations in solutions. This can be seen from the regression models for the sludge treatments showing a significantly higher intercept of the model for pots receiving 50t than from the 25t treatments (Table 9.3). The soil pH was unchanged by the various sludge treatments (Table 9.5) The influence of Cl concentration on Cd concentration in solution was also highly significant with a linear correlation between Cl concentration and Cd concentration in soil solution for control and all sludge treatments. The regression models for the various sludge treatments are listed in Table 9.3. The slopes of the regression models for the soils amended with increasing sludge rates were significantly higher than the slope in the soil without sludge application. However, the influence of Cl on the low and medium sludge treatments (25t, 50t) was quite similar, with regression models showing parallel lines (i.e similar slopes for the models).

9.3.1.2 Plant Cd concentration and uptake

Cadmium concentrations in, and uptake by, plants were significantly increased by the sludge application rate and the Cl concentration in solution. Plant Cd concentrations and uptake values are listed in Table 9.2 and Figure 9.3 and regression models are listed in Table 9.3. The concentration of further cations and anions in plant shoots are listed in the Appendix, Table A.9.2. The dry matter production of plants was similar in the control and the 25t treatments, and only significantly enhanced by the highest sludge application rate of 100t (Table 9.2). Hence for the low sludge treatments a comparison of either Cd concentration or uptake values is sufficient, because both data sets show the same trend. Dry matter production was only slightly decreased by the NaCl treatment.

The increase in sludge application rate from 0t to 25t and 50t increased Cd concentrations in shoots from 0.093 to 0.152 and 0.157 mg Cd kg^{-1} respectively. The difference in Cd concentration between plus and minus sludge treatments were significant, whereas differences between 25t and 50t treatments were insignificant. However, for each sludge level a significant positive correlation between Cl concentration and shoot Cd concentrations was found. Regression models (plant Cd concentration as influenced by Cl concentration in soil solution) for the 25t, 50t treatments showed a significantly higher slope than the control pots. However, there were no differences between the 25t and 50t treatments. The Cd uptake data show the same trends (Tables 9.3 and 9.4).

Table 9.2 The effect of NaCl addition and Cl concentration in soil solution on shoot dry weight and Cd concentration in soil solution and shoots of wheat plants, grown on soil amended with various rates of sludge (0t, 25t, 50t, 100t ha^{-1}) (sludge = SS) (LSD, P=0.05).

Sludge rate [t ha^{-1}]	Irrigation water [mg NaCl l^{-1}]	Cl soil sol. [mM]	Cd soil sol. [µg l^{-1}]	Cd conc. shoot [µg g^{-1}]	Cd uptake shoot [µg pot^{-1}]	Shoot dry weight [g pot^{-1}]
0	0	1	0.2	0.093	0.125	1.32
	400	35	0.1	0.127	0.159	1.25
	800	80	0.6	0.167	0.200	1.18
	1200	108	1.5	0.220	0.235	1.05
	1600	145	2.3	0.265	0.294	1.11
25	0	3	2.0	0.152	0.209	1.38
	400	35	4.4	0.175	0.231	1.35
	800	65	5.3	0.227	0.280	1.22
	1200	88	7.8	0.418	0.428	1.05
	1600	126	8.0	0.413	0.459	1.09
50	0	4	4.6	0.157	0.212	1.34
	400	33	5.9	0.182	0.234	1.32
	800	57	8.3	0.307	0.361	1.18
	1200	99	12.0	0.403	0.463	1.17
	1600	102	16.0	0.439	0.478	1.10
100	0	4	4.2	0.130	0.206	1.65
	400	30	4.1	0.153	0.230	1.48
	800	62	7.8	0.190	0.246	1.29
	1200	94	9.4	0.265	0.416	1.58
	1600	89	7.5	0.279	0.369	1.32
F-Prob. SS rate			#	#	#	0.004
F-Prob. salt rate						0.034
F-Prob. Interaction						n.s.
LSD SS rate						0.168
LSD salt rate						0.188

linear regression models are given in Table 9.3.

Table 9.3 Regression models for the influence of Cl concentration (Cl in [mM]) in soil solution on Cd concentration in soil solution, Cd concentration in plant shoots and Cd uptake by shoots (F significance, * $P< 0.05$; ** $P< 0.01$) (SS=sludge).

SS rate [t ha^{-1}]		Cd$_t$ in solution [µg l^{-1}]	Cd shoot [mg kg^{-1}]	Cd uptake [ug pot^{-1}]
0	Model	0.015(Cl)-0.2	$1.1*10^{-3}$(Cl)+0.09	$1.2*10^{-3}$(Cl)+0.11
25	Model	0.059(Cl)+2.0	$2.2*10^{-3}$(Cl)+0.14	$2.4*10^{-3}$(Cl)+0.17
50	Model	0.113(Cl)+2.7	$2.7*10^{-3}$(Cl)+0.14	$2.9*10^{-3}$(Cl)+0.18
100	Model	0.072(Cl)+2.5	$1.6*10^{-3}$(Cl)+0.12	$2.3*10^{-3}$(Cl)+0.16
0	F-signif.	**	**	**
	R^2	0.71	0.89	0.68
25	F-signif.	**	**	**
	R^2	0.88	0.61	0.71
50	F-signif.	**	**	**
	R^2	0.67	0.77	0.84
100	F-signif.	*	**	**
	R^2	0.31	0.60	0.60

Table 9.4 Pairwise comparisons of regression models describing the influence of Cl concentration in soil solution on Cd concentration in soil solution and shoots and Cd uptake by plants for each sludge rate. The expression 'distinct' describes significantly different slopes, the expression 'parallel' shows significantly different intercepts of the regression lines (P=0.05). The expression 'identical' lines is used when neither slope nor intercept are significantly different.

Regression lines for influence of Cl concentration on Cd concentration in soil solution

Sludge rate	**0**	**25**	**50**	**100**
25	distinct			
50	distinct	parallel *		
100	distinct	identical	parallel	

Regression lines for influence of Cl concentration on Cd concentration in plant shoots

Sludge rate	**0**	**25**	**50**	**100**
25	distinct			
50	distinct	identical		
100	parallel	parallel	distinct	

Regression lines for influence of Cl concentration on Cd uptake by plant shoots

Sludge rate	**0**	**25**	**50**	**100**
25	distinct			
50	distinct	identical		
100	distinct	identical	parallel	

* distinct lines if 2 exceptional high values are left out of the calculation, otherwise parallel lines as listed in the Table.

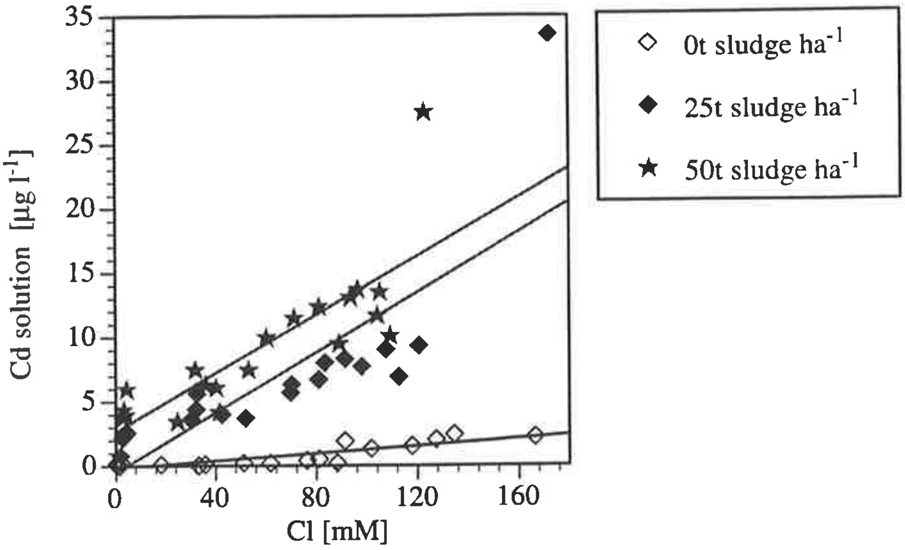

Figure 9.1 Influence of Cl concentration in soil solution on the Cd concentration in soil solution of sludge-amended soils (sludge rates equivalent to 0, 25 or 50t ha^{-1}).

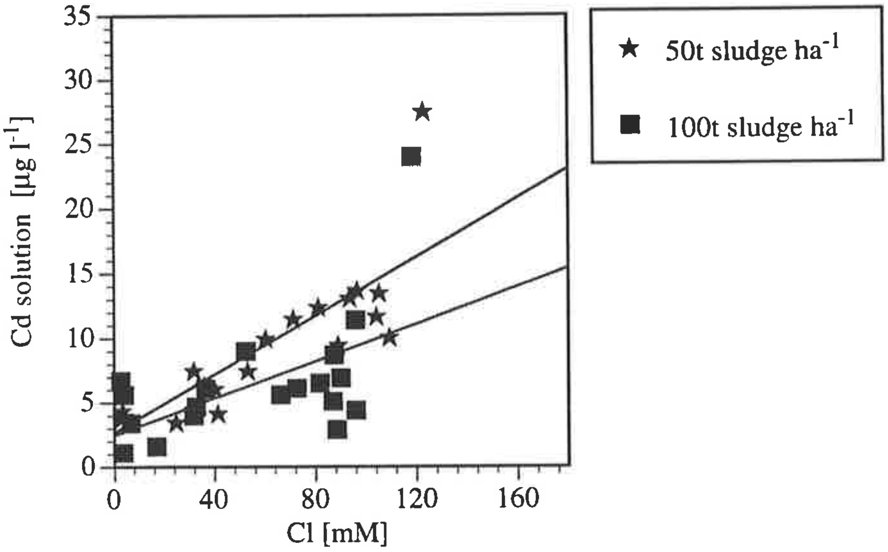

Figure 9.2 Influence of Cl concentration in soil solution on the Cd concentration in soil solution of sludge-amended soils (sludge rates equivalent to 50 and 100t ha^{-1}).

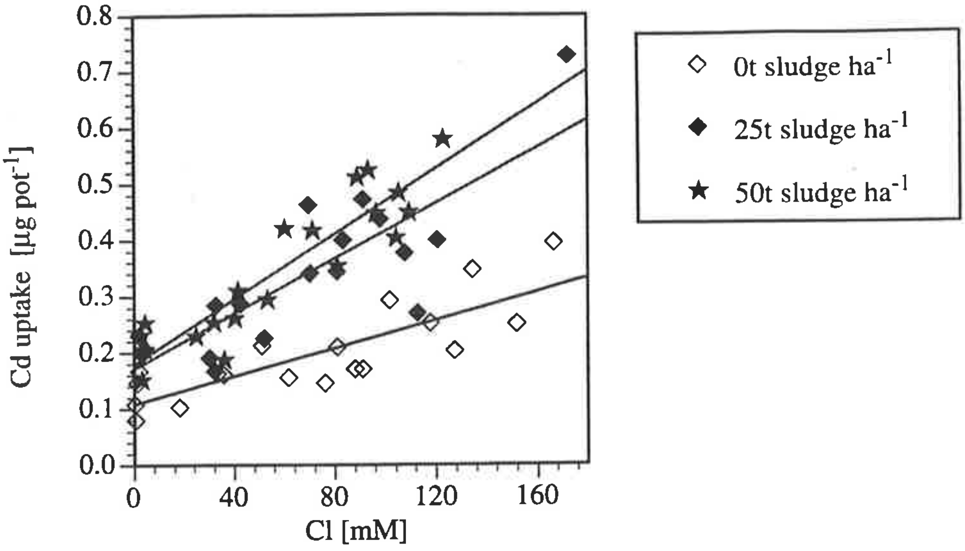

Figure 9.3 Influence of Cl concentration in soil solution on the Cd uptake of wheat shoots when grown in sludge-amended soil. (sludge rates equivalent to 0, 25 or 50t ha^{-1})

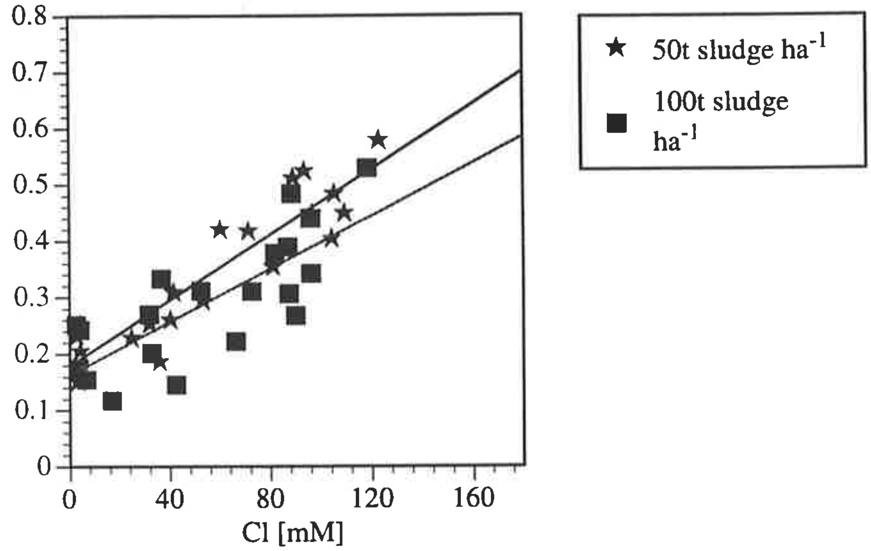

Figure 9.4 Influence of Cl concentration in soil solution on the Cd uptake of wheat shoots when grown in sludge-amended soil (sludge rates equivalent to 50 and 100t ha^{-1}).

9.3.2 Influence of Cl concentration in soil solution on Cd concentration in soil solution and in wheat shoots: high sludge application rates (100t) versus control and lower sludge rates

9.3.2.1 Soil solution Cd

The influence of Cl concentrations and medium to high sludge rates on Cd concentrations in soil solution and in shoots are shown in Table 9.2 and Figure 9.2 and regression models in Table 9.3. The concentrations of further cations and anions in the soil solution are listed in the Appendix, Table A.9.1. Cadmium concentrations in soil solution of the 100t treatment were significantly higher than from control pots, but similar to 25t treatment and lower than in the 50t treatment. A significant positive correlation between Cd concentrations in soil solution and Cl levels in soil solution was measured for the 100t treatment, as was observed for the lower sludge rates. The regression models for all the sludge treatments did not differ in slope, only the intercept of the 100t model was significantly lower than the 50t treatment and similar to the 25t treatment. The regression models for 25t and 100t treatments were similar, thus showing a similar level and increase of Cd concentration in solution with increasing Cl concentrations in the soil solution.

9.3.2.2 Plant concentrations and uptake of Cd

The differences in Cd uptake by wheat shoots showed a somewhat similar trend as the differences in soil solution Cd concentrations. As the 100t sludge treatment had a significant effect on plant growth, the Cd uptake data are more appropriate than plant Cd concentrations for comparison.

The uptake of Cd by plants of the 100t treatment was similar to 25t treatments and slightly lower than from 50t treatment (similar to soil solution data) (see Table 9.3, Figure 9.4). A comparison of regression models (Table 9.4) showed, that in terms of Cd uptake, the regression lines for 25t and 100t were similar and the model for the 50t treatment was parallel, but has a higher intercept. The effect of enhanced Cd phyto-availability due to increased soil Cl levels (slope) therefore was similar in the sludge-amended soils irrespective of the difference in sludge (Cd) application rate.

Table 9.5 The effect of sludge rate (0, 25, 50, 100t ha^{-1}) and irrigation water quality on soil alkalinity, soil pH and Cd speciation in soil solution (LSD, P=0.05).

Sludge rate $[t\ ha^{-1}]$	Irrig. water NaCl $[mg\ l^{-1}]$	NaCl $[mg\ kg^{-1}]$	Alkalinity $[meq\ l^{-1}]$	pH	Cd speciation				
					Cd^{2+}	Cd-OM*	$CdCl_n^{2-n}$ [%]	Cd-SO_4	Cd-CO_3
0	0	0	6.4	8.16	44	2.6	3	11	31
	400	217	7.3	8.14	31	<1	46	4	16
	800	400	5.6	7.94	21	<1	68	3	6
	1200	520	7.0	7.90	17	<1	73	3	6
	1600	681	6.8	7.75	14	<1	80	2	3
25	0	0	5.8	8.19	42	2.1	6	26	20
	400	216	5.8	8.13	30	0.9	41	16	10
	800	391	9.2	8.14	23	0.8	58	9	7
	1200	529	5.3	8.00	20	0.7	65	9	4
	1600	696	6.0	8.00	17	0.5	72	5	4
50	0	0	8.0	8.13	38	4.7	5	33	17
	400	213	6.6	8.10	30	3.2	36	20	9
	800	388	6.8	8.08	25	1.9	51	13	8
	1200	543	7.7	8.03	18	1.0	65	9	6
	1600	684	7.3	8.01	18	1.1	65	10	5
100	0	0	11.5	8.04	35	7.0	5	32	18
	400	233	12.9	8.13	27	5.1	27	23	16
	800	420	13.4	8.07	21	3.0	50	14	10
	1200	665	11.7	8.04	18	2.8	58	12	8
	1600	780	13.7	8.05	19	2.6	57	11	10
F-SS rate		0.025	0.001	n.s.	0.001		0.001	0.001	0.006
F-salt rate		0.001	n.s.	0.006	0.001		0.001	0.001	0.001
F-Interaction		n.s.	n.s.	n.s.	0.001		0.001	0.001	0.001
LSD SS rate		42	1.18	-	1.19		2.78	2.03	2.40
LSD salt rate		47	-	0.114	1.33		3.11	2.27	2.68
LSD-interaction		-	-	-	2.66		6.20	4.52	5.36

* Cd complexed by organic ligands as estimated using the mixture model (Sposito and Bingham, 1981)

9.3.3 Influence of NaCl addition on Cd speciation in soil solution

The influence of the various NaCl treatments on the Cd speciation in soil solution is listed in Table 9.5. The influence of NaCl or, the solution Cl concentration, on the activity of the major Cd-chloro-complexes and the activity of free Cd^{2+} are listed in Table 9.6. With increasing NaCl addition to the soil the various Cd chloro-complexes soon became the dominant Cd species in solution. Sulfate and carbonate complexes of Cd made up a significant percentage of the Cd in solution at low salt levels, even though the free Cd^{2+} ion was the dominant form. Organically-complexed Cd increased with the increase in sludge rate and the resulting dissolved organic carbon level (DOC) in solution. However, the percentage of organically-complexed Cd was low and further decreased with increasing Cl levels in solution (data not shown) (0 NaCl: 3-7%, 1600 mg NaCl l^{-1}: <1-3% organically complexed Cd). Cadmium sulfate complexes less more important in the control treatments than in the sludged soils, where they contributed a significant percentage of the Cd in solution even at high Cl concentrations. Carbonate species of Cd made up a significant proportion of Cd species in all the soils, but they decreased in importance with increases in Cl addition, except in the 100t treatment. At the highest sludge rate (100t), carbonated species still contributed about 10 % of the Cd species in solution even under high salt conditions.

With increases in Cl concentration in soil solution the activity of free Cd^{2+} in solution remained largely unchanged, except for the control treatment (Table 9.6), although there was a significant increase in total Cd concentrations in solution. Using stepwise-multiple regression correlating the increase in shoot Cd concentration with Cd species in solution it was evident that the $CdCl^+$ activity in solution explained most of the variation in shoot Cd concentration (Table 9.7). The free Cd^{2+} activity did not explain any of the variation in Cd concentrations in shoots. Only in the control was the Cd^{2+} activity as closely correlated with the Cd concentration of plants as the $CdCl^+$ activity.

Table 9.6 Total Cd concentration in shoots, Cd-transfer-coefficient and Cd speciation in soil solution as affected by NaCl addition to sludge amended soil. (The Cd-transfer-coefficient is the ratio of Cd in shoots [mg kg^{-1}] to Cd in soil solution [mg l^{-1}]) (LSD, P=0.05).

Irrigation water [mg NaCl l^{-1}]	Cd shoot [mg kg^{-1}]	Cd $^{2+}$	CdCl^{+}	CdCl$_2^0$	Transfer coefficient [l kg^{-1}]
		activity [nM]			
0 sludge					
0	0.093	0.35	0.0	0.00	660
400	0.127	0.11	0.3	0.04	1100
800	0.167	0.38	2.4	0.63	420
1200	0.220	0.74	6.0	1.98	340
1600	0.265	0.69	7.0	2.91	120
25 t ha^{-1} sludge					
0	0.152	3.25	0.9	0.01	94
400	0.175	4.41	11.4	1.21	41
800	0.227	3.80	19.1	4.00	45
1200	0.418	4.42	28.2	7.30	57
1600	0.413	3.89	30.7	9.60	50
50 t ha^{-1} sludge					
0	0.157	5.67	1.6	0.02	36
400	0.182	5.25	13.2	1.35	35
800	0.307	5.94	25.5	4.47	42
1200	0.403	6.10	43.2	12.10	35
1600	0.439	4.94	55.8	16.70	32
100 t ha^{-1} sludge					
0	0.130	4.32	1.3	0.02	53
400	0.153	3.18	7.6	0.75	45
800	0.190	4.62	22.5	4.50	27
1200	0.265	4.13	31.0	8.90	52
1600	0.279	3.08	18.8	4.60	41
F-SSrate		0.001	0.001	0.001	0.001
F-salt rate		n.s.	0.001	0.001	0.001
F-interaction		n.s.	0.010	0.040	0.001
LSD-SSrate		0.93	6.6	2.36	174
LSD-salt rate		-	7.4	2.65	81
LSD-interaction		-	14.7	5.29	227

The transfer-coefficient, which is the ratio of Cd in plant shoots to total Cd concentration in solution, describes the uptake efficiency of a plant under the given environment. With increases in NaCl addition and Cl concentration in soil solution the transfer-coefficient decreased considerably in the control treatment (Table 9.6). The initial increase in the control from the 0 to 400 mg NaCl l^{-1} treatment is due to the low solution Cd concentrations, which did not allow ta distinction in the Cd concentration in solution between those two treatments. However, in the sludge treatments the transfer-coefficient was unaffected by NaCl additions. The higher transfer-coefficient in the 0 NaCl-25t treatment is due to one anonamously low value in Cd concentration in soil solution.

Table 9.7 Analysis of variance in a stepwise forward multiple regression analysis on the influence of Cd species (Cd^{2+}, $CdCl^{+}$, $CdCl_2$) in soil solution as predicted by GEOCHEM-PC on shoot Cd concentration [mg kg^{-1}]: variance accounted for (% v.r.) by the various Cd species.

Change in factor	**0 sludge**	**25t**	**50t**	**100t**	**all treatments**
		[%] variance accounted for			
Cd^{2+}	68.0	3.8	0.0	0.1	22.0
$CdCl^{+}$	59.0	19.0	28.0	9.0	58.0
$CdCl_2$	0.8	0.2	0.1	2.3	2.1

9.4 Discussion

The enhancing effect of Cl ligands on Cd mobility in soils (Doner, 1978) and Cd uptake by plants was demonstrated by a number of studies (Giordano *et al.*, 1983; Bingham *et al.*, 1983 and 1984; McLaughlin *et al.*, 1994; Smolders *et al.*, 1996). In the current study it was intended to determine if Cl complexes sludge-Cd to a similar extent as soil- (or fertiliser-) Cd and thus increases Cd phyto-availability. Therefore it was necessary to distinguish if the Cd, mobilised by Cl ligands and taken up by plants, was either sludge-Cd or soil-Cd. A factorial experiment with sludge rates and NaCl (Cl) rates as factors was chosen to distinguish between the two sources. If sludge-Cd is mobilised by Cl then the amount of mobilised Cd should be dependent on the sludge application rate. In other words, with increasing sludge rates an increase in slopes of the regression models, describing the relation between Cl concentration in solution and Cd concentration in soil solution and in plant shoots would be expected. However, a similar slope in regression models of soils amended with different sludge rates, would indicate that a similar amount of Cd was mobilised irrespective of the sludge Cd additions. This would suggest that mainly or only soil-Cd is mobilised. The following discussion in section 9.4.1 and 9.4.2 will focuss on this issue of distinction between soil-Cd and sludge-Cd.

The influence of sludge application rate on Cd concentrations in solution followed a quadratic curve, with increases in Cd concentration up to an application rate of around 50t , followed by a decrease in Cd concentration when rates were further increased to 100t. Shoot Cd concentrations and Cd uptake data showed the same trend. The phenomenon that Cd uptake of plants actually decreased with high sludge application rate was also observed by Hooda and Alloway (1993). The main difference in soil solutions of the 100t to the other treatments was a higher alkalinity. The possible impact of this and other factors, which may explain the decrease in Cd concentration in solution in the 100t treatment, will be discussed Section 9.4.5.

9.4.1 Influence of NaCl (Cl) additions on Cd in soil solution

Cadmium concentrations in soil solution increased significantly with increases in sludge application rates up to 50t. Cadmium concentrations in solution were clearly enhanced in the 25t treatment compared to the control and from the 25t to the 50t treatment (0-NaCl treatments, Table 9.2). The soil pH was unchanged by sludge application rates. Increases in soil solution Cd concentrations between control and sludge treatments (intercept of regression models, Tables 9.3 and 9.4) suggest that the sludge contributed a sizeable amount of water-soluble Cd.

The effect of Cl ligands on Cd concentration in solution can be assessed from the slope of the calculated regression models describing the influence of Cl concentration on Cd concentration in soil solution. A significantly greater amount of Cd was mobilised in the sludge-treated soils than in the control soil (slope of regression models differed by a factor of 5 between control and 25t or 50t treated soils) with increasing Cl concentrations. The slopes in the regression models of the various sludge treatments were not significantly different. These data indicate that sludge Cd was mobilised by Cl in this experiment.

It is difficult to explain why there were no differences in slope between the 25t and 50t treatments. However, slopes of the regression curves for 25t and 50t- treated soils would have been significantly different if 2 exceptional high values were left out of the regression calculation. Nonetheless, the small differences in solution Cd concentration between 25t and 50t treatments suggest that sludge-Cd is less prone to complexation by Cl ligands as sludge content increases beyond 25t ha^{-1}. In Table 9.8 soluble Cd is expressed as a percentage of the total Cd in the soil-sludge mixture for the various sludge treatments (assumed water content: 20%). For the 0 NaCl treatments soluble Cd expressed as a percentage of the total Cd increases with the increase in sludge application rate up to 50t. This suggests that sludge-Cd is more soluble than soil-Cd. However, when Cl is added to the system, then the soluble

Cd as a percentage of the total Cd is similar for all treatments (at the highest NaCl treatment). Therefore the increase in soluble Cd from low to high NaCl treatments were relatively less marked in the sludge treatments than in the control soil. These results suggest that sludge-Cd is less likely to be mobilised by Cl-ligands than soil Cd. This is in agreement to the comparison of regression models for the influence of Cl on Cd in solution. However, the increase in percentage of Cd in soil solution when Cl concentration were increased indicates that some sludge-Cd was mobilised.

Table 9.8 Soluble Cd as percentage of the total Cd in the soil sludge-mix, calculated for the highest and lowest NaCl treatment.

Sludge rate	Total Cd in soil-sludge mix	Total Cd in solution		Percent of total Cd in solution		
		0 NaCl	1600 NaCl	0 NaCl	1600 NaCl	increase
	[mg 500 g^{-1}]	[ng]	[ng]	[%]	[%]	[%]
0	0.06	20	230	0.033	0.383	0.350
25	0.21	200	800	0.095	0.381	0.286
50	0.36	460	1600	0.128	0.444	0.316
100	0.66	420	750	0.064	0.114	0.050

It may be postulated that the most weakly bound sludge Cd fractions have been eluted in the sludge leaching process prior to the pot experiment. However, it is unlikely that a high proportion of sludge-Cd was lost, because in the preliminary leaching experiment the total sludge Cd increased from 13.9 to 14.8 mg kg^{-1}. The actual increase in Cd concentration was due to a loss in dry matter of approximately 26% (soluble salts and a small fraction of organic matter) with the leaching process. The unleached fractions therefore were concentrated in the remaining material. Taking this concentration effect into account about 20 % of the total Cd was lost.

Cd sludge 13.9 mg kg^{-1} prior leaching

(dry matter loss of 26% concentrates unleached elements by a factor of 1.35)

Cd sludge 18.8 mg kg^{-1} concentration expected after leaching if no losses occured

($13.9*1.35= 18.8$ mg kg^{-1})

Cd sludge 14.8 mg kg^{-1} concentration after leaching

However, the analysis of the leachates predicted a much lower leaching of sludge Cd. The sampled leachates were high in NaCl and dilution was necessary to analyse the samples. The Cd concentration as detected in the diluted leachate samples was 0.01 mg Cd l^{-1} in the first sample and below 0.0015 mg Cd l^{-1} in from leachate number five to the last sample taken (21-28 leachates taken). On average 460 ml leachate was sampled, in subsamples of 20 ml, to leach salts out of 27 g of sludge. The sum of Cd in the leachates, assuming the Cd concentration in the leachates following sample 5 were 0.0015 mg Cd l^{-1} , would have been 1.14 μg Cd per 27 g sludge containing 351 μg Cd. The leached Cd would amount to 0.33 % of the total Cd in sludge. However, Cd analysis in the leachates has to be treated with caution, because the salt content of samples may have interfered with the Cd analysis.

The regression model for the influence of Cl on soil solution Cd of 50t sludge treatments in this study was similar to the model calculated for the Experiments 1, 2, 3 and 4 in Chapter 8. The slope in the current regression models for sludge treatments were lower by the factor of 3 than comparable models in the study of Smolder *et al.* (1995ab) which was done with agricultural, non sludge-amended soil. There are two possible reasons to explain this discrepancy: a) Cl ligands may be less effective in mobilising sludge Cd than soil Cd, b) sludge addition raised soil pH considerably in the study reported here (from pH 6.3 to 8.1) and lime was used to compensate for sludge pH effects. This would reduce considerably the availability of both soil and sludge Cd. The small differences in Cd concentration in soil solution between the 25t and 50t treatments, even though Cd application rates (sludge application rates) differed, suggest that explanation a) is more likely. The effect of Cl on sludge-Cd is dependent on the sludge rate. The comparison of relative amounts of Cd in solution between sludge treatments further clarified this issue. The interaction between sludge application rate and influence of Cl on Cd concentration in solution is particularly obvious in the 100t treatment. This will be discussed in a following section.

Theoretically it could be argued that sludge additions increase the availability of native soil Cd. Changes in soil solution due to sludge addition include: increase in cation concentrations (Ca, Mg, Zn, and Cu) and ionic strength, increases in SO_4 and dissolved organic carbon (DOC) concentrations as well as solution alkalinity. Although an influence of sludge on the availability of the (small pool of) soil-Cd is potentially possible, the increase of soluble Cd as a percentage of the total Cd from the 0 to 25 and from 25 to 50t sludge rates rather suggests that sludge was a major source of Cd in solution; indeed the percentage of Cd in solution from the total Cd was higher in the sludge treatments than in the control at the 0-NaCl level.

9.4.2 Influence of NaCl (Cl) additions on plant Cd uptake

Cadmium concentrations in and Cd uptake by plants increased significantly with increases in soil Cl concentrations. The increases in Cd concentration with Cl levels was more enhanced (slope of regression models) for the sludge treated plants than for the control. However, the enhancement of Cd concentrations was similar for the sludge treatments of 25t or 50t, irrespective of the difference in Cd (sludge) application rate.

Also, there was a significant influence of sludge application rate on Cd concentration and uptake by plants, with a significantly higher Cd concentrations of sludge-amended plants compared to control plants. However, there was no difference in plant Cd concentration with an increase in sludge application rate from 25t to 50t . This once again poses the question if the sludge contributes a major fraction of the plant available Cd as differences between 0t and 25t treated plants suggest, and/or if the sludge amendment influences soil Cd plant availability as the lack of difference between the 25t and 50t regression models suggest.

The Cd soil solution data for 25t and 50t sludge treatments yielded parallel, but significantly different, regression curves . It could be expected that those differences would be reflected in the shoot Cd data. The differences in soil solution data, even though highly significant, may have been too small to cause differences in shoot Cd concentration. Van Erp and Van Lune (1989) found a lower availability of Cd in soil treated with metal contaminated compost compared to untreated soil, although they related Cd uptake of plants to the calculated Cd^{2+} concentration and not total Cd in solution. Taking Cd^{2+} concentration into account, the authors suggested that it was possible to characterize the Cd availability of different soils, but the relations they suggested may not be universal. It was suggested by the authors that on contaminated soils competition between Cd and other heavy metals for root uptake may influence the relationship. However, in the study of Van Erp and Van Lune (1989) Cd^{2+} concentration rather than Cd^{2+} activity was the basis of the calculations, which could have differed in compost and control soils.

It is possible that other sludge factors such as increased levels of Ca, Mg, Cu and Zn in soil solution could have caused a competitive inhibition of Cd uptake by roots. A number of studies suggested that Ca can have an inhibitory effect on Cd absorption (Iwai *et al.*, 1975; Hardiman and Jacoby, 1984; Kawasaki and Moritsugu, 1987) Although this contrasts with the study of Tyler and McBride (1982) who did not find an effect of Ca concentration in solution on Cd absorption by roots, he found that translocation of Cd from roots to top can be depressed. Chaudhry and Loneragan (1972) also reported a reduced absorption of Zn by wheat seedlings, when Ca concentration was increased. However, in the current study the Zn concentration of plants were not decreased but increased by sludge rate and this may imply that cation competition for metal uptake was not a crucial factor in decreasing Cd uptake at higher sludge rates. The inhibitory effect of Ca on absorption of Zn and Cd by excised barley roots was suggested to be more pronounced on the uptake of Cd (Kawasaki and Moritsugu, 1987) and hence an influence of Ca (or Mg) on Cd absorption is still a probability.

The regression models describing plant Cd uptake influenced by Cl levels in sludge amended soil (50t sludge rate) had a higher slope (factor 2) and a lower intercept (factor 1.7) than the comparable model for wheat in Chapter 8 (Exp. 1), although the regression models describing the influence of Cl on Cd concentration in solution were similar. Plant Cd concentrations are dependent on many variables such as plant age, water uptake and growth rate. Plant Cd concentrations are likely to be influenced to a greater extent than soil solution Cd concentrations.

9.4.3 Cadmium speciation in soil solutions

There is increasing evidence that the Cd uptake of plants is dependent on the chemical speciation of Cd in solution. It has been reported that the free (ionic) metal rather than the forms associated with soluble ligands are available to algae and higher plants (Checkai *et al.* 1987).

For a sludge-amended soil, Sposito and Bingham (1981) found the principal Cd species in soil solution are free (ionic) Cd^{2+} (51.7%), chloro-complexes (34.1%) and SO_4 complexes (6.8%). The percentages of free Cd^{2+} for the current experiment were similar to the values of Sposito and Bingham (1981), although a higher percentage of sulfate (30 %) and carbonate (18 %) species of Cd were found. The percentages of chloro complexes in the 0 NaCl treatments were low, because pre-leached sludge was used in the current study. Differences in sulfate and carbonate complexation may be based on soil type, soil pH and incubation time of the soil sludge mixture. Carbonate species of Cd play a more important role in calcareous soils and can constitute 35% to 40% of the total Cd in solution at pH 7.5 to 8 (Hirsch and Banin, 1990). Using the assumptions of the *mixture model* organically complexed Cd was only a small fraction of the Cd in solution as in the studies by Sposito and Bingham (1981) and Hirsch and Banin (1990).

With increases in Cl level in soil solution Cd chloro-complexes became dominant. The activity of Cd^{2+} remained unchanged or increased slightly. An increase in Cd^{2+} activity with increasing Cl concentration was only noticeable in the control treatment, where the total Cd concentrations in the low salt treatments were very low (close to the detection limit for graphite furnace atom absorption spectrometer).

For the sludge treatments the $CdCl^+$ activity in solution explained most of the variation in shoot Cd concentrations. The activity of free Cd^{2+} was only weakly correlated, if at all, with shoot Cd concentrations. This is in agreement with the findings of Smolders *et al.* (1995 and 1996, who found that Cd concentrations in Swiss chard, grown in soils with varying Cl concentrations, did not correlate with Cd^{2+} activity but correlated strongly with $CdCl^+$ activity in solution. In contrast, Bingham *et al.* (1984) found the Cd uptake by Swiss chard grown in soils amended with NaCl or $CaCl_2$ to be mainly correlated with the Cd^{2+} activity in soil solution. However, the very high additions of inorganic Cd to the soil in their study made ion exchange of Na for Cd a more important process than in a soil with naturally low levels of Cd.

The actual mechanism by which Cl enhances Cd uptake by plants is not yet fully resolved. A number of possible reasons have been put forward by Smolders and Mclaughlin (1996a). Firstly, the mobility of Cd in soil is increased at higher Cl concentrations due to the decreased adsorption of Cd-chloro complexes and the resulting increase in Cd concentration in the liquid phase. This effect can be important if the transport of Cd in soil towards plant roots limits the rate of plant uptake from the soil. Secondly, it could be possible that in addition to Cd^{2+} some chloro-complexed species of Cd are also plant available. Although it has been reported that the free (ionic) metal rather than the forms associated with soluble ligands are available to plants (Checkai *et al.*, 1987), some other studies suggest that metal uptake may not be solely dependent on free metal activities in solution (Bell *et al.*, 1991). It has been recently shown in a resin-buffered solution culture system that increasing Cl concentrations increased Cd concentration in solution and shoots of Swiss chard, while Cd^{2+} activity remained unchanged (Smolders and McLaughlin, 1996b). Phytoavailability of chloro-complexed Cd species seemed the most likely explanation for this phenomenon.

The efficiency of plant uptake of a particular element can be measured with the transfer-coefficient, which is the ratio of Cd in shoots to Cd in soil solution. The transfer coefficients for sludge treatments were considerably lower than for control treatments, but were generally similar to those in the previous experiments (Chapter 8, Exp.1 and 3). As the Cl concentration in solution increased, the transfer coefficient for the control treatment was reduced considerably, indicating a lower phytoavailability of Cd in solution. The phytoavailability of chloro-complexed Cd, the dominant Cd species at higher Cl concentrations, seems to be lower than from Cd^{2+}, the Cd species dominant at low Cl levels. This agrees with the study of McLaughlin and Smolders (1996b), where it was estimated that the efficiency of uptake of $CdCl^+$ was 10-20% of that of Cd^{2+}.

However, the transfer coefficient for sludge treatments did not change considerably as the Cl concentration increased. (The somewhat elevated transfer coefficient of the 0 NaCl-25t treatment was based on one anonamously low value for Cd in solution.) The transfer coefficients of sludge compared to control treatments differed in two aspects: a) a considerably lower transfer-coefficient at low NaCl levels, b) no subtsantial decrease in transfer-coefficient at high sludge application rates with an increase in salt rate. This indicates that the soluble Cd in the sludge treatments was less plant available than in the control, which is in agreement with the findings of Van Erp and Van Lune (1989) (see above). The increase in Cl concentration did not decrease the Cd transfer-coefficient any further in sludge treatments than was the case in the control.

9.4.4 Influence of NaCl (Cl) additions on Zn and Mn availability to plants

Increasing soil salinity also had an effect on shoot concentrations of some other cations. The concentrations and uptake of Zn by plant shoots were significantly increased by increasing soil NaCl levels (except Zn uptake in the 100t treatment). However, a significant linear correlation between soil Cl concentrations and soil solution Zn concentration was not found. According to speciation calculations by GEOCHEM-PC Zn was predominantely organically complexed and only a small fraction was chloro-complexed (data not shown). Other salt effects or changes in ionic strength of the solution rather than chloro-complexation of Zn are therefore more likely to account for the increase in Zn phyto-availability.

There was also a significant increase of shoot Mn concentration with increasing NaCl additions. With lower sludge rates the influence of NaCl was more pronounced than at high sludge rates. These increases were more or less a reflection of Mn increases in soil solution, with increases being obvious only at sludge rates of 0t to 50t. This is in agreement with Khattak and Jarrell (1989) who found that saline irrigation water significantly increased the Mn concentration and total Mn accumulation in sugar beet tops (*Beta vulgaris* (l.) USH11). Also the Mn concentration in the leachates were significantly increased in three of the four soils. Hassan *et al.* (1970) reported the same effect for barley plants (*Hordeum vulgare* L.) using saline irrigation water containing NaCl. Also Maas *et al.* (1972) found a significant increase in Mn concentration in tomato and soybean tops due to increases in salinity (NaCl) but a decrease in Mn concentration in squash tops was detected as salinity increased. Although Maas *et al.* (1972) observed a considerable decrease of shoot dry matter in all plant species due to the salinity treatments, the study still may allow the conclusion that interactions between plant species, salinity and Mn uptake can exist. In the study of Smolders *et al.* (1995), no positive effect of Cl concentration on Mn content was recorded. This may be due to the fact that a different plant species was used (Swiss chard) compared to wheat in the current study. In the experiments described in Chapter 8, increases in shoot Mn concentration due to NaCl addition were significant in both experiments using wheat, but only in one experiment using Swiss chard, even though solution concentration of Mn was increased in all four experiments.

9.4.5 Cadmium availability at high rates of sludge addition

Addition of sludge increased Cd concentrations in soil solution and also Cd concentrations in plant shoots. However, with application rates of 100t there was a decrease in solution and shoot Cd concentration compared to the 50t sludge treatment. This trend was also evident in Cd uptake data where dilution effects due to differences in shoot dry matter production of the 100t treated plants are accounted for. Sludge is a complex mix of nutrients and organic material and with increases of sludge application rate an influence on many aspects of soil solution composition can be expected. However, the measured concentrations of Ca, Mg, K, Zn, Cu, PO_4, SO_4 and DOC concentrations increased gradually with each increment of sludge. However, Cd concentrations in soil solution in the 50t treatment were significantly increased, compared to the 25t treatment and significantly decreased in the 100t treatment. There was one factor that disproportionately increased with the 100t sludge application rate. The alkalinity of the soil solution did increase slightly from the 25t to 50t treated soil but doubled in the 100t treated soil. The increase in alkalinity was presumably due to an increase in carbonate and bicarbonate ions, because the soil pH, and thus OH^- concentration, remained unchanged. The increased concentration of DOC in solution may have also contributed to the alkalinity, but DOC levels increased gradually with the increase in sludge application rates.

With increases in carbonate and bicarbonate ions precipitation of $CaCO_3$ is possible as sludge contains a considerable amount of Ca. The soil-sludge mixes were pH buffered by $CaCO_3$ as the pH of the soil was 7.8-8.2. An increase in microbial activity due to addition of sludge, increased CO_2 partial pressure in the soil environment and increased soil solution alkalinity in the 100t treatment. The chemical speciation program GEOCHEM-PC was run as a closed system in terms of CO_2 exchange with the environment, and precipitation was disallowed, because the extracted soil solution was clear. When the program was run as an open system in terms of CO_2 exchange with the environment (See Section 9.2) and precipitation was allowed the precipitation of the following solids were predicted: $CaCO_3$, $CaPO_4$, $MgCO_3$, $FeOH_3$ and $MnCO_3$ (Table 9.9). The predicted precipitation differed according to sludge rates, but not according to NaCl treatments.

Table 9.9 Compounds predicted to precipitate according to GEOCHEM-PC in soil solutions extracted from soils receiving increasing rates of sludge.

sludge rate	$CaCO_3$	$MgCO_3$	$MnCO_3$	$CaPO_4$	$FeOH_3$
[t ha^{-1}]	[mM]		[μM]		
0	4.6	0.5	0	153	1.3
25	9.1	7.1	0	53	1.3
50	13.1	14.5	0	92	1.2
100	19.9	29.0	4.5	108	1.9

The solutions were increasingly oversaturated with $CaCO_3$ and $MgCO_3$ as sludge application rates increased. In the soil solution from the highest sludge treatment, even $MnCO_3$ was oversaturated according to GEOCHEM-PC calculations. However, the concentration of Cd in solution (66 nM) was much lower than from Mn (40 μM) in the 100t treatment. McBride (1980) stated that precipitation of $CdCO_3$ as a separate solid is unlikely to occur at levels encountered in most soils. Although soils in the current experiment received sludge-Cd additions, the total Cd concentration in soil solution were still low and comparable to values found in soils not treated with sludge (Marschner *et al.*, 1991).

It is possible that adsorption of Cd to carbonate surfaces may have reduced the concentration of Cd in solution, when high sludge rates were applied. McBride (1980), Pickering (1983) and Papadopoulos and Rowell (1988) found that Cd can be very effectively retained by calcium carbonate surfaces at very low solution Cd^{2+} activities. McBride (1980) added that chemisorption may control Cd^{2+} activity in some calcareous soils, producing solubilities much lower than predicted by the solubility product of $CdCO_3$. The adsorption reactions of Cd on calcite surfaces seems to be a very selective reaction, because it occured even in solutions containing 100 to 500 times more Ca than Cd (Papadopoulos and Rowell, 1988). The high affinity of Cd for the $CaCO_3$ surfaces can be expected due to the similarity in effective ionic radius of Ca and Cd (Pauling radius of Cd^{2+} is 0.97 A, Ca^{2+} is 0.99 A; McBride, 1980) and the electronic configurations of the two elements are almost the same. However, in the current study, $MgCO_3$ rather than $CaCO_3$ was increasingly predicted to precipitate at high sludge rates. The adsorption behaviour of Cd to $MgCO_3$ was not addressed in the above mentioned studies, but similarities in ionic radius between Mg and Cd are less than between Ca and Mg, and lower adsorption specificity would be expected. Sorption of Cd to sludge sorption sites is unlikely to be the reason for the low Cd concentration in the soil solution of the 100t treatment, because the effect on Cd concentration in solution was not linear with sludge rate.

While the concentration of Cd in solution decreased (high NaCl treatment, or remained stable: 0 NaCl treatment) with high sludge rates, the concentration of Zn in soil solution and plants increased. Pickering (1983) analysed the adsorption or precipitation behaviour of Zn as well as Cd on $CaCO_3$ surfaces. He found that Cd adsorption increased linearly with the weight of $CaCO_3$ in suspension, but suggested that the adsorption behaviour of Zn was completely different from that of Cd. If one accepts the view that the affinity of divalent ions for calcite surfaces is probably a function of hydrated ionic radius, it could be predicted that Zn would be less strongly adsorbed (Pickering, 1983). The amount of Zn ion adsorbed from a suspension, containing $CaCO_3$ and metal nitrates (Zn, Cd, Pb, Cu), was comparatively small and precipitation rather than surface adsorption was suspected to be the dominant process in explaining the loss of Zn from solution. The differential adsorption behaviour of Zn and Cd towards $CaCO_3$ surfaces would explain the contradictory findings for Zn and Cd concentrations in soil solutions and plant shoot Cd and Zn concentrations after high rates of sludge addition (100t) in the current experiment. However, it could also be that some Cd coprecipitated with $CaCO_3$ and $MgCO_3$ and hence reduced Cd concentration in solution. With Ca and Mg concentration in solution in the range of 10^{-2} M and Cd in the range of 10^{-8} M a small amount of coprecipitated Cd would have a considerable impact on the Cd concentration in solution.

Precipitation of Cd phosphate can also reduce Cd concentration in solutions. In the current experiment differences in phosphate concentration in solution between sludge rates existed and furthermore GEOCHEM-PC predicted an oversaturation of $CaHPO_4$, particularly in the control and 100t treatments. However, precipitation of $CdHPO_4$ was not predicted with the low Cd concentrations encountered and thus seems a less likely explanation for the decrease in Cd concentration in soil solution and plants in the 100t treatment.

Hirsch *et al.* (1989) examined the effect of inorganic complexing agents on the adsorption of Cd to montmorillonite. They found that when the complexing agent was HCO_3^-, disappearance of Cd from the equilibrium solution was enhanced compared to the case where the anion was ClO_4^-, which does not form complexes with Cd. They argued that the enhanced dissappearance of Cd from the equilibrium solution of $NaHCO_3$ may be either because the $CdHCO_3^+$ complex has a very high binding coefficient to montmorillonite or because of Cd precipitation as $CdCO_3$. Due to practical constraints neither hypothesis could be tested. However, adsorption of $CdHCO_3^+$ complexes to soil surfaces could also be an explanation for the low Cd concentration in soil solution in the 100t treatment in the current experiment.

The possible influences of alkalinity, oversaturation with $CaCO_3$ and $MgCO_3$ and possibly enhanced adsorption of $CdHCO_3^+$ complexes, on sludge Cd solubility and phyto-availability have to be further investigated to clarify the exact mechanisms. It also must be established how long increased alkalinity after sludge addition is sustained in the soil solution and if Cd availability increases after this period of enhanced microbial activity in the soil diminishes.

9.5 Conclusions

- The addition of NaCl (Cl) enhanced Cd concentrations in soil solution and in plant shoots when grown in sludge amended soil, and Cl-complexation of Cd was the likely reason for this. Sludge-Cd as well as soil Cd, is complexed by Cl-ligands and rendered phytoavailable.

- The activity of $CdCl^+$ and $CdCl_2$ species increased and the Cd^{2+} activity remained unchanged as Cl concentration increased in the sludge treatments. Plant Cd concentrations were positively correlated with $CdCl^+$ activity in solution, whereas the free Cd^{2+} activity was not correlated to plant Cd uptake in the sludge treatments.

- High sludge applications (>100 t ha^{-1}) may reduce Cd availability compared to medium rate sludge applications. It is postulated that increased alkalinity as a result of high rates of sludge applications is likely to have some influence on Cd availability, but the mechanisms have to be further investigated.

- The NaCl (Cl) treatment considerably increased concentrations of Mn in plants, and increased Zn concentrations slightly.

Practical implications

- The Cl concentration of soil and sludges is as important as soil pH in determining Cd availability in soils

- Regulations for sludge application to land need to consider Cl as an important factor governing soil plant transfer of this element as well as soil pH, and soil and sludge metal concentrations. Factors which therefore need consideration are: a) irrigation water quality b) inherent soil salinity (dryland areas) c) sludge Cl loading (see General Discussion).

Chapter 10

General Discussion

10.1 Thesis review

In South Australia there is an increasing need to find further options for the disposal or use of sewage sludge, because ocean dumping of sludge is to be phased out in 1995. A decline in demand for kilned sludge (frequently as a fertiliser-amended sludge product predominately marketed for horticultural crops) has also reinforced the need for additional avenues of sludge usage. The use of sludge in broad scale agriculture has been investigated in a number of studies (Kelling *et al.*, 1977; Kirkham, 1982; Coker, 1983; Page *et al.*, 1987) and is a widespread practice in many countries. However, there was limited information about the effects of sludge applications when applied on Australian soil types and in sandy dryland areas such as South Australia. The initial research emphasis in Australia was on the potential uptake of sludge heavy metals by crops and the contamination of the food chain (De Vries and Tiller, 1978a,b; DeVries and Merry, 1980; DeVries, 1983a,b; Ross *et al.*, 1991). Only limited information existed about the potential fertiliser value of sludge (DeVries and Merry, 1980; DeVries, 1979 and 1981; Willett *et al.*, 1986). Moreover, Adelaide (Bolivar) produces an air dried sludge product which probably has mineralisation patterns different to the liquid digested sludge frequently used in other experiments. There was a need to determine the agronomic value of this particular type of sludge in dryland agriculture in South Australia where micronutrients, such as Zn, Cu and Mn, are frequently low and can reduce plant productivity.

In the field experiments in 1992 and 1993 sludge applications and inorganic fertiliser were compared in their effect on plant productivity during the growing season and their impact on chemical constituents in shoot and grain. It was intended to find a nutrient replacement for a fertiliser rate commonly applied in South Australia (20 kg N, 20 kg P, 2.8 kg Zn, 1.9 kg Cu, 4 kg Mn per hectare). Sludge usually does not contain the nutrients N, P, TE in the balance required for a particular crop. According to assumptions based on information in the literature a sludge rate of 2t contained P and Zn in amounts which could match the nutrient supply of the conventional inorganic fertiliser additions. Treatments with sludge plus inorganic fertiliser (N or N plus P) were included to supply the perceived shortfall in N and investigate the response to increased rates of P at the sites.

A 2t sludge application increased yield of wheat (*T. durum*) and barley (*H. vulgare*) considerably at all of the sites and in both years. The yield of 2t sludge-amended plants was generally equivalent to the yield of the inorganic fertiliser treatments, but where a discrepancy occurred a consistent tendency to lower yield was noticed. The difference was significant when the data of three sites in 1992 were combined, and in 1993 at one of the sites. This suggested that the N nutritional value of 2t sludge was close but below 20 kg N. However, the sludge treatments with additional N had an equivalent (better at one site) yield to the inorganic fertiliser comparison at all sites. Hence, the field data interpreted in a strict sense allowed only a bracketing of the N availability to a range of between 5 and 20 kg N. Further studies focusing on the N availability of sludge may be necessary to confirm the strong indications that 2t sludge contributes closer to the upper value of 20 kg N. The plant responses to sludge in comparison to inorganic fertiliser were much the same at Callington and Freeling in the climatically quite diverse years of 1992 and 1993.

Additional inorganic N with the sludge improved grain yield compared to the sludge only treatment at most sites and sludge plus N showed equal (or better) grain yield than the inorganic fertiliser comparison of 20 kg N ha^{-1}, 20 kg P ha^{-1} at all sites and in both years. This would suggest that the P nutritional value of 2t sludge was similar to the inorganic P application of 20 kg. However, slower plant development of sludge-amended plants compared to inorganic P fertilised plants in 1992 at a number of sites suggested that sludge P availability is low early in the season. This difference compared to inorganic P additions was less obvious later in the season (after booting stage) in 1992 and differences did not occur in 1993 with barley as a test plant. However, differences in P nutrition between sludge and inorganic P fertiliser were measurable in concentrations of P in shoots of barley plants in 1993. Grain yield was not affected by the difference in initial P availability in either years.

Increased rates of sludge up to a level of 10t ha^{-1} caused a logarithmic type response in shoot dry matter production and grain yield at two different sites. A plant response curve to fertiliser additions allows a more refined comparison between the fertiliser value of the two sources. The comparison of P uptake values of inorganic fertilised plants with P uptake values of plants treated with increasing sludge rates up to 10t ha^{-1} revealed that sludge applications of approximately 4t may be closer in their P supply to the inorganic fertiliser comparison than the 2t sludge rate, although a range from 2t - 6t as equivalent can be possible. At the same time shoot and grain yield of (2t+N*) sludge amended barley plants were equivalent to the yield of the inorganic fertilised plants. The physical placement of the two nutrient sources in the soil, with inorganic fertiliser being placed in the close vicinity of the seeds and sludge incorporated in a greater volume of soil may have caused some difference in P availability, particularly early in the season. For practical considerations a low inorganic fertiliser application may enhance the early nutrient supply to plants until the root system is established and sludge nutrients are more plant accessible.

Sludge proved to be a valuable source of micronutrients in the sandy soils of South Australia. The availability of sludge Zn was similar to the inorganic TE fertiliser as judged by growth response at a Zn deficient site and the concentration of Zn in shoots and grain of plants grown at non-deficient sites. The shoot and grain uptake of Zn increased linearly with sludge rates up to 10t ha^{-1}, although at late tillering and in the grain harvest a logarithmic curve would describe the relation equally well. The increase in Zn uptake values with sludge application rates were based on both increased Zn concentration in tissues and increased dry matter production. The results of the field experiments, particularly at Lameroo in 1992, suggest that sludge is a valuable soil amendment to correct Zn deficiency in the Mallee area. At Lameroo in 1992 the addition of TE increased yield by 44 % compared to plants fertilised with N and P only. The TE fertiliser mix applied in the field contained Zn, Cu and Mn, because all three elements are supplied by a sludge application. In Lameroo plants showed low levels of Zn and Cu and the yield increase after TE addition need not necessarily be based on Zn nutrition only. The concentrations of Cu in plants treated with either sludge or inorganic TE fertiliser were similar and higher than in plants treated with N and P only, suggesting that sludge is also a valuable source of Cu.

Using plant growth or ion uptake of plants as a measure of fertiliser efficiency is only possible when plants are not damaged by pests or diseases namely root pest or diseases (for example *Rhizoctonia solani, Pratylenchus ssp.*, Crown rot), or if the damage is similar across the treatments. When comparing different inorganic fertilisers, this is likely but not necessarily always true. In the case of comparing sludge, an organic material, with inorganic fertiliser the influence on soil biota is likely to be different. A possible impact of organic matter on the extent of root damage was not assessed. Application of organic residues to soil has long been considered potentially useful against some root rots and seedling diseases caused by soil borne plant pathogens (Lewis *et al.*, 1992; Hoitink, 1994) and galling caused by plant parasitic nematodes (Linford *et al.*, 1983). It is possible that such influences may have positively influenced grain yield in the sludge treatments. Zinc deficient plants were shown to be more susceptible to *R. solani* (Thongbai, 1993), a disease widespread in the Mallee area. Sludge additions may counteract the disease by improving Zn nutrition, but a direct influence on root diseases is also possible and would be worth further investigation. *(Plant growth in sludge treated plots, Lameroo 1992, seemed to be more even, than in inorganic fertilised plots.)* The application of organic matter on sandy soils with low organic matter content may be relatively more important in terms of influence on soil biota, than in more fertile soils with higher content of organic matter. Most likely sludge is also favourable for soil structure, soil water capacity and organic matter content, but these wider aspects of organic matter applications to soil were not addressed in the current study.

The optimum sludge application rate is the one that can provide the highest possible yield return in relation to the application expenses. The 4t treatment has the advantage in that it provided sufficient P and maybe even sufficient N for the crop. The 2t treatment certainly provided enough of the micronutrients Zn and Cu, but the plant available P seems to be somewhat lower than 20 kg of inorganic P and the N availability may depend on the site (nutritional status of the soil). The 10t treatment promises high yield, but the application could be quite laborious due to the large amount that has to be distributed in broadacre farming. Additionally it has to be confirmed that high sludge addition would not cause a yield depression under certain environmental conditions as has been noticed with elevated N applications in South Australia (Russell, 1967). Also the possible increase in heavy metal content of plants, for example Cd, has to be monitored (see Chapter 7, 8 and 9).

Sludge as a product for agricultural use could be refined if the concentration of Cd (and some other heavy metals), soluble salts and possibly Fe and Al salts were to be reduced. Heavy metals do accumulate in the soil, are taken up by plants and influence soil-biota. Soluble salts can inhibit early plant development and Fe and Al salts can reduce sludge-P availability to plants. However, Fe and Al salts may also reduce the phyto-availability of heavy metals and thus the desired concentration of Al and Fe in sludge has to be balanced between those two aims. Reduction of heavy metal load in the waste water depends on regulations and is already addressed by the appropriate bodies. A reduction in soluble salts would require some drainage of the sludge lagoons, where the sludge currently is air dried. This requires some capital investment. However, this process would enhance the value of sludge for any agricultural, horticultural and environmental use of sludge other than dumping. Stockpiling of sludge for some years may also reduce the content of soluble salts in sludge, but sludge N may also be lost by leaching and volatilisation during that time. A reduction of the Al and Fe content, if intended, may be more easily achieved, by the separate treatment of waste water sludge and water purification sludge. However, some time in the future Al or Fe salts may be required for P flocculation in waste water, as is the case in other countries, and hence a reduction of Al and Fe in the long term may not be possible.

It seems that a careful choice of recommended sludge application rates would allow a beneficial use of sludge nutrients and avoiding the negative impacts that sludge can have. The application process for sludge may need some adjustment in equipment, because sludge is a light and powdery product and quite different from granulated inorganic fertiliser. The results in terms of nutrient availability of sludge cannot directly be applied to granulated sludge, because a granulated product has a smaller surface area and may mineralise more slowly. Small additional experiments would be necessary to compare the products.

The residual value of low sludge applications was measurable in terms of P and Zn concentration in shoot and grain, but was too low to influence dry matter production or grain yield under the given circumstances. The residual value (P, Zn) of inorganic fertiliser compared to sludge nutrients reflected the relative nutrient availability of the two sources in the year of application. The residual value of medium sludge rates (4-10t) may have been underestimated. The experimental year, 1994, was one of the driest years on record in this area and hence growth potential and nutrient demand was low. Basal fertiliser applications may have obscured possible differences between treatments.

The field experiments have shown that sludge enhances plant growth and grain yield of cereals considerably and that sludge can ameliorate Zn and possibly Cu deficiency. But sludge supplies also Cd, a further heavy metal beside Zn and Cu. Cadmium concentration in food is regulated by the Australian National Health and Medical Research Council and must not exceed 0.05 mg Cd kg^{-1} fresh weight in cereal grain. Although the sludge used contained a low amount of Cd (3 mg kg^{-1}), an increase in sludge application rate did increase Cd concentration in shoot and grain of barley at one of the sites (Chapter 7). Indications for elevated Cd concentrations in (10t) treated plant were also noticeable at 2 of the other 7 field experiments (Strathalbyn 1992 and Freeling 1993) listed in the Appendix, Table A 7.1. However, low sludge application rates (2t ha^{-1}) did not enhance Cd levels of plants beyond concentrations measured for the inorganic fertiliser treatment. It has to be emphasised that the Cd addition of Bolivar sludge with 3 mg Cd kg^{-1} , applied at 2t ha^{-1}, was in the same range as the Cd addition in an average phophate fertiliser applied at 20 kg P ha^{-1}.

Recent findings have shown that Cl concentrations in soils are an important factor in determining Cd availability in soils. The Adelaide (Bolivar) sludge contains a comparatively high amount of water-soluble salts including chloride. The 10t sludge amended plants with elevated Cd concentrations at Lameroo 1992 also had slightly elevated Na concentrations (Cl was not measured by the ICP) compared to the inorganic fertilised plants (Appendix, Table A 7.2). This suggests that increased Cl concentration in the soil solution could have occured during the growth period and may have been a factor contributing to Cd availability at this site. However, it is likely that lupins grown in the previous year also had an important influence on Cd availability at this site.

Economic restrictions in terms of transport costs of sludge to agricultural areas make it likely that sludge could be applied on irrigated land or saline soils (Section 8.1). Hence there was a need to investigate the influence of Cl on Cd availability of sludge borne Cd, because research so far concentrated on soil borne or fertiliser borne Cd.

In pot experiments the influence of increasing NaCl additions on Cd availability in sludge amended soil (the equivalent of 50 t ha^{-1}) was investigated. The increase in Cl concentration in soil solution was positively correlated with the Cd concentration in the soil solution and in plant shoots. The increase in Cd concentration in soil solution was more marked than in plant shoots. It was evident that Cd uptake of plants was considerably increased although the sludge application increased soil pH from 6.3 and 4.6 to pH 7.6 and 7.5 for the two soils respectively. The chemical speciation program GEOCHEM-PC was used to calculate the change in Cd species in soil solution in the different NaCl treatments. The Cd concentration of plants correlated best with the increase in $CdCl^+$ activity in soil solution. The free Cd^{2+} activity was generally not significantly correlated with the Cd uptake of plants and remained unchanged in three of the four experiments. This is in agreement with the findings of Smolders *et al.* (1996), where $CdCl^+$ activity explained most of the variance in Cd concentration in shoots, when grown in agricultural soil.

Although sludge contributed the majority of total Cd in the soil-sludge mix in which plants were grown, it cannot be claimed with certainty that mainly sludge borne Cd was mobilised by the NaCl additions, which in turn lead to increases in shoot Cd concentrations of plants. A factorial experiment with sludge rates from 0 to 100t ha^{-1} and increasing NaCl additions was conducted to determine if sludge borne Cd, as well as soil-borne Cd, is mobilised by chloro-ligands. The results of this experiment lead to several conclusions. Firstly, the increase in sludge rates caused an increase in Cd concentrations in soil solution and Cd concentrations of plants. Secondly, with an increase in Cl concentration in solution, sludge borne Cd was mobilised. However, differences in slope of regression models, describing the influence of Cl concentration in solution on Cd uptake by plants, between sludge rates (25t or 50t) were much less striking than the difference in Cd mobilisation between the 0 and 25t sludge rate. The concentrations of Cd in solution confirmed these findings. Hence the results suggest that sludge is a source of easily soluble Cd, but the mobilising influence of Cl in soil solution may be less pronounced on sludge borne Cd than on soil borne Cd.

A third finding in the factorial experiment was that high (~100t ha^{-1}) compared to medium sludge rates did not further increase but rather decreased the Cd concentration in soil solution and Cd uptake by shoots, when grown under high Cl conditions (Table 9.1). The actual cause of this phenomenon could not be fully explained. An increase in adsorption sites due to sludge additions may not be the decisive factor, because the ratio of sludge adsorption sites to sludge borne Cd was identical when more sludge was added. But with the increase in sludge rates an increase in alkalinity in the soil solution was noticed while pH was unchanged. Precipitation of $CaCO_3$ and $MgCO_3$ was predicted by GEOCHEM-PC, when precipitation was allowed. Calcium carbonate was shown to adsorb Cd very effectively and selectively (Pickering, 1983) and may have caused a lower Cd concentration in solution than expected at highest sludge rate. Further investigations into the mechanisms which caused a decrease in Cd availability in high compared to medium sludge treatments are necessary.

10.2 General Discussion

A number of practical implications arise from the current findings. It was shown that sludge can be a significant source of nutrients in dryland cereal agriculture in South Australia. Sludge application rates of 4t seem to be a safe rate to be recommended in terms of N and P supply for agricultural land where 20 kg N and 20 kg P plus TE per hectare were conventionally applied. Sludge is an excellent source of plant available Zn and can be used to ameliorate Zn deficiency in agricultural soils. However, sludge also contains Cd which can potentially be plant available even in soils with a high pH. A measurable increase in Cd concentration in grain at a application rate of 10t ha^{-1} was measured at one site.

It was shown that sludge borne Cd is mobilised by increased concentrations of Cl in soils or soil solutions. Hence it is not advisable to apply sludge with a high content of Cd to agricultural land where plants are likely to be exposed to high concentration of Cl in the root zone, such as saline soils or irrigated land. Although high rates of sludge reduced Cd availability to plants compared to medium rates when exposed to the same Cl concentration in solution (pot experiments), those rates still may not be desirable on most soils, because sludge is also a substantial source of Cl itself. This needs to be considered in dryland agriculture, where leaching of the soluble salts by rainfall may not be guaranteed in every year.

The potential transport distances of sludge from Adelaide, which is determined by economical considerations, is likely to be up to 150 km. This includes areas with horticultural crops and broadscale agricultural land. The results of the current study can add some discussion points when the future use of sludge in the broad area of plant production will be decided. Sludge applications in broadscale agriculture in comparison to horticultural crops seem to have some advantages: Firstly, sludge nutrients are probably exploited more effectively. In the current study rates of only 2t sludge increased the yield of cereal crops considerably in two contrasting growth seasons, but De Vries (1979) could not measure an agronomic value of sludge application rates of below 9t ha^{-1} in vegetable crops. Moreover, heavy metals such as Zn and Cu could be used beneficially in many regions in South Australia, where micronutrient deficiency can be a problem. Thirdly, the Cd uptake of vegetable plants such as Swiss chard is generally higher than from cereal plants and, more importantly, vegetable crops are more likely to be exposed to high Cl levels in soils due to irrigation. A significant influence of sludge borne Cl on Cd uptake of plants at low rates (<10t ha^{-1}) in dryland agriculture is less likely. Although an increase in Cd concentration in shoot and grain at sludge rates of 10t ha^{-1} compared to inorganic fertiliser treatments were measured, absolute increases were low. However, it emphasises again that caution should be taken in applying high rates of sludge to dryland areas or saline soils. Although pot experiments have shown that high rates of sludge can decrease Cd uptake of plants compared to medium rates, they also contain a considerable amount of soluble salts which may lower plant emergence or early plant development until salt gets washed out of the root zone.

Conclusions

Sludge is a valuable source of N, P and Zn in broadscale agriculture in South Australia. The sludge P availability is between 18 and 55 % compared to P in inorganic fertiliser and most likely around 35 %. The mineralisation of sludge N was between 10 to 42 % in the year of application, and most likely closer to the upper margin. Sludge Zn was equivalent to inorganic Zn in elevating plant Zn concentrations grown in deficient and non deficient soils. Adelaide (Bolivar) sludge contains a considerable amount of water-soluble salts. The concentration of Cl in soil solution was found to increase Cd availability of sludge borne Cd, although the effect seemed to be relatively less than for soil Cd. Application rates of sludge can be beneficial when low to medium rates are chosen, which supply sufficient nutrients without being a potential risk in terms of input of Cd and Cl to agricultural land.

The return of nutrients essential to both plants and animals to the land from which they came is fundamentally and environmentally sound. The problem is, in passing these nutrients through the city, they have been contaminated by heavy metals and salts. E&WS (now SA water) needs to look towards their objectives by

a) reducing contaminants
b) increasing entrapment rates of nutrients in the solid phase of the digestion
c) establishing a financially attractive and fair means of returning these nutrients to the macro- and micronutrient (and organic matter) deficient sandy soils of productive regions (>375 mm) east (e.g. Callington - Lameroo) and North-West of Adelaide (e.g. Freeling- Snowtown - Kadina)
d) reducing the Cl concentration in the sludge

Appendices: Chapter 3

Plate 1: Field Plan for all sites in 1992

Border #
1t+N*+P/2+TE/2
2t
nil
#
nil+N+P+TE
2t+N*+P/2
#
nil+N+P
2t+N*

Border #
2t
nil
#
nil+N+P
2t+N*
#
nil+N+P+TE
2t+N*+P/2
1t+N*+P/2+TE/2

nil+N+P
nil
#
nil+N+P+TE
1t+N*+P/2+TE/2
2t+N*+P/2
#
2t+N*
2t

nil
2t+N*
1t+N*+P/2+TE/2
#
nil+N+P+TE
nil+N+P
#
2t
2t+N*+P/2

nil+N+P+TE
2t+N*
#
2t
nil+N+P
2t+N*+P/2
#
nil
1t+N*+P/2+TE/2
Border #

(nil+N+P) applied, plots not used in the current experimental year

Table A.3.1 Plant P concentration in shoot and grain and P uptake values at the three harvests in 1992, Callington.

	nil	nil +N+P	nil +N+P +TE	2t	2t +N*	2t +N*+P/2	1t +N*+P/2 +TE/2	LSD (P= 0.05)	Critical value[a]
				P concentration [mg kg^{-1}]					
H1 shoot	2243	3957	3776	2422	2568	3350	3186	501	3500
H2 shoot	2111	2275	2416	2110	2140	2434	2317	201	2000
Grain	4045	3924	3877	3961	3802	3983	4502	273	2-3000
				P uptake [mg m^{-2}]					
H1 shoot	157	469	385	199	231	316	269	125	
H2 shoot	384	894	791	605	569	740	659	197	
Grain	667	905	867	877	863	1042	1021	107	

[a] approximate critical values for *T.aestivum* (Reuter and Robinson, 1986)

Table A.3.2 Plant P concentration in shoot and grain and P uptake values at the three harvests in 1992, Strathalbyn.

	nil	nil +N+P	nil +N+P +TE	2t	2t +N*	2t +N*+P/2	1t +N*+P/2 +TE/2	LSD (P= 0.05)	Critical value[a]
				P concentration [mg kg^{-1}]					
H1 shoot	3567	5282	5531	3589	3603	4601	4664	482	3500
H2 shoot	1582	1927	2138	2019	1867	2192	1951	196	2000
Grain	3695	3885	3862	3955	3853	3863	3794		2-3000
				P uptake [mg m^{-2}]					
H1 shoot	130	281	300	125	121	219	222	32	
H2 shoot	746	1070	1303	918	861	1167	1110	177	
Grain	1193	1693	1560	1523	1553	1577	1527	154	

[a] approximate critical values for *T.aestivum* (Reuter and Robinson, 1986)

Table A.3.3 Plant P concentration in shoot and grain and P uptake values at the three harvests in 1992, Freeling.

	nil	nil +N+P	nil +N+P +TE	2t	2t +N*	2t +N*+P/2	1t +N*+P/2 +TE/2	LSD (P= 0.05)	Critical value[a]
				P concentration [mg kg^{-1}]					
H1 shoot	2730	3178	3193	3064	2790	3177	3386	268	3500
H2 shoot	1763	1644	1644	1897	1772	1765	1748		2000
Grain	3583	3683	3681	3816	3537	3687	3762	167	2-3000
				P uptake [mg m^{-2}]					
H1 shoot	119	224	251	162	148	225	276	37	
H2 shoot	449	650	707	567	559	720	735	140	
Grain	1305	1516	1484	1491	1463	1681	1604	188	

[a] approximate critical values for *T.aestivum* (Reuter and Robinson, 1986)

Table A.3.4 Plant Zn concentration in shoot and grain and Zn uptake values at the three harvests in 1992, Callington.

	nil	nil +N+P	nil +N+P +TE	2t	2t +N*	2t +N*+P/2	1t +N*+P/2 +TE/2	LSD (P= 0.05)	Critical value[a]
				Zn concentration [mg kg^{-1}]					
H1 shoot	15.2	13.5	13	16	19.2	16.2	15	2.66	20
H2 shoot	11.1	8.7	9.9	11.2	11.3	11.6	12.4	1.60	15
Grain	25.1	20.5	22.4	25.1	24.4	21.6	25.5	3.08	5-10
				Zn uptake [mg m^{-2}]					
H1 shoot	1.04	1.60	1.33	1.32	1.75	1.60	1.24	n.s.	
H2 shoot	2.04	3.42	3.22	3.23	2.99	3.51	3.51		
Grain	4.18	4.74	5.02	5.58	5.54	5.65	5.44	0.73	

[a] approximate critical values for *T.aestivum* (Reuter and Robinson, 1986)

Table A.3.5 Plant Zn concentration in shoot and grain and Zn uptake values at the three harvests in 1992, Strathalbyn.

	nil	nil +N+P	nil +N+P +TE	2t	2t +N*	2t +N*+P/2	1t +N*+P/2 +TE/2	LSD (P= 0.05)	Critical value[a]
				Zn concentration [mg kg^{-1}]					
H1 shoot	40.6	36	35	39.6	42.4	37.2	40.6	3.22	20
H2 shoot	13.8	12	14.2	16.1	15.2	14.3	14.7	1.65	15
Grain	33.4	28.3	30.8	32.8	31.9	30.3	31.6	2.22	5-10
				Zn uptake [mg m^{-2}]					
H1 shoot	1.47	1.91	1.91	1.38	1.41	1.77	1.96	0.31	
H2 shoot	6.48	6.68	8.60	7.30	7.04	7.65	8.47	1.48	
Grain	10.8	12.2	12.4	12.6	12.8	12.4	12.7	1.18	

[a] approximate critical values for *T.aestivum* (Reuter and Robinson, 1986)

Table A.3.6 Plant Zn concentration in shoot and grain and Zn uptake values at the three harvests in 1992, Freeling.

	nil	nil +N+P	nil +N+P +TE	2t	2t +N	2t +N*+P/2	1t +N*+P/2 +TE/2	LSD (P= 0.05)	Critical value[a]
				Zn concentration [mg kg^{-1}]					
H1 shoot	18.9	12.9	14.1	20.5	20.7	19.9	20.1	2.89	20
H2 shoot	10.2	8.7	7.2	9.9	9.4	8.8	8.6	1.17	15
Grain	22.7	21.6	21.5	23.4	21.8	21.8	23.0	n.s.	5-10
				Zn uptake [mg m^{-2}]					
H1 shoot	0.82	0.87	1.12	1.09	1.11	1.40	1.65	0.11	
H2 shoot	2.59	3.47	3.10	2.97	2.98	3.59	3.62	n.s.	
Grain	8.2	8.9	8.7	9.2	9.0	10.0	9.7	n.s.	

[a] approximate critical values for *T.aestivum* (Reuter and Robinson, 1986)

Table A.3.7 Plant copper (Cu) concentration in shoot and grain and Cu uptake values at Lameroo 1992.

	nil	nil +N+P	nil +N+P +TE	2t	2t +N	2t +N*+P/2	1t +N*+P/2 +TE/2	LSD (P= 0.05)	Critical value[a]
				Cu concentration [mg kg^{-1}]					
H1 shoot	3.0	2.4	3.4	3.9	3.7	3.9	3.7	0.67	
H2 shoot	1.2	1.4	1.1	1.3	1.1	1.3	1.1	n.s.	YEB 1.6
Grain	2.5	2.4	2.1	2.3	2.3	2.1	2.3	n.s.	2.5[b]
				Cu uptake [µg m^{-2}]					
H1 shoot	56	77	110	100	117	161	136	24	
H2 shoot	164	209	254	269	267	320	291	102	
Grain	223	237	287	307	380	333	337	88	

[a] approximate critical values for *T.aestivum* (Reuter and Robinson, 1986)
[b] King (1975)

Table A.3.8 Plant manganese (Mn) concentration in shoot and grain and Mn uptake values at Lameroo 1992.

	nil	nil +N+P	nil +N+P +TE	2t	2t +N*	2t +N*+P/2	1t +N*+P/2 +TE/2	LSD (P= 0.05)	Critical value[a]
				Mn concentration [mg kg^{-1}]					
H1 shoot	24.9	25.4	31.0	26.4	31.3	27.5	33.1	n.s.	11-13
H2 shoot	23.8	24.9	18.1	18.7	19.2	14.4	16.6	n.s.	YEB 10
Grain	21.7	22.4	22.1	18.1	19.5	19.2	21.2	n.s.	n.a.
				Mn uptake [mg m^{-2}]					
H1 shoot	0.41	0.81	1.02	0.65	0.97	1.13	1.19	0.209	
H2 shoot	2.84	3.43	4.19	3.99	5.01	3.71	4.10	n.s.	
Grain	1.70	2.10	2.93	2.30	3.17	3.00	3.13	0.58	

[a] approximate critical values for *T.aestivum* (Reuter and Robinson, 1986)

Plate 2: Field Plan: Freeling 1993 and Lameroo 1993

Border	
10t	b
1t+N*+P/2+TE/2	a
2t	a
nil	ab
4t+N*	b
nil+N+P+TE	ab
2t+N*+P/2	a
#	
nil+N+P	a
2t+N*	ab

nil+N+P	a
nil	a
4t+N*	b
nil+N+P+TE	ab
1t+N*+P/2+TE/2	a
2t+N*+P/2	a
10t	b
2t+N*	ab
2t	a

Border	
b	4t+N*
a	2t
ab	nil
b	#
a	nil+N+P
ab	2t+N*
b	10t
ab	nil+N+P+TE
a	2t+N*+P/2
a	1t+N*+P/2+TE/2

a	nil
ab	2t+N*
a	1t+N*+P/2+TE/2
	4t+N*
ab	nil+N+P+TE
a	nil+N+P
b	10t
a	2t
a	2t+N*+P/2

ab	nil+N+P+TE
ab	2t+N*
b	10t
a	2t
a	nil+N+P
a	2t+N*+P/2
b	4t+N*
a	nil
a	1t+N*+P/2+TE/2
Border	

a Results presented in Chapter 4
b Results presented in Chapter 5

Plate 3: Field Plan: Callington, 1993

	Border	Border	
	#	2t	a
	(no label**)	#	
		4t+N*	b
		nil	a
a	2t+N*+P/2	nil+N+P	a
		nil+N+P+TE	ab
		#	
	#	2t+N*	ab
		2t+P/2	a
		10t	b

		2t+N*+P/2	a
		nil	a
a	2t+P/2	2t	a
		nil+N+P+TE	ab
		#	
		#	
ab	2t+N*	nil+N+P	a
		10t	b
		4t+N*	b

	Border	Border	
ab	2t+N*	#	
b	4t+N*		
a	nil		
a	nil+N+P	2t	a
a	2t+P/2		
b	10t		
	#	2t+N*+P/2	a
ab	nil+N+P+TE		
	#		
	#		

a	nil		
b	10t		
	#		
a	2t+N*+P/2	2t	a
ab	nil+N+P+TE		
a	nil+N+P		
ab	2t+N*	2t+P/2	a
b	4t+N*		
	#		

ab	nil+N+P+TE		
b	10t		
a	2t+N*+P/2		
	4t+N*		
a	nil+N+P		
	#		
	#		
a	nil		
	#		
a	2t+P/2	2t+N*	ab
	Border	Border	

a Results presented in Chapter 4.
b Results presented in Chapter 5.
(no label**) Plots without label: Experimental plots used to establish the residual value of sludge and fertiliser applications (Chapter 6).
plots not used in the current experimental year

Appendices: Chapter 5

Table A 5.1 R^2 values for the graphs in Figures 5.3, 5.4 and 5.5 describing the relation of sludge application rate to dry weight production, P uptake and Zn uptake of plants. For a comparison the R^2 values for a linear and logarithmic correlation are given. (**Bold**= correlation shown in the graphs)

	Callington		Freeling	
	linear	logarithmic	linear	logarithmic
Dry weight*				
Harvest 1	0.65	**0.74**	0.82	**0.92**
Harvest 2	0.54	**0.41**	0.62	**0.70**
Grain yield	0.84	**0.90**	0.77	**0.77**
P-uptake				
Harvest 1	0.64	**0.85**	0.72	**0.92**
Harvest 2	**0.65**	0.59	**0.45**	0.44
Grain yield	0.68	**0.90**	0.79	**0.79**
Zn-uptake				
Harvest 1	**0.81**	0.78	**0.82**	0.85
Harvest 2	**0.78**	0.55	**0.75**	0.59
Grain yield	**0.81**	0.82	**0.85**	0.78

(* Only sludge application rates from 0 to 4t ha^{-1} have been included into the curve fitting for the relation between sludge application rate and dry weight production.)

Table A.5.2 Callington, 1993 Concentration of Mn in plant shoots and grain and Mn uptake at the three harvests.

	nil	nil +N+P +TE	2t +N*	4t +N*	10t	LSD (P=0.05)	Critical values[a]
			Concentration [mg kg^{-1}]				
H1 shoot	24.9	24.0	20.8	23.3	27.0	n.s.	13-16
H2 shoot	11.3	11.3	8.1	10.1	11.2	2.55	5-24
Grain	10.4	10.5	9.9	10.4	10.9	0.77	n.a.
			Uptake [mg m^{-2}]				
H1 shoot	3.3	5.6	5.1	6.5	8.5	1.38	
H2 shoot	5.7	8.6	5.7	9.9	11.9	2.98	
Grain	3.9	5.6	5.4	6.3	7.5	0.91	

[a] approximate critical values for *H. vulgare* (Reuter and Robinson, 1986)

Table A.5.3 Freeling, 1993 Concentration of Mn in plant shoots and grain and Mn uptake at the three harvests.

	nil	nil +N+P +TE	2t +N*	4t +N*	10t	LSD (P=0.05)	Critical values[a]
			Concentration [mg kg^{-1}]				
H1 shoot	48.5	38.8	32.6	29.4	26.9	5.33	13-16
H2 shoot	19.7	17.7	17.2	16.0	15.2	3.66	5-24
Grain	13.6	12.7	12.3	12.6	12.1	0.49	n.a.
			Uptake [mg m^{-2}]				
H1 shoot	2.4	4.5	4.1	4.2	4.6	0.87	
H2 shoot	9.2	13.9	14.3	15.2	18.5	4.20	
Grain	2.9	3.3	3.2	3.6	4.1	0.34	

[a] approximate critical values for *H. vulgare* (Reuter and Robinson, 1986)

Table A.5.4 Callington, 1993 Concentration of Cu in plant shoots and grain and Cu uptake at the three harvests.

	nil	nil +N+P +TE	2t +N*	4t +N*	10t	LSD (P=0.05)	Critical values[a]
			Concentration [mg kg^{-1}]				
H1 shoot	7.1	6.0	7.0	7.2	8.6	0.88	4.8
H2 shoot	3.1	2.4	2.9	2.7	3.7	0.55	YEB=1.3
Grain	3.5	3.6	3.6	3.9	4.5	0.31	2
			Uptake [mg m^{-2}]				
H1 shoot	0.93	1.45	1.73	2.01	2.69	0.38	
H2 shoot	1.53	1.84	2.14	2.57	3.87	0.76	
Grain	1.34	1.97	1.95	2.34	3.13	0.32	

[a] approximate critical values for *H. vulgare* (Reuter and Robinson, 1986)

Table A.5.5 Freeling, 1993 Concentration of Cu in plant shoots and grain and Cu uptake at the three harvests.

	nil	nil +N+P +TE	2t +N*	4t +N*	10t	LSD (P=0.05)	Critical values[a]
			Concentration [mg kg^{-1}]				
H1 shoot	8.4	6.7	7.1	6.8	8.1	0.79	4.8
H2 shoot	3.7	2.9	3.1	3.0	3.8	0.45	YEB=1.3
Grain	4.6	4.1	4.2	4.3	4.8	0.39	2
			Uptake [mg m^{-2}]				
H1 shoot	0.46	0.79	0.89	0.99	1.41	0.206	
H2 shoot	1.75	2.30	2.63	2.79	4.64	0.727	
Grain	0.97	1.06	1.08	1.23	1.64	0.131	

[a] approximate critical values for *H. vulgare* (Reuter and Robinson, 1986)

Appendices: Chapter 7

Table A.7.1 Summary of Cd concentration (+/-stdev in brackets) of shoots (Harvest 2) and grain, grown in the field experiments in 1992 (*T.durum*) and 1993 (*H.vulgare*).

	nil	**nil+N+P+TE**	**2t+N***	**5t+N***	**10t**	**LSD (P=0.05)**
1992: Cd concentration in shoots [$\mu g\ kg^{-1}$]						
Callington	52 (+/-9)[2]	69 (+/-12)[2]	59 (+/-16)[2]	<12	<12	*n.a.*
Strathalbyn	30 (+/-5)[3]	52 (+/- 8)[3]	42 (+/- 2)[3]	113[1]	94[1]	*n.a.*
Freeling	Cd was <12 $\mu g\ kg^{-1}$ (detection limit) in the samples analysed					
Lameroo	161 (+/-23)[3]	90 (+/-27)[3]	112 (+/-19)[3]	113[1]	91[1]	*n.a.*
Marion Bay	Cd was <12 $\mu g\ kg^{-1}$ (detection limit) in the samples analysed					
1992: Cd concentration in grain [$\mu g\ kg^{-1}$]						
Callington	38 [1]	33[1]	29[1]	<12[1]	<12[1]	*n.a.*
Strathalbyn	19 (+/-17)[3]	30 (+/- 5)[3]	23 (+/-21)[3]	65[1]	76[1]	*n.a.*
Lameroo	116 (+/-38)[3]	65 (+/-21)[3]	54 (+/-47)[3]	77[1]	59[1]	*n.a.*

	nil	**nil+N+P+TE**	**2t+N***	**4t+N***	**10t**	**LSD**
1993: Cd concentration in shoots [$\mu g\ kg^{-1}$]						
Callington[c]	55	39	64	105	61	**n.s.**
Freeling[c]	66	56	74	83	94	25.6
1993: Cd concentration in grain [$\mu g\ kg^{-1}$]						
Callington[c]	39	47	28	38	40	**n.s.**
Freeling[c]	36	18	16	23	10	**n.s.**

(1,2,3) indicates the number of samples analysed

(c) values below the calibration range, back extraction procedure would have been necessary to analyse the values appropriately; 5 replicates per treatment;

(*n.a.*) not applicable
(**n.s.**) not significant

Table A.7.2 Lameroo, 1993 Concentration of Na in plant shoots and grain at the three harvests.

	nil	nil +N+P +TE	2t +N*	4t +N*	10t	LSD (P=0.05)
			Concentration [mg kg^{-1}]			
H1 shoot	13700	11100	12400	14900	18100	3490
H2 shoot	7100	8300	7800	10600	11100	2710
Grain	223	252	234	274	305	n.s.

Table A.7.3 Callington, 1993 Concentration of Na in plant shoots and grain and Na uptake at the three harvests.

	nil	nil +N+P +TE	2t +N*	4t +N*	10t	LSD (P=0.05)
			Concentration [mg kg^{-1}]			
H1 shoot	8948	9125	9676	9080	10023	n.s.
H2 shoot	3463	4189	4107	4948	4036	n.s.
Grain	262	271	245	233	231	n.s.

Table A.7.4 Freeling, 1993 Concentration of Na in plant shoots and grain at the three harvests.

	nil	nil +N+P +TE	2t +N*	4t +N*	10t	LSD (P=0.05)
			Concentration [mg kg^{-1}]			
H1 shoot	4422	3162	3334	3792	4439	861
H2 shoot	2347	1701	1952	1914	3052	641
Grain	180	153	132	130	114	17

Table A.8.1 Influence of NaCl addition on the concentration of selected cations and anions in soil solution. Wheat grown in sludge-amended Lameroo soil (Exp. 1) and sludge-amended South East soil (Exp.3).

Irrigation water	Ca	Mg	K	Na	P	Zn	Mn	Cu	NO_3-N	SO_4-S	DOC
NaCl [mg l^{-1}]			[mg l^{-1}]				[µg l^{-1}]			[mg l^{-1}]	[mg l^{-1}]
Experiment 1, wheat, Lameroo soil											
0	743	510	18	204	12	420	n.d.	300	15.0	674	718
400	984	682	25	757	14	670	293	498	15.0	931	763
800	1089	746	30	1401	14	560	338	600	0.4	770	756
1200	1068	688	31	1689	13	530	450	525	3.0	770	863
1600	1009	621	29	2142	11	530	527	656	16.0	835	772
LSD	***n.s.***	***n.s.***	***n.s.***	***302***	***n.s.***	***n.s.***	***217***	***n.s.***	***n.s.***	***n.s.***	***n.s.***
Experiment 3, wheat, South East soil											
0	628	421	15	188	11	650	513	258	126	867	1033
800	851	501	24	980	10	700	838	203	126	867	916
1200	973	610	42	1181	12	830	1013	298	168	963	971
1600	1141	651	49	1665	12	780	1070	275	182	1027	1037
LSD	***271***	***n.s.***	***23.7***	***221***	***n.s.***	***n.s.***	***369***	***n.s.***	***n.s.***	***n.s.***	***n.s.***

(n.d. not detected)

Table A.8.2 Influence of NaCl addition on the concentration of selected elements in plant shoots. Wheat grown in sludge- amended Lameroo soil (Exp.1) and sludge-amended South East soil (Exp.3).

Irrigation water quality NaCl [mg l-1]	Ca	Mg	K	Na	P	Zn	Mn	Cu
	[mg kg^{-1}]							
Experiment 1, wheat, Lameroo soil								
0	4576	3470	44997	625	7439	69	17	13
400	3899	3284	50131	1876	8209	74	20	14
800	4088	3162	44617	2675	8633	75	24	13
1200	3460	3035	50183	2492	9407	81	23	13
1600	3631	3074	52785	2619	10396	88	26	14
LSD	***487***	***222***	***5539***	***559***	***436***	***6.3***	***2.1***	***n.s.***
Experiment 3, wheat, South East soil								
0	3286	2577	41635	252	8359	49	24	15
800	3375	2583	42856	1299	8528	49	28	14
1200	3563	2665	45377	1419	9491	52	29	15
1600	3674	2602	44485	1999	8884	52	30	14
LSD	***257***	***n.s.***	***n.s.***	***477***	***580***	***3.1***	***1.3***	***n.s.***
**** critical conc..***	***2000***	***1500***	***41000***	-	***6200***	***20***	***13***	***2***

(* critical concentrations according to Reuter and Robinson (1986)

Table A.8.3 Influence of NaCl addition on the concentration of selected cations and anions in soil solution. Swiss chard grown in sludge-amended Lameroo soil (Exp.2) and sludge-amended South East soil (Exp.4).

Irrigation water	Ca	Mg	K	Na	P	Zn	Mn	Cu	NO_3-N	SO_4-S	DOC
NaCl [mg l-1]			[mg l^{-1}]				[µg l^{-1}]			[mg l^{-1}]	[mg l^{-1}]
Exp.2 Swiss chard, Lameroo soil											
0	1168	745	73	132	17	530	360	268	476	1220	503
400	1394	876	105	456	18	570	768	290	560	1380	467
800	1196	759	93	847	15	530	550	248	350	1188	479
1200	1316	784	106	1222	17	570	865	235	448	1220	456
1600	1435	872	125	1765	17	600	865	323	378	1316	552
LSD	***n.s.***	***n.s.***	***n.s.***	***139***	***n.s.***	***n.s.***	***391***	***n.s.***	***n.s.***	***n.s.***	***n.s.***
Exp. 4, Swiss chard, South East soil											
0	478	307	77	98	10	550	170	128	112	770	640
800	686	405	88	663	10	600	358	150	154	899	755
1200	608	373	111	889	9	480	303	125	154	770	586
1600	837	471	128	1388	10	530	450	153	154	899	773
LSD	***216***	***n.s.***	***31***	***171***	***n.s.***	***n.s.***	***n.s.***	***n.s.***	***n.s.***	***n.s.***	***n.s.***

Table A.8.4 Influence of NaCl addition on the concentration of selected elements in plant shoots. Swiss chard grown in sludge-amended Lameroo soil (Exp.2) and sludge-amended South East soil (Exp.4).

Irrigation water quality NaCl [mg l-1]	Ca	Mg	K	Na	P	Zn	Mn	Cu
	[mg kg^{-1}]							
Exp.2, Swiss chard, Lameroo soil								
0	12031	12790	69067	26486	5555	177	136	18
400	10190	11549	62042	39926	5082	135	141	18
800	9543	10982	58092	46965	5306	144	150	19
1200	9286	11383	57194	47220	5164	143	162	20
1600	9194	11071	56063	51106	5296	138	181	19
LSD	***1647***	***n.s.***	***6961***	***4307***	***n.s.***	***25.8***	***18.2***	***n.s.***
Exp. 4, Swiss chard, South East soil								
0	9500	9443	42053	21889	5989	160	122	17
800	8858	8006	41550	40241	5434	135	119	16
1200	8975	8505	38924	44743	5373	128	133	15
1600	8343	8483	33094	48188	4779	127	129	16
LSD	***n.s.***	***n.s.***	***n.s.***	***5992***	***486***	***19.4***	***n.s.***	***n.s.***
**** sufficient conc.*** ([a])	***25000***	***2000***	***30000***	**-**	***3000***	***20***	***50***	***5***

([a]) most recent fully developped leaf, after 20 days, according to Jones et al. (1991)

Table A.9.1 Influence of NaCl addition on the concentration of selected cations and anions in soil solution of sludge-amended soils with sludge application rates equivalent to 0, 25, 50 and 100t sludge per hectare (SS = sludge). (LSD, P=0.05)

Irrigation water quality	Ca	Mg	K	Na	P	Zn	Mn	Cu	NO_3	SO_4	DOC
NaCl [mg l^{-1}]			[mg l^{-1}]				[µg l^{-1}]			[mg l^{-1}]	
0 t sludge											
0	108	41	64	95	17	26	116	71	9.0	100	83
400	251	78	97	766	10	53	30	82	12.0	103	92
800	413	144	184	1709	15	65	363	120	23.0	149	147
1200	468	169	240	2120	12	68	644	91	34.0	202	119
1600	617	218	244	2876	14	96	964	103	47.0	286	185
25 t sludge ha $^{-1}$											
0	349	242	19	223	7	158	59	275	0.4	514	255
400	441	311	36	792	7	324	189	234	0.0	578	299
800	586	383	54	1449	7	214	467	298	0.0	578	340
1200	677	483	71	1784	8	289	176	436	5.5	738	383
1600	725	468	67	2499	7	326	580	451	13.0	546	510
50 t sludge ha $^{-1}$											
0	555	475	28	365	11	288	199	697	4.3	995	541
400	607	521	46	826	10	387	445	518	14.0	931	569
800	616	485	42	1275	9	277	367	511	14.0	803	440
1200	787	606	58	1941	9	386	518	666	0.7	867	536
1600	856	722	69	2019	11	420	821	625	1.5	1091	567
100 t sludge ha $^{-1}$											
0	821	824	81	560	17	424	1067	652	3.5	1445	1073
400	758	752	64	921	15	385	979	533	0.1	1380	1044
800	758	718	101	1459	13	364	856	589	2.0	1156	911
1200	928	883	90	1909	15	480	1374	778	4.0	1316	1145
1600	878	864	163	1988	15	394	1177	451	0.3	1188	1046
F- Prob. SS rate	0.001	0.001	0.001	n.s.	0.001	0.001	0.001	0.001	n.s.	0.001	0.001
F-Prob. salt rate	0.001	0.001	0.001	0.001	n.s.	0.038	0.001	n.s.	n.s.	n.s.	n.s.
F-Prob. Interaction	n.s.	n.s.	0.006	0.006	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.
SS LSD	86.7	61.9	26.6	-	2.04	63.3	207	138	-	132	85.5
Salt LSD	96.9	69.1	29.8	207	-	70.7	231	-	-	-	-
Interaction LSD	-	-	59.5	413	-	-	-	-	-	-	-

Table A.9.2 Influence of NaCl addition on the concentration of selected cations and anions in wheat shoots grown in sludge-amended soils with sludge application rates equivalent to 0, 25, 50 and 100t per hectare. (SS=sludge) (LSD, P=0.05)

Irrigation water quality	Ca	Mg	K	Na	P	Zn	Mn	Cu
NaCl [mg l^{-1}]	[mg kg^{-1}]							
0 t sludge								
0	4249	1528	45916	375	5768	28	59	6.1
400	4677	1632	47520	1686	6353	35	67	7.0
800	4793	1817	49832	2769	7322	43	77	7.7
1200	4644	1796	49599	3320	7188	47	90	8.0
1600	4632	1807	48048	3978	7131	49	77	8.2
25 t sludge ha $^{-1}$								
0	3086	2205	33594	1097	5729	34	12	7.0
400	3244	2132	32514	2747	6024	36	20	7.2
800	3420	2340	33269	4424	6994	42	21	7.9
1200	4087	2635	38958	5045	8019	57	26	9.6
1600	4002	2602	38304	5966	9116	61	33	10.3
50 t sludge ha $^{-1}$								
0	3476	2940	37478	1543	7764	60	19	10.0
400	3544	2825	38139	3689	8581	61	21	10.1
800	3601	3014	41393	4090	10127	75	29	11.6
1200	3578	3000	42348	4768	10228	84	31	12.0
1600	3462	2987	42716	4976	10969	84	34	12.2
100 t sludge ha $^{-1}$								
0	3044	3201	33038	1800	6409	66	17	10.7
400	2848	3100	33495	3368	6763	70	21	11.0
800	2839	3097	33080	4699	6834	71	21	11.5
1200	2876	3201	32488	5210	8068	83	26	11.9
1600	2765	3015	33996	5501	7500	78	22	12.0
F Prob.SS rate	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
F Prob. salt rate	n.s.	0.011	n.s.	0.001	0.001	0.001	0.001	0.001
F Prob. Interaction	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	0.024	n.s.
SS LSD	317	130	3661	319	709	5.9	4.15	0.790
Salt LSD	-	145	-	357	793	6.6	4.64	0.885
Interaction LSD	-	-	-	-	-	-	9.28	-
***critical conc..**	***2000***	***1500***	***41000***	-	***6200***	***20***	***13***	***2***

(* critical concentrations according to Reuter and Robinson, 1986)

General precautions for trace element analysis in plant tissue, soil solution and sewage sludge

I Field experiments described in chapter 3-6

All digestion tubes were acid washed (10% nitric acid). High grade nitric acid (BDH chemicals Aristar grade, 70 % nitric acid) was used for digestion of the samples. Two blank samples and two laboratory standards were included in every 50 samples to check for possible contamination during digestion and analysis. Samples were diluted approximately 1:25 prior to analysis. Exact dilution was calculated. Samples were further diluted when some elements were highly concentrated in the digest solution, for example Fe and Al in samples of Bolivar sewage sludge.

The detection limit of the ICP for a particular element in the digest solution is given in brackets (in mg l^{-1}) and the detection limit in samples according to the used dilution of approximately 1 : 25 in plant tissue was as follows:

Ca	25 (1.00).mg kg^{-1}	Na	25 (1.00) mg kg^{-1}
K	25 (1.00) mg kg^{-1}	Mn	1.25 (0.05) mg kg^{-1}
P	25 (1.00) mg kg^{-1}	Zn	1.25 (0.05) mg kg^{-1}
Mg	25 (1.00) mg kg^{-1}	Cu	1.25 (0.05) mg kg^{-1}

II Field experiment chapter 7 and pot experiments described in chapter 8-9

Method of sample preparation and detection limit of the ICP for Ca, Mg, K, Na, P, Zn, Mn, Cu in plant tissue are described above.

Detection limits of the ICP for Ca, Mg, K, Na, P, Zn, Mn, Cu in soil solution (undiluted) were as follows:

Ca	0.010 mg l^{-1}	Mg	0.013 mg l^{-1}
K	0.047 mg l^{-1}	Na	0.013 mg l^{-1}
P	0.011 mg l^{-1}	Zn	0.002 mg l^{-1}
Mn	0.001 mg l^{-1}	Cu	0.001 mg l^{-1}

The detection limit of the GFAAS for Cd was 0.0005 mg l^{-1}.Cd in samples. Hence detection limits for undiluted samples of soil solution, was 0.0005 mg l^{-1} and for plant samples (including a 1:25 dilution in the digest solution) was 0.0125 mg kg^{-1}.

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