Muresk Institute

Phosphorus bioavailability from land-applied biosolids in south-western Australia

Deborah L Pritchard

This thesis is presented for the Degree of
Doctor of Philosophy
of
Curtin University of Technology

July 2005

Declaration

This thesis contains no material, which has been accepted for the award of any other degree or diploma in any university. To the best of my knowledge and belief this thesis contains no material previously published by any other person except where due acknowledgment has been made.

Deborah L Pritchard

Acknowledgements

My appreciation is given to the Water Corporation for awarding me a PhD Scholarship and Prof Murray McGregor (past Director, Muresk Institute) who made my study possible. I would like to thank the *'three wise men',* my supervisors: A/Prof Lionel Martin (Curtin University), Dr John William (Bill) Bowden (Department of Agriculture, Western Australia) and Dr David Allen (Chemistry Centre of Western Australia) for their most thought-provoking and masterful comments over a number of years. Not to be forgotten, Dr Bruce Gardiner for setting the pace, his acumen and early direction and final proof reading.

Special thanks to Nancy Penney (Water Corporation), for her advice, support and friendship, for without her this thesis would be without substance. David Collins, who is so much a part of all of the experiments and kept me sane, I thank you with all my heart.

Thank you to the many people who supplied me with useful information and direction early in the development of the thesis, such as T. Gibson, E. Havilah, M. Bolland, R. Gilkes and W. Dougherty. I cannot forget the hospitality of Rob & Anne Chester (the best soil in York); the Department of Agriculture, Northam, especially Mario 'Fantastico' D'Antuono; and the team at the Chemistry Centre, particularly K. Walton, J. Harbord, J. Brown and B. Waddell. To all the NBRP crew on the other side of the desert headed by Mike McLaughlin, a great mentor, you are the best.

I am indebted to the assistance provided at Muresk Institute by Karen Shackleton (library), my helpful buddy Alicia Pasznicki, Gaye Krebs for her positive vibes and the Northam office girls for being there when the going sometimes got a bit tough. My friends and family who provided an interest outside of the biosolids world, thanks to Anna, Bazz and Mandy, the *'mermaids'* Jo and Sue, my five siblings who are always a part of me, my loving Mum and Dad, and the best babysitter in the world, Aunt Jenny.

To my children, who have been so fantastic throughout the duration of the PhD, I thank you. Jeana has known no other existence, being born a PhD child, so loving and yet so quintessentially challenging. Quillan, so young and so blissfully proud of his Mum's experiments in biosolids, as I am so proud of his wonderful achievements. Most importantly to the one who has constantly sacrificed his world to me, my husband Ian, and after approximately 85,000 words, I need say no more; this thesis is dedicated to you.

Abstract

The annual production of biosolids in the Perth region during the period of this study was approximately 13,800 t dry solids (DS), being supplied by three major wastewater treatment plants. Of this, 70% was typically used as a low-grade fertiliser in agriculture, representing an annual land use area of around 1,600 ha when spread between 5 and 7 t DS/ha. Loading rates of biosolids are typically based on the nitrogen (N) requirements of the crop to be grown, referred to as the N Limiting Biosolids Application Rate (NLBAR). A consequence of using the NLBAR to calculate loading rates is that phosphorus (P) is typically in excess of plant requirement.

The resultant high loading rates of P are considered in the guidelines developed for the agricultural use of biosolids in Western Australia, but lack research data specific to local conditions and soil types. Regulatory changes throughout Australia and globally to protect the environment from wastewater pollution have created a need for more accountable and balanced nutrient data. Experiments presented in this thesis were undertaken to ascertain: the percentage relative effectiveness (RE) of biosolids as a source of plant available P compared with inorganic P fertiliser; loading rates to best supply P for optimum crop growth; P loading rates of risk to the environment; and the forms of P in local biosolids. Therefore, both the agronomic and environmental viewpoints were considered.

Anaerobically digested and dewatered biosolids produced from Beenyup Wastewater Treatment Plant, Perth with a mean total P content of 2.97% dry weight basis (db) were used in a series of glasshouse, field and laboratory experiments. The biosolids were sequentially fractionated to identify the forms of P present and likewise in soil samples after applying biosolids or monocalcium phosphate (MCP). The biosolid P was predominantly inorganic (92%), and hence the organic fraction (8%) available for mineralisation at all times would be extremely low. The most common forms of biosolid P were water-soluble P and exchangeable inorganic P (66%), followed by bicarbonate extractable P (19%) and the remaining P as inorganic forms associated with Fe, Al and Ca (14%). Following the application of biosolids to a lateritic soil, the Fe and Al soil fractions sorbed large amounts of P, not unlike the distribution of P following the addition of MCP. Further investigation would be required to trace the cycling of biosolid P in the various soil pools.

The growth response of wheat (*Triticum aestivum* L.) to increasing rates of biosolids and comparable rates of inorganic P as MCP, to a maximum of 150 mg P/kg soil was examined in the glasshouse. The percentage relative effectiveness (RE) of biosolids was calculated using fitted curve coefficients from the Mitscherlich equation: $y = a\ (1\text{-}b\ \exp^{-cx})$ for dry matter (DM) production and P uptake. The initial effectiveness of biosolid P was comparable to that of MCP with the percentage RE of biosolids averaging 106% for DM production of wheat shoots and 118% for shoot P uptake at 33 days after sowing (DAS) over three consecutive crops. The percentage residual value (RV) declined at similar rates for DM production in MCP and biosolids, decreasing to about 33% relative to freshly applied MCP in the second crop and to approximately 16% in the third crop.

The effectiveness of biosolid P was reduced significantly compared with inorganic P when applied to a field site 80 km east of Perth (520 mm annual rainfall). An infertile lateritic podsolic soil, consistent with the glasshouse experiment and representative of a soil type typically used for the agricultural application of biosolids in Western Australia was used. Increasing rates of biosolids and comparable rates of triple superphosphate (TSP), to a maximum of 145 kg P/ha were applied to determine a P response curve. The percentage RE was calculated for seasonal DM production, final grain yield and P uptake in wheat followed by lupin (*Lupinus angustifolius* L.) rotation for the 2001 and 2002 growing seasons, respectively. In the first year of wheat, the RE for P uptake in biosolids compared with top-dressed TSP ranged from 33% to 55% over the season and by grain harvest was 67%. In the second year, and following incorporation with the disc plough at seeding, the RE for P uptake by lupins in biosolids averaged 79% over the growing season compared with top-dressed TSP, and by grain harvest the RE was 60%. The residual value (RV) of lupins at harvest in biosolids compared with freshly applied TSP was 47%.

The non-uniform placement of biosolids (i.e. spatial heterogeneity) was primarily responsible for the decreased ability of plant roots to absorb P. The P was more effective where biosolids were finely dispersed throughout the soil, less so when roughly cultivated and least effective when placed on the soil surface without incorporation. The RE for grain harvest of wheat in the field decreased from 67% to 39% where biosolids were not incorporated (i.e. surface-applied). The RE could also be modified by factors such as soil moisture and N availability in the field, although it was possible to keep these variables constant in the glasshouse. Consequently, absolute values determined for the RE need to be treated judiciously.

Calculations showed that typical loading rates of biosolids required to satisfy agronomic P requirements of wheat in Western Australia in the first season could vary from 0 to 8.1 t DS/ha, depending on soil factors such as the P Retention Index (PRI) and bicarbonate available P value. Loading rates of biosolids were inadequate for optimum P uptake by wheat at 5 t DS/ha (i.e. 145 kg P/ha) based on the NLBAR on high P sorbing soils with a low fertiliser history (i.e. PRI >15, Colwell bicarbonate extractable P <15 mg P/kg). On soils of PRI <2 mL/g however, biosolids applied at identical loading rates would result in high concentrations of available P. Further work on sites not P deficient would be necessary to validate these findings on farmed soils with a regular history of P fertiliser. The sieving of soil samples used in the field experiment to remove stones and coarse organic matter prior to chemical analysis inadvertently discarded biosolids particles >2 mm, and thus their was little relationship between soil bicarbonate extractable P and P uptake by plants in the field.

The risk of P leaching in biosolids-amended soil was examined over a number of different soil types at comparable rates of P at 140 mg P/kg (as either biosolids or MCP) in a laboratory experiment. Given that biosolids are restricted on sites prone to water erosion, the study focussed on the movement of water-soluble P by leaching rather than by runoff of water-soluble P and particulate P. In general the percentage soluble reactive P recovered was lower in soils treated with biosolids than with MCP, as measured in leachate collected using a reverse soil leachate unit. This was particularly evident in acid washed sand with SRP measuring 14% for biosolids and 71% for MCP, respectively, although the differences were not as large in typical agricultural soils. Specific soil properties, such as the PRI, pH, organic carbon and reactive Fe content were negatively correlated to soluble reactive P in leachate and thus reduced the risk of P leaching in biosolids-amended soil. Conversely, the total P and bicarbonate extractable P status of the soils investigated were unreliable indicators as to the amount of P leached.

On the basis of the experiments conducted, soils in Western Australia were categorised according to their ability to minimise P enrichment and provide P necessary for crop growth at loading rates determined by the NLBAR. Biosolids applied at the NLBAR to soils of PRI >2mL/g with reactive Fe >200 mg/kg were unlikely to necessitate P loading restrictions. Although specific to anaerobically digested biosolids cake applied to Western Australian soils, the results will be of relevance to any industry involved in the land application of biosolids, to prevent P contamination in water bodies and to make better use of P in crop production.

Contents

Declaration i

Acknowledgements ii

Abstract iii

Contents vi

List of tables x

List of figures xiv

List of plates xviii

Symbols and abbreviations xix

1 Introduction **1**
1.1 Biosolids in the global context 2
  1.1.1 Trends in wastewater management 2
  1.1.2 Land application of wastewater solids 3
  1.1.3 Biosolids - terminology and history 5
1.2 Thesis rationale 6
1.3 Aims of research 9
  1.3.1 General objective 9
  1.3.2 Specific objectives 9
1.4 Outline of review 10

2 Review of literature **11**
2.1 Biosolids production and use 12
  2.1.1 Major characteristics of biosolids 12
  2.1.2 Wastewater treatment processes 13
  2.1.3 Effluent guidelines and wastewater nutrient removal 16
  2.1.4 Trends in the agricultural land application of biosolids 17
2.2 Major plant nutrients re-cycled by the land application of biosolids 21
  2.2.1 Nutrient recycling in agriculture 21
  2.2.2 Recycling of nitrogen from biosolids 23
  2.2.3 Recycling of phosphorus from biosolids 27
  2.2.4 Biosolids as a source of plant nutrients for soils in south-western Australia 31
2.3 Agricultural land application rates of biosolids based on nutrient loadings 34
  2.3.1 Guidelines for agricultural land application and major crop nutrient requirements 34
  2.3.2 Land application rates based on metals - CLBAR 36
  2.3.3 Land application rates based on nitrogen - NLBAR 37
  2.3.4 Land application rates based on phosphorus - PLBAR 40
2.4 Plant available and environmentally relevant phosphorus in biosolids 44

2.4.1 Measurement for total phosphorus and plant available phosphorus........44
2.4.2 Factors affecting the release of phosphorus from land-applied biosolids........47
2.4.3 Relevance of phosphorus originating from biosolids in the environment........56
2.4.4 Relative effectiveness (RE) of biosolids as a fertiliser........61
2.4.5 Conclusions........65

3 Relative effectiveness and residual value of phosphorus in biosolids-amended soil compared with inorganic fertiliser – glasshouse experiment........66

3.1 Introduction........67
3.2 Materials and methods........68
3.2.1 Trial layout and design........68
3.2.2 Soil........69
3.2.3 Pots and basal nutrients........71
3.2.4 Biosolids........72
3.2.5 Sowing........73
3.2.6 Location........73
3.2.7 Plant measurements and harvest........74
3.2.8 Soil analysis........74
3.2.9 Phosphorus fractionation........76
3.2.10 General........78
3.2.11 Statistical analysis of data........78
3.2.12 Calculation of relative effectiveness........79
3.3 Results........80
3.3.1 Shoot development and dry matter production........80
3.3.2 Shoot phosphorus concentrations and uptake........82
3.3.3 Shoot nitrogen concentrations and uptake........84
3.3.4 Relative effectiveness of biosolids compared with MCP during the growing season........84
3.3.5 Soil analysis........86
3.3.6 Phosphorus fractionation........92
3.4 Discussion........94
3.4.1 Interaction between nitrogen and phosphorus........94
3.4.2 Relative effectiveness (RE) of biosolid P compared with MCP for plant dry matter yield and P uptake........94
3.4.3 Changes in available soil phosphorus and other soil parameters........95
3.4.4 Characterisation of available phosphorus by sequential extraction........97
3.5 Conclusions........98

4 Relative effectiveness and residual value of the phosphorus in biosolids compared with an inorganic fertiliser – field experiment........100

4.1 Introduction........101
4.2 Materials and methods........102
4.2.1 Experimental design........102
4.2.2 Site history and climate........104
4.2.3 Soil type........105
4.2.4 Nutrient application........105
4.2.5 Application of biosolids and TSP........107
4.2.6 Seeding........107
4.2.7 Biosolids analysis........109
4.2.8 Plant density and shoot dry matter........110

4.2.9 Harvest and yield components 110
4.2.10 Plant tissue nutrient analysis 111
4.2.11 Soil analysis 112
4.2.12 Statistical analysis 113
4.2.13 Calculation of relative effectiveness and residual value 113
4.3 Results 115
4.3.1 Initial year of application: wheat crop 115
4.3.2 Residual effects in year two: lupin crop 126
4.3.3 Soil measurements over two years (0-10 cm) 133
4.3.4 Soil changes with depth at 10 months (306 DAS) after sowing the first crop 137
4.4 Discussion 139
4.4.1 Interaction between nitrogen and phosphorus 139
4.4.2 Relative effectiveness of biosolid P compared with TSP 139
4.4.3 Effect of fertiliser placement 141
4.4.4 Use of soil available phosphorus to estimate biosolid P value...............142
4.4.5 Increase in total P loadings and risk of movement of P from biosolids application site 143
4.4.6 Movement of nitrates and other nutrients 145
4.5 Conclusions 146

5 Physical/incorporation factors affecting phosphorus availability in biosolids – glasshouse and field experiments..148
5.1 Introduction..149
5.2 Materials and methods 150
5.2.1 Soil types..150
5.2.2 Biosolids 152
5.2.3 Glasshouse experiment 152
5.2.4 Field experiment 156
5.3 Results 161
5.3.1 Glasshouse..161
5.3.2 Field experiment 171
5.4 Discussion 182
5.4.1 Effect of positional placement of biosolids on crop growth and yield over time..182
5.4.2 Effect of positional placement of biosolids on available soil P and P uptake..183
5.4.3 Relationship between bicarbonate extractable phosphorus and phosphorus uptake 187
5.4.4 Relative effectiveness of surface-applied biosolids compared with incorporated biosolids and relevance to land application rates and the environment..188
5.5 Conclusions..189

6 Leaching of phosphorus in soils following the application of biosolids - laboratory experiment 191
6.1 Introduction..192
6.2 Materials and methods 193
6.2.1 Experimental design 193
6.2.2 Biosolids 193
6.2.3 Soils 195
6.2.4 Reverse soil leachate unit..198
6.2.5 Chemical analysis..200

6.2.6 Statistical analysis 201
6.3 Results 201
6.3.1 Soluble reactive phosphorus and total phosphorus 201
6.3.2 Relationship between soil properties and soluble reactive phosphorus .205
6.3.3 Nitrate and ammonium nitrogen 206
6.4 Discussion 207
6.4.1 Solubility of phosphorus in biosolids compared with MCP 207
6.4.2 Effect of soil properties on water-soluble phosphorus 210
6.5 Conclusions 216

7 General discussion 218
7.1 Introduction 219
7.2 Characteristics of the forms of phosphorus in biosolids produced at the Beenyup Wastewater Treatment Plant 219
7.3 Relative effectiveness of the phosphorus in biosolids compared with an inorganic source of phosphorus 221
7.4 Loading rates of biosolids required to provide agricultural crops with adequate phosphorus 222
7.5 Effect of high loading rates of phosphorus following the application of biosolids at the NLBAR over a range of soil properties 226
7.6 Selection of soils most suitable for the land application of biosolids in Western Australia to best balance phosphorus loadings with the NLBAR 228

8 References 231

9 Appendices 263
9.1 Minimising the nitrogen x phosphorus interaction in biosolids – preliminary glasshouse experiment 264
9.1.1 Introduction 264
9.1.2 Materials and methods 265
9.1.3 Results 270
9.1.4 Discussion 276
9.1.5 Conclusion 279
9.2 List of publications arising from the thesis 280

List of tables

Table 2.1 Chemical composition of selected animal wastes....13

Table 2.2 Historical and future directions for the disposal of communal sewage sludge in the old 12 member countries of the European Union....18

Table 2.3 Comparison of constituents in biosolids sourced from Wastewater Treatment Plants in New South Wales and Western Australia....22

Table 2.4 Quantities of nitrogen and phosphorus removed in one tonne of grain or straw for the main agricultural crops grown in Western Australia....35

Table 2.5 Metal concentrations in animal manure, fertilisers and biosolids compared with *40CFR 503* limits....37

Table 2.6 Maximum phosphorus loadings for four soil characteristics in Western Australia....43

Table 2.7 Chemical extraction methods for phosphorus poorly correlated to bioavailable P in a range of biosolid and organic materials....45

Table 2.8 Characteristics of biosolids, soil and local factors that may affect the release of phosphorus from land-applied biosolids....47

Table 2.9 Phosphorus content in a range of sludges as related to method of treatment in Australia....48

Table 2.10 Eutrophication risk from excess phosphate derived from PRI values, soil characteristics and site....54

Table 2.11 Concentrations of phosphorus and other nutrient elements in common fertilisers....63

Table 3.1 Comparative phosphorus loadings for monocalcium phosphate (MCP) and biosolids treatments....69

Table 3.2 Some properties of the 0-10 cm topsoil (<2 mm fraction) of the Bakers Hill soil....70

Table 3.3 Selected constituents in biosolids collected from the Beenyup Wastewater Treatment Plant on 14 May 2000....72

Table 3.4 Coefficients for the relationships between shoot dry matter and shoot P uptake for three consecutive crops of wheat including relative effectiveness (RE) values....85

Table 3.5 Relationship between concentrations of total soil N and total P applied as MCP or biosolids measured at the completion of three consecutive crops....89

Table 3.6 Sequential extraction of phosphorus for Beenyup biosolids applied at 300 mg P/kg to acid washed sand 92
Table 4.1 Treatment allocation for rates of phosphorus supplied by biosolids or triple superphosphate (TSP) in years one and two of the field experiment...103
Table 4.2 Major soil properties of the top 0-10 cm as determined for a composite soil sample 106
Table 4.3 Selected constituents in biosolids reported from the Beenyup Wastewater Treatment Plant (16 May 2001) as used in the field trial..109
Table 4.4 Mean seasonal production of shoot dry matter of wheat (g/m^2) in response to P applied as triple superphosphate (TSP) or biosolids 117
Table 4.5 Values of coefficients for equation (1) for the relationships between P supply and shoot dry matter of wheat or shoot P uptake over four sampling dates and grain yield including the percentage relative effectiveness (RE) of biosolids (BS) compared with TSP....................122
Table 4.6 Yield components and other harvest measurements of wheat for TSP and biosolids at final hand harvest at 179 DAS..................................125
Table 4.7 Mean seasonal production of shoot dry matter of lupin (g/m^2) in response to P applied as triple superphosphate (TSP), biosolids or freshly applied TSP (TSP 2) 127
Table 4.8 Coefficients of the Mitscherlich equations for biosolids (BS), TSP and freshly applied TSP (TSP2) for seasonal lupin dry matter, shoot P uptake and final grain yield over four sampling dates 132
Table 4.9 Percentage relative effectiveness (RE) of biosolids (BS) compared with TSP and percentage residual value (RV) of BS and TSP compared with freshly applied TSP for seasonal lupin dry matter, shoot P uptake and final grain yield over four sampling dates.............132
Table 4.10 Mean concentrations of bicarbonate extractable soil P (mg P/kg) following the application of triple superphosphate (TSP) and biosolids for over two years after sowing 133
Table 4.11 Soil changes at depth for selected constituents over three treatments at 10 months (306 DAS) in the <2 mm soil fraction 138
Table 5.1. Comparison of the major properties in topsoil (0-10 cm) for soil used in the glasshouse and field experiments 151
Table 5.2 Rate, source and method of incorporation of phosphorus as used for the glasshouse experimental pots 153

Table 5.3 Treatment allocation for rates of phosphorus supplied by biosolids or triple superphosphate (TSP) used in the field experiment....................157

Table 5.4 Effect of phosphorus source on wheat development at 32 days after sowing 162

Table 5.5 Effect of the method of incorporation of biosolids compared with increasing rates of inorganic P on selected soil constituents at 33 days after sowing, as measured in the centre of each pot 170

Table 5.6 Comparison between surface-applied biosolids, incorporated biosolids and nil P for shoot nitrogen and phosphorus uptake over two growing seasons 175

Table 5.7 Comparison between surface-applied biosolids, incorporated biosolids and nil P for grain yield and grain nutrient concentrations of N and P over two growing seasons..176

Table 5.8 Percentage relative effectiveness (RE) of surface-applied biosolids (BS-S) compared with incorporated biosolids (BS) and TSP for shoot dry matter of wheat and shoot P uptake over three sampling dates and final grain yield..177

Table 5.9 Percentage relative effectiveness (RE) of surface-applied biosolids (BS-S) compared with incorporated biosolids (BS), TSP and freshly applied TSP (TSP2) for lupin dry matter and shoot P uptake over three sampling dates and final grain yield 178

Table 5.10 Yield components and other harvest measurements of wheat for surface-applied biosolids, incorporated biosolids and nil biosolids at final hand harvest (year one) at 179 DAS 179

Table 5.11 Concentrations of bicarbonate extractable P (mg P/kg) following the application of surface-applied biosolids, incorporated biosolids and nil P for six sampling dates over two years 181

Table 5.12 Concentrations of ammonium and nitrate forms of N (mg N/kg) for surface-applied biosolids, incorporated biosolids and nil biosolids at four sampling dates over two growing seasons 181

Table 6.1 Description and location of the nine soils used in the leaching experiment ranked in order of sand content. Values are given for texture, pH, EC, organic carbon and gravimetric soil water capacity (GSWC) in the topsoil* 0-10 cm after being sieved <2 mm. 196

Table 6.2 Comparison of selected nutrient properties in the 0–10 cm topsoil* (<2 mm fraction) for the nine soils..197

Table 6.3 Correlation coefficient values between selected soil parameters over nine soils examined and %SRP-R in leachate for MCP, biosolids and the mean of both P sources 205
Table 7.1 Guide to loading rates of biosolids required to obtain optimum wheat yield for soils differing in PRI (mg/L) and available soil P (mg/kg), including values for drilled inorganic P (Pi) and the PLBAR* (kg P/ha)..223
Table 7.2 Soil classification system to ensure high P demand and low risk of P leaching following the application of biosolids**based on the Phosphorus Retention Index (PRI) and bicarbonate extractable P content of the soil 229
Table 9.1 Contaminant and nutrient concentrations for Beenyup WWTP biosolids over four sampling dates for the 1999-2000 period 266
Table 9.2 Calculations for estimating available N and P from biosolids used in the preliminary experiment 267
Table 9.3 Effects of increasing rates of inorganic N and P on shoot dry matter of wheat (g/pot) at 33 days after sowing. 270
Table 9.4 Effects of increasing rates of combinations of nitrogen and biosolids on shoot dry matter of wheat (g/pot) at 33 days after sowing..............272
Table 9.5 Effects of increasing rates of combinations of phosphorus and biosolids on shoot dry matter of wheat (g/pot) at 33 days after sowing 272
Table 9.6 Nutrient concentrations of whole wheat shoots for six different rates of N (mean of all P rates; 0, 10, 20, 40 & 80 mg P/kg) at 33 DAS when shoots were forming tillers (FS2-3)..274
Table 9.7 Selected treatment composites analysed for soil pH, total N, nitrate-N, ammonium-N, total P and available P and K 276

List of figures

Figure 2.1 Estimated biosolids production and use in Australian agriculture, on a state-by-state basis........20

Figure 2.2 Biosolids in the nitrogen cycle........24

Figure 2.3 Components and measurable fractions of the soil P cycle........28

Figure 2.4 The soils of south-western Australia........33

Figure 2.5 Results of different application rate bases and assumed biosolids P availabilities........41

Figure 2.6 Total phosphate fractionation as a function of total P concentration........52

Figure 2.7 Comparison of water extractable P (WEP) for TSP, manures, and typical biosolids........60

Figure 2.8 Comparison of water extractable P (WEP) levels for several biosolids treatment methods........61

Figure 2.9 Relationship between yield and the amount of P applied as superphosphate in the current year (SPF), one year previously (SP1), and four years previously (SP4)........62

Figure 3.1 Relationship between shoot DM of wheat at 33 DAS and total P applied as MCP, biosolids and freshly applied MCP for three consecutive crops........81

Figure 3.2 Relationship between P uptake in shoot DM of wheat and P applied as MCP, biosolids and freshly applied MCP (MCP2) at 33 DAS for three consecutive crops........83

Figure 3.3 Relationship between bicarbonate extractable soil P and total P applied for MCP and biosolids measured at the conclusion of crops one, two and three........87

Figure 3.4 Relationship between soil organic carbon and level of P applied as monocalcium phosphate (MCP) or biosolids measured at completion of crop three........88

Figure 3.5 Relationship between nitrate-N or ammonium-N and total P applied for MCP and biosolids treatments measured in soil samples at the completion of crop three........90

Figure 3.6 Effect of MCP and biosolids treatments for given P rates on soil pH ($CaCl_2$) measured at the completion of crops one, two and three........91

Figure 3.7 Distribution of P in soil extractants at the completion of the experiment in MCP (140 mg P/kg) and biosolids (150 mg P/kg) compared with the control treatment..93
Figure 4.1 Total monthly rainfall, mean monthly maximum and minimum temperature at Inkpen, Western Australia in 2001 116
Figure 4.2 Relationship between P uptake in wheat shoots and the level of P applied in TSP and biosolids over four sampling dates.......................119
Figure 4.3 Relationship between total N uptake in wheat shoots and the level of P applied in TSP and biosolids over four sampling dates....................120
Figure 4.4 Relationship between wheat grain yield and the level of P applied in TSP and biosolids at harvest 121
Figure 4.5 Relationship between the uptake of phosphorus and nitrogen in wheat grain and the level of P applied in TSP and biosolids 124
Figure 4.6 Total monthly rainfall, mean monthly maximum and minimum temperature at Inkpen, Western Australia in 2002 126
Figure 4.7 Relationship between mean total P uptake in lupin and P applied in TSP, biosolids (BS) and freshly applied TSP (TSP 2) at three sampling dates 130
Figure 4.8 Relationship between lupin grain yield and the level of P applied in TSP, biosolids (BS) and freshly applied TSP (TSP2)..........................131
Figure 4.9 Concentrations of total soil N or P in the 0-10 cm profile in three sized soil fractions (<2 mm, 2-4.7 mm, >4.7 mm) in TSP, biosolids (BS) and control treatment at 615 DAS, with predicted N or P concentration for the <2 mm given...135
Figure 4.10 Relationship between total inorganic soil N and total P applied in the highest rate of TSP (120 kg P/ha) or biosolids (145 kg P/ha) at 133 DAS 136
Figure 4.11 Relationship between available soil P at 133 DAS and P uptake by wheat at 123 DAS...143
Figure 5.1 Schematic diagram showing the distribution of biosolids for the four biosolids treatments (each applied at 150 mg P/kg) in the glasshouse experiment...154
Figure 5.2 Effect of method of incorporation of biosolids on shoot dry matter of wheat at 33 days after sowing compared with increasing rates of inorganic P 163

Figure 5.3 Effect of method of incorporation of biosolids on P uptake in wheat shoots compared with increasing rates of inorganic P at 33 days after sowing 164

Figure 5.4 Effect of method of incorporation of biosolids on nitrogen concentration in wheat shoots measured at 33 days after sowing compared with increasing rates of inorganic P 165

Figure 5.5 Effect of incorporation of biosolids on mean bicarbonate extractable soil P compared with inorganic P (MCP) as measured in the centre of each pot at 33 days after sowing 166

Figure 5.6 Schematic diagram highlighting differences in bicarbonate extractable soil P as dependent on the sampling location for the four biosolids treatments 167

Figure 5.7 Relationship between biosolids application rate and percentage incorporation 171

Figure 5.8 Mean seasonal production in shoot dry matter of wheat for biosolids (BS) that are surface-applied compared with incorporated and nil biosolids (control) 172

Figure 5.9 Mean seasonal shoot dry matter of lupin in the second season following the application of biosolids (BS) as surface-applied or incorporated or no biosolids (control) 174

Figure 5.10 Schematic diagram showing growth of wheat shoots and roots in surface-applied biosolids (BT) compared with incorporated treatments (BD, BM & BS) 185

Figure 6.1 Soil leachate unit (Chemistry Centre of Western Australia) 199

Figure 6.2 Relationship between SRP in leachate over nine soil types following the addition of 140 mg P/kg as MCP or biosolids compared with the control soil 202

Figure 6.3 Percentage soluble reactive P recovered (SRP-R) following the addition of MCP or biosolids at 140 mg P/kg for nine soil types 204

Figure 6.4 Concentrations of NO_3-N and NH_4-N measured in leachate following the addition of biosolids (B) compared with the control (C) in nine different soils 207

Figure 6.5 Interaction between PRI (mL/g) and iron content (mg Fe/kg) on percentage SRP-R 211

Figure 6.6 Interaction between percentage sand content and PRI (mL/g) on percentage SRP-R over nine soil types 213

Figure 7.1 Relationship between bicarbonate extractable soil P (Colwell) and total P applied as biosolids and inorganic sources of P, measured at 60 DAS in the field and 66 DAS in the glasshouse 225
Figure 9.1 Effects of increasing rates of combinations of nitrogen and phosphorus on the shoot dry matter of wheat (g/pot) at 33 days after sowing 271
Figure 9.2 Concentrations of P in shoots of wheat at 33 DAS for MCP treatment (80 mg P/kg) for two rates of N (80 and 160 mg N/kg) and biosolids (5 dry g/kg) containing 23,250 mg P/kg 277
Figure 9.3 Comparison between available N in MCP treatment (80 mg P/kg) and two rates of biosolids (5 & 10 dry g/kg) for shoot DM of wheat at 33 DAS..278
Figure 9.4 Comparison between available N in MCP treatment (80 mg P/kg) and two rates of biosolids (5 & 10 dry g/kg) for concentrations of N in shoot DM of wheat at 33 DAS...278

List of plates

Plate 3.1 Vegetative growth differences in wheat at 32 DAS as a result of increasing phosphorus (MCP) applications for crop 1 82
Plate 4.1 Field trial site at York during spreading, May 2001 104
Plate 4.2 Biosolids used in the field experiment, May 2001 108
Plate 4.3 Selected plot showing highest rate of biosolids (4.9 t/ha) following hand application with “pooper scooper”, May 2001 108
Plate 4.4 Vegetative growth differences in wheat between the nil plot (left) and highest rate of biosolids 145 kg P/ha (right) at 96 DAS 116
Plate 4.5 Vegetative growth of lupin in year two at anthesis (flowering) showing responses of the 145 kg P/ha biosolids (left), 120 kg P/ha TSP (right) and nil-P on far left 128
Plate 4.6 Differences in lupin growth at anthesis (flowering) between the nil P treatment (foreground) and the 145 kg P/ha as biosolids treatment (background) 128
Plate 4.7 Fraction of soil >2 mm typically discarded following sieving showing evidence of biosolids (black particles) amongst the gravel stones 134
Plate 5.1 Biosolids applied at 2.9 t DS/ha prior to incorporation on 17 May 2001. 158
Plate 5.2 Biosolids applied at 2.9 t DS/ha following incorporation with the disc plough on 18 May 2001 158
Plate 5.3 Effect of method of incorporation of biosolids on the growth of wheat shoots at 32 days after sowing 161
Plate 5.4 Germination and early development of wheat in 70 kg P/ha as TSP (centre plot), 85 kg P/ha incorporated biosolids treatment (left plot) and 85 kg P/ha surface-applied biosolids (right plot) 173
Plate 5.5 Development of wheat at tillering in 70 kg P/ha as TSP (centre plot), 85 kg P/ha incorporated biosolids treatment (left plot) and 85 kg P/ha surface-applied biosolids (right plot) 173
Plate 6.1 Air-dried biosolids being prepared by mortar and pestle 194
Plate 6.2 Biosolids on completion of grinding and sieving 194
Plate 6.3 White (acid washed) sand before (left) and after (right) the addition of air-dried biosolids 198
Plate 6.4 Reverse soil leachate unit apparatus prior to the leaching stage 200

Symbols and abbreviations

BNR	Biological nutrient removal
CLBAR	Contaminants Limited Biosolids Application Rate
C/N	Carbon-to-nitrogen ratio
DAS	Days after sowing
db	Dry weight basis
DEP	Department of Environmental Protection, Western Australia
DM	Dry matter
DOH	Department of Health, Western Australia
DS	Dry solids
EPA	Environmental Protection Agency, USA
GSWC	Gravimetric soil water capacity
LSD	Least significant difference
MAD	Mesophilic anaerobic digestion
MCP	Monocalcium phosphate
NLBAR	Nitrogen Limited Biosolids Application Rate
N_O	Organic nitrogen
N_T	Total nitrogen content
OM	Organic matter
PAN	Potentially available nitrogen or plant available N
P_i	Inorganic phosphorus
PLBAR	Phosphorus Limited Biosolids Application Rate
P_o	Organic phosphorus
PRI	Phosphorus Retention Index
P_T	Total phosphorus content
RE	Relative effectiveness
RV	Residual value
SRP	Soluble reactive phosphorus
SRP-R	Soluble reactive phosphorus recovered
TSP	Triple superphosphate
WEF	Water Environment Federation
WEP	Water extractable phosphorus
WRC	Waters and Rivers Commission, Western Australia
WSP	Water-soluble phosphorus
WWTP	Wastewater Treatment Plant
Z	Zadoks decimal growth stage

1 Introduction

1.1 Biosolids in the global context

1.1.1 Trends in wastewater management

The problem of human waste disposal has increased in complexity concomitant with global population increases. Historically, wastes were often discarded into streams and rivers; however, major water pollution and health problems arose as communities increased in size. Sewerage systems developed by many civilisations to protect public health often only moved the problems downstream. The development of ‘sewage farms’ in major European and northern American cities in 1875 alleviated many of the water pollution problems, but tended to concentrate wastes onto small areas of land. Elsewhere, such as China, the collection of ‘night soil’ from cities was valued as a agricultural fertiliser in the rural areas (National Biosolids Partnership 2001).

Tomar (1999) regards the management of wastewater as a necessity, not an option in modern and civilised societies with improved and sustainable waste management systems essential to provide for a cleaner environment and safer public health. New legislation to control water pollution, restrictions on marine disposal and population growth has resulted in an increase in the production of wastewater solids worldwide. Consequently, there is a significant and growing investment in waste collection, its management and treatment (Evans 2001; Matthews 2001).

Wastewater treatment plants (WWTPs) consist of a sequence of operations to treat domestic and industrial wastes and refuse, with water being the universal solvent. Correctly treated, effluent can be discharged into the environment without detriment to the ecosystem (Tomar 1999). The resultant by-product of WWTPs is a suspension of solids, often termed sludge, which may account for 0.03% of the total volume of wastewater. Approximately 2.0 to 2.5 L, consisting of about 3% solids, made up of raw faecal and other organic solids are produced per person daily (Matthews 1997).

As outlined by Cameron, Di and McLaren (1997), sludge solids contain a complex mixture of organic and inorganic compounds of biological and mineral origin, that has potential as a soil conditioner and fertiliser. The production of sludges that are amenable to beneficial use and merit the term ‘biosolids’ is a high priority in wastewater treatment (Dentel 2001). Advanced processes are necessary during wastewater treatment to meet stringent new public health guidelines. To avoid contamination of ground and surface waters by nutrients resulting from wastewater treatment, such as nitrogen (N) and phosphorus (P), a high degree of management is required (Cameron, Di & McLaren 1997).

1.1.2 Land application of wastewater solids

The disposal of wastewater solids is often the most expensive component of a WWTP (Vesilind & Spinosa 2001). Current options for sludge management are grouped by Lue-Hing et al. (1997) into three general categories: land application including agriculture and forestry, monofill and co-disposal land-filling, and thermal processing. Most countries have banned the cheaper option of ocean disposal of wastewater solids to restrict the discharge of water-borne pollutants.

Communities create a range of wastes that need to be managed. Common types of wastes include urban solids wastes such as domestic household garbage and agricultural wastes such as manures, various organic and plant wastes and mining wastes (Cameron, Di & McLaren 1997; Hicks & Hird 2000; McCalla, Peterson & Lue-Hing 1977; Pescod 1991). Regardless of the type of waste, the common principles for waste disposal are to reduce the volume, improve environmental acceptance, separate and recover recyclable material or energy, reduce landfill volume and minimise overall costs such as transportation.

1.1.2.1 Monofill and co-disposal land-filling

Traditionally the land disposal of sludge involved high application rates on a regular basis that often exceeded plant nutrient uptake and the soil's capacity for assimilation (Campbell & Beckett 1988; Olsen & Barber 1977). Consequently, environmental problems persisted where sludge was applied in an uncontrolled and repeated manner, particularly in regard to metal contamination. In the review "*Is soil an appropriate dumping ground for our wastes?*" Cameron, Di and McLaren (1997) concluded that the philosophical context of the waste disposal question needs to be changed to recognise the importance of soil and environmental quality and emphasise use of the waste resource. The approach is therefore, on recycling rather than disposal (Sommers & Sutton 1980).

Landfill or surface disposal is the least favoured option for waste disposal, unless the sludge is highly contaminated, but may be convenient where local space is abundant and disposal fees are reasonable (Lue-Hing et al. 1997). However, large amounts of methane are released to the environment during decomposition, which may contribute to global warming. The European Union Landfill Directive has set targets to reduce landfill of biodegradable wastes (Banks & Heaven 2001; von Sothen 2001).

1.1.2.2 Agricultural land application

As with many other organic wastes, wastewater solids are increasingly being valued as a sustainable solution to recycle and exploit non-renewable resources. The role of biosolids management continues to gain priority in terms of holistic waste management and reuse, outlined by Englande and Reimers (2001). Modern WWTPs using a combination of improved technology and regular monitoring ensure that the product falls within guidelines related to nutrient, contaminant and pathogen levels. Land application is likely to remain a major option for smaller plants, which are generally less contaminated by toxic compounds and close to disposal sites (Spinosa 2001).

Wastewater solids are effective as organic soil conditioners and amendments to enhance soil physical properties and the populations of desirable soil microorganisms and earthworms. Changes in properties such as decreased bulk density, increased porosity, aggregate stability and hydraulic conductivity, improved moisture holding capacity, ease of cultivation, reduced wind and water erosion and improvement in plant growth and yields are described by Epstein (2002), Guidi and Hall (1984), Olness and others (1998) and Water Environment Federation (1994). Wastewater sludges are considered an important source of both macronutrients and trace elements for plant growth that are slowly released over several seasons (Epstein 2002; Osborne 1995; Peterson, McCalla & Smith 1971; Pierzynski 1994; Water Pollution Control Federation 1972).

1.1.2.3 Thermal processing

Thermal processing or incineration is common in parts of Europe where sludge production exceeds the amount of available land (Spinosa 2001), but is possibly the most favourable scenario in terms of CO_2 credits (Englande Jr & Reimers 2001). Incineration with energy recovery remains attractive for bigger plants (Mininni 2001) although considered unfavourable in Australia due to problems with air pollution and odour. Levels of carcinogenic dioxins in biosolids formed through combustion processes are at present under review (Christen 2002), with high temperatures and emission controls necessary to minimise toxic gases. Thermal drying can be used to ash sludge, rendering heavy metals immobile and is used as an additive in brick and block making where industrial input is high (Okuno 2001). Energy recovery through thermal processing of sludge to produce oil has been demonstrated using the Enersludge^{TM} Process at Subiaco WWTP in Australia (Bridle 2001).

1.1.3 Biosolids - terminology and history

The term ‘biosolids’ was coined by the Water Environment Federation (WEF), United States of America (USA) in 1991 to promote public acceptance and beneficial re-use for wastewater sludge (Rampton 1998). Biosolids are defined as a modern synonym for sewage sludge, sludge or wastewater solids (Spellman 1997; U.S. Environmental Protection Agency 1997; United States Environmental Protection Agency 1997) with stabilisation and often dewatering essential processes of the wastewater treatment (Spinosa & Vesilind 2001).

Biosolids are conceptually a neologism, the term having evolved with the changing needs of society as a strategy to conserve dwindling non-renewable resources and to create public acceptance for a re-cycled product. To project a more positive image, the terms *‘sludge’* and *‘disposal’* are often replaced by the terms *‘biosolids’* and *‘beneficial use’* (Lue-Hing et al. 1997). For example, the phrase, *‘sludge dumped on land’* conveys a different message than *‘biosolids used in agriculture’*. Public acceptance is variable given concerns with pollution, environmental damage and risk to public health; simplified by Matthews (1997) as a *‘faecal aversion barrier’*.

The USA was instrumental in the development of biosolids standards to protect public health and the environment from concerns related to pathogens, water pollution, synthetic organic compounds, heavy metals, salts or extreme pH values. The Environmental Protection Agency (EPA) of USA promulgated the Federal regulation *40 CFR Part 503 rule* in 1993, based on pathogen content, vector attraction, rate of application and duration of biosolids application (WEF 1994). During this period, Australia lagged behind Europe and North America in the development of re-use guidelines (Rawlinson 1992). Since then, the USA EPA *Part 503 rule* has formed the basis of guidelines for many environmental agencies.

Notwithstanding environmental concerns, there still remains an overarching ecological incentive to use wastewater solids, particularly in agriculture to improve soil physical and nutritional properties. The public has been influential in setting environmental standards for waste disposal as greater emphasis is placed on public health and recycling and recovery of resources (Hadeed 2002). Potential odour problems may require additional processing that are necessary to control the myriad of volatile compounds with evocative names such as putrescine and cadaverine (Kanak, Osborne & Swinton 1995).

1.2 Thesis rationale

Regulatory change in Australia to protect the environment and water bodies from wastewater pollution has forced a shift to land based biosolids use. In Western Australia, the development of new markets is considered an integral step for beneficial biosolids use by key regulators, including the Department of Environmental Protection, Waters and Rivers Commission and Department of Health (DEP, WRC & DOH 2002). New market options for the use of biosolids, such as agricultural land application, urban landscaping (typically following composting), plantation forestry application and use in land rehabilitation such as mine sites, reflects global trends for the use of nutrient-rich organic residuals (Water Corporation 1997b). Agricultural and forestry options in Western Australia have been summarised by L.V. Rawlinson and Associates (Rawlinson 1996a; Rawlinson 1996b; Rawlinson 1997; Rawlinson & Salt 1997).

Much of the early biosolids research in Australia was conducted in New South Wales and included studies on pathogens, metal elements, nitrate movement, crop yield and soil contamination (Havilah & Osborne 1992; Havilah & Davis 1998; Havilah et al. 1996; Joshua et al. 1998; Kanak, Osborne & Swinton 1995; Osborne et al. 1995a; Osborne 1992; Osborne et al. 1995b; Parker & Grant 2001). A few preliminary studies were conducted in Western Australia related to pathogens (Gibbs et al. 1995; Gibbs et al. 1997), forestry application (Dumbrell & McGrath 2002), mine-site rehabilitation, agricultural land application (Priestley & Pritchard 1998; Priestley 1998; Pritchard 1998; Rawlinson 1997) and flies (Penney & Dadour 2002). Guidelines for biosolids use in Australia are constantly being reviewed following interpretation of current research data to ensure they are appropriate (Barry et al. 1995; DEP, WRC & DOH 2002; Gibson et al. 2002; Gough & Fraser 1995).

Overall there are limited research data concerned with plant nutrition, soil physical properties, public health and undesirable soil contamination from biosolids applied to agricultural systems within Australia, and particularly in Western Australia; with information specific to nutrient and chemical release rates in biosolids needed (Cameron, Di & McLaren 1997). The Australian landscape is generally very old by world standards, with many soils low in organic matter and nutrients, complex and highly variable. There is a gap in the literature related to biosolids use in Western Australia to ensure agricultural land application rates are appropriate over a range of environmental conditions.

It has been common for application rates of biosolids in agriculture to be determined by the crop N requirement to reduce nitrate leaching from the root zone. However, the implementation of an N based biosolids nutrient management plan can lead to P being supplied in excess of that required for plant uptake. Therefore, a need exists to demonstrate the agronomic benefit of biosolid P in agriculture and to monitor P loadings to ensure there is minimum risk to the environment. In addition, it is unclear as to whether various additives used in wastewater treatment to reduce the concentration of P in effluent, may affect the bioavailability of P remaining in biosolids (Havilah & Davis 1998; Sakadevan & Bavor 2002).

The Perth region, Western Australia is characterised by three major WWTPs, which annually treat approximately 270 ML/d of raw wastewater and produce 13,800 t DS of biosolids. The WWTPs are located along the coast and discharge effluent via outfalls to the ocean. Beenyup WWTP, north of Perth uses a primary and secondary treatment process involving mesophilic anaerobic digestion at 35^0C for 15 to 20 d, followed by dewatering. The major constituent of the influent is domestically sourced, although 8% is industrial input. Lime (as CaO) is added to the influent channel at a rate of 30 mg/L to maintain pH in the aeration system and to assist with the nitrification/ denitrification process. No chemical precipitation is used to remove P from the effluent stream. The Woodman Point WWTP, south of Perth uses a similar treatment process to Beenyup. The Subiaco WWTP is different in that it stabilises raw sludge by thermal drying or by the addition of lime (Penney, Dumbrell & Pritchard 2003; Water Corporation 1997a).

It is estimated that up to 2040, one percent of agricultural land within a 150 km radius of Perth would be required for land application to utilise biosolids production, with production expected to increase by three percent per annum (Water Corporation 1997a). The agricultural market is considered a beneficial option for biosolids use; with approximately 60% of the Beenyup product, 75% of the Subiaco product and 100% of the Woodman Point product currently being used (Penney, Dumbrell & Pritchard 2003). All WWTPs in Perth achieve significant pathogen reduction, with a grading classification of contaminant grade C2 and pathogen grade P3 required for agricultural land application (DEP, WRC & DOH 2002). Prior to

2002, the biosolids were graded as ‘Restricted Use 2B’ (DEP 2001), making them suitable for direct land application or reprocessing to improve quality.

All experiments presented in this thesis use biosolids sourced from Beenyup, being the major agricultural supplier in Western Australia. Biosolids from the Perth region have been regularly analysed, reported and monitored (Water Corporation 1997a). Long-term averages for constituents in Beenyup biosolids at the commencement of the research over the 1999-2000 period, are given in the Appendices, Table 9.1. During the period of the research, Beenyup used filter belt presses for dewatering, although it has more recently upgraded to a centrifuging system, resulting in a small increase in DM content.

Glasshouse, field and laboratory experiments were designed to collect data as to the bioavailability of P in Beenyup biosolids following application to agricultural land in Western Australia. To ensure a response to P, soil deficient in P was used in all experiments requiring a plant response. As a preliminary study, in an attempt to minimise the interaction between the P and N in biosolids, a glasshouse study was conducted to model and verify the contribution of plant available nitrogen (PAN). The subsequent glasshouse study determined the relative effectiveness of biosolid P using a wheat shoot bioassay compared with inorganic P fertiliser. Three consecutive crops were grown and the residual value determined using freshly applied P for the following two crops, whilst maintaining PAN at constant rates.

Data were collected on a field trial site over a two-year period using a similar design to the glasshouse to determine the relative effectiveness of biosolid P compared with commercial inorganic fertiliser P. The residual value of biosolid P was also determined by applying freshly applied P to extra plots in the second year. The field experiment enabled more realistic land application data to be collected for a wheat/ lupin rotation. Soil extractable bicarbonate P as a measure of P availability was determined and compared with shoot P uptake for both pot and field experiments. In addition, the effect of the incorporation of biosolids into the soil on P availability was investigated concurrently as a factor relevant to land application.

Laboratory experiments included the chemical fractionation of soil into P forms for selected biosolids and inorganic P treatments at the completion of the glasshouse experiment. To investigate issues related to P leaching, soluble reactive P was measured following the addition of biosolids to nine different soil types. Consistent with previous experiments, comparison was made between soluble reactive P in soils amended with biosolids compared with an inorganic P fertiliser.

Data collected from this research will provide specific information as to the bioavailability of P in biosolids produced at Beenyup following application to common agricultural soils. These data will enable environmental regulators to best determine land application rates and validate interim guidelines based on informed decisions concerning the most appropriate P loadings. The results will be of relevance to any industry involved in the land application of biosolids to better utilise biosolid P in crop and pasture production and to prevent P contamination in the environment.

Throughout this review, biosolids, wastewater solids, sewage sludge, or wastewater sludge will be used depending on the reference source. The term biosolids will only be used when defined specifically as such in the literature and where stabilisation has been used in the treatment process. As the emphasis of this review is on phosphorus bioavailability rather than on the level of stabilisation *per se'*, all wastewater solids will be considered if relevant data are available.

1.3 Aims of research

1.3.1 General objective

To study the bioavailability of P in anaerobically digested dewatered biosolids following agricultural land application in south-western Australia.

1.3.2 Specific objectives

To evaluate the relative effectiveness of biosolids as a source of plant available P compared with commercial inorganic P fertiliser;

To determine agricultural land application rates of biosolids to best supply P loadings required for optimum crop growth;

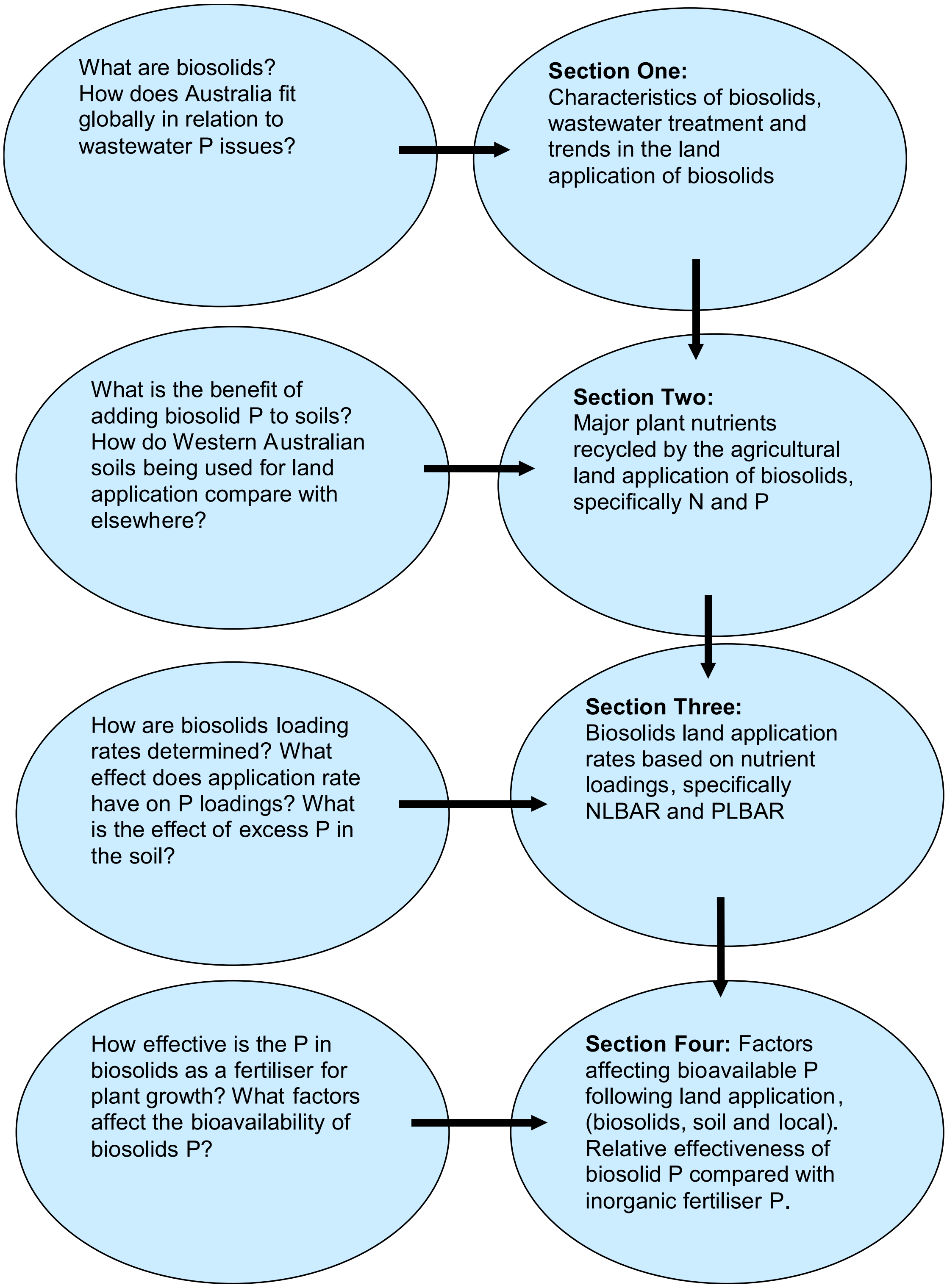
To investigate soil factors affecting P bioavailability following the agricultural land application of biosolids;

To identify P loading rates that may pose a risk to the environment following the agricultural land application of biosolids;

To examine P forms common in biosolids-amended soil, using soil chemical P fractionation.

1.4 Outline of review

The literature review has been divided into four sections with the underlying theme to consider the available and environmentally relevant P in biosolids following land application. The rationale for each section is summarised as follows;



What are biosolids? How does Australia fit globally in relation to wastewater P issues?

Section One: Characteristics of biosolids, wastewater treatment and trends in the land application of biosolids

What is the benefit of adding biosolid P to soils? How do Western Australian soils being used for land application compare with elsewhere?

Section Two: Major plant nutrients recycled by the agricultural land application of biosolids, specifically N and P

How are biosolids loading rates determined? What effect does application rate have on P loadings? What is the effect of excess P in the soil?

Section Three: Biosolids land application rates based on nutrient loadings, specifically NLBAR and PLBAR

How effective is the P in biosolids as a fertiliser for plant growth? What factors affect the bioavailability of biosolids P?

Section Four: Factors affecting bioavailable P following land application, (biosolids, soil and local). Relative effectiveness of biosolid P compared with inorganic fertiliser P.

2 Review of literature

2.1 Biosolids production and use

2.1.1 Major characteristics of biosolids

Biosolids produced on a global basis vary widely in composition and properties. It is widely accepted that wastewater solids are non-homogenous in terms of their chemical, biological and physical properties (Awad, Ross & Lawrie 1989; Cameron, Di & McLaren 1997; Campbell & Beckett 1988; Lawrie, Awad & Ross 1990; McCalla, Peterson & Lue-Hing 1977; Pierzynski 1994; Sommers 1977; Sommers et al. 1972; Sommers, Nelson & Yost 1976; Spinosa & Vesilind 2001). Therefore, a 'normal' form of biosolids is unlikely to exist, which makes comparison between research data difficult.

Differences in composition are determined largely by the wastewater source, such as domestic or industrial, the type of treatment plant and its method of operation (Dentel 2001; Dhir, Limbachiya & McCarthy 2001; Kolarik & Priestley 1995; Sommers et al. 1972; Spellman 1997; Tomar 1999). Source control and industrial wastewater pre-treatment programs in the last 30 years have limited the discharge of industrial constituents into municipal sewers and resulted in a decline in trace elements (Lue-Hing et al. 1997; Smith 2001). In an Australian study, the total concentrations of Cd, Mg, Pb and Zn have declined since 1983 (Oliver, McLaughlin & Merrington 2002). The paper pulp industry has also used the term biosolids to describe the wastes generated by the production of newsprint, also spread on farmland (Schmidt 1997) although it was not considered in this review.

2.1.1.1 Comparison with animal manures and raw sewage

Biosolids are often compared with animal manures and raw sewage, although there are differences. Animal manures and raw sewage have not undergone separation and conditioning, as have biosolids. The elemental content of animal wastes varies with the type of animal, diet, age and degree of decomposition, inclusion of non-wastes such as bedding and waste collection and management facilities (McCalla, Peterson & Lue-Hing 1977). In terms of plant nutrients, animal manures are generally lower in P and higher in potassium (K) than many biosolids, with the chemical composition for selected animal wastes given in Table 2.1. Higher values for these nutrients have been reported by Peterson, McCalla and Smith (1971).

Table 2.1 Chemical composition of selected animal wastes

Type of	Chemical composition of dry matter (% dry weight basis)					
waste	**N**	**P**	**K**	**Ca**	**Mg**	**S**
Hen litter	2.0	1.9	1.9	3.4	0.5	0.5
Dairy cow	2.7	0.5	2.4	1.6	0.6	0.3
Pig	2.0	0.6	1.5	2.0	0.3	0.5
Sheep	4.0	0.6	2.9	1.9	0.6	0.3

(McCalla, Peterson & Lue-Hing 1977)

It is well established that sludge organic matter is as effective as farmyard manures for improving the physical and chemical conditions of soils, particularly degraded soils (Catroux, L'Hermite & Suess 1983). However, the public more favourably accepts the application of animal manures to farmland as a nutrient source and soil amendment. In the USA, a total of 120 million tons DS of animal manure, 50 million tons DS of mineral fertilisers and 2.8 million tons DS of biosolids are applied to farmland annually. Approximately 90% of animal manures produced were land-applied, compared with 40% for biosolids (Spicer 2002). An overview of the types, quantities and characteristics of wastes generated in Australia and New Zealand is reported by Cameron, Di and McLaren (1997).

2.1.2 Wastewater treatment processes

Raw domestic wastewater is treated by various stages that consist of preliminary treatment, primary, secondary, advanced or tertiary treatment, disinfection and sludge treatment; which can all have an effect on the final product. Preliminary treatment includes bar screens and grit collection that uses physical operations such as sedimentation to remove floating and settleable solids. The water-carried solids settling in the bottom of a settling tank are termed raw sewage or primary sludge, which is unsuitable for land application due to many unpleasant characteristics and pathogenic microorganisms (Spinosa & Vesilind 2001; Water Pollution Control Federation 1972). Many WWTPs have converted to advanced treatment processes to meet stringent new guidelines for the agricultural use of wastewater solids, requiring improved management and greater expense.

2.1.2.1 Stabilisation

In secondary treatment, biological and/or chemical techniques are used to remove most of the organic matter. Sludge must be processed to reduce its putrescibility and/or pathogen content. This process is known as ‘stabilisation’ and is essential if the product is to be used for beneficial use programs, such as in agriculture (Spinosa & Vesilind 2001). Alkaline stabilisation, anaerobic digestion, aerobic digestion, composting and heat drying and pelletising are examples of stabilisation processes (Epstein 2002).

Anaerobic digestion has been the favoured biological method for sludge stabilisation since the early 20th century, relying on bacteria to digest organic matter (Bruce, Campbell & Balmer 1984; Wen, Bates & Voroney 1995), and it is used predominantly in the Perth metropolitan area. Aerobic digestion is another biological process that uses long-term aeration using microbes that derive energy from the oxidation of ammonium ions to nitrite and then nitrate, described further by Tomar (1999). Pathogen reduction in aerobic treatment processes is achieved at elevated (thermophilic) temperatures (Spinosa & Vesilind 2001). Thermophilic is defined as temperatures $>54^0$C and mesophilic as $<49^0$C (Holbrook, Henderson & Allison 2002). Reed beds also rely on aerobic bacteria to treat biosolids, although they are more commonly used for treating liquids (Evans 2001).

Sludge stabilisation by the addition of chemicals is an alternative treatment to biological methods (Andreasen 2001), using alkaline materials such as quicklime [CaO] and hydrated lime [$Ca(OH)_2$]. Advanced alkaline stabilisation technologies such as cement and lime kiln dusts, fly ash and calcium sulphate can reduce pathogens, odour and vectors, increase the solid concentration and immobilise metals. Many alkaline processes are marketed privately as N-Viro International Corporation and Chemfix Technologies, Inc (Lane 1994; WEF 1994). Stabilisation and odour control may also be achieved using mineral oxides under thermophilic conditions (Englande & Reimers 2001).

2.1.2.2 Dewatering

In the production of biosolids from sludge, Dentel (2001) has emphasised the need for conditioning, thickening and dewatering to reduce the overall volume and to improve the ease of handling. This has included mechanical dewatering equipment such as centrifuges and belt filter presses, and other methods such as gravity thickening, dissolved air floatation and rotary screen thickening (Australian Water Association 2001; Bruce, Campbell & Balmer 1984). The use of lime, ferric chloride and polymers for sludge conditioning flocculants is explained by Spellman (1997) and non-traditional methods such as freeze-thaw by Dentel (2001). Natural or non-mechanical dewatering includes lagooning and sand drying beds. Sludge drying beds were common prior to urban growth and involved the removal of sludge from primary clarifiers, which were pumped into beds then scraped out and stockpiled following air drying (Australian Water Association 2001).

Physical dewatering can be improved by thermal drying to evaporate water and to produce biosolids from 40 to 98% DS. Drying improves the physical appearance of biosolids, which assists in consumer acceptance, reduces vectors and inactivates pathogens whilst retaining many plant nutrients, often in a more concentrated form. Heat dried products have been marketed in the USA since the 1920s (Evans 2001; Water Pollution Control Federation 1972; WEF 1994). The drying of biosolids uses energy, is expensive and is not considered economic for many plants (Australian Water Association 2001).

In tertiary treatment, additional combinations of chemicals or biological methods are used to remove other constituents from the wastewater, such as N and P, which are not reduced significantly by secondary treatment. Phosphorus treatments are discussed in more detail further in this review. Finally, to reduce pathogens in effluent, a disinfectant such as chlorine may be added (McCalla, Peterson & Lue-Hing 1977; Tomar 1999).

2.1.2.2.1 Composting and vermiculture

Sludge can also be used to make compost or vermicast. Composting is a method of managing sludge wherein organic components are biologically decomposed. Self-heating during composting reduces pathogen numbers and the resultant product is easily handled with fewer vector problems compared with traditional sludges. Various green waste amendments are used to achieve a desirable carbon-to-nitrogen (C/N) ratio, pH, moisture content, aeration and temperature (Evans 2001; Krogmann 2001; Water Pollution Control Federation 1972; WEF 1994; WEF 1995); or municipal waste added (King, Rudgers & Webber 1974; Terman, Soileau & Allen 1973).

Vermiculture describes worm farming whereby worms (*Eisenia foetida*), adapted to high organic environments, are fed a combination of dewatered sludge and shredded green waste or composted green waste. The worm castings or vermicast are used as a fertiliser or soil conditioner, and are regarded as a natural organic fertiliser with pathogens destroyed through the action of worm digestion (Australian Water Association 2001; Evans 2001; Lotzof & Eisenacher 2002; Vermitech 2002).

Irradiation has also been used as a method to eliminate pathogens in digested sludge (US EPA 1998).

2.1.3 Effluent guidelines and wastewater nutrient removal

Wastewater effluent is a potential source of pollution if disposed untreated into any natural water body such as a river or lake due to the presence of suspended solids, biodegradable organics, pathogens responsible for waterborne diseases and trace metals. The nutrients, N and P in domestic, industrial, agricultural wastes and natural runoff have the potential to accelerate eutrophication; the excessive growth of algae and other aquatic plants. The death and decomposition of algae produces an oxygen demand that depletes the level of dissolved oxygen in the water (Pierzynski, Sims & Vance 1994; Tomar 1999). Furthermore, blue-green algae may release toxins into the water when they die (McWaters 1999).

The disposal or re-use of wastewater is governed by international limits and requires that the concentration of P in effluent released to natural drainage systems be <1 mg/L, with eutrophication likely to occur in streams if effluent contains >2 mg P/L and N is present (Tomar 1999). The total P concentration in raw domestic wastewater may vary from 4 to 15 mg/L and N may vary from 20 to 85 mg/L (Havilah & Osborne 1992) and consequently these nutrients must be removed prior to discharge into water bodies. It has been estimated that in 1991, WWTPs discharged 500 t of P and 2,780 t of N into the Murray-Darling Basin’s rivers; more than half the input of both nutrients from all sources in a dry year (Lehane 1995).

2.1.3.1 Phosphorus treatment

The proportion of treated wastewater discharged into river systems has increased with the rise in global population. A number of chemical and biological tertiary treatments are now used to treat P in wastewater to reduce P discharge in effluent (Gestring & Jarrell 1982; Jenkins, Ferguson & Menar 1971; Jeyanayagam & Husband 2002; Raper 1995; Scott & Horlings 1975). Consequently, there has been an increase in the concentration of P in biosolids from WWTPs that use P treatment methods. Phosphorus treatment is not common where effluent is ocean discharged, such as typical for Perth. The maximum P concentration acceptable for ocean discharge of domestic wastewater is 5 mg P/L although other chemical factors are considered. Industrial effluent must have a low total P concentration and be below 100 mg N/L to be acceptable for discharge into municipal sewers or oceans (Tomar 1999).

Treated effluent is becoming a popular source of irrigation water to provide both moisture and plant nutrients, especially in hot, dry climates. The Food and Agricultural Organisation has set a limit of 5 to 30 mg N/L for treated water used for irrigation to prevent ground water contamination by nitrates, although there is no limit for the relatively immobile P. The presence of trace metals may restrict the use of treated effluent sourced from industry, mining, petroleum or metal foundries (Tomar 1999). The use of high quality drinking water in toilets to dispose of human wastes has been questioned by Jenkins (1999).

2.1.4 Trends in the agricultural land application of biosolids

There is no universal approach to the use of wastewater solids, although there is a common strategy to use waste materials to take advantage of the energy content and to recycle nutrients. Agricultural land application is the likely option for beneficial use in highly urbanised countries, such as Australia and North America using modern WWTPs (Lue-Hing et al. 1997). To illustrate differences in end use, a few trends are summarised as follows:

Sommers (1977) calculated that less than 1% of agricultural land in the USA would be required for the land application of biosolids. In 1997, approximately 3,000,000 t DS of biosolids were used in agriculture, accounting for 55% of biosolids production (Spinosa & Vesilind 2001). In general, the land application of biosolids has increased (Womer, Elliott & Brandt 2002), as have trends opposed to land farming, land-filling and/or incineration (Englande & Reimers 2001). Class A and Class B biosolids are the two types of biosolids recognised under the *Part 503* rule (WEF 1995). Class A biosolids have undetectable levels of indicator pathogens for *Salmonella*, enteric viruses, and Helminth ova; or have undergone approved treatment removal and as such are preferred by many municipalities to the partially disinfected Class B (Spicer 2002).

Currently in Europe, sludge production accounts for about 8,000,000 t DS per annum, more than double that produced in the USA, and is expected to increase to 14,000,000 t DS within five years (Bonnin 2000; Lue-Hing et al. 1997; Matthews & Lindner 1997). Increasingly more sludge is being used within agriculture and less sludge is being land filled, although much variation exists between countries. For example, Greece uses 10% of sludge produced in agriculture, whereas Portugal uses 80%. In comparison, many Eastern European countries have poor levels of wastewater treatment with less than 50% mechanically or biologically treated and practically no nutrient removal (Lue-Hing et al. 1997).

The land application of sludges in the European Union, as regulated by *European Directive ED91/156* and *Directive 86/278*, is rapidly evolving (Spinosa 2001) with aspects of sludge disposal under review, i.e. *TC 308 objectives* (Bonnin 2000). Landfill is being restricted under the *European Union Landfill Directive* (Banks & Heaven 2001; Spinosa & Vesilind 2001) and in France, for example, nearly 60% of the sewage sludge has been re-cycled in agriculture with waste disposal in landfills illegal after 2002 (Stenger 2000). Historical and future directions for the disposal of communal sewage sludge in the old 12 member countries of the European Union are summarised in Table 2.2.

Table 2.2 Historical and future directions for the disposal of communal sewage sludge in the old 12 member countries of the European Union

	1984		**1992**		**2000**		**2005**	
Utilisation	2,057	(37)	2,504	(30)	3,617	(40)	4,576	(45)
Incineration	518	(9)	715	(11)	2,088	(24)	3,872	(38)
Landfill	2,988	(54)	3,257	(50)	3,200	(36)	1,615	(17)
Total	5,563	(100)	6,476	(100)	8,906	(100)	10,063	(100)

Figures in 1,000 t DS per year (Percentages given in parentheses).
(Matthews & Lindner 1997).

The use of untreated sludge on food crops was banned in the United Kingdom (UK), following the implementation of the 1998 UK safe biosolids matrix (or safe sludge matrix). Treatment plants in the UK now include thermophilic anaerobic digestion, composting or mesophilic anaerobic digestion and dewatering (MADD) (Gove et al. 2001; Gove et al. 2002), with thermal hydrolysis (Cambi) used for advanced treatment (Evans 2001). In Ireland research is progressing towards the characterisation, treatment and sustainable reuse of biosolids (Bartlett & Kilillea 2001).

The low availability of either landfills or land reclamation sites, such as in Japan, dominates disposal practices throughout much of Asia. Wastewater is typically converted into combustion ash and then melted to produce bricks (Lue-Hing et al. 1997; Okuno 2001). A sludge component of between 10% and 30% is similarly used in Taiwan to produce biobricks. The firing process immobilises toxic metals, destroys hazardous microbes and organic material and is odourless (WME 2002). In contrast, the sludge in South Africa is generally ploughed into specifically designated land areas (i.e. sacrificial) or stockpiled at sewage treatment plants. Much (63%) of the 300,000 t DS sludge in metropolitan and industrial areas in South Africa are high in metals and elements and consequently may not be suitable for land application, although agricultural soils may benefit given their state of deterioration and loss of organic matter (Smollen 1997).

2.1.4.1 Biosolids use in Australia

More than 75% of Australia's agricultural soils have less than 1% organic matter and according to Gillespie (2002), the 60% of organic material it sends to landfill each year would be better re-cycled to agricultural soils. Australia is one of the industrialised world's worst performers in the area of waste disposal and re-use (Environment Australia 2002), and has been slow to adopt the use of organic wastes (Spedding 2002). There has however, been an increase in the land application of biosolids in Australia, particularly in agriculture.

In Australia, the annual total production of biosolids was estimated by Cameron and others (1997) at 250,000 t DS. There is much variation in the end-use of biosolids as evident between different states in Figure 2.1 (Stevens et al. 2002). There are also large variations between country towns and major metropolitan centres. Banks and Heaven (2001) estimated that 76% of sludge in Australia was stockpiled in 1992, although the use of biosolids in agriculture has since developed rapidly. In the Sydney basin for example, 50,000 t DS were produced in 1995 with 58% applied beneficially to agricultural soils (Osborne et al. 1995b), and by 2000 this had increased to 97% (Gibson et al. 2002). This is in stark contrast to ten years previously where ocean disposal accounted for 92% of the sewage sludge produced. Western Australia also has opted for beneficial use programs for biosolids following the discontinuation of incineration in the 1980s (Water Corporation 1997a). More recently, Victoria has reviewed biosolids and composting options (Clements et al. 2002).

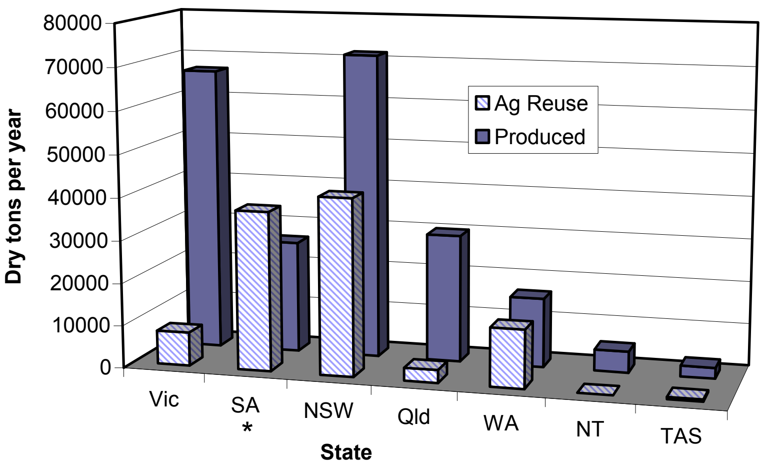


Figure 2.1 Estimated biosolids production and use in Australian agriculture, on a state-by-state basis

(Stevens et al. 2002)

* In South Australia, the availability of stockpiled biosolids resulted in more biosolids being used than produced.

The land application of biosolids in Australia is regulated by specific guidelines. The *'Guidelines for Sewage Systems: Guidelines for Biosolids Management'*, released by the Agriculture and Resource Management Council of Australia and New Zealand (ARMCANZ) in 1995, although based on North American and European guidelines, were used initially. The NSW EPA Environmental Management Guidelines for the *'Use and Disposal of Biosolids Products'* (NSW EPA 1997) was consequently developed and although considered too specific for use on a national basis was adopted by other states, such as Western Australia to develop local guidelines (DEP 2001; DEP, WRC & DOH 2002; Water Corporation 1997a).

Recently a national project has been instigated to research the use of biosolids and other wastes on agricultural land. This coordinated approach aims to gather data to determine the benefits and risks of biosolids applied to a range of soil and crop environments around Australia (McLaughlin et al. 2002). Biosolids management in Australia is undergoing a rapid pace of development and is thus creating a demand for information related to nutrient bioavailability, which is discussed further in the following section.

2.2 Major plant nutrients re-cycled by the land application of biosolids

2.2.1 Nutrient recycling in agriculture

Soil has the capacity to adsorb and by microbial activity transform various solid wastes into useable materials for plant growth. It is generally accepted that chemical elements in wastes can successfully be re-cycled in agricultural production (EPA 1994; Kardos, Scarsbrook & Volk 1977; McCalla, Peterson & Lue-Hing 1977; Page, Lue-Hing & Chang 1986; Peterson, McCalla & Smith 1971). Macronutrients taken up by plant roots from the soil include N, P, K, sulphur (S), calcium (Ca) and magnesium (Mg) (Bolland 1998a).

Nitrogen and phosphorus can be re-cycled by the agricultural use of biosolids with concentrations of these nutrients commonly used to determine land application rates. Biosolids also contain micronutrients essential for plant growth in varying amounts such as manganese (Mn), copper (Cu), zinc (Zn) and molybdenum (Mo) and a number of metal elements not required by plants, such as cadmium (Cd) and mercury (Hg). In land application programs, micronutrient levels need to be balanced, as high quantities of Cu and Zn are toxic to plants, with Cd both phytotoxic and considered a health risk for humans. The metals Cu, Zn and Cd may pose the greatest risk from biosolids use in agriculture because of their potential mobility and uptake by agricultural produce in Australia (Gibson et al. 2002). Biosolids are low in K (Pierzynski 1994) and supplemental K fertiliser may be necessary to maintain productivity in soils receiving sludge (King & Morris 1973).

The range in composition of nutrients in biosolids sourced from a range of WWTPs in New South Wales and Western Australia is highlighted in Table 2.3.

Table 2.3 Comparison of constituents in biosolids sourced from Wastewater Treatment Plants in New South Wales and Western Australia

Parameter	Beenyup, WA [a]	Penrith, NSW [b]	Cronulla, NSW [b]	St Marys, NSW [c]	North Head, NSW [c]
Treatment	Anaerobic digestion	Biological nutrient removal	Anaerobic digestion	Dewatered Ferric chloride	N-Viro Soil
Total dry solids (%)	16 - 22	18	20 - 40	30	46.5
pH	7			6	12.4
Total N (%)	3.3 - 6.7	6.8	4.2	2.4	1.3
Total P (%)	0.9 - 3.6	2.9	2.2	3.8	0.2
Total K (%)	0.1 - 0.24	0.97	0.82		
Ca (%)	2.3 - 9.4	1.1	2.0		
Mg (%)	0.2 -1.0	0.69	0.25		
S (%)				0.6	0.5
Fe (%)				15	0.7
Zn (mg/kg)	640-1,900	470	1,020	432	168
Cu (mg/kg)	1,000-2,200	630	1,220	452	203
Mn (mg/kg)	100-1,500			247	157

[a] (Water Corporation 1997a), [b] (Kanak, Osborne & Swinton 1995), [c] (Bamforth 1996)

Missing values indicate that the given parameter was not supplied by the reference source.
All nutrient constituents are expressed as a dry weight basis.

Biosolids are considered a dilute form of plant nutrients because of the large volume required for application to supply similar quantities compared with commercial fertilisers. Chemical fertilisers in the USA contain from 15% to 82% N and from 8% to 76% P, whereas biosolids may contain from 1% to 11% N and from 0.7% to 7.5% P on a DS basis (Spicer 2002). However, as biosolids contribute directly to soil organic matter and improve physical properties, disadvantages associated with the quantities required for land application compared with inorganic fertilisers are offset. Prior to the manufacture of synthetic fertilisers, agricultural waste products, especially animal manures were recognised as a valuable source of plant nutrients. The concept of elemental recycling is not new, but has resurfaced with the need for more sustainable societies (Kardos, Scarsbrook & Volk 1977).

2.2.2 Recycling of nitrogen from biosolids

Nitrogen is an essential part of many plant compounds such as proteins, amino acids and chlorophyll. Plants require relatively large amounts of N and can easily become deficient unless soil supply is increased by the application of N fertilisers, organic matter and/or by using legumes. Leguminous plants obtain much of their N requirements from the atmosphere by symbiotic fixation with rhizobia bacteria (Mason 1998; Tomar 1999).

A considerable amount of NH_3 is found in wastewater. Animals and humans depend on plant and animal N in the form of protein. This protein undergoes a series of reactions during metabolism to release urea, a N containing waste in faeces and urine (Tomar 1999). A biosolids analysis typically reports total N (N_T), nitrate-N (NO_3-N) and ammonium-N (NH_4-N), with organic N (N_o) estimated as: $N_o = N_T - (NO_3\text{-N} + NH_4\text{-N})$. Sommers (1977) has reported the N_T of a range of sludges to be variable (<1 to 17.6% DS), with median values from 2% to 4% DS likely in Australia (Kanak, Osborne & Swinton 1995). Differences in N_T due to wastewater treatment are described by Havilah et al. (1996) for lime-amended biosolids (0.9% N_T), kiln-dried primary pelleted biosolids (1.5% N_T) and dewatered biosolids (3.3% N_T) compared with urea (46% N_T).

A complete summary of the different forms of N in a range of sludges is reviewed by Hall (1984), with the majority of N in organic forms. Organic combinations may also account for 50% to 90% of N_T in liquid sludge, although they remain to be characterised (Coutinho, Arrobas & Rodrigues 1997; Sommers 1977). Ammonium concentrations are variable with averages ranging from approximately 0.6% to over 2%, mostly due to wastewater treatment processes (Gilmour et al. 2000). Large variations in inorganic N were common in USA cities over a two year period (Sommers, Nelson & Yost 1976). The drying of biosolids can cause changes in the NH_4 content due to the loss of ammonia (Ryan & Keeney 1975).

The majority (80%) of the 3.3% to 6.7% N_T in biosolids produced by anaerobic digestion in Perth is in organic forms. The remainder (20%) consists of NH_4-N, with negligible NO_3–N or nitrite (NO_2) forms (Water Corporation 1997a). These values are typical for fresh anaerobically digested sludge, although NO_3–N can be formed slowly through nitrification when stored prior to analysis. In comparison aerobic sludges will contain some NO_3–N. Dewatering of sludge will further reduce NO_3–N and NH_4-N concentrations (Hall 1984; Ryan & Keeney 1975; Sommers 1977).

2.2.2.1 Plant uptake of nitrogen

Biosolids have been proven as an effective source of N fertiliser for plant growth. Following application to the soil, the N in sludge is or becomes available by the processes of nitrification, immobilisation, volatilisation and mineralisation as illustrated by the soil N cycle in Figure 2.2 (Osborne 1995b). Literature in this area as related to wastewater solids has been described by Kelling et al. (1977) and Osborne (1992).

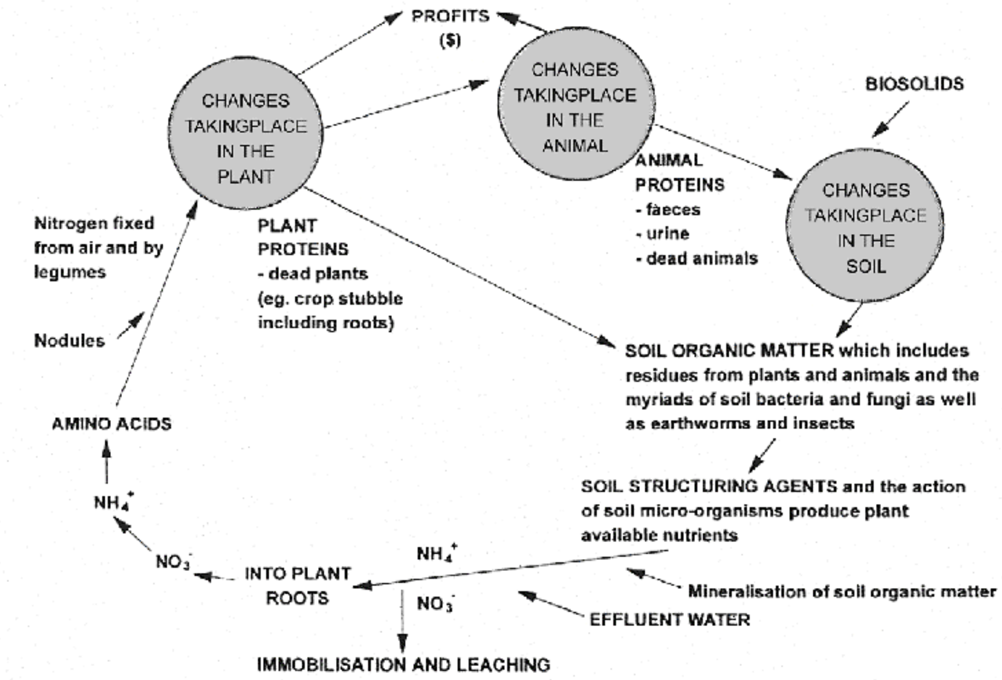


Figure 2.2 Biosolids in the nitrogen cycle

(Osborne 1995b)

Organic forms of N in biosolids are not immediately available for plant uptake, only the inorganic forms of N, such as NO_3^- and NH_4^+. It is essential that inorganic forms of N do not exceed plant agronomic requirements, as NO_3^- being very mobile is liable to be leached quickly beyond the root zone. Ground water contamination with NO_3^- and NH_4^+, for example, has been demonstrated following the ponding of liquid sewage sludge on open porous soils (Lund, Page & Nelson 1976). The management of agricultural N loss to the environment has been discussed by Smith, Schepers and Porter (1990).

2.2.2.2 Mineralisation of organic nitrogen in biosolids

Organic forms of N in biosolids slowly contribute to plant available N, through mineralisation by soil microorganisms to NH_4^+. Mineralisation in sludges can vary from 100% to a low of a few percent and depends on sludge type, C/N ratio of the soil and/or sludge, climate, pH, soil type, method of application, water content (National Research Council 1996) and soil temperature and time since soil incorporation (Smith, Woods & Evans 1998). The irradiation of sludge to reduce pathogens may release NH_4^+ (Wen, Bates & Voroney 1995).

The type of sludge will affect the mineralisation rate of N. Liquid and undigested biosolids have the greatest accumulation of NO_3^-, followed by dewatered digested and then dewatered undigested biosolids being high in available C, which may immobilise N; air dried biosolids are the most resistant to mineralisation (Smith, Woods & Evans 1998). Gilmour et al. (2000) indicated that stabilised biosolids (lagoon, compost) decomposed slower than fresh biosolids. Biosolids high in organic N tended to be more decomposable, leading to increased mineralisation of N. Typical C/N ratios for biosolids range from 7 to 9, with a wide range reported. Biosolids with a C/N ratio >15 may mineralise slowly until substantial decomposition has taken place (Broadbent 1977).

Since the digestion process removes most of the volatile solids in biosolids, mineralisation is less rapid than in other biological material of comparable N content (Broadbent 1977). Plant available N may be reduced in alkaline stabilised biosolids (WEF 1994); however, lime-amended biosolids and kiln dried primary pelleted biosolids were more efficient sources of N compared with dewatered biosolids in New South Wales, which Havilah and others (1996) attributed to the liming effect and N mineralisation. The mineralisation of biosolids follows the same pattern as organic matter decomposition, being dependent on soil temperature and moisture. There is no decomposition below 0^oC as microorganisms are not active, a slow increase up to 17^oC, and a more rapid increase above this. The decomposition of biosolids remains near optimum at a moisture capacity close to 40% of the water holding capacity (i.e. 70% of field capacity). In dry soils (i.e. 10% of field capacity) decomposition may be reduced to one-tenth of the optimum (Gilmour et al. 2000).

Nitrification is an aerobic process whereby NH_4^+ is converted to NO_3^-. The rate of nitrification is increased by temperature, decreased by soil acidity, and affected by moisture and other factors, such as a readily available source of energy for denitrifying bacteria. Hydrogen ions are released into the soil during the conversion from NH_4^+ to NO_3^- contributing to soil acidity. Nitrate can be lost to the atmosphere by denitrification in anaerobic conditions resulting in the production of gases such as nitrogen (N_2), nitrous oxide (N_2O), nitric oxide (NO) and nitrogen dioxide (NO_2) due to denitrifying bacteria, e.g. *Pseudomonas denitrificans* (Tomar 1999). Nitrogen can become temporarily unavailable through fixation by microorganisms during the decomposition of plant material with a high C/N ratio, such as cereal straw. Immobilisation of N may occur shortly after organic wastes are applied to soil, therefore the addition of chemical fertiliser N may be necessary to avoid a deficiency (Wen, Bates & Voroney 1995).

There is equilibrium between NH_4^+ and NH_3 gas in the soil following mineralisation. Under alkaline conditions it swings in favour of NH_3, which can result in volatilisation (gaseous loss) of ammonia. Volatilisation is doubled in alkaline soils (pH >7.5) compared with acidic-neutral soils (pH 5 to 6) and increased in sandy textured soils (>75%) compared with minimal amounts in clay soils. Over 50% of NH_4-N can volatilise when biosolids are surface-applied in a typical situation, which is increased by increasing temperature, soil moisture, humidity and wind speed (Gilmour et al. 2000). Volatilisation losses have been shown to be dependent on the method of soil incorporation (Broadbent 1977; Kardos, Scarsbrook & Volk 1977; National Research Council 1996; Ryan & Keeney 1975; U.S. Environmental Protection Agency 1997).

The potentially mineralisable N varies depending on the type of sludge, ranging from 5% to 10% for composts, 15% for anaerobically digested sludge, 25% for both aerobically digested sludge and raw sludge, 30% for both lime-stabilised and primary sludge, and 40% for waste-activated sludge (Kanak, Osborne & Swinton 1995; Pierzynski 1994); similar rates were reported by Sommers and Barbarick (1986). A mineralisation rate of 10% was used by Wen, Bates and Voroney (1995) to estimate the amount of N available to plants in a range of manures. Following a review of the literature, Osborne (1992) concluded that the soil/climate/crop and biosolids type needs to be considered when determining mineralisation rates.

Under-estimation of the N mineralisation rate in biosolids may result in over-fertilisation thus contributing to the contamination of water-bodies. Estimation of agronomic loading rates based on plant available N (PAN) to calculate agricultural land application rates of biosolids is discussed further in the land application section of the review.

2.2.3 Recycling of phosphorus from biosolids

More P is consumed than is required for normal growth and development by humans. Within a WWTP, approximately 60% of the total P (P_T) content measured in effluent and sludge is derived from faeces and urine. Food ground through garbage disposal units, food wastes from large scale processing plants and synthetic detergents used in household cleaning and soaps also contribute to the P_T. A comprehensive review of the literature, related to biosolid P is reported by Havilah and Osborne (1992).

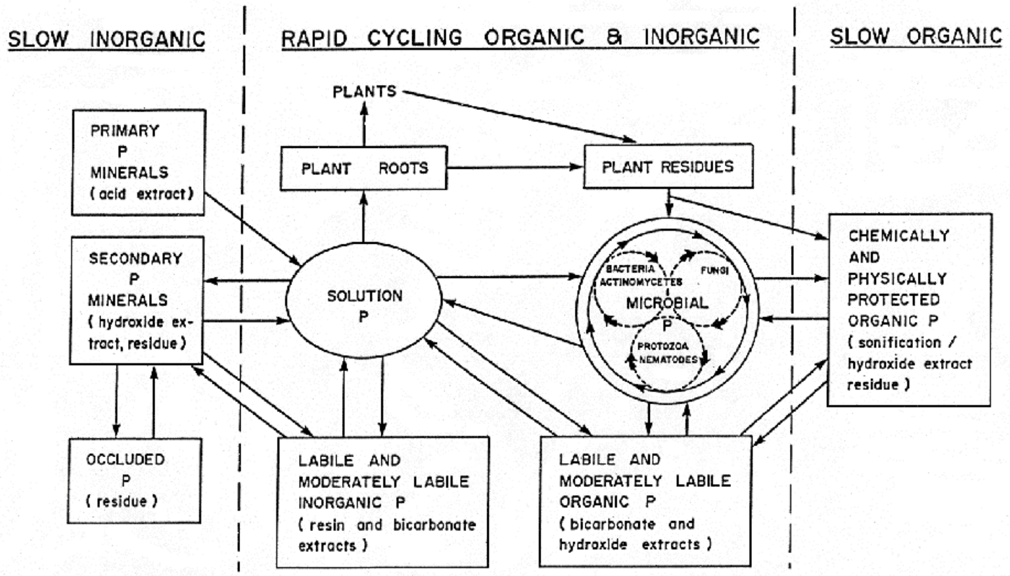
In general the P_T in sludges ranges anywhere from 0.8% to 6.1% DS (National Research Council 1996), being dependent on the nature of the raw sewage and the treatment process (Kirkham 1982; McLaughlin 1984). In the UK for example, the P_T averages from 3% to 4% DS and commonly ranges from 1% to 2% DS with increases up to 8% DS following P treatment (Triner et al. 2001). Aerobically digested sludge has a lower P_T (2.7%) than anaerobically digested sludge (3.0%), based on median values from a range of WWTPs in the late 1970s in the USA (Sommers 1977). In Western Australia, the P_T of biosolids is commonly between 0.9% to 3.6% DS with a mean of 2.2% (Water Corporation 1997a), which is typical for anaerobically digested sludge with no P treatment. In New South Wales, the chemical precipitation of biosolids has resulted in increased P_T from 1.2% to 6.7% DS, with a mean of 3.5% DS (Havilah & Osborne 1992).

In general, sludge P_T concentration has increased from the 1930s due to the use of detergents, garbage grinders, various industrial wastes (Water Pollution Control Federation 1972), and more recently chemical and biological P removal treatments (Havilah & Osborne 1992; Henze et al. 2002; Kirkham 1982; McLaughlin 1984; Raper 1995). The median P_T is now 130% higher in biosolids compared with 1983 in Australia (Oliver, McLaughlin & Merrington 2002).

2.2.3.1 Phosphorus in the soil and plant uptake of P

The role of P in agriculture is well documented and continues to generate considerable research effort and reviews (Foth & Ellis 1988; Khasawneh, Sample & Kamprath 1980; Sanyal & De Datta 1991; Stewart & Sharpley 1987; Tunney et al. 1997; Wild 1988). Plants cannot grow without P and produce little or no grain, with P being an essential component of cell membranes, genetic material and energy storage and transfer systems for chemical reactions. Phosphorus is the most important nutrient element (after N) limiting agricultural production in most regions of the world, particularly on soils derived from old land masses such as Australia (Bolland 1998b; Glendinning 1999; Holford 1997). Soils with low P reserves have little capacity to replace losses from the export of agricultural products and in most soils fertiliser P application is required to produce satisfactory yields.

The widespread deficiency of P in soils is due to its chemically reactive nature, resulting in a complex soil P 'pool' (Holford 1997). The P_T in a majority of soils is relatively low, between 0.02% and 0.08% (Phillips and Webb 1971). Nearly all of the P (98-99%) exists in soil equally as inorganic (P_i) or organic compounds (P_o). Most P_i is combined largely with calcium (Ca), iron (Fe), aluminium (Al) magnesium (Mg), and clay minerals, whereas P_o exists as part of plant and animal residues and products of microbial synthesis. Very small amounts of P compounds are found in the cells of living matter (Brady 1990; Glendinning 1999). The amount of P in soil solution is low, seldom exceeding 0.01% of the total soil P (Brady 1990). The soil P cycle is a system in dynamic equilibrium, with interchanges governed by chemical, physical and biological reactions as in Figure 2.3 (Stewart & Sharpley 1987).



The soil P cycle: Its components and measurable fractions. Source: Adapted from Chauhan et al., (1981); extracts from Hedley et al. (1982).

Figure 2.3 Components and measurable fractions of the soil P cycle
(Stewart and Sharpley, 1987)

Only the P in soil solution P is readily available for plants and is taken up by plant roots as water-soluble orthophosphate (PO_4^{3-}), usually as $H_2PO_4^-$ or HPO_4^{2-} (Black 1968). Soil solution P also reacts rapidly with other elements in the soil (precipitation) and on the surfaces of soil constituents (adsorption) to form a range of insoluble compounds, with the term sorption commonly used to describe precipitation and adsorption events (Barrow 1980; Bolland, Allen & Barrow 2003). The soil microbial biomass can also immobilise P from soil solution (McLaughlin, Alston & Martin 1988a; McLaughlin, Alston & Martin 1988b). The replenishment of soil solution P can occur through the addition of fertiliser, desorption reactions and mineral dissolution of inorganic P or by mineralisation of organic P by microorganisms.

As P is strongly adsorbed by soil particles, very little P is moved over large distances in soil solution. Consequently, absorption of P in soil solution by plant roots is dependent on the interception of P in soil by roots as they grow through moist soil (Bolland 1998b). The concentration of soil solution P required for optimum plant growth is around 0.2 mg P/L (Pierzynski, Sims & Vance 1994). Phosphorus is most critical during early plant growth stages, while the root system is small and consequently early deficiencies are likely to reduce the yield potential. Smith (1967) found it uneconomical to apply P to wheat crops later than ten days after sowing.

Symptoms of P deficiency are often dependent on other factors, such as the N status of the plant, with stunted growth often the only evidence of a deficiency. Phosphorus is mobile in plants and may move from older tissue if a deficiency develops (Glendinning 1999; Phillips & Webb 1971; Snowball & Robson 1983). The critical concentrations of P in a range of plants at different growth stages are available (Bates 1971; Reuter & Robinson 1997).

2.2.3.2 Sources of phosphorus fertiliser

The use of manures, and perhaps rock phosphates and organic sources of P to improve plant growth began as early as recorded time. Phosphorus was recognised as essential for plant growth as early as 1830, with the use of guano and treatment of bone meal with sulphuric acid (H_2SO_4) to increase the solubility of P (Foth & Ellis 1988). The mining of deposits of rock phosphates of marine origin constituted the basis of the chemical P fertiliser industry. Apatite, the principal mineral supplying P before soil has been extensively weathered, accounted for more than 95% of P in igneous rock. Deposits are found worldwide and are generally the beginning for most, if not all mineral P fertilisers (Phillips & Webb 1971; Wild 1988).

Estimates of P reserves vary widely although it is generally accepted that world P supplies are dwindling, with high grade reserves limited (Kirkham 1982; Olsen & Barber 1977). The economic life of the world’s P reserves has been estimated from about 100 years at the present rates of extraction (Evans 2001) to 200 years where future technology may enable geological P reserves to be mined (Glendinning 1999). The continual mining of rock phosphates is finite and does not renew the global P cycle (McLaughlin 1984). Losses of P through wastage to sediments, water and sludges from the soil-plant-animal system is outlined by White (1981).

Soil organic matter may represent 50% of soil P and agricultural management practices that maintain or increase soil P_o are advantageous in that they slowly replenish available soil P and improve long-term P fertility (Glendinning 1999; Stewart & Sharpley 1987). The addition of animal manure and/or crop residues will increase soil organic matter. In the USA, animal manure and crop residues comprise the majority (76%) of the total P distributed in waste products from agricultural products, with 90% and 68% reused on agricultural land, respectively (Havilah & Osborne 1992). The cycling of P between the various pools in a wheat-pasture rotation has been measured using isotope labelled P (McLaughlin, Alston & Martin 1988b), with further long term P cycling examined by Ottabong et al. (1997).

2.2.3.3 Recycling of biosolid phosphorus

The recycling of P from biosolids and related wastes is of benefit in the context of sustainability. The rising costs of phosphatic fertilisers in agriculture and finite natural supplies have ensured that sludge P is considered for recycling, particularly since P removal treatments have increased sludge P concentrations (Kirkham 1982). Global food demands have increased the demand for fertiliser P with biosolids considered more valuable for the P component, rather than the N (Havilah & Osborne 1992). Furrer, Gupta and Stauffer (1984) estimated that 75% of the fertiliser value of sludge is due to the P content.

The per capita output of P by humans is estimated at 1 kg/yr under European conditions (de Hann 1981). Therefore, P passing into the sewage system from a country such as Australia with a population of 19 million would be 19 kt/yr, worth approximately $57 million when valued at $3.00/kg. However, recoveries of P from sewage sludge and municipal refuse are historically low. For example, P in municipal refuse in USA accounted for 132 x10^6 t DS, of which only 1% was reused on land and P in sewage sludge accounted for 4 x 10^6 t DS, of which only 23% was reused on land (Havilah & Osborne 1992). The Swedish government has taken a lead in the sustainable use of P and set an environmental goal of recycling 75% of P by 2010 (Evans 2001).

2.2.4 Biosolids as a source of plant nutrients for soils in south-western Australia

The parent material on which Australian soils are based, is generally older and more heavily weathered and leached than European or North American soils, often with very low levels of P_T (Jackson 1966; McArthur 1991; Wild 1988). A high proportion of Australian soils have a high adsorbing capacity for P, low residual effectiveness, are acidic and have low productivity without the application of P fertiliser (Osborne 1995). South-western Australia is dominated by highly weathered soil with minimal soil renewal resulting in vast areas of infertile soils including shallow, sandy duplex soils and deep sands of lateritic origin. Ferruginous gravels are common in many soils in Western Australia as a result of laterisation. Gravels contain Fe and Al oxides, which are chemically reactive and have the ability to sorb P. Many Western Australian soils would be considered non-arable elsewhere, but due to a relatively reliable rainfall under a Mediterranean climate, agriculture is possible (Weaver, Ritchie & Gilkes 1992).

Newly cleared land used for agriculture in Western Australia was often deficient in N, P, Cu, Zn and sometimes Mo (Robson & Gilkes 1980). Profitable agricultural production was only achieved by the regular application of fertilisers containing these nutrients. The P status of these soils has since been improved, so that maintenance dressings of P are now sufficient (Barrow 1980). Many of these soils required S also, but this was often overlooked in most cases as S was supplied in superphosphate, which was used to improve soil P (Bolland 1998a). Soil N levels are improved by growing legume-based crops and pastures, or by applying inorganic fertilisers. Little residual N is available at the end of a season and depends on many factors other than soil type, such as losses of nitrate through leaching in high rainfall areas and denitrification in waterlogged sites. Inorganic N applied in excess of plant uptake can contribute to nitrate leaching (Mason 1998).

Sandy soils used for horticulture on the coastal plain in Western Australia have poor nutrient retention. Soil amendments that have been suggested to ameliorate this problem include: bauxite residue or “red mud” (Weaver & Summers 1998), red mud combined with gypsum (Alkaloam), possibly fly ash (generated from coal power stations) (Dougherty & Lawrie 2000); organic matter blends such as biosolids, animal manures and cardboard (Tingay 1997).

Biosolids are emerging as a useful and residual source of nutrients for agricultural soils in south-western Australia, preferably within a 150 km radius from Perth to reduce transport costs (Water Corporation 1997a). Soils formed on laterite are common in this area, as described in Figure 2.4 (Mulcahy 1973). A full account of soils and landforms for soils in south-western Australia is available (Lantzke & Fulton 1993; McArthur 1991; Moore 1998; Northcote 1979). The unique characteristics of Australian soils may therefore preclude the adoption of biosolids land application research and management techniques developed elsewhere. Guidelines for the land application are discussed in section 2.3, predominantly in regard to N and P. Organic matter and other plant elements contained in biosolids, such as Cu and Zn, are not discussed in the scope of this review.

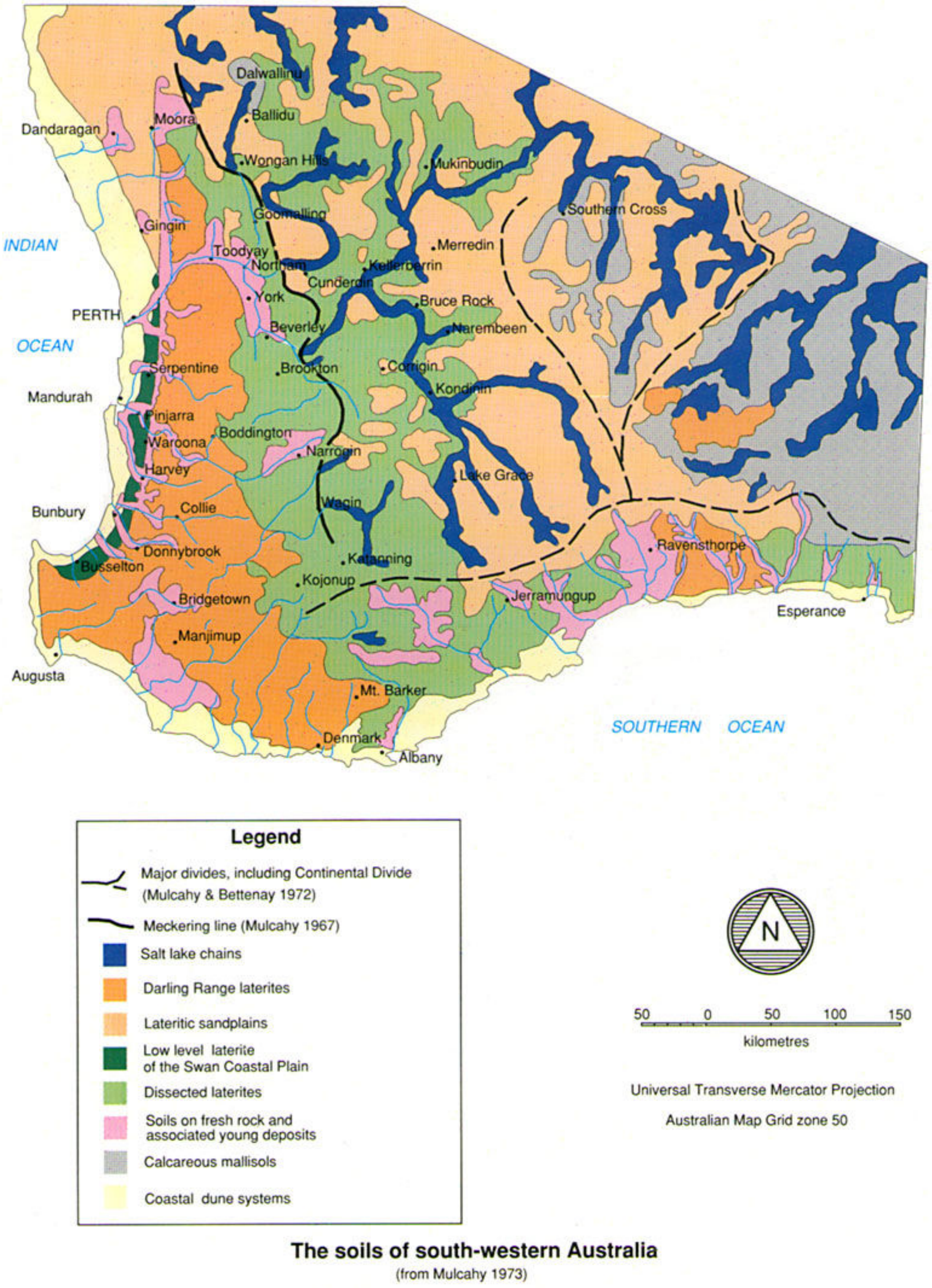


Figure 2.4 The soils of south-western Australia

(Mulcahy 1973)

2.3 Agricultural land application rates of biosolids based on nutrient loadings

2.3.1 Guidelines for agricultural land application and major crop nutrient requirements

The agricultural land application rate of biosolids is often different for various locations throughout Australia and elsewhere. This section will summarise factors that influence the determination of biosolid application rates, primarily based on both the agronomic crop to be grown and nutrient and metal properties of the biosolids. The significance of other factors such as: quantity and quality of the waste, soil characteristics, climate and topographical characteristics, land use and management requirements, and surface water and groundwater issues, to avoid environmental damage are discussed elsewhere by DEP, WRC and DOH (2002), Hardie and Hird (1998), Hicks and Hird (2000), Hird (1998), Hird and Bamforth (1996), Rawlinson and Salt (1997) and Ross and others.

There has been an intense and concerted effort globally to research and collect information relating to the agricultural land application of biosolids (National Biosolids Project 2001). Due to the great regional and temporal variability of biosolids, the specific nutrient/contaminants and their elemental availability need to be assessed on a case-by-case basis (Oliver, McLaughlin & Merrington 2002; Pierzynski 1994; Sommers 1977). The ability of the soil to grow plants and its ability to immobilise any potential contaminants in waste products needs to be considered (Hicks & Hird 2000). Nutrient budgets should include plant uptake requirements, expected plant yield, nutrient recycling from decaying plant material or animal faeces and urine, initial nutrient concentrations and the expected rate of breakdown, and any potential N losses to the atmosphere or soil P sorption (Hicks & Hird 2000; Hird 1998).

The land application of biosolids is regulated to ensure that they are spread evenly and incorporated into the topsoil within 36 h of spreading thus ensuring maximum agronomic benefits (i.e. reduce N volatilisation) and reducing the risk of concentrating contaminants, odours, vectors and surface runoff (DEP 2001; DEP, WRC & DOH 2002). The issue of stockpiling and storage of biosolids is being investigated north of Perth, Australia where the biting stable fly (*Stomoxys calcitrans),* commonly attracted to rotting organic matter such as poultry manure has become a problem (Penney & Dadour 2002). Rydin and Ottabong (1997) noted that sludge spreading did not result in an even homogenous mat, but rather clumps that may influence nutrient release.

The biosolids application rate is generally determined by the contaminant and nutrient loadings, particularly the agronomic needs of N and P for a given site (Awad, Ross & Lawrie 1989; Finney & Rawlinson 1990; National Research Council 1996; Rawlinson & Salt 1997). Typical quantities of N and P removed for several agricultural crops grown in Western Australia are summarised in Table 2.4 (Bolland 1998a; CSBP 1988). Hence, the export of grain products and primary produce in Australia results in large amounts of nutrients exported off farms annually. For example, wheat, the primary export crop in Australia is grown on 11.5 million ha of farmland, yielding on average 1.62 t/ha (2000-03) (ABARE 2003). Thus the removal of P in wheat grain could account for approximately 60,000 t of P exported from farms annually.

Table 2.4 Quantities of nitrogen and phosphorus removed in one tonne of grain or straw for the main agricultural crops grown in Western Australia

Crop	Part	N (kg/t)	P (kg/t)
Wheat	Grain	16-26	2.0-3.5
Wheat	Straw	2-10	0.2-1.5
Narrow-leafed lupins	Grain	50	4
Field Peas	Grain	40	4
	Straw	60	6
Faba beans	Grain	40	4
Chickpeas	Grain	30	3
Canola	Grain	40	6-7
	Straw	10-15	1-2

(Bolland 1998a)

The National Academies of Science, appointed to address environmental issues related to biosolids use in the USA, found no evidence of public health risk from exposure to land-applied biosolids. Mention was made of the limited scientific literature available. It was recommended that chemical and pathogen standards be re-assessed given changes in time with chemical uses, wastewater treatments and technology (Burke 2002).

2.3.2 Land application rates based on metals - CLBAR

Metals are not discussed in any detail in this review, but need to be mentioned briefly to place them in context with N and P loadings. Although metals have been a focal point in the land application of biosolids (McBride 2003; Reid 2002), the average metal concentrations for biosolids fall below most stringent guidelines, e.g. 40 *CFR* 503 biosolids regulations (Spicer 2002). The contaminants limited biosolids application rate (CLBAR) is determined by calculating biosolids application rates that would result in soil contaminants of metal elements remaining below maximum permissible soil concentration (MPC) guidelines after application. Current guidelines ensure that biosolids rates are site specific to prevent excess loading of metal elements (DEP, WRC & DOH 2002).

Preliminary Australian research indicated that biosolids could be applied to agricultural soils as a fertiliser without heavy metal contamination (Lawrie, Awad & Ross 1990; Osborne et al. 1995b). Research is limited in Western Australia, but based on historical nutrient data from Beenyup WWTP, rates of over 56 t DS/ha would be needed to cause metal contamination based on the CLBAR (Rawlinson & Salt 1997). Furthermore, to lessen the risk of contaminant build-up, guidelines in Western Australia recommend application of biosolids no more often than once every five years on any one site (DEP 2001; DEP, WRC & DOH 2002). This is in contrast to sites overseas with higher population pressures, which may have sludges or animal manures applied continually on fertile soils for many years.

Concern about the level of contaminants, mostly arising from the lack of data, has often hindered the use of wastewater solids as fertiliser (McLaughlin 1984; Merrington et al. 2003). Runoff data, soil assessment and soil water sampling over three years by Joshua and others (1998) from New South Wales soils receiving biosolids at rates of up to 120 t DS/ha indicated a low potential for pollution of surface or ground waters by heavy metals. Metal elements are not unique to biosolids; high concentrations are also present in chemical fertilisers and animal manures (Table 2.5, Spicer 2002). Given the higher application rates of manures and biosolids, higher rates of metals however may inadvertently be applied compared with inorganic fertiliser.

Chaney (1994) noted that biosolids are not metal salts, but a mixture of metals that interacted to reduce metal bioavailability and adsorbing, chelating and precipitating materials that also reduce bioavailability even when biosolids are ingested by grazing livestock or children. Similarly, a poor relationship existed between soil Cd concentrations and grain Cd, with bioavailability dependent on biosolids properties rather than soil properties (Zarcinas et al. 2002). Different decomposition rates in anaerobically digested biosolids from WWTPs could explain differences in heavy metal extractability (Walter et al. 2002). Frost and Ketchum (2000) found that trace metal concentrations in wheat were no higher following high metal applications in sludge compared with commercial fertiliser and the metal-free N control. Dissolved organo-metallic complexes significantly depressed Cu and Zn sorption (Burton, Hawker & Redding 2003). The bioavailability of Cd and Zn in vegetables associated with the land application of NuEarth biosolids decreased with time (Cox et al. 2002).

Table 2.5 Metal concentrations in animal manure, fertilisers and biosolids compared with *40CFR 503* limits

Metal (mg/kg)	Biosolids [a]	Poultry manure [b c]	Beef cattle manure [b]	Phosphate fertiliser [d]	40 CFR 503 Limits [e]
Arsenic	5	13	NA	11.3	75
Cadmium	4.4	2.4	NA	65	85
Copper	425	465	NA	56.5	4300
Lead	76	46	36	12.2	840
Molybdenum	12	19	NA	NA	75
Nickel	33	16	4.9	27.5	420
Zinc	735	602	NA	240	7500

(Spicer 2002)

NA = not available; [a]Pietz et al. (1998) averaged and weighted by number of samples from data, [b]American Society of Agricultural Engineers (2000), [c]Texas Agricultural Extension Service (2001), [d]United States Environmental Protection Agency (1999b), [e]Spicer (2002)

Strongly acidic soils increased plant uptake of Zn, Cd, Ni, Mn and Co and increased phytotoxicity from Cu, Zn and Ni (Chaney 1994). Acidic soils in Australia are often characterized by shallow topsoil, low organic matter and low cation exchange capacity and thus further research on these metals is therefore required (Kanak et al., 1995), and over longer periods of time (Whatmuff 1995). Research to examine soil loading limits for metals such as Cd based on bioavailability in Australia is in progress (McLaughlin et al. 2002).

2.3.3 Land application rates based on nitrogen - NLBAR

Agricultural land application rates of biosolids in Australia are commonly based on satisfying crop N requirements (NSW EPA 1997). The N limited biosolids application rate (NLBAR) is calculated using the proportion of N in biosolids, which would provide a crop with sufficient N for growth (Rawlinson & Salt 1997). The amount of N available to plants following biosolids application is referred to as potentially available N (PAN) (Pierzynski 1994) or plant available N or mineralisable N (Kanak, Osborne & Swinton 1995). Land application rates are calculated to ensure that the NLBAR balances PAN in the biosolids and the expected uptake of N by the specific crop to prevent ground water contamination.

A number of different equations have been used to estimate PAN. The concentration of PAN in the first year (typically expressed as percentage by weight) in sludges is estimated by Pierzynski (1994) as:

$$\mathrm{PAN} = \mathrm{N}_{\mathrm{NO3}} + X\mathrm{N}_{\mathrm{NH4}} + Y\mathrm{N}_{\mathrm{O}}$$

Where X is the fraction of NH_4 that does not volatilise (often assumed to be 1) and Y is the fraction of N_O that is expected to mineralise.

Gilmour et al. (2000) used a similar equation in the USA to estimate PAN in year one for biosolids (C/N ratio <15):

$$\mathrm{PAN}_1 = [\%\ \mathrm{NO_3\text{-}N} + \%\mathrm{NH_4\text{-}N} * (1 - \%\mathrm{V}/100) * 20] + [\%\mathrm{D}_{\mathrm{yr1}} * \%\mathrm{N_o} * 0.2]$$

During the growing season, PAN is directly related to the total N content of biosolids with first and second year PAN estimated using a constant organic N mineralisation percentage for a given location. Volatilisation (V) is estimated to be negligible for incorporated biosolids; otherwise a value of 50% is used. Decomposition (D) rates are given in a series of tables, which allow for decreased mineralisation in subsequent years ($_{\mathrm{yr1,\ 2\ etc}}$) (Gilmour et al. 2000).

A number of similar equations have been published, such as six described in detail by Hall (1984).

2.3.3.1 Calculation of NLBAR in Western Australia

In Western Australia, agricultural loading rates for biosolids are calculated using crop N requirements and expected biosolids N release (i.e. PAN) as reported by DEP and others (2002), according to the following equation:

NLBAR (t/ha dry solids (t ha/DS)) = crop requirement (kg/ha)/PAN (kg/t)

Based on overseas data for anaerobically digested dewatered biosolids, a mineralisation rate of 15% and volatilisation rate of 20% have been suggested (Rawlinson 1997), although a higher volatilisation rate of 50% was used in the late 1990s (Penney 1999). Rawlinson (1996b) calculated that 17 t DS/ha of Beenyup biosolids would provide adequate N for a wheat crop on a York soil in Western

Australia although it was postulated that the crop could be N deficient if the N mineralisation rate was not achieved. Priestley (1998) confirmed that this application rate was adequate with little increase in wheat yield at higher rates (24 t DS/ha). Wheat grown with similar rates of biosolids at Calingiri, Western Australia, however, experienced lodging problems. Dewatered cake is commonly applied at 10 t DS/ha in New South Wales, which under typical conditions approximates agronomic N needs with 80 to 100 kg PAN supplied in the first season (Kanak, Osborne & Swinton 1995).

In eastern Australia, Bamforth (1996) showed increased wheat yields with increased rates of dewatered biosolids. Rates higher than 14.4 t DS/ha were considered necessary to allow the determination of both the immediate and residual fertiliser values. Cooper (1996) measured agronomic benefits for cereals at higher rates (24 t DS/ha). Compared with urea, the effectiveness of dewatered biosolids as a source of N has been calculated to be approximately 30% on fertile coastal pasture systems (Havilah et al. 1996).

Overall, there is a lack of data for mineralisation and volatilisation rates in biosolids products and soil types throughout Australia. Nitrogen mineralisation can occur whenever soil conditions are favourable following the application of biosolids and thus N leaching could be a problem if the crop has yet to be sown or has a low N demand. Biosolid application rates on soils high in residual NO_3-N may need adjustment to ensure that N loadings based on the NLBAR are not excessive. Surface and sub-surface movement of nitrates following biosolids application were not detected at rates of 30 t DS/ha in a pasture grazing trial (Joshua et al. 1998).

Little consideration has been given to residual soil N in the determination of NLBAR in Western Australia. Mason (1998) reported that it is difficult to predict how much fertiliser N the soil requires using measurements of total soil N, although this gives a general idea of soil fertility. Inorganic N is generally transitory (except as a comparison between paddocks) and does not indicate how much N will be available during the growing season, although it can be used as a basis for fertiliser recommendations in Western Australia. Tissue testing can be used diagnostically, where the concentration of N in the plant can be compared with established critical levels. The critical range will vary with the season and conditions and stage of growth (Mason 1998).

2.3.4 Land application rates based on phosphorus - PLBAR

Where biosolids are applied as a source of N, almost without exception, the amount of P applied has been more than sufficient to supply the needs of the crop (Pierzynski 1994). Phosphorus levels are often in excess of those used in conventional fertiliser programs and consequently considerable interest in this area has emerged globally. High levels of soil P rarely result in plant toxicity, but are considered an environmental problem due to risk of pollution of water bodies. The P limited biosolids application rate (PLBAR) is an approach to ensure that the P released by biosolids balances the agronomic needs of the crop, i.e. supplied at rates that are not in excess of crop growth and uptake (DEP, WRC & DOH 2002; Rawlinson 1997).

Increased soil P levels as a result of N-based sludge management are widely reported (Chang et al. 1983; Dentel, Sims & Mah 2001; Epstein 2002; Landers 2000; Maguire, Sims & Coale 2000a; Pastene 1981; Pierzynski 1994; Triner et al. 2001). For example, Pierzynski (1994) calculated that the sludge rate required to supply 150 kg PAN/ha (where PAN = 13 g/kg) for corn (*Zea mays* L.) would result in a P_T loading of approximately three times more than removed by plants, i.e. 115 kg P/ha (where P_T = 10 g/kg). To satisfy the N requirement of corn, Dentel, Sims and Mah (2001) calculated that P would be applied at 135 kg P/ha, an oversupply by 540%; whereas Womer, Elliott and Brandt (2002) illustrated a ten fold over-abundance of P. Over a number of sludge applications, the situation can result in tremendous concentrations of soil P_T, for example 2,994 mg P/kg (Kirkham 1982). Soils with a history of sludge and/or animal manure application are often high in P, such sites being more common in Europe and America than Australia.

Environmental guidelines in most developed countries ensure P loadings are based on replenishing total soil P to prevent excessive surface soil accumulation (National Research Council 1996). The extent to which biosolid P is available for crop uptake or transport off-site is unknown; it is however considered to play a very important role in determining the future of biosolids land application rates. Possible scenarios relating to P availability are illustrated by Womer, Elliott and Brandt (2002) in Figure 2.5. Problems associated with the inaccurate estimation of plant available P could include increased spreading costs, extra N fertiliser and the requirement for more land.

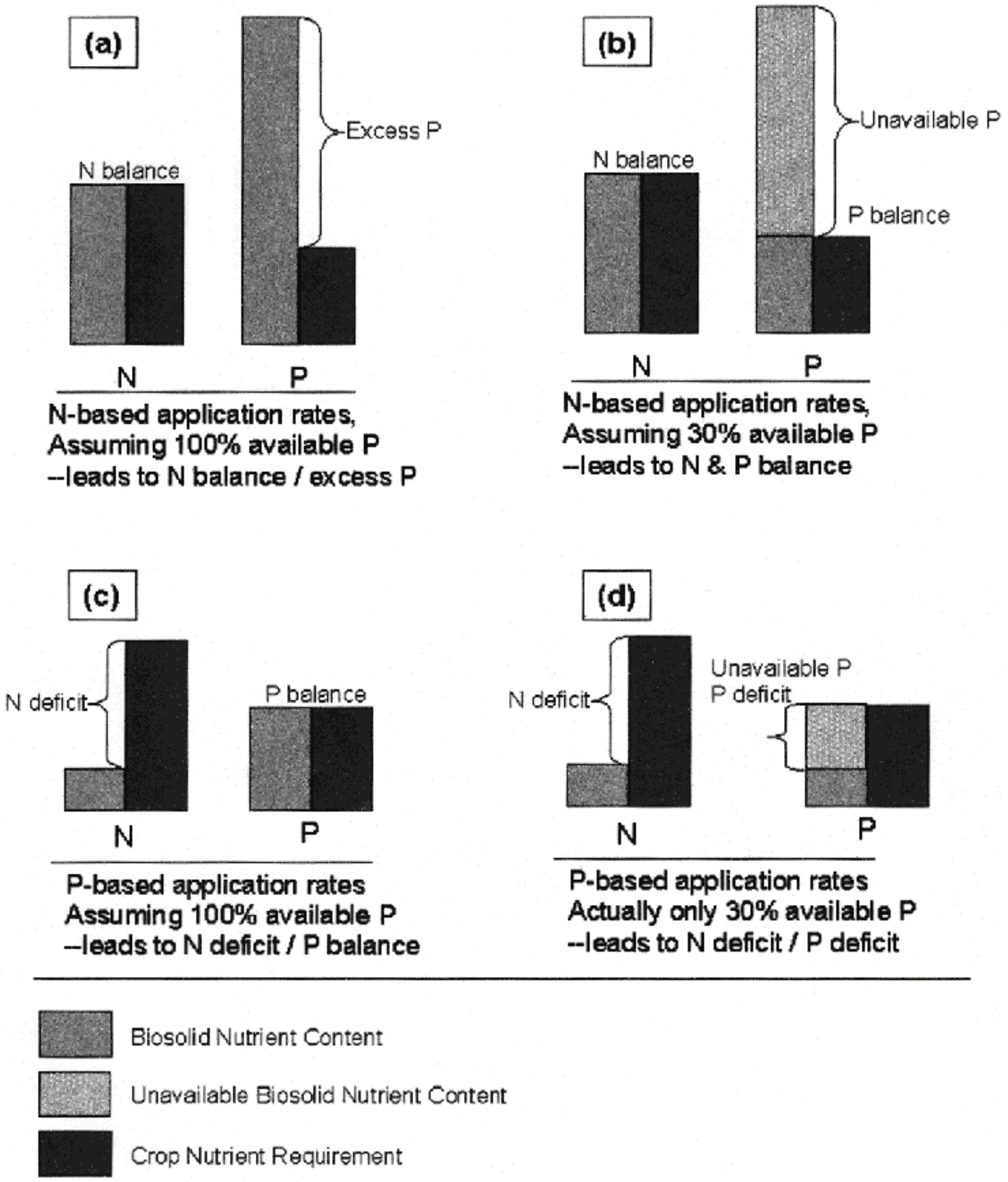


Figure 2.5 Results of different application rate bases and assumed biosolids P availabilities

(Womer, Elliott & Brandt 2002) as adapted from Sharpley and Beegle (1999)

2.3.4.1 Calculation of PLBAR in Western Australia

For the purposes of calculating the PLBAR in Western Australia, all biosolid P is assumed to be readily available to the plant (DEP, WRC & DOH 2002). The PLBAR is therefore:

PLBAR (t/ha) = Crop requirement (kg/ha)/Biosolids P_T (kg/t)

The PLBAR is currently under review in Western Australia, given the concern surrounding the accumulation of P in the soil following the application of biosolids. For example, the predominant export crop grown in Western Australia is wheat: a four tonne crop would remove approximately 84 kg N in grain per hectare (Table 2.4). Biosolids at 5 t DS/ha should provide adequate N for the wheat crop (where N mineralisation = 15%). However, this rate of biosolids would result in the application of 150 kg P/ha (where P_T = 3%), of which the crop would remove only 12 kg P/ha. Based on the PLBAR with 100% of P assumed to be plant available, a biosolid loading rate of 0.4 t DS/ha would be sufficient to satisfy the crop P needs (i.e. annual P requirement of 12 kg/ha and biosolids with a P_T of 30 kg P/t).

It is generally accepted however, that due to the nature of the biosolids and/or the P adsorption properties of the soil, not all biosolid P may be readily available. Michalk et al. (1995) calculated that 21% of biosolid P was plant available in the first season based on soil bicarbonate extractable P data in eastern Australia. This study used incorporated anaerobically digested dewatered biosolids cake (28% DS), similar to Perth biosolids (DEP 2001; Rawlinson 1997). The Water Corporation also used this value during the 1990s to estimate the value of P in land application programs rather than the total P value of the biosolids. Land application programs elsewhere in Australia typically base loading rates of biosolid on N or contaminant levels, rather than P.

2.3.4.2 Influence of soil properties on the PLBAR

There is little information in the literature on appropriate PLBAR for infertile soils typical to Western Australia, which are commonly P deficient or high P sorbing. McLaughlin (1988) described the benefits of soil sequestration using high sludge rates to increase nutrient levels to more productive levels on poor sesquioxide soils in South Africa. Similarly it is recognised that additional P would be beneficial on P deficient soils (Kirkham 1982). Hird (1998) suggested that the ability of a soil to sorb P should be taken into consideration when determining land application rates for biosolids. Barry and others (1995) modelled P loading rates in a lateritic podzolic soil profile in Queensland following the application of biosolids up to 102 t DS/ha (where biosolid P = 1.7%). In this study, the allowed Australian Water Quality Guidelines elemental output of 0.05 mg P/L in leachate was not exceeded as a result of sesquioxide sorption sites at depth. The P increased from 47 kg P/ha in the A 11 horizon to 982 kg P/ha in the B horizon. Soil contamination (metal) and health risks were not considered for this study.

Soil properties are not considered by the current PLBAR equation although the maximum P loading for any site in Western Australia is restricted by four vulnerability categories, as in Table 2.6 (DEP, WRC & DOH 2002). Using a P_T concentration of 3% for Perth biosolids, loading rates would amount to 0.3, 0.6, 1.6 and 4.0 t DS/ha, respectively, for the four categories. Further investigation is warranted to validate the maximum P loadings recommended in Table 2.6.

Table 2.6 Maximum phosphorus loadings for four soil characteristics in Western Australia

Vulnerability category	Soil Description	Maximum P loading (kg/ha/yr)
A	Coarse sandy soils/gravels draining to surface waters with moderate to high eutrophication risk	10
B	Coarse sandy soils/gravels draining to waters with low eutrophication risk	20
C	Loams/clay soils (PRI > 10) draining to waters with moderate/high eutrophication risk	50
D	Loams/clay soils (PRI > 10) draining to waters with low eutrophication risk	120

(DEP, WRC & DOH 2002)

2.4 Plant available and environmentally relevant phosphorus in biosolids

2.4.1 Measurement for total phosphorus and plant available phosphorus

Total loadings of biosolid P provide a guide to soil nutrient balances and soil enrichment (Cottenie & Kiekens 1980). Havilah and Davis (1998) accounted for much of the biosolid P applied to wheat over a period of time by measuring the amount of P removed by plants. Analysis for P_T in the soil can be used determine the extent of recovery of phosphatic fertiliser applied to sandy soils but is not generally related to plant available P (Cottenie & Kiekens 1980). The P_T content in biosolids however, is generally considered an unreliable guide as to the amount of plant available (bioavailable) or environmentally relevant P (Chang et al. 1983; Maguire et al. 2001; Pastene 1981).

The aim of soil P management is to maintain the concentration of soil solution P at a value adequate for plant growth, whilst minimising the movement of soluble P, organic P, and sediment-bound P to sensitive water bodies (Pierzynski, Sims & Vance 1994). The amount of biosolid P that contributes rapidly to the labile P pool is of agricultural and environmental interest. Labile P is readily available to plants but may be transported from the site of application by leaching or runoff if applied in excess of plant requirements. Labile P is of importance in plant nutrition and is the portion that availability indices attempt to measure, with a large number of methods available (Cottenie & Kiekens 1980; Sibbesen & Sharpley 1997; Smith & Scott 1991). Examples of methods used for the extraction of available P in soil fertility studies are described by Olsen and Sommers (1982) and include; dilute acid-fluoride (Bray test), water-soluble, resin, extractable/exchangeable bicarbonate (Olsen) extracts and isotopic dilution.

Phosphorus availability indices for biosolids and organic materials are generally unknown with no readily used P extraction tests successfully correlated with P uptake from biosolids (Womer, Elliott & Brandt 2002). Examples of extraction methods for organic materials and biosolids showing poor correlation with P uptake are summarised in Table 2.7.

Table 2.7 Chemical extraction methods for phosphorus poorly correlated to bioavailable P in a range of biosolid and organic materials

Method of extraction	Comments	Reference
Total of 16 different extraction methods	Inappropriate when high rates of P applied as sewage sludge	(Cottenie & Kiekens 1980)
0.5 M H_2SO_4, P-Bray-1 and P-Olsen	Not accurate measures of plant available P in a range of organic products	(Velthof et al. 1998)
Bray-1, Bray-2, Olsen, ISFEI and $CaCl_2$	Underestimated the effectiveness of sludge P as a fertiliser compared with inorganic P, based on short term P uptake by P-deficient Italian ryegrass	(McLaughlin 1988)
	Extractable P was poorly correlated with P uptake from sewage sludge compost (i.e. overestimated available soil P), whereas extractable soil P (dilute bicarbonate and double acid) was highly correlated with total P uptake from triple superphosphate	(McCoy, Sikora & Weil 1986)
Weak acids or bicarbonate extracts	The concentration of P in the soil solution using 0.01 M $CaCl_2$ was a better indicator of P availability than weak acids or bicarbonate extracts over a range of sludge-amended soils	(Pastene 1981)
Neutral ammonium citrate (NAC), often used by the AOAC to estimate plant available P in fertilisers (i.e. citrate soluble = dicalcium P, hydrated Fe and Al phosphates and portion of tricalcium phosphate)	Poor predictor of bioavailable P in biosolids	(O'Connor et al. 2002; Womer, Elliott & Brandt 2002)

Not all studies have shown a poor correlation between extractable soil P and sludge P application. Correlation between Mehlich 1 and P-Bray-1 extractions and soybean leaf plus stem P and seed P concentrations was achieved for all P forms (including 100 t/ha sludge, where sludge P = 4%) (Folle et al. 1995). Growth and laboratory experiments indicated that the plant utilisable sludge P could be predicted by the citric acid soluble P content of sludge (Furrer, Gupta & Stauffer 1984; Hani, Gupta & Furrer 1981). The Morgan soil test or *in situ* resin extraction related well to levels of P uptake by ryegrass following the application of a range of organic residuals (Montgomery 2002). O'Connor et al. (2002) found the Fe-strip method effective as an effective P soil test for waste-amended soils.

The high organic matter content in biosolids (i.e. up to 70%) may affect the determination of available P (Tiessen & Moir 1993) where standard colorimetric procedures, such as the reduction of a molybdophosphate complex to "molybdenum blue" are used (Smith & Scott 1991). Organic matter can precipitates upon acidification, thereby affecting the intensity of the blue colour, as can iron (III) (Tiessen & Moir 1993) and the sum of Fe and Al. The interest in P based biosolids management has emphasised the need for a suitable method to determination P (other than P_T) for organic P sources (Womer, Elliott & Brandt 2002).

2.4.1.1 Characterisation of phosphorus compounds in biosolids

The use of a single measurement to estimate P availability for sludge-amended soils is limited due to the various P transformations once sludges are applied to soils (McLaughlin 1988). Soil tests used for the determination of available P usually only measure the plant available pool of P in solution and do not identify P that enters the solution during the period used to define availability (desorption or dissolution of P_i) or by the mineralisation of P_o (Tiessen & Moir 1993). The method of Hedley, Stewart and Chauhan (1982) is commonly used by P fractionation studies to characterise the various forms of P, although subsequent authors, such as Tiessen and Moir (1993) have modified the method. Olsen and Sommers (1982) report a fractionation scheme for P, where P_i is fractioned into Fe, Al and Ca phosphates, and P_o is calculated by the difference rather than measured directly. The method of Chang and Jackson (1957) has also been used to fractionate sludge into chemical forms of P (Wild 1988).

Lindo and others (1995) concluded that P_o fractions in sludge-amended soils could probably be partially transformed from one chemical to another through soil biochemical activities and thus contribute to plant available P. Folle and others (1995) noted that most sludge P shifted into Ca and Fe fractions, while that of commercial P_i fertiliser, went into soluble and Al fractions following land application. Of the P fractionation methods used by Velthof and others (1998) in a range of organic products, iron oxide coated filter paper was the best indicator of plant available P.

2.4.2 Factors affecting the release of phosphorus from land-applied biosolids

The release of P from land-applied biosolids has been summarised by Dentel, Sims and Mah (2001) into three main categories related to biosolids, soils and local factors (Table 2.8).

Table 2.8 Characteristics of biosolids, soil and local factors that may affect the release of phosphorus from land-applied biosolids

Biosolid characteristics	Soil properties	Local factors
Type of wastewater treatment used	P concentration in solid, soluble phases	Hydrology
Residuals remaining from water treatment	P speciation and bioavailability	Topography
P removal processes, e.g. biological nutrient removal (BNR), chemical	P binding capacity (eg. presence of Al, Fe)	Crop management practices
Chemical additives used (lime, Fe)	Erosion potential	Other nutrient applications
Stabilisation processes used	Porosity and subsurface drainage	Ditch and stream flow characteristics
		Proximity to surface waters
		Sensitivity of surface waters to elevated P levels

(Dentel, Sims & Mah 2001)

2.4.2.1 Biosolids related factors

Wastewater arriving at a WWTP may have a P_T concentration of 10 mg P/L comprising 5 mg P/L orthophosphate, 3 mg P/L tripolyphosphate, 1 mg P/L pyrophosphate and 1 mg P/L organic phosphate. However, the forms of P vary with the composition of wastewater entering the WWTP and the wastewater treatment. The P_T concentration can be modified by simply changing the amount of P entering the system, such as by restricting detergent use (Havilah & Osborne 1992; Sommers & Sutton 1980).

Only a small proportion of the P in wastewater was captured by sludge in conventional WWTPs and was relatively constant in different types of sludges with 70% to 90% of the P_T present in P_i forms, sorbed onto amorphous hydrous oxides or precipitated as metal phosphate solid phases (Sommers 1977). Chemical P and nutrient treatment processes have increased the P content of sludge. Chemical treatment relies on the precipitation of P as sparingly soluble Fe, Al, Ca or possibly Mg phosphates, whereas biological treatments rely on the absorption of P into the microbial biomass as organic phosphates, as summarised by Havilah and Osborne (1992). The P_T concentration in biosolids for a range of wastewater treatment plants within Australia is given in Table 2.9.

Table 2.9 Phosphorus content in a range of sludges as related to method of treatment in Australia

Source	**Total P content mg/kg of dry matter** (% in parenthesis)	**Treatment**	**Reference**
St Marys, NSW	49,300 (4.9)	Iron P treatment with spent pickle liquor	(Havilah & Davis 1998)
Q.Hill, NSW	34,000 (3.4)	IDAL-continuous flow biological reactor unit	(Kanak, Osborne & Swinton 1995)
Penrith, NSW	29,400 (2.9)	Biological nutrient removal (BNR)	(Kanak, Osborne & Swinton 1995)
Beenyup, WA	23,250 (2.3)	Anaerobic digestion of primary and secondary sludge	(Penney 2000)
Cronulla, NSW	22,500 (2.2)	Anaerobic digestion of primary sludge	(Kanak, Osborne & Swinton 1995)
North Head, NSW	10,000 (1.0)	LAB-Lime amended using cement kiln dust and quicklime	(Havilah & Davis 1998)

2.4.2.1.1 Common phosphorus treatments

Salts used for the precipitation of iron phosphates as described by Havilah and Osborne (1992) include ferric chloride $FeCl_3$, ferric sulphate $Fe_2(SO_4)_3$, ferrous sulphate $FeSO_4$ and ferrous chloride $FeCl_2$ in a pH range of 4.5 to 5.0. Spent pickle liquor, a waste product of the steel industry containing ferrous iron is common in the inland systems in the Sydney region, New South Wales. The iron phosphates formed increase sludge mass by about 25% under aerobic digestion. Aluminium phosphates are precipitated using alum $Al_2(SO_4)_3.18H_2O$ and sodium aluminate $NaAlO_2$ in a pH range of 5.5 to 6.5, but cause a 40% increase in sludge volume making them difficult to dewater. Calcium salts are precipitated using $Ca(OH)_2$ in a preferred pH >10, although the high pH is difficult to maintain. The precipitation of Ca produces up to two times the sludge volume, although the resulting sludge is stable and easy to thicken and dewater. Calcium salts are preferred for agriculture, but pose engineering problems (Havilah & Osborne 1992).

Biological nutrient removal (BNR) and enhanced biological P removal (EBPR) are described by Raper (1995). Up to 85% of P can be removed from wastewater using the bacterium *Acinetobacter,* which incorporates P into a polyphosphate microbial biomass. The remaining P can be precipitated using fewer chemicals than required for conventional chemical precipitation; however, the P can return to solution if the sludge residence time is short. The short sludge retention interval and subsequent death of the bacteria can cause problems with malodorous sludge, dewatering and vectors (Havilah & Osborne 1992; Kanak, Osborne & Swinton 1995).

2.4.2.1.2 Effects of wastewater treatment on phosphorus availability

It is expected that the availability of P in land-applied biosolids will be reduced following chemical P treatment compared with untreated sludge. Dentel, Sims and Mah (2001) reviewed relevant literature (Chang et al. 1983; McCoy, Sikora & Weil 1986; Wen et al. 1997) related to P speciation, availability and mobility in various types of biosolids and concluded that the presence of Al and Fe in biosolids rendered P less available. However, in many studies examined, the effect of treatment processes or soil characteristics on the forms and solubilities of biosolids were not considered.

The effectiveness of biosolid P for plants following the addition of Fe to the processing treatment has been examined in eastern Australia (Davis et al. 2000). Biosolids treated with Fe (i.e. Fe: P ratios between 2.0 and 2.4), decreased the sorption of P by the soil resulting in a decreased need for further P fertiliser at a later time to satisfy plant needs. High sludge Fe decreased the recovery of biosolid P in corn shoots. For example, plants grown in low Fe biosolids (2.6% Fe) recovered 0.88% of biosolid P compared with 0.10% in high Fe biosolids (11.5% Fe). Sludge Fe (and to a lesser extent Al) is thought to decrease P solubility in the sludge and sorb native soil P (Davis et al. 2000; Kanak, Osborne & Swinton 1995; Osborne et al. 1995a). Havilah and Davis (1998) observed a restricted availability of P in sludge chemically treated with Fe compared with pelleted, lime-amended, biological P removal, Al removal or no removal.

Soon, Bates and Moyer (1978) found that Ca treated sludge increased the concentration of P in bromegrass (*Bromus spp.)* and increased bicarbonate extractable soil P more so than Fe treated sludges. Calcium phosphates derived from sludge would be expected to be more available for plant growth on acid soils than on neutral and alkaline soils (Havilah & Osborne 1992). In an alkaline soil, lime-stabilised sludge did not increase the amount of plant available P (Seyhan & Erdincler 2003). Lime-stabilised biosolids contained greater bioavailable soil P than sludge treated by other chemical treatments; due likely to an increase in soil pH rather than any inherent quality of the residual itself (Montgomery 2002). In a study by Dentel, Sims & Mah (2001), the presence of Ca was associated with greater P mobility, although the effect of pH was unknown.

A phosphorus responsive soil is considered necessary to study P uptake by plants and may explain the lack of response in several studies. For example, Gestring and Jarrell (1982) showed no discernable trends in total P uptake by chard grown on soils amended with either Fe, Al or Ca treated sludge. There was no difference in bicarbonate extractable P or P uptake in ryegrass following the addition of either Fe, Al and Ca treated biosolids in two soils in New South Wales (Sakadevan & Bavor 2002). The Ca biosolids, however, contained approximately half the content of P (5.8%) compared with the other treatments (9.2 to 10%). Summer grown crops in New South Wales showed no differences in DM between N-Viro Soil, pelleted biosolids or inorganic fertiliser treatments compared with unfertilised controls. Sufficient concentrations of nutrients present in the soil before treatment application were thought to be responsible for limited nutrient responses (Bamforth 1995).

Biological processes do not appear to immobilise P (Dentel et al. 2000), with aerobic sludges produced by BNR resulting in higher soil available P than sludges using chemical precipitation (Kanak, Osborne & Swinton 1995; O'Connor et al. 2002), and observed to a limited extent by Sakadevan and Bavor (2002). In a study by Amundson and Jarrell (1983), sludge P appeared more available where BNR (aerobic) was used compared with anaerobically digested sludge (Kanak, Osborne & Swinton 1995). Biosolids produced by BNR processes had a higher P bioavailability than biosolids produced by conventional wastewater and solids digestion (O'Connor et al. 2004).

Other factors that have been reported to act to decrease the availability of biosolid P include the addition of cationic polymers during dewatering (Dentel et al. 2000) and composting with sawdust, creating a high C: P ratio (Coutinho, Arrobas & Rodrigues 1997).

2.4.2.1.3 Forms of phosphorus in biosolids

Biosolids are regarded as complex mixtures of P forms (Osborne et al. 1995a). Prior to 2002, there have been few data as to the chemistry of the forms of P (P fractions formed as a consequence of sludge processing methods), how these forms become available to plants, and the availability of P in the organic process (Havilah & Davis 1998). There is no information regarding the forms of P in Perth biosolids although it has been suggested by Barrow (1999) that P is most likely present as dicalcium phosphate. A better knowledge of the forms of P in organic products has been suggested by Velthof et al. (1998) as necessary to improve their use as fertilisers.

Recent investigations into a range of biosolids examined in the USA indicate that P_i forms dominated all P sources (approximately 80% of total P) including biosolids produced by BNR. Inorganic P was predominantly associated with Fe and Al (O'Connor et al. 2002). A comparison of 16 biosolids samples in the USA showed that although the amount of P_T in biosolids varied, its fractionation remained relatively constant. There was very little dissolved P relative to insoluble forms with orthophosphate salts being the predominant insoluble P_i form, with the remaining primarily P_o. A clear correlation existed between total orthophosphate and P_T, with total P_o so weakly related to P_T, it could be regarded as constant, as seen in Figure 2.6. Total ortho-P and total condensed P increased in proportion to P_T (Dentel & Mah 2002; Dentel et al. 2000).

Biosolids are promoted as an organic product; however, they do not typically contain high levels of organic P. For example, sewage sludge produced by cities in the USA in the 1970s typically contained 30% P_o (Sommers 1977). In untreated sludge the P_i is predominant (Sommers, Nelson & Yost 1976), and is characterised by being extractable and predominantly insoluble (Kirkham 1982). Over a two year sampling period, P_o varied by 95% and P_i varied by 25% (Sommers, Nelson & Yost 1976). Up to 50% of the P was separated in the solids as inorganic Fe, Al and Ca compounds and as P_o without any chemical treatment during primary processing (Dougherty & Lawrie 2000). Havilah and Osborne (1992) indicated that aerobically digested sludge may accumulate P_o due to microbial action, whereas anaerobically digested sludge consist mostly of P_i following the mineralisation of P from organic fractions.

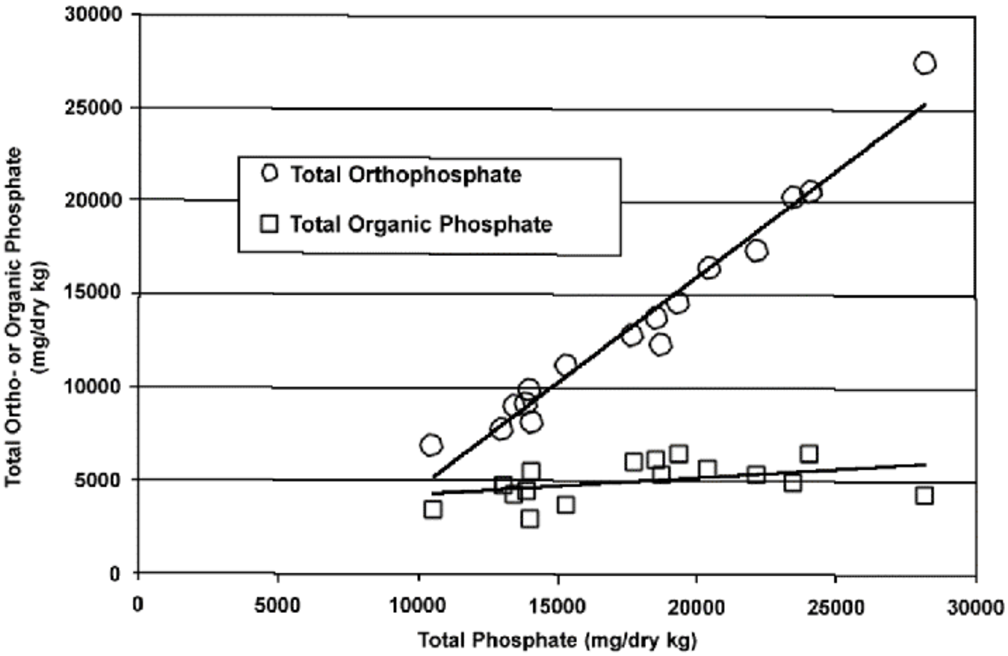


Figure 2.6 Total phosphate fractionation as a function of total P concentration

Dentel, Sims and Mah (2001)

2.4.2.2 Soil related factors

Dentel, Sims and Mah (2001) in Table 2.8, described common soil related factors responsible for the release of P in sludge; although the overall physical, chemical and biological transformations of sludge P in soils have been reported by McLaughlin (1984) as being unclear and in need of further research.

The release of P in soils amended with biosolids was demonstrated by Rydin and Ottabong (1997) to be affected by soil type, sludge type and time. The release of P was slowest in sandy loam and fastest in sandy clay, being more pronounced during the first 20 d. Akhtar, McCallister and Eskridge (2002) showed that in sewage sludge-amended soils, sandy soil maintained a higher concentration of soluble P than finer textured soils. It was demonstrated that soluble P and newly mineralised P were immobilised by microbial action or by chemical mechanisms over time. The release of bioavailable P, extracted in iron-oxide impregnated filter paper strip, was temperature dependent, with concentrations higher at 25°C in all soils than at 37°C for up to 120 d. Overall, the fate of sewage sludge P was difficult to predict due to the interacting effects of soil properties and temperature over time. Pastene (1981) showed that the availability of P in sewage sludge showed a large response to soil P and P sorption at low application rates. However, with time and increased applications, sludge factors exhibited different levels of availability. The decrease in extractable P levels in soil with time after the application of liquid digested sewage sludge was attributed to P sorption (Kelling et al. 1977).

Soil pH can be increased, decreased or not changed by the addition of sewage sludge depending on circumstances, and therefore can have an effect on P availability. As soil acidity increases, P is generally more strongly adsorbed onto Al and Fe compounds with P most soluble at a neutral pH. The addition of lime in the treatment process can increase soil pH and be beneficial in acidic soils (Pastene 1981; Stewart & Sharpley 1987). Kirkham (1982) noted that liming promoted P uptake in sewage sludge-amended soils. At pH from 6.4 to 7.0, the main P sorption constituent was Ca (Folle et al. 1995), as would be expected given the U-shaped solubility principal characteristic of P with pH. Relative to superphosphate, aerobically digested dried sludge was more available to plants in alkaline and calcareous soils (Pomares et al. 1984).

Overall a major key to P fertility is the ability of the soil to replenish readily available phosphates in soil solution following removal by plants as discussed in section 2.2.3.1. Replenishment typically occurs from the addition of inorganic fertilisers or from labile and moderately labile P_i forms in the soil. Following rain, the water-soluble P in fertiliser dissolves rapidly and mostly moves into the soil solution. Aeration, compaction and the effect of other nutrients also affect available soil P (Bolland 1998b; Glendinning 1999; Phillips & Webb 1971; Stewart & Sharpley 1987).

2.4.2.2.1 Phosphorus retention index (PRI)

The adsorption of P onto soil particles is positively correlated to texture, organic matter, Al and Fe (sesquioxides) and carbonate content. The response of crops to P fertiliser is related to a number of factors such as available soil P and ability of the soil to remove P from solution (Bolland 1998b; Bolland, Allen & Barrow 2003; Bowden, Shedley & Burgess 1993; Phillips & Webb 1971).

The P retention index (PRI) is a measure of the relative ability of soils to remove P from solution (Allen & Jeffery 1990; Bolland, Allen & Barrow 2003). In Western Australia, another measure used to rank of the capacity of the soil to sorb P is the amount of iron extracted from soil by ammonium oxalate (AmOx-Fe), or reactive Fe (Bolland & Allen 2003). The PRI measurement is preferred over reactive Fe as soil

PRI will decrease with cumulative fertiliser inputs over time due to saturation of sorption sites, whereas reactive Fe levels remain constant. A soil with a high PRI therefore, has a high capacity for adsorption (Weaver & Summers 1998). Leaching of P has not been observed in Western Australian soils where the PRI >2 mL/g and a reactive Fe content >300 mg/kg (Bolland & Gilkes 2001). Smolinski and Scholz (1997) have classified the eutrophication risk from excess P based on soil PRI values, overall site drainage and flood hazard for soils in West Gingin, Western Australia (Table 2.10).

Table 2.10 Eutrophication risk from excess phosphate derived from PRI values, soil characteristics and site

Numerical rating	Description
1	Soils with a low risk (PRI > 70). Soils are well drained and risk of overland flow is minimal. Includes gravelly clayey sands and reddish brown clayey sands and sandy loams.
2	Soils of low risk (PRI 20 to 70). The risk of overland flow and subsurface lateral flow is minimal. Alternately PRI 5 to 20 and soil depth > 10 m.
3	Soils of moderately low risk. PRI 5 to 20 and soil depth 2 to 10 m. Soils are well drained and risk of overland flow is minimal. Alternatively PRI > 20, lateral flow low to moderate.
4	Soils of moderate risk. PRI 2 to 5 and soil depth 3 to 10 m. Soils are well drained and the risk of overland flow is minimal. Alternatively PRI > 20 and risk of overland and lateral flow is moderate.
5	Soils of high risk. PRI < 2 and/or any soil group with a moderate to high risk of subsurface lateral flow or flooding.

A high level of land management is assumed for all the above categories. Areas <250 m from a natural water body not included in the risk assessment.

(Smolinski & Scholz 1997)

2.4.2.2.2 Mineralisation of organic phosphorus

Very little information exists regarding the mineralisation rate of organic P in biosolids-amended soils. The absolute rate of mineralisation of biosolid P would be expected to be low at all times given that biosolids have been subject to decomposition during treatment (Barrow 1999). Soils treated with high rates of sludge are expected to have low proportions (<5%) of organic forms of P and predominantly (75%) the P would be in forms associated with Fe and Al (McLaughlin 1988). Lindo (1995) observed an initial flush of microbial activity following sludge land application, although Franco-Hernandez and others (2003) noted that biosolids did not significantly increase the mineralisation of P in a sandy clay loam. Chemical factors are thought to be more greatly involved in sludge P availability than biological factors, given that P borne sludge followed a similar type of redistribution to soil native P (Coutinho, Arrobas & Rodrigues 1997).

The mineralisation of P_o may be a major determinant in P fertility in extremely weathered soils with high active Al and Fe properties (Glendinning 1999; Phillips & Webb 1971). Mineralised P reacts rapidly in soil and is removed quickly from solution; with soil P rapidly depleted by cultivation, crop removal and land clearing. The mineralisation of P_o is dependent on soil pH, buffering capacity, soil moisture, root activity (Cottenie & Kiekens 1980; Phillips & Webb 1971), and optimum temperatures (Akhtar, McCallister & Eskridge 2002; Phillips & Webb 1971). A lack of C inputs will slow or stop microbial activity and reduce P supply to plants through mineralisation (Stewart & Sharpley 1987). The relationship between C and P in biosolids needs to be considered to better understand P bioavailability.

2.4.2.3 Local factors

Topography, hydrology, crop management practices and proximity to surface waters (see per Table 2.8, Dentel, Sims & Mah 2001), are important local factors affecting P availability. Management options for biosolid land application programs are designed to ensure that nutrients in biosolids applied to soils are not at risk of contaminating water bodies. Guidelines for the application of biosolids avoid its use on environmentally sensitive sites, such as those prone to water erosion and waterlogging (DEP, WRC & DOH 2002).

General fertiliser management practices and placement can improve the uptake of water-soluble P by crops (Bolland 1998b). The longer fertiliser is in contact with the soil, the greater the chances for P sorption. Therefore P needs to be applied immediately before it is needed in order to maximise plant uptake (Glendinning 1999). Phosphorus drilled with the seed was approximately twice as effective as broadcast P at seeding (Rudd & Barrow 1973). Similarly, sludge applied to the soil surface demonstrated a lower P availability than incorporated sludge (King & Morris 1973; Pastene 1981). This was consistent with findings of the availability of P in sheep dung (Gunary 1968). Bromfield (1961) showed that P in sheep dung had a low water solubility and suggested that P remained positionally unavailable to plants until roots had access to it.

It is difficult to study the effects of biosolid P in isolation from other nutrient constituents within biosolids. In particular, the plant response due to P may be improved by the interaction with the high levels of biosolid N (de Hann 1981; Havilah & Davis 1998; Sommers & Sutton 1980). Prasad (1996) observed that increased sludge levels enhanced N uptake by wheat and vice-versa where the addition of P to sludge increased N uptake by wheat (Gupta, Narwal & Antil 1993). Phosphorus uptake by wheat in pot trials increased in sewage sludge application up to 1% as fertiliser N increased (Gupta, Narwal & Antil 1989).

Little has been done to separate the effects on plant growth, of P (and K) in biosolids from the effects of other metals and nutrients (Olness et al. 1998). At high application rates of sludge, high P rates have induced trace element deficiencies, particularly Zn (Olsen & Barber 1977). In contrast, nutrient deficiencies were not a problem in sludges which contained trace metals (Sommers & Sutton 1980). Giordiano, Mortvedt and Mays (1975) indicated that multiple applications of high rates of compost could lead to potentially toxic accumulations of Zn, although such effects were not observed by Hinesly and others (1976). The Zn: Fe ratio in plants was a better predictor of Zn toxicity associated with decreased P uptake rather than the Zn concentration only (Pommel 1981).

High rates of Al treated sludge increased Zn and Mn concentrations in plant tissue in acid soil, possibly due to a lowering of the soil pH (Gestring & Jarrell 1982). Sludge, soil and plant type affected K, Ca and Mg concentrations in plants treated with a range of chemically treated (Al, Fe or Ca) anaerobically digested sewage sludge (Soon, Bates & Moyer 1978). A molar ratio of total Al plus Fe to P in sludge of less than one (i.e. no chemical precipitation) may result in the release of large quantities of soluble P and a corresponding nutrient imbalance (e.g. Mn toxicity) at high application rates (Pastene 1981). *Brassica* shoot tissue concentrations of N, P, Zn and major cation concentrations increased in biosolids applications of 10% (v/v) in soil in a greenhouse experiment (Wong et al. 2001). Metal salts of Cd, Cu, Ni and Zn decreased the amount of available soil P (Bray-1) and decreased quantities of P in association with Al, Fe and Ca (Folle et al. 1995).

2.4.3 Relevance of phosphorus originating from biosolids in the environment

Phosphorus is both a major plant nutrient and a potential contaminant of water resources. Some controversy has surrounded the role of P in algal blooms in Australia (Rosewell 1997), although P is the nutrient most implicated in eutrophication leading to algal growth in waterways in Western Australia. In rural environments, diffuse (non-point) sources of P such as soil and fertiliser runoff are often a major contributor of nutrients to waterways. In more densely populated areas, point sources such as sewage treatment plants and intensive animal industries may be the main source of contamination (Weaver & Summers 1998). Phosphorus is known to leach from fertilised pastures in the >800 mm rainfall areas of south-western Australia (Bolland & Gilkes 2001).

Excessive levels of P associated with the accelerated growth of toxic *Pfiesteria spp.* in eutrophic waters of the Mid-Atlantic coast (USA), aptly named by the media as *‘Pfiesteria hysteria’* has created public concern (Dentel, Sims & Mah 2001; Womer, Elliott & Brandt 2002). Consequently, factors responsible for P release from a range of land-applied biosolids and manures are being investigated (Dentel et al. 2000; Leopold 2002). Similarly, parts of land most at risk from over-enrichment of P are being examined in the UK (Hogan, McHugh & Morton 2001). Although land application rates of biosolids are regulated according to their nutrient loadings, many animal manures are not and thus are a cause for concern (McCann 1998). The focus of P management from an environmental perspective is now on critical source areas and the factors that trigger the release of potentially mobile P into streams, such as landscape position, waterlogging and overland water flow.

Research supports the premise that P is relatively immobile in most soils and typically remained in the zone of incorporation (Sommers & Sutton 1980). Sludge applied on the soil surface was expected to be less likely to leach P than incorporated sludge (Gove et al. 2001). Soils enriched with P fertilisers, however, have the greatest potential to lose P through surface water runoff and erosion (Weaver & Summers 1998). Water pollution by P may be significant in particulate flow runoff where total P losses are high (Gburek et al. 2005). The erosion of P enriched sediment to streams or lakes could liberate occluded P (P fraction within Al and Fe oxide matrices), even though that form of P is not biologically available under soil surface conditions (Akhtar, McCallister & Eskridge 2002).

Not all P contained in organic sources, however, represents an immediate threat to the surrounding environment (Womer, Elliott & Brandt 2002). Joshua and others (1998) observed reduced runoff and increased rainfall retention in soils treated with dewatered biosolids. The concentration of P measured in runoff was low and not significantly different at rates up to 120 t DS/ha. The low overall loss of sludge P in runoff or by leaching is related to a number of factors, such as rainfall intensity and sludge application rate, with air drying expected to decrease leachate P compared with fluid sludges (Kirkham 1982). In a study by Gove and others (2002) however, the drying of anaerobically digested dewatered biosolids cake had little effect on the loss of P_T following simulated rainfall events in repacked semi-structured soil cores compared with fresh biosolids cake.

Following the land application of high rates of sludge, the leaching of P in soil has not been observed in a number of sites (Cottenie & Kiekens 1980). Similarly, the movement of P downwards through the soil profile was not demonstrated in a UK study following the application of high rates of digested sewage sludge (up to 330 t DS/ha) (Campbell & Beckett 1988). There are many determining factors that affect the leaching of P such as soil type, rate of P application, throughput of water, P_T, CO_2 saturated soluble P and P-sorption indices (Furrer, Gupta & Stauffer 1984). In addition, preferred pathways (preferential flow) for particulate movement of P through soil needs further investigation.

The ability of the soil to adsorb P decreases with successive additions of P, so that more applied P remains in soil solution and is available for plant uptake or loss. This has been noted for a range of organic materials, such as dairy waste (Dougherty & Lawrie 2000) and biosolids (Davis et al. 2000), and attributed both to organic ions and to biosolid P binding with sorption sites. Biosolids increased the P retention in a soil with a low native P sorbing capacity and low Fe_{OX} and Al_{OX} content; but had no effect in soils with a large native P sorbing capacity and abundant Fe_{OX} and Al_{OX} (Lu & O'Connor 2001). Barry and others (1995) considered it appropriate to estimate environmentally acceptable sludge application rates based on soil P sorption characteristics.

Exhumed septic tank drainfields regenerated and regained their capacity to sorb P after drying and wetting cycles with time (Sawhney & Hill 1975). The regeneration of P sorption sites is discussed further by Sommers and Sutton (1980).

There are variable reports as to what constitutes a high soil P value. High soil test values (>200 ppm $NaHCO_3$-extractable P) in sludge-amended soils may indicate excessive levels of available P (Pastene 1981). Available P (Bray-1) of >65 mg P/kg is considered excessively high in the USA (Kelling et al. 1977). Losses of extractable P occurred in soil at Rothamsted in the UK at values >60 mg P/kg (Heckrath et al. 1995). Gestring and Jarrell (1982) estimated that available soil P was saturated by sludge at about 250 kg P/ha, but the amount of biosolids required varied with soil type. McLaughlin (1984) recommended that soil P should not exceed 60 kg P/ha at sludge disposal sites in parts of Canada.

The impetus for P based biosolids management has originated as a consequence of high concentrations of soil P and/or water P. For example, sludge elevated soil P up to 6,582 kg P/ha (Chang et al. 1983) and up to 6,617 kg P/ha were measured in a long-term soil organic matter study at sewage sludge rates of 189 kg P/ha/yr over a period of 35 years (Otabbong et al. 1997). Soil P levels of this magnitude are not typical in Australia, particularly for P deficient soils of the Western Australia wheatbelt. Barrow (1999) used a computer model to predict that the risk of P leaching from land-applied biosolids (i.e. typically 74 kg P/ha) in the wheatbelt of Western Australia would be small and lower than from applications of water-soluble P. Overall there is a scarcity of data related to the pollution of groundwater and water resources in Australia from P resulting from the land application of biosolids. The literature would suggest that P leaching and runoff from land-applied biosolids at current rates in Western Australia (7 t DS/ha) would be unlikely, although it remains to be verified.

2.4.3.1 Water-soluble phosphorus (WSP) and water extractable phosphorus (WEP) in biosolids

To ensure surface runoff and water contamination by excess P are prevented, it is necessary to consider the proportion of water-soluble P (WSP) released from biosolids. The available P fraction of a fertiliser is equivalent to the sum of WSP and citrate soluble P. Extraction of WSP from fertiliser can be measured using water and then citrate soluble P can be extracted using neutral ammonium citrate (Glendinning 1999). Water extractable P (WEP) was used by Brandt, Elliott and O'Connor (2002) to estimate the potential for land-applied manures to enrich P in leachate and runoff. Triple superphosphate had a WEP (% of P_T) of 85% compared with 48% in dairy manure, 21% in poultry manure and 2.5% for typical biosolids, as shown in Figure 2.7 (Brandt, Elliott & O'Connor 2002). Similarly the WSP concentration in a range of biosolids was low (0.3 to 0.4%) compared with poultry and swine manures (17%) (Montgomery 2002). Thus, biosolid P is considered less soluble than animal manure P and chemical fertiliser P and less likely to cause surface water enrichment (Hadeed 2002). Indeed to minimise the leaching of P, biosolids would be preferred as a P source over other sources (Siddique, Robinson & Alloway 2000).

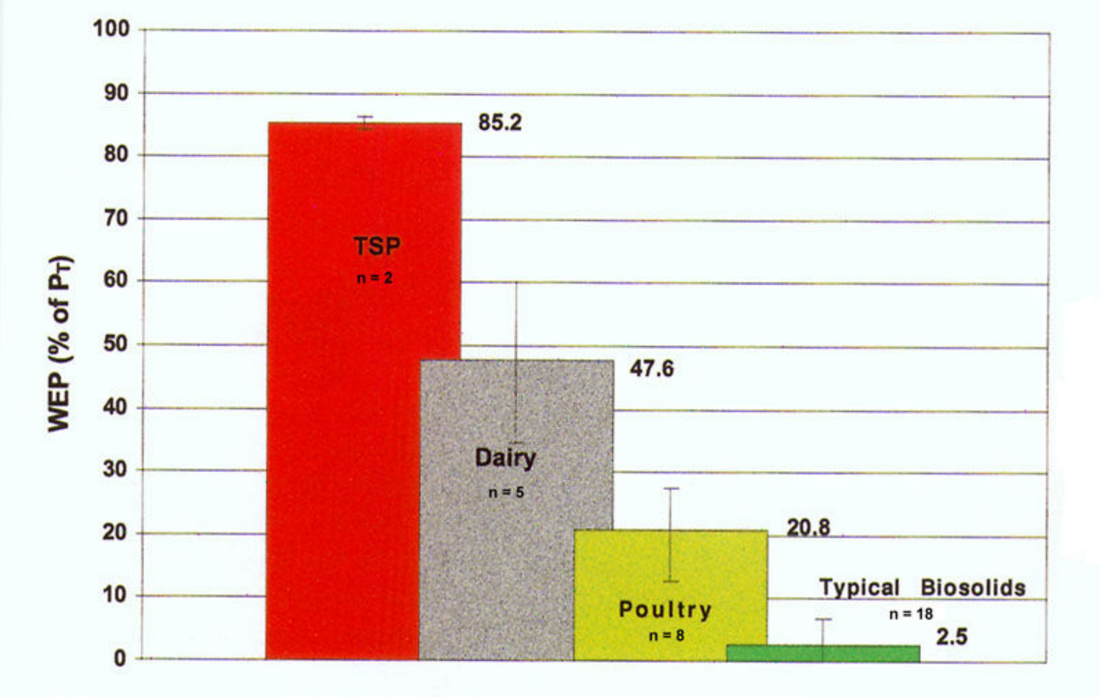


Figure 2.7 Comparison of water extractable P (WEP) for TSP, manures, and typical biosolids

(Brandt, Elliott & O'Connor 2002)

The type of wastewater treatment caused a difference in WEP values for biosolids, particularly for those treated with Fe and Al that tended to sorb P in water insoluble forms, as shown in Figure 2.8 (Brandt, Elliott & O'Connor 2002). Chemical P treatment decreased WEP, whereas enhanced biological removal (EBPR) increased WEP, although not as much as inorganic P fertiliser. Similarly, DeSimone and Dentel (2003) found that biological P removal caused an increase in WEP compared with other wastewater treatments. Elliott, O'Connor and Brinton (2002) found that column leachate P was dominantly inorganic and lower in biosolid sources than TSP. Leaching of P in biosolids was correlated to the P saturation index (PSI = $[P_{\text{oxalate-extractable (ox)}}]/[Al_{ox} + Fe_{ox}]$), with leaching more likely in biosolids cake and pellets with a PSI >1.1.

Concentrations of soluble P in sewage sludge-amended soil was affected by sludge application, soil, time and temperature, peaking at 60 d in 25°C (Akhtar, McCallister & Eskridge 2002). Soluble P was possibly liberated by microbial activity with higher temperatures (37°C) promoting higher biological activity and therefore higher soluble P than measured at lower temperatures (25°C).

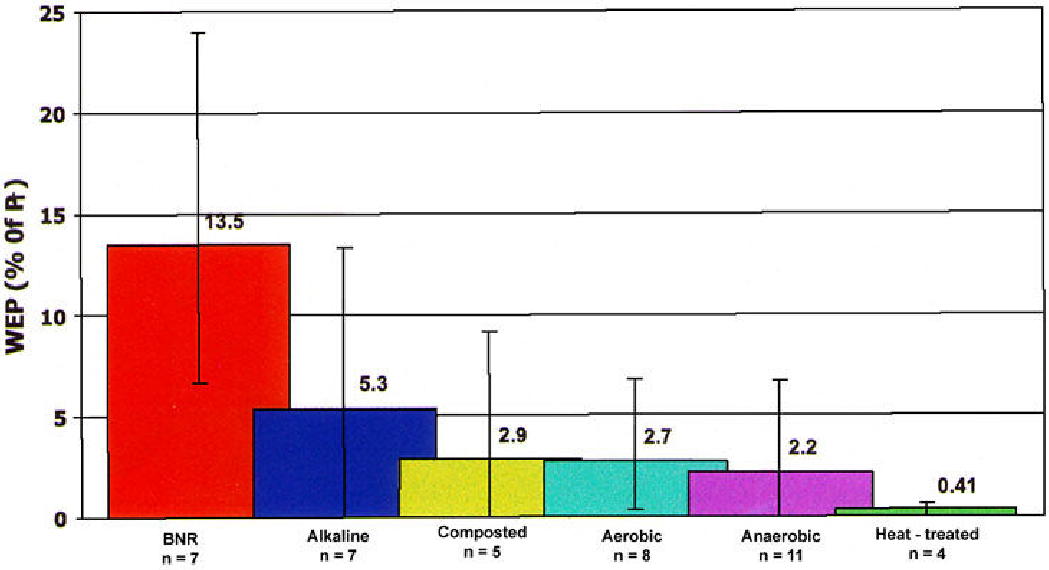


Figure 2.8 Comparison of water extractable P (WEP) levels for several biosolids treatment methods

BNR = biological nitrogen removal. Vertical error bars represent the full range of data included in each category.

(Brandt, Elliott & O'Connor 2002)

2.4.4 Relative effectiveness (RE) of biosolids as a fertiliser

Whereas the previous section examined biosolid P as a possible source of water contamination and pollution, this section is concerned with the effectiveness of biosolid P as a fertiliser. The agricultural value of biosolids as a source of P fertiliser is generally unknown (Osborne et al. 1995a). Barrow (1999) reasoned that it is only possible to measure the “effectiveness” of a fertiliser or its ability to make plants grow better, rather than its “availability”. The term availability is widely used but considered difficult to define and impossible to measure. A general statement may be that biosolid P is (say) 20% available, which Barrow presumed to mean a 20% residual effectiveness compared with fertiliser P such as superphosphate. Thus, biosolids needs to be compared with a standard fertiliser source to allow the RE of biosolids as a source of P to be estimated.

The effectiveness of various sources of P compared with the effectiveness of a standard WSP fertiliser over time has been described in Figure 2.9. In concept, increasing rates of P are applied to a P deficient soil, whilst other nutrients are maintained at adequate levels thereby establishing the yield response curve. The yield response curve is the relationship between plant production (i.e. plant dry matter yield and/or P uptake) and amount of P applied (Bolland & Gilkes 2001). Similarly, the ratio of slopes of regression lines for various sources of sludge P have been used elsewhere to estimate relative efficiency values (%E) (McLaughlin 1988).

The range of values predicted for the effectiveness of P in sewage sludges compared with various WSP fertilisers (de Hann 1981; McLaughlin & Champion 1987; Womer, Elliott & Brandt 2002), highlight the need for data to be collected specific to Western Australian conditions.

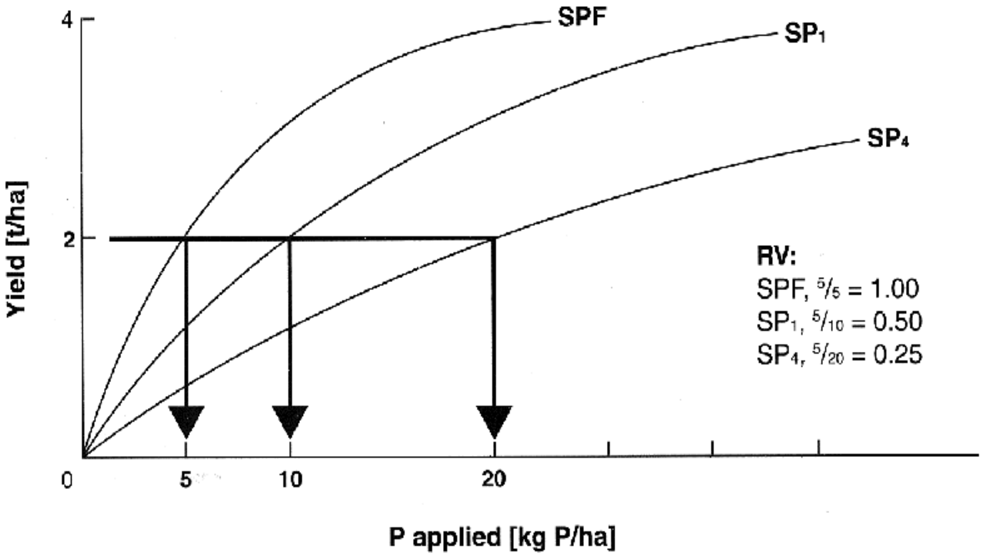


Figure 2.9 Relationship between yield and the amount of P applied as superphosphate in the current year (SPF), one year previously (SP1), and four years previously (SP4)

The residual value of current, one and four year old P is 5/5 = 1.00 for current P: 5/10 = 0.50 for one year old P; and 5/20 = 0.25 for four year old P. Therefore, relative to current P, to produce the same yield (2 t/ha), about twice as much P is required as one-year-old P, and four times P is required as four-year-old P.

(Bolland & Gilkes 2001)

2.4.4.1 Water-soluble fertilisers

The solubility of a fertiliser can influence the nature of soil reactions and its subsequent effectiveness. Fertilisers in which most (>80%) of the P is water-soluble, such as granulated fertiliser manufactured from phosphate rock (Bolland & Gilkes 2001), are most effective for plant production (Barrow 1980). Water-soluble fertilisers are made by adding strong acid such as sulphuric acid or phosphoric acid to rock phosphate to produce single, double and triple superphosphate, or by adding ammonia to phosphoric acid to produce ammonium phosphate fertilisers, such as mono-ammonium phosphate or di-ammonium phosphate (Bolland 1998b; Foth & Ellis 1988; Wild 1988).

Monocalcium phosphate (MCP) is the major component of P in superphosphate, commonly used for agriculture in Australia (Havilah & Osborne 1992). The concentrations of nutrient elements for common P fertilisers are listed in Table 2.11, with various superphosphate and ammonium phosphate fertilisers about equally as effective per unit of P (Bolland 1998b; Glendinning 1999; Phillips & Webb 1971). Rock phosphates contain no WSP and must be converted to more soluble compounds to be effectively utilised by plants. Rock phosphates, for example, are approximately 10% to 20% as effective as superphosphate in the year of application on lateritic soils in Western Australia (Bolland, Gilkes & Allen 1988).

Table 2.11 Concentrations of phosphorus and other nutrient elements in common fertilisers

Fertiliser	Phosphorus %	Sulphur %	Calcium %	Nitrogen %
Single superphosphate	9.1	11.5	20	0
Double superphosphate	17.5	3.5	16	0
Triple superphosphate (TSP)	20	0-1.5	15	0
Di-ammonium phosphate (DAP)	20	0-1	0	17.5
Mono-ammonium phosphate (MAP)	22.6	0-1	0	12
Agras No.1	7.6	17	0	17.5
Summit Topyield	20	1.7	0	18

(Bolland 1998b)

2.4.4.2 Residual phosphorus

Recoveries of fertiliser P are low in the year of application with most annual crops utilising between 5% and 30% of P supplied by an application of WSP fertiliser (Foth & Ellis 1988; Sharpley 1986; Wild 1988). Over time the remaining P converts to insoluble compounds, adsorbed P or organic P. These values decline further over time, although some of the residual is of benefit for following crops.

The residual benefit of biosolid P may increase with time relative to WSP fertilisers. Osborne and others (1995a) proposed that Fe treated sludges in New South Wales are likely to be less than 10% as effective as WSP fertilisers in year one, but increase to (say) 20% in the second and third year. Digested sewage sludge was 15% as efficient as MCP for P uptake by ryegrass after 7 d and increased to 50% as effective after 75 d (Pommel 1981). Rates of P uptake declined rapidly with time in MCP treated soils, whereas sludge-amended soils increased or declined only slowly. This has been attributed to the ability of the sludge to ‘quench’ P-sorbing sites (McLaughlin & Champion 1987). The bioavailability of P decreased with time following the addition of P from various biosolids in an acidic soil after 70 d of laboratory incubation, controlled primarily by an amorphous Al-P mineral (Montgomery 2002).

Kirkham (1982) reported that the type of sludge (i.e. organic sludges, chemical and combined sludges), soil type and plants affect P availability. Other factors that may affect P availability include: the sludge DM content (drying decreased P availability), metal content, soil characteristics, test crop, duration of experiment and inadequate compensation of N (de Hann 1981). For example, P uptake ranged from 36% to 90% for sludges without chemical removal and from 17% to 64% with the addition of Al or Fe salts. Experiments that relate P availability in biosolids with P availability from superphosphate are often complicated in that they fail to take into account the effects of the wide range of other nutrients that are applied, such as N (Havilah & Osborne 1992), thus undermining the applicability of any existing data for Perth’s biosolids and soils.

In Western Australia, fertiliser application rates of P are commonly derived using soil test data, which can be used to predict the crop response to applied P fertiliser. The Colwell (1963) bicarbonate extractable soil P test is recommended for all soil types by the Western Australian Department of Agriculture (Bolland et al. 1987). Furthermore, crop responses to fertiliser P have been predicted by Bowden, Shedley and Burgess (1993) using soil test results, including the PRI, based on over 20 years of trial data in Western Australia. Theoretically, much of their data could be used to extrapolate agronomic P loading rates for biosolids in a range of soils.

Computer software decision tools developed to predict fertiliser requirements include DECIDE; a mathematical model for superphosphate application based on the Mitscherlich response curve that accounts for soil, plant and economic factors in Western Australia and SYN, which is a model to select N rates (Diggle, Bowden & Burgess 2003). A simple spreadsheet model, PAVAIL developed by Bowden (1997) predicts P uptake response of lupins and wheat in Western Australia to variously placed P fertilisers.

2.4.5 Conclusions

The literature suggests that it should be possible to determine the relative effectiveness of biosolids as a source of P compared with water-soluble P fertilisers to enable land application rates in Western Australia to be validated. Given the range of soil types, biosolids and crop management in Australia compared with elsewhere; it has been impossible to extrapolate simply from published reports as to the effectiveness of Perth biosolids as a source of P for plant growth. Experiments related to the release of P in land-applied biosolids in south-western Australia form the basis of the experimental chapters with emphasis given to both agronomic and environmental factors.

3 Relative effectiveness and residual value of phosphorus in biosolids-amended soil compared with inorganic fertiliser – glasshouse experiment

3.1 Introduction

Improvements to soil fertility and soil physical properties following the application of biosolids to agricultural land are well documented (Guidi & Hall 1984; Olness et al. 1998; Osborne et al. 1995a; Water Corporation 1997a; WEF 1994). The Water Corporation, Western Australia has taken advantage of the beneficial properties of biosolids as a soil amendment and currently applies approximately 70% of the 13,800 t DS produced annually to agriculture and forestry surrounding the Perth metropolitan area (Penney, Dumbrell & Pritchard 2003). The use of biosolids in agriculture has become common practice throughout Australia, accounting for 48% of the annual production of 218,000 t DS (Stevens et al. 2002).

In Western Australia, it is usual for land application rates of biosolids to be around 5 to 7 t DS/ha (Penney, Dumbrell & Pritchard 2003), consistent with the N limited biosolids application rate (NLBAR) (DEP, WRC & DOH 2002; NSW EPA 1997; Rawlinson & Salt 1997) and common elsewhere (Gilmour et al. 2000; Havilah et al. 1996). Where biosolids are applied at NLBAR loadings, the total P loadings are in excess of plant requirements with increased soil P levels widely reported (Chang et al. 1983; Dentel, Sims & Mah 2001; Landers 2000; Maguire, Sims & Coale 2000a; Pastene 1981; Pierzynski 1994; Triner et al. 2001; Womer, Elliott & Brandt 2002). Phosphorus applied in excessive amounts presents a risk to the environment, particularly water bodies (Weaver & Summers 1998), and consequently there is a need to investigate biosolid P in more detail. Key characteristics likely to affect the rate of release of P from land-applied biosolids include the type of biosolids, soil characteristics and land management (Dentel, Sims & Mah 2001).

In Australia, there is little information as to the forms of P arising from different types of sludge processing and how these forms are available to plants (Havilah & Davis 1998). Biosolids from Beenyup and Woodman Point Wastewater Treatments Plants (WWTPs) in the Perth region, Western Australia are anaerobically digested and dewatered without chemical P treatment and typically contain between 1.5% to 2.5% total P (P_T) (Water Corporation 1997a). In comparison, sludges and biosolids produced elsewhere may have higher contents of P_T, some up to 6.1% (National Research Council 1996).

Soils surrounding Perth are generally highly weathered, sandy and have low productivity without the application of phosphate fertilisers (Bolland 1998; Moore 1998). The rate of release of P in biosolids-amended soils in Western Australia has not yet been determined. Research elsewhere has shown that the plant response to P is often affected by the interaction with high levels of biosolid N, (Havilah & Davis 1998), with few experiments separating the effects of P from those of metals and other nutrients (Olness et al. 1998).

This investigation aims to compare the relative effectiveness (RE) of anaerobically digested biosolids with an inorganic source of fertiliser P, monocalcium phosphate (MCP), for plant growth and P uptake. The experiment was conducted in a glasshouse using a soil type typically used for biosolids application in Western Australia. The design attempted to ensure that biosolid N was not a factor affecting plant growth. To better understand the forms of P in biosolids, a sequential fractionation procedure was undertaken on selected treatments.

3.2 Materials and methods

3.2.1 Trial layout and design

The experiment consisted of 16 treatments, comprising eight inorganic P (MCP) rates supplying up to 140 mg P/kg and eight rates of biosolids at similar rates of P (Table 3.1). Treatments were replicated three times in a completely randomised design.

Three consecutive crops of wheat were grown in each pot, each for a 33 d period. In addition, new pots treated with freshly applied MCP were established for the second and third crops to enable the residual value of MCP and biosolids to be determined. At the end of each period, the dry matter (DM) of wheat shoots was harvested and a soil sample was collected from each pot. The design concept has been fully explained by Bolland (1993).

The highest rate of biosolids was equivalent to a land application rate of 6 t DS/ha, which is common in Western Australia.

Table 3.1 Comparative phosphorus loadings for monocalcium phosphate (MCP) and biosolids treatments

Treatment	Total P applied (mg P/kg)	MCP (mg/kg)	Biosolids (dry g/kg)
1	0	0	0
2	10	40	0
3	20	80	0
4	40	160	0
5	60	240	0
6	80	320	0
7	110	450	0
8	140	570	0
9	0	0	0
10	21	0	0.7
11	42	0	1.4
12	63	0	2.1
13	84	0	2.8
14	105	0	3.5
15	126	0	4.2
16	150	0	5.0

3.2.2 Soil

The top 10 cm of a yellow gravelly loamy sand, classified as a Yalanbee soil landscape unit (Fulton & Lantzke 1993) was collected from an unfertilised, uncleared bush site on the Allendale Research Station (The University of Western Australia) Bakers Hill, situated 80 km east of Perth (Latitude:-31.7501^{o}S, Longitude: 116.4168^{o}E). The Yalanbee soil unit is formed from deeply weathered laterite in an undulating upland plateau and is mostly (80%) a buckshot gravel soil type. The native vegetation consisted of White gum (*Eucalyptus wandoo*), Marri (*E. calophylla*), some Jarrah (*E. marginata*) with a mix of under-story shrubs (e.g. *Dryandra species*). Gravelly loamy sands, such as these are commonly used for the land application of biosolids in the wheatbelt of Western Australia.

The surface soil consisted of dark, greyish brown loamy sand containing abundant ironstone gravel. The sub-surface soil was a coherent yellowish brown sandy loam containing ironstone gravel with some clay at depth. Gravel and debris were removed by sieving through a 2 mm stainless steel sieve with the <2 mm soil fraction mixed well and stored in 100 kg plastic bins until required. Characteristics of the soil are listed in Table 3.2. Nutrient response curves would be expected for N and P given the low levels of these nutrients in the soil.

Table 3.2 Some properties of the 0-10 cm topsoil (<2 mm fraction) of the Bakers Hill soil

Property	Units
Factual soil key (Northcote 1979)	Dy 4.52
Great Soil Group (GSG) (Stace et al. 1968)	Lateritic podzolic
Australian Soil Classification Scheme (ASCS) (Isbell 1996)	Kurasol
pH ($CaCl_2$) 0.01 M, 1:5	4.8
Total nitrogen	0.093%
Nitrate-nitrogen	6 mg/kg
Ammonium-nitrogen	7 mg/kg
Total phosphorus	69 mg/kg
Bicarbonate-extractable phosphorus	4 mg/kg
Phosphorus Retention Index (PRI)	13 mL/g
Potassium exchangeable	0.09 cmol (+)/kg
Iron $_{(AmOx)}$	500 mg/kg
Aluminium $_{(AmOx)}$	830 mg/kg
Organic carbon (W/B)	2.39%
Conductivity (EC), 1:5	4 mS/m
Carbon/nitrogen ratio	25:1

(CCWA 2000) Report 02A154/1-9

pH ($CaCl_2$) in 0.01 M $CaCl_2$ (Rayment & Higginson 1992i), total N (Blakemore, Searle & Daly 1987; Rayment & Higginson 1992f; Searle 1984), nitrate-N and ammonium-N extracted by 1 M KCl (Rayment & Higginson 1992f) p53, total P (Allen & Jeffery 1990; Murphy & Riley 1962), bicarbonate extractable P extracted by 0.5 M $NaHCO_3$ (1:100) (Colwell 1963; Rayment & Higginson 1992h), PRI (Allen & Jeffery 1990), Fe and Al extracted by 0.2M ammonium oxalate $_{(AmOx)}$, pH 3.25 (Rayment & Higginson 1992c), Organic carbon (W/B)% by Walkley and Black (1934) (Rayment & Higginson 1992g), EC (1:5) at 25°C (Rayment & Higginson 1992b).

(mS/m = milliSiemens per metre, mg/kg = milligrams per kilogram, mL/g = millilitres per gram).

3.2.3 Pots and basal nutrients

Plastic pots (Springdale) measuring 15 cm deep by 15 cm diameter were lined with plastic bags to prevent free drainage and leaching of nutrients and 1.8 kg of air-dried soil was added.

For each crop, basal amounts of K, Cu, Zn, B and Mo were applied per kg soil to all pots as follows: 39 mg K as K_2SO4, 1.2 mg Cu as $CuSO_4.5H_2O$, 1.0 mg Zn as $ZnSO_4.7H_2O$, 0.24 mg B as $H_3BO_{3,}$ 0.05 mg Mo as $Na_2MoO_4.2H_2O$. The levels of nutrients were based on a preliminary glasshouse experiment (Appendix 9.1), to ensure other nutrients (besides P) and trace elements were adequate. However, based on low K shoot tissue analysis in crop one, an additional 78 mg K/kg was applied to all pots at the start of the second crop.

To compensate for the high level of Ca (6.4%) in biosolids (Table 3.3), a once-off Ca application as $CaSO_4.2H_2O$ was applied at a rate of 100 mg Ca/kg to all MCP treatments at the start of the trial only. Ca rates were reduced as the biosolids rate increased to provide 100, 95, 88, 82, 75, 69, 62 or 56 mg Ca/kg to biosolids treatments 9-16, respectively.

For each of the three crops, N was applied in solution as ammonium nitrate (NH_4NO_3) and split over three applications; prior to sowing and at 10 and 20 d. All MCP treatments received a total of 160 mg N/kg. This rate of N resulted in adequate shoot N tissue concentrations in wheat shoots, as determined by a preliminary experiment outlined in Appendix 9.1. The preliminary pot experiment also showed that the N availability from biosolids was approximately 70 mg N/kg biosolids over a 33 d period and consequently this amount was factored into the basal nutrient application rate. Thus, as the rates of biosolids increased, the fertiliser N rates decreased as follows: 160, 150, 140, 130, 120, 112, 102 and 92 mg N/kg, respectively. Plant available N (PAN) was calculated using an organic N mineralisation rate of 20% and ammonium volatilisation rate of 50%, (i.e. approximately 13,700 mg N/kg). Therefore, at the highest rate of biosolids, PAN would be equivalent to 68 mg N/kg.

Monocalcium phosphate [MCP; $Ca(H_2PO_4)_2\ H_2O$] was used as the inorganic source of P and thoroughly mixed dry into the soil for treatments 2 to 8, concurrent with the basal nutrients. No additional P was applied to crop two or three, besides that applied to the new pots to enable residual values to be determined compared with freshly applied P.

3.2.4 Biosolids

Approximately 100 kg of biosolids were collected from Beenyup WWTP, Perth, Western Australia on 14 March 2000. Details specific to the production of biosolids at Beenyup have been explained in section 1.2. A grab sample was used to determine major properties as given in Table 3.3.

Table 3.3 Selected constituents in biosolids collected from the Beenyup Wastewater Treatment Plant on 14 May 2000

Parameter	Units	Method
pH (1:5), H_2O	7.7	PEI-300
Water content	85.2% w/w	PEP-001
Total Kjeldahl Nitrogen (TKN)	50,000 mg/kg	PEI-012
Ammoniacal-nitrogen (NH_3-N)	7,200 mg/kg	PEI-010
Nitrate-nitrogen (NO_3-N)	<5 mg/kg	PEI-011
Total phosphorus	10,000 mg/kg	PEI-015
Total sulphur	10,000 mg/kg	V821
Potassium (extractable)	1,100 mg/kg	PEM-001
Calcium (extractable)	2,700 mg/kg	PEM-002
Calcium (total)	64,000 mg/kg	PEM-002
Magnesium (extractable)	1,400 mg/kg	PEM-002
Copper	1,600 mg/kg	PEM-001
Zinc	810 mg/kg	PEM-001
Cadmium	1.5 mg/kg	PEM-001
Mercury	3.0 mg/kg	PEM-004
Sodium	1,300 mg/kg	PEM-001

(AEL 2000) Report 50817

Analysis carried out by Australian Environmental Laboratories (AEL) on the as received sample and an independent sample used to determine water content. Repeat analysis were conducted on all samples with the average value given. Results for all constituents expressed in mg/kg are reported on a dry weight basis.

Total carbon content determined at 40.6% dry weight basis by combustion (Report 01A360/1-3) (CCWA, 2000).

Biosolids were stored in 30 kg plastic bins at 5°C until required. At the commencement of each glasshouse experiment, a new bin was equilibrated at room temperature for 24 h then mixed for 15 min in a clean cement mixer to ensure homogeneity. The moisture content in the temperature equilibrated, mixed biosolids was determined by drying at 105°C in a fan forced oven for 24 h on large aluminium trays. For each treatment 10-16, the required amount of wet biosolids was weighed (85% moisture), shaken with an equal volume of deionised water in a 500 mL sealed container then evenly mixed through the soil.

Six 100 g biosolids samples collected over the duration of all glasshouse experiments were dried at 40°C for 48 h and then ground through a 1.0 mm screen. The mean P_T was determined using ICP-AES, following digestion with nitric and perchloric acids, which reported macronutrients to 0.01% precision. The mean P_T for biosolids used in the glasshouse experiment was determined to be 2.98% (sd = 0.07) dry weight basis, and is used for all calculations. It should be noted that this value is higher than for the grab sample collected on 14 May 2000 (Table 3.3) and Water Corporation (1999-2000) long-term averages (Appendix 9.1).

3.2.5 Sowing

Soils were watered to a gravimetric soil water capacity (GSWC) of 17% using deionised water and then allowed to incubate in the glasshouse for 7 d prior to sowing. In general, the pots receiving biosolids were close to GSWC and thus required less watering initially. The GSWC was determined as the amount of water remaining after 24 h in the top 5 cm of soil in a 50 cm high free draining soil column covered with plastic wrap to prevent evaporation. The moisture content was determined by drying soil samples at 105°C for 48 h.

For each consecutive crop, ten seeds of wheat (*Triticum aestivum* L. cv. Brookton) were sown in each pot to a depth of 2.5 cm. The seeds were prepared by germinating two days prior to sowing. The three sowing dates were: 18 August 2000, 26 October 2000 and 5 January 2001. Pots were made up to GSWC at least every second day and the position of pots re-randomised. Plants were thinned to five plants per pot at the 2.5 leaf stage, leaving the five most median sized plants.

3.2.6 Location

All glasshouse experiments were conducted in Glasshouse No. 2 at the Centre for Cropping Systems, Department of Agriculture, Northam, Western Australia. The temperature was maintained at 25°C +/-3°C by an air-conditioning system and the relative humidity ranged from 50% to 90%. Pot soil temperatures during the day were constant from 22 to 23°C. During summer the glasshouse roof was painted white to prevent excessive solar radiation and washed clean prior to winter.

3.2.7 Plant measurements and harvest

For each crop, wheat development was recorded at approximately 14 and 33 days after sowing (DAS) using the Zadoks (Z) decimal code for the growth stage of cereals (Zadoks, Chang & Konzak 1974).

Plants were harvested at 33 DAS by cutting the shoots at ground level and then dried at 70°C for 48 h in a forced draught oven. Harvest dates for the three consecutive crops were: 3 October 2000, 1 December 2000 and 12 February 2001. Whole plant shoots were weighed, finely ground using a herb-grinder and then analysed for the concentration of N (Leco N) and P, K, Ca, Mg, Na, S, Fe, Mn, Zn and Cu by Inductively Coupled Plasma Spectrophotometry (ICP) at CSBP, Bayswater (Scheme PTE001). Replications were bulked together where dry matter was less than 800 mg of final sample. Shoot nutrient concentrations were compared with critical nutrient concentration levels in Reuter and Robinson (1997) for whole wheat shoots at the closest comparable growth stage. Total P uptake was determined by multiplying final plant weight by percentage P concentration of shoot tissue.

3.2.8 Soil analysis

Following the first and second harvest, soil was air-dried for 33 d, mixed well and a 10 g sample removed from each pot to enable soil extractable P to be measured. Replicates were bulked together and composite soil samples analysed for total N, pH and the Phosphorus Retention Index (PRI).

Upon completion of the third and final harvest, roots were air-dried for 5 d then physically removed, soil mixed thoroughly, air-dried for 30 d and then sieved to <2 mm. Samples from each pot were analysed for pH, total N, nitrate-N, ammonium-N, total P, PRI, organic carbon and available P.

Characterisation of available P by sequential fractionation was carried out for the highest rate of biosolids (treatment 16), the highest rate of MCP (treatment 8) and the control (treatment 1) at the completion of the experiment, and on air-dried biosolids that had been stored during the experiment. The stored biosolids were prepared by finely milling and then blending with acid washed sand to provide a final concentration of 300 mg P/kg.

3.2.8.1 Soil extractable phosphorus

A sample of soil was extracted in 0.5 M sodium bicarbonate solution (pH 8.5) at 23°C for 16 h (Colwell 1963) and measured by automated colorimetry using a segmented flow auto-analyser (CCWA 2000; Rayment & Higginson 1992h). The Colwell soil test is recommended for all Western Australian soil types and is used by Agriculture Western Australia for predicting phosphate fertiliser requirement.

3.2.8.2 Phosphorus Retention Index (PRI)

Soil samples were equilibrated with a solution containing 10 mg P in 0.02 M KCl by shaking end-over-end at 23°C +/-1°C for 16 h (Allen & Jeffery 1990). The concentration of P in a centrifuged portion of the equilibrated solution was determined by colorimetry as the molybdenum blue complex (Murphy & Riley 1962) on a spectrophotometer. The PRI is expressed as the ratio of P sorbed by the soil (mg P/kg) to the concentration of P remaining in solution (mg P/mL) (Allen & Jeffery 1990).

3.2.8.3 Total phosphorus

Total P was determined using a modification of the Murphy and Riley (1962) molybdenum blue procedure as described by Allen and Jeffery (1990). Soil samples were finely ground (<0.2 mm) in a ring grinder and digested with sulphuric acid in the presence of potassium sulphate and a copper sulphate catalyst at 370°C. The concentration of P_T in the diluted digest was measured by colorimetry (Murphy & Riley 1962) on a spectrophotometer (CCWA 2000).

3.2.8.4 pH

Soil samples were equilibrated with 0.01 M $CaCl_2$ solution (1:5) for one hour using end-over-end shaking then pH was measured in the stirred extract with a calibrated pH meter and combination glass electrode (Rayment & Higginson 1992i).

3.2.8.5 Total Kjeldahl Nitrogen (TKN)

Soil was ground in a ring grinder (<0.2 mm) and digested in a test tube digestion block with a sulphuric acid, potassium sulphate and copper catalyst mixture, converting organic forms of N to ammonium. The digest was diluted and heavy metals complexed with citrate and tartrate. Total N was measured as ammonium-N by automated colorimetry by the nitroprusside-dichloro-S-triazine modification (Blakemore, Searle & Daly 1987) of the Berthelot indophenol reaction reviewed by Searle (1984) and measured using a spectrophotometer at 660 nm. The concentration of total N was reported to the nearest 0.001% (CCWA 2000; Rayment & Higginson 1992a).

3.2.8.6 Ammonium-N (NH_4-N) and nitrate-N (NO_3-N)

Soil samples were air-dried at 40°C for 15-24 h. Ammonium and nitrate ions were displaced from soil by 1 M KCl and end-over-end shaking overnight, then centrifuged at 3,500 rpm for 10 min. Concentrations of NH_4-N in the extract were determined colorimetrically following oxidative coupling with salicyclic acid using sodium dichloroisocyanurate as a source of chlorine. Concentrations of NO_3-N (and NO_2-N) were determined colorimetrically following reduction with hydrazine to the nitrate ion, followed by diazotisation of 1-naphthylethylenediamine and subsequent coupling with sulphanilamide (Rayment & Higginson 1992f).

3.2.8.7 Organic carbon

Organic carbon was measured by the method of Walkley & Black (1934) (W/B)% (Rayment & Higginson 1992g).

3.2.9 Phosphorus fractionation

Characterisation of available P by sequential extraction was based on Tiessen and Moir (1993) modified from Hedley, Stewart and Chauhan (1982) and is used in eastern Australia on biosolids-amended soils (Dougherty 1999).

Air-dried (<2 mm) soil samples of 1 g +/-0.001g, were step-wise extracted with bicarbonate anion resin, 0.5 M $NaHCO_3$ (pH 8.5), 0.1 M NaOH, 1 M HCl, hot concentrated HCl, then extracted with the aid of sonification, H_2SO_4 and H_2O_2 to determine the respective inorganic and organic P fractions. After each step, the soil solution was centrifuged at 3000 rpm for 20 min, the supernatant poured off and the soil dried. The fractions were designated resin-P, bic-P, hyd-P, HCl-P and resid-P, respectively. The bic-P, hyd-P and HCl-P were further analysed for P_T to determine inorganic and organic P (bic-Pi bic-Po; hyd-Pi hyd-Po; HCl-Pi HCl-Po) sub-fractions.

Inorganic P (P_i) in each extract was measured by various modifications of the colorimetric assay of Murphy and Riley (1962) on a spectrophotometer. The concentration of P_T in each extract was measured by either ICP-AES (HCl extracts) or colorimetrically following digestion of an aliquot of the extracts ($NaHCO_3$ and NaOH) with perchloric acid. The amount of organic P (P_o) was calculated from the difference between P_T and P_i. The procedures for measuring inorganic P and P_T at each step were as follows:

3.2.9.1 Resin-P (easily soluble P)

Easily soluble P_i was determined by adding 20 mL 0.5 M HCl to the resin which had been shaking end-for-end in a 3:5 water dilution overnight, then shaking further for 1 h to remove the adsorbed P, which was measured colorimetrically (Murphy & Riley 1962).

3.2.9.2 Bic-P (plant available)

The solution was split into two with plant available P measured colorimetrically as previously described for bicarbonate extractable P and P_T in the leachate determined by perchloric acid (70-72% w/w) digestion to convert organic and colloidal forms of P to P_i. The concentration of P_T in the diluted digest solution was measured colorimetrically (Murphy & Riley 1962), with P_T only suitable for samples containing low levels of dissolved solids and organic matter <20 μg P. The 10 mL aliquot was neutralised with 1.0 mL of perchloric acid. Standards, in 0.5 M $NaHCO_3$, and blank solutions were also taken through the digestion procedure. The calibration curve was constructed from the absorbances of the digested standard solutions and the weight of standard in μg of P. The concentration of P in the leachate was determined as μg of P/aliquot (mL).

3.2.9.3 Hyd-P (Al and Fe bound)

Al and Fe bound P were determined by adding 30 mL 0.1 M NaOH and shaking end-over-end for 16 hrs. The P_T in the leachate was determined by perchloric acid digestion (see bic-P step above), except that 0.65 mL of perchloric acid was added and standards containing 0, 0.5, 1.0 and 2.0 ppm P in 0.1 M NaOH were used (CCWA 2000). Inorganic P was determined as above, without the digestion step.

3.2.9.4 HCl-P (Ca bound)

Ca bound P was measured colorimetrically (Murphy & Riley 1962) following the addition of 30 mL 1 M HCl and shaking end-over-end for 16 h.

3.2.9.5 Residual-P

The soil residue was heated to 80°C with 10 mL conc HCl for 10 min, with a further 5 mL added while vortexing every 15 min for 1 h, and then made to 100 mL using DI water. The solution was split into two with total residual P measured using ICP-AES and P_i procedures described previously.

3.2.9.6 Other P

Remaining P_i was determined by digesting with 5 mL of concentrated H_2SO_4 at 360°C, slowly adding H_2O_2 until clear and then measuring P colorimetrically (Murphy and Riley, 1962).

3.2.10 General

Soil chemical analyses were conducted at the Chemistry Centre of Western Australia (CCWA). Samples were prepared by air-drying (<40°C) and ground to pass through a 2 mm mesh sieve with results expressed by dry weight basis (db).

Standard calibrations were checked for accuracy by ensuring that the mean error of each set of standards was within pre-determined limits. For most colorimetric or ICP methods, the mean of unsigned errors was less than 3%. Reagent blanks were included to be reproducible, being low with respect to the concentrations of the samples. As a guide, the absorbance or peak height of the blank was typically no more than the reporting limit for the method. Control samples were validated against Certified Reference Materials. The control limits were set at the mean +/-3 standard deviations of the sample. Replicates were included to ensure a 95% confidence value for repeatability (CCWA 2000). Digests or extracts of soil samples containing high rates of biosolids often required dilution.

Commonly used models of equipment used for colorimetric analysis included a Technicon AA 2 segmented flow auto-analyser and a Shimadzu UV-101 spectrophotometer set at 882 nm. Inductively coupled plasma optical emission spectrometry analysis was conducted on a Varian ICP-AES.

3.2.11 Statistical analysis of data

Data were prepared for statistical analysis using Microsoft Excel (D'Antuono 2000b). Data were analysed for differences between the biosolids and MCP treatments for final DM yield, P uptake and soil bicarbonate extractable P using an ANOVA model in GENSTAT 5 Release 4.1 program (Lawes Agricultural Trust, Rothamsted

Experimental Station, UK). A single least significant difference (LSD) value of *P* at the 5% level of significance was used for comparing results between treatments at any given sampling date.

3.2.12 Calculation of relative effectiveness

The effectiveness of a P source can be compared with the effectiveness of a standard water-soluble phosphorus (WSP) fertiliser in the year of application by applying different amounts of P to a P deficient soil, whilst maintaining other nutrients at adequate levels. The amount of P required to produce the same yield can be determined to calculate the relative effectiveness (RE) or the residual value (RV) compared with freshly applied fertiliser as described by Bolland and Gilkes (2001), (see Figure 2.9).

Data for the relationship between DM uptake (g/pot) and P applied (mg P/kg) for biosolids, MCP and freshly applied MCP (crop 2 and 3) were fitted to a Mitscherlich equation:

Equation 1

$$y = a\,(1 - b \exp^{-cx}) \qquad (1)$$

The Mitscherlich equation relates the yield to three parameters, where y is the parameter being measured, x is the level of P applied (mg P/kg), and a, b and c are coefficients. The maximum yield when P is no longer limiting is represented by coefficient *a.* The value for b represents the response to P applied so that when b = 1, the yield without P fertiliser is zero and when b = 0, the yield is equal to a (i.e. there is no response to fertiliser). The value for c represents the shape of the response curve so that least effective fertilisers display a flatter curve.

The percentage relative effectiveness (RE) of biosolids compared with MCP was determined by dividing the coefficient (c) value of biosolids by MCP. Thus the RE of MCP will always be 1.00.

The percentage residual values (RV) of biosolids and MCP were similarly determined against freshly applied MCP for the second and third crop by dividing the coefficient (c) value of biosolids or MCP by freshly applied MCP.

To find the parameters that produced the closest fit of a regression model to the observed data, goodness-of-fit statistics were used with a linear solver (Vose 1996).

The solver program in Microsoft Excel was used to fit curve coefficients to a common start and end point for each parameter for biosolids, MCP and freshly applied MCP (crop 2 and 3) using the means of three treatments.

Data for the relationship between P uptake (mg P/pot) and P applied (mg P/kg) for each of biosolids, MCP and freshly applied MCP (crops 2 and 3) were best fitted to a Linear equation:

Equation 2

$$y = b * x \tag{2}$$

where y is the parameter being measured, x is the level of P applied (mg P/kg), and b is the slope coefficient. The Solver program in Microsoft Excel was used to fit the initial slope to a common start point for each parameter for biosolids, MCP and freshly applied MCP (crop 2 and 3) using the means of three treatments. For the lowest rates of P applied, plant material was bulked within treatments to determine the percentage P shoot concentration.

The percentage RE of biosolids compared with MCP was determined by dividing the coefficient (b) value of biosolids by MCP as based on equation (2). Thus the RE of MCP is always 1.00. The percentage RV of biosolids and MCP were similarly determined against freshly applied MCP for the second and third crop by dividing the coefficient (b) value of biosolids or MCP by freshly applied MCP.

3.3 Results

3.3.1 Shoot development and dry matter production

There was a positive relationship between total P applied and DM production of wheat shoots, regardless of the source of P over the three consecutive harvests. No differences in DM were measured between the MCP and biosolids treatments at similar loading rates of P for any of the three consecutive crops (*P* >0.05, Figure 3.1).

In crop one, the lowest DM production was measured in the pots with no added P (0.29 g/pot) and was highest at rates of P >140 mg P/kg (4.90 g/pot in MCP and 4.20 g/pot in biosolids, respectively). The freshly applied MCP in crop 2 and 3 produced significantly more DM relative to residual P (applied as MCP or biosolids) at comparable P rates.

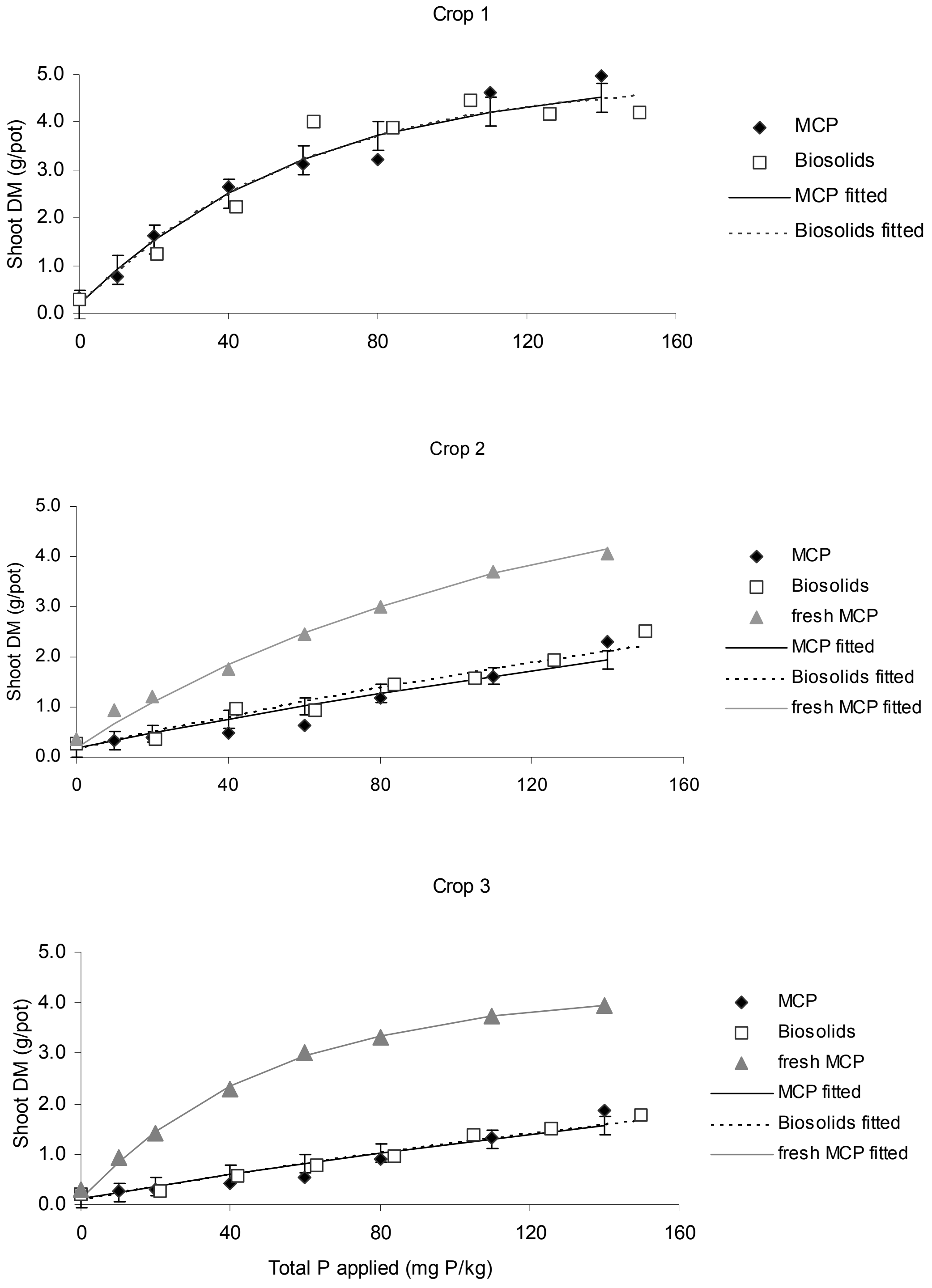


Figure 3.1 Relationship between shoot DM of wheat at 33 DAS and total P applied as MCP, biosolids and freshly applied MCP for three consecutive crops

Fitted lines plotted using Microsoft Excel Solver from equation (1) with coefficients given in Table 3.4. Vertical bars denote LSD (*P* = 0.05) for data from means of three treatment replicates for MCP and biosolids treatments. LSD for fresh MCP crop 2=0.35, fresh MCP crop 3=0.55.

Increases in shoot DM were primarily the result of increased leaf and tiller number. Plants measured at 32 DAS in crop one with no added P averaged 3.5 leaves and showed necrotic symptoms on older leaves (Z13.5). In comparison, the highest rates of P resulted in green plants with an average of up to six leaves and four tillers (Z16/24) as visible in Plate 3.1. In the second consecutive crop, tillering was limited to treatments >105 kg P/kg, and in the third crop tillering was limited to treatments >140 mg P/kg.

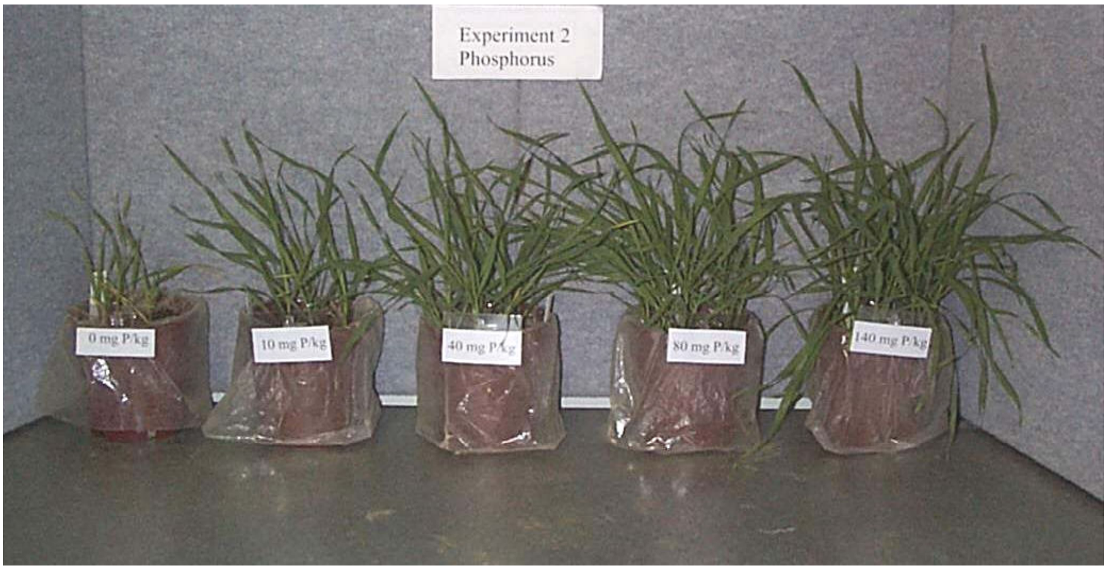


Plate 3.1 Vegetative growth differences in wheat at 32 DAS as a result of increasing phosphorus (MCP) applications for crop 1

(From left to right: 0 mg P/kg, 10 mg P/kg, 40 mg P/kg, 80 mg P/kg, 140 mg P/kg).

3.3.2 Shoot phosphorus concentrations and uptake

The concentration of P in shoot DM of wheat for all three crops increased with increasing P rates from approximately 0.08% in the control to over 0.30% for the highest rates of P. There were no differences between the MCP and biosolids treatments at comparable P loadings (*P* >0.05, data not presented).

A linear relationship existed for shoot P uptake and total P applied for all three crops, with no differences in shoot P uptake between MCP and biosolids at comparable P rates (*P* >0.05, Figure 3.2). Phosphorus uptake declined over each consecutive crop relative to freshly applied MCP.

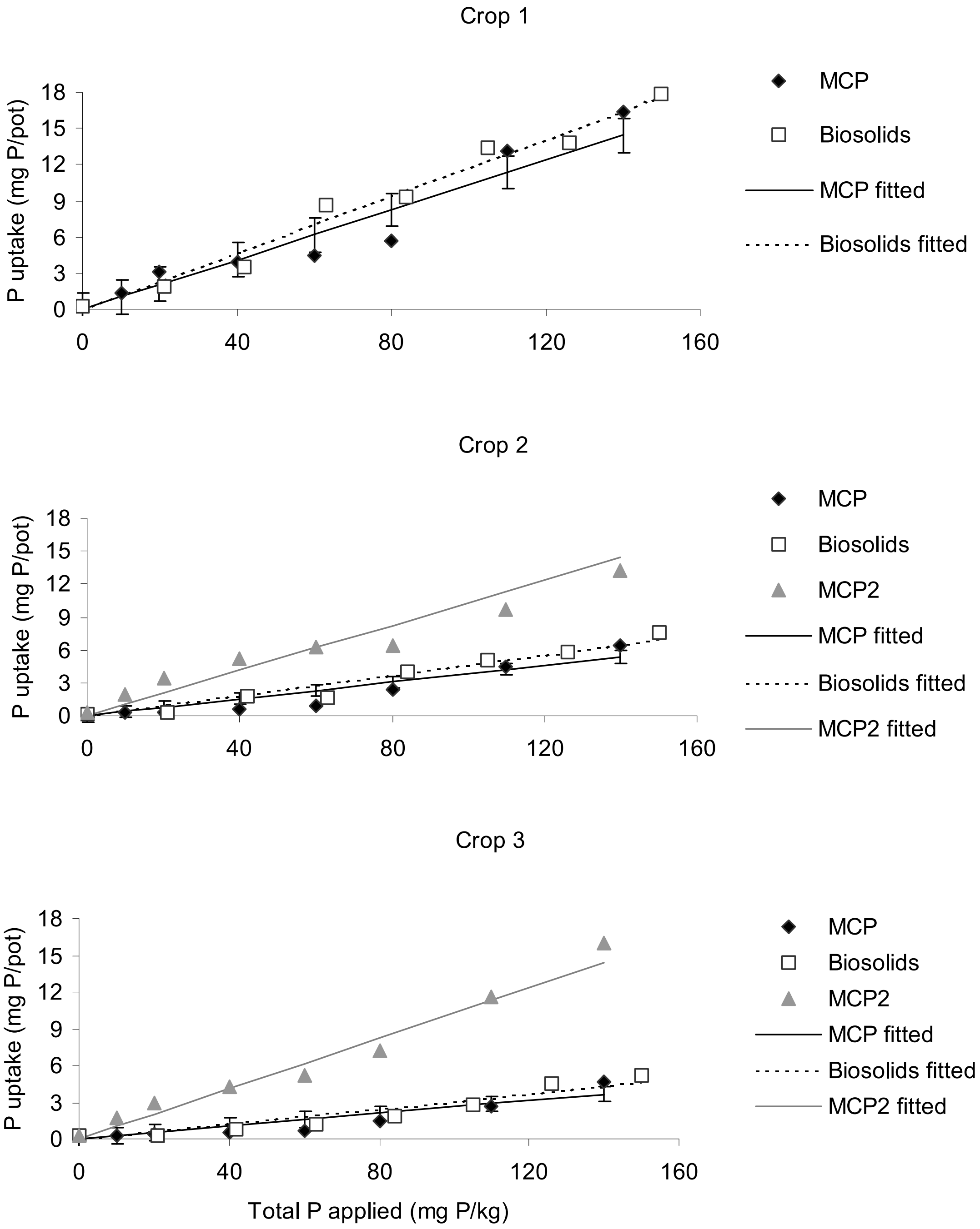


Figure 3.2 Relationship between P uptake in shoot DM of wheat and P applied as MCP, biosolids and freshly applied MCP (MCP2) at 33 DAS for three consecutive crops

Fitted lines plotted using Microsoft Excel Solver from equation (2) with coefficients given in Table 3.5. Vertical bars denote LSD (*P* = 0.05) for data from means of three treatment replicates for MCP and biosolids treatments. LSD for fresh MCP crop 2=1.14, fresh MCP crop 3=1.81.

3.3.3 Shoot nitrogen concentrations and uptake

For crop one, the concentration of N in wheat shoot DM decreased from 5.4% to 3.5% with increasing MCP application rates and from 5.4% to 4.2% with increasing biosolids rates. For crops two and three, the N concentration in wheat shoots measured above 5.8% for all treatments. There were no differences in concentrations of N in shoots at 33 DAS between MCP and biosolids treatments at comparable P loadings ($P > 0.05$, data not presented).

A positive curvilinear relationship existed for shoot N uptake and total P applied for crop one, with N uptake declining with each consecutive crop and becoming linear. There were no differences in shoot N uptake between MCP and biosolid P treatments at comparable P loadings ($P > 0.05$, data not presented). Nitrogen uptake at 33 DAS increased from 17.9 mg N/pot in nil P to 144.0 mg N/pot in the highest rate of biosolids (150 mg P/kg) for crop one. By crop three, N uptakes had declined and were linear, with N uptakes values ranging from 19 mg N/pot to 108 mg N/pot.

3.3.4 Relative effectiveness of biosolids compared with MCP during the growing season

Values for Mitscherlich Equation coefficients for shoot DM accumulation and P uptake for the three consecutive harvests are summarised in Table 3.4. Overall, the percentage relative effectiveness (RE) of biosolids was comparable with MCP at all sampling dates or better. Over time, the percentage residual value (RV) of the P declined in both the MCP and biosolids to similar values relative to that of the freshly applied MCP (Table 3.4).

Table 3.4 Coefficients for the relationships between shoot dry matter and shoot P uptake for three consecutive crops of wheat including relative effectiveness (RE) values

	Crop		
	1st	**2nd**	**3rd**
Parameter			
	Shoot dry matter (g/pot)		
a	4.98	5.78	4.23
b	0.96	0.97	0.97
***c* (MCP)**	0.016	0.0027	0.0031
***c* (Biosolids)**	0.017	0.0031	0.0032
***c* (MCP 2)**	-	0.0088	0.019
%RE (BS/MCP)	101	114	103
%RE (BS/MCPfresh)	-	35	17
%RE (MCP/MCPfresh)	-	31	16
	Shoot P uptake (g/pot)		
***b* (MCP)**	0.10	0.038	0.026
***b* (Biosolids)**	0.12	0.046	0.031
***b* (fresh MCP)**	-	0.10	0.10
%RE (BS/MCP)	114	122	117
%RE (BS/MCPfresh)	-	45	30
%RE (MCP/MCPfresh)	-	37	25

Dry matter calculated using Microsoft Excel Solver for equation (1) and ratio of *c* coefficient determines % relative effectiveness. Shoot P uptake calculated using Microsoft Excel Solver for equation (2) and ratio of *b* coefficient determines % relative effectiveness. The standard error of the RE is approximately 10%.

3.3.5 Soil analysis

3.3.5.1 Bicarbonate extractable phosphorus

Bicarbonate extractable P in the <2 mm fraction increased as the total P applied increased for both MCP and biosolids application. Bicarbonate extractable P was higher for most MCP treatments than for comparable rates of biosolids at the conclusion of all crops *(P* <0.05, Figure 3.3). The differences between the two sources of P became less apparent in crops two and three as bicarbonate extractable P concentrations in the biosolids treatments increased, whereas MCP concentrations remained relatively constant.

3.3.5.2 Total phosphorus

Concentrations of total P in soil samples measured at the completion of crop three were as expected based on the P loading rates. The control treatment contained 72 mg P/kg, which was similar to the initial soil concentration. There were no differences between MCP and biosolids treatments at comparable P loadings. The highest rate of MCP (140 mg P/kg) contained167 mg P/kg, whereas the highest rate of biosolids (150 mg P/kg) contained 177 mg P/kg (data not presented).

3.3.5.3 Phosphorus retention index (PRI)

As application rates of P increased, the PRI declined from 14 mL/g in the control to 8 mL/g in the highest rates of P at the completion of crop one. There were no differences in PRI between MCP and biosolids treatments at comparable P loadings. By the completion of crop three, the PRI values had increased to an average of 23 mL/g in the control to 12 mL/g for the highest P rates regardless of P source (data not presented).

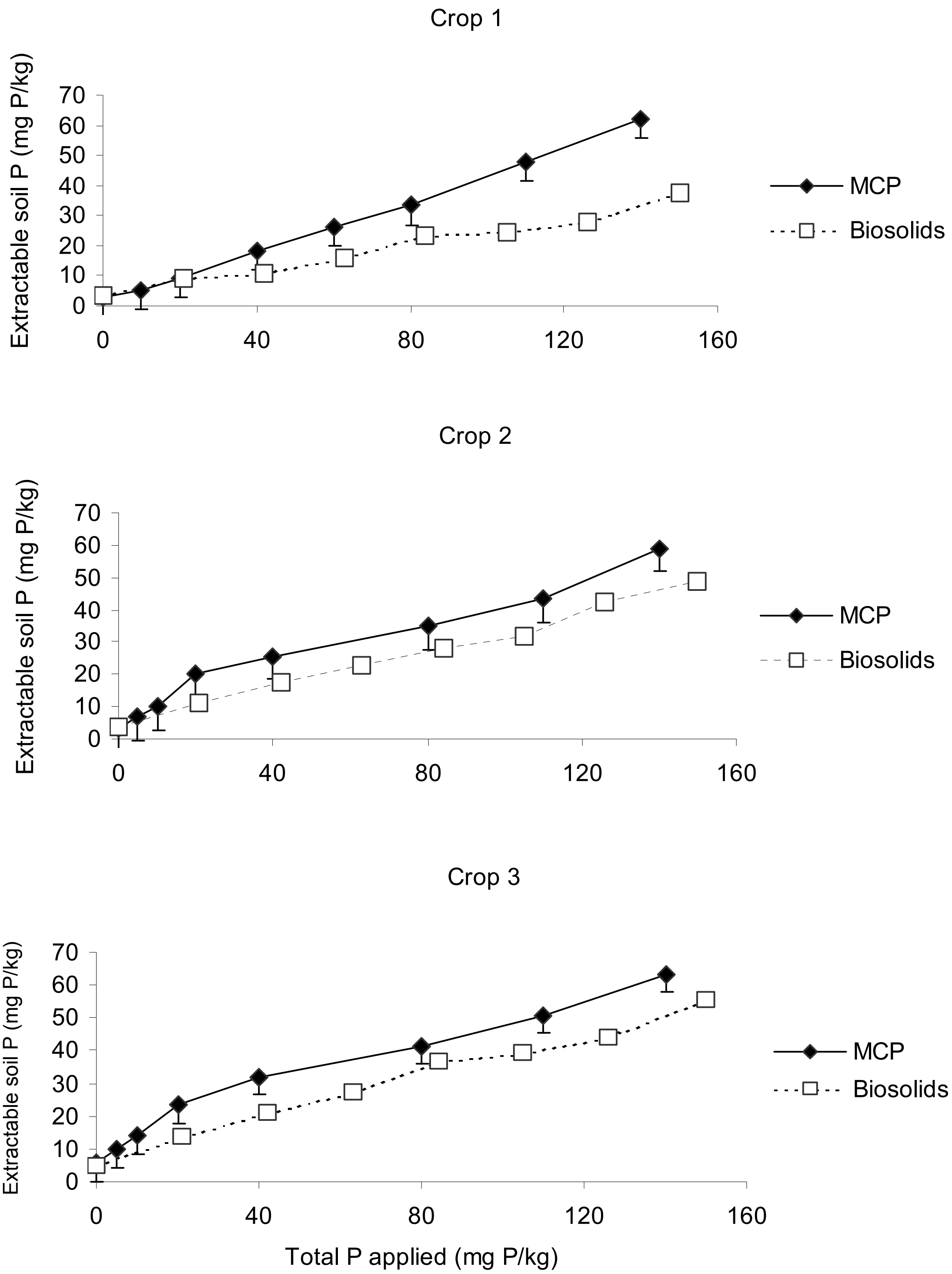


Figure 3.3 Relationship between bicarbonate extractable soil P and total P applied for MCP and biosolids measured at the conclusion of crops one, two and three

Plotted using Microsoft Excel. Vertical bars denote LSD (*P* = 0.05) for data from means of three treatment replicates.

3.3.5.4 *Organic carbon*

The highest rate of biosolids applied increased soil organic carbon by approximately 0.2% (Figure 3.4), which is within the range expected given that biosolids contain 40.6% carbon db (Table 3.3). Soil organic carbon increased linearly with increasing applications of biosolids (slope = 0.001 and correlation coefficient, $r^2 = 0.66$), but no increase was evident for MCP treated soils (slope = -0.0002 and correlation coefficient, $r^2 = -0.15$). At the completion of the experiment, there were no differences in soil organic carbon concentrations between the MCP and biosolid treatments at the application rates used ($P > 0.05$).

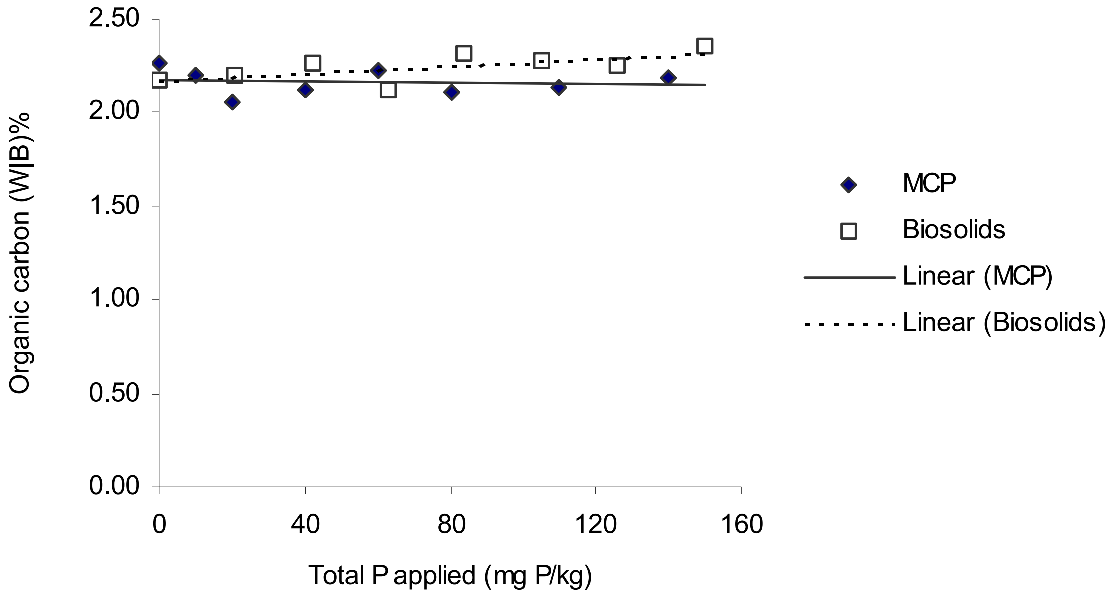


Figure 3.4 Relationship between soil organic carbon and level of P applied as monocalcium phosphate (MCP) or biosolids measured at completion of crop three

Values are means of three treatment replicates. Linear lines plotted using Microsoft Excel.

3.3.5.5 *Total nitrogen*

Over the duration of the experiment, the concentration of total N in the soil was maintained at relatively constant levels (Table 3.5). No significant difference was observed between the MCP and biosolids treatments at the completion of crop 3 ($P > 0.05$). The higher rates of P generally had lower concentrations of soil N, consistent with higher plant N uptakes.

Table 3.5 Relationship between concentrations of total soil N and total P applied as MCP or biosolids measured at the completion of three consecutive crops

Treatment	Total P applied (mg P/kg)	Source	% Concentration of soil total N		
			Crop 1	Crop 2	Crop 3
1	0	0	0.078	0.096	0.124
2	10	MCP	0.086	0.098	0.118
3	20	MCP	0.085	0.096	0.107
4	40	MCP	0.080	0.085	0.112
5	60	MCP	0.088	0.092	0.117
6	80	MCP	0.086	0.079	0.104
7	110	MCP	0.082	0.087	0.096
8	140	MCP	0.077	0.081	0.100
	MCP average		**0.083**	**0.089**	**0.110**
9	0	0	0.094	0.092	0.118
10	21	Biosolids	0.082	0.093	0.115
11	42	Biosolids	0.084	0.09	0.101
12	63	Biosolids	0.105	0.093	0.109
13	84	Biosolids	0.088	0.088	0.107
14	105	Biosolids	0.098	0.086	0.103
15	126	Biosolids	0.104	0.088	0.098
16	150	Biosolids	0.201*	0.093	0.101
	Biosolids average		**0.094**	**0.090**	**0.107**

Crops one and two are values obtained from bulking and analysing three replicates, crop three data are mean values collected from three replicates. No significant difference measured between treatment means in crop three (P >0.05), LSD = 0.0136. * High value measured for crop one biosolids (150 mg P/kg) likely contaminated with biosolids particle and not used to determine average. Data from report number 00A586 Chemistry Centre of WA.

3.3.5.6 Ammonium and nitrate forms of nitrogen

Concentrations of NO_3-N and NH_4-N measured in soil samples at the completion of crop three declined with increasing rates of P for both MCP and biosolids treatments (*P* <0.05, Figure 3.5). There were no differences in concentrations of NO_3-N between MCP and biosolids treatments at comparable P loadings (*P* >0.05). The concentrations of NH_4-N were generally lower than NO_3-N concentrations. Many of the biosolids treatments had lower levels of NH_4-N compared with the MCP treatments (*P* <0.05).

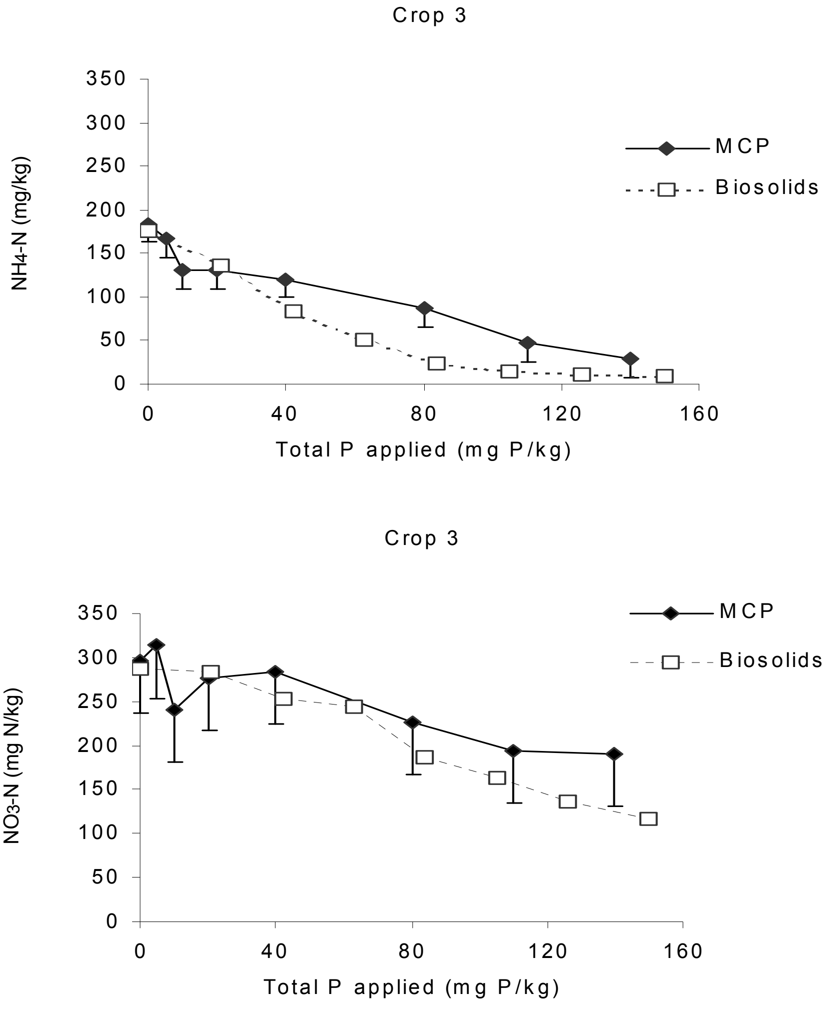


Figure 3.5 Relationship between nitrate-N or ammonium-N and total P applied for MCP and biosolids treatments measured in soil samples at the completion of crop three

Values are the means of three replicates. Lines plotted using Microsoft Excel. Vertical bars denote LSD (*P* = 0.05).

3.3.5.7 Soil pH

The pH ($CaCl_2$) of the soil prior to the start of the experiment was 4.8 (Table 3.2). The MCP treatments showed a general decline in soil pH at the completion of each of the three consecutive crops (Figure 3.6). Soil pH in the highest rates of MCP (> 110 mg P/kg) at the completion of the third crop had decreased to 4.4 and was below all the other treatments (*P* <0.05). In comparison, soil pH in the four highest rates of biosolids showed an initial increase in soil pH, to a maximum of 5.1. Thereafter a gradual decline was measured, so that by the third crop, pH measured 4.8 in the highest rate of biosolids.

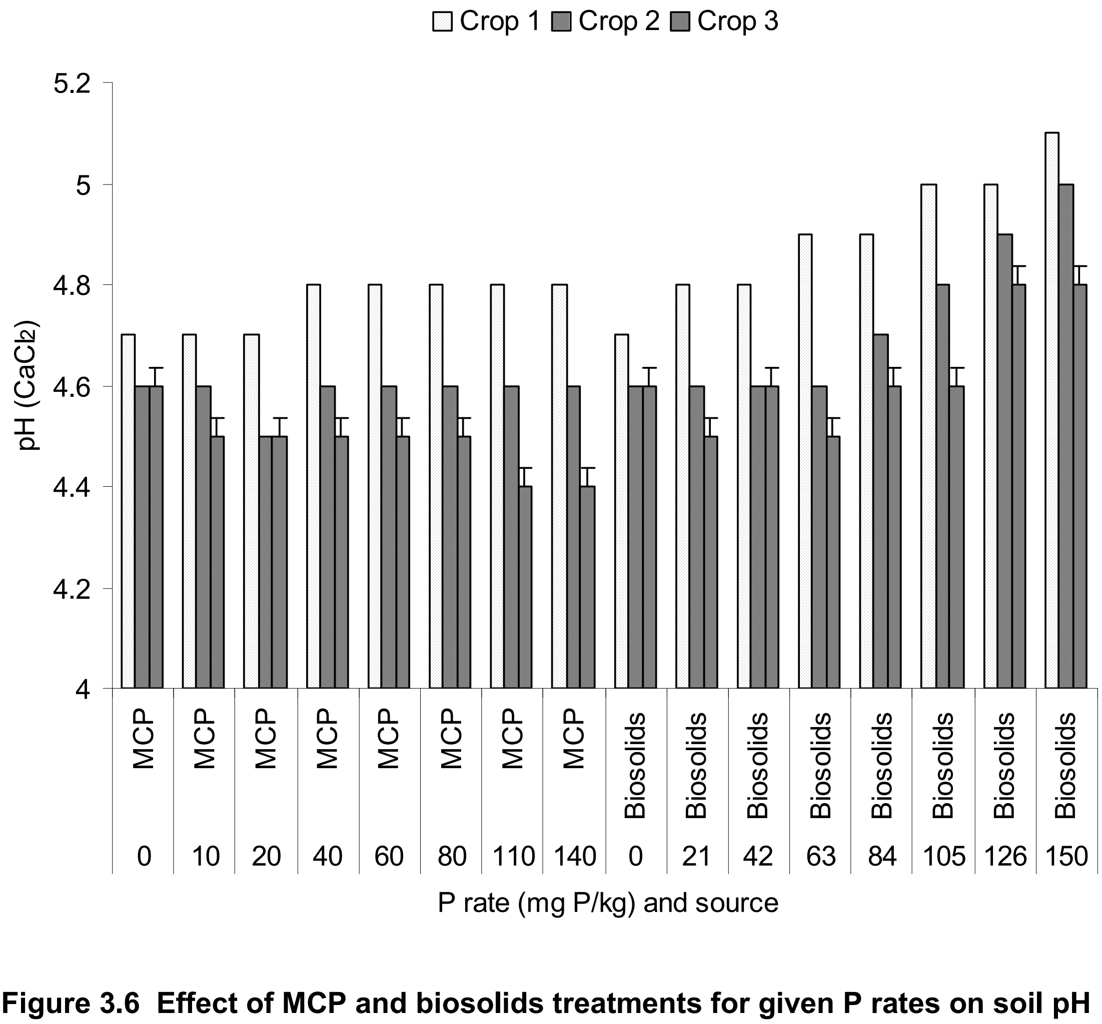


Figure 3.6 Effect of MCP and biosolids treatments for given P rates on soil pH ($CaCl_2$) measured at the completion of crops one, two and three

Data from report numbers 00A286, 00A422 and 00A586, Chemistry Centre of Western Australia. Crops one and two are values obtained from bulking and analysing the soil from three replicates. Crop three is mean values collected from three treatment replicates and vertical bar denotes LSD (*P*=0.05).

3.3.6 Phosphorus fractionation

3.3.6.1 Biosolids

Following the step-wise fractionation of biosolid P: 66% was extracted in resin, 19% in $NaHCO_3$, 5% in NaOH, 7% in HCl, 2% in boiling HCl and 1% residual, expressed as the sum of the total P recovered (Table 3.6). Physical losses and/or analytical errors at each of the steps in the fractionation procedure resulted in a cumulative loss of 14% of the total 300 mg P applied and are not included in the calculation. Overall a relatively small proportion of biosolid P existed in organic forms (8%), predominantly in the $NaHCO_3$ fraction as outlined in Table 3.6.

Table 3.6 Sequential extraction of phosphorus for Beenyup biosolids applied at 300 mg P/kg to acid washed sand

Extractant	P form	Concentration (mg P/kg)	Total P (%) recovered in extract
Resin strips	P_i	171	**66.3**
0.5 M $NaHCO_3$	P_T	50	**19.4**
	P_i	33	12.8
	P_o	17	6.6
1 M NaOH	P_T	13	**5.0**
	P_i	12	4.6
	P_o	1	0.4
1 M HCl	P_i	18	**7.0**
Boiling 1 M HCl	P_T	4	**1.5**
	P_i	2	0.75
	P_o	2	0.75
Digestion	P_T	2	**0.8**
Sum	P_T	**258**	**100**

Chemistry Centre of WA report number 02A155-001, analysis by K. Walton.

3.3.6.2 Comparison between MCP and biosolids

At the completion of crop three, concentrations of P in soil to which biosolids was added increased in the $NaHCO_3$ and NaOH extracts by 36% and 37% respectively, above that of the control treatment. The resin P extract accounted for a 12% increase, boiling HCl by 9%, with less than 4% of biosolid P found in the HCl and residual extracts. The MCP treatment showed similar increases of 47% and 42% for the $NaHCO_3$ and NaOH extracts respectively above that of the control treatment, 11% in the resin P extract and 6% in the boiling HCl at comparable P loadings. The concentrations of P forms measured in selected fractions for each of the treatments are given in Figure 3.7.

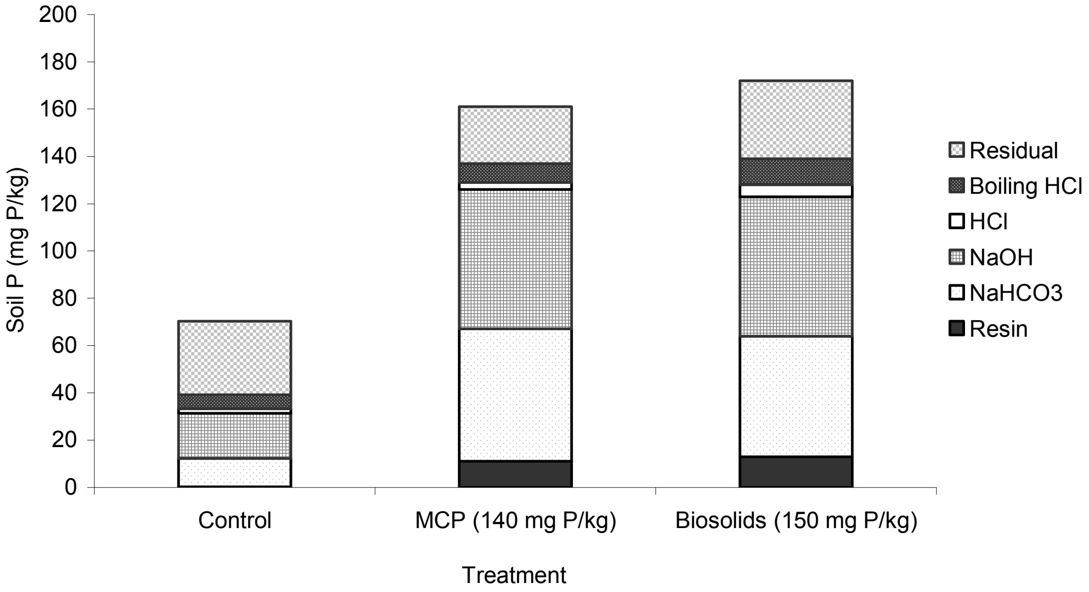


Figure 3.7 Distribution of P in soil extractants at the completion of the experiment in MCP (140 mg P/kg) and biosolids (150 mg P/kg) compared with the control treatment

Values are means of three replicates from soils archived as 00A586, Chemistry Centre of WA.

3.4 Discussion

3.4.1 Interaction between nitrogen and phosphorus

Research on biosolids in eastern Australia has shown that the plant response due to P is often affected by the interaction with the high levels of N in the biosolids (Havilah & Davis 1998). The design of this experiment ensured similar levels of N and other nutrients were available for plant growth, so that P was the only limiting factor in the P responsive soil selected.

Concentrations of N in shoot DM of wheat measured at 33 DAS indicated that concentrations above the critical level of 5.4% (Reuter & Robinson 1997) were achieved overall for crops two and three, although slightly below this for crop one. An N interaction was not considered to favour biosolids treatments as MCP treatments demonstrated similar N concentrations and N uptake compared with comparable P rates of biosolids. Similarly the mean total soil N concentrations in pots following all crops were similar between MCP and biosolids treatments, ranging from 0.083% to 0.110% (Table 3.5). Moreover, all treatments had a substantial surplus of NH_4-N and NO_3-N at the end of the experiment.

On completion of crop three, the levels of nitrate-N and ammonium-N in the soil decreased with total P addition, most likely caused by a higher N uptake by the larger plants. The trend was similar between MCP and biosolids treatments (Figure 3.5), indicating that N did not skew the results.

The percentage shoot concentrations of P were below the critical level of 0.56% reported by Reuter and Robinson (1997) for all levels of P at the most comparable growth stage, meaning that a good response curve was achieved at the P rates applied (Figures 3.1 and 3.2).

3.4.2 Relative effectiveness (RE) of biosolid P compared with MCP for plant dry matter yield and P uptake

The RE of biosolids as a source of P in the present experiment was identical to or better than that of inorganic fertiliser P for plant DM yield; measuring 101%, 114% and 103% for the three consecutive crops respectively, and 114%, 122% and 117% for P uptake (Table 3.4). The responsiveness of wheat to a range of inorganic P fertiliser as an indicator of RE in Western Australia has been used previously by Bolland and Gilkes (2001), but apart from the data presented in this research, there is very little information that has examined the RE of biosolids compared with inorganic P for Australian soils.

Research on sewage sludges and/or sludge composts related to P availability has been carried out by a number of other researchers, often with conflicting results (Coutinho, Arrobas & Rodrigues 1997; de Hann 1981; McCoy, Sikora & Weil 1986; Wen et al. 1997). The P in biosolids or sewage sludge was reported as being from 40% to 100% as available as the P in TSP (Womer, Elliott & Brandt 2002), from 20% to 100% compared with P in MCP (de Hann 1981) and from 90% to over 100% (McLaughlin & Champion 1987). In the present experiment, the RE of biosolids as a source of P compared with MCP was 100%, at the higher range of earlier studies and most similar to results obtained by McLaughlin and Champion (1987), who used P deficient sesquioxide soils in their study.

Direct comparison between research data are often made difficult given the differences in the range of biosolids, crops and type of planting, such as glasshouse (pot) or field experimentation. The literature indicates that it is impossible to generalise as to the fertiliser effectiveness of sludge derived P, primarily due to the varied combinations of soil, biosolids and environmental factors as detailed further by Dentel, Sims and Mah (2001) and McLaughlin (1984).

McLaughlin and others (1988c) used isotopic double labelling to develop an integrated P cycle to trace the amounts of P being taken up by plants and/or being incorporated into the microbial biomass under a wheat-pasture rotation. Much of the inorganic P in pasture residues was not taken up directly by plants, but incorporated into the microbial biomass (22-28%) and then recycled back to the plant available pool later. Most of the P taken up by wheat plants and the microbial biomass was derived from native soil P, rather than from sources of P applied that year as inorganic fertiliser or pasture residues (McLaughlin, Alston & Martin 1988a; McLaughlin, Alston & Martin 1988c). In the present experiment, however, the proportion of P taken up by plants directly from the P supplied in biosolids is unknown, as is the indirect effect of other constituents in biosolids (i.e. 40.6% total C, Table 3.3) on soil microbial activity and thus P availability.

3.4.3 Changes in available soil phosphorus and other soil parameters

There is usually a reasonable correlation between soil extracted P and P uptake by plants, DM yield and crop response to added fertiliser P, where initial soil P is relatively low (Tunney et al. 1997). This was demonstrated to a limited extent in this experiment on the infertile soil used. However, bicarbonate extractable P was slightly higher where MCP was used compared with biosolid P, although differences were not reflected by plant growth (Figures 3.2 and 3.3). The higher levels of extractable P in MCP treatments compared with biosolids did not appear to result in increased shoot DM or P uptake.

Poor correlations between P uptake and soil available P agree with data by a range of researchers (Cottenie & Kiekens 1980; McLaughlin 1988; Pastene 1981; Tiessen & Moir 1993; Velthof et al. 1998; Womer, Elliott & Brandt 2002). The limitations to the various soil P extraction methods have been explained by Wild (1988), Tiessen and Moir (1993) and Tunney (1997). The bicarbonate extractable P (Colwell) test used in this study, which is generally used as a pre-plant predictor, generally underestimated the effectiveness of biosolids as a source of P in this study, although the mechanisms are unclear.

Tiessen and Moir (1993) suggest that the 16 h Colwell extraction partially overcomes problems with organic matter, which has been thought to alter the intensity of the blue colour used to measure P in the colorimetric process. The presence of iron (III) can also affect bicarbonate extractable P results (Tiessen & Moir 1993). The effect of organic matter in biosolids used in the present experiment on the bicarbonate extractable P value, however, is unknown.

The P fertiliser value of sludge cannot be predicted by measuring plant available P directly from a sample of biosolids (Womer et al. 2002), or from laboratory incubations of soil-sludge mixtures and extraction of various forms of P (McLaughlin 1988). For example, P is characterised by a low mobility in soils and the ability of plant roots to explore the soil volume and take up P can be affected by factors such as soil structure and stoniness. Crop roots do not explore soil volume as effectively as chemical extractants; and calibrating does not always give consistent results (Johnston & Poulton 1997). Hence, the use of chemical extractants may overestimate plant available P with the uptake of P by actively growing plants, as was used in the present experiment, often a preferred system of measurement.

It is possible that any number of the complex range of constituents in biosolids may have influenced the concentration of P in soil solution, such as by affecting soil sorption mechanisms and/or microbial activity. The adsorption of P onto the surfaces of soil constituents is affected by many factors, such as soil pH (Bolland, Allen & Barrow 2003). It could be interpreted that the addition of MCP tended to have a net decrease on soil pH, possibly due to the acidifying effects of the greater amounts of ammonium nitrate applied. Soil organic C levels increased only slightly at the biosolids rates applied and in the range expected (Figure 3.4). Being a non-cultivated soil, the C content was initially high (2.39%), with overall changes to total soil C negligible. The resultant C inputs would be unlikely to slow microbial activity or reduce P supply in plants through immobilisation (Stewart & Sharpley 1987).

Over time, the residual P value of both biosolids and MCP decreased, as principles of continuing low reactions and adsorption of P through reaction with soil constituents such as iron and aluminium would suggest (Bolland, Allen and Barrow 2003; Barrow 1980; Glendinning 1999). The lateritic soil used for this experiment had a medium PRI (13 mL/g) and high reactive $_{(AmOx)}$ Fe (500 mg/kg) and Al (830 mg/kg) levels, thus reducing the solubility of P. The decline in PRI with increasing total P rate in both MCP and biosolids was consistent with the findings of Bolland and Allen (2003).

3.4.4 Characterisation of available phosphorus by sequential extraction

Generally, the majority of P in biosolids is present in inorganic forms with its bioavailability dependent on the compounds used for sludge stabilisation (Coutinho, Arrobas & Rodrigues 1997). Biosolids produced by anaerobic digestion are more likely to contain inorganic forms over organic forms (Osborne 1995). This was evident in biosolids used in the present experiment from the Beenyup WWTP, which were found to contain 92% of P in inorganic forms and 8% of P in organic forms (Table 3.6).

Anion exchange resin used in sequential extraction (Tiessen & Moir 1993) absorbed 66% of the P_T from biosolids, indicating that a high amount of exchangeable P_i as well as some soluble P forms constituted the majority of the Beenyup biosolids. A further 19% of biosolid P was measured in the bicarbonate extractable portion, mostly as P_i, but also as easily mineralisable P_o forms. These data further support the plant response data suggesting a high availability of biosolid P compared with the predominantly (80%) water-soluble MCP. Specific mineralogy testing would be required to confirm the presence of large amounts of dicalcium P, proposed by Barrow (1999).

Phosphorus removal techniques are commonly used in eastern Australia and inland southern Western Australia where effluent discharges into creeks and rivers. Phosphorus removal techniques in sludge that use Al or Fe may render P less available (Dentel, Sims & Mah 2001; Havilah & Davis 1998). As P removal techniques are not used by WWTPs on the Perth coastal plain in Western Australia, these additives would not be a factor affecting P bioavailability in the present experiment.

There were no differences in soil P fractions between the highest MCP and biosolids treatment following completion of the final crop on the lateritic soil used in this experiment (Figure 3.7). Compared with the control, the largest increases in soil P were obtained in the NaOH extract, which measured Al and Fe bound Pi, characterised by a lower plant availability than the resin or bicarbonate fractions. Similarly, the predominant forms of P in biosolids treated soils in eastern Australia are mainly in association with Fe and Al (75%), depending on the waste stream and treatment process used, with less than 5% in organic forms (Dougherty & Lawrie 2000). Insoluble compounds are often formed with other constituents in biosolids and in the soil (Cottenie & Kiekens 1980).

The ability of lateritic soils to sorb applied P with time is demonstrated in Figure 3.7 following the addition of either MCP or biosolids, measured at the completion of the third consecutive crop. The P in biosolids has effectively dissolved and distributed itself in the various soil P fractions in the same manner as the MCP. There was no clear evidence in the biosolids treatments of enhanced microbial activity resulting in immobilisation of water-soluble P and a lowering of the bicarbonate extractable P value, towards the end of the growing period. All treatments would have been subjected to the removal of soluble P by plant roots throughout the period of plant growth.

3.5 Conclusions

The glasshouse experiment provided a controlled environment to investigate the relative effectiveness of biosolid P compared with inorganic fertiliser P. The interaction between biosolid N and P was minimised by applying decreasing rates of inorganic N as the rate of biosolids increased. In addition, the soil was deficient in P enabling a P response curve to be established.

There were no differences in shoot DM production of wheat shoots or P uptake between MCP and biosolids at comparable total P loading rates and over three consecutive crops. The residual value of both sources of P decreased similarly over time as P became sorbed by soil particles and/or immobilised by microbial activity, thus reducing the solubility of P.

The bicarbonate extractable P (Colwell) test used in the present study generally underestimated the effectiveness of biosolids as a source of P, although the exact mechanisms are unknown. It is uncertain if the organic matter in biosolids may have possibly interfered with the colorimetric readings used to measure bicarbonate extractable P.

The biosolids used in the present experiment contained 92% of P in inorganic forms and only 8% in organic forms. The inorganic forms of biosolid P were present predominantly as water-soluble P forms (66%) and as bicarbonate extractable P (18%). Following application to the soil, the P in biosolids behaved similarly to MCP being sorbed mostly by Fe and Al soil constituents over time, suggesting that chemical rather than biological factors were responsible for P availability. Further work is warranted to investigate the recycling of P in the various soil pools to establish the source of P taken up by plants following the application of biosolids.

Overall, these results suggest that a higher proportion of P was plant available from anaerobically digested biosolids in Western Australia than previously considered. The mineralisation rate of 21% suggested by DEP and others (2000) and previously used by the Water Corporation of Western Australia to estimate the phosphorus limited biosolids application rate (PLBAR), may play a limited role in P availability given the minor amounts of organic P in biosolids. The term ‘mineralisation rate’ is therefore not appropriate and rather confusing in the context of the Beenyup biosolids.

In order to validate the findings of the current pot experiment in broadacre agriculture, it is necessary to conduct field experimentation on soil types and in areas commonly used for biosolids land applications. It would be appropriate to measure seasonal dry matter production, P uptake, grain yields and changes in available soil P, with values over a number of seasons to determine residual P values. In particular, the soils used in Western Australia for local biosolids application warrant investigation to ensure the P loading rates are optimal and not contributing to an excess of P in the environment. Thus the field trial forms the basis of the following chapter.

4 Relative effectiveness and residual value of the phosphorus in biosolids compared with an inorganic fertiliser – field experiment

4.1 Introduction

Land application rates of biosolids in Western Australia are typically based on the N limiting biosolids application rates (NLBAR) (DEP, WRC & DOH 2002), which may increase total soil P concentrations (Chang et al. 1983; Dentel, Sims & Mah 2001; Epstein 2002; Landers 2000; Maguire, Sims & Coale 2000a; Pastene 1981; Pierzynski 1994; Triner et al. 2001). However, the impact of increased soil P in the agricultural regions used for biosolids application surrounding Perth is unknown. Further work is warranted to investigate the bioavailability of the P contained in biosolids under field conditions specific for Western Australian soils and climate. This is necessary firstly to ensure that adequate P is being applied for plant growth and secondly to ensure that over-fertilisation of P does not pose an environmental risk.

The interim *Western Australia Guidelines for Direct Application of Biosolids and Biosolids Products* (DEP, WRC & DOH 2002) assume that all of the P forms in biosolids are immediately plant available. However, work in eastern Australia by Michalk and others (1995) suggest that the P limiting biosolids application rate (PLBAR) should be based on a 21% mineralisation rate and this has been used previously in Western Australia to calculate P loadings (Rawlinson & Salt 1997). The consequences of using the PLBAR based on total P to limit application rates (rather than N) results in lower biosolids application rates, additional inorganic N fertiliser to supply crop N needs and an increase in land required for application (Womer, Elliott & Brandt 2002).

The literature indicates that it is impossible to generalise as to the fertiliser effectiveness of biosolid derived P compared with various water-soluble phosphorus (WSP) fertilisers from studies elsewhere. Compared with inorganic P sources, the effectiveness of biosolids and sludge P varies from 20% to 100% (de Hann 1981; McCoy, Sikora & Weil 1986; McLaughlin & Champion 1987; Womer, Elliott & Brandt 2002), which is not surprising given the number of soil, biosolids and environmental factors suggested by Dentel and others (2001) as influential to P release. In addition, there are few experiments that have validated glasshouse pot trials against field conditions.

The majority of agricultural soils in Western Australia are derived from ancient, highly weathered parent materials and contain very low levels of native P (Bolland 1998b). Consequently, these soil types may act to reduce the availability of biosolid

P and reduce any risk of P over-fertilisation. The widespread deficiency of P in Australian soils means the reaction of soils with applied fertiliser is an important criterion for determining fertiliser requirement (Holford 1997). The agricultural value of biosolids as a fertiliser needs to be determined (Osborne et al. 1995a), and specifically, the residual value of biosolid P over time to predict subsequent fertiliser requirements. The residual benefit of biosolid P may increase with time relative to WSP fertilisers (McLaughlin & Champion 1987; Osborne et al. 1995a; Pommel 1981) or may decrease with time (Montgomery 2002). In general, recoveries of water-soluble fertiliser P are low in the year of application, with residual values further reduced over time (Foth & Ellis 1988; Wild 1988).

The aim of this experiment was to investigate the relative effectiveness (RE) of biosolids as a source of P compared with inorganic P fertiliser under field conditions common for the application of biosolids in Western Australia. A wheat/lupin rotation was used to gather data over two growing seasons to enable the residual value (RV) of biosolid P over time to be measured. Comparison was made with results obtained in the glasshouse experiment. The results will provide data to better calculate PLBAR for the agricultural land application of biosolids to ensure plant P needs are being met. The change in concentration of P through the soil profile following the application of biosolids was measured to prevent P over-fertilisation and subsequent environmental pollution.

4.2 Materials and methods

4.2.1 Experimental design

The field experiment comprised fifteen treatments as described in Table 4.1, each replicated three times in a randomised block design to give a total of 45 plots. Each plot measured 2.1 m wide x 30 m in length with a buffer control plot placed at each end of the site (Plate 4.1).

To ensure a response to P on this site, fertiliser rates were based on work by Bowden, Shedley and Burgess (1993) with over 20 years of trial data for the response of agricultural plants, Colwell bicarbonate extractable P and P retention index (PRI). In year one, the seven rates of P were top-dressed at 0, 5, 10, 20, 40, 70 & 120 kg P/ha using triple superphosphate [TSP, $Ca(H_2PO_4)_2\ H_2O$] and four rates of biosolids supplied 12, 48, 85 & 145 kg P/ha. The design of the experiment enabled the RE of biosolids as a source of P to be determined compared with an inorganic P fertiliser, similar to the glasshouse experiment described in Chapter 3.

Table 4.1 Treatment allocation for rates of phosphorus supplied by biosolids or triple superphosphate (TSP) in years one and two of the field experiment

	Total P rate (kg P/ha)		TSP applied (kg/ha)	Biosolids applied (t DS/ha)	Plot number
Treatment	Year One	Year Two			
1	0	0	0	0	3,27, 45
2	5	0	25	0	13, 25, 35
3	10	0	50	0	9, 23, 40
4	20	0	100	0	4, 26, 33
5	40	0	200	0	11, 17, 37
6	70	0	350	0	6, 20, 41
7	120	0	600	0	2, 18, 34
8*	0	20	100	0	8, 28, 36
9*	0	40	200	0	12,16, 31
10*	0	80	400	0	15, 24, 43
11	12	0	0	0.41	14, 21, 39
12	48	0	0	1.64	10, 30, 38
13	85	0	0	2.86	5, 22, 32
14	145	0	0	4.91	1, 19, 44
15	85	0	0	2.86**	7, 29, 42

*Plant and soil samples were not collected from treatments 8, 9 and 10 in the first year, 2001. **Biosolids surface-applied to Treatment 15.

Three extra treatments had no P applied in year one to enable freshly applied TSP to be added in the following year, consequently no measurements were made on these plots in year one. In 2002, freshly applied TSP was broadcast to these plots on 9 May 2002 at rates of 20, 40 and 80 kg P/ha. There was one additional biosolids treatment at 85 kg P/ha to examine P availability from surface-applied biosolids compared with sub-surface incorporation (treatment 15), which is discussed separately in Chapter 5.

Plate 4.1 Field trial site at York during spreading, May 2001

4.2.2 Site history and climate

The field experiment was conducted over two years, during 2001-2002. The 0.5 ha site was located 20 km west of York on Rob and Anne Chester's property "Allawuna" on the eastern edge of the Darling Range laterite (Latitude: -31.7501°S, Longitude: 116.5501°E). The site had been cleared in 1999 and sown to wheat (*Triticum aestivum* L. cv. Aroona) in 2000 with a basal dressing of superphosphate and urea. The native vegetation was predominantly Wandoo (*Eucalyptus wandoo*), Marri (*E. calophylla*) and Jarrah (*E. marginata*) woodland with a mix of under-storey shrubs, such as *Dryandra* species.

The climate is Mediterranean, typified by a short wet winter and long dry summer. The average annual rainfall is 520 mm, with 70% falling during a seven-month growing season. Daily measurements of minimum and maximum air temperatures and rainfall were recorded at Inkpen weather station (Latitude: -31.8000°S, Longitude: 116.4300°E) located 15 km north-east of the site. The Queensland Department of Natural Resources and Mines maintain the weather station data.

4.2.3 Soil type

To ensure a P response, the site was chosen for its low fertility and high P sorbing capacity. The soil type is commonly described as a yellow gravelly loamy sand, and is classified as belonging to the Leaver soil landscape unit by Fulton and Lantzke (1993). This soil type is representative (90%) of all the gravelly, loamy sand soils that occur on dissected lateritic hillslopes within the Darling Range. The topsoil consists of brown loamy sand, which overlies yellowish brown sandy loam subsoil, which increases to clay at depth. More commonly the soil is referred to as a “gravelly loam” and is very similar in properties to the soil used in the glasshouse experiments. The major soil properties are described in Table 4.2.

This soil type is common in an area within close proximity to the Perth region and potentially suitable for the land application of biosolids. The Yalanbee and Leaver soil landscape units (Fulton & Lantzke 1993) comprise 60% or 73,000 ha of the Darling Range and West Kokeby Zones (Lantzke & Fulton 1993).

4.2.4 Nutrient application

To ensure nutrients besides P were adequate for plant growth, basal amounts of N, potassium (K), calcium (Ca), copper (Cu), zinc (Zn), sulphur (S) and manganese (Mn) were applied prior to seeding in year one as follows: gypsum 100 kg/ha, muriate of potash 50 kg/ha, zinc sulphate 13.3 kg/ha (Zn 2.0 kg/ha), copper sulphate 6.7 kg/ha (Cu 1.0 kg/ha) and manganese sulphate 12.5 kg/ha (Mn 4.0 kg/ha). All basal nutrients were mixed together except for urea and incorporated using a disc plough, working across plots. A total of 92 kg N/ha was applied as urea (i.e. 200 kg urea/ha) and split over two applications; at seeding and top-dressed at 11 weeks after sowing to minimise the interaction with biosolid N. An additional application of N was planned but cancelled due to dry seasonal conditions. No additional nutrients were applied in year two.

Table 4.2 Major soil properties of the top 0-10 cm as determined for a composite soil sample

Property	Description
Great Soil Group (GSG) (Stace 1968)	Lateritic podzolic
Australian Soil Classification Scheme (ASCS) (Isbell 1996)	Kurasol
Stones > 2mm	35%
Properties of < 2mm soil fraction	
Sand	87.5%
Silt	7.5%
Clay	5.0%
pH ($CaCl_2$) 0.01 M, 1:5 ratio	5.5
Total nitrogen	0.08%
Nitrate-nitrogen	1 mg/kg
Ammonium-nitrogen	11 mg/kg
Total phosphorus	110 mg/kg
Bicarbonate-extractable P	6 mg/kg
Phosphorus Retention Index (PRI)	100 mL/g
Bicarbonate-extractable K	180 mg/kg
Sulphur (KCl extract)	12 mg/kg
Organic carbon (W/B)%	2.68%
Reactive iron	370 mg/kg
Electrical conductivity (EC), 1:5	6 mS/m
Carbon/nitrogen ratio	33:1

Report 00A634/1-3 (CCWA 2000)

pH ($CaCl_2$) in 0.01 M $CaCl_2$ (Rayment & Higginson 1992i), total N (Blakemore, Searle & Daly 1987; Rayment & Higginson 1992f; Searle 1984), nitrate N and ammonium N extracted by 1 M KCl (Rayment & Higginson 1992f) p53, total P (Allen & Jeffery 1990; Murphy & Riley 1962), bicarbonate extractable P extracted by 0.5 M $NaHCO_3$ (1:100) (Colwell 1963; Rayment & Higginson 1992h), PRI (Allen & Jeffery 1990), Fe and Al extracted by 0.2M ammonium oxalate pH 3.25 (Rayment & Higginson 1992c), Organic carbon by Walkley and Black (1934) (Rayment & Higginson 1992g), EC (1:5) at $25^{o}C$ (Rayment & Higginson 1992b).

(mS/m = milliSiemens per metre, mg/kg = milligrams per kilogram, mL/g = millilitres per gram).

4.2.5 Application of biosolids and TSP

Approximately 2 t of fresh biosolids were delivered to the field site directly from Beenyup WWTP on 16 May 2001. Details specific to the production of biosolids at Beenyup are explained in section 1.2.

Biosolids rates were selected to fall within the TSP response surface, with initial target predictions of 10, 40, 70 and 120 kg P/ha based on long-term average composition for Beenyup WWTP (P_T of 2.2% db and 15% DM, Table 9.1). Slightly higher P_T loading were realised however, following subsequent analysis of biosolids samples used in the experiment (P_T of 2.96% db and 13.5% DM), section 4.2.7. Dry matter was determined on sub-samples of biosolids collected on the day of spreading, after they had been dried in a fan forced oven at 105^{o}C for 48 h.

Plots were marked out using coloured 3 mm rope and divided into six sub-plots using marking tape (every 5 m) and biosolids applied on a wet weight basis (Plate 4.2). Electronic Ruddweigh loading bars were used to weigh biosolids and wire-sieve livestock manure “pooper-scoopers” used to hand spread accurately over each sub-plot (Plate 4.3). Biosolids were spread within 72 h of being delivered to the site and incorporated to a maximum depth of 10 cm by discs during seeding, 48 h later. TSP was hand-broadcast to sub-plots to ensure an even rate and incorporated by discs during seeding.

4.2.6 Seeding

In year one, wheat (*Triticum aestivum* L. cv. Carnamah) was sown at 58.4 kg/ha to a depth of 2.5 cm in each plot on 18 May 2001 following the application of fertiliser treatments. Weeds were not a problem on this newly cleared site and in the first year herbicides were not required with a small number of capeweed, wild radish, tomato and ryegrass removed by hand weeding. The trial was not grazed over summer by livestock during the experimental period.

In year two, lupins (*Lupinus angustifolius* L. cv. Tallerack) were sown at a rate of 93 kg/ha on 10 May 2002. The site was sprayed with 2.0 L/ha of Simazine and 1.0 L/ha Glyphosphate one week prior to sowing. Fusilade was sprayed at 150 mL/ha to control self-sown wheat 6 weeks post seeding. For both crops a 12-row disc plough combine with 18 cm spacings between each row was used. The end rows were blocked off resulting in a 30 cm buffer between each treatment.

Plate 4.2 Biosolids used in the field experiment, May 2001

Plate 4.3 Selected plot showing highest rate of biosolids (4.9 t/ha) following hand application with “pooper scooper”, May 2001

4.2.7 Biosolids analysis

The major nutrient concentrations of biosolids used in the trial are presented in Table 4.3. Approximately 30 kg of biosolids from the stockpile used for the trial was frozen including three 100 g sub-samples collected at random on the day of spreading for analysis.

Table 4.3 Selected constituents in biosolids reported from the Beenyup Wastewater Treatment Plant (16 May 2001) as used in the field trial

Constituent	Value
Total nitrogen (N)	6.17%
Ammoniacal nitrogen (NH_3-N)	0.715%
Nitrate nitrogen (NO_3-N)	<10 mg/kg
Carbon (C)	40.6%
Total phosphorus (P)	2.96%
Potassium (K)	0.18%
Calcium (Ca)	4.47%
Zinc (Zn)	733 mg/kg
Copper (Cu)	1,500 mg/kg
Iron (Fe)	>4,000 mg/kg
H_2O	7.5% aa

Report 01A360/1-3 (CCWA 2000)

Total N by combustion; nitrate-N and ammonium-N by analysis in a continuous segmented flow auto-analyser (SFA); total P, K, Ca, Cu, Zn and Fe by ICP-AES; Total carbon, C by combustion.

Values are means of three sub-samples. Biosolids oven dried and reported as percent dry weight basis (%db), mg/kg = milligrams per kilogram, % aa = percent as analysed.

Biosolids sub-samples were dried at 40°C for 48 h, ground and passed through a 1 mm screen with P_T determined following digestion with nitric and perchloric acids using ICP-AES, which reported macronutrients to 0.01% precision (CCWA 2000; McQuaker, Brown & Kluckner 1979). The mean P_T of 2.96% db (sd = 0.08) was similar to the P_T in the glasshouse trials. In addition, three identical samples, freeze dried at minus 47°C for 48 h in a Heto Freeze Drier, gave a comparable P_T value of 3.0% db, with P_T determined by Allen and Jeffery (1990).

Plant available N (PAN) in Year One was estimated from N values in Table 4.3 using formula (1) (DEP, WRC & DOH 2002).

Available N (year one) = ammonium-N + 0.15 (total Kjeldahl N – ammonium-N), thus 15,335 mg N/kg (i.e. 7,153 + 8,182). This would provide approximately 6, 25, 44 and 75 kg N/ha respectively, for the four biosolids rates in addition to the basal 92 kg N/ha applied to all treatments.

4.2.8 Plant density and shoot dry matter

4.2.8.1 Wheat

Plant establishment counts were made on five, 0.5 m lengths of three rows in each plot (i.e. 1.35 m^2) with wheat plants counted at 26 days after sowing (DAS). Shoot dry matter (DM) was determined at 27, 67, 96 and 123 DAS from plants cut at ground level selected at random from the centre six rows and dried at 70^{o}C for 48 h in a forced draught oven. For the first three sampling dates, 40 plants were selected and for the final sampling date, 30 plants were selected. The average plant density for each plot was used to determine DM/m^2. Plant development including leaf number and tiller number was scored using the Zadoks (Z) decimal growth stage for cereals (Zadoks, Chang & Konzak 1974), using ten median plants measured at random in each plot every 6 weeks.

4.2.8.2 Lupins

Plant establishment counts were made on five, 0.5 m lengths of three rows in each plot at 28 DAS. Shoot DM was determined at 47, 98 and 165 DAS from plants cut at ground level, selected at random from the centre six rows and dried at 70^{o}C for 48 h in a forced draught oven. For the first sampling date, 30 plants were used, thereafter 20 plants. The calculated average plant density of 37 plants/m^2 was used to determine DM/m^2. Plant development (i.e. leaf number) was scored as described by Dracup and Kirby (1996) with ten median plants measured at random in each plot every 8 weeks.

4.2.9 Harvest and yield components

4.2.9.1 Wheat

Grain yield and above ground DM were determined at the final harvest at 179 DAS on four, 0.5 m by 6 rows in each plot (i.e. total area=2.16 m^2). The number of ears was counted, weighed, the ears threshed and 1,000 grain weight measured.

Ear weight was calculated by dividing grain yield by ear number. The number of grains per ear was calculated by dividing the ear weight by the weight of the grain.

Grain and DM samples were dried at 70°C for 48 h in a forced draught oven and then Harvest Index (HI) was determined by dividing grain yield by the total biomass of the crop (grain plus straw). A detailed description of wheat yield components is reported by Anderson and Garlinge (2000).

Spikelet rows per ear and grains per ear were determined from a sub-sample of 20 ears taken from a randomly selected 50 ears per plot.

In addition, the centre eight rows were mechanically harvested at 210 DAS and grain yield (kg/ha) calculated over the non-disturbed area (42 m^2).

4.2.9.2 Lupins

Lupins were mechanically harvested 211 DAS on 6 December 2002 using the centre eight rows and grain yield (kg/ha) calculated for each plot.

4.2.10 Plant tissue nutrient analysis

Whole dried plant samples collected from the determination of DM were used to determine plant concentrations of N and P. Grain sub-samples collected during machine harvest were used to determine grain N and P.

In wheat samples, a combustion technique was used to determine plant and grain N concentration. Total N was measured using a Leco FP-428 analyser. Samples were combusted in pure oxygen at 850°C whereby nitrogen oxides were converted to nitrogen with the removal of water, oxygen and carbon dioxide, and nitrogen measured by thermal conductivity by method PCM P03 (CCWA 2000).

Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) was used to determine plant and grain P concentrations. Plant material was milled through a 1.0 mm screen and organic material digested by heating to 250°C with nitric and perchloric acids followed by evaporation of nitric acid and addition of water. The solution was analysed by ICP-AES, which measured precision of macro-nutrients to 0.01% and trace elements to 1 µg/g (CCWA 2000; McQuaker, Brown & Kluckner 1979). ICP-AES also provided results for K, Ca, Mg, Na, S, Fe, Mn, Zn, and Cu, although the data are not presented.

Lupin grain samples were finely ground then analysed for N, P and K in a continuous segmented flow auto-analyser (SFA). Organic material was digested at 340°C with a mixture of salicyclic acid, sulphuric acid and hydrogen peroxide. Dilution was followed by automated colorimetry and flame photometry in a four-channel auto-analyser (CCWA 2000).

4.2.11 Soil analysis

4.2.11.1 Surface 0-10 cm

Bicarbonate extractable soil P (Colwell) was determined from composite samples consisting of 30 x 2 cm diameter random cores in the 0 - 10 cm depth from each plot. Over the duration of the experiment, soil samples were collected six times: 5 June 2001, 17 July 2001, 28 September 2001, 20 March 2002, 27 June 2002 and 24 January 2003, which covered periods throughout the growing season and following harvest for both crops. In addition, selected treatments were measured for nitrate-N, ammonium-N, total N and P_T over the growing season during these sampling dates.

Soil pH, organic carbon, nitrate-N, ammonium-N, total N and P_T were measured for all plots 10 months after the commencement of the trial on 20 March 2002 (305 DAS).

Bicarbonate extractable soil P (Colwell 1963) was determined and measured by automated colorimetry using a Technicon AA 2 segmented flow auto-analyser (CCWA 2000; Rayment & Higginson 1992h). Total P was determined as described by Allen and Jeffery (1990) using a modification of the Murphy and Riley (1962) molybdenum blue procedure. Soil samples were finely ground (< 0.2 mm) in a ring grinder and digested with sulphuric acid in the presence of potassium sulphate and a copper sulphate catalyst at 370^{o}C. The concentration of P_T in the diluted digest was measured by colorimetry as the phosphomolybdenum blue complex (Murphy & Riley 1962) on a spectrophotometer (CCWA 2000).

Ammonium-N and nitrate-N were extracted in 1 M KCl (Rayment & Higginson 1992f) and total N was measured as ammonium-N by automated colorimetry by the nitroprusside-dichloro-S-triazine modification (Blakemore, Searle & Daly 1987) of the Berthelot indophenol reaction reviewed by Searle (1984) and measured using a spectrophotometer at 660 nm (Rayment & Higginson 1992f). The concentration of total N was reported to the nearest 0.001%.

Soil pH (1:5) was measured in 0.01 M $CaCl_2$ (Rayment & Higginson 1992i). Organic carbon was measured by the method of Walkley and Black (1934) as described by Rayment & Higginson (1992g).

4.2.11.2 Depth sampling to 30 cm

Soil composite samples consisting of five, 50 mm diameter cores were collected in the 0-10 cm, 10–20 cm and 20–30 cm depths for control plots and the top rates of TSP and biosolids (i.e. 0 kg P/ha, 120 kg P/ha as TSP and 145 kg P/ha as biosolids) on 21 March 2002 at 10 months (306 DAS crop 1) to monitor nutrient movement, particularly N and P. Measurements were conducted for ammonium-N, nitrate-N, total N, pH, organic carbon and P_T as described previously in section 4.2.11.1, electrical conductivity EC (1:5) at 25°C (Rayment & Higginson 1992b), potassium extracted in 0.5 M NaHCO3 (1:100) (Rayment & Higginson 1992d); PRI (Allen & Jeffery 1990), iron and aluminium (AmOx) extracted in 0.2 M ammonium oxalate pH 3.25 (Rayment & Higginson 1992c), sulphur extracted in 0.25 M KCl (Blair et al. 1991); and exchangeable calcium, magnesium, sodium and potassium extracted in 1 M NH_4Cl at pH 7.0 (Rayment & Higginson 1992e).

4.2.11.3 Soil fractions (<2 mm, 2 to 4.7 mm and >4.7 mm)

During the final sampling on 24 January 2003, almost two years after the initial application, the soil fraction >2.0 mm typically discarded for nutrient analysis was further separated into the 2.0 to 4.7 mm, and >4.7 mm soil fractions. Three treatments were analysed: the control; the highest rate of TSP; and the highest rate of biosolids. Soil samples were ground and analysed for total P and total N as described in section 4.2.11.1.

4.2.12 Statistical analysis

Data were analysed for differences between the biosolids and TSP treatments in DM production, N uptake, P uptake and grain yield using an ANOVA model in GENSTAT as previously described in section 3.2.11. A single least significant difference (LSD) value of probability (*P*) at the 5% level of significance was used for comparing results between treatment means.

4.2.13 Calculation of relative effectiveness and residual value

Data for the relationship between P rates and the DM production (kg/ha), P uptake (kg P/ha) and grain yield (kg/ha) for each of the biosolids, TSP and TSP (year 2) treatments were fitted to a Mitscherlich equation:

Equation 1

$$y = a\,(1 - b \exp^{-cx}) \qquad (1)$$

where y is the parameter being measured, x is the level of P applied (kg P/ha), and a, b and c are coefficients.

To find the parameters that produce the closest fit of a distribution to the observed data, goodness-of-fit statistics were used with a linear solver (Vose 1996). The solver program in Microsoft Excel was used to fit curve coefficients to a common start and end point for each parameter for biosolids, TSP and TSP (year 2) using the means of three replicates.

The percentage RE of biosolids compared with TSP for any year was determined by dividing the coefficient (c) value of biosolids by TSP as based on equation (1). Thus the RE of freshly applied TSP is always 1.00. The percentage RV of biosolids and TSP was similarly determined against freshly applied TSP in year two by dividing the coefficient (c) value of biosolids or TSP by freshly applied TSP.

4.3 Results

4.3.1 Initial year of application: wheat crop

4.3.1.1 Weather conditions

During the first year of the field experiment (2001), the growing season (May-October) was 35% below average and followed a seven-month dry spell, with 339 mm rainfall recorded for the year. The trial was sown into dry conditions on 18 May 2001 following 41 mm of rain with a further 34 mm of rain recorded over the next four weeks. Rainfall continued to be below average, with July one of the driest on record, apart from a 58 mm fall on the last day of the month. The total monthly rainfall, which highlights the dry conditions, and mean monthly temperatures have been shown in Figure 4.1. The average June rainfall for this area is typically 100 mm. The dry conditions meant that penetration with the disc plough could not be fully achieved and less N was top-dressed than planned. The season finished reasonably well.

4.3.1.2 Plant establishment and development

Wheat establishment in year one ranged from 116 to 154 plants/m^2 with a mean of 137 plants/m^2. The mean plant density in each plot was used to calculate the DM of wheat shoots in kg/ha. A small number (22 plants/m^2) of *'Aroona'* wheat germinated from stubble residue from the previous season's crop, but were not very vigorous and therefore not used to calculate plant density.

Poor growth and development in wheat plants were noted where no P was applied compared with the highest rates of P (Plate 4.4). Control plants failed to produce tillers, with necrotic symptoms developing on old leaves. Tillering was observed at >10 kg P/ha treatments as early as 27 DAS for both TSP and biosolids. Tiller numbers were variable within plots, with plants typically ranging from nil to up to five tillers by 123 DAS at the highest rates of P and averaging 1.7 tillers. Plant development was variable in biosolids treatments consistent with the uneven mixing of biosolids into the soil. In particular, plant growth appeared to be improved in rows where the biosolids had been compacted by vehicle tyres during seeding, although this became less obvious with time. Plant sampling at random ensured that representative plants were collected for analysis.

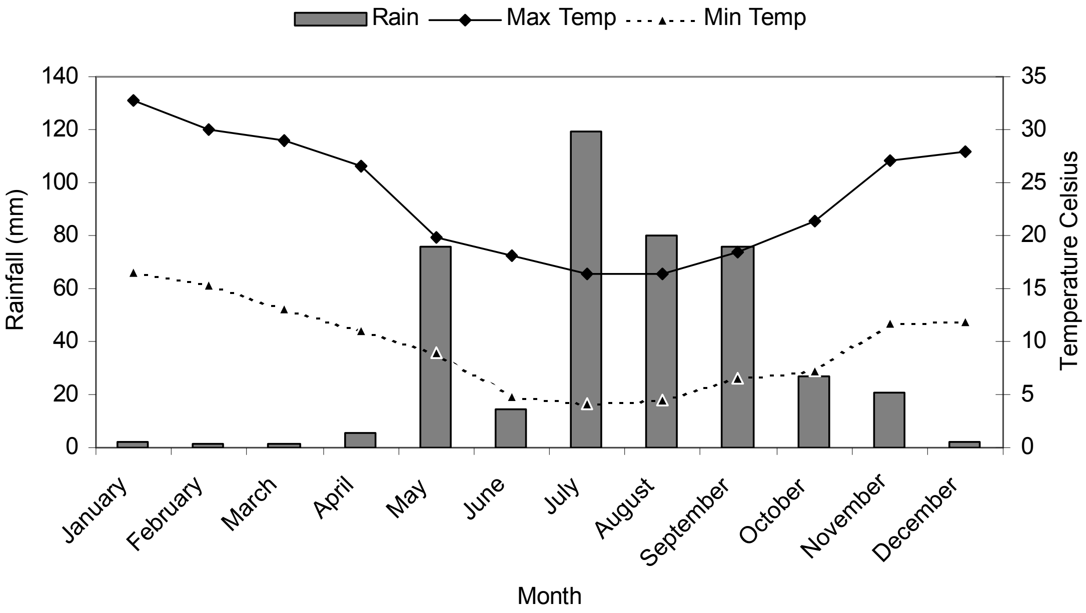


Figure 4.1 Total monthly rainfall, mean monthly maximum and minimum temperature at Inkpen, Western Australia in 2001

Rainfall is the cumulative for each month, whereas temperature is the mean of daily values for each month.

Plate 4.4 Vegetative growth differences in wheat between the nil plot (left) and highest rate of biosolids 145 kg P/ha (right) at 96 DAS

4.3.1.3 Dry matter accumulation

The seasonal DM of wheat shoots showed a positive response to increasing rates of both TSP and biosolids, which became more apparent with time on the infertile yellow gravelly loamy sand (Table 4.4). Plant growth improved as P_T loadings increased, irrespective of the P source, with top-dressed TSP showing a greater rate of response than biosolids.

Table 4.4 Mean seasonal production of shoot dry matter of wheat (g/m^2) in response to P applied as triple superphosphate (TSP) or biosolids

Total P rate and source (kg P/ha)	**Days after sowing (DAS)**			
	27	**67**	**96**	**123**
0 Control	3.9	13.8	41.0	163
TSP				
5	4.7	17.8	55.3	189
10	5.1	25.6	98.0	308
20	5.8	38.5	141	411
40	6.0	48.3	169	498
70	6.4	51.1	173	532
120	7.3	56.6	201	467
Biosolids				
12	4.5	23.5	76.0	240
48	4.9	30.6	126	363
85	6.0	44.4	170	530
145	7.0	42.8	168	564
LSD (P = 0.05)	**1.6**	**9.2**	**47.4**	**92.8**

Where the difference between any two values in any column is greater than the LSD, then those values are significantly different at P <0.05. Values are the means of three replicates. Coefficients of variation for each sampling time are as follows: 27 DAS = 16.5%, 67 DAS = 15.7%, 96 DAS = 22%, 123 DAS = 13.8%

4.3.1.4 Phosphorus and nitrogen uptake

The concentration of P in the DM of whole shoots of wheat showed a positive response to increasing levels of P. Over the duration of the growing season, mean concentrations of P in shoot DM declined with the overall means: 0.27% (sd = 0.081), 0.26% (sd = 0.04), 0.22% (sd = 0.032) and 0.086% (sd = 0.014) for 27, 67, 96 and 123 DAS, respectively. Compared with critical values given in Reuter and

Robinson (1997), wheat shoots were P deficient for all sampling dates with the only exception being at 96 DAS for rates >70 kg P/ha.

Mean total P uptake by wheat plants for each of the four sampling dates (Figure 4.2) followed similar trends for DM uptake. At all P loading rates and sampling dates the application of TSP resulted in higher P uptake than similar rates of P in biosolids. Differences were significant (*P* <0.05) at 27 and 67 DAS between TSP and biosolids. However by 96 DAS the differences became less apparent.

Over the duration of the growing season, N concentrations declined with overall means as follows, 4.7% (sd=0.014), 3.7% (sd=0.25), 2.9% (sd=0.29) and 1.28% (sd=0.16) for 27, 67, 96 and 123 DAS, respectively. At all sampling dates and for all rates, the N concentrations were below the critical concentration required for maximum yield based on equivalent growth stages (Reuter & Robinson 1997).

Mean total N uptake by wheat shoots increased with increasing rates of either TSP or biosolids at all sampling dates (Figure 4.3). There were no differences in N uptake at 27, 67 and 96 DAS between TSP and biosolids at comparable P loadings. However by 123 DAS, the highest rate of TSP (120 kg P/ha) displayed low N uptake relative to the highest rate of biosolids (*P* <0.05). Nitrogen uptake in the highest rate of TSP reached a plateau, whereas N uptake in the highest rate of biosolids had not.

4.3.1.5 Grain yield

Mean grain yields of wheat for TSP and biosolids treatments at all rates of P for machine harvests are presented in Figure 4.4. Overall, TSP produced higher grain yields at comparable P loadings with significant differences in grain yield at the lowest levels of P (*P* <0.05). At rates above 70 kg P/ha there were no differences in grain yield between the two P sources (*P* <0.05). The improvement in grain yield in biosolids treatments at the higher rates of P was concomitant with N uptake curves.

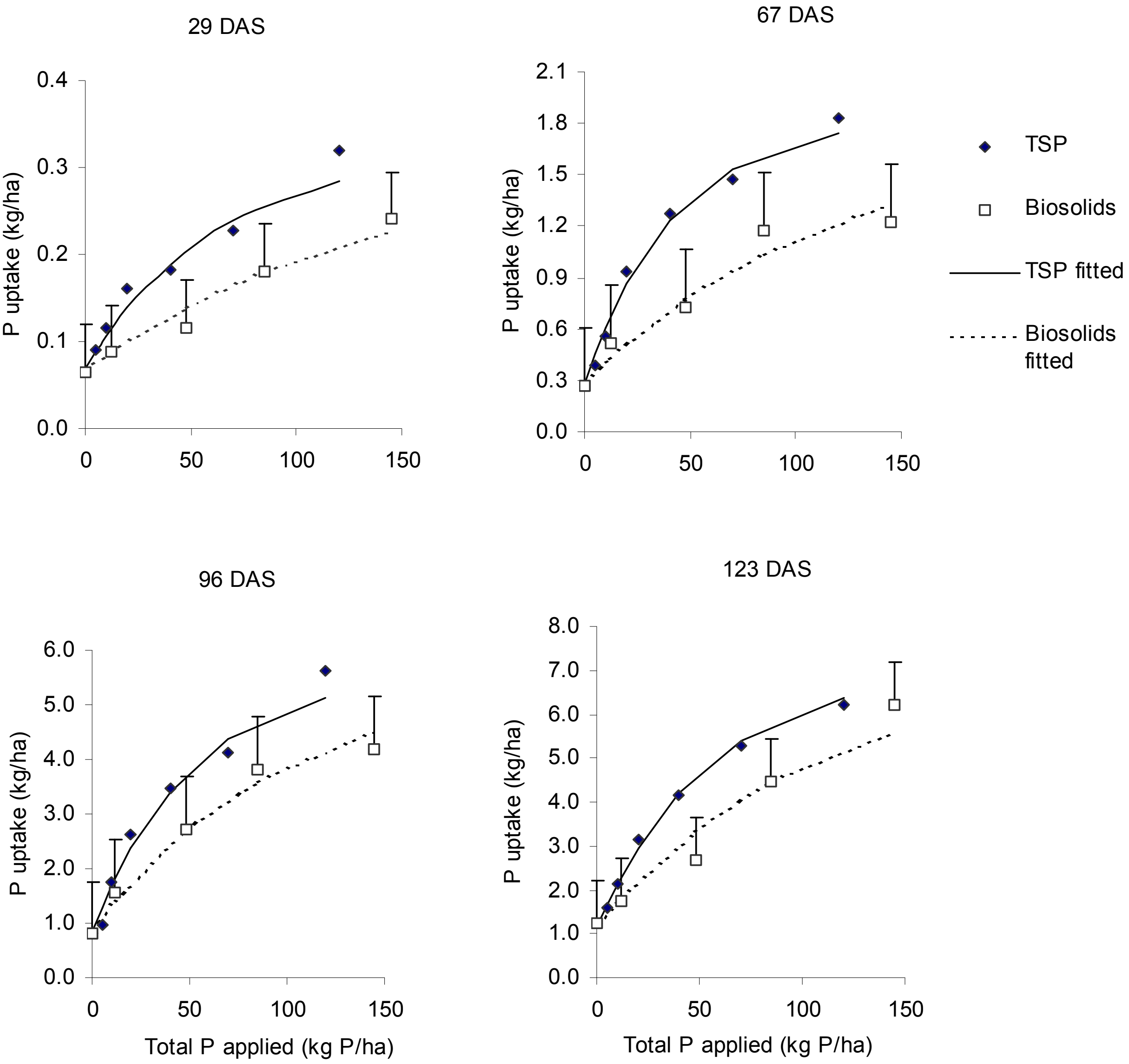


Figure 4.2 Relationship between P uptake in wheat shoots and the level of P applied in TSP and biosolids over four sampling dates

Values are the means of three replicates. Lines are fitted to equation (1) and coefficients are listed in Table 4.5. BS=biosolids. Vertical bars denote LSD (P = 0.05) for data from all treatment means. Note that the *y-axis* is plotted on different scales.

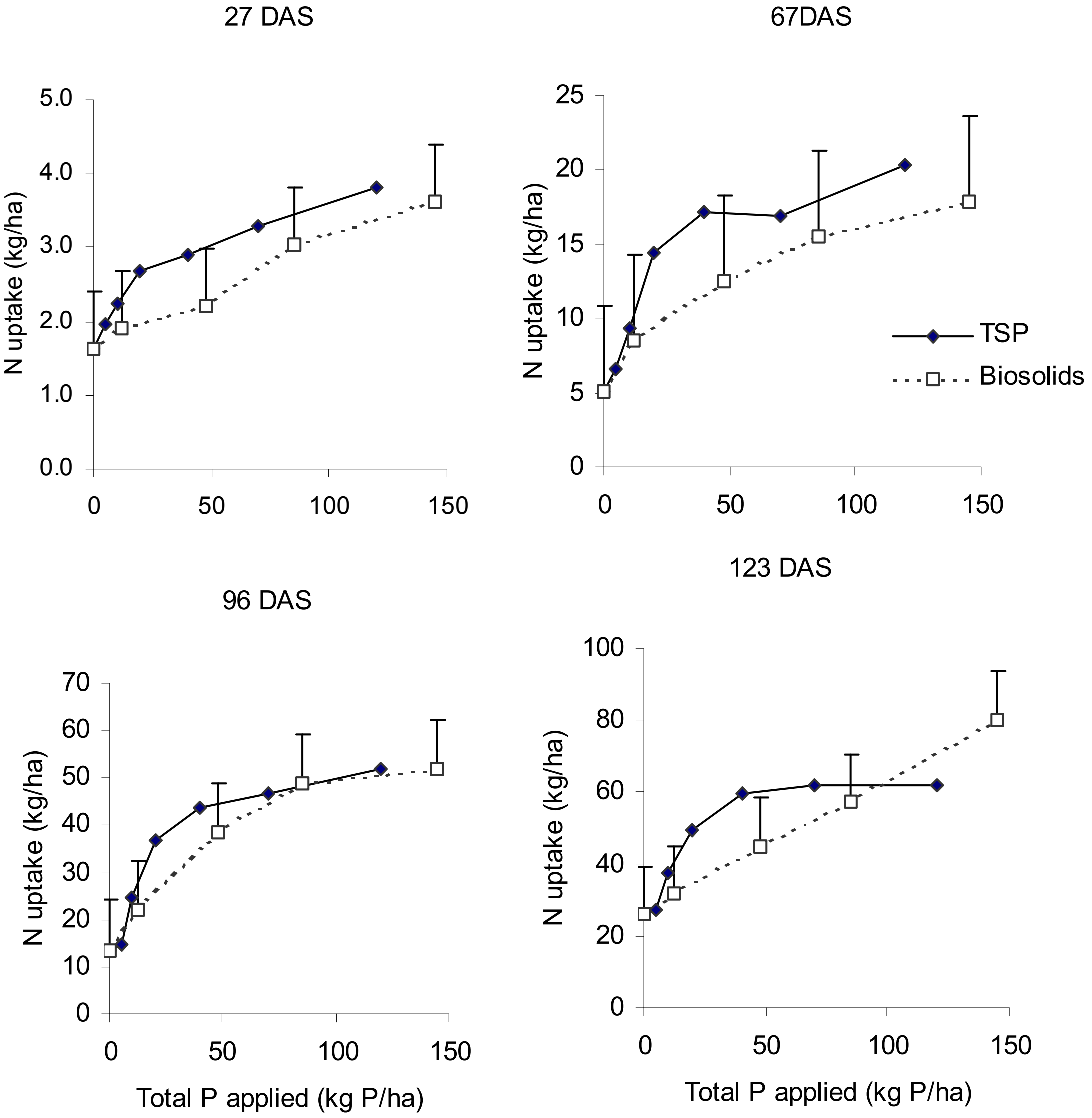


Figure 4.3 Relationship between total N uptake in wheat shoots and the level of P applied in TSP and biosolids over four sampling dates

Values are the means of three replicates. Line plotted using Microsoft Excel. Vertical bars denote LSD (*P* = 0.05) for data from all treatment means. Note that the *y-axis* is plotted on different scales.

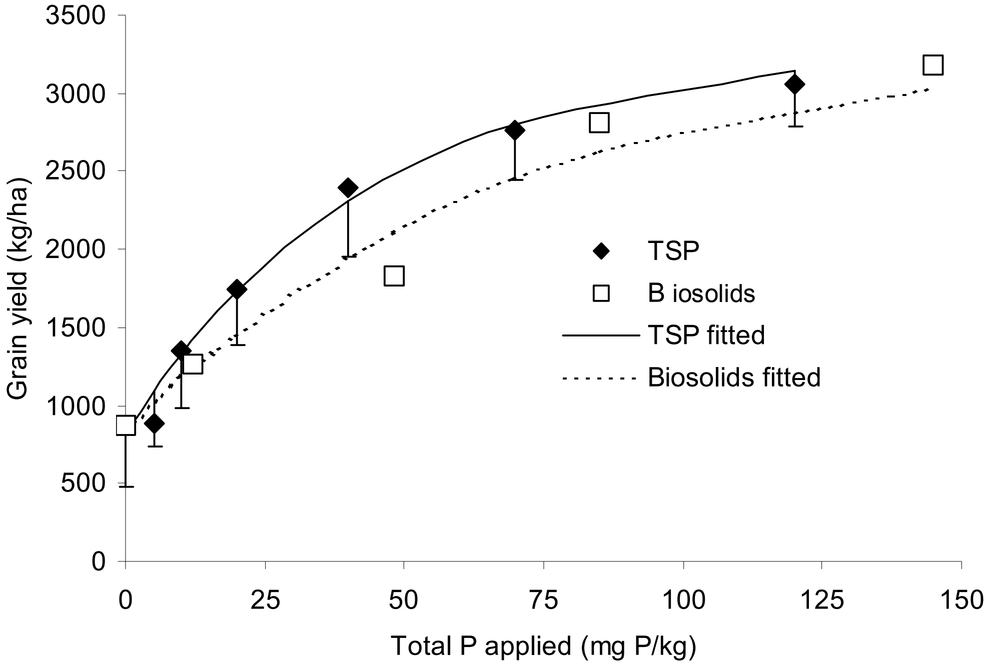


Figure 4.4 Relationship between wheat grain yield and the level of P applied in TSP and biosolids at harvest

Values are the means of three replicates. Lines are fits to equation (1) with coefficients listed in Table 4.5. Vertical bars denote LSD (*P* = 0.05) for data from all treatment means. Coefficient of Variation CV% = 10.8.

4.3.1.6 Relative effectiveness of biosolids compared with TSP during the growing season

Values for Mitscherlich coefficients for DM production, P uptake and grain yield in wheat over the four sampling dates are summarised in Table 4.5. The ratio of the *c* coefficients was used to obtain percentage RE value of biosolids compared with TSP. Overall the RE of biosolids compared with TSP increased as the growing season progressed, with the highest value of 67% determined at grain yield.

Table 4.5 Values of coefficients for equation (1) for the relationships between P supply and shoot dry matter of wheat or shoot P uptake over four sampling dates and grain yield including the percentage relative effectiveness (RE) of biosolids (BS) compared with TSP

	Coefficients				
Days after sowing	***a***	***b***	***c* (TSP)**	***c* (BS)**	**%RE**
		Dry matter (g/m^2)			
27	6.7	0.42	0.050	0.015	**31**
67	59.4	0.75	0.032	0.0096	**30**
96	200.0	0.79	0.040	0.016	**40**
123	584.7	0.74	0.037	0.018	**46**
		Shoot P uptake (kg/ha)			
27	0.32	0.78	0.016	0.0068	**42**
67	1.83	0.84	0.024	0.0079	**33**
96	5.60	0.85	0.019	0.010	**53**
123	7.00	0.84	0.018	0.0099	**55**
		Grain Yield (kg/ha)			
210	3,300	0.75	0.023	0.015	**67**

Calculated using Microsoft Excel Solver for equation (1) and ratio of *c* coefficient determines % relative effectiveness. Coefficent values for *a* and *b* were identical for TSP and biosolids. Grain yield based on machine harvest at 210 DAS. The standard error of the RE is approximately 10%.

4.3.1.7 Yield components and other harvest measurements

Total DM production, grain yield, harvest index, ear weight, ear number/m^2, number of grains per ear, grain number/m^2 and 1,000 grain weight of wheat increased as applied P increased in the final hand harvest sampling at 179 DAS ($P < 0.05$;Table 4.6). There was a strong correlation between grain yields in the hand harvest at 179 DAS compared with the machine harvest at 210 DAS ($r^2 = 0.89$). The coefficient of variation in grain weight in the hand harvest measured 24%, whereas the machine harvest showed less variation at 10.8%. The machine harvest results were used to calculate the RE values, given the lower CV% and the larger sampling area used.

The mean concentration of P in grain from all treatments was 0.14% with the highest concentration of 0.18% at the highest rate of TSP. The mean concentration of P in grain was slightly higher for all rates of TSP compared with biosolids, although the difference was not significant ($P > 0.05$). The mean concentration of N in grain was 1.67% over all treatments and generally decreased as P loading rates increased. Biosolids treatments resulted in higher concentrations of grain N compared with TSP treatments at similar P loadings.

Mean total P and N uptake values by wheat grain are shown in Figure 4.5, indicating P uptake in TSP to be significantly higher at P rates between 25 and 75 kg P/ha compared with biosolids ($P < 0.05$). At loading rates >75 kg P/ha, the N uptake in wheat grain for TSP was steady whilst N uptake for biosolids continued to increase, with significant differences apparent above that for TSP ($P < 0.05$, Figure 4.5).

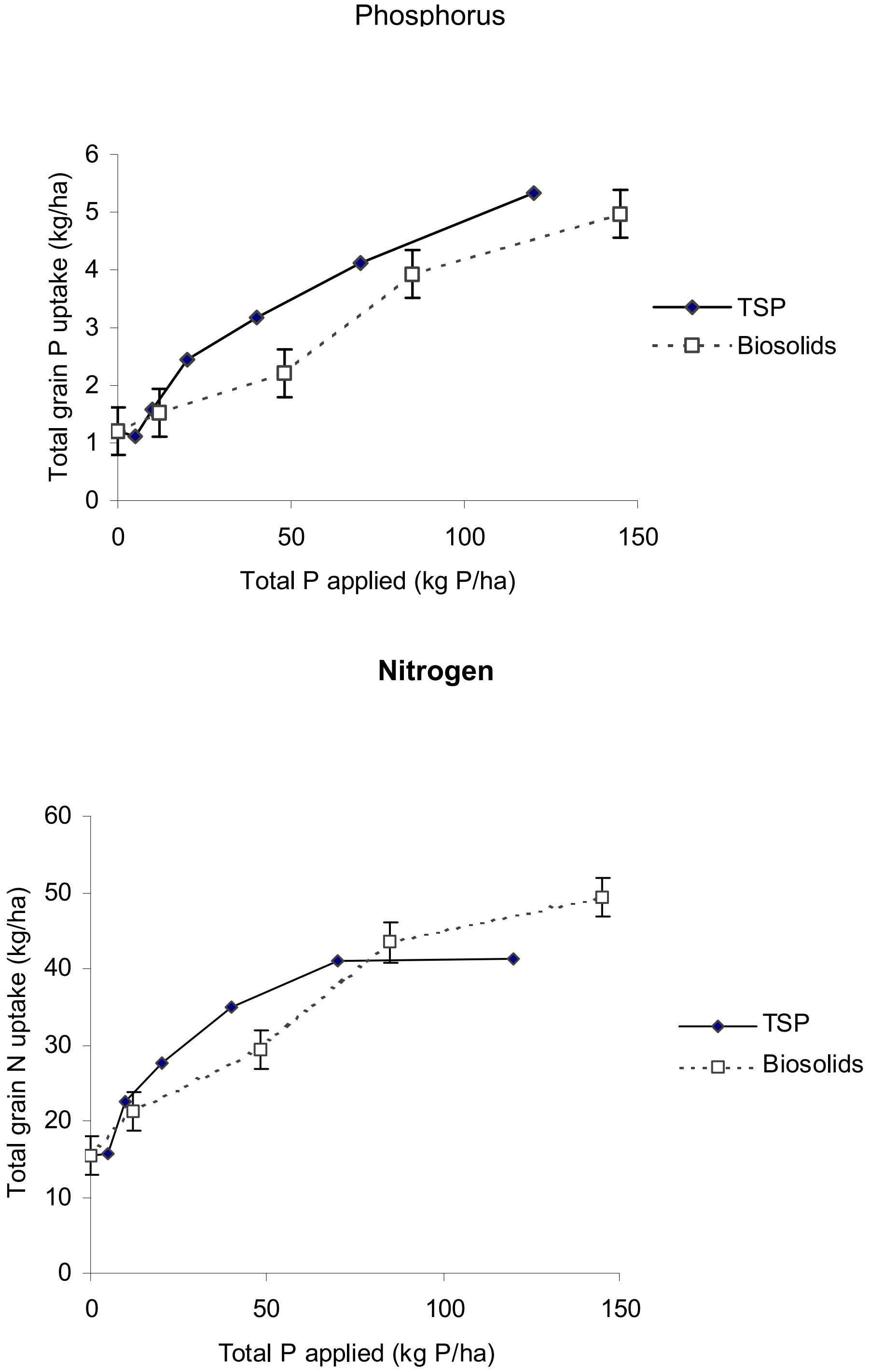


Figure 4.5 Relationship between the uptake of phosphorus and nitrogen in wheat grain and the level of P applied in TSP and biosolids

Values are the means of three replicates. Vertical bars denote LSD (*P* = 0.05). Lines between points plotted using Microsoft Excel. Coefficient of Variation for phosphorus CV = 17.1%, Nitrogen CV = 9.8%.

Table 4.6 Yield components and other harvest measurements of wheat for TSP and biosolids at final hand harvest at 179 DAS

P source and rate (kg/ha)	Total dry matter (g/m^2)	Harvest index	Ear weight (g)	Number of grains/ ear	Ear number/ m^2	Grain number/ m^2	1000 grain weight (g)	Grain yield (g/m^2)
Control	241	0.31	0.43	10.4	174	1,826	41.3	75
TSP								
5	273	0.29	0.42	10.3	183	1,883	40.9	77
10	347	0.32	0.54	13.0	209	2,686	41.7	112
20	414	0.28	0.59	13.7	198	2,708	43.2	117
40	579	0.28	0.62	14.1	259	3,682	44.0	162
70	577	0.37	0.87	19.2	241	4,648	45.4	211
120	697	0.37	0.91	20.0	287	5,749	45.4	261
Biosolids								
12	314	0.29	0.45	11.0	204	2,244	41.0	92
48	423	0.27	0.52	12.0	219	2,639	43.2	114
85	510	0.33	0.78	17.5	219	3,854	44.6	172
145	585	0.36	0.83	18.7	261	4,876	44.3	216
LSD (P = 0.05)	**111**	**0.08**	**ND**	**ND**	**ND**	**ND**	**1.4**	**60.7**

ND = Determined through calculation, so LSD not determined. Where the difference between any two values in any column is greater than the LSD, then those values are significantly different at P <0.05.

All methodology and calculations described in Chapter 4, section 4.2.9.1.

.

4.3.2 Residual effects in year two: lupin crop

4.3.2.1 Weather conditions

In year two (2002), lupins were sown on 10 May following opening rain, which was then followed by a dry spell. Adequate rainfall in June and July (126 mm and 121 mm, respectively) ensured lupins established well, although August was relatively dry. A reasonable spring rain in September ensured potential yields were not limited. The total rainfall for the year (520 mm) was similar to the long-term average (Figure 4.6).

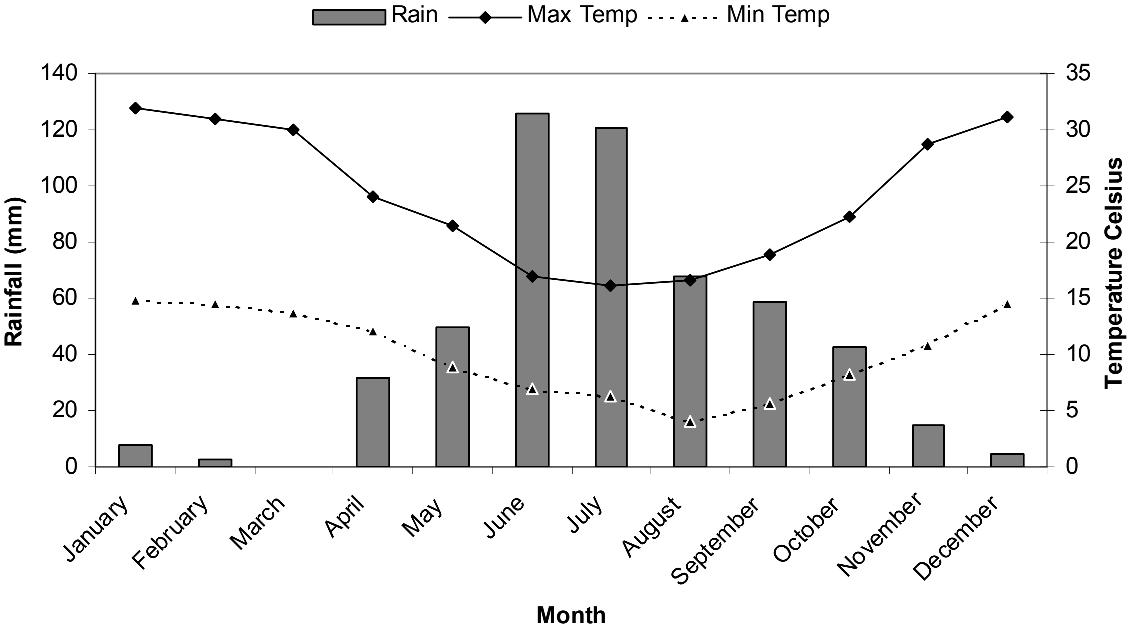


Figure 4.6 Total monthly rainfall, mean monthly maximum and minimum temperature at Inkpen, Western Australia in 2002

Rainfall is the cumulative for each month, whereas temperature is the mean of daily values for each month.

4.3.2.2 Plant establishment, development and dry matter accumulation

The wheat stubble residue from the previous season interfered with seed placement and hence germination of lupin seedlings in all plots, which ranged from 23 to 53 plants/m^2. The mean plant density of 37 plants/m^2 was used to determine DM in kg/ha (data not presented).

There were only slight differences in seasonal DM production of lupin shoots between the residual TSP and residual biosolids treatments at most P loading rates (Table 4.7, Plate 4.5). The dry growing conditions early in the season contributed to slow lupin growth as evident at 47 DAS. By 98 DAS, the DM accumulation in TSP treatments exceeded that for lupins grown in biosolids (*P* <0.05), except at the highest rates. By 165 DAS, lupin DM accumulation was significantly higher in the highest TSP treatment only. At all sampling dates, the freshly applied top-dressed TSP contributed to greater DM production compared with the P applied from both sources in the previous year.

Table 4.7 Mean seasonal production of shoot dry matter of lupin (g/m^2) in response to P applied as triple superphosphate (TSP), biosolids or freshly applied TSP (TSP 2)

P rate and source (kg P/ha)	Days after Sowing (DAS)		
	47	**98**	**165**
0 (Control)	7.9	10.1	26.9
TSP			
5	8.4	16.2	33.9
10	7.1	22.6	113.6
20	8.4	31.3	239.9
40	7.9	60.9	506.5
70	8.1	96.7	675.5
120	8.7	111.3	1,136*
Biosolids			
12	8.6	15.4	58.5
48	8.4	37.6	427.4
85	9.0	81.5	844.5
145	9.5	133.3	1,035
TSP (2)			
20	9.0	42.3	224.3
40	9.2	89.5	783.1
80	10.4	136.0	1,021
LSD (*P = 0.05*)	**1.4**	**23.6**	**198.4**

Values are the means of three replicates. Where the difference between any two values in any column is greater than the LSD, then those values are significantly different at *P* <0.05. Coefficients of variation for each sampling time as follows: 47 DAS = 9.7%, 98 DAS = 21.7%, 165 DAS = 22.4%. * Value of two means only.

Plate 4.5 Vegetative growth of lupin in year two at anthesis (flowering) showing responses of the 145 kg P/ha biosolids (left), 120 kg P/ha TSP (right) and nil-P on far left

Plate 4.6 Differences in lupin growth at anthesis (flowering) between the nil P treatment (foreground) and the 145 kg P/ha as biosolids treatment (background)

4.3.2.3 Shoot phosphorus and nitrogen uptake

Throughout the growing season, P uptake in lupin shoots increased with increasing P applied and with progressive sampling dates (Figure 4.7). Uptake of P in shoots was similar between TSP and biosolids over all sampling dates, whereas freshly applied TSP showed greater P uptake ($P < 0.05$) compared with the previous season's TSP or biosolids at 47 and 98 DAS. At 47 DAS, P deficiency in shoot tissue DM was not apparent with the mean whole shoot concentration of P being 0.22%. However, at 98 and 165 DAS lupin shoot tissue concentrations of P in most treatments were P deficient (Reuter & Robinson 1997). The mean total percentage P in shoots over all treatments at 98 DAS was 0.24% (0.12 to 0.34%) and by 165 DAS had decreased to 0.10% (0.08 to 0.14%).

There were no significant differences in N uptake in lupin shoots between TSP and biosolids treatments at comparative P loadings from 98 DAS ($P > 0.05$, data not presented). However, earlier in the season at 47 DAS, N uptake was greater in biosolids treatments ($P < 0.05$). Freshly applied TSP produced greater N uptake than either TSP or biosolids, which also increased proportionately to P uptake.

4.3.2.4 Grain yield and phosphorus and nitrogen uptake

The relationship between lupin grain yield and freshly applied TSP, residual P from biosolids and TSP are shown in Figure 4.8. Fitted curves indicate decreasing yields in the order TSP2 > TSP > biosolids at comparable rates of P.

Grain P concentrations increased from 0.22% to 0.30% as applied P increased, with total grain P uptake from 0.1 kg P/ha to 7.2 kg P/ha. Mean total grain P uptake was greater in TSP compared with biosolids at P application rates >20 kg P/ha ($P < 0.05$). As the trend was similar to grain yield (Figure 4.8), the data are not presented.

The mean grain N concentration over all treatments was 5.62% (sd = 0.014%) and not significantly different ($P > 0.05$) for treatments, irrespective of P rate or source. Grain N uptake resembled Figure 4.8 for grain yield and therefore data are not presented (ranged from 2.6 to 136 kg N/ha). The mean total N uptake was greater in TSP treatments than biosolids at comparable P loadings ($P < 0.05$).

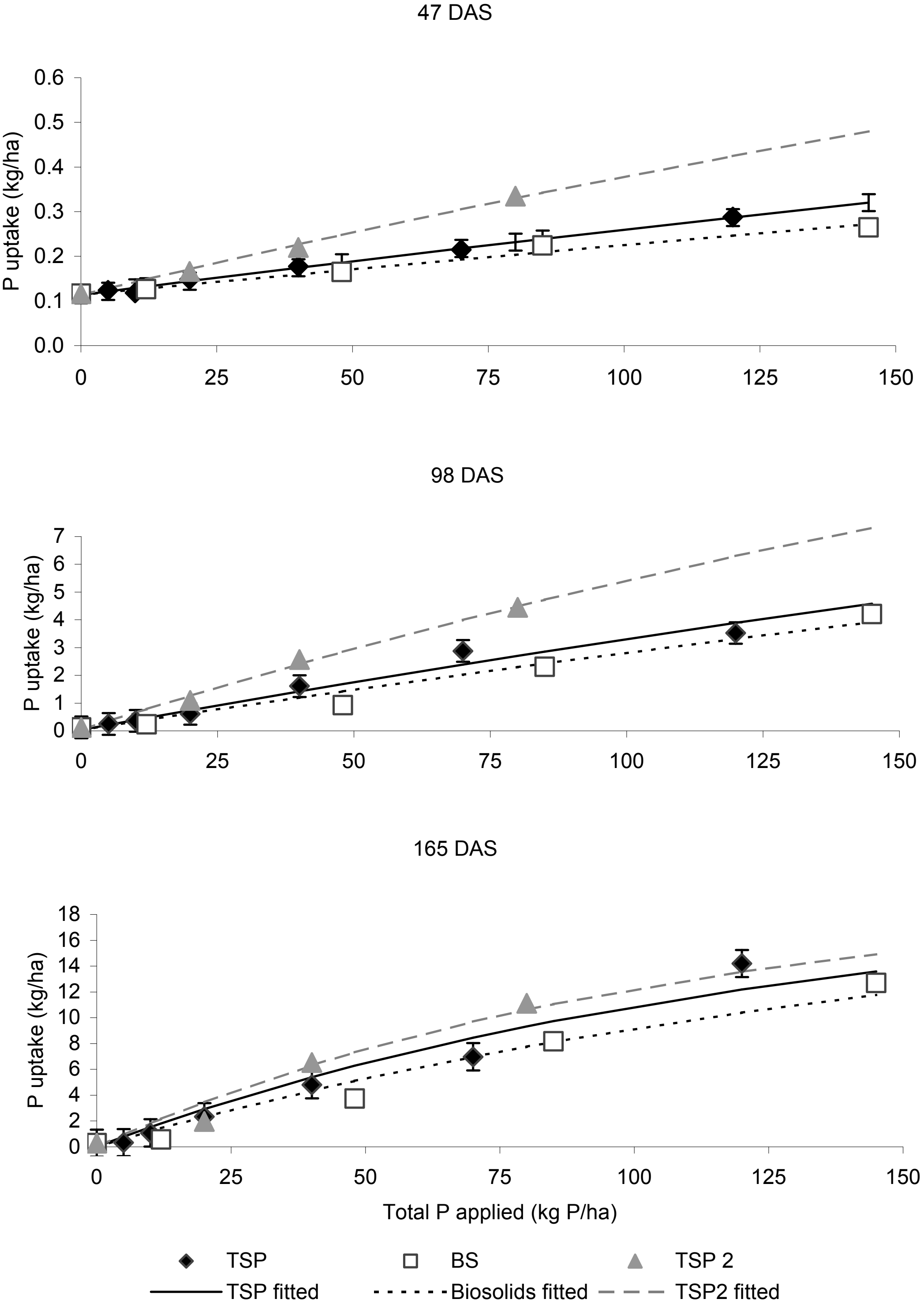


Figure 4.7 Relationship between mean total P uptake in lupin and P applied in TSP, biosolids (BS) and freshly applied TSP (TSP 2) at three sampling dates

Fitted lines plotted using Microsoft Excel Solver from equation (1) with coefficients given in Table 4.8. Vertical bars denote LSD (P = 0.05). Values are means from three replicates. Note that the *y*-axis is plotted on different scales.

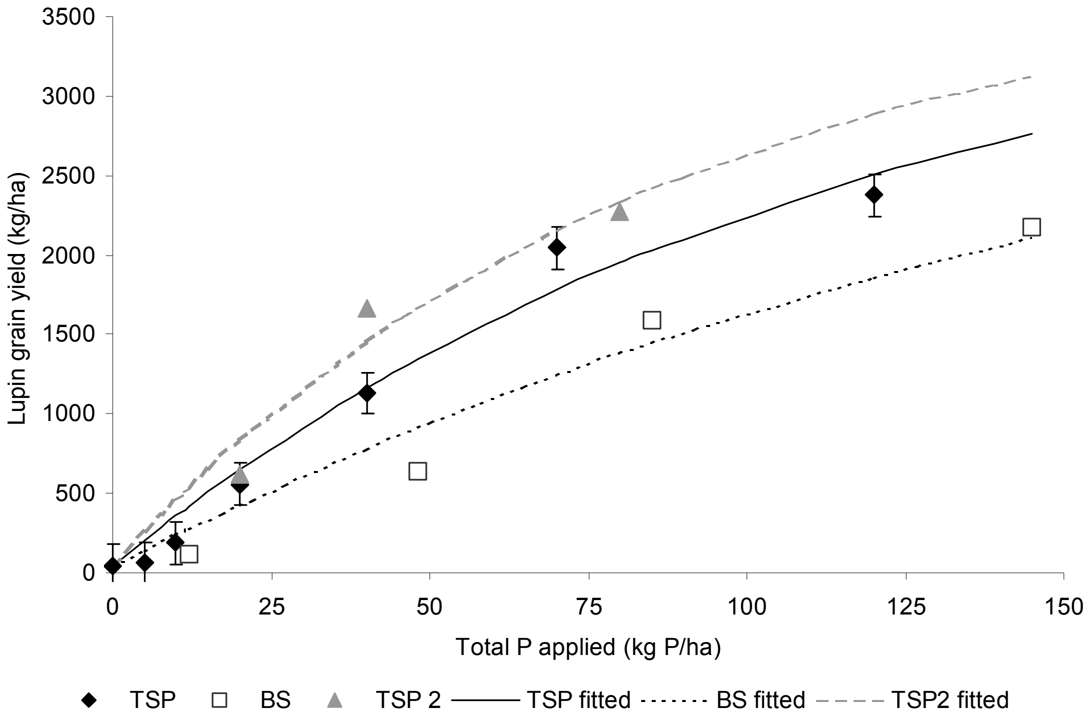


Figure 4.8 Relationship between lupin grain yield and the level of P applied in TSP, biosolids (BS) and freshly applied TSP (TSP2)

Values are the means of three replicates. Vertical bars denote LSD (P = 0.05) from all treatment means. Fitted curve coefficients determined from equation (1) using Microsoft Excel Solver with values listed in Table 4.8.

4.3.2.5 Relative effectiveness of biosolids compared with TSP during growing season and residual effectiveness compared with freshly applied TSP

The RE for biosolid P in the second season compared with TSP (year 1) was 84% for DM and 78% for P uptake at 165 DAS (Tables 4.8 and 4.9). The RE for the P value in biosolids compared with TSP for final lupin grain yield was 60%.

Freshly applied TSP was more effective as a source of P than comparable P loadings from either TSP or biosolid P from the previous season, as indicated by the RV for DM and P uptake over all sampling dates (Tables 4.8 and 4.9). The RV of biosolids was lower than that of TSP when compared with freshly applied TSP (TSP 2), at 45% and 75%, respectively for grain yield at 211 DAS (Table 4.9).

Table 4.8 Coefficients of the Mitscherlich equations for biosolids (BS), TSP and freshly applied TSP (TSP2) for seasonal lupin dry matter, shoot P uptake and final grain yield over four sampling dates

Days after sowing	*a*	*b*	*c* (TSP)	*c* (BS)	*c* (TSP2)
			Dry matter (g/m^2)		
98	135	0.92	0.014	0.010	0.025
165	1,400	0.99	0.011	0.009	0.016
			Shoot P uptake (kg/ha)		
47	0.5	0.78	0.0048	0.0036	0.0095
98	6.0	0.98	0.0077	0.0062	0.0143
165	18.0	0.99	0.0089	0.0061	0.0095
			Grain yield (kg/ha)		
211	3,000	0.99	0.0129	0.0070	0.0107

Calculated using Microsoft Excel Solver for equation (1) and ratio of *c* coefficient determines % relative effectiveness. Coefficent values for *a* and *b* were identical for TSP and biosolids. Values for DM at 47 DAS not presented due to plants being of insufficient size to accurately determine coefficients.

Table 4.9 Percentage relative effectiveness (RE) of biosolids (BS) compared with TSP and percentage residual value (RV) of BS and TSP compared with freshly applied TSP for seasonal lupin dry matter, shoot P uptake and final grain yield over four sampling dates

Days after sowing	%RE of (BS/TSP)	%RV (BS/TSP2)	%RV (TSP/TSP2)
		Dry matter (g/m^2)	
98	76	42	55
165	84	57	68
		Shoot P uptake (kg/ha)	
47	74	38	50
98	80	43	54
165	78	65	83
		Grain yield (kg/ha)	
211	60	45	75

Ratio of *c* coefficient presented in Table 4.8 determines % relative effectiveness. Values for DM at 47 DAS not presented due to plants being of insufficient size to accurately determine coefficients. The standard error of the RE is approximately 10%.

4.3.3 Soil measurements over two years (0-10 cm)

4.3.3.1 Bicarbonate extractable soil P

Bicarbonate extractable P in the <2 mm soil fraction increased with increasing TSP rates, with major changes noticeable at 18 DAS in year one, thereafter values decreased with progressive sampling dates (P <0.05, Table 4.10). There was little change in bicarbonate extractable soil P with any biosolids application over the first year of the sampling dates.

Table 4.10 Mean concentrations of bicarbonate extractable soil P (mg P/kg) following the application of triple superphosphate (TSP) and biosolids for over two years after sowing

	Days after sowing of first crop and sampling date					
	18	**60**	**133**	**305**	**405**	**615**
	5/6/01	**17/7/01**	**28/9/01**	**20/3/02**	**27/6/02**	**24/1/03**
P rate (kg P/ha)						
0 (Control)	6.3	6.0	4.7	5.0	4.0	5.0
TSP						
5	9.0	9.3	5.3	8.3	5.7	5.0
10	12.3	9.0	9.7	8.3	7.0	6.0
20	19.7	13.3	11.3	7.3	7.0	6.7
40	23.3	32.7	18.3	14.0	11.0	10.3
70	44.0	33.0	22.7	17.3	21.3	18.7
120	112.0	51.0	46.0	28.0	28.7	21.3
Biosolids						
12	8.7	6.3	6.0	5.7	5.7	6.0
48	9.3	7.3	8.0	6.0	9.7	9.0
85	10.3	9.0	9.0	8.7	10.3	9.3
145	11.0	9.7	8.7	12.7	19.3	13.3
LSD (*P* = 0.05)	**25.4**	**8.2**	**15.7**	**3.0**	**6.3**	**5.6**

Values are means of three replicates. Where the difference between any two values in any column is greater than the LSD, then those values are significantly different at $P < 0.05$. Bicarbonate extractable P extracted by 0.5 M $NaHCO_3$ (1:100), Chemistry Centre (WA). Report numbers 00A778, 01A111, 01A217, 01A629, 02A01 and 03A73.

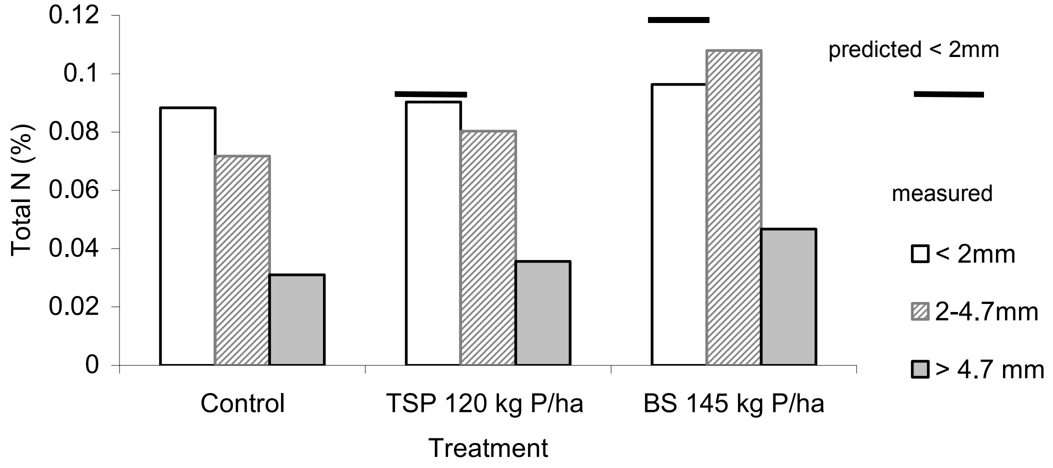
4.3.3.2 Total phosphorus and nitrogen

The <2 mm soil fraction in the highest rates of biosolids at 305 DAS and 405 DAS, showed a low recovery of total P compared with predicted values. Total P was 100 mg P/kg and 133 mg P/kg in the highest biosolids treatment, giving typical recoveries of 21% and 43%, respectively. In comparison, typical total P recoveries in the highest rate of TSP treatment were 106% at 305 DAS (167 mg P/kg) and 117% at 405 DAS (187 mg P/kg).

Evidence of biosolids particles were noted in the >2 mm fraction upon observation (Plate 4.7). Where the total soil fraction including the >2 mm fraction was ground and analysed at 405 DAS, total P recoveries increased to 95% for the biosolids, whereas the TSP recoveries remained similar at 101%.

Plate 4.7 Fraction of soil >2 mm typically discarded following sieving showing evidence of biosolids (black particles) amongst the gravel stones

Measurement of mean total N and P concentrations in the <2 mm, 2 to 4.7 mm and >4.7 mm soil fraction for the highest rates of biosolids, TSP and the control treatment at 615 DAS are summarised in Figure 4.9. The predicted values are based on the initial nutrient loading rates of biosolids and show that much of the P (and to a lesser extent N) remains in the 2 to 4.7 mm soil fraction.



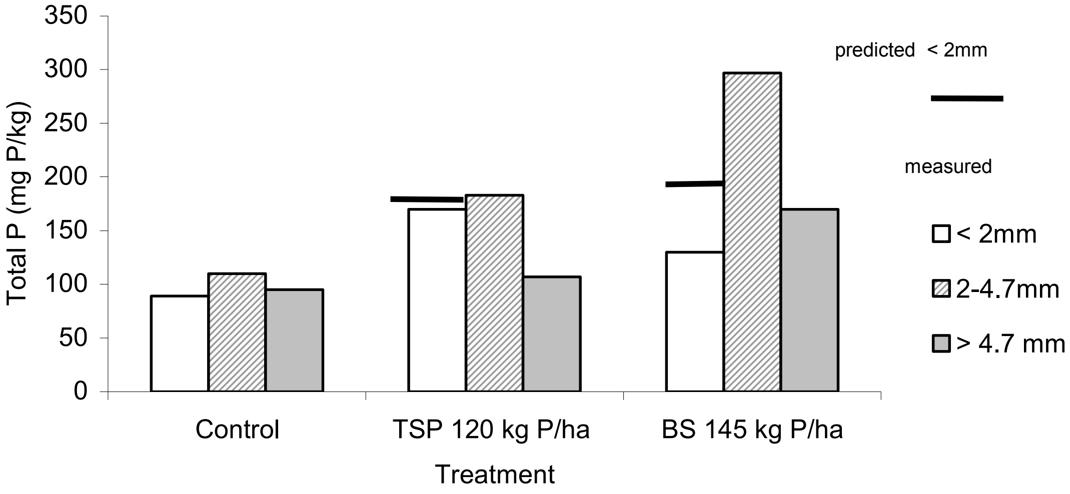


Figure 4.9 Concentrations of total soil N or P in the 0-10 cm profile in three sized soil fractions (<2 mm, 2-4.7 mm, >4.7 mm) in TSP, biosolids (BS) and control treatment at 615 DAS, with predicted N or P concentration for the <2 mm given

Predicted values for total N (kg/ha) and total P (kg/ha) in the <2 mm fraction of either the TSP or biosolids treatment were calculated using the N and/or P content of the product at the loading rate applied. A bulk density of 1.3 g/cm^3 was used to convert values to mg/kg. The 2 to 4.7 mm and >4.7 mm fractions would be predicted to have similar values to the control. Values are means of three replicates. Data from report 03A45 Chemistry Centre (WA).

4.3.3.3 Nitrate and ammonium nitrogen

Soil measurements for NO_3–N and NH_4–N at 18 DAS and 60 DAS showed little differences between the biosolids treatments compared with the control treatment. Mean total inorganic N concentrations (sum of nitrate-N and ammonium-N) over these plots during this sampling period decreased from 57 to 52 mg N/kg in the control treatment and from 61 to 53 mg N/kg over all biosolids treatments (data not presented). However, at 133 DAS total inorganic N concentrations were lower in some TSP treatments compared with biosolids treatments (*P* <0.05, Figure 4.10). The proportion of NO_3–N and NH_4–N that would remain in the >2 mm soil fraction in the biosolids treatments is uncertain, given the high solubility of inorganic N, especially in the NO_3–N form.

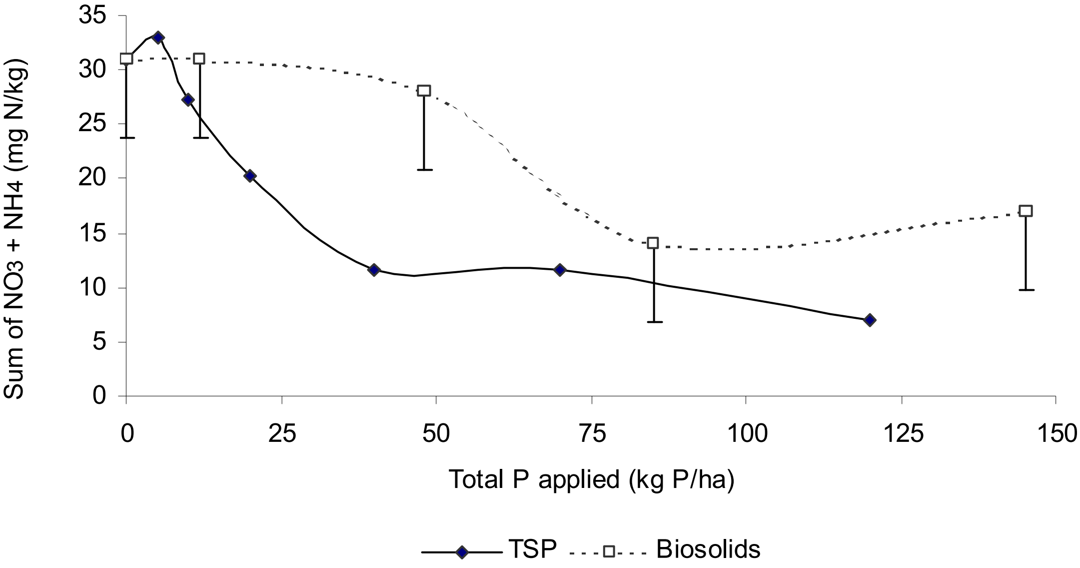


Figure 4.10 Relationship between total inorganic soil N and total P applied in the highest rate of TSP (120 kg P/ha) or biosolids (145 kg P/ha) at 133 DAS

Values are means of three replicates. Total inorganic soil N is the sum of ammonium-N and nitrate-N. Lines plotted using Microsoft Excel. Vertical lines denote LSD (*P* = 0.05) from all treatment means.

4.3.3.4 Soil pH and organic carbon

Soil pH ($CaCl_2$) measured at 305 DAS ranged from 5.5 to 5.7 over all treatments with no differences (*P* >0.05) between the TSP and biosolids plots (data not presented). There were no differences in soil pH (*P* >0.05) at 615 d after the commencement of the experiment between any treatment means, with an average overall soil pH of 5.6 (data not presented).

Soil organic carbon (W/B)% measured at 305 DAS showed no differences between the initial TSP and biosolids treatments (*P* >0.05) with ranges from 2.7% to 3.0% (data not presented). There were no differences between TSP and biosolids treatments for organic carbon at 615 DAS in the <2 mm soil fraction, with C/N ratios constant at approximately 32:1.

The effect of soil sieving on pH and organic carbon was not measured. However, only a small maximum increase up to 0.2% in organic carbon would be expected in the 0-10 cm soil depth following biosolids land application rates of 5 t DS/ha.

4.3.4 Soil changes with depth at 10 months (306 DAS) after sowing the first crop

There were large differences in NO_3–N and NH_4–N concentrations between the highest rate of TSP and biosolids at 306 DAS for soil composite samples in three depths (0-10 cm, 10-20 cm, 20-30 cm) (Table 4.11). The 145 kg P/ha biosolids treatment had higher inorganic N levels than the TSP treatment at all depths.

Bicarbonate extractable P increased at depth in the 120 kg P/ha TSP and 145 kg P/ha biosolids treatment compared with the control treatment. Total P was highest at all depths for the 120 kg P/ha TSP treatment. There was no evidence of increased total P levels in the highest rate of biosolids at soil depths >20 cm.

The pH was slightly lowered in the highest biosolids treatment. There were no measurable differences in extractable Fe, Al, S, and exchangeable Ca, Mg, Na or K (data not presented).

Nutrient changes below 10 cm would be due to the leaching of nutrients given that treatments were only incorporated to a depth of 10 cm. Below 30 cm the ground was too hard to penetrate by hand auger.

Table 4.11 Soil changes at depth for selected constituents over three treatments at 10 months (306 DAS) in the <2 mm soil fraction

Treatment and P rate (kg P/ha)	Depth (cm)	pH ($CaCl_2$)	OrgC (W|B)%	Total N (%)	NH_4-N (mg/kg)	NO_3–N (mg/kg)	Total P (mg/kg)	HCO_3-P (mg/kg)	EC (1:5) (mS/m)
Control nil P	0-10	6.0	2.6	0.080	8.3	9.0	71.7	4.3	10.0
	10-20	6.0	2.4	0.072	9.0	7.7	68.7	3.7	10.0
	20-30	6.0	2.2	0.069	7.7	7.0	88.3	3.7	10.3
TSP at 120 kg P/ha	0-10	6.0	2.2	0.067	5.0	1.7	112.7	13.7	8.3
	10-20	5.9	1.9	0.061	3.7	1.3	99.3	14.3	7.3
	20-30	5.8	1.7	0.058	3.7	1.3	97.3	12.7	6.0
Biosolids at 145 kg P/ha	0-10	5.6	2.4	0.075	16.3	6.0	96.0	14.7	6.7
	10-20	5.5	1.9	0.063	14.3	5.7	93.3	15.3	6.0
	20-30	5.5	1.9	0.064	12.3	5.3	88.0	10.3	6.0

CCWA Laboratory Report 01A630; pH ($CaCl_2$) in 0.01 M $CaCl_2$ (Rayment & Higginson 1992i), total N (Blakemore, Searle & Daly 1987; Rayment & Higginson 1992f; Searle 1984), nitrate N and ammonium N extracted in 1 M KCl (Rayment & Higginson 1992f) p53, total P (Allen & Jeffery 1990; Murphy & Riley 1962), bicarbonate extractable P extracted in 0.5 M $NaHCO_3$ (1:100) (Colwell 1963; Rayment & Higginson 1992h), Organic carbon by Walkley and Black (1934) (Rayment & Higginson 1992g), EC (1:5) at 25^oC (Rayment & Higginson 1992b).

(mS/m = milliSiemens per metre, mg/kg = milligrams per kilogram, mL/g = millilitres per gram).

4.4 Discussion

4.4.1 Interaction between nitrogen and phosphorus

The design of the experiment attempted to ensure that biosolid N was not a confounding factor influencing plant growth as implied by other researchers (de Hann 1981; Gupta, Narwal & Antil 1989; Gupta, Narwal & Antil 1993; Havilah & Davis 1998; Prasad 1996; Sommers & Sutton 1980). It was recognised that the highest biosolids rates in this study would supply greater N than TSP treatments, with plant available N (PAN) in Year One estimated from formula (1) as 15,335 mg N/kg (Section 4.2.7); supplying 6, 25, 44 and 75 kg N/ha respectively for the four biosolids rates. This would be in addition to the basal urea applied at 200 kg/ha, supplying 92 kg N/ha to all treatments.

In the first year, the highest rates of TSP appeared to be have been disadvantaged by the lower levels of available soil N, which became more apparent as the season progressed. The urea application planned at 28 DAS was deferred due to the dry seasonal conditions and inadequate rainfall to 77 DAS. Soil sampling at 133 DAS for inorganic N concentrations (Figure 4.10), and percentage shoot tissue N concentrations at 123 DAS (Figure 4.3) provided evidence of N deficiency in the highest TSP treatments. By comparison, the higher rates of biosolids, although still considered below critical nutrient levels for N, were not affected to the same degree.

In the second year, lupins inoculated with N fixing bacteria were grown to minimise the effect of N as it was envisaged that they would be capable of fixing much of their required N. In addition, lupins require a good P status for maximum vegetative growth and yield and will respond to high rates of P on P deficient soils, requiring twice as much P as wheat on new land (Nelson & Delane 1990). There were no differences in N uptake in lupin shoots between TSP and biosolids treatments at comparative P loadings, which would suggest that P uptake was not influenced by an interaction with the supply of N.

4.4.2 Relative effectiveness of biosolid P compared with TSP

The infertile soil type selected for the study and the rates of P applied ensured that a P response was achieved. In the first year, the RE of biosolids compared with top-dressed TSP increased as the season progressed, as shown by seasonal DM and P uptake. The RE of biosolids compared with top-dressed TSP ranged from 31% to

46% for DM and from 42% to 55% for P uptake over the season. At final grain harvest, the RE had increased to 67%.

In the second year, following incorporation with the disc plough at seeding, the biosolid P compared with TSP had increased to be at most 84% as effective in lupin shoots (shoot DM at 165 DAS). However, by grain harvest, results were similar to the first year with biosolids being 60% as effective as TSP. It is uncertain as to whether the lupin root system, which has an effective cluster root production under low P levels, was more effective than wheat plants in sourcing P in the biosolids treatments.

In the field experiment in the first season, the progressive increase in RE over time may be due to a number of factors such as: the P in biosolids becoming more available over time; the biosolid P being accessed more effectively by larger plant roots; increased soil moisture increasing the solubility of soil P; or alternatively, the higher rates of TSP being limited by the lower levels of soil N. There was evidence to suggest that plants in the highest rates of TSP may have been disadvantaged in terms of N nutrition during later growth stages, thereby biasing the results in favour of biosolids. However, there was no evidence to suggest that soil N contributed to improvement in RE during the second year (Table 4.9).

A number of researchers have found that the relative efficiency of biosolid P or sewage sludge P compared with mineral P either increased with time or declined only slowly (McLaughlin & Champion 1987; Pommel 1981) or decreased with time (Montgomery 2002) . Following the land application of sludge, Akhtar, McCallister and Eskridge (2002) suggest that organic ligands from the partial decomposition of sludge, form complexes with Al, Fe and Ca, thus making P more available. Further investigation into the cycling of P into various soil pools following the application of biosolids is warranted to better understand the mechanisms involved in P availability.

In the present experiment, the residual values of P in both TSP and biosolids were less than that of freshly applied TSP. This would be expected as Wild (1988) indicated that the recovery of P from a fertiliser application not used by a crop continues to be of value to succeeding crops, although the uptake each year is usually less than in the first year. McLaughlin and others (1988b) used isotope labelling of P to show that recently applied inorganic fertiliser P moved from available fractions to those more difficult to extract. The cycling of P was subject to uptake by wheat plants and microorganisms, as well as by adsorption, precipitation and exchange reactions in the soil. The RE values in the field experiment were much lower than would be expected from the results of the pot experiment (Chapter 3), given the similarity between the inorganic sources of P. Therefore, a number of environmental factors need to be investigated to further explain these differences, which forms the basis of the following Chapter.

4.4.3 Effect of fertiliser placement

The effectiveness of inorganic P fertilisers is reduced where fertilisers are top-dressed rather than drilled with the seed due to positional placement. Orthophosphate (as TSP) can be from two to four times more effective for cropping if drilled with the seed rather than top-dressed (Rudd & Barrow 1973). For this field experiment both TSP and biosolids were top-dressed and incorporated, which would have resulted in a reduced P positional availability than if drilled with the seed. Therefore, if TSP had been drilled with the seed rather than top-dressed, as in the present experiment, the RE of biosolids compared with top-dressed TSP would be reduced by a factor of between two and four.

Based on the reasoning given above, it is postulated that the RE of biosolids P compared with drilled inorganic P fertiliser may range from 8 to 17% early in the growing season, increase from 12% to 24% towards the end of the season, and range from 17% to 33% for grain yield in the first season. These values are higher than those obtained by Osborne and others (1995a), who proposed that Fe treated sludges in New South Wales are likely to be less than 10% as effective as WSP fertilisers in year one, but increase to (say) 20% in the second and third year. Other studies suggest higher RE values than obtained in the present study: from 40% to 100% as effective as inorganic sources of P (Womer, Elliott & Brandt 2002), 44% to 100% on sesquioxide soils (McLaughlin & Champion 1987) and 20% to 100% in the Netherlands (de Hann 1981).

Throughout the two years of this study, the soil remained dry for extended periods. The dry conditions were due to low opening rains and below average rainfall, particularly for year one of the experiment. Thus, climatic differences need to be taken into account when comparing data from elsewhere that may cite higher RE. The annual rainfall over much of the agricultural areas where biosolids are applied in Western Australia is typically 450 mm, of which 70% falls during the growing season. Uneven distribution of rainfall would be experienced in the field, although not a problem in regularly watered glasshouse experiments.

The current PLBAR used in Western Australia assumes that 100% of biosolid P is available for plant uptake, which would overestimate the P value and appear highly unlikely under field conditions. In comparison, the literature indicates that the uptake of P by agricultural crops during the current year is between 5% to 30% of that applied by a single application of WSP fertiliser (Foth & Ellis 1988; McLaughlin, Alston & Martin 1988c; Wild 1988). Therefore, one should further question the basis for assuming that biosolid P is 100% plant available in the first year. It is likely that anywhere from three to six times more biosolid P would be required to obtain wheat yields comparable to that of drilled inorganic P fertiliser on a similar soil type and rainfall zone in Western Australia. An annual fertiliser P application of 120 kg Superphosphate (11 kg P/ha) drilled with the seed to replace soil P removed by crop harvest would require a minimum equivalent of 1.2 to 2.2 t DS/ha of biosolids (i.e. Beenyup WWTP) to provide similar P nutrition.

4.4.4 Use of soil available phosphorus to estimate biosolid P value

Increasing rates of TSP increased bicarbonate extractable soil P proportionately, with increases noticeable at 18 DAS in year one (Table 4.10). Bicarbonate extractable soil P then peaked at 60 DAS, but decreased at 133 DAS, possibly due to higher plant demands, immobilisation by soil microbial activity and/or soil sorption of P over time. In contrast, there was little change in bicarbonate extractable soil P following the application of biosolids. Furthermore, the relationship between bicarbonate extractable soil P and shoot P uptake in the biosolids treatments over the duration of the present experiment was poor (Figure 4.11), and could not be used to predict P availability.

Less than 5% of the total P applied was measured as available P (Colwell) compared with approximately 60% in TSP. It is suggested that soil sieving to <2 mm for bicarbonate extractable P determination removes many particles of biosolids. Thus, it would be expected that crushing soil to pass through a 2 mm sieve would improve the accuracy of bicarbonate extractable P and total P tests.

Michalk and others (1995) used soil available P to estimate that 21% of the P in biosolids was plant available in the first spring following the application of biosolids. The Bray test was used to determine soil extractable P and the percentage of plant available P was estimated from the total P applied. The method used to prepare the soil for analysis was not given, but the soil may possibly have been ground based on value increases in available soil P.

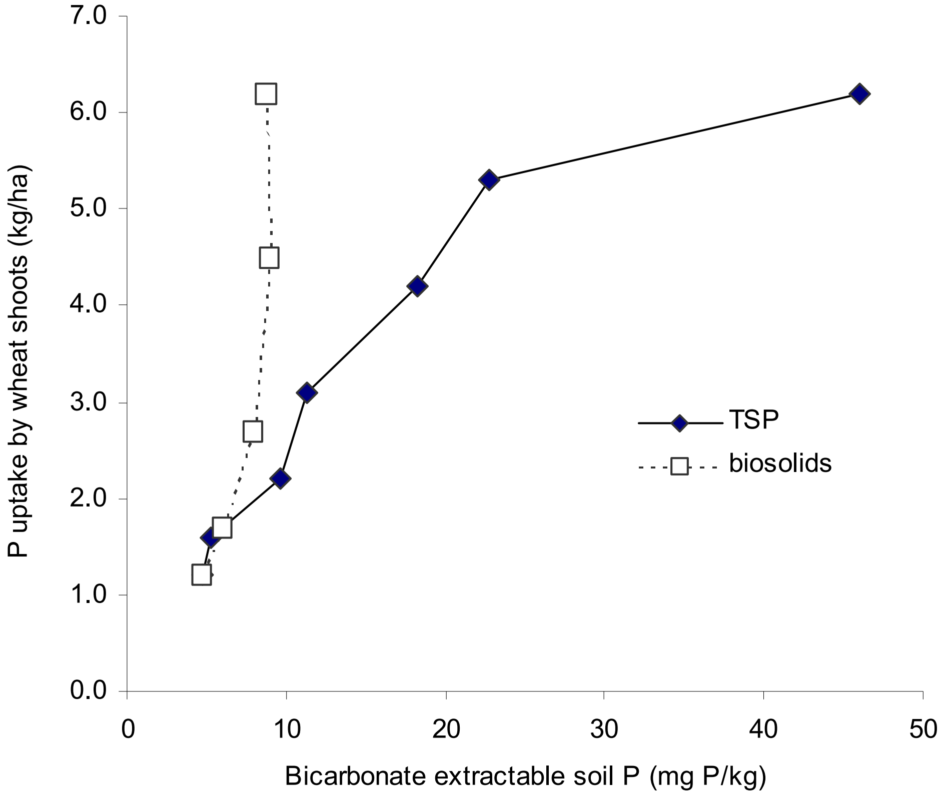


Figure 4.11 Relationship between available soil P at 133 DAS and P uptake by wheat at 123 DAS

Values mean of three replicates. Lines plotted using Microsoft Excel.

4.4.5 Increase in total P loadings and risk of movement of P from biosolids application site

In Australia, the land application rates of biosolids based on crop N needs have generally resulted in an excess of P, as the N: P ratio in biosolids does not match crop nutrient requirements. For example, a four tonne wheat crop may remove approximately 84 kg N/ha in grain (Table 2.4). The application of 5 t DS biosolids per ha could provide adequate N where a 15% mineralisation rate was expected. However, the same biosolids application would result in the application of 150 kg P/ha, of which the crop would remove only 12 kg P/ha. It is unknown if the excess of total P is a potential problem over a range of soil types in Western Australia.

The repeated use of various sludges in land application overseas has resulted in problems with excessive soil P enrichment (Cottenie & Kiekens 1980; Furrer, Gupta & Stauffer 1984; Maguire, Sims & Coale 2000a). In Australia, excessive soil P enrichment following the application of biosolids has not yet occurred, possibly due to factors such as the short land management history and low inherent soil fertility. In addition, many treatment processes designed to remove P from wastewater, as a result of more stringent effluent disposal regulations, have resulted in higher concentrations of P in biosolids (Scott & Horlings 1975). However, Perth's WWTPs do not use P removal processes, therefore the P content in biosolids may be lower than used in land application programs elsewhere.

While excess P is generally not an agronomic problem and P deficient soils would benefit from additional P enrichment, excess P in the environment has the potential to cause contamination of water bodies (Leopold 2002; National Research Council 1996; Womer, Elliott & Brandt 2002). In the UK, biosolids applied to soils has become more focused on meeting the P needs of crops, whilst N needs are met by supplementary nitrate fertilisers (Gove et al. 2002). Contamination of water bodies by excess P derived from soils is generally caused by leaching or surface runoff.

There was no evidence of P leaching from biosolids at rates up to 5 t DS/ha to depths below 20 cm by the end of the first growing season in the lateritic soil type investigated. Total P at depths of 20 to 30 cm in 145 kg P/ha biosolids treatment had not increased above the control treatment (88 mg P/kg), whereas 120 kg P/ha TSP treatment increased total soil P to 96 kg P/ha. In addition, much of the biosolid P remained in the 0-10 cm depth in the 2.0 - 4.7 mm soil fraction, as evident in Figure 4.9. The experiment, however, was conducted on a P deficient soil to obtain a response to P. Most farmed soils now have a substantial history of P application; therefore it would be useful to investigate the movement of biosolid P on a more fertile soil types. There was no leaching of P, however, on a deep Karrakatta coastal sand in Western Australia following biosolids application up to 34 t DS/ha (where biosolid P_T =1.4%) in a *Pinus pinaster* plantation (Dumbrell & McGrath 2002), nor in a UK study following the application of high rates of digested sewage sludge (up to 330 t DS/ha) (Campbell & Beckett 1988).

The potential for biosolids to cause surface water enrichment with P would depend on factors such as the amount of water-soluble P (WSP) present, the P adsorption capacity of the soil and runoff. Biosolids are considered to have a lower WSP compared with animal manures or chemical fertiliser, thus would be less likely to cause surface water enrichment with P (Hadeed 2002). A low WSP in biosolids would suggest that the movement of particles of biosolids would be necessary for surface water enrichment to occur. Management guidelines in Western Australia, attempt to minimise the risk of runoff by ensuring that biosolids are not applied on sites prone to runoff or in close proximity to water bodies (DEP, WRC & DOH 2002). The experiments in Chapter 6 further investigate WSP concentrations following the application of biosolids in a range of soil types compared with inorganic P. As management guidelines attempt to minimise the risk of runoff by restricting biosolids application on high-risk sites, the main focus will be on the risk of leaching loss rather than runoff.

4.4.6 Movement of nitrates and other nutrients

Ten months after sowing, the <2 mm soil fraction to which 5 t DS/ha of biosolids had been applied showed the largest increases in inorganic soil N and to depths of 30 cm compared with the control and TSP treatments. It would be expected that nitrate and ammonium being soluble would move out of biosolids into the soil during periods of rainfall, whereas the P being less soluble would not.

The NLBAR has been investigated in eastern Australia to ensure groundwater contamination with nitrates does not occur following the application of biosolids (Havilah & Davis 1998; Havilah et al. 1996; Osborne 1992; Salt, Hird & Bamforth 1996) and is not discussed in detail here. Nitrates have been demonstrated to leach through the soil profile following application of high rates of biosolids, whereas P has not (Campbell & Beckett 1988; Dumbrell & McGrath 2002). To reduce the risk of nitrate leaching, plants with low N uptake, such as lupin should be avoided in biosolids land application programs in the first year of application.

Slightly lowered pH values observed in the soil with the highest biosolids application were not expected due to the biosolids having a pH of 7.7 (H_2O, 1:5) prior to application. The decrease in pH following application may be due to acidification via the nitrification process as a result of higher levels of ammonium forms of N. There were no other major changes recorded in soil properties resulting from the application of biosolids up to 5 t DS/ha; however, sieving may have skewed the results in the 0-10 cm samples.

4.5 Conclusions

The field experiment enabled Perth biosolids to be studied in a Mediterranean climate and lateritic soil type typically used by the Water Corporation in agricultural land application programs in Western Australia. The soil was P deficient to enable a P response to be achieved, although most farming properties, through the regular application of P fertilisers, now have improved soil P status. In the first season, wheat grain yield indicated biosolid P to be 67% as effective as top-dressed TSP and in the second season lupin grain yield indicated the RE to be 60% (SE of the mean=+/-10%). Plants were able to uptake relatively more P from biosolids as the season progressed, with RE for P uptake increasing from 33% to 55%. In comparison, RE values in the field were much lower than the RE of 100% achieved in the glasshouse experiment.

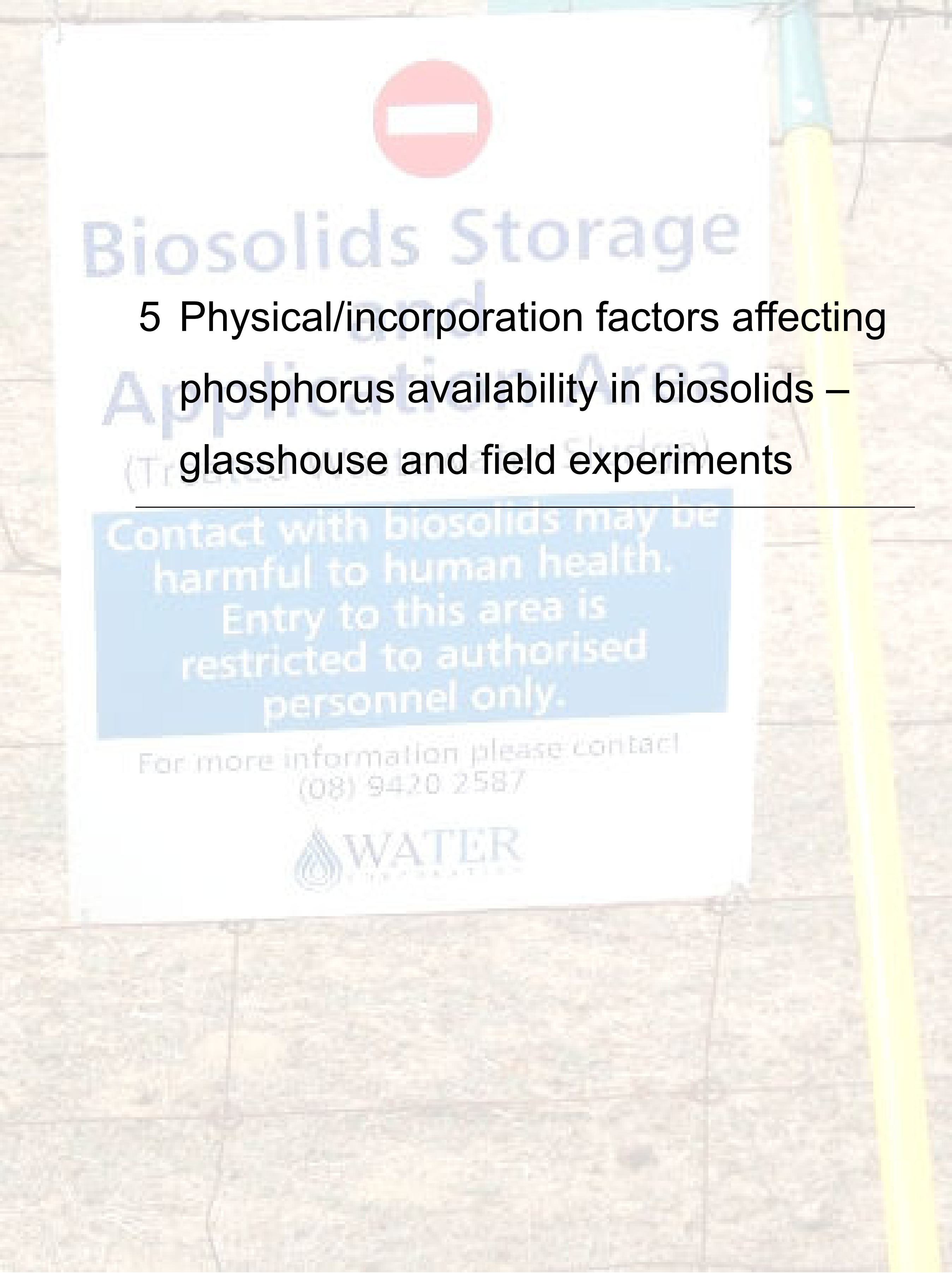
Factors that may have contributed to low initial RE values in the field (given the high RE in the glasshouse) included the low and variable rainfall affecting the solubility of the P in biosolids and microbial reactions within the soil. The placement of biosolids in the soil may have impacted directly on these reactions as biosolids in the glasshouse were well mixed with the soil and kept moist throughout the experiment. A deficiency of N in the higher TSP treatments as the season progressed may have restricted potential yield in the TSP treatments relative to biosolids treatments and confounded the RE values for later in the season.

Bicarbonate extractable soil P increased proportionately with increasing TSP rates and was positively correlated with P uptake, whereas a poor relationship was observed between P uptake and bicarbonate extractable P in soils to which biosolids had been applied. Sieving soil <2 mm, a routine operation prior to chemical analysis in Western Australia to remove stones and debris, may have contributed to these poor predictions of P uptake by soil test values as particles of biosolids were inadvertently discarded. Inorganic forms of N, being more soluble than P were not affected to the same extent. There was no evidence of leaching of P at depths of 20-30 cm (below the placement of biosolids) based on soil test values at the highest rate of biosolids used (5 t DS/ha, 150 kg P/ha), although concentrations of NH_4-N increased.

The RE value obtained for biosolids compared with inorganic fertiliser may be affected by the method by which the fertiliser is applied. For example, TSP drilled with the seed would result in approximately two to four times better uptake of P by plants than broadcast TSP. Therefore the RE of biosolids may be reduced from 8%

to 33% as effective as drilled TSP for grain yield compared with broadcast TSP. The effect of the physical placement of biosolids on P availability will be investigated in the following experiment (Chapter 5) to further understand differences between the glasshouse and field.

It is proposed that positional availability and incorporation of biosolids plays a large role in determining the availability of P. Further experimentation in the glasshouse and field should enable more accurate determination of the PLBAR calculation to ensure best practice land application programs, which will be covered more fully in the general discussion (Chapter 7). Other effects of biosolids on soil organic matter, soil structure and soil water are not considered further in this study although they may all play a role in P cycling.



5 Physical/incorporation factors affecting phosphorus availability in biosolids – glasshouse and field experiments

5.1 Introduction

Biosolids applied to agricultural land in Australia are required to meet, as a minimum, the National Guidelines – Guidelines for Sewage Systems, Biosolids Management (draft Feb 2003) (DEP, WRC & DOH 2002); with additional restrictions on use in environmentally sensitive sites, such as those prone to water erosion and waterlogging (Hird & Bamforth 1996). Biosolids are required to be incorporated as fully as possible into the topsoil within 36 h of land application to maximise agronomic benefits, reduce the risk of excess contaminants to isolated sections of land, to reduce odour and vector attraction properties, and to minimise nitrogen loss through volatilisation and biosolids loss through surface runoff (DEP 2001).

Incorporation methods differ between application sites. Methods have included: surface spreading liquid or dewatered material with or without incorporation into the plough layer; liquid material injected below the soil surface; light incorporation with scarifiers and harrows; rotary hoes or mouldboard ploughs that would completely invert the biosolids (EPA 1994; Salt, Hird & Bamforth 1996; WEF 1994); or one-way disc plough or an off-set disc plough as preferred in Western Australia by the Water Corporation. Salt, Hird & Bamforth (1996) showed that the amount of biosolids remaining on the soil surface was reduced with more complete incorporation methods, although the differences may be small at application rates of 10 to 15 t DS/ha. Overall, there is a trend towards less tillage and less topsoil inversion by tillage to be used in Australian agriculture in an attempt to prevent unnecessary soil structure decline.

A number of physical, chemical and environmental factors in soils affect the reactions of biosolid P following land application (McLaughlin 1988). At each site, local factors such as topography, hydrology and proximity to surface waters are involved in the release of P from land-applied biosolids (Dentel, Sims & Mah 2001). Very few studies have investigated the effect of incorporation on nutrient release from biosolids and subsequent interaction with the plant, soil and/or environment in detail. The degree by which biosolids are mixed with the soil may result in large differences in nutrient availability. In addition, the relationships between glasshouse and field experiments have not been considered, with estimates of nutrient availability in land application programs based on results from either without adequate verification that they generate similar results. Depending on the type of incorporation, biosolids may remain on the soil surface in various amounts in the field, whereas they are more likely to be fully incorporated in soil in glasshouse pot trials as noted in the previous experimental Chapters.

The placement of fertiliser P affects its subsequent uptake by plants (Bolland 1998b; Bolland, Allen & Barrow 2003). Surface-applied sludge had a lower P availability than incorporated sludge and was not immediately available to the roots of growing crops (King & Morris 1973; Pastene 1981); as also demonstrated by positional availability of P in sheep dung (Bromfield 1961; Gunary 1968). Plant roots had a better chance of taking up water-soluble P when fertiliser was sown or drilled with the seed, with drilled P approximately twice as effective as broadcast P at seeding (Rudd & Barrow 1973). However, the longer that fertiliser and soil are in contact, the greater the chances for P sorption, with fertiliser best applied immediately before needed for maximum plant uptake (Glendinning 1999). The aim of this study was to investigate the effects of the availability of biosolid P for plant growth following a range of incorporation techniques. These data should provide further insight as to the relationship between glasshouse and field experiments reported in the previous two Chapters.

5.2 Materials and methods

The basic methodology for both the glasshouse and field experiments are described in Chapters 3 and 4 and will not be repeated in detail here.

In this experiment, the growth and P uptake by wheat *(Triticum aestivum* L.) grown with biosolids following a range of incorporation treatments were compared with similar levels of inorganic P supplied by MCP in the glasshouse and TSP in the field. The residual value of P in the second season following incorporation was examined in the field experiment using narrow-leaf lupin (*Lupinus angustifolius* L.) with growth and grain yield analysed. Bicarbonate extractable soil P was measured at the conclusion of each experiment.

5.2.1 Soil types

Table 5.1 summarises the properties of the infertile, yellow gravelly loamy sands used for both the glasshouse and field experiments.

Table 5.1. Comparison of the major properties in topsoil (0-10 cm) for soil used in the glasshouse and field experiments

Soil Property	Glasshouse	Field
Soil Location	Bakers Hill (70 km north-east of Perth, WA)	York (70 km east of Perth, WA)
Soil Series	Yalanbee	Leaver
Great Soil Group	Lateritic podzolic	Lateritic podzolic
Australian Soil Classification (ASC)	Kurasol	Kurasol
Stones >2 mm	66%	35%
Properties of <2 mm soil fraction		
Sand	95%	87.5%
Silt	4%	7.5%
Clay	1%	5%
pH ($CaCl_2$), 1:5 ratio	4.8	5.5
Total nitrogen	0.10%	0.08%
Nitrate-N	1.5 mg/kg	1 mg/kg
Ammonium-N	3.5 mg/kg	11 mg/kg
Total P	61.5 mg/kg	110 mg/kg
Bicarbonate-extractable P	5.2 mg/kg	6 mg/kg
Phosphorus Retention Index (PRI)	15 mL/g	100 mL/g
Bicarbonate-extractable K	76 mg/kg	180 mg/kg
Organic carbon (W|B)	2.50%	2.68%
Reactive iron	770 mg/kg	370 mg/kg
Conductivity (EC), 1:5	4 mS/m	6 mS/m
Carbon/nitrogen ratio	25:1	33:1

Values determined from three replicates, sieved to <2 mm. All chemical analysis as per Reports 02A28(1-3), 02A154(1-9) and 02A634 (CCWA 2000) .

Soil Series (Fulton & Lantzke 1993), Great Soil Group (Stace et al. 1968), Australian Soil Classification (ASC) (Isbell 1996).

pH ($CaCl_2$) in 0.01 M $CaCl_2$ (Rayment & Higginson 1992i), total N (Blakemore, Searle & Daly 1987; Rayment & Higginson 1992f; Searle 1984), nitrate-N and ammonium-N extracted by 1 M KCl (Rayment & Higginson 1992f), total P (Allen & Jeffery 1990; Murphy & Riley 1962), bicarbonate extractable P extracted by 0.5 M $NaHCO_3$ (1:100) (Colwell 1963; Rayment & Higginson 1992h), PRI (Allen & Jeffery 1990), Fe and Al extracted by 0.2 M ammonium oxalate pH 3.25 (Rayment & Higginson 1992c), Organic carbon (W/B) (%) by Walkley and Black (1934) (Rayment & Higginson 1992g), EC (1:5) at 25°C (Rayment & Higginson 1992b).

(mS/m = milliSiemens per metre, mg/kg = milligrams per kilogram, mL/g = millilitres per gram).

5.2.2 Biosolids

Biosolids from Beenyup WWTP were used in this experiment as detailed in section 1.2. For the glasshouse experiment, biosolids were sourced on 14 March 2000 (mean P_T content = 2.96% db, DM = 15%) as described in section 3.2.4 and Table 3.3. Biosolids used in the field experiment were sourced on 16 May 2001 (mean P_T = 2.96% db, DM = 13.5%) as described in sections 4.2.5, 4.2.7 and Table 4.3.

5.2.3 Glasshouse experiment

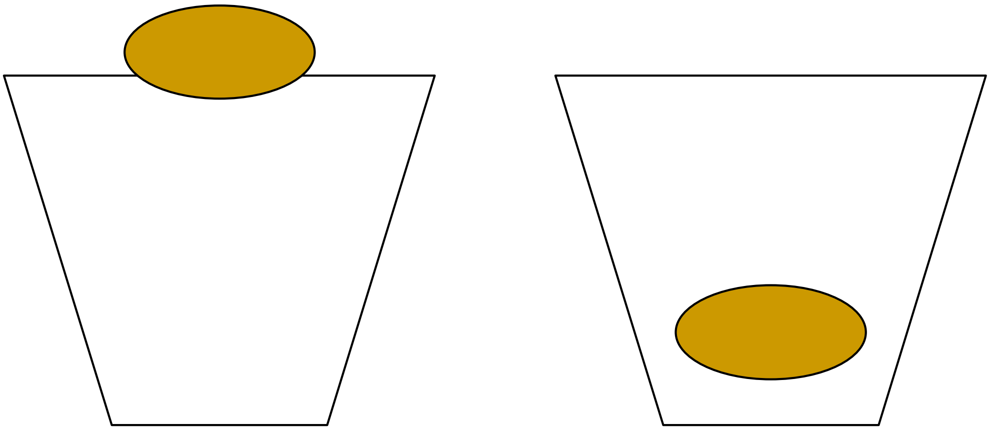
5.2.3.1 Treatment and trial design

A total of twelve treatments comprising four biosolids and eight inorganic P treatments were arranged in a randomised block design with three replicates. The four biosolids treatments were applied at 150 mg P/kg each (i.e. 5 dry g biosolids/kg soil), with the method of incorporation varying from nil incorporation to full incorporation, as outlined in Table 5.2 and schematically in Figure 5.1.

Table 5.2 Rate, source and method of incorporation of phosphorus as used for the glasshouse experimental pots

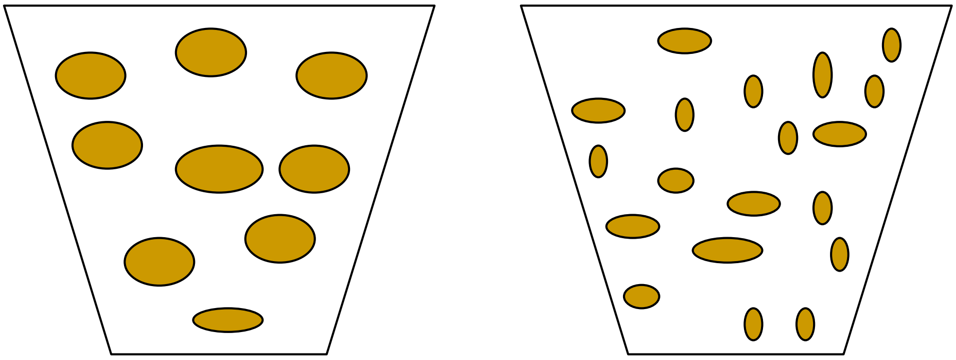
Treatment	P rate (mg P/kg) and source	Method of incorporation	Key
1	0 Nil	Completely mixed	P0
2	10 MCP	Completely mixed	P10
3	20 MCP	Completely mixed	P20
4	40 MCP	Completely mixed	P40
5	60 MCP	Completely mixed	P60
6	80 MCP	Completely mixed	P80
7	110 MCP	Completely mixed	P110
8	140 MCP	Completely mixed	P140
9	150 Biosolids	No incorporation: applied on Top of soil surface only	BT
10	150 Biosolids	High level of incorporation: mixed in three times the volume of water and applied as a wet Slurry evenly throughout the soil	BS
11	150 Biosolids	Moderate incorporation: mixed roughly into soil	BM
12	150 Biosolids	Incorporated at Depth only: applied at 10cm below the soil surface only. No biosolids placed in the top 10 cm of soil.	BD

See also figure 5.1 for a schematic representation of biosolids application methods.



BT = biosolids top

BD = biosolids at 10cm depth



BM = biosolids moderately incorporated

BS = biosolids incorporated as wet slurry

Figure 5.1 Schematic diagram showing the distribution of biosolids for the four biosolids treatments (each applied at 150 mg P/kg) in the glasshouse experiment

Prior to the start of the pot experiment, biosolids were mixed for 15 min in a clean cement mixer to ensure homogeneity and then all treatments were applied on a wet weight basis. This experiment was established concurrently with the experiment described in Chapter 3 to enable comparison with a P response curve, using eight rates of MCP. Monocalcium phosphate was applied as a fine powder and mixed throughout the soil at rates from 0 to 140 mg P/kg, with the highest rate comparable to the biosolid treatments.

5.2.3.2 Basal nutrients, pot size and sowing

Non-draining pots, 15 cm in depth by 15 cm diameter at the surface, were filled with 1.8 kg of air-dried soil. Basal amounts of N, K, Ca, Cu, Zn, B and Mo were mixed throughout all pots, and then the corresponding P treatment applied (see Table 5.2). Nitrogen was split over three applications and applied at sowing, and at 10 and 20 days after sowing (DAS). The MCP treatments received a total of 160 mg N/kg, whereas the biosolids treatments received 92 mg N/kg as an inorganic salt, with less N applied to compensate for the extra biosolid N as described in section 3.2.3.

Ten pre-germinated seeds of Brookton wheat were sown to a depth of 2.5 cm on 5 January 2001 into pots incubated to gravimetric soil water capacity (GSWC). Thereafter pots were watered to GSWC at least every second day using distilled water. Following germination, plants were thinned to five median plants per pot at the 2.5 leaf stage and harvested 33 DAS on 12 February 2001. The experiment was conducted in an air-conditioned glasshouse, described fully in Chapter 3.

5.2.3.3 Plant and soil data

Wheat development was recorded at 14 and 32 DAS using the Zadoks (Z) decimal code for the growth stage of cereals (Zadoks, Chang & Konzak 1974). Plants were harvested at 33 DAS and shoots were dried at 70°C for 48 h to determine DM, then milled and analysed for the concentration of N by combustion (Leco N) and P, K, Ca, Mg, Na, S, Fe, Mn, Zn and Cu by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), as described in section 3.2.7. Tissue concentrations of nutrients were compared with critical levels as published by Reuter & Robinson (1997) using an equivalent growth stage.

Immediately following harvest a 10 g sample of soil was collected from each pot to measure soil pH, total N, nitrate-N, ammonium-N, total P, PRI and available P as described in Chapter 3, Section 3.2.8. The biosolids treatments, BT and BD were partitioned and sampled in more detail to examine P movement throughout the soil profile relative to the initial biosolids placement. In treatment BT, the clump of biosolids was removed prior to the collection of 10 g of soil to a depth of 1 cm. In treatment BD, a soil sample was taken from the soil surface, the centre of the pot and at the bottom of the pot (10 cm) where biosolids had originally been positioned. In all other pots the soil was mixed thoroughly in the bag prior to soil removal. Surface samples of biosolids were ground <2 mm prior to analysis.

5.2.3.4 Statistical analysis

Wheat shoot data from the four biosolids treatments and eight MCP treatments at harvest were compared for differences in DM production, P uptake, P shoot concentration and N shoot concentration. Soil samples collected from the centre of each pot were compared for differences in bicarbonate extractable soil P, total P, soil pH, total N, nitrate-N, ammonium-N, total P and PRI. All statistical analyses used an ANOVA model in GENSTAT as previously described in Section 3.2.11. A single least significant difference (LSD) value at the 5% level of significance was used for comparing results between treatment means.

5.2.4 Field experiment

5.2.4.1 Experimental design

This study reports two years of field trial data during the 2001-2002 growing seasons on the field experiment site described fully in Chapter 4. The extended version of this experiment consisted of a total of 15 treatments established to determine the relative effectiveness (RE) and residual value (RV) of biosolids compared with inorganic P. Data specific to this experiment are reported from treatments 1, 13 and 15; consisting of a nil biosolids treatment, incorporated biosolids at 85 kg P/ha and surface-applied biosolids at 85 kg P/ha, as highlighted in Table 5.3. Each treatment was replicated three times in a randomised block design.

5.2.4.2 Application of basal nutrients, TSP and biosolids

Biosolids for each plot were weighed and spread by hand within 72 h of delivery. All plots were incorporated to a depth of 10 cm during seeding, except for the surface-applied biosolids (treatment 15), which was applied the day after seeding to ensure no incorporation took place.

The effectiveness of the disc plough used to incorporate biosolids was determined at 26 DAS on 13 June 2001 from treatments 1, 13, 14 and 15 by measuring biosolids remaining on the soil surface from five, 0.25 m^2 quadrats. Biosolids collected were oven dried at 110^{o}C for 48 h to determine dry weights and to calculate the percentage incorporation.

Table 5.3 Treatment allocation for rates of phosphorus supplied by biosolids or triple superphosphate (TSP) used in the field experiment

Treatment	**P year one (2001)** (kg P/ha)	**P year two (2002)** (kg P/ha)	**Total TSP** (kg/ha)	**Biosolids** (t DS/ha)	**Biosolids** (wet t/ha)
1	**0**	**0**	**0**	**0**	**0**
2	5	0	25	0	0
3	10	0	50	0	0
4	20	0	100	0	0
5	40	0	200	0	0
6	70	0	350	0	0
7	120	0	600	0	0
8	0	20	100	0	0
9	0	40	200	0	0
10	0	80	400	0	0
11	12	0	0	0.41	3.03
12	48	0	0	1.64	12.15
13	**85**	**0**	**0**	**2.86**	**21.18**
14	145	0	0	4.91	36.37
15	**85**	**0**	**0**	*** 2.86**	*** 21.18**

N.B. Treatments 1, 13 and 15 specific to Chapter 5 are in bold, *Biosolids surface-applied rather than incorporated. Plant and soil samples were not collected from treatments 8, 9 and 10 in the first year (2001), since fresh rates of TSP were applied only in 2002.

Plates 5.1 and 5.2 show biosolids before and after incorporation to illustrate initial placement and final burial.

To ensure that nutrients besides P were adequate for plant growth, basal nutrients including N, K, Ca, Cu, Zn, S and Mn were top dressed prior to seeding on all plots as described in section 4.2.10. Triple superphosphate (TSP) was top dressed on all plots requiring inorganic P. The seven rates of inorganic P used ensured that a P response curve could be determined in the first season. To enable the residual value of P to be determined, freshly applied TSP was broadcast in the second season to treatments 8, 9 and 10.

Plate 5.1 Biosolids applied at 2.9 t DS/ha prior to incorporation on 17 May 2001

Plate 5.2 Biosolids applied at 2.9 t DS/ha following incorporation with the disc plough on 18 May 2001

5.2.4.3 Seeding

Full details of seeding methods, site management and weed control are described in section 4.2.6, with Carnamah wheat sown on 18 May 2001 and Tallerack lupin sown on 10 May 2002.

5.2.4.4 Shoot dry matter and plant density

The full methodology for determination of plant establishment at 26 DAS, seasonal shoot DM and plant density (DM/m^2) at 27, 67, 96 and 123 DAS, and plant development (Zadoks, Chang & Konzak 1974) for wheat has been described in section 4.2.8.1.

The full methodology for determination of plant establishment at 28 DAS, seasonal shoot DM and plant density (DM/m^2) at 47, 98 and 165 DAS and plant development (Dracup & Kirby 1996) for lupin has been described in Chapter 4, section 4.2.8.2.

5.2.4.5 Harvest and yield components

Wheat was harvested manually at 179 DAS to determine the yields of grain, DM of shoots and various yield components as described in Chapter 4, section 4.2.9.1. In addition, the centre eight rows were mechanically harvested at 210 DAS and grain yield (kg/ha) calculated.

Lupins were mechanically harvested at 211 DAS and grain yield (kg/ha) calculated as described fully in Chapter 4, section 4.2.9.2.

5.2.4.6 Plant tissue nutrient analysis

All analyses are described fully in Chapter 4, section 4.2.10. Shoot and grain N concentrations were determined in wheat by combustion using a Leco FP-428 analyser and shoot and grain P concentrations determined using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). In lupin, grain samples were analysed for the concentration of N, P and K in a continuous segmented flow auto-analyser (SFA) after sample digestion (CCWA 2000).

5.2.4.7 Soil analysis

5.2.4.7.1 Surface 0-10 cm

Soil samples were collected on six dates: 5 June, 17 July and 28 September 2001; 20 March and 27 June 2002; and 24 January 2003, which covered periods throughout the growing season and following harvest for both crops. Bicarbonate extractable soil P, nitrate-N, ammonium-N, total N and total P were measured over the growing season for selected plots during these sampling dates as described fully in Chapter 4, Section 4.2.11.

5.2.4.8 Statistical analysis

Data were analysed for differences between treatment means for DM production, P uptake, N uptake and grain yield using an ANOVA model in GENSTAT as described in Section 3.2.11. A single least significant difference (LSD) value at the 5% level of significance was used for comparing treatment means.

Data for the relationship between P applied and DM yield (kg/ha), P uptake (kg P/ha) and grain yield (kg/ha) for each of: biosolids, TSP and TSP2 (year 2), were fitted to equation (1).

Equation 1

$$y = a\,(1 - b \exp^{-cx}) \tag{1}$$

where y is the parameter being measured, x is the level of P applied (kg P/ha), and a, b and c are coefficients.

To find the parameters that produced the closest fit of the regression to the observed data, goodness-of-fit statistics were used with a linear solver (Vose 1996), as described fully in section 4.2.13.

The percentage RE of surface-applied biosolids compared with incorporated biosolids, TSP and TSP2 will only be presented here. The percentage RE was determined by dividing the coefficient (c) value of surface-applied biosolids by that for incorporated biosolids or TSP as based on equation (1).

5.3 Results

5.3.1 Glasshouse

5.3.1.1 Wheat shoot development

The method by which biosolids were incorporated into the soil had a significant effect on wheat growth and development. Overall, the surface application of biosolids (BT) resulted in the poorest development and plant growth of all the biosolids treatments at equivalent P loadings (Plate 5.3).

Plate 5.3 Effect of method of incorporation of biosolids on the growth of wheat shoots at 32 days after sowing

From left to right of plate: BT= biosolids applied to surface, no incorporation, BD = biosolids placed at bottom of pot only, BM = biosolids moderately incorporated, BS = biosolids incorporated as wet slurry, All biosolids treatments applied at 150 mg P/kg.

At 14 DAS, wheat shoots in the biosolids applied to the soil surface treatment (BT) were pale with necrotic symptoms developing on old leaves. Plants averaged two leaves/plant (Z12), and were most similar to the nil P treatment (P0). In comparison, all other biosolids treatments averaged three leaves/plant (Z13). Throughout the experiment, plants continued to grow poorly at nil P (P0). At 32 DAS, a positive growth response to increasing rates of MCP was observed. In addition, tillers were observed only in plants at the highest rates of inorganic P (80, 110 and 140 mg P/kg) and where biosolids had been fully incorporated (BM and BS) (Table 5.4).

Table 5.4 Effect of phosphorus source on wheat development at 32 days after sowing

Treatment number	Treatment	Zadoks leaf and tiller number
1	P0	13.1/20
2	P10	14.8/20
3	P20	15.1/20
4	P40	15.312.1
5	P60	15.5/21.7
6	P80	15.6/22.1
7	P110	15.7/22.7
8	P140	15.7/22.8
9	BT	14.5/20.3
10	BS	15.9/22.3
11	BM	15.8/22.9
12	BD	15.9/22.7

Values are means of five plants per pot for three replicates.

Zadoks decimal growth stages (Zadoks, Chang & Konzak 1974)

The roots of wheat had fully explored the soil volume and had grown to the depth of the pot (15 cm), with root size proportional to shoot growth. In the biosolids applied at depth (BD), the plant roots had invaded the clump of biosolids placed at the bottom of the pot. In the biosolids applied to the surface of the pot (BT), the plant roots had attempted to grow upwards into the biosolids.

5.3.1.2 Shoot dry matter

Shoot DM of wheat in the four biosolids treatments supplying 150 mg P/kg ranged from 0.76 to 3.64 g/pot at 33 DAS, which was dependent on the incorporation technique used (*P* <0.05, Figure 5.2). There were no differences in shoot DM of wheat where biosolids had been incorporated wet as slurry (BS), moderately mixed (BM) or applied at depth (BD). However, biosolids applied to the surface of the soil (BT) resulted in a lower shoot DM (*P* <0.05). In comparison, shoot DM of wheat at an equivalent rate of P (140 mg P/kg) supplied as MCP, measured 3.95 g/pot and was no different to BS, BM and BD (*P* >0.05). Shoot DM of wheat grown in biosolids applied to the surface of the pot (BT) were comparable to the nil P (P0) and 10 mg P/kg (P10) pots only.

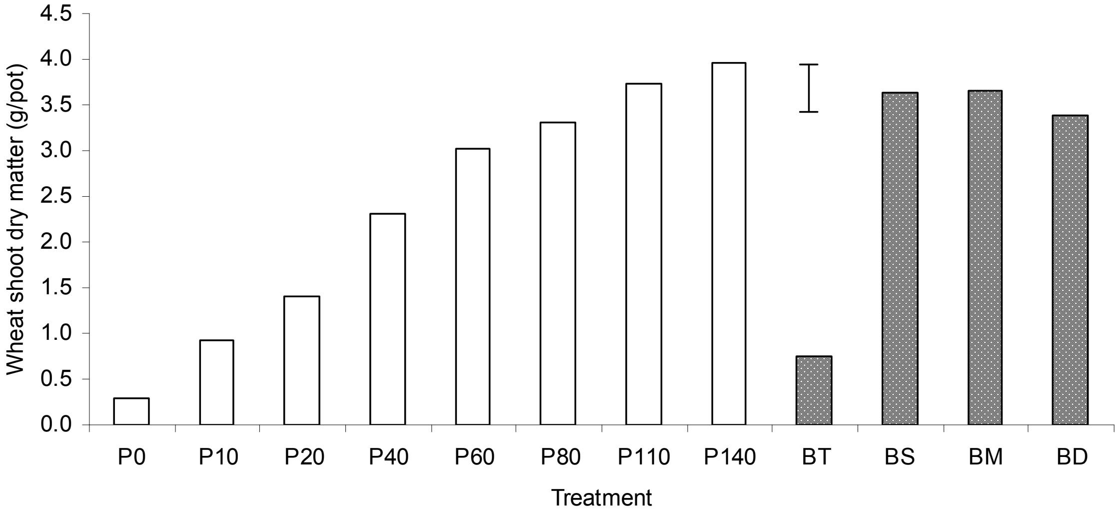


Figure 5.2 Effect of method of incorporation of biosolids on shoot dry matter of wheat at 33 days after sowing compared with increasing rates of inorganic P

BT=biosolids applied to surface, no incorporation, BS=biosolids incorporated as wet slurry, BM=biosolids moderately incorporated, BD=biosolids placed at bottom of pot only. All biosolids treatments applied at 150 mg P/kg. MCP given as P rate (mg P/kg). All values are the means of three replicates. Vertical line represents LSD (*P*=0.05).

5.3.1.3 *Shoot phosphorus concentrations*

Shoot concentrations of P in wheat at 33 DAS in soil with the highest levels of MCP (110 mg P/kg and 140 mg P/kg) and all biosolids treatments (150 mg P/kg) applied with a degree of incorporation (i.e. BT, BS and BD) ranged between 0.31% and 0.42%. There were no differences in shoot P concentrations among these treatments (*P* >0.05). Plants grown in the lower rates of MCP (<80 mg P/kg) and biosolids applied to the surface of the soil (BT) were considered to be P deficient, ranging from 0.092% in nil P (P0) to 0.22% in 80 mg P/kg and 0.22% in BT, respectively (data not presented).

5.3.1.4 *Shoot phosphorus uptake*

Biosolids applied to the soil surface (BT) resulted in significantly lower uptakes of P (1.65 mg P/pot) than the other biosolids treatments (*P* <0.05, Figure 5.3). Plants grown with biosolids incorporated into the soil (BS, BM, and BD) removed 14.16 mg P/pot, 14.86 mg P/pot and 14.05 mg P/pot, respectively at 32 DAS, being similar to plants in comparable rates of inorganic P (140 mg P/kg), which removed 15.94 mg P/pot.

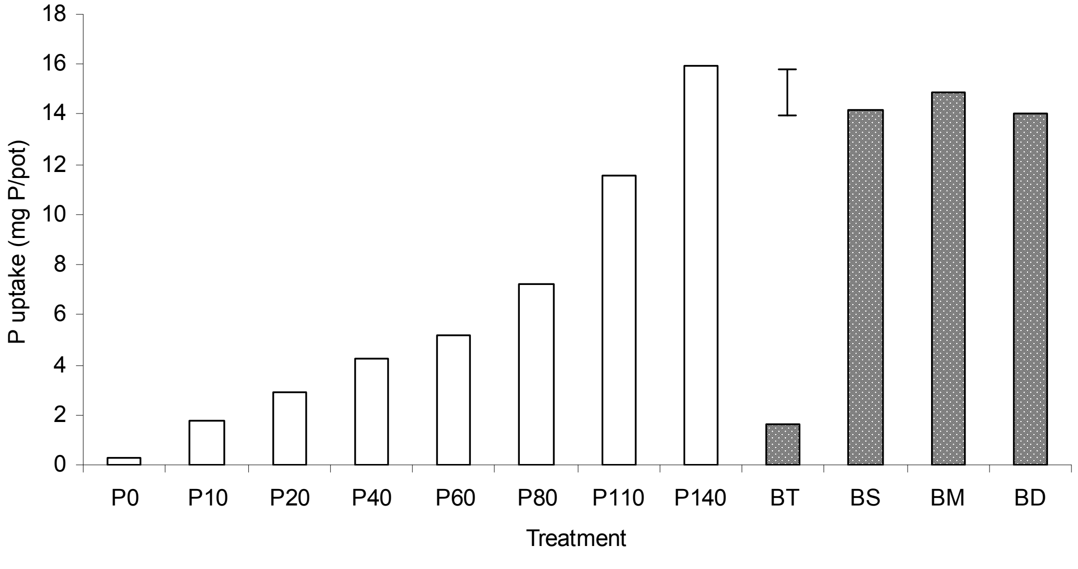


Figure 5.3 Effect of method of incorporation of biosolids on P uptake in wheat shoots compared with increasing rates of inorganic P at 33 days after sowing

BT=biosolids applied to surface, no incorporation, BS=biosolids incorporated as wet slurry, BM=biosolids moderately incorporated, BD=biosolids placed at bottom of pot only. All biosolids treatments applied at 150 mg P/kg. MCP given as P rate (mg P/kg). All values are means of three replicates (except BS, which is mean of two sample replicates only). Vertical line represents LSD (*P*=0.05).

5.3.1.5 Shoot nitrogen concentrations

The only significant difference in shoot concentrations of N in wheat at 33 DAS in the biosolids treatments was in the biosolids applied as slurry (BS), being lower than biosolids applied at depth (BD) (P <0.05). Shoot N concentrations in the biosolids mixed as wet slurry (BS) were similar to comparable rates of inorganic P (P >0.05, Figure 5.4). It should be noted that all MCP treatments received extra N to compensate for the biosolid N as discussed in the methods section. As noted in the highest MCP rates in Chapter 3, concentrations of shoot N decreased as shoot DM production increased.

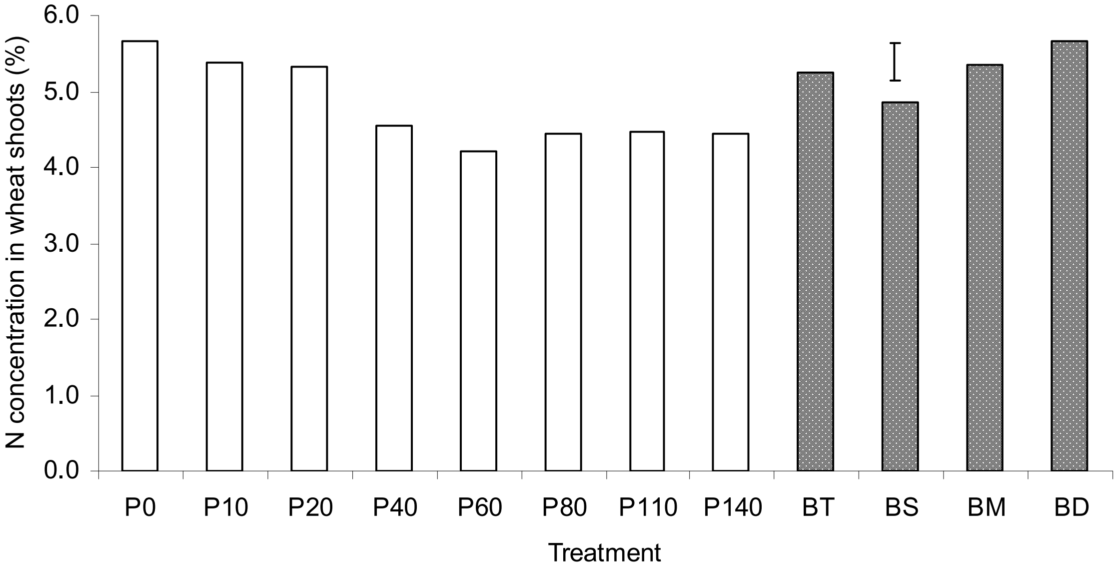


Figure 5.4 Effect of method of incorporation of biosolids on nitrogen concentration in wheat shoots measured at 33 days after sowing compared with increasing rates of inorganic P

BT=biosolids applied to surface, no incorporation, BS=biosolids incorporated as wet slurry, BM=biosolids moderately incorporated, BD=biosolids placed at bottom of pot only. All biosolids treatments applied at 150 mg P/kg. MCP given as P rate (mg P/kg). All values are means of three replicates. Vertical line represents LSD (P=0.05).

5.3.1.6 Bicarbonate extractable soil phosphorus

Soil samples collected from the centre of pots at 33 DAS showed variation in bicarbonate extractable P between the four biosolids treatments. Biosolids placed on the surface (BT) and at depth (BD) were similar to each other and showed little increase above the nil P (P0) and rates of MCP up to 20 mg P/kg (P20) (Figure 5.5). In comparison, biosolids mixed into the soil (BS and BM) resulted in increased bicarbonate extractable P (*P* <0.05) of up to 52 and 41 mg P/kg, respectively.

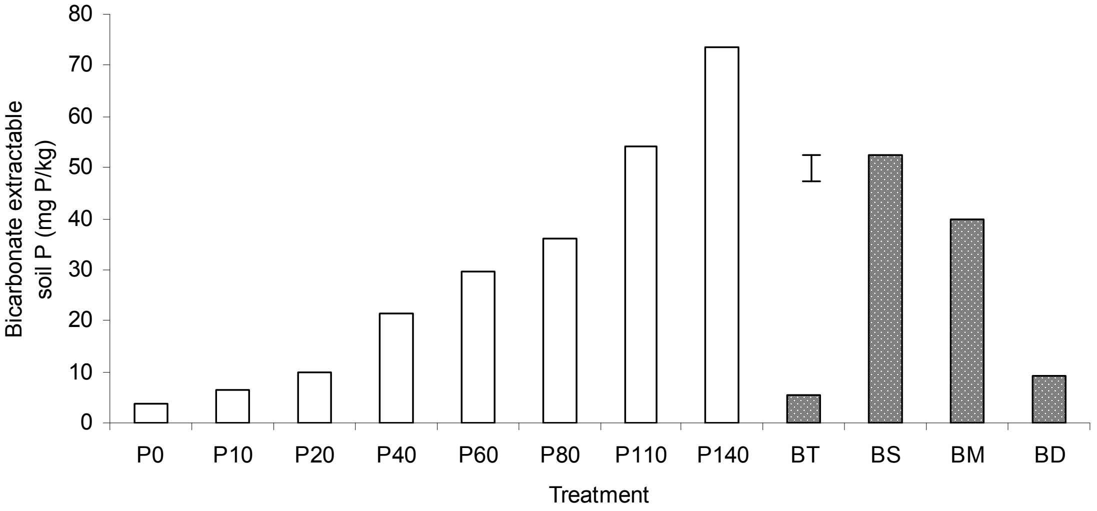
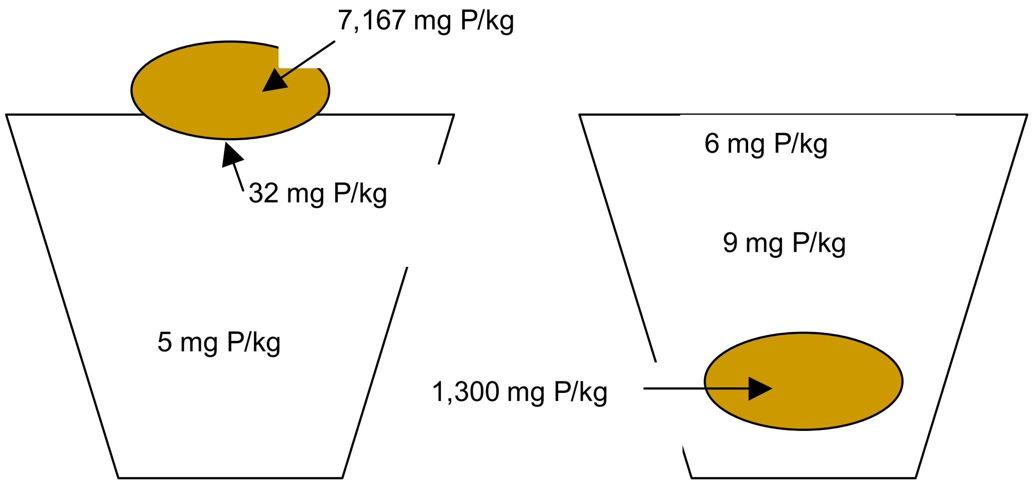


Figure 5.5 Effect of incorporation of biosolids on mean bicarbonate extractable soil P compared with inorganic P (MCP) as measured in the centre of each pot at 33 days after sowing

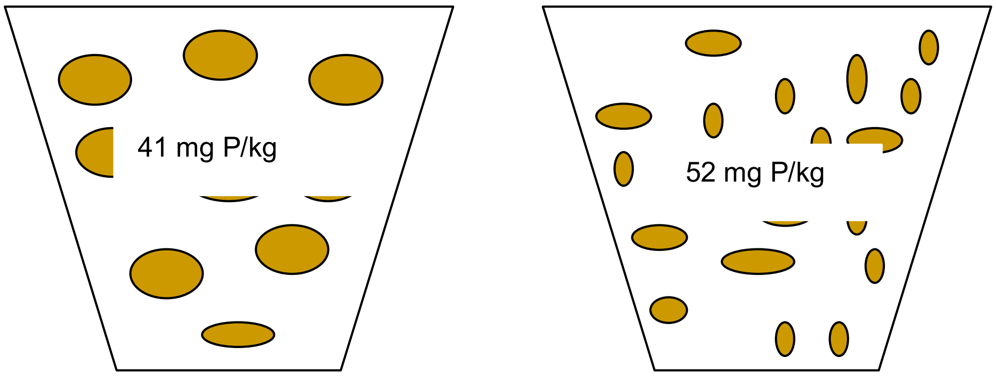
BT=biosolids applied to surface, no incorporation, BS=biosolids incorporated as wet slurry, BM=biosolids moderately incorporated, BD=biosolids placed at bottom of pot only. All biosolids treatments applied at 150 mg P/kg. MCP given as P rate (mg P/kg). All values are means of three replicates. Vertical line represents LSD (*P*=0.05).

Soil sampling at depth in selected treatments highlighted major differences in bicarbonate extractable P, with values represented schematically in Figure 5.6. Soil samples collected from the soil surface in BT measured 7,167 mg P/kg and decreased rapidly to 32 mg P/kg in the 1 cm of soil directly below this. Biosolids placed at depth (BD) resulted in low bicarbonate extractable soil P (6 mg P/kg) on the surface of the pot and the centre of the pot (5 mg P/kg), but increased to high levels (1,300 mg P/kg) at the depth of 10 cm where biosolids were initially placed.



BT = biosolids top

BD = biosolids at 10cm depth



BM = biosolids moderately incorporated

BS = biosolids incorporated as wet slurry

Figure 5.6 Schematic diagram highlighting differences in bicarbonate extractable soil P as dependent on the sampling location for the four biosolids treatments

Values are the means of three replicates.

5.3.1.7 Total soil phosphorus

There was a strong relationship between total P concentrations of soil samples and bicarbonate extractable P values. As the MCP rate increased, total P increased proportionately to a maximum of 180 mg P/kg measured at 33 DAS. Biosolids incorporated into the soil (BS and BM) corresponded with the highest measured total P concentrations (i.e. 193 and 183 mg P/kg, respectively). Where biosolids were not incorporated throughout the soil profile (BT and BB), total P was lower measuring 69 and 95 mg P/kg, respectively (Table 5.5).

5.3.1.8 Phosphorus Retention Index (PRI)

The PRI values decreased with increasing rates of MCP, from 16.7 mL/g in nil P to 7.0 mL/g in the highest rate of MCP, similar to Chapter 3. Interestingly the biosolids treatments placed at depth (BD) or on the surface (BT) increased the PRI to 21.3 mL/g and 22.3 mL/g, respectively ($P < 0.05$). Biosolids mixed into the soil thoroughly (BS and BM) increased soil PRI to a lesser extent with the PRI increased more so than for comparable amounts of MCP, (i.e. 11.3 and 13.0 mL/g) (see Table 5.5). Further increases in soil PRI following biosolids application were not measured in a third consecutive harvest (Chapter 3).

5.3.1.9 Soil nitrogen

There were no differences in concentrations of total soil N between the four biosolids treatments ($P > 0.05$), although the total soil N decreased with increasing rates of MCP ($P < 0.05$, Table 5.5).

Mineral N was examined further for the four biosolids treatments to investigate the method of incorporation on soil N forms, given that the biosolids treatment pots received less mineral N than the MCP pots. There were no differences in nitrate-N in biosolids treatments due to the method of incorporation, although ammonium-N was higher in soil from the biosolids on the surface (BT) ($P > 0.05$, Table 5.5). Surface-applied biosolids (BT) treatments produced smaller plants with lower requirements for N. In comparison, soil mineral N decreased with increasing MCP rates, corresponding to larger plants with increased demands.

5.3.1.10 Other soil constituents

Prior to application, the mean pH (H_2O, 1:5) in biosolids from Beenyup WWTP was 7.7 (Chapter 3, Table 3.3). Soil pH ($CaCl_2$), as sampled from the centre of each pot, increased where biosolids were incorporated fully (BS and BM) compared with select placement (BT and BB) (*P* <0.05). In comparison, MCP treatments were lower than for fully incorporated biosolids with no differences in pH values across rates (*P* >0.05, Table 5.5).

All biosolids treatments increased soil organic carbon concentrations above the MCP treatments; however, there were no differences among the four biosolids treatments (*P* >0.05, Table 5.5).

Table 5.5 Effect of the method of incorporation of biosolids compared with increasing rates of inorganic P on selected soil constituents at 33 days after sowing, as measured in the centre of each pot

Soil constituent	pH ($CaCl_2$)	NO_3-N (mg N/kg)	NH_4-N (mg N/kg)	Total N (%)	Total P (mg P/kg)	PRI (mL/g)	Org C W|B (%)
Treatment and rate (mg P/kg)							
P0	4.8	72.0	50.0	0.076	59.0	16.7	1.85
P10	4.7	73.3	33.7	0.078	64.3	16.0	1.86
P20	4.7	62.3	22.7	0.070	68.3	15.0	1.81
P40	4.7	45.7	11.3	0.071	86.7	13.3	1.83
P60	4.7	29.7	8.0	0.072	98.3	12.0	1.95
P80	4.7	18.0	6.3	0.064	117	9.8	1.74
P110	4.7	7.0	5.7	0.065	147	8.7	1.80
P140	4.7	4.3	6.3	0.067	180	7.0	1.84
BT150	4.7	67.0	51.7	0.088	69.0	22.3	2.22
BS150	5.0	79.3	22.3	0.100	193	11.3	2.19
BM150	5.0	59.0	23.0	0.101	183	13.0	2.31
BD150	4.7	52.0	25.7	0.095	94.0	21.3	2.35
LSD (*P* = 0.05) *(biosolids treatments only)							
	0.07	ns	14.10	ns	47.17	2.64	ns
LSD (*P* = 0.05) **(all treatment means)							
	0.08	15.94	11.20	0.009	24.72	1.54	0.193

BT=biosolids applied to surface, no incorporation, BS=biosolids incorporated as wet slurry, BM=biosolids moderately incorporated, BD=biosolids placed at bottom of pot only. All biosolids treatments applied at 150 mg P/kg. MCP given as P rate (mg P/kg).

Values are means of three replicates. Where the difference between any two values in any column is greater than the LSD, then those values are significantly different at $P < 0.05$ unless stated ns (not significant). ANOVA analysed for *biosolids treatments separately and then for **all twelve treatment means.

Data from report number 00A586 Chemistry Centre of Western Australia. pH ($CaCl_2$) by 0.01 M $CaCl_2$, total N, nitrate N and ammonium N extracted by 1 M KCl, total P, bicarbonate extractable P extracted by 0.5 M $NaHCO_3$ (1:100), Organic carbon by Walkley and Black method, EC (1:5) at 25°C,

(mg/kg = milligrams per kilogram, mL/g = millilitres per gram)

5.3.2 Field experiment

General details such as germination and seasonal weather conditions relating to the field trial are presented in Chapter 4. There were no differences in plant establishment between the surface-applied or incorporated biosolids treatments over the two seasons. Wheat averaged 195 and 191 plants/m^2, respectively and lupins averaged 33 and 27 plants/m^2, respectively over the two treatments.

5.3.2.1 Incorporation of biosolids

Biosolids were surface-applied at a rate of 2.86 t DS/ha (treatment 15). Sub-sampling of biosolids remaining of the soil surface at 26 DAS resulted in 100% recovery. Incorporation with disc ploughs using the same rate of biosolids (treatment 13) resulted in 38% of biosolids being incorporated below the soil surface. Incorporation with the disc plough was greatest at the lowest rates of biosolids. Figure 5.7 shows that almost 70% of the biosolids applied at 0.41 t DS/ha were incorporated, whereas less than 30% were incorporated at the highest rate of 4.91 t DS/ha.

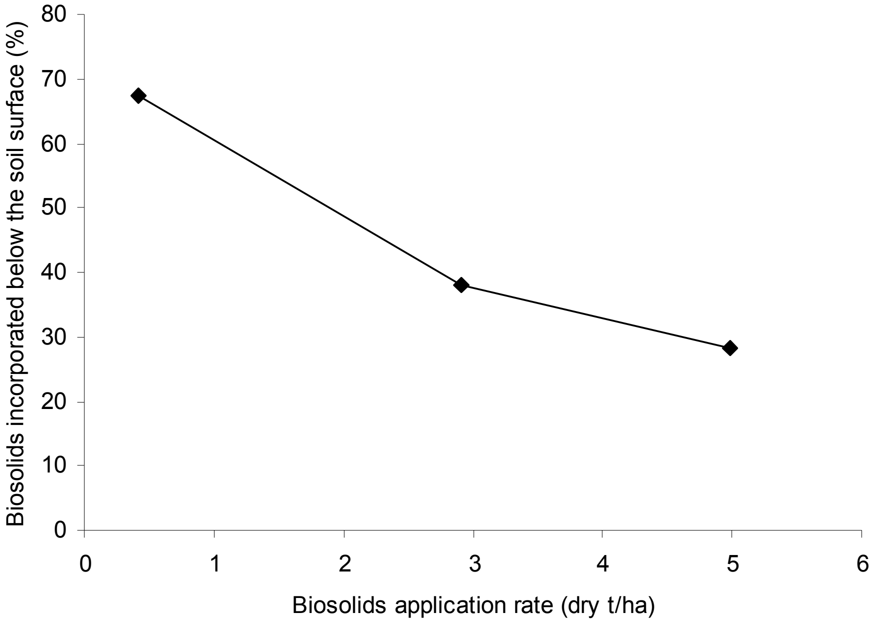


Figure 5.7 Relationship between biosolids application rate and percentage incorporation

Values are means of three replicates.

5.3.2.2 Dry matter accumulation and plant development

Throughout the first growing season, the incorporated biosolids treatment resulted in higher shoot DM of wheat compared with surface-applied biosolids or nil biosolids (control) (Figure 5.8). Differences between the two biosolids treatments became more apparent over time (Plate 5.4 and Plate 5.5), and were significant from 67 DAS (*P* <0.05).

Plant development over the growing season was similar for all treatments. At 27 DAS, wheat shoots were forming their third leaf and tillering was just commencing (Z12.8/20.1 to Z13/20.1). At 67 DAS, all treatments were producing their sixth leaf and all treatments still had less than one tiller on average (Z15.3/20.3 to Z15.9/20.7). At 96 DAS, both biosolids treatments averaged one tiller, whereas the control had not progressed any further.

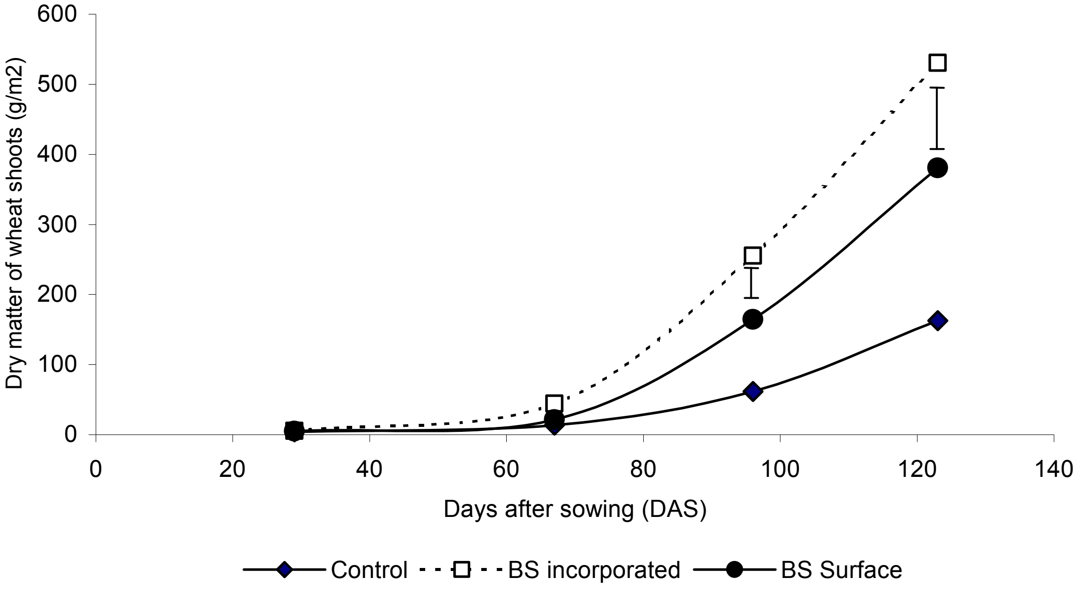


Figure 5.8 Mean seasonal production in shoot dry matter of wheat for biosolids (BS) that are surface-applied compared with incorporated and nil biosolids (control)

Values are means of three replicates. Vertical line represents LSD (*P*=0.05) for each sampling date.

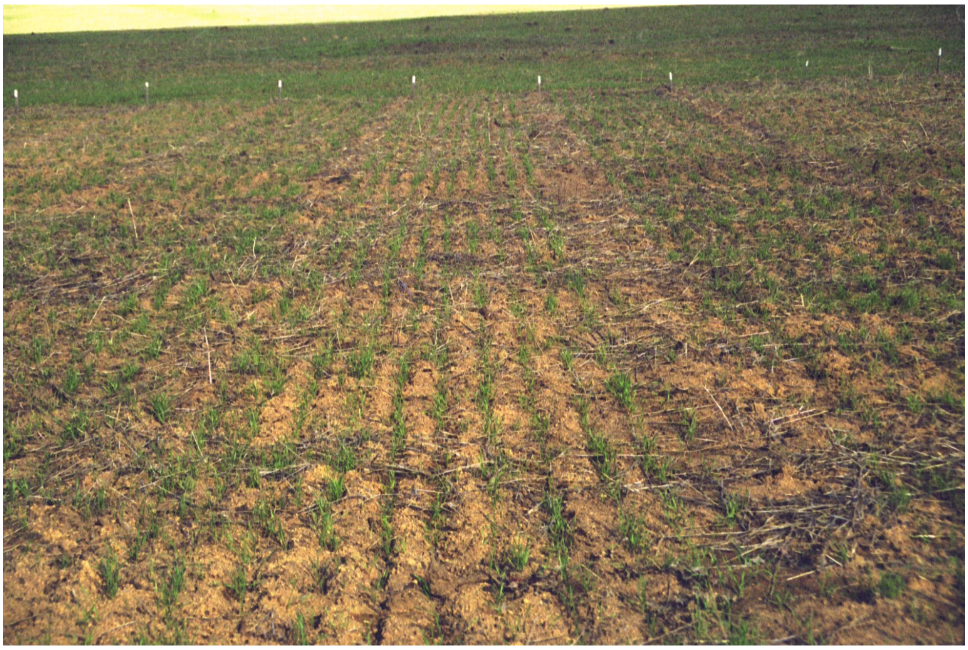


Plate 5.4 Germination and early development of wheat in 70 kg P/ha as TSP (centre plot), 85 kg P/ha incorporated biosolids treatment (left plot) and 85 kg P/ha surface-applied biosolids (right plot)

Plate 5.5 Development of wheat at tillering in 70 kg P/ha as TSP (centre plot), 85 kg P/ha incorporated biosolids treatment (left plot) and 85 kg P/ha surface-applied biosolids (right plot)

By the second growing season, there was no significant difference in shoot DM of lupin between surface and incorporated biosolids treatments, applied the previous season (*P* >0.05, Figure 5.9). Both biosolids treatments produced more shoot DM than the nil biosolids at all sampling dates (*P* >0.05).

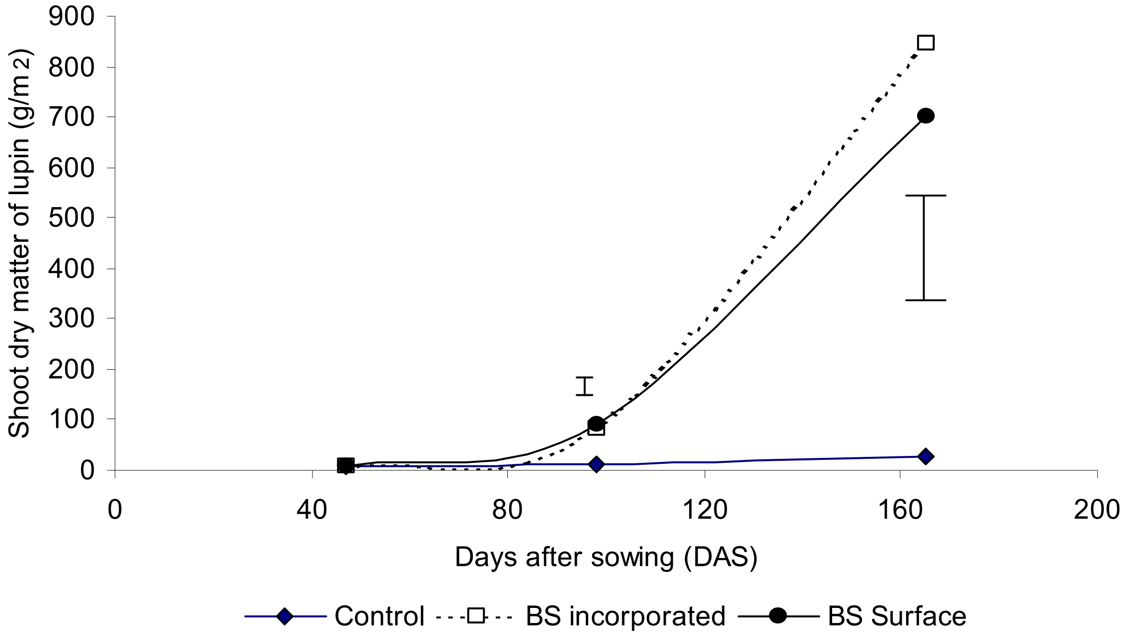


Figure 5.9 Mean seasonal shoot dry matter of lupin in the second season following the application of biosolids (BS) as surface-applied or incorporated or no biosolids (control)

Values are means of three replicates. Vertical line represents LSD (*P* = 0.05) at each sampling date.

5.3.2.3 Nitrogen and phosphorus uptake

From Table 5.6, N and P uptake by wheat shoots tended to be highest in the incorporated biosolids treatment as compared with surface-applied biosolids in the first season. Differences however, were mostly not significant (*P* >0.05). Concentrations of P in wheat shoots at 67 DAS were as follows: nil P = 0.20%, incorporated biosolids = 0.26% and surface-applied biosolids = 0.24%.

In the second season, N and P uptake by lupin shoots showed no differences between the two biosolids treatments, regardless of the method of incorporation. The nil P treatment resulted in low P and N uptake over both years.

Table 5.6 Comparison between surface-applied biosolids, incorporated biosolids and nil P for shoot nitrogen and phosphorus uptake over two growing seasons

Days after sowing	**Control (nil P)**	**Biosolids incorporated (85 kg P/ha)**	**Biosolids surface (85 kg P/ha)**	**LSD (*P* = 0.05)**
Nitrogen uptake in wheat shoots (year one) (kg N/ha)				
27	1.63	3.03	2.19	0.78
67	5.11	15.5	8.81	5.77
96	13.2	48.7	37.6	10.7
123	25.9	57.2	52.2	13.3
Phosphorus uptake in wheat shoots (year one) (kg P/ha)				
27	0.06	0.18	0.21	0.06
67	0.27	1.18	0.51	0.34
96	0.80	3.81	2.93	0.96
123	1.25	4.45	3.43	0.98
Nitrogen uptake (removal) in lupin shoots (year two) (kg N/ha)				
47	3.93	3.98	4.15	ns
98	4.11	32.3	33.5	8.96
165	7.52	204	181	45.9
Phosphorus uptake in lupin shoots (year two) (kg P/ha)				
47	0.12	0.22	0.19	0.04
98	0.13	2.31	2.28	0.78
165	0.28	8.18	6.77	2.10

Values are the means of three replicates. Where the difference between any two values in any row is greater than the LSD, then those values are significantly different at *P* <0.05 unless stated not significant (ns). LSD calculated for all treatment means as outlined in Chapter 4.

5.3.2.4 Grain yield

Grain yield of wheat in the first year was significantly lower in surface-applied biosolids (2.04 t/ha) compared with incorporated biosolids (2.67 t/ha), although both biosolids treatments yielded higher than the nil P treatment (0.83 t/ha) (*P* <0.05, Table 5.7). The uptake of N and P in wheat grain was similarly affected, although not apparent from grain N and P concentrations. By the end of the second year, grain yield of lupin was unaffected by the initial biosolids treatment.

Table 5.7 Comparison between surface-applied biosolids, incorporated biosolids and nil P for grain yield and grain nutrient concentrations of N and P over two growing seasons

Treatment	N conc. (%)	N uptake (kg N/ha)	P conc. (%)	P uptake (kg P/ha)	Grain yield (t/ha)
Wheat grain (year one)					
Control (nil P)	1.90	15.5	0.14	1.20	0.83
Biosolids incorporated (85 kg P/ha)	1.63	43.5	0.15	3.93	2.67
Biosolids surface (85 kg P/ha)	1.65	33.4	0.14	2.79	2.04
LSD (*P*=0.05)	0.09	5.27	ns	0.83	0.35
Lupin grain (year two)					
Control (nil P)	5.78	2.60	0.25	0.12	0.045
Biosolids incorporated (85 kg P/ha)	5.48	87.2	0.25	3.99	1.59
Biosolids surface (85 kg P/ha)	5.73	80.5	0.26	3.61	1.41
LSD (*P*=0.05)	ns	17.9	ns	0.79	0.26

Values are the means of three replicates. Where the difference between any two values in any column is greater than the LSD, then those values are significantly different at *P* <0.05 unless stated not significant (ns).

5.3.2.5 Relative effectiveness of surface-applied biosolids compared with incorporated biosolids

At harvest in year one, the RE for grain yield in surface-applied biosolids was 58% relative to incorporated biosolids and 39% as effective as that of TSP (Table 5.8). The RE for DM production in surface-applied biosolids compared with incorporated biosolids ranged from 20% to 41% over the growing season. The RE for shoot P uptake in surface-applied biosolids compared with incorporated biosolids was higher than DM, increasing from 24% at 67 DAS to 67% at 98 DAS and 59% at 165 DAS.

Table 5.8 Percentage relative effectiveness (RE) of surface-applied biosolids (BS-S) compared with incorporated biosolids (BS) and TSP for shoot dry matter of wheat and shoot P uptake over three sampling dates and final grain yield

	% Relative effectiveness (RE)			**Coefficient**
	BS-S/BS	BS-S/TSP	BS/TSP	*c* (BS-S)
Days after sowing (DAS)				
		Dry matter (g/m^2)		
67	20	6	30	0.0019
96	41	16	40	0.0067
123	35	16	46	0.0064
		Shoot P uptake (kg/ha)		
67	24	8	33	0.0019
96	67	35	53	0.0068
123	59	32	55	0.0058
		Grain Yield (kg/ha)		
210	58	39	67	0.0090

Calculated using Microsoft Excel Solver for equation (1) and ratio of *c* coefficient determines % relative effectiveness. Complete values of a, b and c coefficients for equation (1) for the relationships between wheat shoot dry matter and shoot P uptake over four sampling dates and grain yield are given in Chapter 4 (Table 4.5).

Values for DM and P uptake at 27 DAS not presented due to plants being of insufficient size to accurately determine coefficients. The standard error of the RE was approximately 10%.

At lupin harvest in year two, the RE for surface-applied biosolids applied in the previous year had improved to be 95% relative to incorporated biosolids and 57% as effective as TSP (Table 5.9). Improvements were also noted for P uptake and seasonal DM production.

Table 5.9 Percentage relative effectiveness (RE) of surface-applied biosolids (BS-S) compared with incorporated biosolids (BS), TSP and freshly applied TSP (TSP2) for lupin dry matter and shoot P uptake over three sampling dates and final grain yield

	Percentage relative effectiveness (%RE)				Coefficient
	BS-S/ BS	BS-S/ TSP	BS/ TSP	BS-S/ TSP2	*c* (BS-S)
Days after sowing					
			Dry matter (g/ha)		
98	118	89	76	49	0.0120
165	88	74	84	50	0.0080
			Shoot P uptake (kg/ha)		
47	75	57	75	30	0.00064
98	93	78	84	44	0.0015
165	79	62	78	51	0.0049
			Grain yield (kg/ha)		
211	95	57	60	43	0.0073

Calculated using Microsoft Excel Solver for equation (1) and ratio of *c* coefficient determines % relative effectiveness. Complete values of a, b and c coefficients for equation (1) for the relationships between wheat shoot dry matter and shoot P uptake over four sampling dates and grain yield are given in Chapter 4 (Tables 4.8 and 4.9). Values for DM at 47 DAS not presented due to plants being of insufficient size to accurately determine coefficients. The standard error of the RE was approximately 10%.

5.3.2.6 Yield components and other harvest measurements

There were no differences in DM, grain yield and harvest index between the surface-applied biosolids treatment and incorporated biosolids treatment measured on four, 0.5 m by 6 rows in wheat (year one) at 178 DAS (*P* >0.05, Table 5.10); although 1,000 grain weights were highest in the incorporated biosolids treatment (*P* <0.05). The control (nil P) had significantly lower yield components and grain yield compared with the biosolids treatments (*P* <0.05). Grain yields 32 d later (210 DAS) in the machine harvest, were highest where biosolids had been incorporated (*P* <0.05, Table 5.7).

Table 5.10 Yield components and other harvest measurements of wheat for surface-applied biosolids, incorporated biosolids and nil biosolids at final hand harvest (year one) at 179 DAS

Treatment	Total dry matter (g/m^2)	Harvest index	Ear weight (g)	Number of grains/ ear	Ear number/ m^2	Grain number/ m^2	1,000 grain weight (g)	Grain yield (g/m^2)
Control (nil P)	241	0.31	0.43	104	174	1,826	41.34	75.5
Incorporated biosolids (85 kg P/ha)	510	0.33	0.79	177	219	3,854	44.62	172
Surface-applied biosolids (85 kg P/ha)	529	0.35	0.78	181	238	4,328	42.98	186
LSD (*P*=0.05)	**111.7**	**ns**	**ND**	**ND**	**ND**	**ND**	**1.38**	**60.7**

The LSD was not determined (ND) for all of the measurements. Where the difference between any two values in each column is greater than the LSD (where calculated), those values are significantly different at *P* <0.05, unless stated not significant (ns).

All methodology and calculations described in Chapter 4, section 4.2.9.1.

5.3.2.7 Soil measurements over two years (0–10 cm)

There were no differences in bicarbonate extractable P in the <2 mm soil fraction between the two biosolids treatments over the two years at any sampling date (*P* >0.05, Table 5.11). There were no differences in total N and total P between surface-applied and incorporated biosolids at 305, 405 and 615 DAS (*P* >0.05). However, the soil preparation method of sieving through a 2 mm sieve was considered unreliable where biosolids were applied to the soil (Chapter 4).

Basal applications of urea were applied in year one over all treatments and consequently differences in nitrate-N and ammonium-N would be expected to be minor. Nitrate-N and ammonium-N measured in the 0–10 cm fraction generally decreased in incorporated biosolids more so than for surface-applied biosolids or nil P (control), consistent with larger plants with higher N requirements (Table 5.12).

Soil pH ($CaCl_2$) values at the final sampling (305 DAS) were 5.7, 5.7 and 5.5 for the control, incorporated biosolids and surface-applied biosolids, respectively and were not significantly different (*P* >0.05). Organic carbon (W/B)% concentrations at the final sampling date were 2.7%, 2.8% and 2.7% for the control, incorporated biosolids and surface-applied biosolids, respectively and were not significantly different (*P* >0.05).

Table 5.11 Concentrations of bicarbonate extractable P (mg P/kg) following the application of surface-applied biosolids, incorporated biosolids and nil P for six sampling dates over two years

	Days after sowing first crop and sampling date					
	18	**60**	**133**	**305**	**405**	**615**
Treatment & P rate (kg P/ha)	**5/6/01**	**17/7/01**	**28/9/01**	**20/3/02**	**27/6/02**	**24/1/03**
Control (nil P)	6.3	6.0	4.7	5.0	4.0	5.0
Incorporated biosolids (85 kg P/ha)	10.3	9.0	9.0	8.7	10.3	9.3
Surface-applied biosolids (85 kg P/ha)	7.7	7.0	7.3	7.3	14.7	12.3
LSD (*P*=0.05)	ns	ns	ns	3.0	6.3	5.6

Values are the means of three replicates. Where the difference between any two values in any column is greater than the LSD, then those values are significantly different at $P < 0.05$ unless stated not significant (ns). Bicarbonate extractable P extracted by 0.5 M $NaHCO_3$ (1:100), Chemistry Centre (WA). Report numbers 00A778, 01A111, 01A217, 01A629, 02A01 and 03A73.

Table 5.12 Concentrations of ammonium and nitrate forms of N (mg N/kg) for surface-applied biosolids, incorporated biosolids and nil biosolids at four sampling dates over two growing seasons

Days after sowing	**Control (nil P)**	**Incorporated biosolids** (85 kg P/ha)	**Surface-applied biosolids** (85 kg P/ha)
27 DAS (year one)			
NH_4-N (mg/kg)	16	12	19
NO_3-N (mg/kg)	15	2	7
60 DAS (year one)			
NH_4-N (mg/kg)	41	46	36
NO_3-N (mg/kg)	11	7	12
133 DAS (year one)			
NH_4-N (mg/kg)	16	12	19
NO_3-N (mg/kg)	15	2	7
405 DAS (year two)			
NH_4-N (mg/kg)	53	60	46
NO_3-N (mg/kg)	10	3	3

Values are the means of three replicates. LSD ($P = 0.05$) calculated for 133 DAS only as follows: NH_4-N = 8.9 (not significant), NO_3-N = 4.6 (all treatments significant).

5.4 Discussion

5.4.1 Effect of positional placement of biosolids on crop growth and yield over time

The positional placement of biosolids and its mixing with the soil influenced crop growth and yield under both glasshouse (Table 5.4, Figure 5.2 and Plate 5.3) and field conditions (Figure 5.8). Biosolids placed on the surface of the pot, or not fully incorporated in the field reduced plant yields. Where soil moisture and temperature conditions were optimum for plant growth, such as in the glasshouse, differences between surface-applied biosolids and incorporated biosolids were observed as early as 33 DAS. In the field, plant growth differences between surface-applied and incorporated biosolids were not observed until 67 DAS. Wheat growth rate was increased in the glasshouse and responses to incorporation were more pronounced than in the field.

The pot and field experiments differed in a number of properties. The pot experiment was characterised by: higher rates of biosolid P (150 mg P/kg) as compared with the field (57 mg P/kg); a more homogenous distribution of biosolids (incorporated treatments); more reliable and consistent soil moisture in the non-draining pots; a confined area for root growth; higher average soil temperatures; regular applications of basal N; and the use of pre-germinated seed. Wheat plants in the glasshouse at 33 DAS (Table 5.4) were at a similar stage of development to plants in the field at 67 DAS due to environmental conditions, such as warmer temperatures (25^{o}C), being optimum for wheat growth. The warmer soil temperature in the pots would also be expected to increase soil microbial activity. The pot and glasshouse experiments both used soils of lateritic origin, albeit from different sites, and the soil in the glasshouse was sieved.

In the field experiment, plant growth differences between surface-applied and incorporated biosolids became less significant as the season progressed, and disappeared after the soil was disturbed during seeding of the second crop. In comparison, where surface-applied biosolids were not disturbed in another glasshouse experiment for three consecutive wheat crops, there was no improvement in growth with surface-applied biosolids relative to incorporated biosolids (Pritchard et al. 2002). Each crop was grown for 33 d and soil fallowed for an equal period of time, with biosolids removed carefully and then replaced on the surface post sowing. Hence in the pots, there was negligible opportunity for mixing of surface-applied biosolids in the soil.

The inclusion of increasing rates of MCP in the pot trial enabled a comparison to be made for a fixed rate of biosolids against the P response curve. Concentrations of P in wheat shoots in the glasshouse experiment were below 0.56%, and therefore P deficient (Reuter & Robinson 1997), as was wheat grown in the field experiment at 67 DAS with shoot P concentrations below 0.35%. Therefore the rates of inorganic P complemented the P deficient soil type chosen for both experiments and achieved a positive response to applied P.

Basal applications of N to all biosolids and inorganic P treatments were included in an attempt to ensure N did not confound the effects of P. This was taken into consideration when comparing N concentrations of shoots and inorganic soil N forms, as discussed in detail in Chapters 3 and 4. In the glasshouse experiment, comparison between biosolids could be made directly as the same biosolids rates and basal N had been applied, with the only variable being the method of incorporation.

In the glasshouse experiment, N concentrations in shoots of wheat in all biosolid treatments at 33 DAS were >5.0% (Figure 5.4), being the value reported as critical at 90% of maximum yield at a comparable stage of development (Reuter & Robinson 1997). There were no differences for percentage total soil N and levels of nitrate-N amongst the four biosolids treatments at 33 DAS (Table 5.5). Higher amounts of ammonium-N in the surface-applied biosolids were probably due to reduced requirements for N by the smaller plants. In the field experiment, there were no discernable patterns for concentrations of ammonium-N or nitrate-N over four sampling dates following the application of biosolids and urea (Table 5.12).

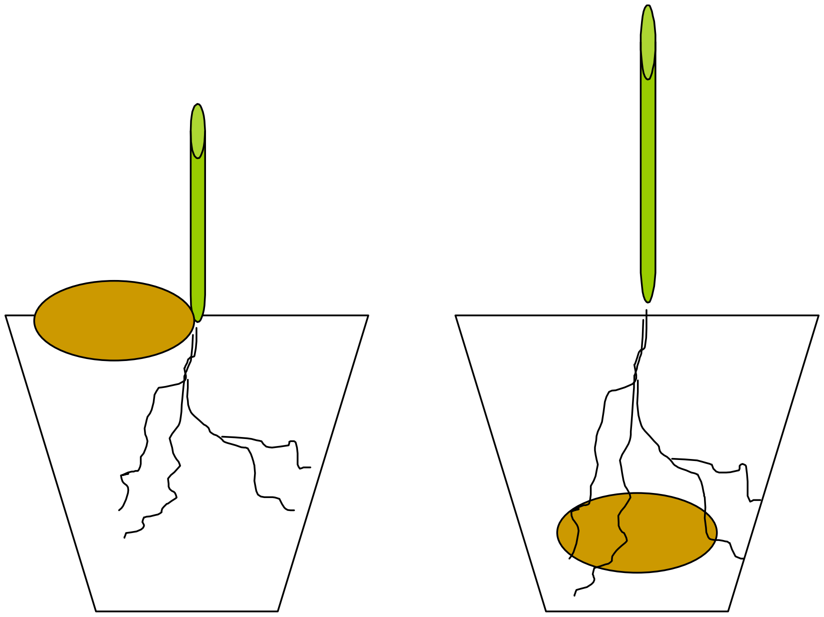
5.4.2 Effect of positional placement of biosolids on available soil P and P uptake

There was limited movement of plant available P into the soil surrounding the biosolids as measured by differences in bicarbonate extractable P at different depths in the pot experiment (Figure 5.6). Bicarbonate extractable P measured directly above or below the placed biosolids was low, which indicated little movement of P through the soil. Rydin and Ottabong (1997) attributed differences in nutrient release in biosolids to the application of non-homogenous clumps of biosolids. Particles of biosolids in the soil were shown to remain as discrete aggregates for at least three months after biosolids application (Sort & Alcaniz

2001). Hedley and McLaughlin (2004) concluded that the spatial heterogeneity of applied biosolids in the soil matrix had a large effect on initial P reactions in the soil, with the transformation and release of biosolid P to soluble orthophosphate determined by several key chemical reactions.

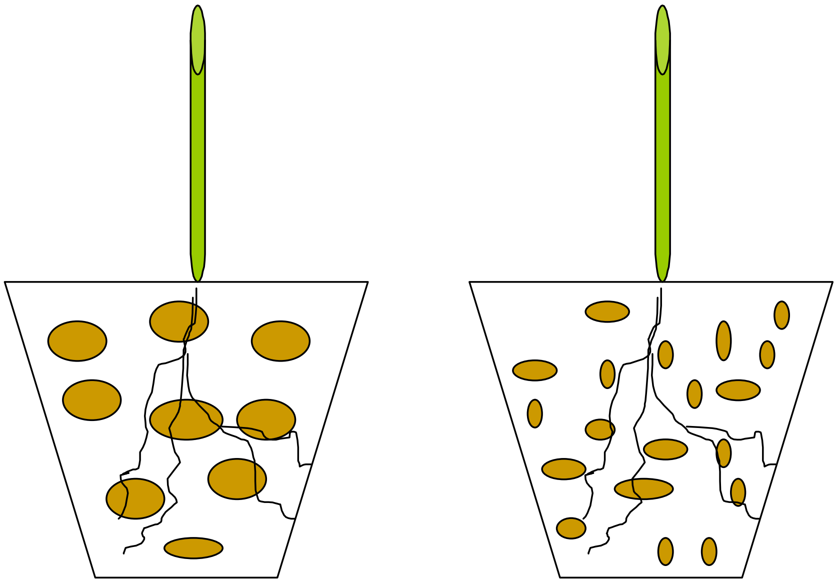
Shoot P uptake (Figure 5.3) and bicarbonate extractable P (Figure 5.5) values indicated that the interception of P by plant roots played a large role in sourcing P, dependent largely on the mixing of the biosolids. The schematic diagram in Figure 5.10 illustrates in concept the poor uptake of P in surface-applied biosolids, given the limited movement of P out of biosolids and into the soil. Absorption of P by plant roots is dependent on interception by roots as they grow, with P in solution strongly sorbed by soil particles (Bolland & Allen 2003; Glendinning 1999). In the early stages of the growth of wheat plants, the uptake of fertiliser P was influenced to a large extent by root distribution (McLaughlin, Alston & Martin 1988c). The uptake of P by plants grown in sludge (King & Morris 1973; Pastene 1981) and ground sheep dung mixed with the soil (Bromfield 1961; Gunary 1968) highlight the role of plant roots in the interception of P.

In the pot experiment at 14 d after sowing, plants were able to source P in biosolids placed 10 cm below the seed, as implied by improved Zadoks scores measured at 14 DAS relative to the control treatment, with no reduction in wheat development at 32 DAS (Table 5.4). Bicarbonate extractable P at the depth of 10 cm was 1,300 mg P/kg, whereas in contrast the topsoil was 6 mg P/kg (Figure 5.6). Plants were unable to obtain adequate P when biosolids were placed on the soil surface, yields being most similar to the nil P treatment. Watering was necessary on most days, which resulted in the surface-applied biosolids continually being wetted. Even so, there was little movement of water-soluble P out of biosolids into the soil. Bicarbonate extractable P in the clump of biosolids on the surface was 7,167 mg P/kg and at a depth of 1 cm was 232 mg P/kg.



BT = Biosolids top

BD = biosolids at 10cm depth



BM = biosolids moderately incorporated

BS = biosolids incorporated as wet slurry

Figure 5.10 Schematic diagram showing growth of wheat shoots and roots in surface-applied biosolids (BT) compared with incorporated treatments (BD, BM & BS)

Plant roots were capable of sourcing P, given adequate soil moisture and an even distribution of biosolids in the soil profile. The distribution and density of plant roots, however, was not investigated although it may be expected that root density would be increased where P concentration is highest, i.e. unmixed lumps of biosolids. The results of the present experiment support the premise by Barrow (1999), in that Perth biosolids, although of a low solubility, would be an effective source of P provided that the biosolids are mixed with the soil so that plant roots can get close to the P source and induce the dissolution of P. A low solubility of biosolid P would be expected given that much soluble P is removed during processing.

The supply of P is crucial during the first 10 d of wheat seedling growth (Smith 1967), highlighting the importance of adequate seed sources of P and initial soil P concentration. Primarily, the native soil P (i.e. P not added that season) contributes more to P nutrition in wheat plants than does freshly applied fertiliser P. McLaughlin and others (1988a) recovered only 11.6% of fertiliser P applied that season in a wheat crop at 95 DAS, and similarly Sharpley (1986) recovered 9-23% of fertiliser P applied to a wheat crop at 70 DAS under field conditions. The availability of native soil P is therefore important in supplying plants with P early in the growing season. It is unknown if the biosolids used in the experiments presented herein affected mineralisation of native soil P_o, for example through increased carbon inputs.

The forms of P in Perth biosolids were described in Chapter 3, with the P in biosolids used in this study predominantly inorganic in form (i.e. 92%, Table 3.6). The final distribution of soil P fractions following the application of biosolids was similar to that obtained by inorganic fertiliser P (Figure 3.7), which would suggest similar uptake of P by plants, microorganisms and soil reactions. Given the low initial organic P fraction in Perth biosolids (i.e. 8%, Table 3.6) the mineralisation of the organic P pool in biosolids would be expected to be minor initially. However, more detailed investigation through the use of isotope labelled P, as studied by McLaughlin and others (1988c), would be necessary to establish the source of P uptake by plants.

There was no evidence of P leaching down the soil profile in the remainder of the pot at 33 DAS, as measured by low bicarbonate extractable P values at depth. However, the risk of P leaching in a range of soil types other than the high P sorbing lateritic soil used in the present experiment needs to be investigated. Guidelines for the land application of biosolids in Western Australia restrict the application of biosolids on sites prone to water erosion, therefore research preference needs to be given to the risk of P leaching rather than to P in surface runoff. The findings would assist the Water Corporation in determining soils that pose a risk to P leaching and that should be avoided for land application. As a result of low P solubility properties, the leaching of P is expected to be less in sludges that have been surface-applied than incorporated sludges (Gove et al. 2001).

5.4.3 Relationship between bicarbonate extractable phosphorus and phosphorus uptake

In the field, low extractions of soil P were demonstrated at three sampling dates over 12 months (Table 5.11) and showed little relationship to mean seasonal production of DM over two seasons (Figures 5.8 and 5.9) and P uptake (Table 5.6). In the second season, and following cultivation (incorporation) of surface-applied biosolids, bicarbonate extractable P increased slightly. In comparison, biosolids fully mixed into the soil in the pot experiment as slurry, resulted in a strong relationship between bicarbonate extractable P and shoot P uptake (Figures 5.3 and 5.5).

Concentrations of bicarbonate extractable P in soil following the application of biosolids was influenced by soil sieving as discussed in detail in Chapter 4. Sieving of soil <2 mm in the field experiment resulted in particles of biosolids inadvertently being discarded. Biosolids were dispersed into the soil during incorporation as slurry and consequently there were no sieving abnormalities. Biosolids that were more homogenously distributed in the soil resulted in a stronger relationship between P uptake in shoots and bicarbonate extractable P values.

Overall, it is not uncommon for a poor correlation to exist between P extraction tests and P uptake for soil application of a range of biosolids products (Cottenie & Kiekens 1980; McCoy, Sikora & Weil 1986; McLaughlin 1988; Pastene 1981; Velthof et al. 1998; Womer, Elliott & Brandt 2002). Chemical extractants are renown for underestimating the potential for P release to plants, which Hedley and McLaughlin (2004) attributed to factors such as plant roots promoting dissolution of precipitated P or by modifying conditions in the rhizosphere. This was apparent in the glasshouse study, but in the field experiment, the poor correlation was attributed to physical effects.

There were little changes in bicarbonate extractable P (<10 mg P/kg, Table 5.11) following the incorporation of biosolids applied at 85 kg P/ha with a disc plough in the field. In comparison, in the glasshouse at biosolid application rates of 150 mg P/kg, bicarbonate extractable P increased up to 52 mg P/kg (Figure 5.6). These large discrepancies could be attributed to a combination of uneven mixing and soil sieving to <2 mm in the field experiment. Experiments by other researchers do not always specify how the biosolids were incorporated into the soil and whether sieving was used as a preliminary to nutrient analysis, (i.e. stone removal). The results presented in Table 5.11 underestimated available soil P, with the biosolids treatments no higher than the nil P (control) on several sampling dates and therefore these results need be treated cautiously. The number of soil samples collected to make the final composite soil sample would also affect soil results due to the 'hit or miss' characteristic of sampling biosolids.

Measurements for total N and total P are not presented, given the low recoveries of biosolid P in the <2 mm fraction as discussed previously in Section 4.3.3. For example, recoveries of total P in the 85 kg P/ha incorporated biosolids treatment were 26% at 305 DAS and 29% at 405 DAS following sieving.

5.4.4 Relative effectiveness of surface-applied biosolids compared with incorporated biosolids and relevance to land application rates and the environment

A full account of the RE of incorporated biosolids compared with inorganic P is given in Chapters 3 and 4 and will not be repeated here. Surface-applied biosolids reduced potential grain yield of wheat in the field on the P deficient soil in the first year following application to 58% relative to incorporated biosolids (Table 5.8). However, in the second year and following cultivation during the seeding process, differences in grain yield of lupin were negligible (i.e. 95% as effective, Table 5.9). Throughout the first growing season, the uptake of P by plant roots following the incorporation of biosolids was greater than for surface-applied biosolids. Following incorporation of all treatments in the second season, the biosolids were mixed throughout the soil and hence P became more available due to better soil contact.

Differences in incorporation and soil moisture throughout the season explain why the RE of biosolids in the glasshouse (Chapter 3) was higher than in the field (Chapter 4). There were also marked differences in grain yield between incorporated and surface-applied biosolids compared with TSP (Table 5.8). The RE for grain yield of incorporated biosolids compared with TSP was 67%; however, in the year of application without incorporation, the RE was reduced to 39%.

In practical terms, the effectiveness of biosolid P may be reduced where the soil is difficult to cultivate or dries out throughout the growing season (i.e. lower rainfall zones). In these situations, consideration may need to be given to possible incorporation difficulties encountered in land application programs, particularly where the soil has low reserves of P.

The experiment presented herein concentrated on the bioavailability of P in soils that were P deficient and highly P sorbing. It is generally accepted that soils high in clays, particularly Fe and Al oxides and hydroxides have higher P sorption characteristics than sands, with pH also affecting the release of P (Bolland, Allen & Barrow 2003). The addition of biosolids may reduce soil pH as a result of mineralisation and leaching of nitrate (Hedley & McLaughlin 2004). In the pot experiment, soil pH increased following the mixing of biosolids into the soil (Table 5.5), presumably increasing the solubility of P initially. Over time, differences in pH became less apparent, as noted in the field experiment in the second season at 305 days after the start of the experiment. Loading rates of biosolids higher than those used in the present experiment may have had a larger effect on soil pH.

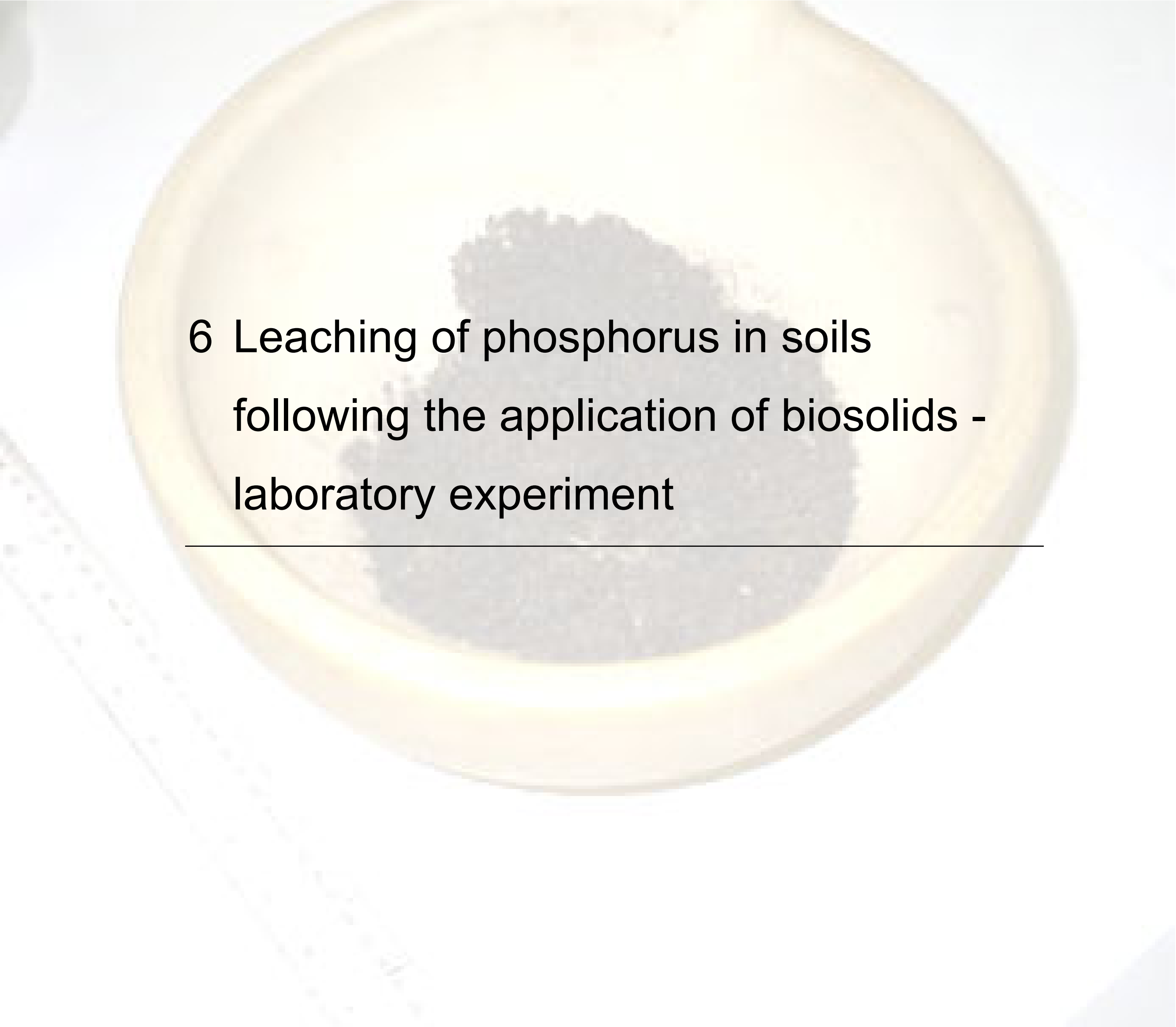
5.5 Conclusions

The positional placement of biosolids and subsequent mixing with the soil affected plant yield, which could be directly attributed to P uptake. The uptake of P by plant roots was optimal where biosolids were well mixed into the soil and the soil remained at field capacity throughout the growing season, such as in the glasshouse experiment. For the effectiveness of P in biosolids to be maximised, the incorporation method needed to be effective in burying biosolids and thoroughly mixing it into small lumps. The initial P reactions in the soil were affected by the spatial heterogeneity of applied biosolids in the soil matrix.

In comparison to inorganic P, biosolids were not as effective in supplying P, which was attributed to physical or positional availability rather than chemical soil reactions. In the Mediterranean climate where this field investigation was conducted, the surface-applied biosolids were reduced to 58% as effective as incorporated biosolids in the first season, although by year two both were approximately similar (i.e. 95% as effective) on the lateritic soil. It is common practice for biosolids used in land application programs in Western Australia to be fully incorporated into the soil. However, rainfall and soil type may need to be taken into consideration when determining the effectiveness of biosolid P and agronomic loading rates. The rainfall during the period of the experiment was moderate to low and the results may have been different under extreme rainfall conditions. An under-estimation of P may lead to an excess of P in the environment, whereas over-estimation of P may result in inadequate amounts for plant growth.

The relationship between the bicarbonate extractable soil test and P uptake by plants in the glasshouse was poorer in the biosolids than the MCP treatments although the reasons for this are unclear. One possibility may be due to the preferential growth of roots within the biosolids matrix. In the field experiment, the poor correlation between bicarbonate extractable P and P uptake in plants grown with biosolids was attributed to physical effects, such as sieving and discarding of biosolids prior to chemical analysis.

Preliminary results from the experiment presented herein indicates a limited movement of plant available P into the lateritic soil surrounding the biosolids, as measured by differences in bicarbonate extractable P at different depths in the pot experiment; and hence a low solubility of P. There is a need to investigate the release of P in biosolids over a range of soil types, differing in chemical and physical properties, as distinct from the infertile lateritic soils used in the present and previous experiments. Loading rates of P are generally high following the land application of biosolids, and are applied to soils with a previous history of P fertiliser. Therefore the potential for P pollution following the application of biosolids needs to be identified. More emphasis will be given to the risk of P leaching than to runoff, as guidelines for the land application of biosolids restricts the application on sites prone to water erosion. There is currently a lack of data in Australia on this topic and consequently this forms the basis of Chapter 6.



6 Leaching of phosphorus in soils following the application of biosolids - laboratory experiment

6.1 Introduction

Increased concentrations of P in water bodies can contribute to eutrophication, the main cause being excessive fertiliser application of P to land areas prone to runoff by water-soluble P and sediments enriched with P, such as by water moving across or through soils, and/or by P leaching downwards (Pierzynski, Sims & Vance 1994). Events have occurred in Australia where P pollution from sewage and animal manure has occurred on poorly adsorbing sands, under intensive agriculture such as piggeries or horticulture or where the population pressure is high, such as the Peel-Harvey Inlet (Barrow 1999; McWaters 1999). The over-use of fertilisers containing P, resulting in high concentrations of P in soil and water bodies has been of global concern, although there is little evidence that P, originating from the land application of biosolids is involved (Dentel, Sims & Mah 2001; Elliott, O'Connor & Brinton 2002; Womer, Elliott & Brandt 2002).

It is common for up to ten times more total P (P_T) to be applied annually using biosolids compared with maintenance dressings of superphosphate in Western Australia (Pritchard & Penney 2003). Therefore, given the high loading rates of P_T in biosolids, data need to be collected to ensure that the risk of contamination of water bodies by water-soluble P and/or sediments enriched with P originating from biosolids is low. The accumulation of P from biosolids and animal manures has been examined elsewhere (Brandt, Elliott & O'Connor 2004; Elliott, O'Connor & Brinton 2002; Maguire, Sims & Coale 2000a; Maguire, Sims & Coale 2000b; Maguire et al. 2001; Sharpley & Moyer 2000; Sims 1998), although there is no information available for the environmental consequence of P enriched soils in the wheatbelt of Western Australia following the land application of biosolids.

Water-soluble P can be extracted from fertiliser using water (Glendinning 1999) with about 80% of the P_T in single, double and triple superphosphates readily water-soluble. The concentrated fertiliser solution reacts with soil constituents in a series of precipitation and adsorption events that are positively correlated to factors such as texture, Al and Fe (sesquioxides) and carbonate content (Bolland, Allen and Barrow 2003). High P retention in many Australian and New Zealand soils result in a low risk of P leaching, except for sandy soils (Cameron, Di & McLaren 1997). Soils with a high PRI increase the capacity for P sorption and reduce the amount of P lost by leaching, but may increase the P lost by erosion (Allen & Jeffery 1990). Soils in Western Australia can be characterised by their risk of P loss, including runoff and/or leaching, based on the soil type, rate of P applied and throughput of water. The time taken for P to move through sandy soils is generally less than for lateritic soils (Weaver & Summers 1998). In Western Australia, the leaching of P has not been observed in soils that showed a PRI >2 mL/g and reactive Fe content >300 mg/kg (Bolland & Gilkes 2001).

The aim of this study was to measure the proportion of water-soluble P in biosolids compared with inorganic P when applied to a range of soil types typically found in the wheatbelt of Western Australia and subjected to a standard leaching procedure. Thus the potential risk of leaching of P in soils treated with biosolids could be made relative to an inorganic source of P applied at comparable rates. Given the restriction of biosolids in Western Australia on sites prone to water erosion, the leaching of P was chosen as the focus for this investigation rather than the measurement of water-soluble P or particulate P in runoff.

6.2 Materials and methods

6.2.1 Experimental design

The experiment consisted of three treatments applied to nine different soils and replicated twice as a completely randomised design. The three treatments consisted of: 140 mg P/kg as biosolids, 140 mg P/kg as monocalcium phosphate (MCP) and a nil P (control). A reverse soil leachate unit (Figure 6.1) was set up to enable measurement of soluble reactive P, total P, nitrate-N and ammonium-N.

6.2.2 Biosolids

Sub-samples of Beenyup biosolids sourced from the field experiment stockpile (Chapter 4) on 16 May 2001 were air-dried at 40°C for 6 d. During this slow drying period, biosolids were regularly broken into smaller pieces to enhance drying and then ground in a mortar and pestle to pass through a 2 mm stainless steel sieve (Plates 6.1 and 6.2).

The major concentrations of nutrients in these biosolids on a dry weight basis were as follows: P_T = 2.96%, total N = 6.17%, NH_4-N = 0.72% and NO_3-N <10 mg/kg (Table 4.3). Full details of Beenyup WWTP biosolids have been described in sections 1.2, 4.2.5 and 4.2.7. Inorganic forms of P were predominant (92.2%), with anion exchange resin extracting 66% of the P_T (Table 3.6 & section 3.3.6). The Al and Fe content of air-dried and milled biosolids were measured at 0.62% and 0.40%, respectively (CCWA Report 02A155_001).

Plate 6.1 Air-dried biosolids being prepared by mortar and pestle

Plate 6.2 Biosolids on completion of grinding and sieving

6.2.3 Soils

Full descriptions of the physical and chemical properties of the nine soils chosen for the study are given in Tables 6.1 and 6.2. Overall the nine soils varied in a range of properties, such as percentage sand content from 34% to 99.5%, pH ($CaCl_2$) from 4.1 to 7.0, EC from 1 mS/m to 140 mS/m, PRI from 0.2 mL/g to 95 mL/g and PRI* from 0.4 mL/g to 97.3 mL/g.

Both the PRI and modified PRI (PRI*) values are reported. The standard PRI calculation is P sorbed /P solution, where P sorbed is the amount of P removed from solution by the soil (mg P/kg) and P solution is the concentration of P remaining in solution (mg P/L) after the PRI test equilibration (i.e. shaking 19 mg/L in a soil: solution ratio of 1:20 for 16 hrs). The PRI* considers the amount of P already adsorbed by the soil from previous applications of P fertiliser and is calculated as: (P sorbed + Colwell P)/P solution, i.e. [20*(10 - P solution) + Colwell P]/P solution, where P solution = 10 (Allen, Barrow & Bolland 2001).

The white sand (AW) was selected to represent a worst-case scenario in terms of P leaching and is not considered an agricultural soil type. It was sourced from a plant nursery in Perth and then prepared by washing with dilute hydrochloric acid to remove any residual phosphate as well as calcium, iron and aluminium which may absorb the phosphate, effectively to produce an inert supporting matrix.

Soil from the Bakers Hill (BH) site and Chester's site (CH) were included to ensure comparability as they were used in both the glasshouse and field experiment respectively. They are described in detail in sections 3.2.2 and 4.3.2. Both of these lateritic soil types are typically used for the land application of biosolids in Western Australia.

Two soils were collected from the Moora district where the land application of biosolids is a common occurrence. Soil was sourced from Brennan (BR) and Wilson (WI) paddocks on P, O & J Cocking's farm, Gillingarra, being research sites used by the National Biosolids Research Program (research described at *http://www.awa.asn.au/NSIG/bio/biosolids.pdf*).

The soil samples designated C10, C42, C50 and LIS are reference soil standards used by the Chemistry Centre of Western Australia originating from Merredin, Boddington, Jerramungup and Wongan Hills, respectively. They were chosen as they showed extremes in a number of chemical and physical properties.

Table 6.1 Description and location of the nine soils used in the leaching experiment ranked in order of sand content. Values are given for texture, pH, EC, organic carbon and gravimetric soil water capacity (GSWC) in the topsoil* 0-10 cm after being sieved <2 mm.

Sample	Description	Location	EC	pH	Sand	Silt	Clay	Org C	GSWC
			(1:5) mS/m	($CaCl_2$)	%	%	%	(W/B)%	%
AW	White acid washed sand	Perth	1	5.0	99.5	<0.5	0.5	0.02	17
C50	Orange sand	Jerramungup	3	5.1	97.5	1.0	1.5	0.80	17
LIS	Grey sand	Wongan Hills	5	4.1	95.5	1.5	3.0	0.98	19
BH	Gravel loamy sand	Bakers Hill	4	4.8	94.5	3.0	2.5	2.39	23
BR	Grey silicious loamy sand	Moora (Brennan's)	2	4.1	94.0	1.5	4.5	0.80	20
WI	Gravelly loamy sand	Moora (Wilson's)	5	4.6	91.5	4.0	4.5	1.83	24
CH	Yellow gravelly loamy sand	York (Chester's)	6	6.1	85.0	8.5	6.5	1.83	23
C10	Brown sandy loam	Merredin	18	7.0	57.0	24.0	19.0	1.01	25
C42	Brown clay	Boddington	140	5.6	34.0	37.0	29.0	4.14	40

(CCWA 2002) Report 02A154/1-9

pH ($CaCl_2$) by 0.01 M $CaCl_2$ (Rayment & Higginson 1992i), EC (1:5) at 25°C (Rayment & Higginson 1992b); sand (2mm-0.02mm), silt (0.02mm-0.002mm), clay (<0.002mm) by plummet method in a suspension of soil in water with sodium hexametaphosphate/sodium hydroxide (McDonald et al. 1990), organic carbon (W/B) (%) by Walkley and Black (1934) (Rayment & Higginson 1992g), GSWC = Gravimetric soil water capacity, * LIS was a sub-soil sample.

(mS/m = milliSiemens per metre).

Table 6.2 Comparison of selected nutrient properties in the 0–10 cm topsoil* (<2 mm fraction) for the nine soils

Sample	N total	NH_4-N	NO_3-N	P total	P (HCO_3)	PRI	PRI*	Fe	Al	Ca	Mg	Na	K	Al	Mn
	%	mg/kg	mg/kg	mg/kg	mg/kg	mL/g	mL/g	(AmOx) mg/kg	(AmOx) mg/kg	(exch) cmol (+)/kg	(exch) cmol (+)/kg	(exch) cmol (+)/kg	(exch) cmol (+)/kg	(exch) cmol (+)/kg	(exch) cmol (+)/kg
AW	<0.005	<1	<1	9	2	0.2	0.4	5.9	11	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
C50	0.047	2	4	110	4	2.1	2.5	210	230	1.84	0.25	0.03	0.02	0.08	0.03
LIS	0.066	2	13	78	18	1.2	3.1	110	230	1.56	0.18	0.07	0.06	0.42	<0.02
BH	0.093	7	6	69	4	13	13.7	500	830	2.80	0.76	0.07	0.09	0.34	0.06
BR	0.058	2	3	110	27	4	7.2	200	240	0.72	0.13	0.02	0.12	0.46	<0.02
WI	0.125	11	16	230	34	13	18.6	280	940	1.71	0.22	0.06	0.11	0.56	0.02
CH	0.063	3	6	64	4	95	97.3	420	2700	5.76	1.62	0.18	0.43	0.08	<0.02
C10	0.096	12	31	160	28	12	16.5	290	470	8.71	3.09	0.28	1.12	0.04	0.07
C42	0.324	32	28	260	12	72	77.5	7800	1800	10.83	16.72	7.91	0.23	0.07	0.20

(CCWA 2002) Report 02A154/1-9

Total N (Blakemore, Searle & Daly 1987; Rayment & Higginson 1992f; Searle 1984), nitrate-N and ammonium-N extracted in 1M KCl (Rayment & Higginson 1992f), total P (Allen & Jeffery 1990; Murphy & Riley 1962), bicarbonate extractable P extracted by 0.5 M $NaHCO_3$ (1:100) (Colwell 1963; Rayment & Higginson 1992h), PRI (Allen & Jeffery 1990), PRI* = (P sorbed + Colwell P)/P solution (Allen, Barrow & Bolland 2001).Fe and Al extracted by 0.2 M ammonium oxalate pH 3.25 (Rayment & Higginson 1992c); calcium (Ca exchangeable), magnesium (Mg exchangeable), sodium (Na exchangeable), potassium (K exchangeable), aluminium (Al exchangeable), manganese (Mn exchangeable) extracted by 0.1M BaCl by method S21 (CCWA 2000). *LIS was a sub-soil sample.

mg/kg = milligrams per kilogram, mL/g = millilitres per gram, cmol (+)/kg =cmol (+) per kilogram

6.2.4 Reverse soil leachate unit

All nine soils were prepared by air-drying, sieving <2 mm and then 600 g batches of soil weighed. Biosolids and MCP treatments were both applied dry and well mixed into the soil (Plate 6.3). The biosolids were applied at a rate of 4.14 dry g biosolids per kg soil to achieve the desired P loading of 140 mg P/kg. This rate was selected to be comparable to rates used in the previous experiments and to reflect loading rates currently used in Western Australia.

Plate 6.3 White (acid washed) sand before (left) and after (right) the addition of air-dried biosolids

The design of the reverse soil leachate unit is given in Figure 6.1, with the apparatus handling batches of 14 leachates at any one time. Prior to soil being placed in the soil leachate unit, all treatments were incubated at gravimetric soil water capacity (GSWC), described in section 3.2.5 at 40°C for 7 d.

Following incubation, soils were loosely packed into the 250 mL leachate unit (135 mm x 50 mm diameter) to 80% of volume. The weighed leachate bottles were prepared by applying cotton wool filters (top and base) to 10 mm dry depth. Deionised water was delivered at 1 mL/min via a 1.8 mm diameter plastic tube to the base of the leachate via inlet nipples. Water moved upwards through the soil mix and was collected by a 1,000 mL plastic receiver bottle (Plate 6.4).

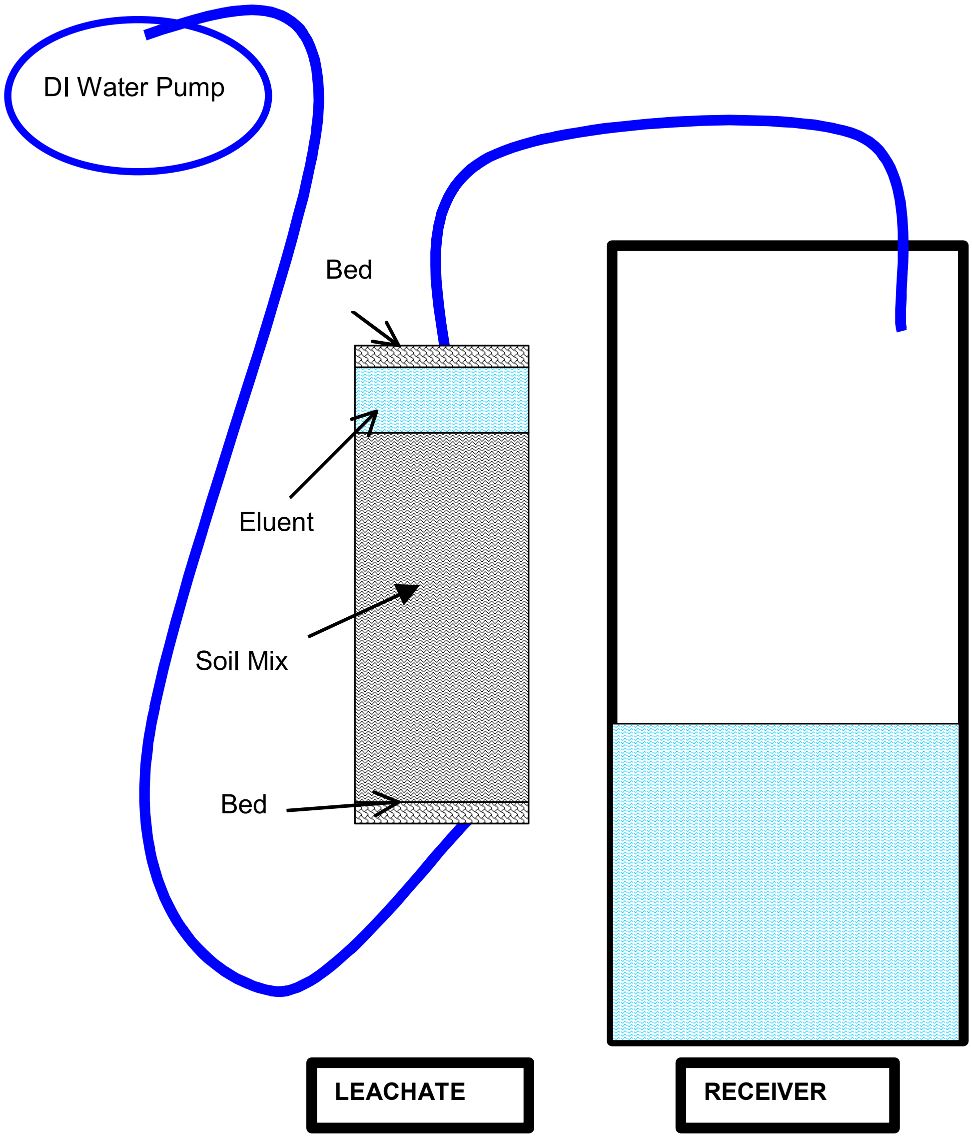


Figure 6.1 Soil leachate unit (Chemistry Centre of Western Australia)

Leachate unit = 250 mL plastic bottle of 135 mm x 50 mm diameter fitted with inlet nipples at each end. Filter beds (top & base) = cotton wool of 10 mm dry depth. Soil mix sample = loosely packed at 80% column volume. Deionised water delivered at 1 mL/min via 1.8 mm diameter plastic tube. Receiver = 1000 mL plastic bottle with received volume ~ 800 mL measured.

(Source: CCWA)

Plate 6.4 Reverse soil leachate unit apparatus prior to the leaching stage

In addition to the placement of soil into the leachate units, a sub-sample of each soil was oven-dried to determine the dry weight of the soil used. The volume of the leachate collected after approximately 12 h was measured for each treatment and the concentration of dry soil in solution (g/mL) determined. Sub-samples of the leachate were frozen prior to the chemical determination of soluble reactive phosphorus (SRP) and P_T (all treatments) and NO_3-N and NH_4-N (biosolids and control treatments only).

6.2.5 Chemical analysis

Samples of leachate were thawed at room temperature prior to analysis. The concentration of SRP in a centrifuged portion (3,500 rpm for 10 min) of the equilibrated solution was determined by colorimetry as the molybdenum blue complex (Murphy & Riley 1962) using the PRI colour reagent and read on a spectrophotometer at 882 nm (Allen & Jeffery 1990). The concentration of P_T in the diluted digest was measured directly by ICP-AES.

The mean percentage SRP recovered (SRP-R) was determined as the percentage recovery of P_T applied as either MCP or biosolids, minus the SRP present in leachate from the control soil, calculated as follows:

% SRP-R = (treatment SRP (mg/kg) – control SRP (mg/kg)) /applied P_T) * 100.

where treatment SRP (mg/kg) = SRP (mg/L)/solution (g/mL) as MCP or biosolids, control SRP (mg/kg) = SRP (mg/L)/solution (g/mL), P_T = 140 mg P/kg, SRP concentration (mg/L) and solution = dry soil per leachate volume.

Concentrations of NH_4-N in leachates were determined by colorimetry following oxidative coupling with salicyclic acid using sodium dichloroisocyanurate as a source of chlorine. Concentrations of NO_3-N were determined by colorimetry following reduction with hydrazine to the nitrite ion, followed by diazotisation of 1-naphthylethylenediamine and subsequent coupling with sulphanilamide (CCWA 2000).

6.2.6 Statistical analysis

Data were analysed for differences between treatment means for SRP, total P, SRP-R, ammonium and nitrate in leachate using an ANOVA model in GENSTAT as previously described in section 3.2.11. A single LSD value ($P = 0.05$) was used for comparing treatment means between the MCP and biosolids treatments for all soils for SRP (mg/L) and percentage SRP-R; and for comparing treatment means between the biosolids and control for all soils for ammonium-N and nitrate-N.

Microsoft Excel was used to calculate the correlation between SRP in leachate of MCP or biosolids treatments against several soil constituents such as: soil texture, pH, EC, organic carbon and exchangeable cations.

6.3 Results

6.3.1 Soluble reactive phosphorus and total phosphorus

The concentration of SRP measured in leachate (mg/L) was influenced by both the source of P (i.e. biosolids or MCP treatments) and the soil type (Figure 6.2). The addition of MCP increased the concentration of SRP to a greater extent than biosolids in the acid washed sand (AW), orange sand (C50), grey sand (LIS), siliceous sand (BR), and gravelly loamy sand (WI) ($P < 0.05$).

The soil type had a large effect on the concentration of SRP, which was highest in leachate from the acid washed sand for the MCP treatment at 28.5 mg P/L. In comparison, the concentration of SRP in leachate collected from the acid washed sand for the biosolids treatment was significantly lower at 6.0 mg P/L ($P < 0.05$). The highest concentration of SRP for biosolids was for the grey sand (LIS), which measured 9.4 mg SRP/mL.

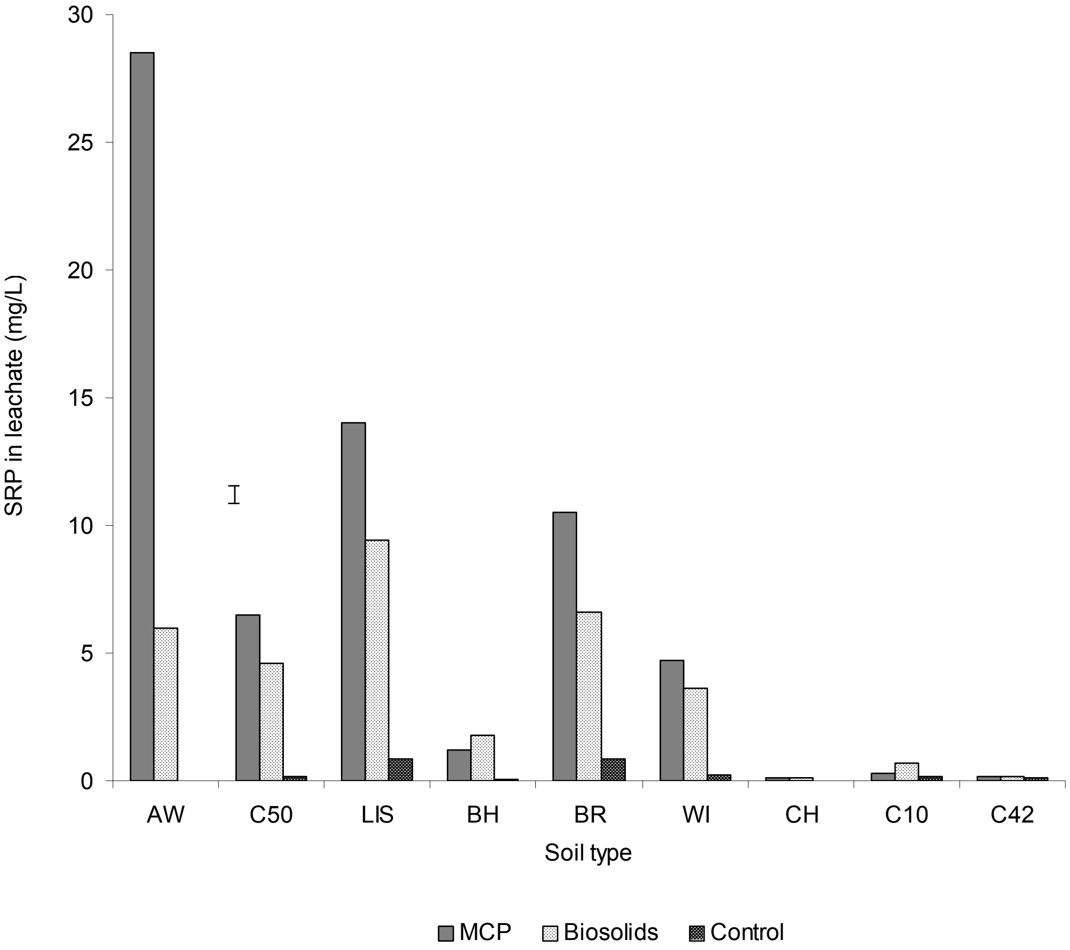


Figure 6.2 Relationship between SRP in leachate over nine soil types following the addition of 140 mg P/kg as MCP or biosolids compared with the control soil

AW=acid washed sand, C50=orange sand, Jerramungup, LIS=grey sand, Wongan Hills, BH= gravelly sand, Bakers Hill, BR=siliceous sand, Brennans, Moora; WI=gravelly loamy sand, Wilsons, Moora, CH=yellow gravelly loam Chesters, York; C10=brown sandy loam, Merredin; C42=brown clay, Boddington.

(Soils ranked by texture from highest sand content from left to right).

66% of biosolid P extracted by anion resin (Table 3.6).

Vertical bar denotes LSD (*P* = 0.05) for soil*source = 2.11, with LSD not shown for soil type = 1.22 and treatment source = 0.70.

Very low concentrations of SRP (< 1.8 mg P/L) were measured in leachate from the soil types: gravelly sand (BH), yellow gravelly loam (CH), brown sandy loam (C10) and brown clay (C42). The concentration of SRP in leachate over all control treatments (nil P) measured <0.86 mg P/L. The highest concentration of SRP for the control treatment was measured in the grey sand (LIS), representing 4.11% of the P_T following leaching (calculated by dividing SRP by the total soil P concentration given in Table 6.2).

The mean percentage SRP-R for all nine soils on completion of 12 h of leaching following the addition of MCP (140 mg P/kg) was 18.6% and was halved for biosolids (140 mg P/kg) (P<0.05). The highest value for SRP-R was for acid washed sand (AW) with the percentage recovery of P in leachate 71.2%, following the addition of MCP. In comparison, SRP-R of acid washed sand was significantly lower at 14.2% in the biosolids treatment (*P* <0.05, Figure 6.3). However, the variation in SRP-R in the acid washed sand for the two biosolids replicates was large, ranging from 6.0 to 22.4%.

The percentage SRP-R was very low (<1.4%) for the yellow gravelly loam (CH), brown sandy loam (C10) and brown clay (C42), with no differences between the sources of P (*P* >0.05). In the gravelly sand (BH), percentage SRP-R was low (<5.0%) for both P treatments, although slightly higher in the biosolids treatment than the MCP treatment (*P* <0.05). Overall, the mean percentage SRP-R for all agricultural soils, excluding the acid washed sand was only marginally higher (*P* <0.05) for the MCP (11.2%) than the biosolids (7.9%).

A high correlation existed between SRP and total P in leachate (r = 1.00) with the SRP comprising 95.7% of the P_T measured, and therefore the results for total P are not presented.

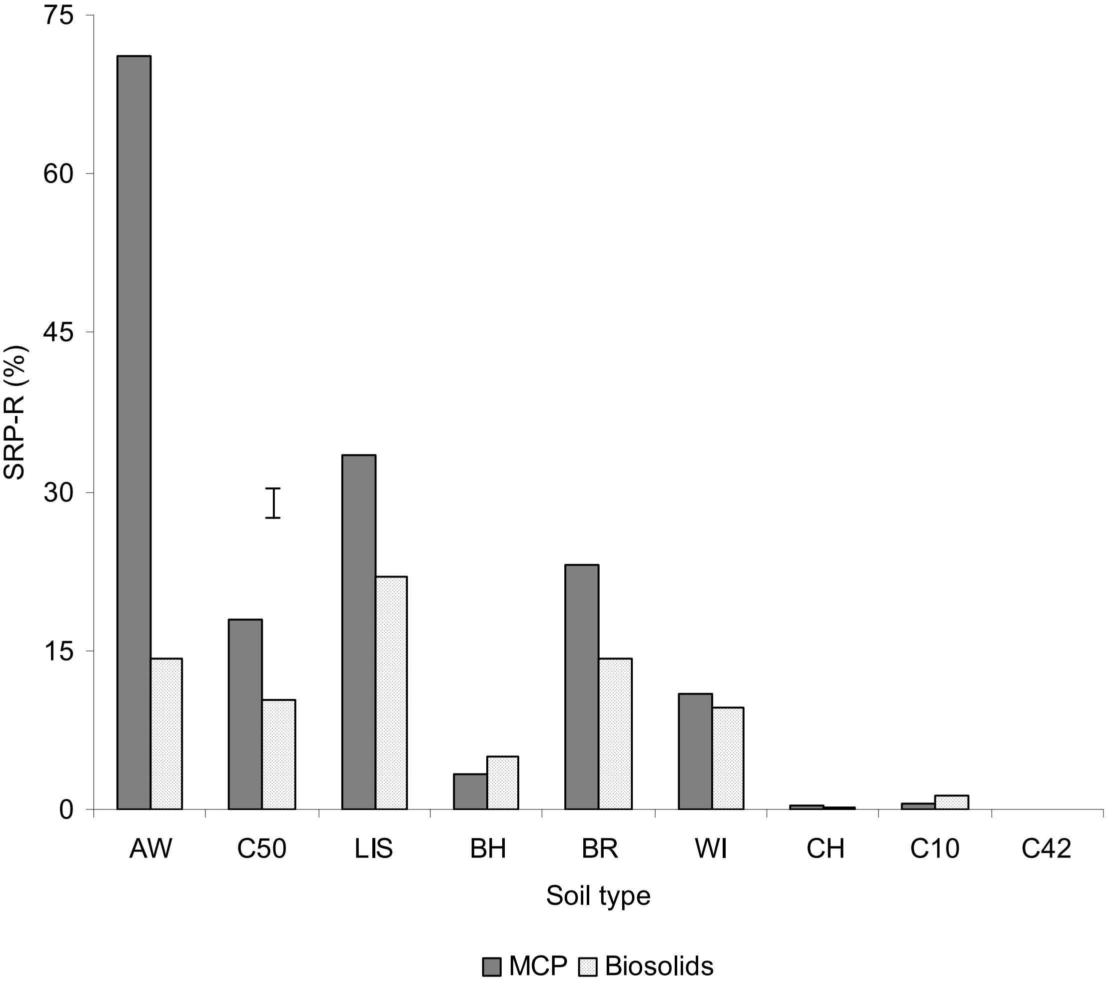


Figure 6.3 Percentage soluble reactive P recovered (SRP-R) following the addition of MCP or biosolids at 140 mg P/kg for nine soil types

AW=acid washed sand, C50=orange sand, Jerramungup, LIS=grey sand, Wongan Hills; BH= gravelly sand, Bakers Hill, BR=siliceous sand, Brennans, Moora; WI=gravelly loamy sand, Wilsons, Moora, CH=yellow gravelly loam Chesters, York; C10=brown sandy loam, Merredin; C42=brown clay, Boddington.

Vertical line denotes LSD (*P* =0.05) for soil*source = 6.61, with LSD not shown for P source = 2.20 and soil type = 4.67.

% SRP-R = (treatment SRP (mg/kg) – control SRP (mgkg)) /applied P_T) * 100.

Where treatment SRP (mg/kg) = SRP (mg/L)/solution (g/mL) as MCP or biosolids, control SRP (mg/kg) = SRP (mg/L)/solution (g/mL), P_T = 140 mg P/kg, SRP concentration (mg/L) and solution = dry soil per leachate volume.

6.3.2 Relationship between soil properties and soluble reactive phosphorus

Correlation values between soil properties for the nine soils and percentage SRP-R in leachate are summarised in Table 6.3.

Table 6.3 Correlation coefficient values between selected soil parameters over nine soils examined and %SRP-R in leachate for MCP, biosolids and the mean of both P sources

Soil parameter	MCP (r)	Biosolids (r)	Mean (r)
Fe $_{(AmOx)}$ (mg/kg)*	-0.87	-0.76	-0.82
Organic C (W/B)%	-0.67	-0.62	-0.64
pH ($CaCl_2$) 1:5	-0.44	-0.79	-0.62
PRI (mL/g)	-0.52	-0.70	-0.61
Sand (%)	0.53	0.67	0.60
Clay (%)	-0.52	-0.64	-0.58
Ca $_{exch}$ (cmol(+)/kg)	-0.56	-0.51	-0.54
Total P (mg/kg)	-0.58	-0.40	-0.49
Total N (mg/kg)	-0.46	-0.46	-0.46
Mn $_{exch}$ (cmol(+)/kg)	-0.37	-0.47	-0.42
EC (1:5, mS/m)	-0.34	-0.47	-0.41
Mg $_{exch}$ (cmol(+)/kg)	-0.35	-0.45	-0.40
Na $_{exch}$ (cmol(+)/kg)	-0.30	-0.42	-0.36
PRI* (mL/g)	-0.32	-0.20	-0.26
K $_{exch}$ (cmol(+)/kg)	-0.32	-0.17	-0.25
Al $_{(AmOx)}$ (mg/kg)	-0.34	-0.14	-0.24
Al $_{exch}$ (cmol(+)/kg)	-0.01	0.41	0.20
P (HCO_3) (mg/kg)	-0.23	0.13	-0.05

Correlation coefficient is calculated over nine soil types. Description of soil chemical methods are given in Tables 6.1 and 6.2. %SRP-R = (treatment SRP (mg/kg) – control SRP (mgkg)) /applied P_T) * 100, where treatment SRP (mg/kg) = SRP (mg/L)/solution (g/mL) as MCP or biosolids, control SRP (mg/kg) = SRP (mg/L)/solution (g/mL), P_T = 140 mg P/kg, SRP concentration (mg/L) and solution = dry soil per leachate volume. *Correlation for Fe $_{(AmOx)}$ does not include C42, due to the extreme value of 7,800 mg Fe/kg.

Soil Fe $_{(AmOx)}$ content was negatively correlated (r = -0.82) with SRP-R for both biosolids and MCP over eight soils. Only eight soils were used to calculate the correlation for Fe $_{(AmOx)}$, after C42 was excluded as its extreme Fe value of 7,800 mg/kg complicated the calculation (Table 6.2). Organic carbon negatively correlated to the SRP-R in leachate for both MCP and biosolids treatments for the nine soils (r = -0.64), whereas the percentage sand content was positively correlated (r = 0.60).

In the biosolids treatments, the pH ($CaCl_2$) and PRI were negatively correlated to SRP-R in leachate (r = -0.79 and r = 0.70, respectively), although the relationship was weaker in MCP treatments. However, the correlation for pH and PRI in the MCP treatments was improved (r = -0.77 and r = -0.63, respectively) when the acid washed sand was not included in the calculation. The exclusion of acid washed sand from the correlation calculations did not affect the majority of the other values.

Soil factors that showed the least effect (r <0.55) on the concentration of SRP-R in leachate included: PRI*, bicarbonate extractable P; Al$_{(AmOx)}$ content, exchangeable Al, Na, K, Mg, Ca and Mn; EC; total P and total N content.

6.3.3 Nitrate and ammonium nitrogen

The addition of biosolids at 4.14 dry g/kg soil significantly increased the concentration of NH_4-N in leachate as compared with the control, following 12 h of leaching (*P* <0.05, Figure 6.4). The highest increases above that of the control soils were measured in the orange sand (C50) = 9 mg N/L and the grey sand (LIS) = 8 mg N/L; and was lowest in the brown clay (C42) = 2 mg N/L. There was no increase in NH_4-N above that of the control in the yellow gravelly loam (CH), which only contained 1 mg N/L (*P* >0.05). There was no increase in NO_3-N (*P* >0.05) over all soils, except for the gravelly loamy sand (WI), which was also high in the control prior to the addition of biosolids.

Mineral N recovered in leachate after 12 h of leaching was at most 3.9% of the total N applied in biosolids (i.e. orange sand, C50), accounting for 30% of biosolid NH_4-N. Given the overall low recovery of mineral N, the correlation with soil properties was of limited value. However, soil pH and PRI were negatively correlated to mineral N (r = -0.61 and –0.78, respectively) and sand content was positively correlated (r = 0.54).

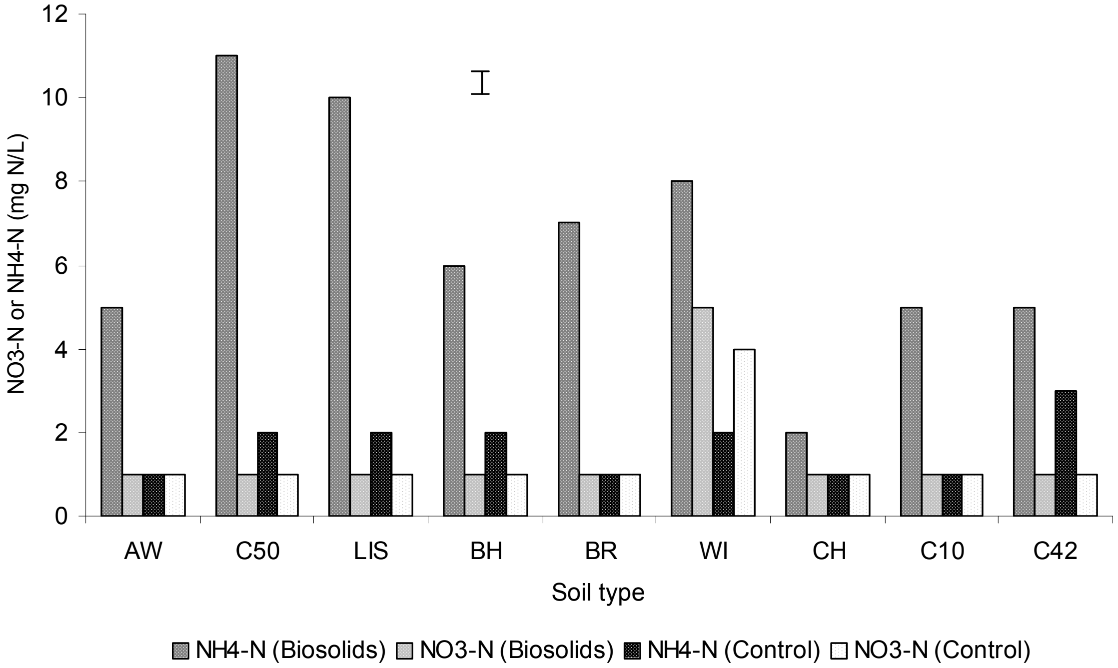


Figure 6.4 Concentrations of NO_3-N and NH_4-N measured in leachate following the addition of biosolids (B) compared with the control (C) in nine different soils

AW=acid washed sand, C50=orange sand, Jerramungup, LIS=grey sand, Wongan Hills, BH=gravelly sand, Bakers Hill, BR=siliceous sand, Brennans, Moora; WI=gravelly loamy sand, Wilsons, Moora, CH=yellow gravelly loam Chesters, York; C10=brown sandy loam, Merredin; C42=brown clay, Boddington.

Vertical bar denotes LSD (*P* =0.05) for NH_4-N across the means of the soil types.

6.4 Discussion

6.4.1 Solubility of phosphorus in biosolids compared with MCP

The addition of MCP increased the mean concentration of SRP (mg/L) in leachate to a greater extent than the addition of comparable rates of biosolid P (Figure 6.2). The percentage SRP-R (i.e. recovery of SRP in leachate expressed as a percentage of the total P applied) was used to compare soils as it took into consideration the SRP leached by the control and the leachate volumes collected. The percentage SRP-R was highly variable, being dependent largely on the soil type and P source (Figure 6.3). Across all soil types the mean percentage SRP-R for the MCP treatments was higher than for the biosolids treatments, being 17.8% and 8.6%, respectively.

The acid washed sand (AW) represented a worst-case scenario in terms of P leaching for the MCP treatment and resulted in 71.1% SRP-R compared with 14.2%

in the biosolids treatment. As inorganic fertilisers are intended to be highly water-soluble (Glendinning 1999), the higher percentage SRP-R for the MCP treatment (in acid washed sand) was as expected. In comparison, the percentage SRP-R for the biosolids in the acid washed sand was similar to other sands used, suggesting that other constituents in biosolids, such organic carbon, Fe, Ca or Al content may act to decrease the sorption properties of P following the incubation period of one week; or that the porosity of the biosolids particles limits the release of soluble P.

Whereas the determination of SRP in the present experiment involved a soil leachate unit, values for WEP are commonly determined in the absence of soil. The WEP was initially proposed by Sharpley and Moyer (2000) to estimate the potential for land-applied manures and composts to enrich drainage and surface runoff P. Dried biosolids or manure samples are agitated in a solid: deionised water solution of 1:250 for 1 hr, with the concentration of P measured by ICP-AES analysis following the addition of 0.5 mL HNO_3 (1:1) to 24.5 mL of filtrate.

Brandt, Elliott and O'Connor (2002) used WEP to measure the potential for land-applied biosolids and manures to enrich P in leachate and runoff. The WEP in triple superphosphate (TSP) was higher (85.2%) than animal manures (20.8 to 47.6%) and low for typical biosolids (2.5%). Sharpley and Moyer (2000) found that WEP was 51% for dairy manure and 26% for poultry manure. Similarly, WSP measured for a range of biosolids was low (0.3 to 0.4%) compared with poultry and swine manures (17.0%) (Montgomery 2002). Cooke and others (2001) showed no evidence of a high P solubility in biosolids, as did Elliott, O’Connor and Brinton (2002).

The inert acid washed sand (AW) used in the present study provided the most direct comparison between SRP and WEP. In the present study, the SRP-R in MCP measured 71.1%, whereas Brandt, Elliott and O’Connor (2002) measured WEP in TSP to be 85.2%. Interestingly, the percentage SRP-R in acid washed sand for Perth biosolids was 14.2% (Figure 6.3), and although lower than reported for most animal manures, was higher than the WEP reported for other biosolids. A value of 14% was most similar to that found by Brandt, Elliott and O'Connor (2002) in biosolids undergoing biological nitrogen removal (BNR).

In all of the reported studies, biosolids were established to have lower WSP than animal manures and these authors explained that unlike manures, biosolids must be stabilised prior to land application and often alum or iron salts may be added to precipitate metal phosphates to reduce P in effluent. In addition, treatment plants undergo removal of labile P in the process of producing biosolids. In digestion, the super natant in the digester is frequently removed and mechanical dewatering further removes water-soluble P, as noted by Barrow (1999) for Perth biosolids. Overall, chemical P removal using Fe or Al decreased WEP to total P percentage (PWEP = 0.5%), as did treatment processes to reduce pathogens (i.e. heat treatment), whereas enhanced biological phosphorus removal (EBPR) increased PWEP (i.e. 14%) (Brandt, Elliott & O'Connor 2004).

Brandt, Elliott and O'Connor (2002) reported an inverse relationship between WEP and levels of Al plus Fe in biosolids and manures. Dairy and poultry manures often contain <0.1 g/kg of Fe_T plus Al_T. In contrast, Perth biosolids are less likely to leach P than animal manures as they contain approximately 10.2 g/kg of Fe_T plus Al_T with a molar value of 0.30 moles/kg of Fe_T + Al_T. The leaching of P in biosolids was correlated to the P saturation index ($PSI=[P_{ox}]/[Al_{ox} + Fe_{ox}]$) with leaching more likely in biosolids cake and pellets with a PSI >1.1 (Elliott, O'Connor & Brinton 2002). The PSI was inversely related to the molar ratio of (Fe_T + Al_T) to P_T value and was recommended by Pastene (1981) to characterise biosolids P availability. Similarly, a strong correlation was obtained between Mehlich-3 P and the molar ratio of Al plus Fe in biosolids (measured by oxalate extraction or acid-peroxide digestion) for WSP (Maguire et al. 2001).

Perth biosolids were air-dried and ground through a 2 mm sieve possibly resulting in a higher surface area than for biosolids reported in the WEP studies that used a 6 mm sieve. This combined with the longer incubation and shaking time may also explain why Perth biosolids had higher SRP than WEP values reported for biosolids elsewhere. The slow leaching used in the present study to extract SRP, however, may be more effective than a single water extraction for sparingly soluble materials. It was established in Chapter 3 that 66% of the P in Beenyup biosolids was easily extracted by resin following the sequential fractionation of biosolids in acid washed sand (Table 3.6) indicating a high amount of exchangeable P_i as well as water-soluble P forms.

It is doubtful whether drying of biosolids would affect the solubility of P compared with fresh biosolids unless the surface was rendered hydrophobic. In the study by Gove and others (2002), little difference was observed between dried and composted mesophilic anaerobically digested dewatered biosolids cake compared with conventional biosolids (fresh cake or liquid) on the movement of P following simulated rainfall events in repacked semi-structured soil cores.

The mean percentage SRP-R for all agricultural soil types examined (i.e. exclusion of acid washed sand) showed little difference between the MCP and biosolids treatments, being 11.2% (ranged from 0.06 to 33.4%) and 7.9% (ranged from 0.08 to 22.0%), respectively. There were no significant differences in percentage SRP-P between biosolids and MCP for the yellow gravelly loam (CH), brown sandy loam (C10) and brown clay (C42), with SRP-R very low (<1.4%). In contrast, the percentage SRP-P following MCP application was higher on the sandier soil types and will be discussed further under soil properties.

6.4.2 Effect of soil properties on water-soluble phosphorus

Sibbensen and Sharpley (1997) indicated that P release was governed by P sorption characteristics of the soil plus climatic, edaphic and agronomic factors. In the experiment presented herein, soil factors that usually affect P sorption showed a relationship to SRP-R. For example, the percentage of sand correlated positively with SRP-R (r = 0.60; Table 6.3). Negatively correlated with SRP-R were soil Fe ($_{\mathrm{AmOx}}$ mg/kg) content (r = -0.82), organic carbon (r = -0.64), pH (r = -0.62) and PRI (r = -0.61), which would be as expected given soil sorption characteristics (Bolland & Allen 2003).

Leaching of P has not been observed in Western Australian soils that showed a PRI >2 mL/g and reactive Fe content >300 mg/kg (Bolland & Gilkes 2001). The gravelly sand (BH), yellow gravelly loam (CH) and brown clay (C42) were therefore not expected to leach P, regardless of the source of P. Soils with very low risk of eutrophication of drainage waters from excess P, derived from soil PRI values, overall site drainage and flood hazard in West Gingin, Western Australia also included those with a PRI >70 mL/g, such as gravelly clayey sands and sandy loams (Smolinski & Scholz 1997). Clearly therefore, the yellow gravelly loam (CH) and the brown clay (C42) used in this study (PRI >70 mL/g) confirm that the risk of leaching of P on these soils would be negligible. In addition, the gravelly loam (CH) used in Chapter 4 showed no evidence of the movement of P down the soil profile to depths below 20 cm by the end of the first growing season at biosolid application rates providing 145 kg P/ha (Table 4.11).

The relationship between soil PRI, Fe content and percentage SRP-R for the present experiment is shown in Figure 6.5, with SRP depicted as the size of the bubble marker. The concentration of SRP in leachate was likely to decrease as both the PRI value and Fe content increased. The soil Fe concentration gave a better correlation with percentage SRP-R than the PRI value (Table 6.3). As indicated by

Weaver and Summers (1998), the soil PRI will decrease with cumulative fertiliser inputs over time and saturation of P sorption sites, whereas reactive Fe levels remain constant.

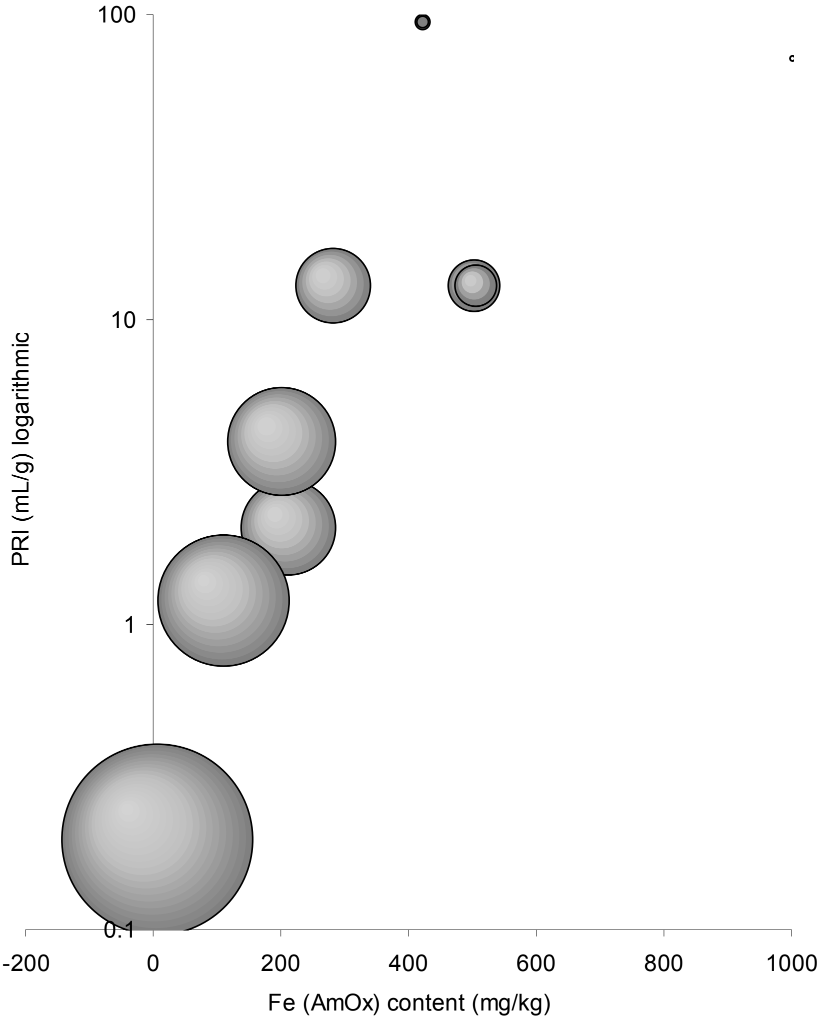


Figure 6.5 Interaction between PRI (mL/g) and iron content (mg Fe/kg) on percentage SRP-R

The size of the bubble indicates the relative % SRP-R. Values include both biosolids and MCP treatment means.

Soils classified by Smolinski and Scholz (1997) as being of moderately low risk of P leaching, that is those having a PRI from 5 to 20 mL/g, included the brown sandy loam (C10), gravelly sand (BH) and gravelly loamy sand (WI). As expected, these treatments resulted in low concentrations of SRP (<5 mg/L) in leachate across all treatments (Figure 6.2). The gravelly loamy sand (WI) generated the highest percentage SRP-R in this moderately low risk category, which coincided with the lowest soil pH of 4.1 in 0.01 M $CaCl_2$.

The siliceous sand (BR) and orange sand (C50) are soils designated as being of moderate risk of leaching (PRI 2 to 5 mL/g). This was apparent from Figure 6.3 with 25% of SRP recovered from MCP in the siliceous sand (BR), and was halved for biosolids. Therefore, assuming soils are well drained and the risk of overland flow is minimal, the risk of P leaching from biosolids in these sands would be less than for similar rates of inorganic P. The siliceous sand (BR) and gravelly loamy sand (WI) are soil types being investigated by the National Biosolids Research Program (NBRP) (2003-05) to examine long-term changes in nutrients and movement to depth (including P) (McLaughlin et al. 2002). The study by the NBRP uses higher biosolid application rates than used in the present experiment, up to 31.5 t DS/ha, and will therefore extend the present findings.

In soils classified as being of high risk of leaching P (PRI <2 mL/g), such as the acid washed sand (AW) and grey sand (LIS), the source of P (either biosolids or MCP), was, of greater significance. Biosolids treatments, however, were more similar to SRP results obtained in the moderate risk category. In general, the sandier soils tended to have the highest SRP values (Figure 6.3); which is not surprising given their low buffering capacities and lower pH values in Western Australia. The increase in SRP in leachate from biosolids in the grey sand (LIS) relative to the acid washed sand (AW) may be due to its lower pH (Table 6.2).

Texture alone was not a good predictor of SRP concentration in the present experiment, indicating that interactions with a number of other soil properties, such as PRI and reactive Fe were also important. The relationship between percentage sand content, PRI (mL/g) and percentage SRP-R is shown in Figure 6.6, with percentage SRP-R depicted as the size of the bubble marker. As the sand content in soil decreased and the PRI increased, the concentration of SRP was likely to decrease. Maguire and others (2001) also reported greater increases in WSP for sandy, low organic matter soil than fine textured, higher organic matter soil in the USA. The leachable fraction in sandy soils was small (<5%), although the type of biosolids applied affected WSP. Biosolids produced in BNR facilities, without the addition of Al or Fe salts for P removal, released more WSP.

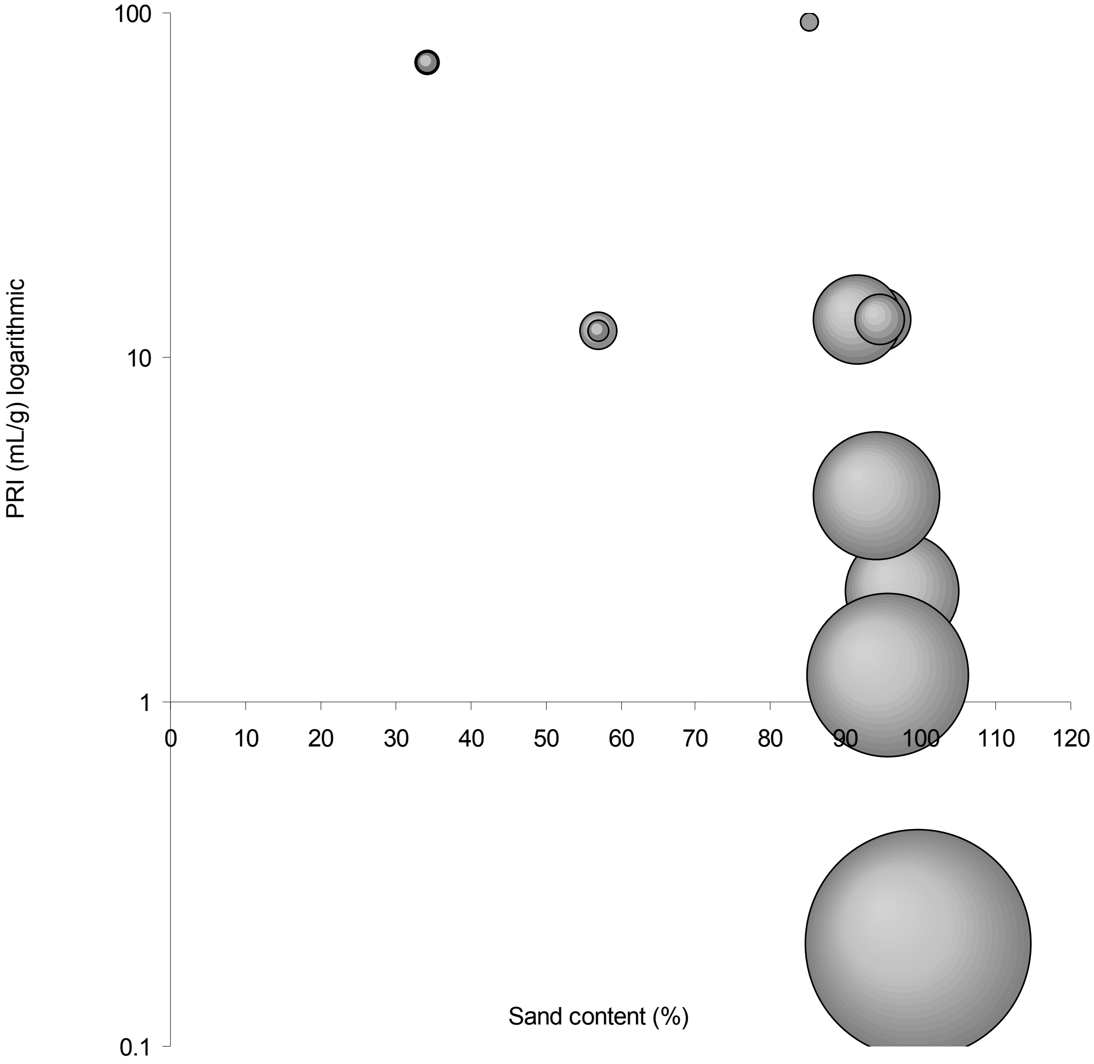


Figure 6.6 Interaction between percentage sand content and PRI (mL/g) on percentage SRP-R over nine soil types

The size of the bubble indicates the relative % SRP-R. Values include both biosolids and MCP treatment means.

There are soil types common to the USA with sufficient P-sorptive capacity (Al and Fe oxides) to prevent significant P leaching and mask inherent differences in the P solubilities of biosolids materials (Elliott, O'Connor & Brinton 2002). Kardos and Hook (1976) showed that leaching of P was <3% of the total P applied following the application of high rates of sewage effluent over a number of soil types and years. Fractionation of mineral P in the different soils used for the study showed that P had increased in the Al and Fe fractions, indicating that the sesquioxide content of the soil influenced its ability to sorb P. Although the leaching of P by biosolids has not been examined in Western Australia, P sorption plays a large role in the leaching of P. Gerritse (1990) predicted the time taken for P to move 1 m in a range of soils as: Darling Plateau (lateritic surface soil) = 15,000 years; Darling Plateau (clay subsoil) = 170 years; yellow Spearwood sand (subsoil) = 30 years; and Gavin sand (surface soil) = 2.5 years; based on a P accumulation of 20 kg/ha/yr and recharge of 100 cm/year (Weaver & Summers 1998)..

In the present study, SRP-R was negatively correlated to soil organic carbon (Table 6.3). The reduced leaching of P from biosolids, even on the acid wash sand was an unexpected result and could be due to a number of factors. It is suggested that the various constituents in biosolids, (i.e. organic carbon and various soil cations) acted to immobilise or sorb P in the acid washed sand, resulting in the lower solubility of biosolid P relative to MCP. High C: P ratios provide substantial energy and stimulate microbial growth that can consume all available P (Pierzynski, Sims & Vance 1994). The addition of biosolids to the acid washed sand may have introduced a microbial population, which immobilised a portion of the water-soluble P. In contrast, microbial activity would be absent in the MCP treatment on the acid washed sand, thus explaining the relatively higher SRP. Alternatively biosolids changed the nature of surfaces interacting with inorganic P by changing pore size distribution. Another possibility is that the addition of biosolids to the poorly buffered sands may have changed the soil pH, which acted to decrease the solubility of P.

The total P content of the soil and concentration of bicarbonate extractable P were poorly correlated with SRP (r = -0.49 and -0.05, respectively) and as such were not likely to be reliable predictors of the release of P to surface water and groundwater (Table 6.3). Total P was also considered by Pastene (1981) and Maguire and others (2001) to give a poor estimate of extractable P. For a particular soil type, a long history of P use will reduce the PRI as the capacity of the soil to adsorb additional P decreases. The modified PRI (PRI*) showed less correlation to SRP (r = - 0.26) than

PRI (r = - 0.61) and is logical given that bicarbonate extractable P values are used in the calculation.

Soil vulnerability guidelines and maximum N and P loadings presently recommended by DEP, WRC and DOH (2002) for the land-application of biosolids in Western Australia include four categories based on soil texture and PRI, as presented in Table 2.6 (Chapter 2). However, it would seem unnecessary to restrict the maximum recommended biosolid P loading to 120 kg P/ha (Table 2.6) in soils characterised by a PRI >5 mL/g and reactive iron content of >300 mg/kg. There was no evidence in the literature and this experiment to suggest that P would leach following the application of biosolids in these soils.

Further work is needed to establish the risk of P being moved off-site through surface runoff, including eroded sediments, although the risk would be expected to be low given that guidelines specify that biosolids not be applied to land prone to erosion (i.e. steep slopes) and/or near water bodies. Variability in runoff volume and erosion as a result of climatic, topographical and agronomic factors plays a larger role than soil-test P in determining the amount of P losses from agricultural land (Sibbesen & Sharpley 1997).

Soluble reactive P was negatively correlated with pH between values of 4.1 to 7.0 ($CaCl_2$) for biosolids in the present experiment, with concentrations of SRP in leachate higher in the more acidic soils. The relationship was weaker between SRP and pH in MCP. At pH values less than 7, the solution concentration of P is controlled by adsorption, which is not uniquely related to pH (Wild 1988). Therefore, the addition of biosolids to the soils used in the experiment is likely to have provided greater sites for P sorption, rather than by pH affecting the solubility of P directly. DEP, WRC and DOH (2002) recommend that biosolids should not be applied to soils of pH <5.0 ($CaCl_2$). Plants can take up toxic amounts of aluminium on acidic soils that interfere with P nutrition in plants; therefore the addition of lime is commonly used to raise pH (Wild 1988).

It was interesting to note that recovery of mineral N during this time period was less than for the recovery of SRP, with soil factors such as pH, and sand content likely to be involved. However, further research on N mineralisation in land-applied biosolids in Western Australia is warranted to justify N loading rates, given the tendency for excess inorganic N to dissolve and move off-site. Biosolids application rates up to 34 t DS/ha (biosolid P_T = 1.4%) in a *Pinus pinaster* plantation on deep Karrakatta coastal sand in Western Australia resulted in continual mineralisation and percolation of anions, such as nitrates down to the 40-60 cm horizon. Nitrate levels increased for a short period below the stockpile area only, with no increases in critical P soil concentrations in bore water samples (Dumbrell & McGrath 2002). Although biosolids application rates for agricultural crops in the wheatbelt are commonly less than used for forestry (i.e. 7 t DS/ha), there may be a need to select stockpile sites carefully, due to the concentration of high rates of nutrients in a small area.

6.5 Conclusions

Overall, biosolid P was of lower solubility than inorganic sources of P and applied to soil would be less likely to leach P following high rainfall events. There was almost complete recovery of the water-soluble portion of MCP applied to the inert, acid washed sand (AW) with 71.1% SRP-R as compared with 14.2% for biosolids. Similarities would be expected between values for SRP in the acid washed sand (AW) obtained in this experiment and WEP for biosolids obtained elsewhere, i.e. approximately 14%, although this remains to be verified. The relationship between WEP (agitation in water) and SRP (soil leachate unit) was limited due to the different methodologies used by each study; including the agitation time, biosolids particle size and presence of soil. Perth biosolids are produced without the addition of iron or aluminium salts in the treatment process, therefore higher SRP values would be expected than for biosolids produced using chemical P treatment.

Over a range of eight agricultural soils (excluding the acid washed sand), the mean percentage of SRP recovered in leachate subjected to standard leaching procedure was higher ($P < 0.05$) following the addition of MCP (11.2%) than for comparable rates of P in biosolids (7.9%). However, values for SRP-R ranged significantly from 0.06% to 33.4% in the MCP and from 0.08% to 22.0% in the biosolids, respectively largely dependent on the specific agricultural soil properties. The risk of P leaching following the application of biosolids was dependent on chemical, physical or biological properties unique to the biosolids although the reasons for this are unclear. The acid washed sand (AW) would be the least chemically and biologically reactive of all the soils examined in the present study, and interestingly large differences in SRP values existed between MCP and biosolids.

The type of soil and inherent soil properties determined the percentage SRP-R for both the MCP and biosolids under a standard leaching procedure. The solubility of P in both biosolids and inorganic P was most likely to be decreased by increasing concentrations of Fe, organic carbon, and increasing values of pH and PRI. The total soil P concentrations and bicarbonate extractable P concentrations were not good indicators for WSP released following the application of biosolids in the low to moderate P soils studied (i.e. total soil P <260 mg P/kg and bicarbonate extractable P <34 mg P/kg). Consequently, the previous P fertiliser history of the soil may not accurately predict changes in WSP following the application of biosolids.

The Western Australian soils used in the present experiment, ranked according to their risk of P leaching following the application of biosolids were as follows: negligible risk = gravelly sand (BH), yellow gravelly loam (CH) and brown clay (C42); moderately low risk = brown sandy loam (C10), gravelly sand (BH), gravelly loamy sand (WI), siliceous sand (BR) and orange sand (C50); and moderate risk = acid washed sand (AW) and grey sand (LIS). There was no evidence in the literature to suggest that P would leach on soils where PRI > 2 mL/g and reactive iron content >300 mg/kg, as indicated by the results in the present study. Further, following the application of biosolids, soils were of lower risk of P leaching than inorganic sources of P where the PRI >2 mL/g and reactive iron >200 mg/kg.

It is suggested that no P loading restrictions be placed on Western Australian soils characterised by a PRI >2 mL/g and an appreciable reactive iron content (e.g. >200 mg/kg). Existing management issues relating to the land application of biosolids in Western Australia, such as selecting for well-drained sites away from watercourses would ensure that sensitive land areas and water resources are avoided. However, this is a management issue rather than a soil type restriction. Further work could be conducted to establish the risk of water-soluble P or particulate P being carried off-site in runoff following high rainfall events. In addition, further investigation needs to be conducted to determine N mineralisation rates specific to the wheatbelt of Western Australia to establish the risk of runoff and leaching by mineral N.

7 General discussion

7.1 Introduction

Prior to the studies presented in this thesis, there was a lack of data in Western Australia concerning the forms of P in local biosolids, how effective the P was for plant growth and the significance of high loading rates of P in the environment as a result of typical biosolids application rates being used in agriculture. This section will discuss and summarise the major findings of glasshouse, field and laboratory experiments under the following headings: characteristics of the P forms in Perth biosolids; relative effectiveness of biosolid P compared with water-soluble inorganic P fertiliser; loading rates of biosolids required to provide agricultural crops with adequate P; and selection of soils most suitable for the land application of biosolids.

Biosolids from the Beenyup WWTP were used throughout all experiments to ensure comparability. Beenyup uses mesophilic anaerobic digestion and then dewatering of primary domestic sourced influent. There is no chemical precipitation of P, as is common in many inland WWTPs throughout Australia, with effluent from Beenyup WWTP discharged directly to the ocean (Water Corporation 1997a). As anaerobic digestion is a widely used method for sludge stabilisation (Bruce, Campbell & Balmer 1984; Lue-Hing et al. 1997; Wen, Bates & Voroney 1995), it would be expected that the results of this thesis would be applicable to anaerobically digested dewatered biosolids cake produced without chemical precipitation of P elsewhere; and particularly from Perth's other major WWTP, Woodman Point, which uses a similar treatment process to Beenyup.

7.2 Characteristics of the forms of phosphorus in biosolids produced at the Beenyup Wastewater Treatment Plant

The total P content of Beenyup biosolids was consistent for all experiments ranging from 2.98% db (Chapters 3 & 5) to 2.96% db (Chapters 4, 5 & 6). Total P measured by ICP-AES was approximately 0.5% higher than the long-term average reported by the Water Corporation (1999-2000), highlighting variation in the methodologies used to extract and report total P by different laboratories. Although Beenyup does not use chemical precipitation of P, lime is added to the influent channel to maintain pH in the aeration system (Water Corporation 1997a). Thus much of the water-soluble P is discharged in effluent, with P remaining in biosolids thought to precipitate to $CaHPO_4$ (Barrow 1999).

Sequential fractionation of P indicated that 92% of P was in inorganic forms and a much smaller proportion (8%) in organic forms (Chapter 3), consistent with that expected of anaerobically digested biosolids (Coutinho, Arrobas & Rodrigues 1997; Dentel et al. 2000; Dentel & Mah 2002; O'Connor et al. 2002; Osborne 1995). Exchangeable inorganic P and water-soluble P forms constituted the majority of Beenyup biosolids (66.3%). The bicarbonate extractable portion (19.4%) was the second highest fraction and consisted of inorganic P (12.8%) and easily mineralisable organic P forms (6.6%). The remainder of P (14.3%) was typically present as inorganic forms associated with Fe, Al and Ca. Consequently, the term 'mineralisation rate' often used to describe the percentage release of biosolid P over time (Michalk et al. 1995; Rawlinson & Salt 1997) is of little consequence to Perth biosolids.

Therefore, given the predominantly soluble inorganic P forms in the Beenyup biosolids, it was reasonable that the glasshouse experiment reported in Chapter 3, showed biosolid P to be comparable with MCP for shoot dry matter production and P uptake by wheat shoots on a P deficient lateritic soil. The biosolids were dispersed in water and well mixed into the soil, which remained at gravimetric soil water capacity for the duration of three consecutive crops, each of 33 days. Values for Mitscherlich equation coefficients showed the RE of biosolid P to be comparable with that of MCP for each of the three consecutive crops. In addition, the residual values of both biosolid P and MCP relative to freshly applied MCP decreased and were similar over time as similar processes presumably sorbed P.

On completion of the third harvest in the glasshouse (Chapter 3), there were no differences in fractions of soil P between the two sources of P as measured in the 140 mg P/kg MCP treatment and the 150 mg P/kg biosolids treatment. Compared with the control treatment, the largest increases were in the Al and Fe bound inorganic P fraction, similar to that obtained in eastern Australia (Dougherty and Lawrie 2000), showing a shift from the predominant resin or bicarbonate fractions measured at the start of the experiment. To establish the source of P taken up by plants following the application of biosolids, further investigation is required to trace the cycling of P in the various soil pools.

Many studies have shown a poor correlation between soil extractable P and plant uptake following the application of biosolids or sludges (Cottenie & Kiekins 1980; McLaughlin 1988; Pastene 1981; Tiessen & Moir 1993; Velthof et al. 1998; Womer, Elliott & Brandt 2002), with results for bicarbonate extractable P in the glasshouse (Chapter 3) similarly underestimating P uptake.

7.3 Relative effectiveness of the phosphorus in biosolids compared with an inorganic source of phosphorus

The field experiment (Chapter 4) measured plant and soil data collected over a two-year wheat and lupin rotation. The site represented Mediterranean climatic conditions typically experienced in agricultural regions of Western Australia where biosolids are applied. The infertile lateritic soil type was P responsive and similar in properties to that used in the glasshouse experiment. A contrast in seasons was encountered, with the first year (2001) being relatively dry (390 mm annual rainfall) and the second year (2002) more typical of the district average (520 mm annual rainfall).

In the first season and following incorporation by disc plough, the RE of P in biosolids was significantly less than the inorganic source of P (TSP), and lower from that obtained in the glasshouse. In the first season, RE values for Mitscherlich equation coefficients for P uptake in the dry matter of wheat shoots for biosolids compared with top-dressed TSP at 67 DAS was 33%, although this gradually improved over the season at 123 DAS to 55%. By grain harvest of wheat at 210 DAS, the RE of biosolids compared with top-dressed TSP was 67% indicating that P availability in biosolids increased with time, consistent with other studies (Osborne et al. 1995a; McLaughlin and Champion 1987). In the second season, and following incorporation by the disc plough during seeding, P uptake in shoot dry matter of lupins over three sampling dates at 47, 98 and 165 DAS was similar, averaging 78%. At grain harvest of lupin at 211 DAS, the RE of biosolids compared with top-dressed TSP was 60% (Chapter 4).

After one season, the residual P value in biosolids relative to P in freshly applied top-dressed TSP was lower, for each of four sampling dates. The RV of biosolids determined at grain yield of lupin at 211 DAS compared with freshly applied top-dressed TSP was 45%, whereas last year’s top-dressed TSP was higher at 75% of that of freshly applied top-dressed TSP (Chapter 4). Therefore, the reduced RV of biosolids compared with inorganic P fertiliser needs to be taken into consideration in the context of determining follow-up P fertiliser rates in the second season.

Factors such as reduced and variable soil moisture throughout the growing season and the spatial heterogeneity of biosolids in the soil matrix contributed to the lower effectiveness of biosolid P under field conditions (Chapter 5). Glasshouse experiments similarly indicated that reduced P uptake was due to physical effects resulting from the extent of mixing or placement of biosolids into the soil, rather than chemical or biological reactions in the soil when moisture was not limiting. In the field experiment, the RE of biosolids relative to top-dressed TSP for grain yield of wheat was reduced from 67% to 39% where biosolids were placed on the soil surface without incorporation. Relative to incorporated biosolids, the RE of surface-applied biosolids was 58%. However, in the second season, all treatments including the surface-applied biosolids were incorporated with a disc plough at seeding. The resultant incorporation of biosolids ensured that P was accessible to plant roots and thus little difference in lupin grain yield was measured. Similarly, the availability of P in sludges and animal manures is reduced when surface-applied rather than incorporated (Bromfield 1961; Gunary 1968; King and Morris 1973; Pastene 1981).

7.4 Loading rates of biosolids required to provide agricultural crops with adequate phosphorus

Estimations of loading rates of biosolids that may be required, on a range of soils, to satisfy the P requirement of a wheat crop and optimise yield are presented in Table 7.1. Data pertaining to the response of wheat to inorganic P over a range of soils, differing in PRI and bicarbonate extractable soil P (Colwell) was adapted from Bowden, Shedley and Burgess (1993). All values are specific to a wheat crop and assume that top-dressed TSP is approximately 30% as effective as fertiliser drilled with the seed (Rudd and Barrow 1973); and the RE of biosolids P is 67% that of top-dressed TSP.

From Table 7.1, for example, 41 kg P/ha would be required for maximum crop yield on the P responsive Chester’s site (Chapter 4) (Bowden, Shedley & Burgess 1993), requiring approximately 6.9 t DS/ha biosolids. Data from Chapter 4 confirmed that rates of biosolids applied below the NLBAR (5.0 t DS/ha) were P deficient (Reuter & Robinson 1997) at all growth stages when applied to a P deficient soil. Therefore, on high P sorbing sites, biosolids applied at the NLBAR may still require additional inorganic P for optimal wheat yield.

A number of scenarios are possible where the NLBAR and the PLBAR are in balance (Table 7.1). However, where maintenance dressings of P had been applied regularly to increase bicarbonate extractable soil P, lower biosolids loading rates would be required to satisfy the P requirements of the crop. It is essential to balance P loadings as Womer, Elliott and Brandt (2002) concluded that unfairly restrictive

PLBAR estimates would require more land, increase spreading costs and may also result in N deficient crops or require extra applications of N.

Table 7.1 Guide to loading rates of biosolids required to obtain optimum wheat yield for soils differing in PRI (mg/L) and available soil P (mg/kg), including values for drilled inorganic P (Pi) and the PLBAR* (kg P/ha)

	PRI <2			**PRI 2 to 15**			**PRI > 15**		
Colwell P (mg P/kg)	Pi (kg P/ha)	PLBAR (kg P/ha)	BS rate (t DS/ha)	Pi (kg P/ha)	PLBAR (kg P/ha)	BS rate (t DS/ha)	Pi (kg P/ha)	PLBAR (kg P/ha)	BS rate (t DS/ha)
<2	35	175	5.9	44	220	7.4	48	240	8.1
4	30	150	5.1	37	185	6.3	44	220	7.4
6	27	135	4.6	34	170	5.7	41	205	6.9
8	24	120	4.1	31	155	5.2	39	195	6.6
10	22	110	3.7	27	135	4.6	37	185	6.3
12	19	95	3.2	24	120	4.1	31	155	5.2
15	15	75	2.5	19	95	3.2	26	130	4.4
18	11	55	1.9	15	75	2.5	20	100	3.4
21	7	35	1.2	8	40	1.4	15	75	2.5
25	2	10	0.3	2	10	0.3	9	45	1.5
30	0	0	0.0	0	0	0.0	4	20	0.7

*PLBAR=Phosphorus Limited Biosolids Application Rate.

Original data sourced from Bowden, Shedley and Burgess (1993); where top-dressed inorganic P is 30% as effective as drilling fertiliser with the seed, biosolid P content is 2.96% and percentage relative effectiveness (RE) of biosolid P compared with top-dressed inorganic P (Pi) is 67% (Chapter 4). The NLBAR (Nitrogen Limited Biosolids Application Rate) is not considered in this Table.

The data in Table 7.1 needs to be substantiated over sites with a higher P availability, i.e. soils that have received regular applications of fertiliser P. Thus, nutrient data presently being collected on the moderately P sorbing gravelly loamy sand (WI) and the grey siliceous loamy sand (BR) at Moora, Western Australia (Chapter 6) within the National Biosolids Research Program (NBRP) (McLaughlin 2002) could extend the present findings. The Moora study is characterised by higher rates of biosolids, up to 42 t DS/ha, and moderate levels of soil available P due to regular dressings of P fertiliser over a number of years (Pritchard & Collins 2005).

The absolute values for RE obtained in this study need to be treated judiciously given the complexity of the wheatbelt environment, including differences in season, type of crops, farm management practices and farm machinery used. Potentially, the effectiveness of biosolids in the first season, relative to the inorganic source of P was highly variable and consistent with extreme ranges cited elsewhere (de Hann 1981; McLaughlin & Champion 1987; Womer, Elliott & Brandt 2002).

Management factors such as the placement of fertiliser P are considered crucial in the determination of yield, such that drilling TSP with the seed, rather than top-dressing improves its effectiveness two to four times (Rudd and Barrow 1973). The implications are that the RE of biosolids compared with drilled TSP (rather than top-dressed TSP) could be reduced from 67% (Chapter 4) to anywhere from 8% to 33% for grain yield in the first season. The improvement in RE over time during the first season may be due to factors such as improved soil moisture, ability of larger plants to locate the heterogeneously distributed biosolids or to induce solubility around the rhizosphere, or other constituents in the biosolids affecting P availability indirectly by stimulating microbial biomass and activity, or blocking P sorption sites.

In some circumstances, the application of biosolids has resulted in a change in soil pH, with the solubility of P increased at a neutral pH (Stewart & Sharpley 1987). However, no change in soil pH was measured in the 0-10 cm depth at 305 DAS in the field experiment at biosolids rates up to 5 t DS/ha (Chapter 4), although soil pH in the glasshouse increased ($P < 0.05$) under a similar rate of biosolids. Other major constituents in biosolids, such as organic carbon, showed no significant increase in soil samples after application, although at the biosolids rates used (<5 t DS/ha) only small increases of up to 0.2% would be expected.

The relationship between bicarbonate extractable soil P test and shoot uptake of P in plants grown with biosolids in the field experiment (Chapter 4) was poor. Soil sieving to <2 mm removed many particles of biosolids and consequently underestimated P values. Less than 5% of the total P applied was measured as bicarbonate extractable P as compared with approximately 60% of the applied TSP. In comparison, there were no such discrepancies in the glasshouse experiment (Chapter 3) because the soil was sieved to <2 mm prior to use and as biosolids were dispersed in a wet slurry, sieving <2 mm was not necessary. Changes in bicarbonate extractable soil P measured at 60 DAS in the field experiment and 66 DAS in the glasshouse experiment for all P loading rates are plotted in Figure 7.1.

The lack of relationship between increasing application rates of biosolid P and bicarbonate extractable soil P in the field highlights the importance in ensuring biosolids particles are not inadvertently sieved from the sample during routine soil preparation.

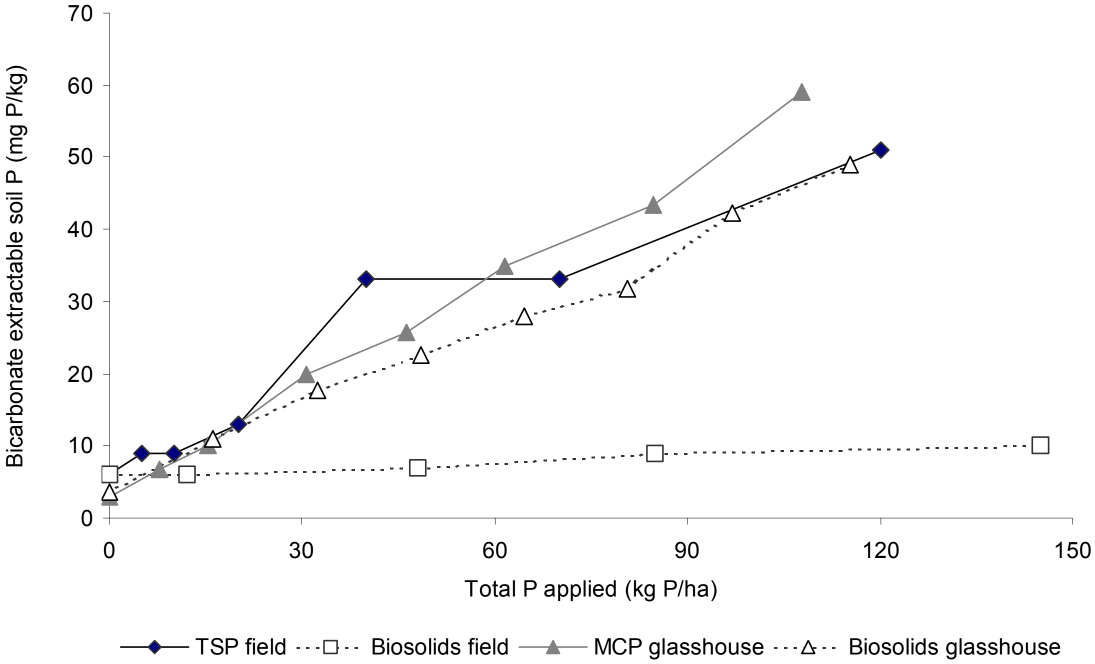


Figure 7.1 Relationship between bicarbonate extractable soil P (Colwell) and total P applied as biosolids and inorganic sources of P, measured at 60 DAS in the field and 66 DAS in the glasshouse

TSP = triple superphosphate, MCP = monocalcium phosphate. Values are the mean of three replicates. Lines plotted using Microsoft Excel. Bulk density of 1.3 g/cm^3 used to convert P applied in kg/ha in the 0-10 cm depth of the field trial to mg/kg.

The influence of biosolid N (de Hann 1981; Gupta, Narwal & Antil 1989; Gupta, Narwal & Antil 1993; Havilah & Davis 1998; Prasad 1996; Sommers & Sutton 1980) was largely minimised in the glasshouse experiment (Chapter 3) by applying decreasing rates of inorganic N as the rates of biosolids increased. An N interaction was not considered to favour the biosolids treatments as MCP treatments exhibited similar concentrations of N in dry matter of shoots and N uptake. In the field experiment (Chapter 4), basal applications of urea were applied to all treatments in an attempt to minimise the response to N. However, in the first year, the highest TSP treatment appeared to be disadvantaged by lower levels of available soil N as evident by low N concentrations in shoots at 123 DAS and low inorganic soil N at 133 DAS. The deficiency became more apparent as the season progressed, which may have contributed to improvement in the RE of biosolids relative to top-dressed TSP. In the second year, lupins inoculated with N fixing bacteria overcame confounding effects of variable soil N, with little change in the RE throughout the season. However, further research on N mineralisation in land-applied biosolids in Western Australia is warranted to ensure N loading rates are being met, given that excess inorganic N is soluble and has the potential to move off-site.

7.5 Effect of high loading rates of phosphorus following the application of biosolids at the NLBAR over a range of soil properties

Loading rates of biosolids determined by the NLBAR, are commonly reported to have resulted in large loadings of P (Chang et al. 1983; Dentel, Sims & Mah 2001; Epstein 2002; Landers 2000; Maguire, Sims and Cole 2000; National Research Council 1996; Pastene 1981; Pierzynski 1994; Triner et al. 2001; Womer, Elliott & Brandt 2002). In Western Australia, a typical biosolids land application may result in soil enrichment of P with up to 120 kg P/ha, or 10 times more P than removed by plant uptake (Pritchard and Penney 2003). High levels of soil P of this magnitude rarely result in plant toxicity, with high application rates of P vital to maximise crop yield on many high P sorbing soils (Table 7.1). However, the fate of high loadings of biosolid P, particularly on the lower P sorbing soils is unknown.

Very little soluble P remains in Beenyup biosolids, being largely discharged to the ocean in effluent (Barrow 1999), typical of wastewater treatment plants where chemical precipitation of P is absent (Havilah & Osborne 1992; Kirkham 1982). In Chapter 6, concentrations of SRP-R in leachate collected from the reverse soil leachate unit in acid washed sand (AW) measured 71.1% in the MCP treatment as compared with 14.2% for the biosolids treatment. All treatments had been maintained at gravimetric soil water capacity (GSWC) for one week prior to leaching. The P in biosolids was of a lower solubility than MCP, and therefore biosolids would be less likely to leach P than comparable rates of inorganic P. It is suggested that biosolids may change the nature of the surfaces of soil particles that interact with inorganic P, or immobilise P through the stimulation of microbial activity; although the exact process is unclear and warrants further study. Water extractable P values reported for biosolids are generally lower elsewhere than obtained in this study (Brandt, Elliott & O'Connor 2002; Elliott, O'Connor & Brinton 2002; Montgomery 2002), possibly due to a difference in the methodology and/or different biosolid types.

The mean proportion of SRP recovered in leachate from eight agricultural soils (excluding acid washed sand), subjected to a standard leaching procedure was significantly higher following the addition of MCP (11.2%) than for comparable rates of P as biosolids (7.9%), ranging from 0.06% to 33.4% in the MCP treatments and from 0.08% to 22.0% in the biosolids treatments (Chapter 6). Effective P sorption mechanisms are known to occur in many Western Australian soils (Bolland 1998b; Bolland, Allen & Barrow 2003; Smolinski & Scholz 1997); and not surprisingly, soil characteristics such as Fe, organic carbon, pH and PRI were negatively correlated to SRP. In the leaching experiment (Chapter 6), the previous P fertiliser history and present total P and bicarbonate extractable P status of the soils used in the study were not reliable predictors of the proportion of water-soluble P released following the application of biosolids.

Soils considered to be of negligible risk of P leaching following the application of biosolids at typical agricultural rates (5 t DS/ha) included gravelly sand (BH), yellow gravelly loam (CH) and brown clay (C42); moderately low risk included brown sandy loam (C10), gravelly sand (BH), gravelly loamy sand (WI), siliceous sand (BR) and orange sand (C50); those of moderate P leaching risk included acid washed sand (AW) and grey sand (LIS). In addition, the risk of P leaching in the yellow gravelly loam (CH) was shown to be negligible with no increase in P measured at depths to 20 cm at loading rates of 5 t DS/ha after one season (Chapter 4). Likewise, the gravelly sand (BH) used in the glasshouse experiments (Chapter 5), showed no increase in bicarbonate extractable P at depths to 10 cm following the placement of biosolids on the soil surface after 33 days of continual watering to GSWC in a non-draining pot. The physical placement of biosolids is of environmental relevance, with surface-applied biosolids expected to be less prone to leaching than incorporated sludges (Gove et al. 2002), although surface-applied fertiliser may contribute to P in runoff (Pierzynski, Sims & Vance 1994).

Given the P forms in Beenyup biosolids and its high RE in the glasshouse (Chapter 3), the P could be as effective as inorganic P if dispersed in water and injected into the soil as slurry, cultivated throughout the soil and the site maintained at field capacity throughout the growing season. However, this method of land application would be improbable in the agricultural sector (Chapters 4 & 5). Furthermore, agricultural crops typically allow the recovery of between 5% and 30% of water-soluble P fertiliser during the year of application (Sibbensen & Sharpley 1997; Foth & Ellis 1988; Wild 1988), with biosolids expected to be less effective given consistently lower RE values (Chapter 4 & 5). Therefore it would be erroneous to base the PLBAR on an assumption that the P is 100% plant available, given that only a small proportion of the P in biosolids contributes immediately to soil solution P.

It is certain that biosolids loading rates based on the NLBAR would result in enrichment in total soil P, with only about 10% of the P removed annually by the crop. However, much of the biosolid P is positionally unavailable to plants (Chapter 5), accentuated by its low solubility (Chapter 6) and over time the P becomes less available (Chapter 4). Biosolids are distributed heterogeneously in the soil matrix (Chapter 5), with large amounts of P sorbed by soil constituents, typically Fe and Al (Chapter 3), consistent with highly weathered lateritic soils in Western Australia. In addition, other constituents or properties in the biosolids acted to sorb or immobilise P, as evident by lower SRP values in the acid washed sand compared with the MCP treatment (Chapter 6).

7.6 Selection of soils most suitable for the land application of biosolids in Western Australia to best balance phosphorus loadings with the NLBAR

Guidelines developed to provide acceptable practices for the beneficial reuse of biosolids on agricultural land in Western Australia (DEP, WRC & DOH 2002), presently include four categories for maximum P loadings based on soil texture and PRI (Chapter 2). Based on the present study, an alternative approach is to prioritise land application programs based on agronomic P requirement (see Table 7.1), combined with the risk of leaching and off-site movement of P (Chapter 6).

A classification is proposed in Table 7.2, with no P loading restrictions placed on soils characterised by a PRI >2 mL/g and a reactive iron content >200 mg/kg: that is on such soils, biosolids loading rates would be determined by the NLBAR. Soils to be used in biosolids land application programs should be selected in order of priority, thus category 1 > category 2 > category 3. Soils in category 4 are least likely to be selected and category 5 soils are not recommended. Category 1 soils may not be able to provide plants with adequate P at 1 x NLBAR loadings due to high P sorption of the soil. Fertiliser P may be needed in subsequent years, particularly as the residual value of biosolid P was shown not to be as effective as TSP.

Table 7.2 Soil classification system to ensure high P demand and low risk of P leaching following the application of biosolidsbased on the Phosphorus Retention Index (PRI) and bicarbonate extractable P content of the soil**

PRI (mL/g)	Bicarbonate extractable P (Colwell) (mg P/kg)	Agronomic demand for P	Risk of P leaching	Category*
>70	<15	High	Negligible	1
	>15	Moderate	Negligible	1
15-70	<15	High	Low	1
	15-25	Moderate	Low	2
	>25	Low	Low	3
2-15	<10	High	Low	1
	10-20	Moderate	Low	2
	>20	Low	Low	3
<2	<15	Moderate	Moderate	4
	>15	Low	High where <200 mg Fe/kg	5

***Soil categories ranked in order of preference for use from highest (1) to lowest (5).**

Categories preferred for land application and which impose no P loading restrictions are 1>2>3. Soils in category 4 are least suitable. Category 5 soils are not recommended for biosolids application and include all soils with a reactive Fe content <200 mg Fe/kg.

**** Biosolids applied at 1xNLBAR = Nitrogen Limiting Biosolids Application Rate**

Sites eligible for biosolids land application programs are required to be well drained, of good soil depth, further than >250 m from a natural water body, have minimal risk of overland flow and subsurface lateral flow and demonstrate a good level of land management.

Bicarbonate extractable P extracted by 0.5 M $NaHCO_3$ (1:100) (Colwell 1963; Rayment & Higginson 1992h), PRI (Allen & Jeffery 1990), Fe extracted by 0.2M ammonium oxalate pH 3.25 (Rayment & Higginson 1992c) (mg/kg = milligrams per kilogram, mL/g = millilitres per gram).

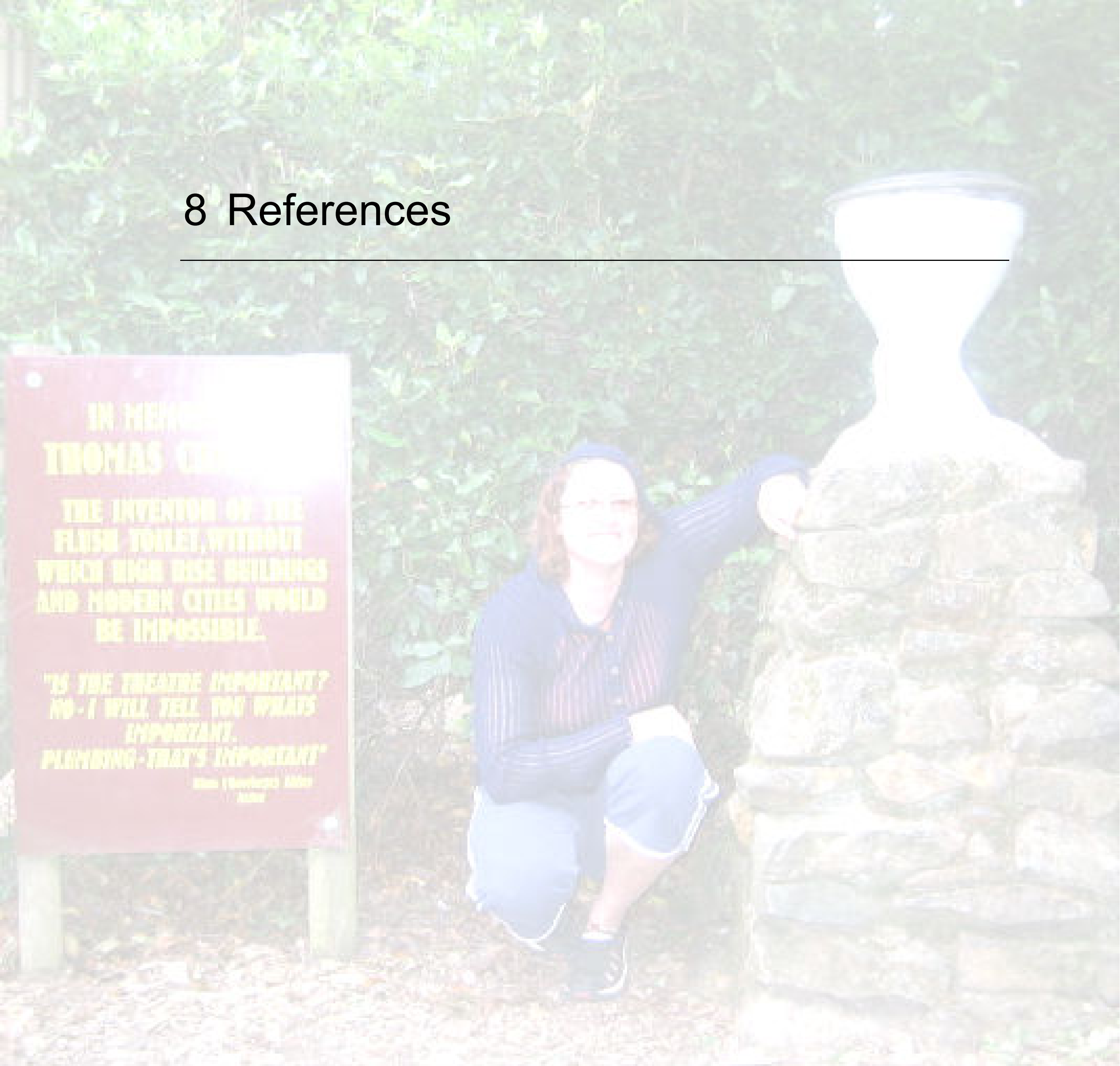
Table adapted from information by Smolinski and Scholz (1997) and Bowden, Shedley and Burgess (1993), combined with Chapter 6 data.

The Water Corporation (1997a) predicted that only 1% of the agricultural land within a 150 km radius surrounding Perth would be required for biosolids land application programs to the year 2040. Biosolids are in high demand at present for use in broadacre agriculture (Penney, Dumbrell & Pritchard 2003), and with large land areas available, the selection of suitable soils from the categories in Table 7.2 is envisaged to be workable. In the selection of suitable sites for the land application of biosolids in Western Australia, consideration also needs to be given to DEP, WRC and DOH (2002) guidelines to ensure existing management issues are included. These include well-drained sites away from watercourses to ensure that sensitive land and water resources are especially avoided and that water-soluble P and particulate P originating from biosolids is not washed into streams through surface runoff and/or flooding.

Repeat applications on each site, no more frequent than every five years, as currently recommended, would ensure that excessive soil P enrichment was minimised. Plants can take up toxic amounts of aluminium on acidic soils that interfere with P nutrition in plants (Wild 1988). Liming would therefore be recommended on soils of pH <5.0 ($CaCl_2$) to raise pH, consistent with current guidelines, particularly given that soil pH was negatively correlated to SRP at values up to 7.0 ($CaCl_2$).

Based on the findings from the experiments conducted, it is recommended that loading rates of biosolids should be continued to be based on the NLBAR in Western Australia with further investigation warranted to validate current N mineralisation and volatilisation rates. Table 7.2 should be used as a guide in the initial selection of sites for the application of biosolids to ensure that P issues are considered.

8 References



ABARE 2003, *Australian Commodity Statistics 2003*, Australian Bureau of Agricultural and Resource Economics, Commonwealth of Australia, Canberra.

AEL 2000, *Laboratory report 50817 to Water Corporation Western Australia*, Australian Environmental Laboratories, Welshpool, Perth, p 1-7.

Akhtar, M, McCallister, D L & Eskridge, K M 2002, 'Availability and fractionation of phosphorus in sewage sludge-amended soils', *Communications in Soil Science and Plant Analysis,* vol. 33, no. 13 &14, pp. 2057-2068.

Allen, D G, Barrow, N J & Bolland, M D A 2001, 'Comparing simple methods for measuring phosphate sorption by soils', *Australian Journal of Soil Research,* vol. 39, no. 6, pp. 1433-1442.

Allen, D G & Jeffery, R C 1990, *Methods for analysis of phosphorus in Western Australian soils*, Agricultural Chemistry Laboratory, Chemistry Centre of Western Australia, East Perth, Report 37.

American Society of Agricultural Engineers 2000, *ASAE standards 2000: standards, engineering practices and data*, American Society of Agricultural Engineers, St. Joseph, Mich.

Anderson, W K & Garlinge, J (eds.) 2000, *The wheat book: principles and practice*, Agriculture Western Australia, South Perth.

Andreasen, P 2001, 'Chemical stabilisation', in L. Spinosa & P. A. Vesilind, (eds.), *Sludge into biosolids: processing, disposal and utilisation*, IWA Publishing, London, pp. 242-258.

Australian Water Association 2001, *Sludge and biosolids. We all use water: a users guide to water and wastewater management*, AWA and NHT and Sunshine Coast Environmental Council, Report 26.

Awad, A S, Ross, A D & Lawrie, R A 1989, *Guidelines for the use of sewage sludge on agricultural land,* 2nd edn, New South Wales Agriculture and Fisheries, Rydalmere, Sydney.

Bamforth, I 1995, *The growth and yield response to sewage sludge of a range of summer crops - SAP core unit trials final report*, New South Wales Agriculture Organic Waste Recycling Unit, Richmond, Sydney, Project 16.

Bamforth, I 1996, 'The growth and yield response of wheat to biosolids products', in G. J. Osborne, R. L. Parkin, D. L. Michalk & A. M. Grieve, (eds.), *Biosolids research in New South Wales: proceedings of the biosolids summit, a research conference on the use of biosolids in agriculture and forestry held at the Biological and Chemical Research Institute, Rydalmere June 1995*, NSW Agriculture Organic Waste Recycling Unit, Richmond, pp. 103-111.

Banks, C J & Heaven, S 2001, 'Landfilling', in L. Spinosa & P. A. Vesilind, (eds.), *Sludge into biosolids: processing, disposal and utilisation*, IWA Publishing, London, pp. 74-101.

Barrow, N J 1980, 'Evaluation and utilization of residual phosphorus in soils', in F. E. Khasawneh, E. C. Sample & E. J. Kamprath, (eds.), *The role of phosphorus in agriculture*, American Society of Agronomy, Madison, Wis., pp. 333-359.

Barrow, N J 1999, *Report on the expected reactions of P in biosolids when used for land application*, Water Corporation, Perth.

Barry, G A, Chudek, P J, Best, E K & Moody, P W 1995, 'Estimating sludge application rates to land based on heavy metal and phosphorus sorption characteristics of soil', *Water Research,* vol. 29, no. 9, pp. 2031-2034.

Bartlett, J & Kilillea, E 2001, 'The characterisation, treatment and sustainable reuse of biosolids in Ireland', *Water Science and Technology,* vol. 44, no. 10, pp. 35-40.

Bates, T E 1971, 'Factors affecting critical nutrient concentrations in plants and their evaluation: a review', *Soil Science,* vol. 112, no. 2, pp. 116-125.

Black, C A 1968, *Soil plant relationships,* 2nd edn, John Wiley & Sons, New York.

Blair, G R, Chinoim, N, Lefroy, R D B, Anderson, G C & Croker, G C 1991, 'A soil sulphur test for pastures and crops', *Australian Journal of Soil Research,* vol. 29, pp. 619-626.

Blakemore, L C, Searle, P L & Daly, B K 1987, *Methods for chemical analysis of soils*, NZ Soil Bureau, Department of Scientific and Industrial Research, Lower Hutt, NZ, Scientific Report 80.

Bolland, M 1998a, 'Chapter 6.1 Introduction', in G. Moore, (ed.) *Soilguide: a handbook for understanding and managing agricultural soils*, vol. Bulletin 4343, Agriculture Western Australia, South Perth, pp. 161-163.

Bolland, M 1998b, 'Chapter 6.3 Phosphorus', in G. Moore, (ed.) *Soilguide: a handbook for understanding and managing agricultural soils*, vol. Bulletin 4343, Agriculture Western Australia, South Perth, pp. 168-175.

Bolland, M & Gilkes, R J 2001, *Comparison of sources of phosphorus for pasture production on phosphorus leaching soils of Western Australia*, Department of Agriculture, South Perth, Bulletin 4524.

Bolland, M D A 1993, *Evaluation of coastal superphosphate, Ecophos and North Carolina rock phosphate compared with superphosphate*, Division of Plant Industries, Department of Agriculture, South Perth, Technical Report 59.

Bolland, M D A & Allen, D G 2003, 'Phosphorus sorption by sandy soils from Western Australia: effect of previously sorbed P on P buffer capacity and single-point P sorption indices', *Australian Journal of Soil Research,* vol. 41, no. 7, pp. 1360-1388.

Bolland, M D A, Allen, D G & Barrow, N J 2003, *Sorption of phosphorus by soils: how it is measured in Western Australia*, Department of Agriculture, South Perth, Bulletin 4591.

Bolland, M D A, Baker, M J, Allen, D G & Gilkes, R J 1987, *Effectiveness of phosphatic fertilisers and an evaluation of three soil tests for phosphate in Western Australia*, Department of Agriculture, South Perth, Technical Bulletin 10.

Bolland, M D A, Gilkes, R J & Allen, D G 1988, 'The residual value of superphosphate and rock phosphates for lateritic soils and its evaluation using three soil phosphate tests', *Fertilizer Research,* vol. 15, pp. 253-280.

Bonnin, C 2000, 'CEN TC 308: sludge characterization - a way to promote and preserve sludge disposal routes', In *Sludge Management Newsletter: International Water Association specialist group on sludge management*, pp. 6-8.

Bowden, B 1997, *Better phosphorus recommendations for lupins, final report prepared for the Grains Research and Development Corporation*, Agriculture Western Australia, South Perth, Report DAW 352 WR.

Bowden, J W, Shedley, C & Burgess, S J 1993, *Soil test and phosphorus rate*, Department of Agriculture, South Perth, Technote 5/93.

Brady, N C 1990, *The nature and properties of soil,* 10th edn, Macmillan, New York.

Brandt, R C, Elliott, H A & O'Connor, G A 2002, 'Comparative evaluation of water extractable phosphorus in biosolids and livestock manures', in *Proceedings of the 16th annual residuals and biosolids management conference, CD-Rom*, ed. Water Environment Federation, WEF, Austin, Texas, 3-6 March 2002.

Brandt, R C, Elliott, H A & O'Connor, G A 2004, 'Water-extractable phosphorus in biosolids: implications for land based recycling', *Water Environment Research,* vol. 76, no. 2, pp. 121-129.

Bridle, T 2001, 'Other thermal processes', in L. Spinosa & P. A. Vesilind, (eds.), *Sludge into biosolids; processing, disposal and utilisation*, IWA Publishing, London, pp. 130-146.

Broadbent, F E 1977, 'Cycling of nitrogen in 'Recycling of carbon and nitrogen through land disposal of various wastes'', in H. A. Elliott & F. J. Stevensen, (eds.), *Organic wastes and waste waters*, Soil Science Society of America, American Society of Agronomy, Crop Science Society of America, Madison, Wis., pp. 181-193.

Bromfield, S M 1961, 'Sheep faeces in relation to the phosphorus cycle under pastures', *Australian Journal of Agricultural Research,* vol. 12, pp. 111-123.

Bruce, A M, Campbell, H W & Balmer, P 1984, 'Developments and trends in sludge processing techniques', in P. L'Hermite & H. Ott, (eds.), *Processing and use of sewage sludge: proceedings of the third international symposium held at Brighton, 27-30 September 1983*, D. Reidel Publishing Co., Dordrecht, Holland.

Burke, T A 2002, *NAS Biosolids panel chair clarifies findings of biosolids applied to land: advancing standards and practices report*, Available: [webmaster@biosolids.policy.net] (9 September 2002).

Burton, E D, Hawker, D W & Redding, M R 2003, 'Estimating sludge loadings to land based on trace metal sorption in soil: effect of dissolved organo-metallic complexes', *Water Research,* vol. 37, no. 6, pp. 1394-1400.

Cameron, K C, Di, H J & McLaren, R G 1997, 'Is soil an appropriate dumping ground for our wastes?' *Australian Journal of Soil Research,* vol. 35, no. 5, pp. 995-1035.

Campbell, D J & Beckett, P H T 1988, 'The soil solution in a soil treated with digested sewage sludge', *Journal of Soil Science,* vol. 39, pp. 283-298.

Catroux, G, L'Hermite, P & Suess, E (eds.) 1983, *The influence of sewage sludge application on physical and biological properties of soils*, D. Reidel Publishing Co., Dordrecht, Holland.

CCWA 2000, *Methods manual*, Natural Resources Chemistry Laboratory, Land Resources Section, Chemistry Centre of Western Australia (CCWA), Perth, Issue 1.

Chaney, R L 1994, 'Trace metal movement: soil-plant systems and bioavailability of biosolids-applied metals', in C. E. Clapp, W. E. Larson & R. H. Dowdy, (eds.), *Sewage sludge: land utilization and the environment*, American Society of Agronomy, Crop Science Society of America, Soil Science Society of America, Madison, Wis.

Chang, A C, Page, A L, Sutherland, F H & Grgurevic, E 1983, 'Fractionation of phosphorus in sludge-affected soils', *Journal of Environmental Quality,* vol. 12, no. 2, pp. 286-290.

Chang, S C & Jackson, M L 1957, 'Fractionation of soil phosphorus', *Soil Science,* vol. 84, pp. 133-144.

Christen, C 2002, 'Dioxins in biosolids: to regulate or not?' In *Water Environment and Technology*, vol. September 2002, pp. 22-26.

Clements, J, Rajendram, W, Reid, H & Hill, C 2002, 'Sustainable use of biosolids and other organic wastes', in *Proceedings of Enviro 2002 Convention and Exhibition and IWA 3rd World Water Congress, CD-Rom*, IWA, Melbourne, 7-12 April 2002.

Colwell, J D 1963, 'The estimation of the phosphorus fertilizer requirements of wheat in southern New South Wales by soil analysis', *Australian Journal of Experimental Agriculture and Animal Husbandry,* vol. 3, no. August, pp. 190-197.

Cooke, C M, Gove, L, Nicholson, F A, Cook, H F & Beck, A J 2001, 'Effect of drying and composting biosolids on the movement of nitrate and phosphorus through repacked soil columns under steady-state hydrological conditions', *Chemosphere,* vol. 44, no. 4, pp. 797-804. Retrieved: 1 August 2001, from Science Direct database.

Cooper, J L 1996, 'The agronomic value of biosolids in cropping systems on acid soils in central New South Wales', in G. J. Osborne, R. L. Parkin, D. L. Michalk & A. M. Grieve, (eds.), *Biosolids research in NSW: proceedings of the biosolids summit, a research conference on the use of biosolids in agriculture and forestry held at the Biological and Chemical Research Institute, Rydalmere June 1995*, NSW Agriculture Organic Waste Recycling Unit, Richmond, pp. 87-94.

Cottenie, A & Kiekens, L 1980, 'Phosphorus analysis in soils', in *Phosphorus in sewage sludge and animal waste slurries*, eds. T. W. G. Hucker & G. Catroux, D. Reidel Publishing Co., Groningen, Netherlands.

Coutinho, J, Arrobas, M & Rodrigues, O 1997, 'Effect of composted sewage sludge amendment on soil nitrogen and phoshorus availability', *Communications in Soil Science and Plant Analysis,* vol. 28, no. 19&20, pp. 1845-1857.

Cox, A, Granato, T, Pietz, R & Tata, P 2002, 'Uptake of Cd and Zn by garden vegetables grown in NuEarth biosolids-amended soil', in Water Environment Federation, (ed.) *Proceedings of the 16th annual residuals and biosolids management conference, CD-Rom*, WEF, Austin, Texas, 3-6 March 2002.

CSBP 1988, *A crop and pasture nutrition guide for farmers*, CSBP and Farmers Ltd, Perth.

D'Antuono, M 2000a, *Report 1 on experiment 1 (Biosolids N x P interaction)*, Agriculture Western Australia, South Perth, 14 June 2000, 6 July 2000, 20-22 August 2000.

D'Antuono, M 2000b, *StatsPrep: preparing data in microsoft Excel for statistical analysis in Genstat*, Agriculture Western Australia, South Perth.

Davis, J, Blair, G J, MacLeod, D & Till, R 2000, 'The fertiliser value of chemically treated biosolids', The University of New England, New South Wales.

de Hann, S 1981, 'Sewage sludge as a phosphate fertiliser', in T. W. G. Hucker & G. Catroux, (eds.), *Phosphorus in sewage sludge and animal waste slurries: proceedings of the EEC Seminar organised jointly by the CEC and the Institute for Soil Fertility, Haren (Gr.) and held at Groningen, Netherlands, 12-13 June 1980*, D. Reidel Publishing Co., Boston, Mass.

Dentel, S K 2001, 'Conditioning, thickening, and dewatering: research update/research needs', *Water Science and Technology issue. Conference* *proceedings: sludge management entering the 3rd Millenium - industrial, combined, water and wastewater residues,* vol. 44, no. 10, pp. 9-18.

Dentel, S K & Mah, J T 2002, 'Chemical treatment effects on phosphorus availability in sludges', in H. H. Hahn, E. Hoffman & H. Odegaard, (eds.), *Chemical Water and Wastewater Treatment VII*, IWA Publishing, London, pp. 339-348.

Dentel, S K, Sims, J T & Mah, J T 2001, 'Nutrient limitations: an update on issues with phosphorus', in *Symposium on innovative processes to produce useful materials and energy from biosolids and animal manure*, eds. USEPA Region V. & Water Environment Federation, WEF, Chicago, p. 12.

Dentel, S K, Sims, J T, Mah, J T, Khadar, Y & Maguire, R O 2000, 'Availability and environmental impact of phosphorus in soils amended with biosolids: effect of wastewater treatment on the forms, solubility, and biological availability of phosphorus in municipal biosolids', in *WEFTEC 2000*, ed. Water Environment Federation, WEF, USA.

DEP 2001, *Interim guidelines for direct land application of biosolids and biosolids products*, Department of Environmental Protection, Perth, Key Stakeholder Review, May 2001.

DEP, WRC & DOH 2002, *Western Australian guidelines for direct land application of biosolids and biosolids products*, Department of Environmental Protection, Waters and Rivers Commission & Department of Health, Perth.

DeSimone, C & Dentel, S K 2003, *The relation of biosolids source and process type to phosphorus availability in biosolids-amended soils*, Department of Civil and Environmental Engineering, University of Delaware.

Dhir, R K, Limbachiya, M C & McCarthy, M J (eds.) 2001, *Recycling and reuse of sewage sludge*, Thomas Telford, Herin Quay, London.

Diggle, A, Bowden, B & Burgess, S 2003, *Select your nitrogen (SYN): a decision tool for quantifying nitrogen availability and crop response in broadacre farming systems*, Department of Agriculture, South Perth, Bulletin 4600.

Dougherty, W 1999, 'P fractionation methods for Glenfield soils', New South Wales Agriculture, Richmond.

Dougherty, W & Lawrie, R 2000, 'Agricultural production and environmental protection: biosolids, sewage ash and other waste products', in *Biosolids Conference*, New South Wales.

Dracup, M & Kirby, E J M 1996, *Lupin development guide*, University of Western Australia, Nedlands.

Dumbrell, I C & McGrath, J F 2002, 'Biosolids produce significant increases in growth and nutrient status in a Western Australian pine plantation without contamination of groundwater', in *Biosolids Specialty Conference I, CD-Rom*, ed. Australian Water Association, Sydney, 19-20 June 2002.

Elliott, H A, O'Connor, G A & Brinton, S 2002, 'Phosphorus leaching from biosolids-amended sandy soils', *Journal of Environmental Quality,* vol. 31, pp. 681-689.

Englande Jr, A J & Reimers, R S 2001, 'Biosolids management - sustainable development status and future direction', *Water Science and Technology issue. Conference proceedings: sludge management entering the 3rd Millenium - industrial, combined, water and wastewater residues,* International Water Association, vol. 44, no. 10, pp. 41-46.

Environment Australia 2002, 'Recycling organics - Australia's sustainable, untapped wealth', In *Envirobusiness update; news from Environment Australia's Environment Protection Divisions, Department of Environment and Heritage*, p. 14.

EPA 1994, *Biosolids recycling: Beneficial technology for a better environment*, United States Environmental Protection Agency, Washington, DC, 4204.

Epstein, E 2002, *Land application of sewage sludge and biosolids*, Lewis Publishers, Boca Raton, Fla.

Evans, T 2001, 'The journey to sustainable treatment and use or disposal of wastewater solids', in R. K. Dhir, M. C. Limbachiya & M. J. McCarthy, (eds.), *Recycling and reuse of sewage sludge*, Thomas Telford, Heron Quay, London, pp. 1-18.

Finney, I & Rawlinson, L 1990, 'Sludge and wastewater re-use', in *The agricultural and horticultural use of sewage sludge*, eds. D. Elmes & J. Mallen-Cooper, New South Wales Branch of the Australian Institute of Agricultural Science, University of Western Sydney, Hawkesbury Campus.

Folle, F, Shuford, J W, Taylor, R W, Mehadi, A A & Tadesse, W 1995, 'Effect of sludge treatment, heavy metals, phosphate rate, and pH on soil phosphorus', *Communications in Soil Science and Plant Analysis,* vol. 26, no. 9&10, pp. 1369-1381.

Foth, H D & Ellis, B G 1988, *Soil fertility*, John Wiley & Sons, New York.

Franco-Hernandez, O 2003, 'Dynamics of carbon, nitrogen and phosphorus in soil amended with irradiated, pasteurised and limed biosolids', *Bioresource Technology,* vol. 87, no. 1, pp. 93-102.

Frost, H L & Ketchum Jr., L H 2000, 'Trace metal concentration in durum wheat from application of sewage sludge and commercial fertiliser', *Advances in Environmental Research,* vol. 4, no. 4, pp. 347-355.

Fulton, I & Lantzke, N 1993, *Soils of the Northam advisory district: vol. 3 - the Darling Range and West Kokeby zones*, Department of Agriculture, South Perth, Bulletin 4257.

Furrer, O J, Gupta, S K & Stauffer, W 1984, 'Sewage sludge as a source of phosphorus and consequences of phosphorus accumulation in soils', in P. L'Hermite & H. Ott, (eds.), *Processing and use of sewage sludge: proceedings of the third international symposium held at Brighton, September 27-30, 1983*, D. Reidel Publishing Co., Dordrecht, Holland, pp. 279-294.

Gburek, W J, Barberis, E, Haygerth, P M, Kronvang, B & Stamm, C 2005, 'Phosphorus mobility in the landscape', in J. T. Sims & A. Sharpley, (eds.), *Phosphorus: Agriculture and the Environment*, vol. Agronomy Monograph 46, ASA/CSSA/SSSA, Wisconsin, pp. 941-979.

Gerritse, R G 1990, 'Impact of horticultural landuse on water quality in the Darling Range and Coastal Plain of Western Australia', in *Proceedings of horticulture and the environment, Division of Horticulture Seminar, held at Mandurah 7-8 June 1990*, Western Australian Department of Agriculture, South Perth.

Gestring, W D & Jarrell, W M 1982, 'Plant availability of phosphorus and heavy metals in soils amended with chemically treated sewage sludge', *Journal of Environmental Quality,* vol. 11, no. 4, pp. 669-675.

Gibbs, R A, Hu, C J, Ho, G E, Philips, P A & Unkovich, I 1995, 'Die-off of human pathogens in sludge amended soil', in *Proceedings of the Australian Water and Wastewater Association 16th Federal Convention. Vol. 1*, Australian Water and Wastewater Association, pp. 667-674.

Gibbs, R A, Hu, C J, Ho, G E & Unkovich, I 1997, 'Regrowth of faecal coliforms and salmonellae in stored biosolids and soil amended with biosolids', *Water Science and Technology,* vol. 35, no. 11-12, pp. 269-275.

Gibson, T, Whatmuff, M, Michalk, D L & Eamens, G 2002, 'New South Wales Agriculture and Sydney Water's biosolids research program 1993-2000: implications for the NSW biosolids guidelines', in *Biosolids Specialty Conference I*, *CD-Rom*, ed. Australian Water Association, Sydney, 19-20 June 2002.

Gillespie, G 2002, 'Waste management or soil management', in *Proceedings of Enviro 2002 Convention and Exhibition and IWA 3rd World Water Congress, CD-Rom paper e20028b*, IWA, Melbourne, 7-14 April 2002.

Gilmour, J, Wilson, S, Cogger, C G, Jacobs, L, Evanylo, G & Sullivan, D 2000, 'Estimating plant available nitrogen in biosolids: a revision', in Water Environment Federation, (ed.) *Proceedings of the residuals and biosolids management conference*, WEF, Alexandria, VA, pp. 1-13.

Giordiano, P M, Mortvedt, J J & Mays, D A 1975, 'Effect of municipal wastes on crop yields and uptake of heavy metals', *Journal of Environmental Quality,* vol. 4, no. 3, pp. 394-399.

Glendinning, J S (ed.) 1999, *Australian soil fertility manual: Fertilizer Industry Federation of Australia, Inc.*, CSIRO, Collingwood.

Gough, D & Fraser, R 1995, 'Long term planning for biosolids management in Sydney', in L. O. Kolarik & A. J. Priestley, (eds.), *Modern techniques in water and wastewater treatment*, CSIRO, East Melbourne, pp. 177-181.

Gove, L, Cooke, C M, Nicholson, F A & Beck, A J 2001, 'Movement of water and heavy metals (Zn, Cu, Pb and Ni) through sand and sandy loam amended with biosolids under steady-state hydrological conditions', *Bioresource Technology,* vol. 78, no. 2, pp. 171-179.

Gove, L, Nicholson, F A, Cook, H F & Beck, A J 2002, 'Comparison of the effect of surface application and subsurface incorporation of enhanced treated biosolids on the leaching of heavy metals and nutrients through sand and sandy loam soils', *Environmental Technology,* vol. 23, no. 2, pp. 189-198.

Guidi, G & Hall, J E 1984, 'Effects of sewage sludge on the physical and chemical properties of soils', in P. L'Hermite & H. Ott, (eds.), *Processing and use of* *sewage sludge: proceedings of the third international symposium held at Brighton, 27-30 September 1983*, D. Reidel Publishing Co., Dordrecht, Holland, pp. 295-306.

Gunary, D 1968, 'The availability of phosphate in sheep dung', *Journal of Agricultural Science (Cambridge),* vol. 70, pp. 33-38.

Gupta, A P, Narwal, R P & Antil, R S 1989, 'Effect of different levels of nitrogen and sewage sludge on wheat', *Journal of the Indian Society of Soil Science,* vol. 37, pp. 576-578.

Gupta, A P, Narwal, R P & Antil, R S 1993, 'Effect of different levels of phosphorus and sewage sludge on wheat', *Journal of the Indian Society of Soil Science,* vol. 41, no. 2, pp. 304-307.

Hadeed, S 2002, *Addressing concerns with land application of biosolids-part 5 & 6 in a continuing series, editors column* (Sent 9 February 2002 4:57, webmaster@biosolids.policy.net).

Hall, J E 1984, 'Predicting the nitrogen value of sewage sludges', in P. L'Hermite & H. Ott, (eds.), *Processing and use of sewage sludge: proceedings of the third international symposium held at Brighton, 27-30 September 1983*, D. Reidel Publishing Co., Dordrecht, Holland, pp. 268-277.

Hani, H, Gupta, S K & Furrer, O J 1981, 'Availability of phosphorus fractions in sewage sludge', in T. W. G. Hucker & G. Catroux, (eds.), *Phosphorus in sewage sludge and animal waste slurries: proceedings of the EEC Seminar organised jointly by the CEC and the Institute for Soil Fertility, Haren (Gr.) and held at Groningen, Netherlands, 12-13 June 1980*, D. Reidel Publishing Co., Boston, Mass.

Hardie, A & Hird, C 1998, *Landform and soil requirements for biosolids and effluent reuse*, New South Wales Agriculture, Richmond, NSW, Advisory Bulletin 14.

Havilah, E G & Osborne, G J 1992, 'Phosphorus', in *Review of published literature on the land application of sewage sludge - an internal document for the Sydney Water Corporation*, New South Wales Agriculture, Richmond, NSW, pp. 231-250.

Havilah, E J & Davis, J M 1998, *Biosolids as nitrogen and phosphorus fertiliser in coastal New South Wales: part 2 - phosphorus*, New South Wales Agriculture, Richmond.

Havilah, E J, Davis, J M, Rawlinson, L V & Osborne, G J 1996, *Sewage products as nitrogen and phosphorus fertilisers in coastal New South Wales: part 1 - nitrogen*, NSW Agriculture Organic Waste Recycling Unit, Richmond, Project 2, Final report.

Heckrath, G, Brookes, P C, Poulton, P R & Goulding, K W T 1995, 'Phosphorus leaching from soils containing different phosphorus concentrations in the Broadbalk Experiment', *Journal of Environmental Quality,* vol. 24, pp. 770-775.

Hedley, M J & McLaughlin, M J 2004, 'Reactions of phosphate fertilisers and by-products in soils', in M. J. Hedley & M. J. McLaughlin, (eds.), *Phosphorus in Agriculture*, American Society of Agronomy & Soil Science Society of America, Madison, Wis., p. 76.

Hedley, M J, Stewart, J W B & Chauhan, B S 1982, 'Changes in inorganic and organic soil phosphorus fractions induced by cultivation practices and by laboratory incubations', *Journal of Soil Science Society of America,* vol. 46, pp. 970-976.

Henze, M, Aspregren, H, la Cour Jansen, J, Nielsen, P H & Lee, N 2002, 'Effect of solids retention time and wastewater characteristics on biological phosphorus removal', *Water Science and Technology,* vol. 45, no. 6, pp. 137-144.

Hicks, R W & Hird, C 2000, 'Soils and urban land use', in P. E. V. Charman & B. W. Murphy, (eds.), *Soils: their properties and management*, 2nd edn, Oxford University Press, pp. 386-389.

Hinesly, T D, Jones, R L, Tyler, J J & Ziegler, E L 1976, 'Soybean yield responses and assimilation of Zn and Cd from sewage-amended soil', *Journal Water Pollution Control Federation,* vol. 48, pp. 2137-2152.

Hird, C 1998, 'Land suitability assessment for applying liquid and solid wastes to soil', In *Australian Collaborative Land Evaluation Program*, vol. 7, Issue 2, pp. 14-16.

Hird, C & Bamforth, I 1996, 'Selection of sites suitable for application of biosolids products', in G. J. Osborne, R. L. Parkin, D. L. Michalk & A. M. Grieve, (eds.), *Biosolids research in New South Wales: proceedings of the biosolids summit, a research conference on the use of biosolids in agriculture and* *forestry held at the Biological and Chemical Research Institute, Rydalmere June 1995*, NSW Agriculture Organic Waste Recycling Unit, Richmond.

Hogan, F, McHugh, M & Morton, S 2001, 'Phosphorus availability for beneficial use in biosolids products', *Environmental Technology,* vol. 22, no. 11, pp. 1347-53.

Holbrook, R F, Henderson, R C & Allison, R 2002, 'A class-A act', In *Water Environment and Technology, Water Environment Federation, February 2002*, pp. 44-48.

Holford, I C R 1997, 'Soil phosphorus: its measurement, and its uptake by plants', *Australian Journal of Soil Research,* vol. 35, no. 2, pp. 227-239.

Isbell, R F 1996, *The Australian Soil Classification*, CSIRO, Collingwood, Vic.

Jackson, E A 1966, *Phosphorus fertilizer research in Australia*, CSIRO, Melbourne, Bulletin 284.

Jenkins, D, Ferguson, J F & Menar, A B 1971, 'Chemical processes for phosphate removal: review paper', *Water Research,* vol. 5, no. 7, pp. 369-389.

Jenkins, J 1999, *The humanure handbook: a guide to composting human manure*, Jenkins Publishing, Grove City, PA.

Jeyanayagam, S & Husband, J 2002, 'BNR Sludges', In *Water Environment and Technology, Water Environment Federation, October 2002*, pp. 39-45.

Johnston, A E & Poulton, P R 1997, 'Factors affecting critical soil phosphorus values', in H. Tunney, O. T. Carton, P. C. Brookes & A. E. Johnston, (eds.), *Phosphorus loss from soil to water*, CAB International, Oxon, UK, pp. 445-448.

Joshua, W D, Michalk, D L, Curtis, I H, Salt, M & Osborne, G J 1998, 'The potential for contamination of soil and surface waters from sewage sludge (biosolids) in a sheep grazing study, Australia', *Geoderma,* vol. 84, no. 1-3, pp. 135-156.

Kanak, A, Osborne, G & Swinton, E A 1995, 'Beneficial Use of Biosolids in the Sydney region', In *Water magazine*, vol. July/August, pp. 9-12.

Kardos, L T & Hook, J E 1976, 'Phosphorus balance in sewage effluent treated soils', *Journal of Environmental Quality,* vol. 5, pp. 87-90.

Kardos, L T, Scarsbrook, C E & Volk, V V 1977, 'Recycling elements in wastes through soil-plant systems', in American Society of Agronomy, Crop Science Society of America & Soil Science Society of America, (eds.), *Soils for management of organic wastes and waste waters*, ASA, CSSA, SSSA, Madison, Wis., pp. 301-322.

Kelling, K A, Walsh, L M, Keeney, D R, Ryan, J A & Peterson, A E 1977, 'A field study of the agricultural use of sewage sludge: II. Effect on soil N and P', *Journal of Environmental Quality,* vol. 6, no. 4, pp. 345-352.

Khasawneh, F E, Sample, E C & Kamprath, E J (eds.) 1980, *The role of phosphorus in agriculture,* 2nd edn, American Society of Agronomy, Crop Science Society of America, Soil Science Society of America, Madison, Wis.

King, L D & Morris, H D 1973, 'Land disposal of liquid sewage sludge: IV. Effect of soil phosphorus, potassium, calcium, magnesium, and sodium', *Journal of Environmental Quality,* vol. 2, no. 3, pp. 411-414.

King, L D, Rudgers, L A & Webber, L R 1974, 'Application of municipal refuse and liquid sewage sludge to agricultural land: 1. Field study.' *Journal of Environmental Quality,* vol. 4, pp. 361-366.

Kirkham, M B 1982, 'Agricultural use of phosphorus in sewage sludge', *Advances in Agronomy,* vol. 35, pp. 129-163.

Kolarik, L O & Priestley, A J (eds.) 1995, *Modern techniques in water and wastewater treatment*, CSIRO, East Melbourne.

Krogmann, U 2001, 'Composting', in L. Spinosa & P. A. Vesilind, (eds.), *Sludge into biosolids: processing, disposal and utilisation*, IWA Publishing, London, pp. 259-277.

Landers, J 2000, 'Phosphorus research addresssing biosolids runoff concerns', In *Biosolids Technical Bulletin, Water Environment Federation, USA*, vol. 6, pp. 1-5.

Lane, C 1994, 'The N-Viro process for biosolids reuse', Logan City Council, February 1994, Brisbane.

Lantzke, N & Fulton, I 1993, *Land resources of the Northam district*, Department of Agriculture, South Perth, Land Resources Series 11.

Lawrie, R A, Awad, A S & Ross, A D 1990, 'Using sewage sludge as fertiliser', in *The agricultural and horticultural use of sewage products*, eds. D. Elmes & J.

Mallen-Cooper, New South Wales Branch of the Australian Institute of Agricultural Science, Hawkesbury Campus, University of Western Sydney.

Lehane, R 1995, *Effluent-irrigated plantations: design and management*, CSIRO Division of Forestry, Canberra, Technical paper 2.

Leopold, R P 2002, 'Phosphorus assessment tool for Texas', in Water Environment Federation, (ed.) *Proceedings of the 16th annual residuals and biosolids management conference, CD-Rom*, WEF, Austin, Texas, 3-6 March 2002.

Lindo, P V, Taylor, R W, Adriano, D C & Shuford, W 1995, 'Fractionation of residual phosphorus in a highly weathered sludge-treated soil: organic phosphorus', *Communications in Soil Science and Plant Analysis,* vol. 26, no. 15&16, pp. 2639-2653.

Lotzof, M & Eisenacher, K 2002, 'Vermicomposting achieves pathogen stabilisation of biosolids at mesophilic temperatures', in Water Environment Federation, (ed.) *Proceedings of the 16th annual residuals and biosolids mangement conference, CD-Rom*, WEF, Austin, Texas, 3-6 March 2002.

Lu, P & O'Connor, G A 2001, 'Biosolids effects on phosphorus retention and release in some sandy Florida soils', *Journal of Environmental Quality,* vol. 30, no. 3, pp. 1059-1063.

Lue-Hing, C, Matthews, P, Na'mer, J, Okuno, N & Spinosa, L 1997, 'Sludge management in highly urbanised areas', in P. Matthews, (ed.) *A global atlas of wastewater sludge and biosolids use and disposal*, International Association on Water Quality (IAWQ), London, pp. 7-12.

Lund, L J, Page, A L & Nelson, C O 1976, 'Nitrogen and phosphorus levels in soils beneath sewage disposal ponds', *Journal of Environmental Quality,* vol. 5, pp. 26-30.

Maguire, R O, Sims, J T & Coale, F J 2000a, 'Phosphorus fractionation in biosolids-amended soils', *Journal of the Soil Science Society of America,* vol. 64, pp. 2018-2024.

Maguire, R O, Sims, J T & Coale, F J 2000b, 'Phosphorus solubility in biosolids-amended farm soils in the Mid-Atlantic region of the USA', *Journal of Environmental Quality,* vol. 29, no. 4, pp. 1225-1233.

Maguire, R O, Sims, J T, Dentel, S K, Coale, F J & Mah, J T 2001, 'Relationships between biosolids treatment process and soil phosphorus availability', *Journal of Environmental Quality,* vol. 30, no. 3, pp. 1023-1033.

Mason, M 1998, 'Nitrogen', in G. Moore, (ed.) *Soilguide: a handbook for understanding and managing agricultural soils*, Agriculture Western Australia, South Perth, pp. 164-167.

Matthews, P (ed.) 1997, *A global atlas of watewater sludge and biosolids use and disposal*, International Association on Water Quality, London.

Matthews, P 2001, 'Agricultural and other land uses', in L. Spinosa & P. A. Vesilind, (eds.), *Sludge into Biosolids*, IWA Publishing, London, pp. 43-73.

Matthews, P & Lindner, K H 1997, 'European Union', in P. Matthews, (ed.) *A global atlas of wastewater sludge and biosolids use and disposal*, International Association on Water Quality, London, pp. 49-64.

McArthur, W M 1991, 'Reference soils of south-western Australia', in D. A. W. Johnstin & L. J. Snell, (eds.), Department of Agriculture, South Perth, p. 265.

McBride, M B 2003, 'Toxic metals in sewage sludge-amended soils: has promotion of beneficial use discounted the risks?' *Advances in Environmental Research,* vol. 8, no. 1, pp. 5-19.

McCalla, T M, Peterson, J R & Lue-Hing, C 1977, 'Properties of agricultural and municipal wastes', in American Society of Agronomy, Crop Science Society of America & Soil Science Society of America, (eds.), *Soils for management of organic wastes and waste waters*, ASA, CSSA, SSSA, Madison, Wis., pp. 11-41.

McCann, L 1998, *Farmers' attitudes to policies to reduce phosphorus runoff* (18/12/98).

McCoy, J L, Sikora, L J & Weil, R R 1986, 'Plant availability of phosphorus in sewage sludge compost', *Journal of Environmental Quality,* vol. 15, no. 4, pp. 403-409.

McDonald, R C, Isbell, R F, Speight, J G, Walker, J & Hopkins, M S 1990, *Australian soil and land survey: field handbook,* 2nd edn, Inkata Press, Melbourne.

McLaughlin, M 1984, 'Land application of sewage sludge: phosphorus considerations', *South African Journal of Plant and Soil,* vol. 1, pp. 21-29.

McLaughlin, M J 1988, 'A comparison between short-term chemical and biological methods to measure phosphorus availability in sludge-amended sesquioxide soils', *South African Journal of Plant and Soil,* vol. 5, no. 3, pp. 137-141.

McLaughlin, M J, Alston, A M & Martin, F G 1988a, 'Phosphorus cycling in wheat-pasture rotations. II. The role of the microbial biomass in phosphorus cycling', *Australian Journal of Soil Research,* vol. 26, pp. 333-342.

McLaughlin, M J, Alston, A M & Martin, J K 1988b, 'Phosphorus cycling in wheat-pasture rorations. III. Organic phosphorus turnover and phosphorus cycling', *Australian Journal of Soil Research,* vol. 26, pp. 343-353.

McLaughlin, M J, Alston, A M & Martin, J K 1988c, 'Phosphorus cycling in wheat-pasture rotations. I. The source of phosphorus taken up by wheat', *Australian Journal of Soil Research,* vol. 26, pp. 323-31.

McLaughlin, M J & Champion, L 1987, 'Sewage sludge as a phosphorus amendment for sesquioxide soils', *Soil Science,* vol. 143, no. 2, pp. 113-119.

McLaughlin, M J, Stevens, D P, Barry, G, Bell, M, Whatmuff, M & Warne, M 2002, 'A national research program for beneficial reuse of biosolids and other wastes in agriculture; and scientifically defensible guidelines for metals', in *Biosolids Specialty Conference I, CD-Rom*, ed. Australian Water Association, Sydney, 19-20 June 2002.

McQuaker, N R, Brown, D F & Kluckner, P D 1979, 'Digestion of environmental samples for analysis by inductively coupled plasma-atomic emission spectrometry', *Analytical Chemistry,* vol. 51, pp. 1082-4.

McWaters, V 1999, 'What's happening in NEMP - the National Eutrophication Management Program', In *Rivers for the Future Magazine, Land and Water Resources Research and Development Corporation, Summer, Issue no. 8*, pp. 20-22.

Mead, R, Curnow, R N & Hasted, A M 1993, *Statistical Methods in Agriculture and Experimental Biology,* 2nd. edn.

Merrington, G, Oliver, I, Smernik, R J & McLaughlin, M J 2003, 'The influence of sewage sludge properties on sludge-borne metal availabilty', *Advances in Environmental Research,* vol. 8, pp. 21-36.

Michalk, D L, Curtis, I H, Seaman, J T, Langford, C M, Simpson, P C & Osborne, G J 1995, 'Benefits and risks associated with the application of biosolids to pastures grazed by sheep', in *Biosolids Research in NSW*, eds. G. J. Osborne, R. L. Parkin, D. L. Michalk & A. M. Grieve, NSW Agriculture Organic Waste Recycling Unit, Rydalmere, NSW, pp. 62-84.

Mininni, G 2001, 'Incineration with energy recovery', in L. Spinosa & P. A. Vesilind, (eds.), *Sludge into biosolids: processing, disposal and utilisation*, IWA Publishing, London, pp. 101-129.

Montgomery, M 2002, 'unpublished Masters thesis', University of Maine, USA.

Moore, G 1998, *Soilguide: a handbook for understanding and managing agricultural soils*, Agriculture Western Australia, Perth, Bulletin 4343.

Mulcahy, M J 1973, 'Landform and soils of south-western Australia', *Journal of the Royal Society of Western Australia,* vol. 56, pp. 16-22.

Murphy, J & Riley, J D 1962, 'A modified single solution method for the determination of phosphate in natural waters', *Analytica Chimica Acta,* vol. 27, pp. 31-36.

National Biosolids Partnership 2001, *History of biosolids*, Available: [http://biosolids.policy.net/toolbox/history.vtml] (5 December 2001).

National Research Council 1996, *Use of reclaimed water and sludge in food crop production*, National Academy Press, Washington, D.C.

Nelson, P & Delane, R 1990, *Producing lupins in Western Australia*, Western Australian Department of Agriculture, South Perth, Bulletin 4179.

Northcote, K H 1979, *A factual key for the recognition of Australian soils*, Rellim Technical Publications, Glenside, SA.

NSW EPA 1997, *Environmental Guidelines: use and disposal of biosolids products*, Environmental Protection Authority, New South Wales, Sydney.

O'Connor, G A, Elliott, H A, Graetz, D A, Sarkar, D & Brinton, S 2002, *Characterising forms, solubility, bioavailabilities, and mineralisation rates of phosphorus in biosolids, commercial fertilisers and manures: phase 1*, Water Environment Federation, Alexandria, VA, Report 99-PUM-2T.

O'Connor, G A, Sarkar, D, Brinton, S R, Elliott, H A & Martin, F G 2004, 'Phytoavailability of biosolids phosphorus', *Journal of Environmental Quality,* vol. 33, pp. 703-712.

Okuno, N 2001, 'Production of usable materials', in L. Spinosa & P. A. Vesilind, (eds.), *Sludge into biosolids: processing, disposal and utilisation*, IWA Publishing, London, pp. 147-171.

Oliver, I W, McLaughlin, M J & Merrington, G 2002, 'Temporal trends in biosolids characteristics', in *Biosolids Specialty Conference I, CD-Rom*, ed. Australian Water Association, Sydney, 19-20 June 2002.

Olness, A, Clapp, C E, Liu, R & Palazzo, A J 1998, 'Biosolids and their effects on soil properties', in A. Wallace & R. E. Terry, (eds.), *Handbook of soil conditioners: substances that enhance the physical properties of soil*, Marcel Dekker, New York, pp. 141-165.

Olsen, S R & Barber, S A 1977, 'Effect of waste application on soil phosphorus and potassium', in H. A. Elliott & F. J. Stevensen, (eds.), *Soils for management of organic wastes and waste waters*, ASA, CSSA, SSSA, Madison, Wis., pp. 197-213.

Olsen, S R & Sommers, L E 1982, 'Phosphorus', in A. L. Page, (ed.) *Methods of soil analysis: part 2 - chemical and microbiological properties*, 2nd edn, American Society of Agronomy, Soil Science Society of America, Madison, Wis., pp. 403-430.

Osborne, G, Holford, I C R, Havilah, E G, Bamforth, I S & Cooper, J L 1995a, *The land disposal of chemically treated sewage sludge*, New South Wales Agriculture Organic Waste Recycling Unit, Richmond.

Osborne, G J 1992, 'Nitrogen', in *Review of published literature on the land application of sewage sludge - an internal document for the Sydney Water Corporation*, New South Wales Agriculture, Richmond, pp. 217-229.

Osborne, G J 1995, 'Fertiliser value of biosolids - a review', in *Biosolids summit: a research conference on the use of biosolids in agriculture and forestry*, eds. G. J. Osborne, R. L. Parkin, D. L. Michalk & A. M. Grieve, NSW Agriculture Organic Waste Recycling Unit, Biological and Chemical Research Institute, Rydalmere, pp. 227-236.

Osborne, G J, Parkin, R L, Michalk, D L & Grieve, A M (eds.) 1995b, *Biosolids research in New South Wales: proceedings of the biosolids summit, a research conference on the use of biosolids in agriculture and forestry held at the Biological and Chemical Research Institute, Rydalmere June 1995*, NSW Agriculture Organic Waste Recycling Unit, Richmond.

Osborne, L 2000, 'Nutrients for biosolids experiment, email 29 February 2000', The University of Western Australia, Nedlands.

Otabbong, E, Persson, J, Iakimenko, O & Sadovnikova, L 1997, 'The Ultuna long-term organic matter experiment: II. Phosphorus status and distribution in soils', *Plant and Soil,* vol. 195, no. 1, pp. 17-23.

Page, A L, Lue-Hing, C & Chang, A C 1986, 'Introduction and general objectives: utilisation, treatment, and disposal of waste on land', in Soil Science Society of America, (ed.) *Utilisation, treatment, and disposal of waste on land*, vol. 3rd printing 1990, Soil Science Society of America, Madison, Wis., pp. 1-12.

Parker, T & Grant, C 2001, 'Biosolids and coal mine rehabilitation', In *Natural Resource Management, AANRM, Canberra,* vol. 4, pp. 29-34.

Pastene, A J 1981, *Factors affecting the crop availability of phosphorus in sewage-sludge-amended soils*, M.Science (Soil Science) Thesis, University of Wisconsin.

Penney, N 1999, *Review of environmental factors: biosolids land application - Annadale Farm, Gillingarra*, Water Corporation of Western Australia, Leederville, Appendix 1: based on Occasional paper WTC No 1/95.

Penney, N 2000, 'Beenyup WWTP: contaminant and nutrient concentrations', Water Corporation of Western Australia.

Penney, N & Dadour, I 2002, 'Biosolids and flies', in *Biosolids Specialty Conference I, CD-Rom*, ed. Australian Water Association, Sydney, 19-20 June 2002.

Penney, N, Dumbrell, I & Pritchard, D 2003, 'Biosolids: wanted not wasted', in *Proceedings of the fourth international conference of ORBIT, Association on biological processing of organics: advances for a sustainable society,* ed. Organic recovery & biological treatment (ORBIT), Perth, 30 April-2 May 2003.

Pescod, M B 1991, *Urban solid waste management,* 1991-1993 edn, World Health Organisation Office for Europe by IRIS, Copenhagen.

Peterson, J R, McCalla, T M & Smith, G E 1971, 'Human and animal wastes as fertilizers', in R. A. Olson, T. J. Army, J. J. Hanway & V. J. Kilmer, (eds.), *Fertilizer technology & use*, Soil Science Society of America, Madison, Wis., pp. 557-596.

Phillips, A B & Webb, J R 1971, 'Production, marketing and use of phosphorus fertilizers', in R. A. Olson, T. J. Army, J. J. Hanway & V. J. Kilmer, (eds.), *Fertilizer technology & use*, Soil Science Society of America, Madison, Wis., pp. 271-301.

Pierzynski, G M 1994, 'Plant nutrient aspects of sewage sludge', in C. E. Clapp, W. E. Larson & R. H. Dowdy, (eds.), *Sewage sludge: land utilization and the environment*, American Society of Agronomy, Crop Science Society of America, Soil Science Society of America, Madison, Wis., pp. 21-25.

Pierzynski, G M, Sims, J T & Vance, G F 1994, 'Soil phosphorus and environmental quality', in G. M. Pierzynski, J. T. Sims & G. F. Vance, (eds.), *Soils and environmental quality*, Lewis Publishers, CRC Press, Inc, Boca Raton, Florida, USA.

Pietz, R, Johnson, R, Sustich, R, Granato, T A, Tata, P & Lue-Hing, C 1998, *Biosolids - reaping the benefits of pre-treatment: a 1996 sewage sludge survey*, Association of Metropolitan Sewage Agencies Members.

Pomares, F, Roca, J, Tarazona, F & Estela, M 1984, 'Aerobically digested sewage sludge as N and P fertiliser', in P. L'Hermite & H. Ott, (eds.), *Processing and use of sewage sludge: proceedings of the third international symposium held at Brighton, 27-30 September 1983*, D. Reidel Publishing Co., Dordrecht, Holland, pp. 313-315.

Pommel, B 1981, 'Phosphorus value of sludges related to their metal content', in T. W. G. Hucker & G. Catroux, (eds.), *Phosphorus in sewage sludge and animal waste slurries: proceedings of the EEC Seminar organised jointly by the CEC and the Institute for Soil Fertility, Haren (Gr.) and held at Groningen, Netherlands, 12-13 June 1980*, D. Reidel Publishing Co., Boston, Mass., pp. 137-147.

Prasad, R 1996, 'Effect of phosphate and sewage sludge on wheat and fertility of Calciorthent', *Journal of the Indian Society of Soil Science,* vol. 44, no. 3, pp. 536-538.

Priestley, M & Pritchard, D 1998, 'Biosolids: benefits and concerns in the environment', in *Understanding your environment conference, held at Murdoch University, 1-3 May 1998*, ed. The Australian Association for Environmental Education, unpublished, Western Australia.

Priestley, M H 1998, *The effect of biosolids application on wheat establishment, growth and yield*, Honours thesis, Muresk Institute of Agriculture, Curtin University of Technology, Northam.

Pritchard, D & Collins, D 2005, *The national biosolids research program: research studies on the impact of heavy metals on sustainable fertilisation and intensive agricultural applications of biosolids*, Curtin University of Technology, Muresk Institute, Northam, Progress report to Water Corporation of Western Australia, Contract XX-03-11200, July 2005.

Pritchard, D L 1998, *Are you interested in the future of biosolids research in Western Australia?*, Curtin University of Technology, Bentley.

Pritchard, D L, Martin, L D, Bowden, J W & Penney, N 2002, 'Biosolids down-under: effect of soil incorporation on phosphorus availability', in *Proceedings of the 16th annual residuals and biosolids management conference, CD-Rom*, ed. Water Environment Federation, WEF, Austin, Texas, 3-6 March 2002.

Pritchard, D L & Penney, N 2003, 'Validation of biosolids land application guidelines in Western Australia through innovative research', in *'Innovations in Water' Ozwater Convention and Exhibition Conference, CD-Rom*, ed. Australian Water Association, Perth, 6-10 April 2003.

Rampton, S 1998, *Let them eat nutri-cake: Merriam-Webster thinks our 'biosolids' don't stink - how the word became a dictionary term*, Available: [http://www.findarticles.com/cf_dls/m1111/n1782_v1782_v297/21281405?p1/article.jhtml] (20 May 2002).

Raper, W G C 1995, 'An overview of all-biological removal of N and P from sewage', in L. O. Kolarik & A. J. Priestley, (eds.), *Modern techniques in water and waterwater treatment*, CSIRO, East Melbourne, pp. 99-102.

Rawlinson, L 1992, 'The use of sludge in land rehabilitation', In *Rehabilitate Victoria, La Trobe Valley magazine, 14-15 November*, pp. 97-99.

Rawlinson, L V 1996a, *Biosolids land application trials in agriculture and pine plantations for the Water Corporation of Western Australia*, L.V. Rawlinson and Associates, Berry, NSW, Proposal, July 1996.

Rawlinson, L V 1996b, *Proposal to conduct biosolids land application trial in agriculture and forestry for Western Australian Water Corporation*, L.V. Rawlinson and Associates, Berry, NSW, Project 96/0013.

Rawlinson, L V 1997, *Biosolids land application trial at Muresk Institute of Agriculture (Northam) for the Water Corporation of Western Australia*, L.V. Rawlinson & Associates Pty Ltd, Berry, NSW.

Rawlinson, L V & Salt, M 1997, *Review of environmental factors for trial application of biosolids to agricultural land*, L.V. Rawlinson and Associates and Water Corporation of Western Australia (John Tonkin Water Centre), Leederville.

Rayment, G E & Higginson, F R 1992a, *Australian laboratory handbook of soil and water chemical methods*, Inkata Press, Melbourne.

Rayment, G E & Higginson, F R 1992b, 'Electrical conductivity', in *Australian laboratory handbook of soil and water chemical methods*, Inkata Press, Melbourne, pp. 15-16.

Rayment, G E & Higginson, F R 1992c, 'Extractable iron, aluminium and silicon, section 13A1', in *Australian laboratory handbook of soil and water chemical methods*, Inkata Press, Melbourne.

Rayment, G E & Higginson, F R 1992d, 'Extractable potassium, section 18A1', in *Australian laboratory handbook of soil and water chemical methods*, Inkata Press, Melbourne, pp. 203-204.

Rayment, G E & Higginson, F R 1992e, 'Ion-exchange properties, section 15A2', in *Australian laboratory handbook of soil and water chemical methods*, Inkata Press, Melbourne, NSW, p. 144.

Rayment, G E & Higginson, F R 1992f, 'Nitrogen, sections 7C2 & 7A2', in *Australian laboratory handbook of soil and water chemical methods*, Inkata Press, Melbourne, pp. 41-42, 53-57.

Rayment, G E & Higginson, F R 1992g, 'Organic carbon, section 6A1', in *Australian laboratory handbook of soil and water chemical methods*, Inkata Press, Melbourne, pp. 29-30.

Rayment, G E & Higginson, F R 1992h, 'Phosphorus, section 9B1', in *Australian laboratory handbook of soil and water chemical methods*, Inkata Press, Melbourne, pp. 66-67.

Rayment, G E & Higginson, F R 1992i, 'Soil pH, section 4A1, 4B1 and 4B2', in *Australian laboratory handbook of soil and water chemical methods*, Inkata Press, Melbourne.

Reid, H 2002, 'Biosolids to land: international regulations - part 1: contaminants', *Water, Journal of Australian Water Association,* vol. 29, no. 8, pp. 40-46.

Reuter, D J & Robinson, J B (eds.) 1997, *Plant analysis: an interpretation manual,* 2nd edn, CSIRO Publishing, Collingwood, Vic.

Robson, A D & Gilkes, R J 1980, *Fertilizer responses (N, P, K, S and micronutrients) on lateritic soils in south-western Australia - a review*, Oxford and IBM Publishing Co., Oxford, England.

Rosewell, C J 1997, *Potential sources of sediments and nutrients: sheet and rill erosion and phosphorus sources*, Department of the Environment, Sport and Territories, Canberra.

Rudd, C L & Barrow, N J 1973, 'The effectiveness of several methods of applying superphosphate on yield response by wheat', *Australian Journal of Experimental Agriculture and Animal Husbandry,* vol. 13, no. August, pp. 430-433.

Ryan, J A & Keeney, D R 1975, 'Ammonia volatilisation from surface-applied wastewater sludge', *Journal Water Pollution Control Federation,* vol. 47, pp. 386-393.

Rydin, E & Ottabong, E 1997, 'Potential release of phosphorus from soil mixed with sewage sludge', *Journal of Environmental Quality,* vol. 26, no. 2, pp. 529-534.

Sakadevan, K & Bavor, J 2002, 'Phosphorus availability in soils receiving different types of biosolids', in *Proceedings of Enviro 2002 Convention and Exhibition and IWA 3rd World Water Congress, CD-Rom*, IWA, Melbourne, 7-14 April 2002.

Salt, M, Hird, C & Bamforth, I 1996, 'Assessment of biosolids application rates, degrees of incorporation and movement of mineral nitrogen in biosolids-treated plots', in G. J. Osborne, R. L. Parkin, D. L. Michalk & A. M. Grieve, (eds.), *Biosolids research in New South Wales: proceedings of the biosolids summit, a research conference on the use of biosolids in agriculture and forestry held at the Biological and Chemical Research Institute, Rydalmere June 1995*, NSW Agriculture Organic Waste Recycling Unit, Richmond, pp. 18-27.

Sanyal, S K & De Datta, S K 1991, 'Chemistry of phosphorus transformations in soil', in B. A. Stewart, (ed.) *Advances in soil science*, vol. vol.16, Springer-Verlag, New York, pp. 1-120.

Sawhney, B L & Hill, D E 1975, 'Phosphate sorption characteristics of soils treated with domestic waste water', *Journal of Environmental Quality,* vol. 4, pp. 342-346.

Schmidt, A T 1997, 'Biosolids from ANM's Albury Mill diverted from landfill in breakthrough spreading scheme', In *Waste Disposal and Water Management in Australia*, pp. 15-19.

Scott, D S & Horlings, H 1975, 'Removal of phosphates and metals from sewage sludges', *Environmental Science Technology,* vol. 9, pp. 849-855.

Searle, P L 1984, 'The Berthelot or indophenol reaction and its use in the analytical chemistry of nitrogen - a review', *Analyst,* vol. 109, pp. 549-68.

Seyhan, D & Erdincler, A 2003, 'Effect of lime stabilisation of enhanced biological phosphorus removal sludges on the phosphorus availability to plants', *Water Science and Technology,* vol. 48, no. 1, pp. 155-162.

Sharpley, A & Beegle, D 1999, *Managing phosphorus for agriculture and the environment*, The Pennsylvania State University, College of Agricultural Sciences, Cooperative Extension.

Sharpley, A & Moyer, B 2000, 'Phosphorus forms in manure and compost and their release during simulated rainfall', *Journal of Environmental Quality,* vol. 29, no. 5, pp. 1462-1469.

Sharpley, A N 1986, 'Disposition of fertiliser P applied to winter wheat', *Journal of Soil Science Society of America,* vol. 50, pp. 953-8.

Sibbesen, E & Sharpley, A N 1997, 'Setting and justifying upper critical limits for phosphorus in soils', in H. Tunney, O. T. Carton, P. C. Brookes & A. E. Johnston, (eds.), *Phosphorus loss from soils to water*, CAB International, USA, pp. 151-175.

Siddique, M T, Robinson, J S & Alloway, B J 2000, 'Phosphorus reactions and leaching potential in soils amended with sewage sludge', *Journal of Environmental Quality,* vol. 29, no. 6, pp. 1931-1938.

Sims, J T 1998, 'Phosphorus soil testing: innovations for water quality protection', *Communications in Soil Science and Plant Analysis,* vol. 29, no. 11-14, pp. 1471-1489.

Smith, A N 1967, 'Late applications of superphosphate to wheat are ineffective', *Agriculture Gazette of New South Wales,* vol. 78, pp. 539-542.

Smith, K A & Scott, A 1991, 'Continuous-flow, flow injection, and discrete analysis', in K. A. Smith, (ed.) *Soil analysis: modern instrumental techniques*, 2nd edn, Marcel Dekker, New York, p. 659.

Smith, S J, Schepers, J S & Porter, L K 1990, 'Assessing and managing agricultural nitrogen losses to the environment', *Advances in Soil Science,* vol. 14, pp. 2-43.

Smith, S R 2001, 'The scientific basis to recycling sewage sludge in agriculture', in R. K. Dhir, M. C. Limbachiya & M. J. McCarthy, (eds.), *Recycling and reuse of sewage sludge*, Thomas Telford Publishing, Heron Quay, London, pp. 141-158.

Smith, S R, Woods, V & Evans, T D 1998, 'Nitrate dynamics in biosolids-treated soils. I: Influence of biosolids type and soil type', *Bioresource Technology,* vol. 66, no. 2, pp. 139-149.

Smolinski, H & Scholz, G 1997, *Soil assessment of the West Gingin area*, Agriculture Western Australia, South Perth, Land Resources Series 15.

Smollen, M 1997, 'South Africa', in P. Matthews, (ed.) *A global atlas of wastewater sludge and biosolids use and disposal*, IWA Publishing, London, pp. 125-127.

Snowball, K & Robson, A D 1983, *Symptoms of nutrient deficiencies: subterranean clover and wheat*, Department of Soil Science and Plant Nutrition, University of Western Australia, Nedlands.

Sommers, L E 1977, 'Chemical composition of sewage sludges and analysis of their potential uses as fertilizers', *Journal of Environmental Quality,* vol. 6, pp. 225-231.

Sommers, L E & Barbarick, K A 1986, 'Constraints to land application of sewage sludge', in Soil Science Society of America, (ed.) *Utilisation, treatment, and disposal of waste on land*, vol. 3rd printing 1990, SSSA, Madison, Wis., pp. 193-216.

Sommers, L E, Nelson, D W, Yahner, J E & Mannering, J V 1972, 'Chemical composition of sewage sludge from selected Indiana cities', *Indiana Academy of Science,* vol. 82, pp. 424-432.

Sommers, L E, Nelson, D W & Yost, K J 1976, 'Variable nature of chemical composition of sewage sludges', *Journal of Environmental Quality,* vol. 5, no. 3, pp. 303-306.

Sommers, L E & Sutton, A L 1980, 'Use of waste materials as sources of phosphorus', in F. E. Khasawneh, E. C. Sample & E. J. Kamprath, (eds.), *The role of phosphorus in agriculture*, American Society of Agronomy, Crop Science Society of America, Soil Science Society of America, Madison, Wis., pp. 515-544.

Soon, Y K, Bates, T E & Moyer, J R 1978, 'Land application of chemically treated sewage sludge: II - effects on plant and soil phosphorus, potassium, calcium and magnesium and soil pH.' *Journal of Environmental Quality,* vol. 7, no. 2, pp. 269-273.

Sort, X & Alcaniz, J M 2001, 'Application of x-ray microanalysis to study the distribution of organic wastes in soil', *Geoderma,* vol. 104, no. 1-2, pp. 1-15.

Spedding, M 2002, 'Twelve years in the Australian waste management industry: a personal view', in *Proceedings of Enviro 2002 Convention and Exhibition and IWA 3rd World Water Congress, CD-Rom paper e20002b*, IWA, Melbourne, 7-14 April 2002.

Spellman, F R 1997, *Dewatering biosolids*, Technomic Publishing, Pennsylvania.

Spicer, S 2002, 'Fertilisers, manures or biosolids?' In *Water Environment and Technology, Water Environment Federation, July 2002*, pp. 32-35.

Spinosa, L 2001, 'Evolution of sewage sludge regulations in Europe', *Water Science and Technology issue. Conference proceedings: sludge management entering the 3rd Millenium - industrial, combined, water and wastewater residues,* vol. 44, no. 10, pp. 1-8.

Spinosa, L & Vesilind, P A (eds.) 2001, *Sludge into biosolids*, IWA Publishing, London.

Stace, H C T, Hubble, G D, Brewer, R, Northcote, K H, Sleeman, J R, Mulchay, M J & Hallsworth, E G 1968, *A handbook of Australian soils*, Rellim Technical Publications, Glenside, Adelaide.

Stenger, A 2000, 'Experimental valuation of food safety application to sewage sludge', *Food Policy*, no. 25, pp. 211-218.

Stevens, D, Kelly, J, Liston, C & Oemcke, D 2002, 'Biosolids management in England and France', *Water, Journal of Australian Water Association*, pp. 56-61.

Stewart, J W B & Sharpley, A N 1987, 'Controls on dynamics of soil and fertilizer phosphorus and sulfur', in R. F. Follett, J. W. B. Stewart & C. V. Cole, (eds.), *Soil Fertility and Organic matter as Critical Components of Production Systems*, vol. SSSA Special Publication 19, Soil Science Society of America, Inc., American Society of Agronomy, Inc.,, Madison, WI, USA, pp. 101-121.

Terman, G L, Soileau, J M & Allen, S E 1973, 'Municipal compost: effects on crop yields and nutrient content in greenhouse pot experiments', *Journal of Environmental Quality,* vol. 2, no. 1, pp. 84-89.

Texas Agricultural Extension Service 2001, *Nutrient management planning certificate 2001*, Texas.

Tiessen, H & Moir, J O 1993, 'Characterisation of available P by sequential extraction', in M. R. Carter, (ed.) *Soil sampling and methods of analysis*, Canadian Society of Soil Science, Lewis Publishers, Canada.

Tingay, A 1997, 'Potential uses of soil amendments in horticulture', Alan Tingay & Associates.

Tomar, M 1999, *Quality assessment of water and wastewater*, Lewis Publishers, Boca Raton, Fla.

Triner, N G, Rudd, T, Smith, S R & Dearley, T 2001, 'Phosphorus and agricultural recycling of sewage sludge', in R. K. Dhir, M. C. Limbachiya & M. J. McCarthy, (eds.), *Recycling and reuse of sewage sludge*, Thomas Telford Publishing, Heron Quay, London, pp. 125-140.

Tunney, H, Carton, O T, Brookes, P C & Johnston, A E (eds.) 1997, *Phosphorus loss from soil to water*, CAB International, Oxon, UK.

United States Environmental Protection Agency 1997, *Land application of biosolids: process design manual*, Technomic Publishing Company, Pennsylvania.

United States Environmental Protection Agency 1999b, *Standard for the use or disposal of sewage sludge: proposed rule*, United States Environmental Protection Agency,, Federal Register 64 (246): 72045-72062.

US EPA 1998, *How wastewater treatment works: the basics*, United States Environmental Protection Agency Office of Water (4204), Washington, DC, EPA 833-F-98-002.

Velthof, G L, van Beusichem, M L, Raijmakers, W M F & Janssen, B H 1998, 'Relationship between availability indices and plant uptake of nitrogen and phosphorus from organic products', *Plant and Soil,* vol. 200, no. 2, pp. 215-226.

Vermitech 2002, *Corporate capability statement*, Vermitech Limited, Darlinghurst, New South Wales, February 2002.

Vesilind, P A & Spinosa, L 2001, 'Productions and regulations', in L. Spinosa & P. A. Vesilind, (eds.), *Sludge into Biosolids*, IWA Publishing, London, pp. 3-19.

von Sothen, F 2001, 'Prognosis about the reuse of sewage sludge for agricultural purposes in Germany', in R. K. Dhir, M. C. Limbachiya & M. J. McCarthy, (eds.), *Recycling and reuse of sewage sludge*, Thomas Telford Publishing, Heron Quay, London, pp. 305-316.

Vose, D 1996, *Quantitative risk analysis: a guide to Monte Carlo simulation modelling*, John Wiley & Sons, Chichester, West Suffolk.

Walkley, A & Black, I 1934, 'An examination of the Degtjareff method for determining soil organic matter and a proposed modification of the chromic acid titration method', *Soil Science,* vol. 37, pp. 29-38.

Walter, I, Martinez, F, Alonso, L, de Gracia, J & Cuevas, G 2002, 'Extractable soil heavy metals following the cessation of biosolids application to agricultural soil', *Environmental Pollution,* vol. 117, no. 2, pp. 315-321.

Water Corporation 1997a, *Biosolids 2040: a long term strategy for the management of Perth's wastewater biosolids*, Water Corporation of Western Australia, Leederville.

Water Corporation 1997b, *Working with nature: biosolids*, Wastewater Treatment Technical Services Section, Water Corporation of Western Australia, Leederville.

Water Corporation 2000, 'Beenyup WWTP: contaminant and nutrient concentrations, electronic database retrieved 20/03/2000 and based on Occasional paper WTC No. 1/95', Water Corporation of Western Australia, Leederville.

Water Pollution Control Federation 1972, *Utilisation of municipal wastewater sludge*, Water Pollution Control Federation: prepared under the direction of the Technical Practice Committee by the Subcommittee on Utilization of Wastewater Sludge, Washington, D.C., No. 2.

Weaver, D & Summers, R 1998, 'Chapter 7.3 Soil factors influencing eutrophication', in G. Moore, (ed.) *Soilguide: a handbook for understanding and managing agricultural soils*, vol. Bulletin 4343, Agriculture Western Australia, South Perth, pp. 243-250.

Weaver, D M, Ritchie, G S P & Gilkes, R J 1992, 'Phosphorus sorption by gravels in lateritic soils', *Australian Journal of Soil Research,* vol. 30, pp. 319-330.

WEF 1994, *Beneficial use programs for biosolids management: a special publication*, Water Environment Federation, Alexandria, VA.

WEF 1995, *Biosolids composting: a special publication*, Task Force on Biosolids Composting, Water Environment Federation, Alexandria, VA.

Wen, G, Bates, T E & Voroney, R P 1995, 'Waste management: evaluation of nitrogen availability in irradiated sewage sludge, sludge compost and manure compost', *Journal of Environmental Quality,* vol. 24, pp. 527-534.

Wen, G, Bates, T E, Voroney, R P, Winter, J P & Schellenbert, M P 1997, 'Comparison of phoshorus availability with application of sewage sludge, sludge compost and manure compost', *Communications in Soil Science and Plant Analysis,* vol. 28, no. 17&18, pp. 1481-1497.

Whatmuff, M S 1995, 'Heavy metal chemistry and plant uptake', in *Biosolids summit: a research conference on the use of biosolids in agriculture and forestry*, eds. G. J. Osborne, R. L. Parkin, D. L. Michalk & A. M. Grieve, NSW Agriculture Organic Waste Recycling Unit, Biological and Chemical Research Institute, Rydalmere, New South Wales, pp. 44-51.

White, R E 1981, 'Pathways of phosphorus in soils', in T. W. G. Hucker & G. Catroux, (eds.), *Phosphorus in sewage sludge and animal waste slurries*, D. Reidel Publishing Co., Boston, Mass., pp. 21-46.

Wild, A 1988, 'Plant nutrients in soil: phosphate', in A. Wild, (ed.) *Russell's soil conditions and plant growth*, 11th edn, Longman Scientific and Technical, Essex, England, pp. 695-742.

WME 2002, *Biobrick breakthrough* (04-09-02).

Womer, J, Elliott, H A & Brandt, R C 2002, 'Determining phosphorus in biosolids: using a neutral ammonium citrate extraction', in *Proceedings of the 16th annual residuals and biosolds management conference, CD-Rom*, ed. Water Environment Federation, WEF, Austin, Texas, 3-6 March 2002.

Wong, J W, Lai, K M, Su, D C, Fang, M & Zhou, L X 2001, 'Effect of applying Hong Kong biosolids and lime on nutrient availability and plant growth in an acidic loamy sand', *Environmental Technology,* vol. 22, no. 12, pp. 1487-95.

Zadoks, J C, Chang, T T & Konzak, C F 1974, 'A decimal code for the growth stages of cereals', *Weed Research,* vol. 14, pp. 415-421.

Zarcinas, B A, Stevens, D P, Lammerhirt, M, McLaughlin, M J, Smart, M K & Nolan, A I 2002, 'Bioavailability of cadmium in biosolids: effect of biosolids and soil type', in *Biosolids specialty conference I, CD-Rom*, ed. Australian Water Association, Sydney, 19-20 June 2002.

9 Appendices

9.1 Minimising the nitrogen x phosphorus interaction in biosolids – preliminary glasshouse experiment

9.1.1 Introduction

In plant nutrition experiments involving increasing rates of biosolids, it has been difficult to isolate the effects of N from that of P due to the cumulative effects of one element with another and resulting interactions (Havilah & Davis 1998). Previous attempts to study the P component in biosolids have included a succession of high N using crops (Havilah & Osborne 1992). This preliminary glasshouse experiment was established to determine the contribution of N to plant growth in biosolids to enable P uptake to be measured without interaction with N.

Nitrogen and phosphorus are the two major plant nutrients supplied in biosolids, providing a useful fertiliser substitute. In general, the N content in biosolids has more commonly been used than the P content to determine land application rates where contaminants (metals) are not an issue. These are referred to as the nitrogen limiting biosolids application rate (NLBAR) and the phosphorus limiting biosolids application rate (PLBAR), respectively (Rawlinson 1996a). Consequently the NLBAR and PLBAR should ensure that environmental problems caused by excess nutrients are avoided (Osborne et al. 1995b).

A large proportion of N applied to soil in biosolids is organic N, which must first be mineralised by microorganisms to inorganic forms such as nitrate and ammonium before being taken up by plants (Coutinho, Arrobas & Rodrigues 1997; Osborne 1995). In addition, a proportion of the ammonium form may be volatilised, depending on the method of soil incorporation (National Research Council 1996; United States Environmental Protection Agency 1997). Similarly, it is often assumed that a large proportion of the P in biosolids is organic, requiring mineralisation prior to plant uptake. Consequently, the concentrations of total N and total P in biosolids do not necessarily indicate the amount of these nutrients immediately available for plant growth. In Western Australia, N mineralisation rates of 20%, N volatilisation rates of 50% and P mineralisation rates of 21% have been commonly used to calculate the NLBAR and PLBAR, respectively, based on current land application guidelines in the initial year of application (Penney 1999).

The aim of this study was to establish an N X P response surface using inorganic fertiliser on a nutrient responsive soil. The dry matter production of wheat shoots and uptake of N and P following the application of biosolids was compared with inorganic N and P combinations. The hypothesis to be tested was that 20% of the total N and 21% of the total P in biosolids were available for plant growth, being approximately the value calculated for biosolids land application rates within Western Australia over the first growing season. The results of this study were used to determine the N rates in subsequent glasshouse experiments.

9.1.2 Materials and methods

9.1.2.1 Treatments and trial design

The experiment consisted of a total of 60 treatment combinations and two replicates arranged in a completely randomised design. There were six rates of N (0, 10, 20, 40, 80 and 160 mg N/kg), five rates of P (0, 10, 20, 40 and 80 mg P/kg) and three rates of biosolids (5, 10 and 15 dry g/kg) set out as three x two-way interactions (at the zero level of the other factor).

This included 30 treatments of a N x P matrix with no added biosolids to plot a nutrient response curve, 18 treatments to examine three rates of biosolids at six rates of N, with no added P and 15 treatments to examine three rates of biosolids at five rates of P with no added N.

9.1.2.2 Biosolids

Biosolids were sourced from Beenyup WWTP on 14 March 2000, with full details given in sections 1.2 and 3.2.4. The three rates of biosolids applied (5, 10 and 15 dry g/kg) were equivalent to agricultural land application rates of approximately 6, 12 & 18 t DS/ha.

The expected proportions of available N and P applied at these loadings were estimated using projected averages for these nutrients from Beenyup (Table 9.1), with mineralisation and volatilisation estimates provided by the Water Corporation (2000). The proportion of plant available N (PAN) was calculated at 13,164 mg N/kg (Table 9.2), equivalent to 66, 132 & 198 mg N/kg at the rates of biosolids applied. The expected amount of available P was calculated at 5,460 mg P/kg (Table 9.2). This was expected to be equivalent to 27, 55 & 82 mg P/kg from biosolids at the three rates applied.

Table 9.1 Contaminant and nutrient concentrations for Beenyup WWTP biosolids over four sampling dates for the 1999-2000 period

Sample Date	07/09/99	05/10/99	02/11/99	04/01/00	Mean	SD
Parameter						
Total solids (%)	16.8	16.5	16.6	13.7	**16.4**	0.9
pH (1:5)	7.0	7.3	7.1	7.9	**7.3**	0.3
Nitrogen and phosphorus concentrations (mg/kg)						
TKN	51,000	50,000	49,000	61,000	**52,750**	5,560
Nitrate	140	5.0	5.0	5.0	**38.7**	67.5
Nitrite	120	2.0	2.0	2.0	**31.5**	59.0
Ammonium	9,200	7,500	4,400	1,300	**8,525**	3,585
Total P	22,000	29,000	26,000	16,000	**23,250**	5,620
Contaminant concentrations (mg/kg)						
Arsenic	3.7	4.5	2.1	3.0	**3.2**	0.3
Cadmium	1.1	1.2	1.3	1.3	**1.0**	0.1
Chromium	49	60	51	48	**51**	6.6
Copper	1,100	1,200	1,300	1,700	**1,219**	191
Lead	47	60	44	47	**45**	5.1
Mercury	1.1	1.9	1.8	1.5	**1.8**	0.3
Molybdenum	7	6	6	9	**6.5**	1.0
Nickel	18	22	21	20	**20**	2.2
Selenium	5.5	5.9	5.6	3.0	**4.9**	1.0
Zinc	650	550	540	620	**558**	65

Values extracted from Occasional paper WTC No 1/95. Sampling carried out by Australian Environmental Laboratories (AEL) with all values in mg/kg expressed as a dry weight basis.

Biosolids were applied as wet slurry by shaking and dispersing with an equal volume of deionised water in a 500 mL sealed container to ensure even mixing throughout the soil.

Ammonium nitrate (NH_4NO_3) and monocalcium phosphate (MCP; $Ca(H_2PO_4)_2 H_2O$) were used as the inorganic sources of N and P, respectively. The MCP was weighed and applied dry to pots requiring inorganic P and the soil was mixed thoroughly. The inorganic N treatments were added in solution, with the N split over three applications and applied prior to sowing and at 10 and 20 d.

Table 9.2 Calculations for estimating available N and P from biosolids used in the preliminary experiment

Available N *

= nitrate + nitrite + 50% ammonium + (20% of organic N)

= 39.7 + 31.5 + (50% of 8,525)+ (20% of 44,155)

= 70 + 4262.5 + 8831

= 13,164 mg N/kg

Available P **

= 21% of total P

= 21% of 23,250

= 4,882 mg/kg

Formula as per Water Corporation (2000) and based on projected averages of nutrients from biosolids at Beenyup WWTP (Table 9.1).

*Available N based on 50% ammonium volatilisation and 20% nitrogen mineralisation rate, where organic N is equal to TKN minus inorganic fraction (nitrate + nitrite + ammonium).

** Available P based on 21% mineralisation rate of total P.

9.1.2.3 Soil

The top 10 cm of a soil type, commonly referred to as a Yellow gravelly loamy sand, classified within the Yalanbee soil landscape unit (Fulton & Lantzke 1993) was collected from an unfertilised, uncleared bush site as described in Chapter 3. The soil was selected for its low N and P content to enable a responsive nutrient curve to be established. Gravel stones were removed by sieving through a 2 mm stainless steel sieve and the soil fraction <2 mm retained for the experiment. Soil characteristics are listed in detail in Chapter 3.

9.1.2.4 Basal nutrients

Basal amounts of K, Ca, Cu, Zn, B and Mo were applied to all pots to ensure limited supply of trace elements would not confound the results. The levels of nutrients based on the work of Bolland (1993) and personal communication with Lorraine Osborne, University of Western Australia (2000), were as follows: 39 mg K as K_2SO4, 1.2 mg Cu as $CuSO_4.5H_2O$, 1.0 mg Zn as $ZnSO_4.7H_2O$, 0.24 mg B as $H_3BO_{3,}$ 0.05 mg Mo as $Na_2MoO_4.2H_2O$ and applied as solution to all pots. In addition, 56 mg Ca as $CaSO_4.2H_2O$ was applied as a powder and mixed thoroughly through the soil.

9.1.2.5 Pots and sowing

Plastic pots measuring 15 cm deep by 15 cm diameter were lined with plastic bags to prevent free drainage and leaching of nutrients and filled with 1.8 kg of air-dried soil. Soils were watered to gravimetric soil water capacity (GSWC) of 17% as described in Chapter 3, and allowed to incubate in the glasshouse for 7 d prior to sowing. Ten pre-germinated seeds of wheat (*Triticum aestivum* L. var. Brookton) were sown to a depth of 2.5 cm on 10 April 2000. Plants were thinned to five plants per pot at the 2.5 leaf stage, leaving the five most uniform plants. Pots were made up to 17% GSWC at least every second day using deionised water and the position of pots were re-randomised. Plant shoots were cut at ground level, 33 days after sowing (DAS) and dried at 70°C for 48 h in a fan-forced oven. The experiment was conducted in the glasshouse described in Chapter 3.

9.1.2.6 Plant harvest

Plant development was recorded at 31 DAS using Zadoks (Z) decimal code for the growth stage of cereals (Zadoks, Chang & Konzak 1974). Plants were harvested at 33 DAS (10 May 2000) by cutting shoots at ground level and DM determined. Shoots were finely ground using a herb-grinder, then analysed for the concentration of N (Leco N) and P, K, Ca, Mg, Na, S, Fe, Mn, Zn and Cu by Inductively Coupled Plasma Atomic Emission Spectrophotometry (ICP-AES). Replicates were bulked together where total dry matter was less than 800 mg; otherwise analysis was on two replicates for each treatment.

Shoot nutrient concentrations were compared with critical nutrient concentration levels reported in Reuter & Robinson (1997) for whole wheat shoots at the closest comparable growth stage. Concentrations of N and P in wheat shoots grown in combinations of these nutrients were compared with concentrations in wheat shoots grown in the three rates of biosolids.

9.1.2.7 Soil analysis

Roots were air-dried for 5 d, and were physically removed. Soil was mixed thoroughly, air-dried for 30 d and was passed through a 2 mm sieve. Six treatments were selected to compare the effects of biosolids with inorganic N and P on selected soil properties such as pH, total N, nitrate-N, ammonium-N, total P and available P and K. The treatments included the two lowest rates of biosolids, the three highest rates of N combined with the highest rate of P and the control.

9.1.2.8 Statistical analysis of data

Data were prepared for statistical analysis using Microsoft Excel (D'Antuono 2000b). Genstat 5 was used to fit an ANOVA-type model to dry weights of shoots using the REML procedure to handle the three sets of 2-way interactions. The REML procedure was selected as it could handle unbalanced data. The Least Significant Difference (LSD) was computed at the 5% level of significance using the residual degrees of freedom where;

$LSD = SED * t$ where $SED = \sqrt{2 * RMS / npots}$

ANOVA-tables were computed for each of the 2-way interactions with both linear and quadratic trends plotted using trellis graphing (D'Antuono 2000b; Mead, Curnow & Hasted 1993).

Genstat was used to model the curve for the two-way N x P response surface (i.e. NxP for biosolids=0) using an exponential form, (related to the Mitscherlich) with:

y = a + b*exp (cN + dP + eN*P +….) for biosolids=0

assuming a non-linear parameter or curvature (D'Antuono 2000a). The response surface for the P, N and biosolids was constructed using the three x two-way interaction tables with data between yield of dried wheat shoots fitted to:

y = a + b*exp (cN + dP + eN*P + fB + gNP + hBxP) where B = biosolids

Therefore, the availability and individual contribution of biosolid N and P could be estimated from shoot yields compared with the N x P response surface.

9.1.3 Results

9.1.3.1 Shoot development and dry matter yield

9.1.3.1.1 N and P response surface (Increasing rates of N and P, with nil biosolids)

At 33 DAS, the dry matter (DM) of shoots increased with increasing combinations of rates of N and P from 0.27 g/pot to a maximum of 2.36 g/pot (Table 9.3). At the highest rates of N and P, plants had developed up to two tillers and five leaves per plant. Wheat grown at the lowest rates of N and P showed reduced growth and development with chlorotic symptoms evident on the oldest leaves. Plants had developed their fourth leaf and tillers were absent.

Overall, a strong positive interaction existed between N and P. As N increased from 0 to 160 mg N/kg, shoot yield did not increase significantly (*P* <0.05) where levels of P were low. In contrast, as P increased from 0 to 80 mg P/kg, wheat growth at low levels of N increased (Figure 9.1).

Table 9.3 Effects of increasing rates of inorganic N and P on shoot dry matter of wheat (g/pot) at 33 days after sowing.

		Inorganic N rate (mg N/kg)						
		0	10	20	40	80	160	Mean
Inorganic P rate (mg P/kg)	0	0.27	0.32	0.32	0.32	0.36	0.32	0.32
	10	0.43	0.67	0.72	0.96	0.86	0.83	0.75
	20	0.51	0.74	0.97	1.33	1.40	1.40	1.06
	40	0.47	0.89	1.09	1.82	1.93	1.62	1.30
	80	0.51	0.95	1.31	1.72	2.36	2.34	1.53
	Mean	0.44	0.71	0.88	1.23	1.38	1.30	

LSD (*P*=0.05) 0.19

Values are the means of two replicates. Values greater than the LSD between any treatment means are significantly different at *P* <0.05.

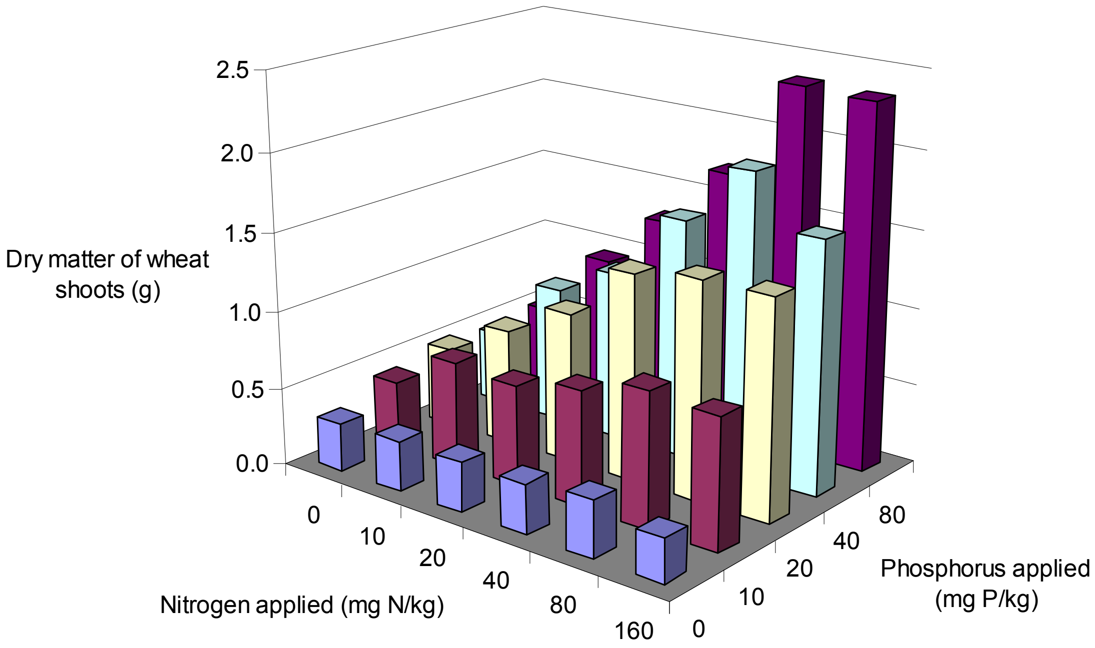


Figure 9.1 Effects of increasing rates of combinations of nitrogen and phosphorus on the shoot dry matter of wheat (g/pot) at 33 days after sowing

9.1.3.1.2 Increasing rates of N and biosolids, without added P

There was little response to the application of N between the three rates of biosolids for shoot DM of wheat at 33 DAS, without added P (Table 9.4). Plant development was similar for all biosolids treatments with five leaves and two tillers per plant. However, wheat plants in the highest rate of biosolids were more prostrate and darker green than the other two rates and generally yielded less as the rate of N increased (*P* <0.05). Mean shoot DM declined from 2.44 g/pot to 2.01 g/pot as rates of biosolids increased from 5 dry g/kg to 15 dry g/kg, respectively across all levels of N.

Table 9.4 Effects of increasing rates of combinations of nitrogen and biosolids on shoot dry matter of wheat (g/pot) at 33 days after sowing

		Inorganic N rate (mg N/kg)						
		0	10	20	40	80	160	Mean
Biosolids rate (dry g/kg)	5	2.35	2.38	2.32	2.40	2.57	2.60	2.44
	10	2.52	2.44	2.02	2.25	2.09	2.44	2.29
	15	2.23	1.81	2.03	2.03	2.04	1.89	2.01
	Mean	2.37	2.21	2.12	2.23	2.23	2.31	

LSD (*P* =0.05) = 0.42

Values are the means of two replicates. Values greater than the LSD between any treatment means are significantly different at *P* <0.05.

9.1.3.1.3 Increasing rates of P and biosolids, without added N

Plant development between all biosolids and inorganic P treatments were similar with an average of 5 leaves and two tillers per plant. However, increasing applications of P tended to decrease shoot DM of wheat over all biosolids treatments, which was significant at the highest rates of applied P (*P* <0.05,Table 9.5).

Table 9.5 Effects of increasing rates of combinations of phosphorus and biosolids on shoot dry matter of wheat (g/pot) at 33 days after sowing

		Inorganic P rate (mg P/kg)					
		0	10	20	40	80	Mean
Biosolids rate (dry g/kg)	5	2.35	2.35	2.39	2.23	2.14	2.29
	10	2.52	2.59	2.67	2.57	2.09	2.49
	15	2.23	2.31	2.60	2.51	2.17	2.36
	Mean	2.37	2.42	2.55	2.44	2.13	

LSD (*P* =0.05) = 0.40

Values are the means of two replicates. Values greater than the LSD between any treatment means are significantly different at *P* <0.05.

9.1.3.1.4 Regression analysis

The non-linear regression analysis for the N x P response surface (i.e. biosolids=0) showed significant interactions for DM with different shapes for each level of N or P across the other factor. The DM responses with N x biosolids for P=0 showed significant main effects only for biosolids. The DM responses with biosolids x P for N=0 showed the main effects of biosolids to be significant, only the effects of biosolids swamped the response curves which were flat but high (D'Antuono 2000a). Therefore due to the different response curves, it was not possible to fit an exponential model as planned.

9.1.3.2 Plant tissue analysis

9.1.3.2.1 N and P response surface (Increasing rates of N and P, with nil biosolids)

Nutrient concentrations of wheat shoots measured over the N x P response surface (biosolids=0) differed with the N and/or P rate. For ease of reporting, these are averaged over the six different N rates (i.e. average of all P rates: 0, 10, 20, 40 & 80 mg P/kg) (Table 9.6). The concentrations of K, Mg, Mn, Ca, Cu, S, B, Fe and Zn were considered adequate for wheat growth.

Concentrations of N in wheat shoots for the N x P response surface at 160 mg N/kg were adequate for shoot growth (5.6% N). Rates of N below 160 mg N/kg resulted in wheat shoots below the critical concentration of N, with values from 2.6% to 5.1% (Table 9.6), which coincided with a decrease in DM production at the highest MCP rate of 80mg P/kg (Figure 9.1).

Wheat shoots were deficient in P at all combinations of N and P (at nil biosolids). Generally the P concentrations in wheat whole shoots at 80mg P/kg decreased as inorganic N rates increased. However, if the different plant growth stages were considered, P was adequate at 80 mg P/kg.

Table 9.6 Nutrient concentrations of whole wheat shoots for six different rates of N (mean of all P rates; 0, 10, 20, 40 & 80 mg P/kg) at 33 DAS when shoots were forming tillers (FS2-3).

	N level (mg N/kg)							
Nutrient	0	10	20	40	80	160	**Critical level**	**How critical level derived**
N%	**2.60**	**2.93**	**3.63**	**4.17**	**5.08**	5.60	5.39-5.64	WS, F, FS3,
P%	**0.42**	**0.36**	**0.38**	**0.29**	**0.31**	**0.27**	0.70-0.38	WS, F, ZS 12/21-15.5/2+
K%	5.9	6.0	6.0	5.3	5.2	5.2	4.1-3.2	FS2-FS3, WS, F
S%	0.60	0.53	0.52	0.46	0.54	0.51	0.3	FS 2, WS, F
Ca%	0.26	0.26	0.27	0.29	0.30	0.36	<0.2	FS 2, YEB, S
Mg%	0.17	0.18	0.21	0.23	0.31	0.25	0.15	FS 1-6, YEB, F, S
Cu (mg/kg)	13.7	14.0	15.0	15.0	14.0	14.0	7.0	60 DAS, WS, Soil
Zn (mg/kg)	55.3	59.6	69.4	79.0	89.5	93.6	20	45 DAS, WS, Soil
Mn (mg/kg)	442	317	286	204	221	195	11-13	FS3-4, WS, F
Fe (mg/kg)	101.1	94.6	93.3	87.2	108.4	116.7	<25	FS 10.1, WS, Lit
B (mg/kg)	33.3	33.6	30.4	28.0	29.9	28.7	<6	FS 5-6, WS, Lit

Nutrient concentration means from CSBP Future Farm Report Number JCP00 (23/06/00) 370239

DAT=days after transplanting, WS=whole shoot, F = field, FS3 = Feeke's growth stages of cereals.

Critical values for tissue nutrient concentrations and how derived are included (Reuter & Robinson 1997).

Figures in bold are deemed to be deficient in that nutrient.

9.1.3.2.2 Increasing rates of N and/or P and biosolids

Wheat shoots were deficient in N where biosolids were applied without the addition of inorganic N. Shoot N concentrations measured 5.2% across all rates of P, regardless of the biosolids application rate. The addition of at least 10 mg N/kg resulted in adequate concentrations of shoot N. Wheat shoots were adequate in P for all biosolids applications irrespective of the level of inorganic P applied, measuring a minimum of 0.63%. The concentrations of K, Mg, Mn, Ca, Cu, S, B, Fe and Zn in shoots were considered adequate for wheat growth for all treatments.

9.1.3.3 Soil analysis

Soil analysis for six selected biosolids and inorganic fertiliser treatments showed a number of differences in soil properties (Table 9.7). The addition of biosolids tended to increase soil pH ($CaCl_2$) from 4.9 (control) to 5.2 and 5.5 in the biosolids at 5 and 10 dry g/kg, respectively, whereas no change was noted in the inorganic fertiliser treatments. The lowest rate of biosolids (5 dry g/kg) increased bicarbonate extractable P (Colwell) to a greater extent than the highest MCP treatments at 80 mg P/kg. This was more than anticipated, given the low mineralisation rate of biosolid P assumed. Large increases in soil inorganic N levels were not consistent with the total N loading supplied by biosolids. The biosolids at the rates used, more closely resembled MCP treatments where the addition of inorganic N was between 80 and 160 mg N/kg.

Table 9.7 Selected treatment composites analysed for soil pH, total N, nitrate-N, ammonium-N, total P and available P and K

Loading rate	**Treatment**					
	Control	Biosolids 5 g/kg	Biosolids 10 g/kg	80 MCP + 40 N	80 MCP +80 N	80 MCP + 160 N
Total N (mg N/kg)	Nil	264	527	40	80	160
PAN* (mg N/kg)		66	132			
Total P (mg P/kg)	Nil	116	233	80	80	80
Parameter measured						
pH ($CaCl_2$)	4.9	5.2	5.5	4.9	4.9	4.7
Nitrate-N (mg N/kg)	6	27	86	9	10	77
Ammonium-N (mg N/kg)	2	3	4	2	2	7
Total N (%)	0.11	0.11	0.24	0.07	0.17	0.10
Colwell P (mg P/kg)	9	57	115	37	37	45
Total P (mg P/kg)	47	173	294	101	111	107
Colwell K (mg K/kg)	76	36	55	31	23	28

CSBP Future Farm Report Number INSOO (26/06/00) 00633610. * PAN = Plant Available Nitrogen, estimated from Table 9.2, applies to biosolids treatments only.

9.1.4 Discussion

9.1.4.1 Estimating the amount of available N and P from biosolids compared with the N x P response surface

The growth and response of wheat shoots to the P supplied in biosolids was much higher than initially predicted. Significantly more P was available to plants than the 21% of total P than expected (Table 9.2). Comparison with the N x P response surface (Figure 9.1) and P concentrations (Table 9.6) would indicate that the expected values of 24, 48 & 72 mg P/kg at the three biosolids treatments, respectively were too low to enable accurate comparison or regression modelling to be conducted. Therefore, comparison with the N x P response matrix was limited to the highest rates of inorganic P, being 80 mg P/kg. Loadings of biosolid P were at most (i.e. 100% availability) equivalent to 116, 232 and 348 mg P/kg for the three rates of biosolids applied, respectively. Concentrations of P in wheat shoots at 33 DAS are shown in Figure 9.2 plotted against total P applied and therefore not closely aligned. Further investigation into the availability of P from biosolids is presented in Chapter 3.

The highest rate of MCP used in the N X P response surface (i.e. 80 mg P/kg) and the lowest rates of biosolids were plotted for DM and concentrations of N in wheat shoots at 33 DAS (Figure 9.3). Estimates for plant available N (PAN) were calculated at 13,164 mg N/kg (Table 9.2). The PAN calculation for shoot DM (Figure 9.3) and N concentrations (Figure 9.4) fitted reasonably well for the lowest rates of biosolids at 33 DAS. The soil analysis data (Table 9.7) also tended to verify that the levels of inorganic N in biosolids applied at 5 g/kg were intermediate between the ammonium nitrate applications of 80 and 160 mg N/kg, where MCP=80 mg P/kg at 33 DAS. In addition, rates of inorganic N applied at 160 mg N/kg were above the critical concentration required for adequate N nutrition (Table 9.6).

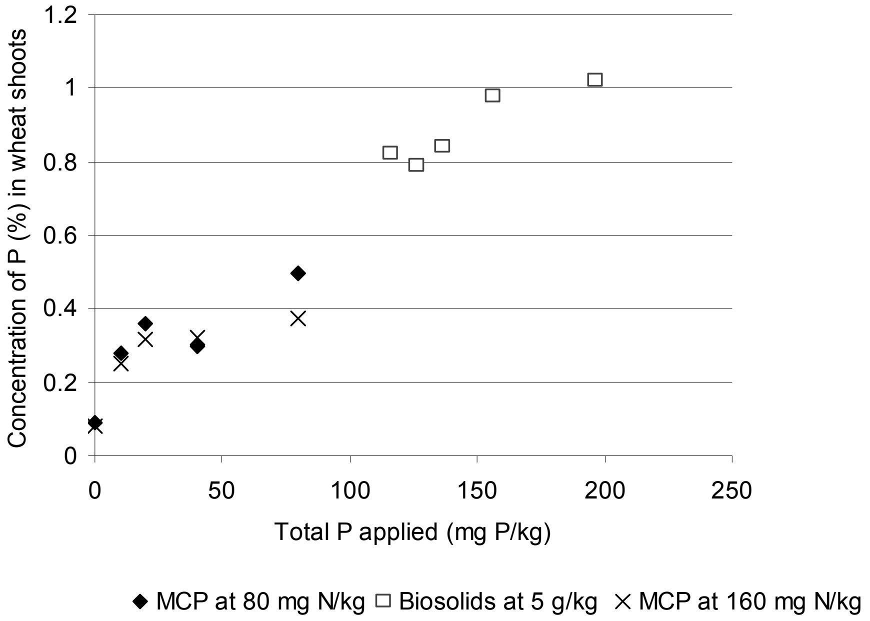
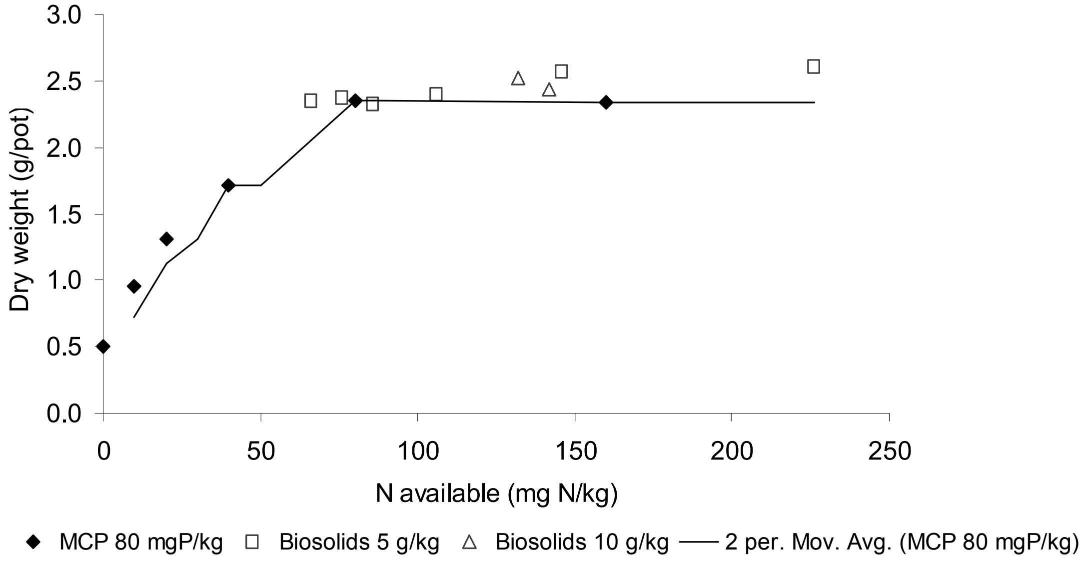
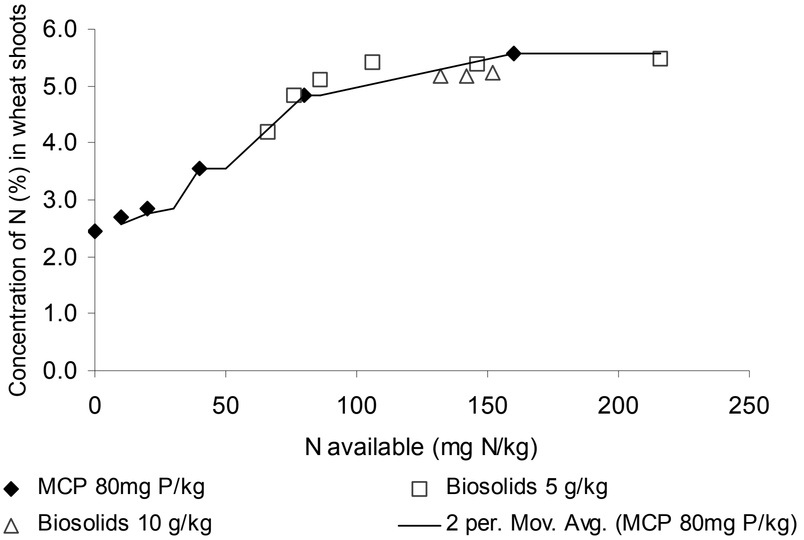


Figure 9.2 Concentrations of P in shoots of wheat at 33 DAS for MCP treatment (80 mg P/kg) for two rates of N (80 and 160 mg N/kg) and biosolids (5 dry g/kg) containing 23,250 mg P/kg



Nitrogen available in biosolids calculated at 13,164 mg N/kg from Table 9.2.

Figure 9.3 Comparison between available N in MCP treatment (80 mg P/kg) and two rates of biosolids (5 & 10 dry g/kg) for shoot DM of wheat at 33 DAS



Nitrogen available in biosolids calculated at 13,164 mg N/kg from Table 9.2.

Figure 9.4 Comparison between available N in MCP treatment (80 mg P/kg) and two rates of biosolids (5 & 10 dry g/kg) for concentrations of N in shoot DM of wheat at 33 DAS

9.1.5 Conclusion

In order to study the effect of increasing rates of P in biosolids without an interaction with biosolid N, experiments need to be designed to ensure that N is constant between treatments. Therefore as the rates of biosolids increase, the amount of inorganic N needs to decrease proportionately. The formula for PAN, suggested by the Water Corporation (2000), Table 9.2, was a reasonable estimate of the portion of inorganic N available at 33 DAS under the specific glasshouse conditions. Therefore, it is proposed that subsequent pot experiments will use the PAN calculation consisting of a 50% volatilisation rate and 20% mineralization rate, with values determined on a sub-sample of biosolids specific to that experiment. It was determined that the N application rate of 160 mg N/kg was adequate for the growth of wheat shoots at 33 DAS and would be used in further glasshouse experiments.

In contrast, the amount of plant available P in biosolids was much higher than the 21% expected from the total P applied, and thus forms the basis of further experimentation. All other basal nutrients were considered adequate for plant growth on the soil type used and were repeated in subsequent experiments.

9.2 List of publications arising from the thesis

Pritchard, D L and Penney, N 2003, ‘Validation of biosolids land application guidelines in Western Australia through innovative research’ in *Innovations in Water’ Ozwater Convention and Exhibition,* CD-ROM, ed. Australian Water Association, Perth, 6-10 April 2003.

Penney, N, Dumbrell, I & Pritchard, D 2003, ‘Biosolids: Wanted not wasted’ in *Proceedings of the Fourth International Conference of ORBIT Association on Biological Processing of Organics: Advances for a Sustainable Society, Organic Recovery & Biological Treatment*, CD-ROM, ed. ORBIT, Perth, 30 April-2 May 2003.

Pritchard, D L, Bowden, J W, Martin, L D & Penney, N 2002, ‘How available is the phosphorus in anaerobically digested biosolids?’, in *3rd World Water Congress*, CD-ROM, ed. International Water Association (IWA), Melbourne, 7-12 April 2002.

Pritchard, D L, Martin, L D, Bowden, J W & Penney, N 2002, ‘Biosolids down under: effects of incorporation on phosphorus availability’, in *16th Annual Residuals and Biosolids Management Conference 2002 Privatization, Innovation and Optimisation – How to do More for Less,* CD-ROM, ed. Water Environment Federation, Renaissance Austin Hotel, Austin, Texas, 3-6 March 2002.

Pritchard, D L., Martin, L D, Bowden, J W & Penney, N 2002, ‘Biosolids phosphorus and environmental best practice’, in Proceedings *Australian Soil Science Society (ASSI) FutureSoils 2002 Conference*, ed. The University of Western Australia, Perth, 2-6 December 2002.

Pritchard, D L, Penney, N, Martin, L D, Bowden, J W & Collins, D 2002, ‘Taking a closer look at the PLBAR’, in *Biosolids Specialty Conference I*, ed. Australian Water Association, Sydney, 19-20 June 2002.

Pritchard, D, Bowden, J W, Martin, L 2001, Phosphorus uptake by wheat shoots: investigations using biosolids, in *Fifth WA Symposium on Ions in the Soil-Water-Plant Continuum*, ed. The University of Western Australia, Perth, 27 April, 2001.