



**THE EFFECT OF MINERALOGY AND
EXCHANGEABLE MAGNESIUM ON THE
DISPERSIVE BEHAVIOUR OF WEAKLY SODIC
SOILS.**

Thesis submitted by

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to

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TABLE OF CONTENTS.

Abstract	iv
Declaration	vi
Acknowledgments	vii
List of Figures	viii
List of Tables	xi
List of Appendices	xii
1. INTRODUCTION	1
2. LITERATURE REVIEW	11
2.1. INTRODUCTION	11
2.2. DEFINING SODICITY AND SODIC SOILS	14
2.3. THE RELATIONSHIP BETWEEN CARBONATE, PH AND SODICITY	16
2.4. CLAY MINERALOGY	17
2.4.1. <i>Kaolinite</i>	19
2.4.2. <i>Smectite</i>	20
2.4.3. <i>Illite</i>	21
2.5. THE NATURE OF DISPERSION AND ITS EFFECT ON SOIL PROPERTIES	22
2.6. THE EFFECT OF DISPERSION ON SOIL PROPERTIES	23
2.6.1. <i>The effect of soil conditions on hydraulic conductivity</i>	23
2.6.2. <i>The effect of dispersion on infiltration rate</i>	24
2.6.3. <i>The effect of dispersion on soil stability and strength</i>	24
2.7. THE EFFECT OF INTERPARTICLE FORCES ON DISPERSION	25
2.7.1. <i>Van der Waals forces</i>	26
2.7.2. <i>Diffuse double layer repulsion</i>	29
2.7.3. <i>Derjaguin, Landau, Verwey, Overbeek (DLVO) theory</i>	30
2.7.4. <i>Structural (hydration) forces</i>	31
2.7.5. <i>Ion-ion correlation forces</i>	33
2.7.6. <i>Swelling</i>	34
2.8. THE EFFECT OF POTASSIUM AND MAGNESIUM ON SOIL STABILITY	36
2.8.1. <i>Potassium</i>	36
2.8.2. <i>Magnesium</i>	37
2.9. THE EFFECT OF SOIL PH ON SODIC SOIL STABILITY	44
2.10. THE EFFECT OF MINERALOGY ON SODIC SOIL STABILITY	45
2.11. THE ROLE OF CEMENTING AGENTS IN SOIL STABILITY	47
2.12. WEAKLY SODIC AND NON-SODIC SOILS	49
3. MATERIALS AND METHODS	50
3.1. SOILS	50
3.2. MECHANICAL ANALYSIS	50
3.3. CLAY MINERALOGY	54
3.4. EXCHANGEABLE CATIONS	55
3.5. SURFACE AREA OF SOIL AND SOIL CLAY	56
3.6. OTHER MEASUREMENTS	58
3.7. CATION EXCHANGE SATURATION	58
3.8. SODIC SOIL PREPARATION	61
3.9. MECHANICAL DISPERSION	61
3.10. SPONTANEOUS DISPERSION	62
3.11. TURBIDITY CALIBRATION CURVE	62
3.12. PARTICLE SIZE MEASUREMENT	67
3.13. INDUCTION OF SODICITY IN NATURAL AGGREGATES	68
4. EFFECT OF GROUP II CATIONS ON THE DISPERSION OF SOIL	70
4.1. INTRODUCTION	70
4.2. MATERIALS AND METHODS	71
4.3. RESULTS	72
4.3.1. <i>Mechanical Dispersion</i>	73
4.3.2. <i>Particle size</i>	88

4.3.3. <i>Spontaneous dispersion</i>	91
4.4. DISCUSSION.....	95
4.4.1. <i>Mechanical dispersion</i>	95
4.4.2. <i>Particle size</i>	105
4.4.3. <i>Spontaneous dispersion</i>	106
4.5. CONCLUSIONS.....	107
5. DISPERSION OF SOIL IN A MIXED CALCIUM-MAGNESIUM-SODIUM SYSTEM.....	110
5.1. INTRODUCTION.....	110
5.2. MATERIALS AND METHODS.....	111
5.3. RESULTS.....	113
5.3.1 <i>Mechanical dispersion</i>	114
5.3.2 <i>Particle size</i>	139
5.3.3 <i>Zeta potential</i>	142
5.4. DISCUSSION.....	146
5.4.1 <i>Mechanical Dispersion</i>	146
5.4.2 <i>Particle size and zeta potential</i>	155
5.5. CONCLUSION.....	155
6. A METHOD FOR INDUCING SODICITY IN SOIL WITH MINIMAL STRUCTURAL DISTURBANCE.....	158
6.1. INTRODUCTION.....	158
6.2. A METHOD FOR INDUCING SODICITY IN SOIL WITH MINIMAL STRUCTURAL DISTURBANCE	158
6.2.1. <i>Materials and methods</i>	158
6.2.2. <i>Analysis of the method</i>	159
6.2.3. <i>Results</i>	162
6.2.4. <i>Discussion and conclusions</i>	171
6.3. COMPARISON OF THE CLAY DISPERSED BY SAMPLES PREPARED BY REMOULDING AND WITH MINIMAL DISTURBANCE.....	172
6.3.1. <i>Materials and methods</i>	172
6.3.2. <i>Results</i>	172
6.3.3. <i>Discussion</i>	183
6.4. CONCLUSIONS.....	184
7. GENERAL DISCUSSION AND CONCLUSIONS.....	186
7.1. DISCUSSION.....	186
7.1.1. <i>Introduction</i>	186
7.1.2. <i>Relevance of a sodium percentage to define a sodic soil</i>	187
7.1.3. <i>The effect of magnesium on soil stability</i>	190
7.1.4. <i>The influence of mineralogy on soil stability</i>	194
7.1.5. <i>Evaluation and comparison of methods used to produce samples with particular ESP values</i>	201
7.2. CONCLUSIONS.....	204
8. REFERENCES.....	207
9. APPENDICES.....	218

ABSTRACT

The influence on soil stability of interactions between exchangeable magnesium, calcium and sodium, where all three cations are present, has rarely been investigated. Therefore, the effect of mineralogy and exchangeable magnesium on the dispersive behaviour of six weakly sodic Australian soils was investigated. Soils were subjected to spontaneous and mechanical dispersion, and the percentage of dispersed clay was measured.

The extent of clay dispersion from soils bearing group II exchangeable (Mg, Ca, Sr, Ba) cations was also measured. The six soils studied generally dispersed more clay when saturated with exchangeable magnesium. The amount of clay dispersed from each soil with calcium, strontium or barium as the dominant exchangeable cation was similar. This shows that Group II cations do not produce effects on the dispersion of soil which are reflected in the chemical trends within the series.

In mixed magnesium calcium systems the dispersive effects of exchangeable magnesium generally occurred when magnesium dominated the exchange phase. Soils which were more susceptible to the effects of sodium also exhibited significant increases in the amount of clay dispersed, as exchangeable magnesium increased. This result indicated that these soils may be more susceptible to the presence of exchangeable magnesium and require amelioration even when only weakly sodic.

It was evident that soils containing significant amounts of smectitic Randomly Interstratified Minerals (RIM) were particularly susceptible to the effects of

exchangeable magnesium. There were also some similarities in the response of soils with similar dominant clay minerals. The clay mineralogy clearly played a very important role soil behaviour. However, classification by dominant minerals only, could not be used to explain the results observed. More detailed mineralogical information, as well as surface charge density and pore size distribution all contributed to the response of a soil to various conditions. Thus the nature of the dominant mineral alone is not indicative of potential soil dispersivity, and further details about soil/clay properties are required before possible predictions can be made.

A method for inducing sodicity in soils without disturbing the aggregate structure was developed. The undisturbed aggregates prepared using this method were subjected to the same mechanical dispersion regime as the samples studied for the effects of magnesium and mineralogy. Comparisons of the amount of dispersed clay were made. Unexpectedly, the undisturbed samples generally dispersed to give more clay. This implies that clay dispersion may be underestimated in soils where the structure is disturbed during preparation. Further work on the method is required.

DECLARATION

I declare that 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 or written by another person, except where due reference is made in the text of the thesis.

I give consent to this copy of my thesis being available for loan and photocopying.

SIGNED:

.....

DATE:.....2/11/99.....**Gayle R Grieger.**

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LIST OF FIGURES

FIGURE 2-1 ARID, SEMI-ARID AND SALT-AFFECTED AREAS OF AUSTRALIA (BASED ON ISBELL, (1983) AND MCGINNIES <i>ET AL.</i> , (1968))	12
FIGURE 2-2 MINERAL STRUCTURE OF KAOLINITE, (AFTER GRIM, 1968)	20
FIGURE 2-3 MINERAL STRUCTURE OF SMECTITE, (AFTER GRIM, 1968)	21
FIGURE 2-4 MINERAL STRUCTURE OF ILLITE, (AFTER GRIM, 1968)	22
FIGURE 2-5 MONOVALENT COUNTERION CONCENTRATION PROFILE BETWEEN TWO CHARGED SURFACES, 2.1 NM APART IN WATER. THE SMOOTH CURVE IS OBTAINED FROM THE POISSON-BOLTZMANN EQUATION; THE OTHER IS FROM A MONTE CARLO SIMULATION BY JONSSON <i>ET AL.</i> (1980) FROM ISRAELACHVILLI, 1985).	27
FIGURE 2-6 VARIATION IN ELECTRIC POTENTIAL WITH DISTANCE FROM THE SURFACE AND ITS DEPENDENCE ON ELECTROLYTE CONCENTRATION: (I) LOW, (II) MEDIUM, (III) HIGH ELECTROLYTE CONCENTRATION. $1/\kappa$ IS CALLED THE "THICKNESS OF THE DOUBLE LAYER" (EVERETT, 1988)	30
FIGURE 2-7 SCHEMATIC ENERGY VS DISTANCE PROFILES OF DLVO INTERACTION (ISRAELACHVILLI, 1985).....	31
FIGURE 2-8 ORIENTATION OF WATER AROUND A POSITIVE ION IN SOLUTION (BOCKRIS <i>ET AL.</i> , 1974).....	32
FIGURE 2-9 RELATIVE HYDRAULIC CONDUCTIVITY OF WILLOWS SOILS LEACHED WITH NA-CA, NA-MG, AND NA-MG-CA SOLUTIONS OF SODIUM ADSORPTION RATIO (SAR) 10 AND 20 (CURTIN <i>ET AL.</i> , 1994B).	42
FIGURE 3-1 LOCATION OF BELALIE, NEAR BOOBOROWIE, AND BORDERTOWN SOILS, SOUTH AUSTRALIA, AUSTRALIA.	51
FIGURE 3-2 LOCATION OF WIMMERA SOIL AT LONGERENONG, NEAR HORSHAM, AND TATURA SOIL, VICTORIA, AUSTRALIA.	51
FIGURE 3-3 LOCATION OF TOMKI SOIL, NEAR LISMORE, NEW SOUTH WALES, AUSTRALIA.	52
FIGURE 3-4 LOCATION OF MT MADDEN SOIL, NEAR RAVENSTHORPE, WESTERN AUSTRALIA. ...	52
FIGURE 3-5 SCHEMATIC DIAGRAM OF APPARATUS USED TO MEASURE SPONTANEOUS DISPERSION	63
FIGURE 3-6 THE STANDARD TURBIDITY CURVES FOR CALCIUM- AND SODIUM-SATURATED ILLITIC BELALIE AND TATURA SOILS.	65
FIGURE 3-7 THE STANDARD TURBIDITY CURVES FOR CALCIUM- AND SODIUM-SATURATED WIMMERA, TOMKI, BORDERTOWN AND MT MADDEN SOILS.	66
FIGURE 4-1 AVERAGE CLAY DISPERSION PRODUCED BY END-OVER-END INVERSION OF THE SOIL SUSPENSION TWICE BY HAND, EXPRESSED AS A PERCENTAGE OF THAT PRODUCED BY 1 MINUTE SONIFICATION.	74
FIGURE 4-2 AVERAGE CLAY DISPERSION AT ESP 0 AND 5 PRODUCED FROM TOMKI AND BORDERTOWN SOILS BY END-OVER-END INVERSION OF THE SOIL SUSPENSION TWICE BY HAND AND EXPRESSED AS A RATIO TO THAT PRODUCED BY 1 MINUTE SONIFICATION.	75
FIGURE 4-3 CLAY DISPERSION PRODUCED BY 1 MINUTE END-OVER-END SHAKING EXPRESSED AS A PERCENTAGE OF THAT PRODUCED BY 1 MINUTE SONIFICATION.	78

- FIGURE 4-4 CLAY DISPERSION OF TOMKI, BORDERTOWN, MT MADDEN AND TATURA AT ESP 0 AND 5 PRODUCED BY 1 MINUTE END-OVER-END SHAKING AND EXPRESSED AS A PERCENTAGE OF THAT PRODUCED BY 1 MINUTE SONIFICATION. 79
- FIGURE 4-5 AVERAGE CLAY DISPERSION PRODUCED BY 15 MINUTES END-OVER-END SHAKING, EXPRESSED AS A PERCENTAGE OF CLAY PRODUCED BY 1 MINUTE SONIFICATION. 82
- FIGURE 4-6 AVERAGE CLAY DISPERSION PRODUCED BY BORDERTOWN AND TATURA ESP 0 AND 5 AT 15 MINUTES END-OVER-END SHAKING EXPRESSED AS A PERCENTAGE OF THAT PRODUCED BY 1 MINUTE SONIFICATION. 83
- FIGURE 4-7 AVERAGE CLAY DISPERSION PRODUCED BY 2 HOURS END-OVER-END SHAKING EXPRESSED AS A PERCENTAGE OF THAT PRODUCED FROM 1 MINUTE SONIFICATION. 85
- FIGURE 4-8 AVERAGE CLAY DISPERSION PRODUCED BY 16 HOURS END-OVER-END SHAKING EXPRESSED AS A PERCENTAGE OF THAT PRODUCED FROM 1 MINUTE SONIFICATION. 87
- FIGURE 4-9 PERCENTAGE OF CLAY SPONTANEOUSLY DISPERSED FROM SOILS WITH ESP 0. ERROR BARS ARE STANDARD DEVIATIONS OF AVERAGE CLAY DISPERSION..... 92
- FIGURE 4-10 PERCENTAGE OF CLAY SPONTANEOUSLY DISPERSED FROM MT MADDEN ESP 5,10 AND 20 AND TOMKI ESP 10 AND 20. ERROR BARS ARE STANDARD ERRORS OF AVERAGE CLAY DISPERSION. 94
- FIGURE 5-1 CLAY DISPERSION FROM NON-SODIC SOIL TREATMENTS (ESP/EMGP) PRODUCED BY END-OVER-END SHAKING TWICE AND EXPRESSED AS A PERCENTAGE OF THAT PRODUCED BY 1 MINUTE SONIFICATION. LETTERS INDICATE THE RESULTS OF A TUCKEY'S TEST FOR EACH ESP. THE LETTERS INDICATE STATISTICALLY SIGNIFICANT DIFFERENCES BETWEEN THE MEANS OF EACH TREATMENT *WITH THE SAME ESP*. 115
- FIGURE 5-2 CLAY DISPERSION OF SODIC SOIL TREATMENTS (ESP/EMGP) PRODUCED BY END-OVER-END SHAKING TWICE AND EXPRESSED AS A PERCENTAGE OF CLAY PRODUCED BY 1 MINUTE SONIFICATION. LETTERS INDICATE THE RESULTS OF A TUCKEY'S TEST FOR EACH ESP. THE LETTERS INDICATE STATISTICALLY SIGNIFICANT DIFFERENCES BETWEEN THE MEANS OF EACH TREATMENT *WITH THE SAME ESP*. 117
- FIGURE 5-3 CLAY DISPERSION OF TOMKI ESP 7 AND 10 TREATMENTS PRODUCED BY END-OVER-END SHAKING TWICE AND EXPRESSED AS A PERCENTAGE OF CLAY DISPERSED BY 1 MINUTE SONIFICATION. LETTERS INDICATE THE RESULTS OF A TUCKEY'S TEST FOR EACH ESP. THE LETTERS INDICATE STATISTICALLY SIGNIFICANT DIFFERENCES BETWEEN THE MEANS OF EACH TREATMENT *WITH THE SAME ESP*. 118
- FIGURE 5-4 CLAY DISPERSION OF BORDERTOWN ESP 7 AND 10 TREATMENTS PRODUCED BY END-OVER-END SHAKING TWICE AND EXPRESSED AS A PERCENTAGE OF CLAY PRODUCED BY 1 MINUTE SONIFICATION. LETTERS INDICATE THE RESULTS OF A TUCKEY'S TEST FOR EACH ESP. THE LETTERS INDICATE STATISTICALLY SIGNIFICANT DIFFERENCES BETWEEN THE MEANS OF EACH TREATMENT WITH THE SAME ESP..... 119
- FIGURE 5-5 CLAY DISPERSION FROM NON-SODIC SOIL TREATMENTS (ESP/EMGP) PRODUCED BY 1 MINUTE END-OVER-END SHAKING AND EXPRESSED AS A PERCENTAGE OF CLAY PRODUCED BY 1 MINUTE SONIFICATION. LETTERS INDICATE THE RESULTS OF A TUCKEY'S TEST FOR EACH ESP. THE LETTERS INDICATE STATISTICALLY SIGNIFICANT DIFFERENCES BETWEEN THE MEANS OF EACH TREATMENT *WITH THE SAME ESP*. 121
- FIGURE 5-6 CLAY DISPERSION FROM SODIC SOIL TREATMENTS (ESP/EMGP) PRODUCED BY 1 MINUTE END-OVER-END SHAKING AND EXPRESSED AS A PERCENTAGE OF CLAY PRODUCED BY 1 MINUTE SONIFICATION. LETTERS INDICATE THE RESULTS OF A TUCKEY'S TEST FOR EACH ESP. THE LETTERS INDICATE STATISTICALLY SIGNIFICANT DIFFERENCES BETWEEN THE MEANS OF EACH TREATMENT *WITH THE SAME ESP*. 123
- FIGURE 5-7 CLAY DISPERSION OF TOMKI ESP 7 AND 10 TREATMENTS (ESP/EMGP) PRODUCED BY 1 MINUTE END-OVER-END SHAKING AND EXPRESSED AS A PERCENTAGE OF CLAY PRODUCED BY 1 MINUTE SONIFICATION. LETTERS INDICATE THE RESULTS OF A TUCKEY'S

- TEST FOR EACH ESP. THE LETTERS INDICATE STATISTICALLY SIGNIFICANT DIFFERENCES BETWEEN THE MEANS OF EACH TREATMENT *WITH THE SAME ESP*. 124
- FIGURE 5-8 CLAY DISPERSION OF TATURA ESP 7 AND 10 TREATMENTS (ESP/EMGP) PRODUCED BY 1 MINUTE END-OVER-END SHAKING AND EXPRESSED AS A PERCENTAGE OF CLAY PRODUCED BY 1 MINUTE SONIFICATION. LETTERS INDICATE THE RESULTS OF A TUCKEY'S TEST FOR EACH ESP. THE LETTERS INDICATE STATISTICALLY SIGNIFICANT DIFFERENCES BETWEEN THE MEANS OF EACH TREATMENT *WITH THE SAME ESP*. 124
- FIGURE 5-9 CLAY DISPERSION OF MT MADDEN ESP 7 AND 10 TREATMENTS (ESP/EMGP) PRODUCED BY 1 MINUTE END-OVER-END SHAKING AND EXPRESSED AS A PERCENTAGE OF CLAY PRODUCED BY 1 MINUTE SONIFICATION. LETTERS INDICATE THE RESULTS OF A TUCKEY'S TEST FOR EACH ESP. THE LETTERS INDICATE STATISTICALLY SIGNIFICANT DIFFERENCES BETWEEN THE MEANS OF EACH TREATMENT *WITH THE SAME ESP*. 125
- FIGURE 5-10 CLAY DISPERSION OF NON-SODIC SOIL TREATMENTS (ESP/EMGP) PRODUCED BY 15 MINUTES END-OVER-END SHAKING AND EXPRESSED AS A PERCENTAGE OF CLAY PRODUCED BY 1 MINUTE SONIFICATION. LETTERS INDICATE THE RESULTS OF A TUCKEY'S TEST FOR EACH ESP. THE LETTERS INDICATE STATISTICALLY SIGNIFICANT DIFFERENCES BETWEEN THE MEANS OF EACH TREATMENT *WITH THE SAME ESP* 126
- FIGURE 5-11 CLAY DISPERSION OF SODIC SOIL TREATMENTS (ESP/EMGP) PRODUCED BY 15 MINUTE END-OVER-END SHAKING AND EXPRESSED AS A PERCENTAGE OF CLAY PRODUCED BY 1 MINUTE SONIFICATION. LETTERS INDICATE THE RESULTS OF A TUCKEY'S TEST FOR EACH ESP. THE LETTERS INDICATE STATISTICALLY SIGNIFICANT DIFFERENCES BETWEEN THE MEANS OF EACH TREATMENT *WITH THE SAME ESP*. 129
- FIGURE 5-12 CLAY DISPERSION OF NON-SODIC SOIL TREATMENTS (ESP/EMGP) PRODUCED BY 2 HRS END-OVER-END SHAKING AND EXPRESSED AS A PERCENTAGE OF CLAY PRODUCED BY 1 MINUTE SONIFICATION. LETTERS INDICATE THE RESULTS OF A TUCKEY'S TEST FOR EACH ESP. THE LETTERS INDICATE STATISTICALLY SIGNIFICANT DIFFERENCES BETWEEN THE MEANS OF EACH TREATMENT *WITH THE SAME ESP*. 131
- FIGURE 5-13 CLAY DISPERSION OF SODIC SOIL TREATMENTS (ESP/EMGP) PRODUCED BY 2 HRS END-OVER-END SHAKING AND EXPRESSED AS A PERCENTAGE OF CLAY PRODUCED BY 1 MINUTE SONIFICATION. LETTERS INDICATE THE RESULTS OF A TUCKEY'S TEST FOR EACH ESP. THE LETTERS INDICATE STATISTICALLY SIGNIFICANT DIFFERENCES BETWEEN THE MEANS OF EACH TREATMENT *WITH THE SAME ESP* 134
- FIGURE 5-14 CLAY DISPERSION OF NON-SODIC SOIL TREATMENTS (ESP/EMGP) PRODUCED BY 16 HOURS END-OVER-END SHAKING AND EXPRESSED AS A PERCENTAGE OF CLAY PRODUCED BY 1 MINUTE SONIFICATION. LETTERS INDICATE THE RESULTS OF A TUCKEY'S TEST FOR EACH ESP. THE LETTERS INDICATE STATISTICALLY SIGNIFICANT DIFFERENCES BETWEEN THE MEANS OF EACH TREATMENT *WITH THE SAME ESP*. 136
- FIGURE 5-15 CLAY DISPERSION OF SODIC SOIL TREATMENTS (ESP/EMGP) PRODUCED BY 16 HOURS END-OVER-END SHAKING AND EXPRESSED AS A PERCENTAGE OF CLAY PRODUCED BY 1 MINUTE SONIFICATION. LETTERS INDICATE THE RESULTS OF A TUCKEY'S TEST FOR EACH ESP. THE LETTERS INDICATE STATISTICALLY SIGNIFICANT DIFFERENCES BETWEEN THE MEANS OF EACH TREATMENT *WITH THE SAME ESP* 137
- FIGURE 6-1 CLAY DISPERSED FROM SIX SOILS THAT WERE MINIMALLY DISTURBED DURING SAMPLE PREPARATION AS A PERCENTAGE OF THAT PRODUCED BY SONIFICATION. SAMPLES WERE EXPOSED TO SHAKING TWICE END-OVER-END BY HAND. ERROR BARS INDICATE THE STANDARD ERROR OF THREE REPLICATES. 164
- FIGURE 6-2 CLAY DISPERSED FROM SIX SOILS THAT WERE MINIMALLY DISTURBED DURING SAMPLE PREPARATION AS A PERCENTAGE OF THAT PRODUCED BY SONIFICATION. SAMPLES WERE EXPOSED TO 1 MINUTE END-OVER-END SHAKING. ERROR BARS INDICATE THE STANDARD ERROR OF THREE REPLICATES 165
- FIGURE 6-3 CLAY DISPERSED FROM SIX SOILS THAT WERE MINIMALLY DISTURBED DURING SAMPLE PREPARATION AS A PERCENTAGE OF THAT PRODUCED BY SONIFICATION. SAMPLES

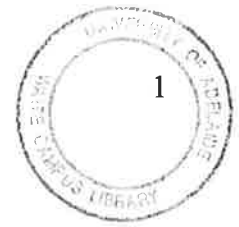
- WERE EXPOSED TO 15 MINUTES END-OVER-END SHAKING. ERROR BARS INDICATE THE STANDARD ERROR OF THREE REPLICATES. 167
- FIGURE 6-4 CLAY DISPERSED FROM SIX SOILS THAT WERE MINIMALLY DISTURBED DURING SAMPLE PREPARATION AS A PERCENTAGE OF THAT PRODUCED BY SONIFICATION. SAMPLES WERE EXPOSED TO 2 HOURS END-OVER-END SHAKING. ERROR BARS INDICATE THE STANDARD ERROR OF THREE REPLICATES. 168
- FIGURE 6-5 CLAY DISPERSED FROM SIX SOILS THAT WERE MINIMALLY DISTURBED DURING SAMPLE PREPARATION AS A PERCENTAGE OF THAT PRODUCED BY SONIFICATION. SAMPLES WERE EXPOSED TO 16 HOURS END-OVER-END SHAKING. ERROR BARS INDICATE THE STANDARD ERROR OF THREE REPLICATES. 170
- FIGURE 6-6 COMPARISON OF THE AVERAGE DISPERSION OF THREE REPLICATES OF WIMMERA SOIL PREPARED USING TWO METHODS. ERROR BARS ARE THE STANDARD ERROR OF THE AVERAGE DISPERSION. DARK BARS ARE THE "NATURAL" AGGREGATES AND THE LIGHT BARS ARE THE "SYNTHETIC" AGGREGATES. 174
- FIGURE 6-7 COMPARISON OF THE AVERAGE DISPERSION OF THREE REPLICATES OF TOMKI SOIL PREPARED USING TWO METHODS. ERROR BARS ARE THE STANDARD ERROR OF THE AVERAGE DISPERSION. DARK BARS ARE THE "NATURAL" AGGREGATES AND THE LIGHT BARS ARE THE "SYNTHETIC" AGGREGATES. 176
- FIGURE 6-8 COMPARISON OF THE AVERAGE DISPERSION OF THREE REPLICATES OF TATURA SOIL PREPARED USING TWO METHODS. ERROR BARS ARE THE STANDARD ERROR OF THE AVERAGE DISPERSION. DARK BARS ARE THE "NATURAL" AGGREGATES AND THE LIGHT BARS ARE THE "SYNTHETIC" AGGREGATES. 178
- FIGURE 6-9 COMPARISON OF THE AVERAGE DISPERSION OF THREE REPLICATES OF BELALIE SOIL PREPARED USING TWO METHODS. ERROR BARS ARE THE STANDARD ERROR OF THE AVERAGE DISPERSION. DARK BARS ARE THE "NATURAL" AGGREGATES AND THE LIGHT BARS ARE THE "SYNTHETIC" AGGREGATES. 179
- FIGURE 6-10 COMPARISON OF THE AVERAGE DISPERSION OF THREE REPLICATES OF BORDERTOWN SOIL PREPARED USING TWO METHODS. ERROR BARS ARE THE STANDARD ERROR OF THE AVERAGE DISPERSION. DARK BARS ARE THE "NATURAL" AGGREGATES AND THE LIGHT BARS ARE THE "SYNTHETIC" AGGREGATES. 181
- FIGURE 6-11 COMPARISON OF THE AVERAGE DISPERSION OF THREE REPLICATES OF MT MADDEN SOIL PREPARED USING TWO METHODS. ERROR BARS ARE THE STANDARD ERROR OF THE AVERAGE DISPERSION. DARK BARS ARE THE "NATURAL" AGGREGATES AND THE LIGHT BARS ARE THE "SYNTHETIC" AGGREGATES. 182

LIST OF TABLES

TABLE 2-1 THE RATIO OF SODIC TO SALINE SOILS FOR EACH CONTINENT.	13
TABLE 2-2 SUMMARY OF THE CHARGE CHARACTERISTICS OF THREE MINERALOGICAL TYPES. ...	19
TABLE 2-3 FRACTION OF MAGNESIUM PRESENT IN THE SOIL SOLUTION AS THE ION PAIR $MgOH^+$	39
TABLE 3-1 SOILS INFORMATION.	53
TABLE 3-2 COMPARISON OF SOIL AND CLAY CEC.	56
TABLE 3-3 REPLICATE WATER CONTENTS OF SOILS AND CLAYS USED TO DETERMINE SURFACE AREA.	57
TABLE 3-4 SOME CHEMICAL AND PHYSICAL CHARACTERISTICS OF THE SOILS.	59
TABLE 3-5 ELECTRICAL CONDUCTIVITY ($\mu S/CM$) OF 1:5 EXTRACT OF SOILS AFTER	60
TABLE 4-1 PH RANGE OF DISPERSED CLAY SUSPENSIONS.....	73
TABLE 4-2 SUMMARY OF RESULTS FOR MECHANICAL DISPERSION OF SIX SOILS SATURATED WITH MAGNESIUM, CALCIUM, STRONTIUM AND BARIUM, EACH WITH ESP VALUES OF 0 - 20.	96
TABLE 4-3 CHARGE PROPERTIES OF THE SOILS USED IN THE STUDY.	98
TABLE 4-4 WATER ADSORPTION AT 100 CM SUCTION OF SOILS USED IN THIS STUDY.	100
TABLE 5-1 THE EXCHANGEABLE CATIONS PRESENT IN EACH TREATMENT.....	112
TABLE 5-2 SUMMARY OF RESULTS FOR MECHANICAL DISPERSION OF SIX SOILS WITH DIFFERING CALCIUM AND MAGNESIUM RATIOS AND ESP VALUES RANGING FROM 0 TO 20.....	147
TABLE 5-3 COMPARISON OF SOME FEATURES OF THE WIMMERA AND TOMKI SOILS.....	149
TABLE 6-1 FINAL ESP OF SAMPLES PRODUCED USING A METHOD FOR ACHIEVING TARGET ESP VALUES OF 2 AND 6, WHICH INVOLVED MINIMAL DISTURBANCE OF THE SOIL STRUCTURE.	160
TABLE 6-2 CALCULATED GAPON CONSTANTS FOR EACH TARGET ESP OF THE SIX SOILS.	162

LIST OF APPENDICES

APPENDIX 1 XRAY DIFFRACTION PATTERNS FOR WHOLE AND FINE CLAY OF THE SIX SOILS CHARACTERISED.	218
APPENDIX 2 PORE SIZE DISTRIBUTION DATA OF WHOLE NATURAL SOIL (1-2 MM AGGREGATES) FOR THE SIX SOILS CHARACTERISED.	224
APPENDIX 3 MEAN PARTICLE SIZE DISTRIBUTION OF DISPERSED CLAY FROM SAMPLES WITH VARIOUS ESP VALUES AND THE EXCHANGE COMPLEX COMPLETED FROM THE GROUP II CATIONS.	230
APPENDIX 4 MEAN PARTICLE SIZE OF CLAY DISPERSED FROM TREATMENTS WITH DIFFERENT CALCIUM:MAGNESIUM RATIOS AND ESP VALUES.	235
APPENDIX 5 ZETA POTENTIAL MEASUREMENTS OF DISPERSED SOIL SAMPLES CALCIUM OR MAGNESIUM DOMINATED AND WITH VARIOUS ESP VALUES.	241
APPENDIX 6 MEAN PARTICLE SIZE MEASUREMENTS OF DISPERSED CLAY FROM REPLICATE "NATURAL" AGGREGATE SAMPLES PREPARED WITH MINIMAL DISURBANCE TO AGGREGATE STRUCTURE.	242
APPENDIX 7 COMPARISON OF MEAN PARTICLE SIZES OF DISPERSED CLAY SAMPLES PREPARED BY REMOULDING ("SYNTHETIC") AND WITH MINIMAL DISTURBANCE ("NATURAL") TO AGGREGATE STRUCTURE.	243



1. Introduction

Sodic soils are a widespread problem for Australian land managers, with 25% of the land mass being sodic (Rengasamy & Olsson 1991). Many land managers may not even be aware that they have sodic soils, and this knowledge would improve the sustainability of the land. Sodicty causes dispersion of clay throughout the soil profile resulting in infiltration problems and hardsetting. Sodic topsoils form crusts which contribute to surface erosion. Sodic soils have traditionally been defined in terms of exchangeable sodium percentage (ESP). A soil is generally defined as sodic on the basis of a critical ESP value. The US Salinity Laboratory Staff (1954) defined a soil as sodic if it had an ESP of 15 or higher, while in Australia the more commonly accepted value is 6 (Northcote & Skene, 1972). The differences in critical ESP values between the two countries was discussed by Shainberg *et al.*, (1980), Shainberg & Letey (1984) and McIntyre (1979) and the electrolyte concentration of the water used to determine the limits resulted in the different critical ESP values. The ESP for Australian soils related to soil exposure to pure water. Permeability studies by Quirk & Schofield (1955) showed that there was no basis for dividing soils into sodic and non-sodic using a critical ESP value. They observed that, with increasing ESP, soil permeability decreased as the solute concentration decreased below a critical level (threshold level). Later work by Emerson & Chi (1977), Shainberg *et al.* (1980) and Alperovitch *et al.* (1985) also indicated that soils with ESP values lower than 6 dispersed spontaneously, giving further support to the suggestion that use of a critical ESP value to define sodic soils is not suitable. Despite these results, soils continue to be defined as sodic and non-sodic by ESP in the

literature and this distinction will be used in this study since it is a widely accepted practice.

The most effective treatment of sodic soils is the application of gypsum, which has a two-fold effect. One, the exchangeable sodium is replaced by exchangeable calcium on clay surfaces thereby decreasing the propensity for dispersion (Shainberg *et al.*, 1991). Two, flocculation is promoted by increasing the electrolyte concentration in soil (Rengasamy *et al.*, 1984b). The influence of organic matter on sodic soil stability is still controversial with some studies indicating that the presence of organic matter can increase dispersion (Emerson, 1983; Durgin & Chaney, 1984). Recent work on organic matter and sodic soils has demonstrated many benefits from the incorporation of organic matter into sodic soils (Nelson & Oades, 1996) and further investigation in this area may lead to amelioration practices using organic matter that compliment, and partly replace, of gypsum.

The most obvious visual indication of a sodic soil is clay dispersion. Spontaneous dispersion of clays is governed by interparticle forces in situations where no outside force is imparted into the system. Interparticle forces result from the charge on the clay surfaces (due to isomorphous substitutions in the crystal lattice) and the exchangeable cations in the system. There are attractive and repulsive forces that operate over a range of distances. The attractive forces between particles are van der Waals and ion-ion correlation forces. Van der Waals forces arise from the fluctuating dipoles between atoms and decay much more slowly between macroscopic bodies than single atoms. This makes van der

Waals forces more effective over a longer range which results in a force that can still be important at relatively large distances. The ion-ion correlation forces, in contrast, are only important at close distances of surface approach (1nm or less). Ion-ion correlation forces only occur when polyvalent ions balance the surface charge or when the clay has a high density of surface charge (Kjellander & Marcelja, 1988). Ion-ion correlation forces between overlapping particles in Ca-illite and Ca-montmorillonite result in the stability of these clays and, ultimately, to their insensitivity to changes in electrolyte concentration.

The repulsive forces are due to diffuse double layers and hydration forces. Diffuse double layers consist of a layer of ions near the surface of the clay (the Stern layer), which is approximately 0.55nm thick (Quirk, 1994), and a second more diffuse layer, the Gouy layer, where there is an excess of counter-ions over co-ions. The width of the diffuse layer is affected by electrolyte concentration and cation valency. It decreases in size as the electrolyte concentration increases (Everett, 1988) and is much less populated when calcium, rather than sodium is the counter ion. The swelling observed in Na-montmorillonites is a result of the formation of diffuse layers near the clay surfaces. Double layers also explain the changes in basal spacings observed with changes in sodium chloride concentration (Norrish, 1954). Hydration or structural forces are also repulsive and arise from disruption of the solvation zone, the area around a cation where the properties of water are significantly different from the bulk solution (Israelachvili, 1988). The strength of these forces depends on the energy required to ultimately dehydrate the two particle surfaces as they come together. The hydration force only occurs when a critical number of cations, different for

each cation, have been adsorbed onto the surface of the clay. Between smooth mica surfaces in salt solutions of high concentration the strength and range of the hydration force decreased in the order $Mg > Ca > Li \sim Na > K > Cs$ (Pashley, 1981a,b; Pashley & Israelachvili, 1984).

The percentage of dispersible clay in a soil has been shown to control the physical condition of the soil (Shanmuganathan & Oades, 1982). Many soil properties are affected by clay dispersion. The ability of soil to conduct water (hydraulic conductivity) is one of these soil properties. Generally hydraulic conductivity decreases with increasing ESP when distilled water is used to leach soil (Alperovitch *et al.*, 1985). Most changes in hydraulic conductivity occur in the ESP range 5 –15 (Martin *et al.*, 1964). Like most soil properties, the exact electrolyte concentration and ESP required to reduce hydraulic conductivity is soil specific (Frenkel *et al.*, 1978). Soil strength is also affected by dispersion. Barzegar *et al.* (1994) found that in remoulded soils the amount of clay spontaneously dispersed was more dependent on clay content than on ESP. However exchangeable cations still play an important role in soil strength with sodium-magnesium soils having higher strengths than sodium-calcium soils over the ESP range 0-20 (Aylmore & Sills, 1982; Dexter and Chan, 1991).

The effects of sodium and calcium on soil properties are widely documented (Yaron & Thomas, 1968; Agassi *et al.*, 1981; Shainberg, 1985; Mullins *et al.*, 1987) and some of these effects were mentioned above. However, the effects of the cations potassium and magnesium on soil are perhaps less well documented. The potassium content of Australian soils is generally quite low (Williams &

Raupach, 1983). Quirk and Schofield (1955) found the permeability of potassium-soils was less sensitive to electrolyte concentration than sodium-soils. Furthermore, Brooks *et al.* (1956) observed that despite various combinations of sodium and potassium in soil, the effect of sodium on permeability dominated. Increases in exchangeable potassium have been shown to decrease hydraulic conductivity and infiltration rate in illitic and kaolinitic soils (Levy & van der Watt, 1990).

Exchangeable magnesium, in contrast to potassium, is present in many Australian soils in similar proportions to exchangeable calcium (Isbell, 1986). The selectivity of soils for calcium over magnesium has been investigated extensively. Vermiculites seem to be the only clay mineral that preferentially absorbs magnesium over calcium (Peterson *et al.*, 1965), especially when magnesium is present as 30 to 40% of the exchange cations (Levy & Shainberg, 1972). The other major body of work on selectivity has been conducted on montmorillonites. The majority of studies indicate a preference for calcium over magnesium (Krishnamoorthy & Overstreet, 1950; Dolcater *et al.*, 1968; Levy & Shainberg, 1972, Rahman & Rowell, 1979; Hagnia & Pratt, 1988). Some studies indicate that the preference for calcium and magnesium differs in soils and clays, however these results are contradictory (Levy & Shainberg, 1972; Van Bladel & Gheyi, 1980). Gheyi and Van Bladel (1975) and Fletcher *et al.* (1984b) observed that the presence of organic matter seemed to contribute to the selectivity of either calcium or magnesium. It has been proposed that montmorillonite soils have specific sites for magnesium and calcium and once these sites have been filled then no preference is displayed (Beckett, 1965). Although there has been

less work on kaolinites and illites, these studies again indicated contradictory results on calcium and magnesium selectivity (Chi *et al.*, 1972; Hunsaker & Pratt, 1971; Tucker, 1985).

The most commonly observed effect of magnesium on soils seems to be its enhancement of sodic behaviour. In smectitic soils, behaviour would indicate that at a given SAR, more exchangeable sodium is present in a sodium-magnesium system than a calcium-sodium system (Curtin *et al.*, 1994b). For an illitic soil an ESP of 3 was found to be sufficient for a sodium-magnesium soil to disperse, compared with the ESP of 6 required in a sodium-calcium soil (Emerson & Bakker, 1973). Hydraulic conductivity has also been shown to be more affected in a sodic soil when magnesium is the complimentary ion as opposed to calcium (Curtin *et al.*, 1994b). The dominant result seems to be that the unfavourable effects of exchangeable magnesium are only observed when the calcium:magnesium ratio is greater than a value specific for that soil (Rengasamy *et al.*, 1984a). Emerson and Chi (1977) proposed that calcium soils are more stable than magnesium soils due to calcium ions being more strongly adsorbed on the clay surface. This was disputed by Bakker *et al.* (1973) who found the strengths of adsorption for calcium and magnesium to be similar. Instead they proposed that differences in the hydration energy may explain soil stability differences.

Another proposed explanation for decreased stability in magnesium soils has been the presence of single charged species such as $MgCl^+$ and $MgOH^+$. Sposito *et al.* (1983a) found that the $CaCl^+$ complex was more stable and had a higher

affinity for clay than MgCl^+ , while Tucker (1985) discounted the effects of MgCl^+ and MgOH^+ on the basis of CEC calculations. The role of magnesium in soil structure is of particular importance in Australia since some soils contain equivalent amounts of exchangeable calcium and magnesium (Isbell, 1986). To further understand the influence of magnesium on structural stability, the impact of the group II cations magnesium, calcium, strontium and barium on dispersion was investigated here to observe any trends in the response of soils to these cations.

The majority of the research into the effect of exchangeable magnesium has been carried out on soils that have magnesium as the dominant exchangeable cation (Rowell & Shainberg, 1979; Alperovitch *et al.*, 1981; Rengasamy *et al.*, 1986). This situation is unusual in the field, where soils usually contain a mixture of cations, mainly calcium, magnesium and sodium, plus various other cations in small amounts. Therefore it seems important to investigate the dispersion of soils that have a range of exchangeable sodium percentages and a range of calcium and magnesium ratios. This will determine if a threshold percentage of magnesium is required resulting in significantly more dispersion in soils.

The effects of sodicity on soils has also been investigated with respect to their mineralogy. Montmorillonites are considered the clay minerals most sensitive to sodicity (Frenkel *et al.*, 1978), and appear to have the most influence on soil erodibility. Soils with only a small amount of montmorillonite present can behave as montmorillonite dominant soils and disperse readily. Of interest in calcium dominated montmorillonite soils is the formation of quasi-crystals

containing 4 – 9 particles, which make them prone to “de-mixing” (Shainberg & Otoh, 1968). De-mixing is the process where the external surfaces of the quasi-crystals are saturated with sodium while the calcium ions remain on the internal surfaces. Shainberg and Otoh (1968) found that this explained why montmorillonitic soils with ESP 10 can be structurally sound. They also found that the quasi-crystal did not break up until ESP 15, and only separated completely at ESP 50. The stability of illitic soils seems to depend on the particle size and shape of the clay (Grim, 1962). De-mixing has also been detected in illites (Lebron *et al.*, 1993). For kaolinites the stability of the sodium form depends on many factors, including pH and domain formation. Sodic kaolinites are less stable at low pH (Lebron & Suarez, 1992). Well crystallised kaolinites disperse less readily than poorly crystallised kaolinites. The amount of montmorillonite in a kaolinite soil can also affect the ability of the soil to disperse, the more montmorillonite present the less stable the soil (Frenkel *et al.*, 1978). Prediction of sodic soil behaviour on the basis of mineralogy is difficult, however if similarities due to mineralogy can be found this will make it easier to define soil behaviour.

Much of the research on sodicity has been conducted on soils with ESP values greater than 10 (McNeal & Coleman, 1966; McNeal *et al.*, 1968; Frenkel *et al.*, 1978; Shainberg *et al.*, 1980; Shainberg *et al.*, 1981; Astarai & Chauhan, 1992). Little work has been done on weakly or non-sodic soils. Their importance cannot be overlooked simply because they are not classified as sodic and therefore not considered a problem. Most of the work that has been done on weakly and non-sodic soils has been conducted on American (Shainberg *et al.*,

1980) and Israeli (Pupisky & Shainberg, 1979; Kazman *et al.*, 1983) soils. The ramifications of this work on the area of land considered as affected by sodium are huge. Areas traditionally determined as non-sodic may respond to amelioration resulting in increased productivity and sustainability. Hence investigations into the response of soils to conditions where exchangeable sodium is present but which are described as non-sodic (Northcote & Skene, 1972) is important for land management.

There is a wide body of literature on the stability of soil under sodic conditions. Many of the soils used are disturbed from their original condition and exposed to agitation and disruption in the laboratory. The applicability of these results to field conditions, where the soil has not been disturbed by shaking and repeated washing, are unknown. A method to induce sodic conditions in "natural" aggregates (soils that have not been crushed and/or sieved) with minimal disturbance of aggregate structure is needed. This would enable a comparison of the dispersion of soils that have been vigorously manipulated ("artificial" soils) with that of soils which are still in a relatively "natural" state. This should provide an indication of the applicability of laboratory data to field situations.

Therefore the aims of this research were:

- 1) To observe the response of six Australian soils with a range of exchangeable sodium values to various levels of mechanical disturbance.
- 2) To investigate the effect of magnesium on the dispersion of six Australian soils exposed to various levels of mechanical dispersion.

- 3) To detail any mineralogical influences upon the response of the six Australian soils to the various conditions in the first two aims, and
- 4) To develop a method for inducing sodicity in soils that does not vigorously disrupt the aggregate structure and to then use these soils to compare the applicability of results from more artificially manipulated soils to those in the field.

2. Literature Review

2.1. Introduction

Australian soils, due to their extreme age, are relatively fragile, especially when compared to those of the northern hemisphere where the soils are the result of relatively recent glacial periods. Australian soils have generally not responded well to European settlement (Jenkin, 1986) and the demand for a highly productive agricultural industry is partly to blame. Australian soils are plagued by low organic matter, weak structural development, hard-setting characteristics, water repellence, strong textural contrasts, bleached A₂ horizons, acidification and salt accumulation. These features make Australian soils particularly prone to erosion and can restrict plant establishment and growth.

Salt-affected soils are endemic in the arid and semi-arid areas of the world, with these areas particularly susceptible to degradation from salt problems. Arid and semi-arid areas constitute about 70% of Australia (Figure 2-1), which makes this land particularly prone to the effects of salt. Salt-affected soils are divided into two classes, sodic and saline. Saline soils contain substantial concentrations of soluble salt (usually sodium chloride) in the soil solution, while sodic soils contain exchangeable sodium on the surfaces of the soil particles. It follows then that virtually all saline soils are sodic but all sodic soils are not necessarily saline. Australia has the highest area of salt-affected soils in relation to total surface area of any continent of the world. Approximately one quarter of the landmass is covered by sodic soil while only 5% is affected by salinity (Table 2-1). It is difficult to get an accurate global estimate of the extent of sodic and saline soils because severity is extremely variable and the area affected increases constantly (Szabolcs, 1989). Also, unless the problem is well advanced, the

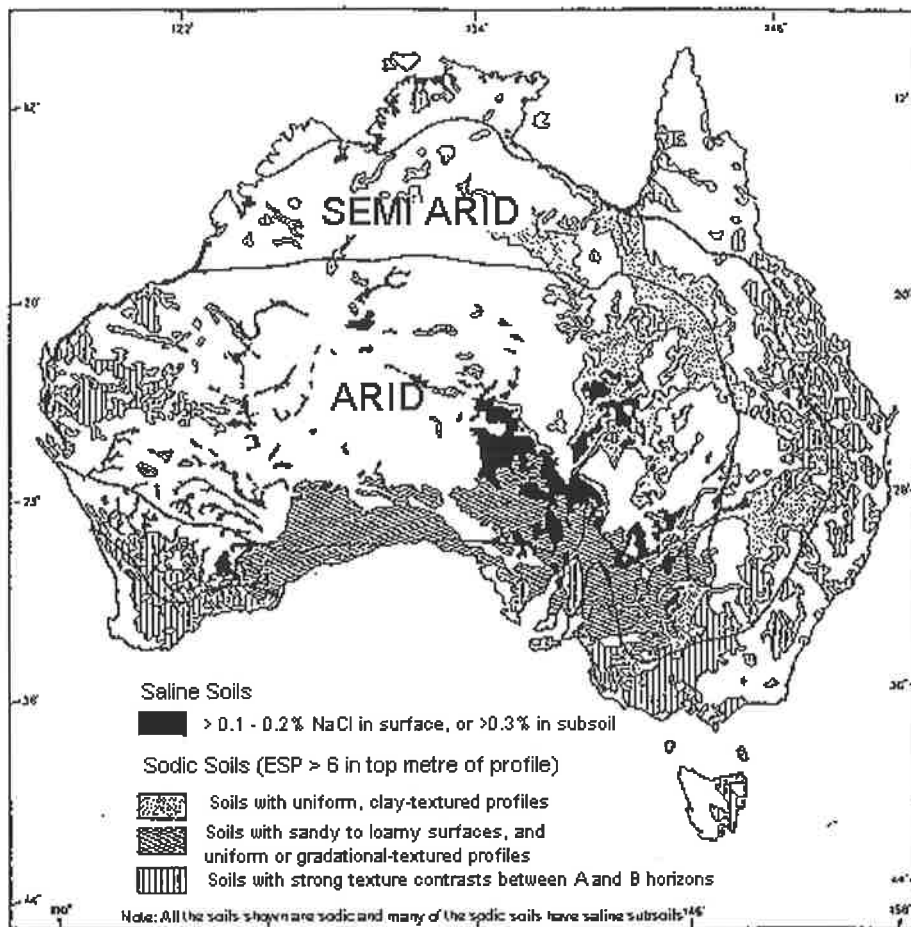


Figure 2-1 Arid, semi-arid and salt-affected areas of Australia (based on Isbell, (1983) and McGinnies *et al.*, (1968))

Table 2-1 The ratio of sodic to saline soils for each continent.

Continent	Sodic soils % of total area	Saline soils % of total area	Ratio of sodic to saline soils.
Australia*	25	5	5:1
North America*	0.3	0.3	1:1
South America*	3.3	4.0	0.8:1
Africa*	0.8	1.8	0.4:1
Europe ^o	2.6	0.75	3.5:1
Asia*	2.8	4.5	0.6:1

* Rengasamy and Olsson, (1991).

^o Szabolcs, (1989).

effects of sodicity are insidious. There may be few perceived effects of sodification but crop yields or the range of possible land uses for an area may be significantly affected.

According to estimates of competent international organisations affiliated with the United Nations, more than half of all irrigated lands in the world are becoming salt-affected. These estimates do not include soils affected as a result of dryland farming. This indicates how urgently more research into salt-affected soils is required.

Sodic soils are formed in two ways; either the high levels of exchangeable sodium are produced in-situ from the weathering of parent rock material, or, saline profiles are leached of salts. The most effective way of treating sodic soils is by replacing the exchangeable sodium or by minimising its effect. At this time, the best treatment appears to be the application of gypsum, which has a twofold effect on sodic soils. It replaces some of the exchangeable sodium with exchangeable calcium (Shainberg *et al.*, 1989) and raises electrolyte concentration in the soil, promoting flocculation (Rengasamy *et al.*, 1984b). Further improvements occur if stubble retention and incorporation are included as part of the soil management strategy (Robbins, 1986).

2.2. Defining sodicity and sodic soils

No universal definition of sodic soils has been accepted, but Northcote & Skene (1972) define a sodic soil as one that contains sufficient exchangeable sodium to interfere with the growth of most crop plants. Traditionally, a critical ESP value is used to distinguish sodic from non-sodic soils. The US Salinity Laboratory Staff (1954) defined sodic soils as those with an ESP of 15 or higher; in Australia the more generally accepted value is 6 (Northcote & Skene, 1972). This difference in the critical ESP value is very important as soils with low ESP values (between 6 and 15) are widespread in arid and semi-arid regions (Shainberg *et al.*, 1989). Thus the occurrence of dispersive and unstable soils that might respond to gypsum application is much wider than previously thought if one accepts the Australian definition of a sodic soil. The reason for the difference in critical sodium level between America and Australia is necessary for an understanding of dispersive soils. In the U.S. Salinity Laboratory, the hydraulic conductivities of disturbed soil samples were measured using tap water whose electrolyte concentration was 5-10 mmol(+)/l (Shainberg *et al.*, 1980; Shainberg & Letey, 1984). At these electrical conductivities, relatively high ESP values are needed to reduce hydraulic conductivity (Shainberg *et al.*, 1980). Conversely, in Australia, distilled water with an electrical conductivity of only 0.7 mmol(+)/l was used (McIntyre, 1979). This is not sufficient to offset the dispersive effect of exchangeable sodium, even at very low levels. When Australian soils are exposed to rainwater (distilled water), susceptibility to small amounts of exchangeable sodium is further exacerbated by raindrop impact, which causes mechanical dispersion along with spontaneous dispersion (Oster & Schroder, 1979; Agassi *et al.*, 1985). The notion of a critical level of exchangeable sodium defining a sodic soil may not be valid since it has been shown that soils with ESP values lower than six can also disperse spontaneously (Emerson & Chi, 1977; Shainberg *et al.*, 1980; Alperovitch *et al.*, 1985). Hence,

the definition of sodicity needs to be based on the behaviour of soil when sodium is present rather than on the ESP alone.

An important consideration in sodic soils is the composition of solution from which exchangeable sodium may derive. A useful index for predicting this tendency is the sodium adsorption ratio, (SAR), defined as:

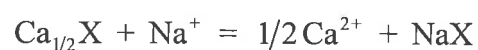
$$\text{SAR} = \frac{[\text{Na}^+]}{([\text{Ca}^{2+}] + [\text{Mg}^{2+}])^{\frac{1}{2}}}$$

Where:

[] signifies concentration in mmol/l.

SAR is a good indicator of the relative degree to which exchangeable sodium accumulates on the exchange sites of soil exposed to a given solution. Although ESP was originally used as the main criterion for excessive sodium levels, emphasis has shifted more recently to the use of the SAR of the equilibrium solution (Bresler *et al.*, 1982).

The ESP of a soil depends the SAR. Cation exchange equations describe the distribution of cations between the exchanger phase (in this case the clay surface) and its equilibrium solution. Of the numerous equations proposed (Bolt, 1967) linking the relative activities of ions in solution to their relative proportions as exchangeable ions, the Gapon equation is the simplest. The Gapon constant, resulting from the Gapon equation, gives a measure of the relative tightness with which a cation is held to the clay. The Gapon equation is derived from the modified mass-action equation,



and results in the following equilibrium constant (Tan, 1993):

$$K_G = \frac{[Ca^{2+}]^{1/2} (NaX)}{[Na^+] (Ca_{1/2}X)}$$

Where:

() and [] refer to the concentrations of adsorbed and free ions respectively.

Although ion activities can be quite different from ion concentrations, over the concentration ranges common to salt-affected soil, the ratio of ion concentrations is of similar magnitude to the corresponding ratio of ion activities (Shainberg & Letey, 1984).

2.3. The relationship between carbonate, pH and sodicity

The maximum concentration of many cations in the soil solution is limited by the presence of carbon dioxide, with the presence of solid phase carbonates stabilising the concentration of other cations in the soil solution. The most abundant carbonate-forming cation is calcium and many soils contain solid calcium carbonate due to its low solubility. In a calcareous soil, the pH of the soil depends on the partial pressure of carbon dioxide in the soil atmosphere. Modification of soil pH is one way of improving the soil response to sodic conditions. The pH of soil can be modified by adding calcium and magnesium carbonates to neutralise acidic soils, or by adding sulfur, ammonia, ammonium salts, iron or aluminium sulphates to acidify soil.

If water with an appreciable concentration of bicarbonates is used for irrigation, some of the bicarbonate will precipitate as calcium carbonate. This precipitation causes a decrease in soil salinity but an increase in the proportion of sodium in

the soil solution and on the exchange complex of the soil. The tendency of calcium carbonate to precipitate from water is a useful way to appraise water quality. Langelier devised the "saturation index" to predict in a closed system whether flowing water would precipitate or dissolve calcium carbonate. The saturation index is defined as the actual pH of the water (pH_a) minus the theoretical pH (pH_c) that the water would have if it were in equilibrium with calcium carbonate ($\text{Saturation index} = \text{pH}_a - \text{pH}_c$). Langelier's equation for calculating pH_c from water analysis is:

$$\text{pH}_c = (\text{pK}'_2 - \text{pK}'_c) + \text{pCa} + \text{pAlk}$$

where:

pK'_2 = the negative logarithms of the second dissociation constant of H_2CO_3

pK'_c = the solubility product of CaCO_3 .

pCa = the negative logarithm of the calcium concentration of the water (mol/l).

pAlk = the negative logarithm of the titratable base (carbonate plus bicarbonate) concentration of the water (eq/l).

Langelier's equation was derived for a closed system and modifying the index to measure the tendency of irrigation water to precipitate calcium carbonate (pH_c) in a soil of a given pH is possible. The pH of the highly buffered soil is substituted for that of the poorly buffered irrigation water (pH_a , Bower *et al.*, 1965).

2.4. Clay mineralogy

The following section is based on Grim (1968), Dixon & Weed (1977), Greenland & Hayes (1978) and Brindley & Brown (1980). Clay minerals are distinguished from other mineral groups because they are small imperfect crystals that largely determine the surface chemical and bulk physical properties of soils. Clay minerals are mainly of the phyllosilicate class, structurally based

on sheets of silica tetrahedra linked to aluminium octahedra. The bonds between the sheets vary in strength, and the oxygen exposed at the edges of the lattice structure can also form weak bonds with other ions.

The tetrahedral and octahedral sheets of clay minerals can be stacked with different repeat patterns eg. 1:1, 2:1 (the ratio of tetrahedral to octahedral sheets in each type of crystal unit). This enables the clay minerals to be divided into major groups.

The surface charge on clays has two origins; isomorphous substitution in the lattice of silicon and aluminium by cations with generally lower valencies leading to permanent surface charge. The other source is variable charge, and is due to the interaction of exposed hydroxyl groups and oxygen atoms of the lattice structure with the solution. Variable charge is pH-dependent because of adsorption and desorption of H^+ ions onto or from the exposed clay mineral edges. The magnitude of total charge varies with the mineralogy of the clay and the extent of exposed surfaces; both types of charge contribute to the cation exchange capacity. The different physical properties of clays also impact on sodic soil stability and this is discussed later.

The clay mineral groups of concern here are kaolinite, mica (illites), and smectites (montmorillonite). No other types of clay minerals were important in the soils in this study. The particular characteristics that identify each group of minerals from the others are shown in Table 2-2.

Table 2-2 Summary of the charge characteristics of three mineralogical types.

Structure type	Name	Species	Variable charge	CEC (meq/100gm)
1:1	kaolin	kaolinite	high	3-15*
2:1	smectite	montmorillonite nontronite beidellite	low	80-150*
	mica	illite	low	10-40*

*Grim, (1968)

2.4.1. Kaolinite

Kaolinite is usually abundant in strongly weathered soils. The kaolinite crystal has a 1:1 non-expandable structure (Figure 2-2) with a single silica tetrahedral sheet and a single alumina octahedral sheet combining to form a unit. There is little isomorphous substitution in kaolinite and consequently there is little or no permanent charge. However, due to the presence of exposed hydroxyl groups, kaolinite has some variable, or pH-dependent charge. The cation exchange capacity is very small (3-15 meq/100g) and changes with pH (Grim, 1968). Due to the close association of adjacent units in a crystal, kaolinite particles are not easily broken down and the kaolinitic soils have low plasticity, shrinkage and swelling properties (Grim, 1962a). The low negative charge of kaolinite makes it generally less dispersive when compared to the other clay mineral types (Velasco-Molina *et al.*, 1971; Frenkel *et al.*, 1978). The positive edge sites under low pH conditions and the presence of exchangeable cations held firmly on the surface of the clay also contribute to the tendency of kaolinites to flocculate in acidic environments.

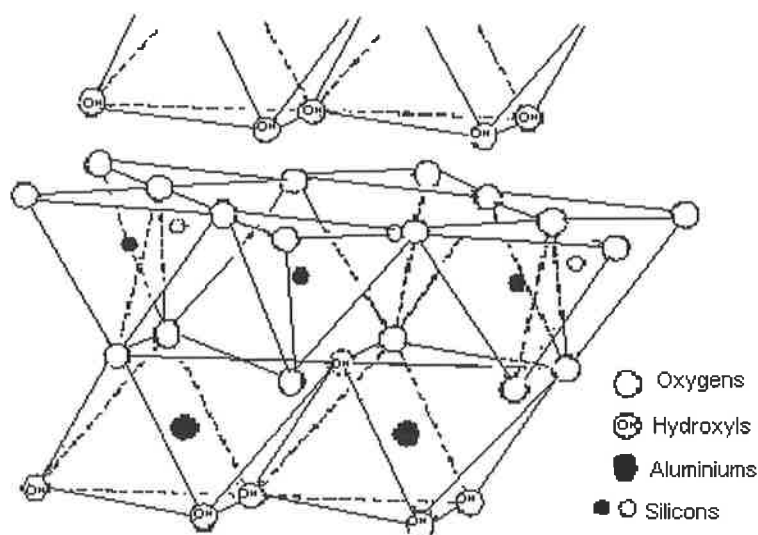


Figure 2-2 Mineral structure of kaolinite, (after Grim, 1968)

2.4.2. Smectite

Smectites are 2:1 expanding layer minerals (Figure 2-3) with a symmetric unit cell structure. The 2:1 mineral has one aluminium octahedral sheet sandwiched between two silica tetrahedral sheets with the tips of the silica tetrahedra pointing into the centre of the unit. The bonds holding the layers together are relatively weak, allowing interlamellar regions to expand with increasing moisture content. Isomorphous substitution of magnesium and ferrous iron for aluminium in the octahedral positions, and aluminium for silicon in the tetrahedral positions of smectites, creates a large permanent negative charge on the clay surface resulting in a relatively high CEC (80-150 meq/100g, Grim, 1968). Smectites have low variable charge, since many of the hydroxyl groups are located in sub-surface planes and so their CEC is only slightly pH dependent. The large CEC of smectitic soils makes them important in soil fertility as nutrient cations are secured against leaching.

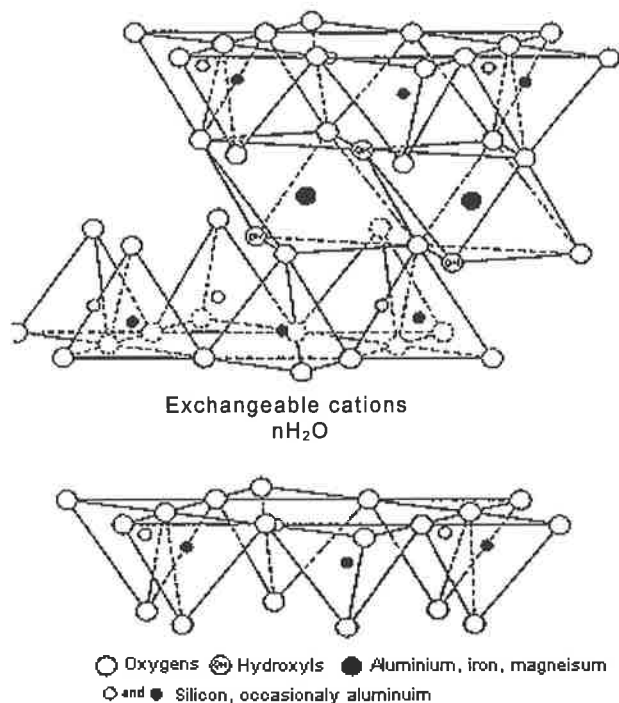


Figure 2-3 Mineral structure of smectite, (after Grim, 1968)

2.4.3. Illite

Illites are also 2:1 layer clays (Figure 2-4) but unlike smectites they do not expand. Isomorphous substitutions occur in both the tetrahedral and octahedral sheets causing a high permanent charge. The main difference between illites and montmorillonite is that illites contain interlayer potassium strongly held in the ditrigonal holes of the oxygen planes of two adjacent tetrahedral sheets. This produces stronger bonds between the unit layers than in montmorillonite, preventing swelling on the same scale. The potassium also reduces the availability of sites for cation exchange, and so the cation exchange capacity of illites is smaller than that of montmorillonites, about 10-40 meq/100g (Grim, 1968), despite the higher degree of isomorphous substitution. The physical properties of illites are more similar to those of kaolinites than montmorillonites.

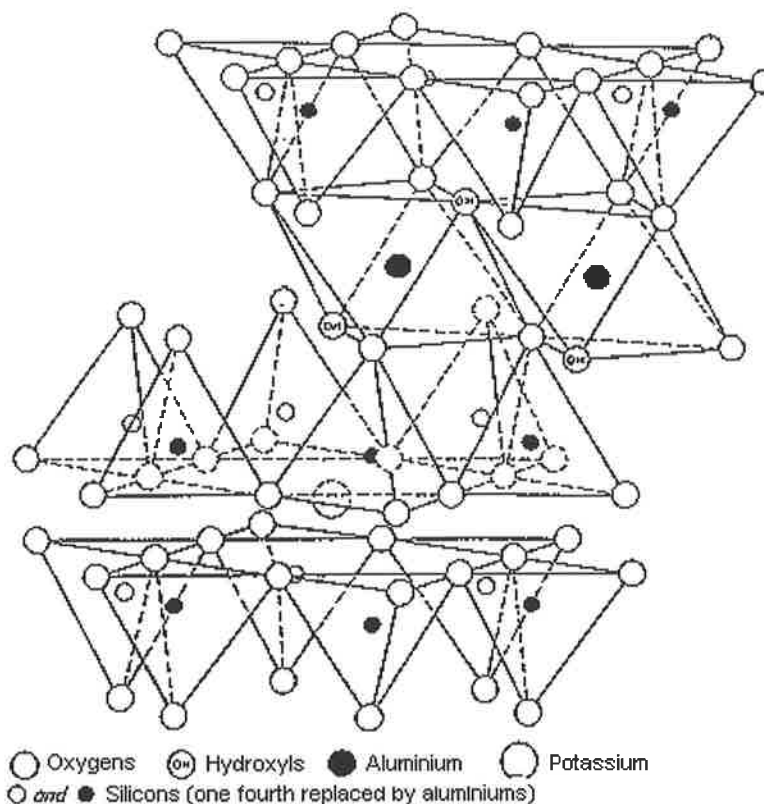


Figure 2-4 Mineral structure of illite, (after Grim, 1968)

2.5. The nature of dispersion and its effect on soil properties

Dispersion is the most obvious visual characteristic of sodic soils. Dispersion can be defined simply as the detachment of clay particles from soil aggregates and their subsequent mobilisation in suspension. Dispersion is a consequence of either/or both the repulsive forces between aluminosilicate layers (spontaneous dispersion) or the separation of clay particles by mechanical energy (mechanical dispersion). Spontaneous dispersion arises with no physical input of energy from an external source. It occurs when dry aggregates are wet slowly and interparticle forces move the clay particles away from each other. Mechanical dispersion occurs when some form of physical energy has been imparted to the

system. This energy overcomes the attractive forces between clay particles that contribute to soil stability. It is difficult to compare dispersivity by energy inputs alone; under given conditions dispersion is related to the total amount of dispersible clay available in that particular soil. This is important because the percentage of dispersible clay controls, to a large degree, the physical condition of the soil (Shanmuganathan & Oades, 1982). Levy *et al.*, (1993b) investigated dispersion in soils with different mineralogies and found that clay dispersion in distilled water was significantly correlated with clay content.

2.6. The effect of dispersion on soil properties

2.6.1. The effect of soil conditions on hydraulic conductivity

Hydraulic conductivity is a measure of the ability of soil to transmit water and is affected by the electrolyte concentration of the soil solution, clay content and mineralogy, and by exchangeable cations. There are two mechanisms proposed for the hydraulic conductivity changes that arise from soil dispersion. The percolating solution causes clay particles to dislodge from soil aggregates and physically move down the soil profile blocking transmission pores, or alternatively, the clay swells and blocks the pores. Generally hydraulic conductivity decreases with increasing ESP when distilled water is used to leach the soil (Alperovitch *et al.*, 1985), which Shainberg *et al.* (1980) proposed was probably due to slaking, rather than mobilisation of clay particles.

In soil with nearly uniform clay mineralogy, a reduction in hydraulic conductivity can be correlated with the percentage of clay present (McNeal *et al.*, 1968) and the susceptibility of soils to sodic conditions increased with clay content (Frenkel *et al.*, 1978). When sodium was added to the system, most

hydraulic conductivity changes occurred in the ESP range 5-15 (Martin *et al.*, 1964), with the same quantities of sodium reducing the hydraulic conductivity more in acid soils than in neutral or alkaline soils. The exact level of exchangeable sodium and electrical conductivity at which hydraulic conductivity is appreciably reduced was soil specific (Frenkel *et al.*, 1978).

2.6.2. The effect of dispersion on infiltration rate

Infiltration rate is a dynamic measure of the rate of movement of water through soil; hydraulic conductivity, by contrast, is a static measurement. Surface crusts are washed-in layers in soils that are easily dispersed (Agassi *et al.*, 1981) and have a greater density, higher strength, and finer pores than bulk soil (McIntyre, 1958). Crust formation in soils exposed to rain is due to two mechanisms: (1) physical dispersion caused by the impact of raindrops, and (2) "chemical" dispersion that depends on the ESP of the soil and the electrolyte concentration of applied water (Agassi *et al.*, 1981). The above mechanisms were proposed for a weakly sodic soil subjected to high intensity rain, with the drop impact disintegrating the soil aggregate and compacting the soil into a thin seal (Agassi *et al.*, 1985). Under conditions of high ESP and low electrolyte concentration in soil, the "chemical" dispersion process plays an increasing role in determining the infiltration rate of the soil. Comparisons of infiltration rate and hydraulic conductivity data indicate that infiltration rate is affected more than hydraulic conductivity at low ESP values (Shainberg & Letey, 1984).

2.6.3. The effect of dispersion on soil stability and strength

Dispersion of clay affects the structural stability and therefore the strength of soil. Structural stability is a measure of the ability of soil to retain its structural form, over time, against external forces such as wheel traction and rainfall, and

can be quantified by measuring tensile strength. Tensile strength is calculated indirectly from the load applied to an aggregate at the point of failure. The tensile strength of remoulded soils increases as the clay content increases due to the increased number of contact points between the clay particles (Barzegar *et al.*, 1994). Analysis of spontaneous dispersion in remoulded soils showed that clay content was more important than ESP in determining the amount of clay dispersed (Barzegar *et al.*, 1994). The exchangeable cations on clay surfaces can play an important role in soil strength. The strength of sodium-magnesium and sodium-calcium soils were compared over a range of ESP values (0-20), and it was found that the sodium-magnesium soils had higher strengths (Aylmore & Sills, 1982); similar observations were made by Dexter & Chan (1991).

2.7. The effect of interparticle forces on dispersion

Forces between clay colloids are largely responsible for the dispersive behaviour of soil, and most of these forces arise from the presence of exchangeable ions on the clay surface. Attractive forces between particles promote flocculation and soil stability, while repulsive forces reduce soil stability by increasing the dispersive behaviour.

The electrostatic forces between clay particles depend, to a large degree, upon the distribution of ions near the clay surface. The Poisson-Boltzmann equation provided one of the first descriptions of the distribution of ions near a charged surface and this equation is derived in many texts (e.g. Verwey & Overbeek, 1948; van Olphen, 1963). For flat, charged clay particles suspended in a solution of a single symmetrical electrolyte the Poisson-Boltzmann equation takes the form (Low, 1981):

$$\frac{d^2 y}{d\xi^2} = \sinh y$$

Where:-

$$y = \frac{ze\psi}{kT}$$

z is the ionic valence; e is the electronic charge; ψ is the electrostatic potential at any distance, x , from the particle surface; k is the Boltzmann constant; T is the absolute temperature.

$$\xi = \kappa x$$

κ is the Debye-Huckel constant given by $\kappa^2 = 8\pi n e^2 z^2 / \epsilon k T$, where n is the number of ions per unit volume in the solution beyond the electric fields of the particles, and ϵ is the dielectric constant.

The solution of the Poisson-Boltzmann equation provides a profile of the density of ions away from the clay surface. For the ionic distribution between particles (Figure 2.5), Israelachvili (1985) calculated that the counter ion concentration on the surface of the particle was 18.5 times greater than at the midplane that is only 1 nm away. In reality the Poisson-Boltzmann equation does not allow for hydration and ion-ion interactions, which contribute to the stability of soils in conditions under which the Poisson-Boltzmann theory predicts dispersion.

2.7.1. Van der Waals forces

Van der Waals force is a term that covers the predominantly attractive forces between polar and non-polar molecules. The attractive forces between atoms arise from fluctuating dipoles caused by the motions of outer electrons. In 1937, Hamaker introduced the idea that, for conglomerates of atoms, the attractive forces are pair-wise additive, ie. the interaction of all atoms contributes to the total energy and force of interaction (Everett, 1988).

This resulted in the Hamaker constant, which is used to calculate the sum of the attractive potentials of two bodies and is dependent on the intervening media.

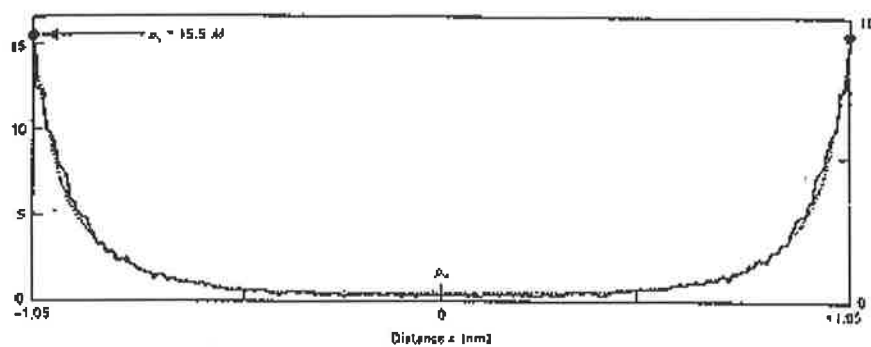


Figure 2-5 Monovalent counterion concentration profile between two charged surfaces, 2.1 nm apart in water. The smooth curve is obtained from the Poisson-Boltzmann equation; the other is from a Monte Carlo simulation by Jonsson *et al.* (1980) from Israelachvili, 1985).

The Hamaker constant is only an approximation because it ignores the influence of neighbouring atoms on the interaction between any other two atoms.

The forces between molecules and particles at large separations lose coherence and decline more rapidly and are said to be "retarded". The distance between atoms results in the dipole of the issuing atom having changed when the original force returns, which makes the atoms less favourably disposed to attraction, resulting in the retardation effect. This produces a force between atoms that decays faster than the $1/r^6$ predicted by the London equation. When applied to macroscopic bodies, the van der Waals interaction energy decays much more slowly with distance (D) than it does for two atoms ($1/D$ for spheres; $1/D^2$, for planar surfaces), and is therefore more effective over a much longer range. This becomes important when macroscopic bodies interact in a liquid medium because attractive forces can still be important at large distances.

Hamaker's simple additivity theory breaks down when many atoms are present, because the multiple reflections and extra force terms cannot be processed by the Hamaker constant. The problem of additivity is completely avoided in Lifshitz theory that relates the forces between the particles to the dielectric properties of the solids and the intervening medium. The main difference mathematically between the Hamaker and Lifshitz theories is the way the Hamaker constant is calculated. In Lifshitz theory the Hamaker constant varies with the separation between the particles, and is called the Hamaker function, $A(H)$. Lifshitz theory enables the numerical values of $A(H)$ to be calculated with some certainty, whereas the Hamaker constant for simple additivity depends on estimates of values, which are not always reliably known. The main shortcoming of the Lifshitz theory is that at very small separations, where the molecular structure of each solid is "seen" by the other, the theory becomes less reliable and some arbitrary approximations have to be made (Everett, 1988).

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2.7.2. Diffuse double layer repulsion

The diffuse double layer (DDL) consists of the charge on the clay mineral surface and the compensating counter ions. The compensating counter ions are divided into two layers. The Stern layer is closest to the clay surface and is approximately 2 water monolayers thick (Quirk, 1994). The second layer is the Gouy layer which contains an excess of counter ions. The counter ions are subject to two opposing tendencies: electrostatic attraction to the negatively charged clay surface, and the tendency for the cations to diffuse from the surface of the particle, where their concentration is high, into the bulk solution, where their concentration is lower. The two opposing tendencies result in decreasing counter ion concentrations (a diffuse layer) when moving away from the clay surface into the bulk solution.

Divalent ions are attracted to the surface with a larger force than monovalent ions, thus the diffuse double layer in divalent systems is more compressed towards the surface of the clay particle. Increasing the electrolyte concentration in the bulk solution also diminishes the tendency for the counterions to diffuse away from the surface, which compresses the DDL (Figure 2-6). Further DDL theory can be found in Bresler *et al.* (1982).

Most studies of the diffuse double layer of clay minerals have been carried out on smectites where it has been observed that most of the exchangeable cations reside on the surface of the clay (Kjellander, *et al.*, 1988a; Miller & Low, 1990). Low (1981) calculated the percentage of cations on the surface of sodium-saturated soil and found that less than 2% of the cations were in the diffuse layer with most on clay surfaces.

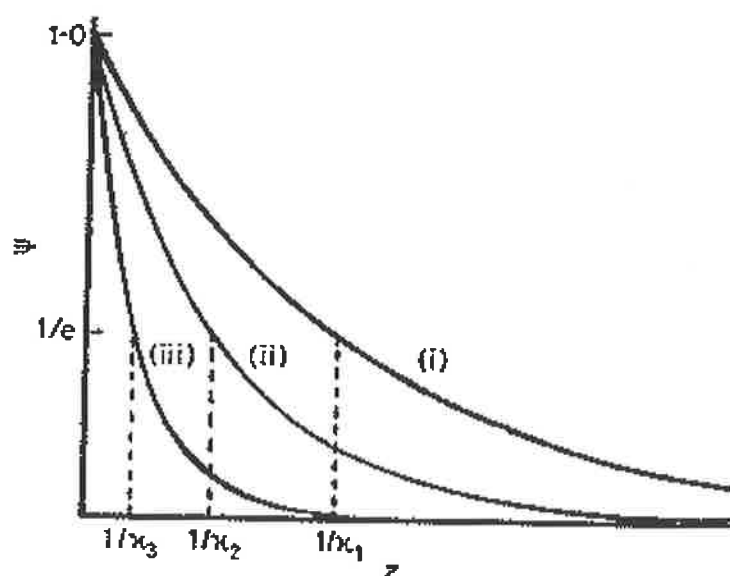


Figure 2-6 Variation in electric potential with distance from the surface and its dependence on electrolyte concentration: (i) low, (ii) medium, (iii) high electrolyte concentration. $1/\kappa$ is called the "thickness of the double layer" (Everett, 1988)

2.7.3. Derjaguin, Landau, Verwey, Overbeek (DLVO) theory

The first theory to incorporate more than one type of interparticle force was promoted by Derjaguin & Landau (1941), and Verwey & Overbeek (1948), and is called the DLVO theory. It combines van der Waals attraction and double layer repulsion. The resultant force (Figure 2-7) determines stability in colloids. In this model, the dispersed particles are not "hydrated" and hence do not have an additional repulsive force (or attractive force) when they approach one another in solution. Any deviations in the forces from those expected by DLVO theory can usually be traced to the existence of some other force (eg, solvation force) and not because of a breakdown in the DLVO interaction.

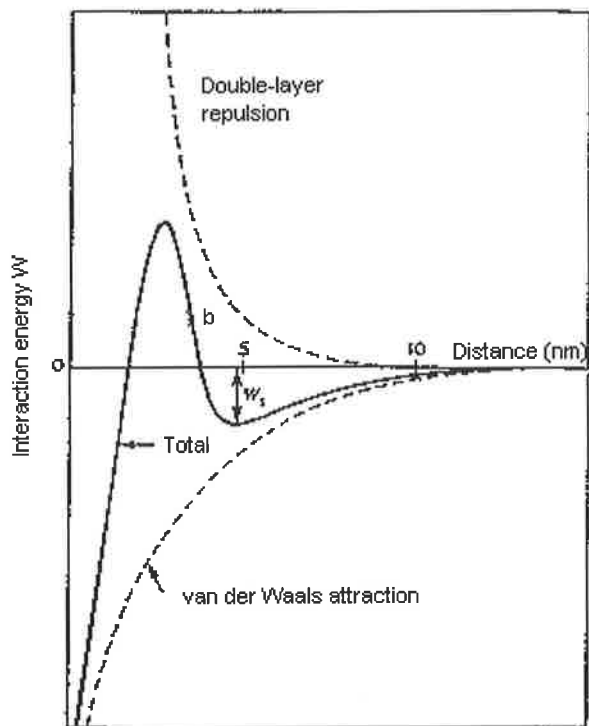


Figure 2-7 Schematic energy vs distance profiles of DLVO interaction (Israelachvili, 1985).

2.7.4. Structural (hydration) forces

Hydrated ions hold water around the ion in layers (Figure 2-8). The first shell of water molecules around a strongly solvated ion is usually referred to as the primary hydration shell. These water molecules are relatively immobile, being held tightly by short-range ion-dipole forces. In the second shell the water molecules are freer to rotate and exchange with the bulk water, in the third shell even more so, and so on (Israelachvili, 1985). The region where the properties of the solvent are significantly different from the corresponding bulk value is referred to as the solvation zone (Israelachvili, 1985). Structural forces result from disruption of the solvation zone around the ion. The strength of the solvation force depends on the energy needed to disrupt the ordered water

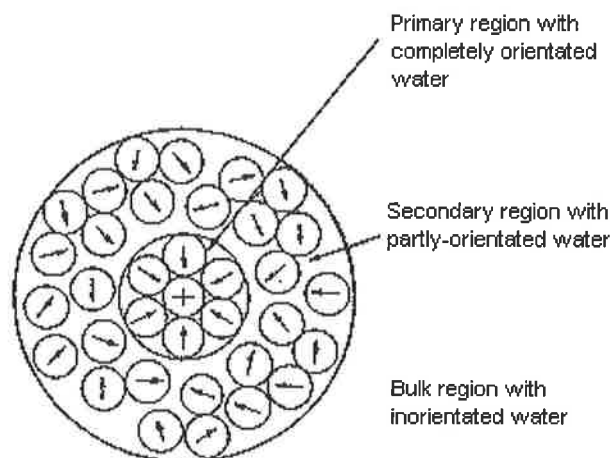


Figure 2-8 Orientation of water around a positive ion in solution (Bockris *et al.*, 1974)

structure and ultimately to dehydrate the two particle surfaces as they approach each other. This results in the measured force between the surfaces being more repulsive than expected due to the additional energy needed to dehydrate the ions. Structural forces only occur when a critical number of cations, which is particular for each cation, have been adsorbed onto the surface of the soil.

The size of the hydrated cation also plays an important role in determining the percentage of the surface that needs to be covered before structural forces became significant. The larger the cation the more easily it is displaced and so the higher the fraction of surface area that must be covered. Pashley (1981a, b), and Pashley & Israelachvilli (1984) found that in high salt concentrations, the hydration force between molecularly smooth mica surfaces was specific for each electrolyte. The strength and range of the hydration force decreased with the hydration number of the cations in the order $Mg > Ca > Li \sim Na > K > Cs$. This indicates hydration forces can be modified or regulated by exchanging ions with different hydration behaviour onto clay surfaces.

Quirk (1994) indicated that the surface density of charge of clay minerals may affect the ability of their surfaces to come into close approach. For clay minerals of high surface density of charge the pressure required to bring the surfaces into contact is too high for the apparatus of Israelachvili and Adams (1978, in Quirk, 1994). Quirk (1994) surmised that with surfaces of lower density of charge, it would be possible to bring them close enough together so that each surface has a layer of exchangeable cations in two layers of water.

2.7.5. Ion-ion correlation forces

Deviations from the standard Poisson-Boltzmann treatment of the double layer force for divalent counter ions were first discovered theoretically from Monte Carlo calculations by Guldbrand *et al.*, (1984). Using a simple model they discovered that instead of the repulsion at small distances predicted by DLVO theory, attraction occurred. The deviations were due to two causes: (1) the inclusion of the effect of ion-ion correlations, and (2) correlated fluctuations in the ion clouds of the two surfaces. For moderately low ion concentrations and fairly small ionic radii, the ion-ion correlation can fairly simply be described as a local reduction in the average density of the ion cloud around each ion due to the electrostatic repulsion (Kjellander & Marcelja, 1986). One consequence of ion-ion correlations is that, compared to the Poisson-Boltzmann theory, more ions are allowed closer to the clay surface. The region between each ion and the closest surface is, on average, depleted of other ions. The gathering of ions closer to the clay surfaces leads to a lowering of the concentration at the midplane between the surfaces (Kjellander & Marcelja, 1986). This reduces the overlap between double layers (Guldbrand *et al.*, 1984). Furthermore, ion-ion correlations across the midplane lead to a local reduction in density at one side due to an ion at the other side. This results in an attractive interaction of a van der Waals type force between the two clay surfaces (Guldbrand *et al.*, 1984;

Kjellander & Marcelja, 1986). This attractive force occurs when polyvalent ions balance the surface charge and clay surfaces need to be at a close distance of approach (about 1nm or less) for this force to have any impact (Quirk, 1994).

The mechanism of the ion-ion correlation force is analogous to the normal van der Waals force, and could be considered a further contribution to it. Both are electrostatic fluctuation forces but, while the van der Waals force originates from the dielectric polarisation of atoms due to outer electron movement, the ion-ion correlation force originates from the polarisation response in the ion cloud due to permanent ionic charges.

The density of surface charge of the minerals affects the positive force that results from ion-ion correlations. Surfaces with higher charge densities experience attractive forces due to the large ion-ion correlation forces. In contrast, as the surface density of charge decreases the attractive force decreases. This occurs due to the greater separation between exchangeable cations when the density of surface charge is lower. Quirk (1994) indicated that as the surface density of charge became less than one unit per 2.0 nm^2 , the pressure between surfaces became increasingly repulsive.

2.7.6. Swelling

Generally, limited swelling of clay in aqueous solutions results when repulsive forces between particles are constrained by attractive forces. In the field, swelling is mainly restricted by the availability of water (suction) and the physical constraints of the soil profile. In a laboratory situation swelling seems to be influenced by clay mineralogy, salt concentration and exchangeable cations. Crystalline swelling can be measured from the basal spacings observed with low angle X-ray diffraction. Observations of sodium-montmorillonites

reveal the influence of electrolyte concentration on swelling. Measurements on the basal spacings indicate that as the sodium chloride concentration decreased from 0.5M to 0.3M, the basal spacings increased from 1.9nm to 4.3nm (Norrish, 1954). This also translated to a large change in the volume of the clay, and is due mainly to the formation of diffuse double layers. As sodium chloride concentration increased, the double layer thickness decreased which reduces repulsion and so swelling is reduced. Sodium illites exhibit inter-crystalline swelling and a sensitivity to electrolyte concentration similar to that of sodium montmorillonite. However, Aylmore and Quirk (1962) measured the solution contents of montmorillonites and illites over a range of salt concentrations and found that they were less in illites. They attributed this to the lower surface area of the illites used. Slade *et al.* (1991) conducted a study on the swelling of sodium smectites that emphasised the importance of the structural origin of the charge on the swelling behaviour. Smectites with high tetrahedral charge did not exhibit crystalline swelling in water, but as the tetrahedral and total charge decreased, clay swelling increased.

In contrast to the extensive swelling observed in sodium montmorillonites as electrolyte concentrations decreased, Norrish and Quirk (1954) reported that calcium montmorillonite maintained a basal spacing of 1.9 nm regardless of electrolyte concentration. Aylmore and Quirk (1962) measured the solution contents of Wyoming calcium-montmorillonite over the concentration range 1M CaCl_2 to distilled water and found little variation. The solution contents of calcium-illites over a similar range were almost identical. The stability of calcium-montmorillonite and illites under these conditions is due to the operation of ion-ion correlation forces (Kjellander *et al.*, 1988a). These forces operate at areas of overlap between the crystals maintaining them in a primary potential well (Quirk, 1994). This results in calcium-illite and calcium-montmorillonite being relatively insensitive to electrolyte concentration.

The lack of swelling in kaolinite is thought to add to its higher stability when compared to illite and montmorillonite (El-Swaify & Henderson, 1967; Aylmore & Quirk, 1966; El-Swaify & Emerson, 1975).

2.8. The effect of potassium and magnesium on soil stability

2.8.1. Potassium

The potassium content of Australian soil ranges from 0.01 to over 3% in surface soils (Williams & Raupach, 1983). Most agricultural soils of the United States have 1 to 2% potassium and the proportion of total potassium in soils held in soluble and exchangeable forms is usually relatively small (Bear, 1964). Soil permeability is less sensitive to electrolyte concentrations for potassium-saturated soil than for sodium-saturated soil (Quirk & Schofield, 1955). Brooks *et al.* (1956) found that various combinations of exchangeable sodium and potassium did not seem to appreciably alter the dominant effect of sodium on the permeability of soils. Hesterberg & Page (1990) observed that potassium was three times more effective than sodium for coagulating illite, due to the greater attraction for potassium by illite. When the hydraulic conductivity of soils with different exchangeable potassium percentages (EPP) was investigated, the effects were found to depend on the charge density of the clays. The effect of $EPP < 20$ on the hydraulic conductivity of smectites with high charge density was negligible. The hydraulic conductivity of smectites having low charge density changed markedly when leached with dilute solutions. For smectites, the low hydration energy of the potassium cations, coupled with the strong electrostatic attraction forces between platelets of smectites with high charge density, accounts for the "inefficiency" of potassium in dispersing them (Shainberg *et al.*, 1987). Levy & van der Watt (1990) investigated the effect of potassium on the

hydraulic conductivity and infiltration rate of illitic and kaolinitic soils and found increasing potassium resulted in decreases in hydraulic conductivity and infiltration rate. Potassium was found to be intermediate between calcium and sodium in its effect on the hydraulic properties of soils and cannot be grouped together with either calcium or sodium as ions having similar effects on the hydraulic properties of soils.

2.8.2. Magnesium

The effect of magnesium on sodic soil has long been a source of conflict amongst researchers. It is a problem of particular pertinence to Australia as many arid and semi-arid soils contain exchangeable calcium and magnesium in fairly similar proportions, especially at depth (Isbell, 1986). The investigation of exchangeable magnesium has been piecemeal at best, and in many cases the resulting information is contradictory.

2.8.2.1. The properties of group I and II elements and magnesium complexes

Comparison of the group I (alkaline earth) and II (alkali) elements indicate that the alkaline earth series does not follow the trends of the periodic table as closely as the alkali metals. Group II comparisons show calcium, strontium, barium and radium form a closely allied series, but magnesium and beryllium do not fit smoothly into this series. The chemical and physical properties of calcium, strontium and barium and their compounds vary systematically down the group in much the same manner as in group I. Magnesium does not have a similar chemistry to either the heavier group II elements (Ca, Sr, Ba and Ra), or beryllium, which also behaves differently to the heavier elements. Beryllium

consistently forms covalent bonds but magnesium has less of a tendency to form covalent bonds, this is consistent with the high charge/radius ratio of beryllium.

A comprehensive discussion of the solubility of magnesium complexes in soil is found in Lindsay (1979). The carbonate and oxide minerals of magnesium are too soluble to persist in the soil solution and are generally leached. Magnesium nitrate and magnesium chloride are insignificant at normal chloride and nitrate levels and contribute very little to the total soluble magnesium. In contrast there are several magnesium complexes that contribute heavily to total magnesium in solution. The MgSO_4° and MgHPO_4° ion pairs are among these and their importance increases as sulphate and phosphate activity increases and pH rises. The presence of single charged species like MgCl^+ and MgOH^+ was thought to contribute to the increased effect of magnesium on dispersion. The single charge of the above complexes was thought to act like the single charge of the sodium ion. Sposito *et al.* (1983a) found that the CaCl^+ complex is thermodynamically much more stable and has a greater affinity for clay than the MgCl^+ complex. If single charged magnesium complexes form in a soil it would be expected that the CEC measured for that soil would be higher than if it were calcium saturated. Tucker (1985) found the CEC's of calcium and magnesium soils to be equivalent, discounting the presence of MgCl^+ . MgOH^+ was also dismissed as a possibility by Tucker (1985) because it is not expected to occur in significant concentrations in soils with a pH below 8. The fraction of magnesium present as MgOH^+ was calculated by the author (Table 2-3) and it showed the concentrations of MgOH^+ are only significant at very high pH's.

Table 2-3 Fraction of magnesium present in the soil solution as the ion pair MgOH^+ .

pH	Fraction of Mg present as MgOH^+
4	0.006
7	0.012
8	0.032
9	0.086
10	0.234

2.8.2.2. Selectivity of soil for calcium and magnesium

Most research on magnesium in soils has been conducted on soil selectivity for calcium over magnesium or vice versa. Of the mineralogical groups investigated, vermiculites are the only mineral group that prefers magnesium to calcium (Peterson *et al.*, 1965). This occurred especially when magnesium exceeds 30 to 40% of the exchangeable cations (Levy & Shainberg, 1972); below this level calcium is the preferred cation. X-ray evidence indicates that in vermiculites the inter-layer magnesium occupies the central position with a single layer of water separating it from the silica layer (Peterson *et al.*, 1965). This magnesium-water structure appears exceedingly stable, perhaps due primarily to the high charge of the silicate lattice. The calcium-water structure of calcium vermiculites is looser and would more freely admit the magnesium ion; however the larger calcium ion is not readily accommodated into the magnesium-vermiculite and would require disruption and expansion of the magnesium-water structure, hence the preference for magnesium.

Montmorillonites seem to have a slight preference for calcium over magnesium (Krishnamoorthy & Overstreet, 1950; Dolcater *et al.*, 1968; Levy & Shainberg, 1972; Rahman & Rowell, 1979; Hagnia & Pratt, 1988). There are contradictory results from studies of the preferences of montmorillonite soil and montmorillonite clay. Levy & Shainberg (1972) found a calcium preference in

montmorillonite clays while Van Bladel & Gheyi (1980) found the calcium preference was stronger in montmorillonite soils. This highlights the difficulty of producing consistent, replicable results when working with soils. Originally the presence of hydroxy-aluminium polymers on the surface of clays was thought to have no significant effect on the selectivity of a soil for calcium or magnesium. However, Hunsaker & Pratt (1971) discovered that montmorillonite clays coated with hydroxy-aluminium had a higher preference for calcium than without the hydroxy-aluminium coating. Organic matter was also shown to contribute to the selectivity of a montmorillonite soil for calcium over magnesium (Gheyi & Van Bladel, 1975; Fletcher *et al.*, 1984b). Further studies have found montmorillonite soils have equal affinities for calcium and magnesium (Sposito *et al.*, 1983b; Fletcher *et al.*, 1984a). Beckett (1965) proposed that montmorillonitic soils had specific sites for magnesium and calcium and once these sites were filled, no preference for either ion was displayed. It has also been found that magnesium saturation needed to be over 30% before soils show equal affinity for calcium and magnesium (Levy, *et al.*, 1972).

The body of literature on the selectivity of kaolinites and illites is much smaller. Some researchers found no preference for calcium and magnesium on illites and kaolinites (Chi *et al.*, 1977), but Hunsaker & Pratt (1971) and Tucker (1985) found calcium adsorbed preferentially in kaolinites and illites.

2.8.2.3. The effect of magnesium on sodic soil

The most commonly observed effect of magnesium in soil seems to be its apparent enhancement of sodic behaviour. Smectitic soils have been observed to contain 17 to 37% more exchangeable sodium in a magnesium-sodium system than in a calcium-sodium system, over the SAR range of 0 to 40 (Curtin *et al.*,

1994b). Emerson & Bakker (1973) observed the behaviour of dominantly illitic soils over the ESP range 0-10. With magnesium present, only 3% of the exchange sites need to be occupied by sodium to cause a dry aggregate to disperse in water. When calcium was the complementary cation, nearly double the proportion of sodium was required to achieve similar dispersion to that observed in the magnesium system. In illite and illite-montmorillonite soils, comparisons of equivalent magnesium-sodium and calcium-sodium systems found between 3-5 times more sodium present in the magnesium-sodium soil (Rahman & Rowell, 1979).

The effect of magnesium on hydraulic conductivity has been investigated more extensively than its effect on other soil characteristics. A soil containing smectite and illite, saturated with exchangeable magnesium at SAR 10 had a substantially lower hydraulic conductivity than the equivalent calcium soil, but a mixed calcium-magnesium system was only slightly less stable than the calcium system (Curtin *et al.*, 1994b). However, if one observes the graphs from Curtin *et al.* (1994b, Figure 2-9), it is very difficult to observe any real difference in the hydraulic conductivity between the calcium system and the calcium-magnesium system at SAR 10. The results for the SAR 20 system are similar to SAR 10, but the decrease in hydraulic conductivity is more obvious. Even at SAR 20, the difference in the calcium system and the calcium-magnesium system is not dramatic. Therefore, it can be concluded that there are large differences in the saturated hydraulic conductivity of the calcium and magnesium systems, with the mixed calcium-magnesium system being closer to the calcium than to the magnesium system. Curtin *et al.* (1994b) also proposed that with the similarities between the SAR 10 magnesium system and the SAR 20 calcium system, magnesium could have a significant adverse effect on structural stability when present as the dominant divalent cation. This was also found by Misopolinos *et al.* (1988), who observed that the erodibility of a soil increased when magnesium

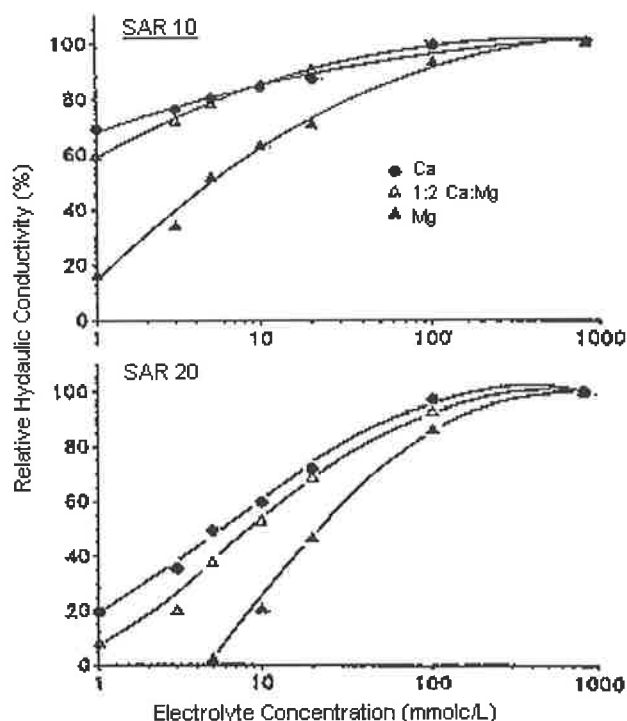


Figure 2-9 Relative hydraulic conductivity of Willows soils leached with Na-Ca, Na-Mg, and Na-Mg-Ca solutions of sodium adsorption ratio (SAR) 10 and 20 (Curtin *et al.*, 1994b).

was the dominant cation. Both papers support the view that, in soils with a mixture of calcium and magnesium on the exchange complex, the unfavourable effect of magnesium is evident only when the magnesium/calcium ratio is greater than some critical value specific to that soil (Rengasamy *et al.*, 1984a).

2.8.2.4. How magnesium affects sodic soil stability

Many explanations for the effect of magnesium on sodic soil have been proposed. Most are in terms of the physical and chemical properties of the magnesium ion. Emerson & Chi (1977) proposed that calcium soils are more stable than magnesium soils due to the calcium ion being more strongly adsorbed onto the clay colloid surface. The difference in adsorption strength could be due to the diameter of a hydrated calcium ion (0.42 nm) being slightly less than that

of a magnesium ion (0.47 nm, Stern & Amis, 1959; Emerson & Chi, 1977). The electrostatic force with which a hydrated calcium ion is held at the clay surface will be stronger. Another reason for the strong calcium adsorption on clay surfaces could be due to the larger size of the unhydrated ion. Since calcium has a larger ion size it is more easily polarised and hence more strongly adsorbed on the surface. Strong adsorption of counterions is thought to cause a sharp decrease of the Stern layer potential, decreasing the flocculation value (van Olphen, 1963).

Bakker *et al.* (1973) observed the strengths of adsorption of calcium and magnesium cations on soil and found them to be similar. This was concluded by calculating the Gapon constants for each system in dilute solution. The Gapon constants were similar for the illitic soil used, so there could be little difference in the strength with which the ions are held on the surfaces of clays. Instead Bakker *et al.* (1973) proposed that the hydration energy of the cations played a role in the magnesium effect on sodic soil, since magnesium has a 20% higher hydration energy than calcium. A similar difference in the hydration energy between lithium and sodium ions was calculated by Shainberg & Kemper (1966b). They discovered that for montmorillonite in a dilute chloride solution, the difference in hydration energies between sodium and lithium leads to a much greater fraction of lithium ions in the diffuse double layer, compared with sodium ions. If the same occurred with magnesium and calcium, which have a similar energy difference to lithium and sodium, then the larger number of magnesium ions in the diffuse double layer would lead to an increase in repulsive pressure resulting in the magnesium soil being more dispersive.

It can be seen that the role of magnesium in soil structural stability is still unclear. There seems to be little appreciation of whether magnesium disperses more than would be expected when compared to the dispersion of clay from soils

containing the other group II cations. Comparisons of soil saturated with cations of the group II series would indicate the actual nature of the dispersion caused by magnesium. Since some researchers have observed an effect on dispersion caused by magnesium, it is reasonable to expect that, with the range of soils investigated in this study, some of them will display increased dispersion in the presence of magnesium. There has been little work on soils with a mixture of calcium and magnesium on the exchange sites. Most have been conducted on soils saturated with or at least dominated by magnesium (Emerson & Bakker, 1973; Rahman & Rowell, 1979). The few studies using mixed calcium and magnesium systems have not been comprehensive or conclusive. A wide ranging study using a number of calcium/magnesium ratios would indicate if any effects of magnesium could be mineralogically based, and/or if there is a threshold percentage of magnesium at which the dispersion of sodic soils is significantly increased.

2.9. The effect of soil pH on sodic soil stability

The deleterious effect of increasing pH on soil structure has been observed by many researchers (Gupta *et al.*, 1984; Suarez *et al.*, 1984; Lebron & Suarez, 1992). A change in pH from 6 to 9 can cause changes in hydraulic conductivity equivalent to a change in SAR from 20 to 40 (Lebron & Suarez, 1992). The stability of kaolinite is the most pH dependent. In acidic solutions kaolinite has been shown to have negatively charged faces and positively charged edges (Theisen, 1942 cited by Herrington & Midmore, 1993). At low pH these can form strong edge-to-face associations producing three-dimensional voluminous "card-house" structures (van Olphen (1956) cited in Herrington & Midmore, 1993). The edge-to-face attraction collapses to a face-to-face structure, resulting in densely packed flake-like aggregates (Herrington & Midmore, 1993). As the

pH increases, the positive edge charges are reversed from positive to negative and the attraction between platelets is reduced. Therefore alkaline kaolinitic soils are more susceptible to dispersion. A mixture of kaolinite and montmorillonite behaves more like montmorillonite (Goldberg & Glaubig, 1987). When kaolinite and illite are mixed the soil behaves most like illite (Goldberg *et al.*, 1991). This is probably due to the low CEC of kaolinites; the CEC of other minerals dominate any surface effects in the kaolinitic soil because they are generally much larger. However, the pH dependence of mixed illite and kaolinite is greater than that of illite and montmorillonite (Goldberg *et al.*, 1991). Changing pH changed the net negative charge on the soil, resulting in increased dispersion (Chorom *et al.*, 1994), with whole soils and soil clays varying in the magnitude of their response to pH. Soil clays had a much higher flocculation value than whole soils at all pH values (Goldberg *et al.*, 1991). It was concluded that the presence of organic matter in whole soils enhanced the net negative charge. However, the destruction of aggregates and removal of cementing agents in the clay separation procedure means that soil clays will have more surfaces exposed than whole soils and it is likely that this will also increase the net negative charge (Chorom *et al.*, 1994).

2.10. The effect of mineralogy on sodic soil stability

Of the three common soil clay minerals, kaolinites have the lowest negative charge. In water, well-crystallised kaolinites cannot be readily dispersed into smaller units but poorly crystallised kaolinites are mechanically weak with a coarse structure of thick particles that are relatively easily dispersed. Calcium kaolinites are stable even in distilled water (Arora & Coleman, 1979); in contrast the stability of sodium kaolinites depends on many factors. Dispersion of kaolinite soil can occur after the addition of small amounts of montmorillonite

(Frenkel *et al.*, 1978). The montmorillonite particles are negatively charged and adsorbed on to the positively charged edges of the kaolinite particles, disrupting bonds between the kaolinite particles and allowing dispersion to occur more easily. In soils of mixed mineralogy illites have a less dispersive effect on kaolinites than montmorillonites, probably due to the shape of the illite particles (Stern, *et al.*, 1991).

Montmorillonites have the highest negative charge and have been considered the most sensitive to sodic conditions (Frenkel *et al.*, 1978). Montmorillonite, as a percentage of the clay fraction, affects soil erodibility more than illite and kaolinite (Frenkel *et al.*, 1978). As stated above, even soil with only small amounts of montmorillonite present can behave as montmorillonite-dominant soils that disperse readily. Montmorillonites when calcium saturated form "quasi-crystals" that contain between 4 - 9 particles as opposed to sodium montmorillonite which, when dispersed, tend to form single particles (Shainberg & Otoh, 1968). The formation of the quasi-crystals makes montmorillonites prone to the "demixing" phenomenon (Shainberg & Otoh, 1968). The external surface of the quasi-crystal is saturated with sodium with the calcium ions remaining on the internal surfaces. As long as there is only a small amount of sodium inside the quasi-crystal, the size and shape of the particles are not affected due to the presence of the calcium. As further sodium is added, more penetrates into the quasi-crystals causing disintegration. Shainberg & Kemper (1966a) studied the mobility of homo-ionic clays and concluded that the mobility of adsorbed calcium is low due to most of the calcium being on the internal surfaces of quasi-crystals. Clays with calcium adsorbed between these internal surfaces appear to have much lower electrophoretic mobility than clays with calcium on the external surface (which have mobilities in the same order of magnitude as sodium clay). Since the forces between quasi-crystals depend on the external exchangeable cation, demixing explains why soils with small

amounts of sodium (10%) can be structurally unstable. The calcium quasi-crystals do not break up until at least 10-15% of the exchangeable ions are sodium, and they separate completely when 50% of the calcium ions are replaced by sodium (Shainberg & Otoh, 1968).

Illites have a negative charge between that of kaolinite and montmorillonite. They can consist of small, poorly defined flakes and are commonly grouped together in irregular aggregates. When placed in water, poorly crystalline illites tend to dis-aggregate considerably and well crystalline varieties only slightly (Grim, 1962). Dis-aggregation of illite occurs by cleavage between the aluminosilicate units. The ease of cleavage varies from that of montmorillonite, in the degraded varieties, to about that of kaolinite, in the well crystalline varieties (Grim, 1962). Illites disperse easier than kaolinites due to the poor contact between the terraced planar surfaces and edges. Despite similar structural characteristics to montmorillonites, they can disperse more than montmorillonites (Alperovitch *et al.*, 1985). Surface illitic soils tend to disperse spontaneously at SAR > 3 and even when the SAR < 3, these soils are easily dispersed mechanically (Rengasamy *et al.*, 1984b). Demixing has also been detected in illites, as indicated by the increase in electrophoretic mobility of the particles in the SAR range 2 to 10 (Lebron *et al.*, 1993). The stability of illite quasi-crystals to sodium was similar to that observed in smectites.

2.11. The role of cementing agents in soil stability

Organic matter was once generally accepted as having only a positive effect on all aspects of soil properties, but this has subsequently been disproved. It was suggested that organic bonds stabilise aggregates against slaking and dis-aggregation but once these bonds are broken and dis-aggregation occurs, organic

matter then acts a dispersing agent (Emerson, 1983). This idea was refined when it was suggested that the size of the organic anion was important in the effect of organic matter (Durgin & Chaney, 1984). If the organic anion was smaller than the clay particle size then excess negative charge resulted and dispersion was increased, whereas if the organic anion was larger than the clay particle then it was able to attach to several particles and bind them together, increasing soil stability. The humic fraction of organic matter has been known to contribute to aggregate stabilisation; it has also been suggested that humic substances are particularly involved in the formation of micro-aggregates (Chaney & Swift, 1986). One positive aspect of organic matter is its role as a binding agent reducing the preferences of soil colloids for sodium (Gupta *et al.*, 1984). There are many other benefits of organic matter (Nelson & Oades, 1996) that have led to the improvement of sodic soils.

Iron and aluminium complexes are also binding agents in soil, with aluminium generally more effective at maintaining soil structure (Frenkel & Shainberg, 1980; Alperovitch *et al.*, 1985). While aluminium complexes are more effective than iron at decreasing swelling in montmorillonites (Deshpande *et al.*, 1964), iron complexes are effective at stabilising illites (Blackmore, 1973). Aluminium can be such an effective binding agent that even soils with high ESP values do not disperse when it is present (Alperovitch *et al.*, 1985). The removal of aluminium and iron can increase the dispersibility of clay indicating the important role they play in soil structural stability (Goldberg *et al.*, 1990). The shape of the aluminium and iron compounds could explain why aluminium is better at stabilising soil. Aluminium-hydroxy compounds are flat, making them more conducive to direct bonding over a large contact area in clay particles, whereas iron precipitates are rounded, producing a more open structure with less bond formation (El-Swaify & Emerson, 1975).

2.12. Weakly sodic and non-sodic soils

Much of the work on the effects of sodicity has been focussed on soil with an ESP greater than 10 (McNeal & Coleman, 1966; McNeal *et al.*, 1968; Frenkel *et al.*, 1978; Shainberg *et al.*, 1980; Shainberg, *et al.*, 1981; Astarai & Chauhan, 1992). Little work has been done on weakly sodic or non-sodic soils (ESP 0 to 10), with much of it on American or Israeli soils. Studies of Israeli soil showed that the hydraulic conductivity of soils was sensitive to ESP at low salt concentrations and low ESP values (Pupisky & Shainberg, 1979; Kazman *et al.*, 1983). Similar trends were observed in American soils (Shainberg *et al.*, 1980), with susceptibility increasing when the rate of mineral dissolution was low. Studies of Australian soil have mainly concentrated on the red-brown earths. Rengasamy *et al.* (1984b) investigated 138 samples from 69 red-brown earth profiles, and found that surface soils with a SAR > 3 (1:5 extracts) would disperse spontaneously, whereas those with SAR < 3 dispersed only after mechanical shaking. Swelling, dispersion and water movement have also been observed to be adversely affected in a red-brown earth with ESP < 5 (Bakker & Emerson, 1973).

The studies reviewed in this chapter illustrate that little emphasis has been placed on the responses of soils to exchangeable sodium percentages below six, since soils with this ESP are generally not considered sodic. This has been shown in the few cases investigated to be an oversight since some soils display symptoms of sodicity when the ESP < 6. The implications of this for land management are important since it increases the current estimates of the land area affected by sodicity immensely, and suggests that improvements in sustainability and possibly productivity might be gained if these soils are treated and ameliorated as though they were sodic. Therefore, further study of the response of a range of soils to essentially non-sodic conditions could be considered a priority.

3. Materials and Methods

3.1. Soils

Six soils were chosen from the agricultural areas of Australia to obtain two representing each of the three major clay mineralogical groups (viz. illite, kaolinite and smectite). To eliminate most of the effects of organic matter, subsoils were chosen where possible. These six soils included illitic red-brown earths, from near Booborowie, South Australia (Belalie - Figure 3-1), and Tatura, Victoria (Figure 3-2). The smectitic grey/black earths were from the Wimmera, Victoria (Figure 3-2), and Lismore, New South Wales, (Tomki - Figure 3-3), and the kaolinitic soils, from Bordertown, South Australia (Figure 3-1), and Mt Madden, Western Australia (Figure 3-4). The Belalie and Tomki soils were existing samples from the CSIRO Division of Soils where they were stored as < 2 mm samples. The other four soils were collected, air dried and divided in two, one half was gently crushed to pass through a 2 mm sieve and the other was left in its natural state. Soil classification and general information about areas of collection are in Table 3-1.

3.2. Mechanical analysis

Particle size distributions were determined on all six soils by sedimentation of salt-free sodium-saturated soil (method of sodium-saturation in section 3.7). No chemical or stringent mechanical methods were used to dis-aggregate the soil, resulting in removal of only the easily dispersible clay present in the soil.

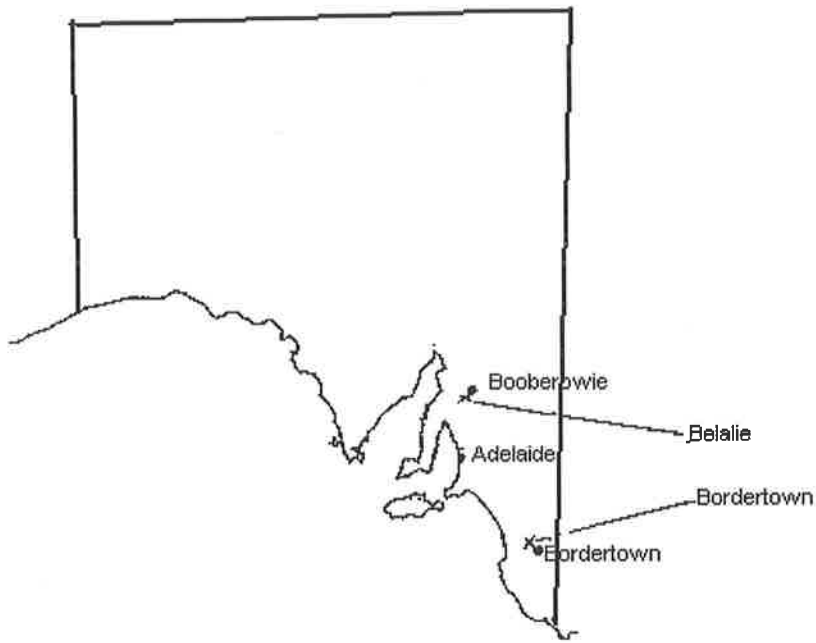


Figure 3-1 Location of Belalie, near Booborowie, and Bordertown soils, South Australia, Australia.

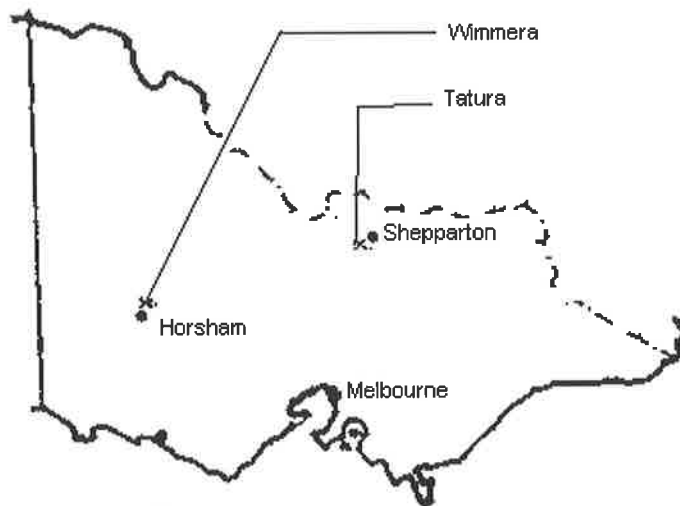


Figure 3-2 Location of Wimmera soil at Longerenong, near Horsham, and Tatura soil, Victoria, Australia.

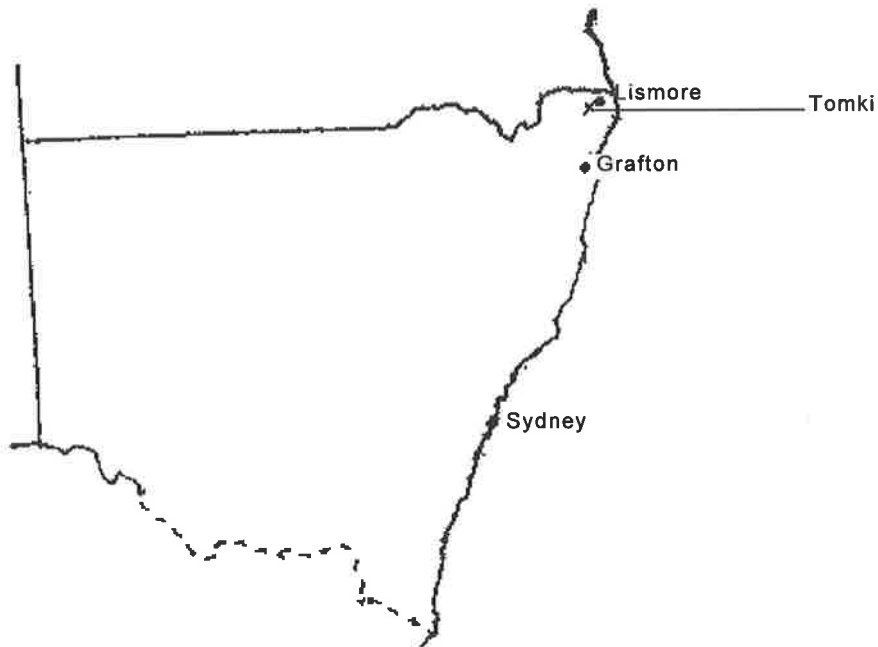


Figure 3-3 Location of Tomki soil, near Lismore, New South Wales, Australia.

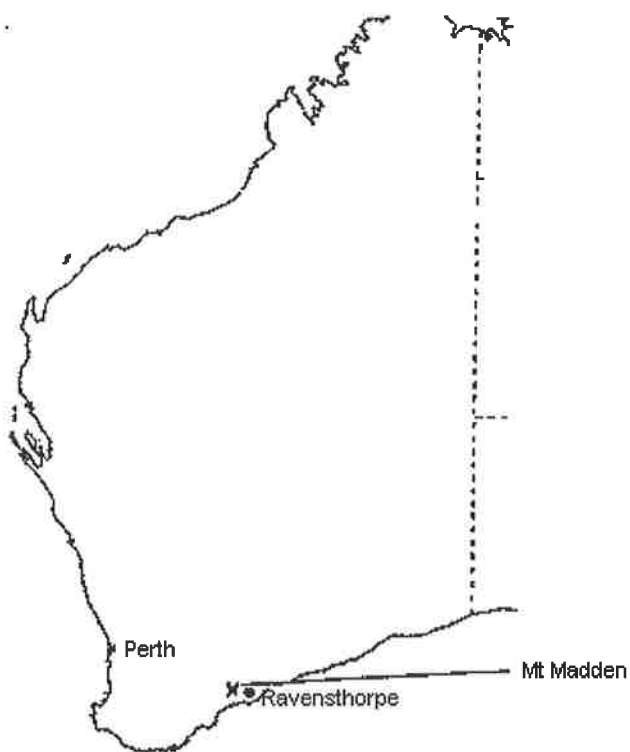


Figure 3-4 Location of Mt Madden soil, near Ravensthorpe, Western Australia.

Table 3-1 Soils information.

Soil	Depth (cm)	Location	Land Use	Aspect	Classification ^a	USDA Taxonomy ^b	Map
Wimmera ^c	50-60	Approximately 30 m north of Wimmera research station buildings, Horsham, Vic.	Dryland field crops	Flat	Calcareous-Epihypersodic Self-mulching, Grey Vertisol: non-gravelly, medium fine/medium fine, very deep	Chromic Calcixert	3.2
Tomki ^d	70-120	Northern Rivers, County Rous, Military grid ref. Lismore 373-149 North Codrington, NSW.	Rough pasture grazing	Gilgai	Halpic, Pedal, Grey Vertisol: non-gravelly, very fine/very fine, very deep.	Ustic Epiquert	3.3
Belalie ^e	10-20	Near north-west corner of manure plot of former experimental farm near Booborowie, SA	Wheat cropping	Flat	Calcic, Subnatric, Red Sodosol: medium, non-gravelly, clay loamy/clayey, very deep	Typic Natrixeralf	3.1
Tatura	20-45	Old apple orchard at Katunga, Tatura, Vic.	Old apple orchard	Flat	Lemnos Loam. Calcic, subnatric, red sodosol: medium, non-gravelly, loamy/ clayey, very deep	Typic Natrixeralf	3.2
Bordertown	10-30	2 km north of farmhouse on Wayne Dodd's farm, 5 km along the Pinaroo road, Bordertown, SA	Cereal cropping	Gently undulating rise	Calcic, Mottled-Mesonatric, Brown Sodosol: medium, non-gravelly, sandy/clayey, very deep.	Typic Natrixeralf	3.1
Mt. Madden	2-5	25 km south of Lake King on Lake King/Ravensthorpe road, WA	Salt scald approximately 15 m from active farmland	Flat	Salic Hydrosol.	Halaquept	3.4

^a Isbell, (1996) ^b Soil Survey Staff (1992), (1994) ^c Northcote & Skene, (1972) ^d Nicholls & Tucker, (1956) ^e Stephens *et al.*, (1945)

This clay is the most likely to be mobile during a dispersion event. The clay not removed by the above method would not normally be dispersed in the field and is not considered relevant to this work. The suspensions were mixed and separated by gravity sedimentation, using Stokes' Law, into clay ($< 2 \mu\text{m}$) and silt ($< 20 \mu\text{m}$) fractions. The percentage of clay, silt and sand was calculated on an oven dry basis.

The fine clay fraction ($< 0.2 \mu\text{m}$) was also separated by centrifugation from a portion of the clay fraction for X-ray diffraction analysis. A soil/solution slurry was made from 10 g of clay and 10 ml of a solution containing 0.5% sodium hexametaphosphate and 1% sodium carbonate. This slurry was made up to 60 ml with distilled water, and shaken on a Spex mill for 10 minutes. The solution was transferred to a centrifuge bottle and made up to 100 mls with distilled water. The solutions were centrifuged at 6000 rpm for 10 minutes (6158g) to remove the $< 0.2 \mu\text{m}$ fraction.

3.3. Clay mineralogy

The clay mineralogy was determined on clay recovered from mechanical analysis. Following a method described by Churchman *et al.* (1994), the $< 2 \mu\text{m}$ fraction was analysed by: X-ray diffraction (XRD) on randomly orientated clay and magnesium-saturated, glycerol solvated clay and X-ray fluorescence (XRF) on barium-saturated clay to determine cation exchange capacity. The relative proportion of kaolinite and illite was given by twice the ratio of the height of the 7\AA peak for kaolinite to the height of the 10\AA peak for illite in the XRD pattern of the magnesium-saturated, glycerol solvated orientated sample. The

percentages of smectite, kaolinite and illite were then determined by an iterative process. The result, including the previously determined percentages of uncharged non-clay minerals, accounted for the cation exchange capacity obtained from XRF analysis.

X-ray diffraction analysis of magnesium-saturated, glycerol solvated orientated samples of the $< 0.2 \mu\text{m}$ clay fractions was also made. XRD patterns for the whole clay and fine clay fraction are given in Appendix 1.

3.4. Exchangeable cations

The exchangeable cations were measured on a 1:20 soil solution, by displacement of adsorbed cations with 0.5 M ammonium chloride at pH 7. Soils with EC > 0.3 dS/m were pre-treated for soluble salts by washing with aqueous ethanol and aqueous glycerol before extraction (Rayment & Higginson, 1992). Exchangeable potassium and sodium were measured by flame photometry, and exchangeable magnesium and calcium by atomic absorption spectrometry (AAS).

The soil used in the exchangeable cation determination was washed with aqueous ethanol to remove entrained salts. Soil was leached overnight with 200 ml of acidified M sodium chloride solution. The filtrate was collected and made up to 200 ml with acidified sodium chloride and mixed. Cation exchange capacity (CEC) of the whole was determined by the ammonium saturation and displacement method (Rayment & Higginson, 1992). Table 3 – 2 compares the CEC's of the whole soil and the CEC of the whole soil calculated from the % clay and the Clay CEC. The similarity between the two values is an indication of

how well the clay dispersed from the soil when sodium saturated. Since only the easily dispersible clay was of interest it would be expected that some discrepancies would be observed between the two CEC values.

Table 3-2 Comparison of soil and clay CEC.

Soils	CEC Clay (meq/100g)	%Clay	CEC Soil (meq/100g)	CEC Calculated ^a (meq/100g)
Wimmera	52 ^b	63	18	33
Tomki	50	81	42	40.5
Belalie	20	21	4	4.2
Tatura	30	46	14	14
Bordertown	39	38	20	15
Mt Madden	29	45	11	12

^a CEC calculated from the % clay and the CEC of the clay fraction

^b CaCO₃ present results in higher than expected value

3.5. Surface area of soil and soil clay

Surface areas of calcium saturated soils and soil clays were determined by water and nitrogen adsorption. For water adsorption, duplicate samples of soil and soil clay were dried over fresh silica gel in an evacuated desiccator for 1 week; the silica gel was replaced with saturated potassium acetate solution ($p/p_0 = 0.22$) and the desiccator evacuated and left to equilibrate for two weeks. A stopwatch was started on the release of the vacuum and the samples were removed from the desiccator and weighed immediately. The soils were then weighed a further five times, noting the time at weighing. Changes in weight over time were plotted and the plot was extrapolated to give the sample mass at time zero, that is before samples started to absorb water from the atmosphere on release of the vacuum. The water content of the soils and clays is given in Table 3-2. The specific surface area of the soil and clay was calculated assuming water vapour at 20% humidity produces a mono-layer of water around the particles (Quirk, 1955).

Assuming the normal packing area of water in physical adsorption is 10.8 \AA^2 per molecule (Mooney *et al.*, 1952), then the equivalent surface areas were calculated from:

$$SSA(m^2 g^{-1}) = 3610 \theta_m (g / g)$$

where:

SSA = specific surface area

θ_m = gravimetric water content

Table 3-3 Replicate water contents of soils and clays used to determine surface area.

Soil		Gravimetric water content (g/g) replicates				Ave
Wimmera	Soil	0.051	0.051	0.056	0.056	0.053
	Clay	0.078	0.066	0.078		0.074
Tomki	Soil	0.066	0.067	0.069	0.075	0.069
	Clay	0.099	0.087	0.105	0.110	0.100
Belalie	Soil	0.007	0.007			0.007
	Clay	0.023	0.030	0.024		0.026
Tatura	Soil	0.025	0.025	0.022		0.024
	Clay	0.054	0.043	0.065		0.054
Bordertown	Soil	0.025	0.022	0.024		0.024
	Clay	0.120	0.099	0.130	0.105	0.113
Mt Madden	Soil	0.016	0.016	0.019	0.019	0.017
	Clay	0.089	0.074	0.095		0.086

For the surface area measurements by water adsorption, the replicates for each soil were within 20% of the average. The total surface areas noted in Table 3-3 are calculated from the surface area measurements of both water and nitrogen. This takes into account the shared monolayer of water on the internal surface of smectitic clay when the water surface area is calculated.

The nitrogen surface area of the soil and soil clays was measured on a Quantachrome AUTOSORB 1, and determined using the B.E.T. method (Brunauer *et al.*, 1938). Pore size distribution was also measured on the Quantachrome AUTOSORB 1.

3.6. Other measurements

Electrical conductivity (EC) and pH was determined in triplicate on 1:5 soil water extracts after shaking for 1 hour and filtering. The pH of soils in 0.01 M calcium chloride was determined similarly. Carbonate concentration in the soil was calculated from the volume of carbon dioxide evolved when the soil was treated with acid (Loveday & Reeve, 1974).

Some relevant physical and chemical properties of the soils are presented in Table 3-3.

3.7. Cation exchange saturation

Before cation exchange saturation, calcium carbonate was removed from the Wimmera soil by treatment of 10% soil solutions with acidified 1M sodium chloride, shaken vigorously then left standing for two hours. The soil solutions were shaken overnight in the acidified sodium chloride, then centrifuged and washed with water. After treatment soil pH was approximately 7. Calcium-, magnesium-, strontium- and barium-saturated soils were prepared by washing with 0.1 M chloride solutions of the respective cations three times (firstly for 3 hours then twice overnight). Excess salts were removed by washing with deionised water until the soil began to disperse. Salt-free soil was obtained by

Table 3-4 Some chemical and physical characteristics of the soils.

Soil	Clay Mineralogy	Particle Size			ESP	CEC ^a meq/100g	Surface Area				pH ^b		EC ^b μS/cm	Carbonate %
		Sand	%				Soils		Clays		H ₂ O	CaCl ₂ ^d		
			Silt	Clay			Total ^c	N ₂	Total ^c	N ₂				
Wimmera	K,S	27	10	63	36	36	193	127	267	121	9.0	8.7	740	5.7
Tomki	RIM>>I,K	5	13	82	9	43	250	96	364	105	6.6	5.4	177	<0.1
Belalie	I>>K	52	25	23	4	4	25	14	94	67	6.2	5.2	89	<0.1
Tatura	I>K,RIM	28	22	50	17	14	86	60	194	91	7.3	6.8	236	0.2
Bordertown	K,RIM,I	59	2	39	27	20	85	64	405	70	8.7	7.4	336	<0.1
Mt Madden	K>>RIM>I	50	2	47	77	12	65	51	310	60	7.9	6.3	199	<0.1

K = Kaolinite, S = Smectite, RIM = Randomly Interstratified Mineral, I = Illite.

^a CEC determined by the Kjeldahl method.

^b 1:5 soil solution extract.

^c Total surface area calculated from surface area measured by water and nitrogen adsorption (Mooney *et al.*, 1952)

^d Concentration of CaCl₂ was 0.01 M.

freezing the suspensions, causing the dispersed clay to flocculate (*pers. comm.* Murray, 1993). On thawing, the soil remained flocculated and the water was removed and replaced. The soil was then re-suspended by shaking overnight and the procedure repeated until the electrical conductivity of the solution was $< 10 \mu\text{S/cm}$ ($< 0.001 \text{ dS/m}$). Sodium-saturated soil was prepared using the same procedure as above, but with 1 M sodium chloride; excess salts were removed by dialysis until the electrical conductivity was $< 10 \mu\text{S/cm}$. Soils were dried at 50°C , remoulded at a water content where the soils were easily workable, dried and then sieved to 2 mm before use. The electrical conductivity of the soils after exchangeable cation saturation is presented in Table 3-4. The higher electrical conductivity in sodium soils indicates that the dialysis was not as complete as first thought. It seems that dialysis of soil, as opposed to dilute clay suspensions, requires fairly vigorous mixing of the soil when in the dialysis tubing; this is a delicate operation as the tubing can be quite fragile.

Table 3-5 Electrical conductivity ($\mu\text{S/cm}$) of 1:5 extract of soils after saturation of exchange capacity with each of the cations.

Soil	Na	Mg	Ca	Sr	Ba
Wimmera	600	100	87	104	95
Tomki	164	32	30	26	31
Belalie	53	26	22	19	20
Tatura	108	44	44	37	32
Bordertow	228	40	43	26	24
Mt	500	37	49	32	36

3.8. Sodic soil preparation

A range of soil samples with ESP 0 to 20 were prepared by weight. All samples were remoulded at a water content which enabled easy working. After remoulding, the samples were covered and left overnight before drying at 40°C. The dry samples were gently crushed and sieved to < 2 mm. The 1-2 mm aggregates were removed and spray wet gently to minimise structural disruption, then dried. This wetting procedure was repeated before use, making a total of three wetting and drying cycles including the remoulding and drying.

3.9. Mechanical dispersion

Triplicate 1 g samples of each soil were weighed into containers with the dimensions; 28 mm in diameter and 110.5 mm in length with a tapered bottom. 20 ml of RO water was added slowly down the side of the container to minimise soil disturbance. Each sample was subjected to a range of mechanical disturbance following Churchman & Foster (1994): gently end-over-end twice by hand, 1 minute, 15 minutes, 2 hours and 16 hours end-over-end shaking on a mechanical shaker at 13.5 rpm, and finally sonified for 1 minute at 40% of the output power of the sonifier. After standing for 1 hour, 1 ml or 0.1 ml (depending on the amount of clay dispersed) of the < 2 μm fraction was sampled with the pipette tip just above the calculated 2 μm depth, diluted to 30 mls and the turbidity was measured on a Hach turbidimeter. Turbidities were converted to clay concentration from the calibration curves of sodium- and calcium-saturated clay; turbidity measurement and calibration curves of the clay are discussed in more detail later. The amount of clay dispersed at each stage was calculated as a percentage of the amount derived from mechanical analysis (section 3.2). Finally the clay percentage dispersed was itself expressed as a

percentage of the clay dispersed by 1 minute sonification, which was considered the point at which all the easily dispersible clay would be dispersed. Since one minute sonification may be more destructive than sodium saturation alone, more clay may be produced by this method. This accounts for some of the soils having more than 100% dispersion.

3.10. Spontaneous dispersion

Spontaneous dispersion was measured by placing 0.5 g of artificial aggregates (section 3.8), in a single layer on a plate 9 cm in diameter and suspended to a depth of 8 cm in a 2 L beaker. The beaker was filled to the 1500 ml mark with distilled water, using a funnel to minimise soil disturbance. The solution was continuously pumped through the turbidimeter and back into the beaker (Figure 3-5) at a rate of 40 mls/min. Turbidity data was collected continuously until the turbidity remained relatively constant. The amount of clay dispersed was expressed as a percentage of clay derived from mechanical analysis (section 3.2). Triplicate measurements were made on the soils which appeared to disperse spontaneously.

3.11. Turbidity calibration curve

The turbidity of the suspensions was used to determine the concentration of dispersed clay for each disturbance event. Turbidity can be associated with particle concentration by Rayleigh theory (Keren & Klein, 1995). Rayleigh theory predicts that light scattering is proportional to the number of non-absorbing spherical particles in the suspension with volume V , the dimensions of which are small compared with the wavelength of the light.

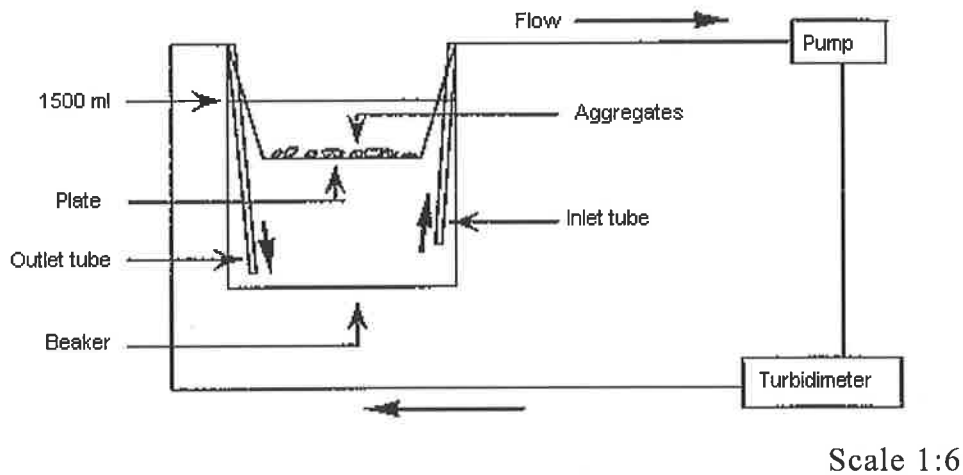


Figure 3-5 Schematic diagram of apparatus used to measure spontaneous dispersion

The total scattered light intensity is related to particle concentration by:

$$I_s = I_0 24\pi^3 \frac{V^2}{\lambda^4} \nu \left(\frac{n_1^2 - n_0^2}{n_1^2 + 2n_0^2} \right)^2$$

where:

ν is the number of particles per unit volume

V is the volume of a particle

λ is the wavelength of the scattered light

n_0 & n_1 are the refractive indexes of the medium and the particle, respectively (Keren & Klein, 1995).

Therefore the scattered light intensity is affected by the number of particles in suspension and the volume of those particles. At a given suspension concentration (g/g), as the number of particles per unit volume increases, the volume of the particles decreases. The particles studied in this work are neither

spherical nor small when compared with the wavelength of the scattering light. Instead, light scattering of the particles is dependent on the number of centres on the particle which scatter light and the orientation of the particle with respect to the direction of illumination (Keren & Klein, 1995). This means that Rayleigh theory is not strictly applicable here and may only be used for comparisons. The size and shape of particles in suspension vary and the light scattering depends on both the particle size and shape and the number of particles per unit volume. These two factors should be considered when determining the concentration of clay in suspension. The clays used for standard curve determination were saturated with calcium or sodium, since the exchangeable cation determines to some extent the size of the particles present and therefore affects turbidity. The particle shape is determined by the mineralogy of the soil clay and the mode of clay particle break-down when subjected to 1 minute sonification. The number of particles per unit volume increases as the concentration of clay increases. Although the particle size in the suspensions is larger than the wavelength of the scattering light, the standard curves of most soils are straight lines.

Of the six soils investigated, only the illitic soils (Figure 3-6) displayed higher turbidity for the sodium-saturated clay than the calcium-saturated clay. This is probably due to the larger number of particles with smaller volume that are present in the sodium-saturated suspension. The other four soils (Figure 3-7) all have calcium-saturated clays that exhibit higher turbidity than sodium saturated clay. This may be due to the larger volume of the particles in these solutions and hence each particle contains a number of light scattering centres. The

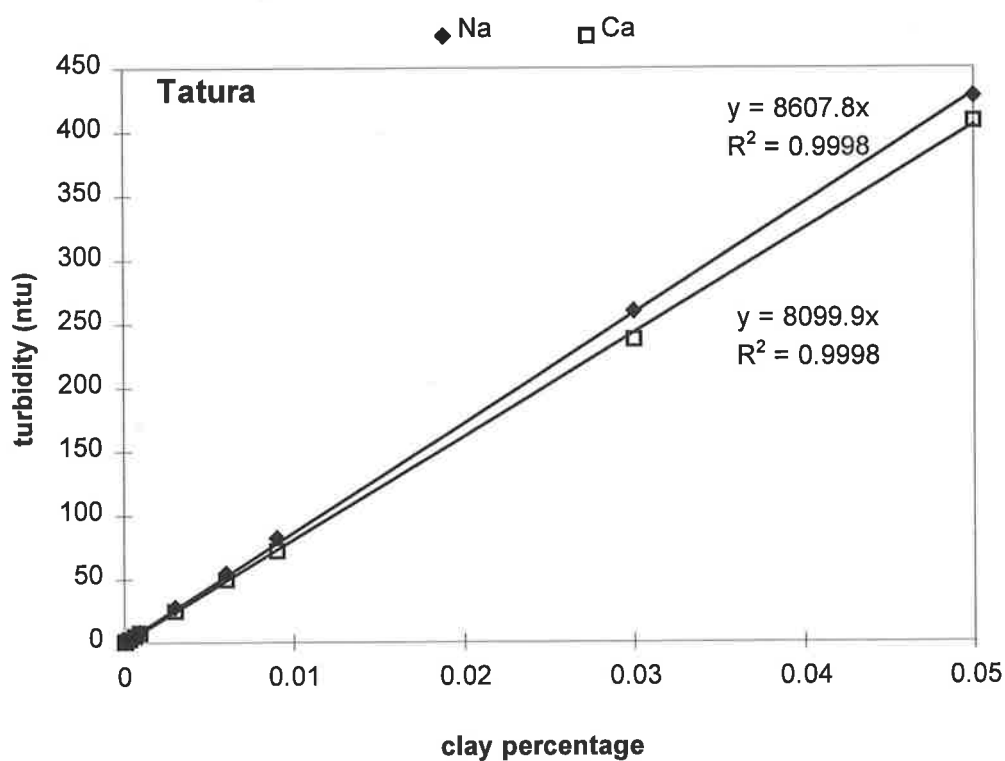
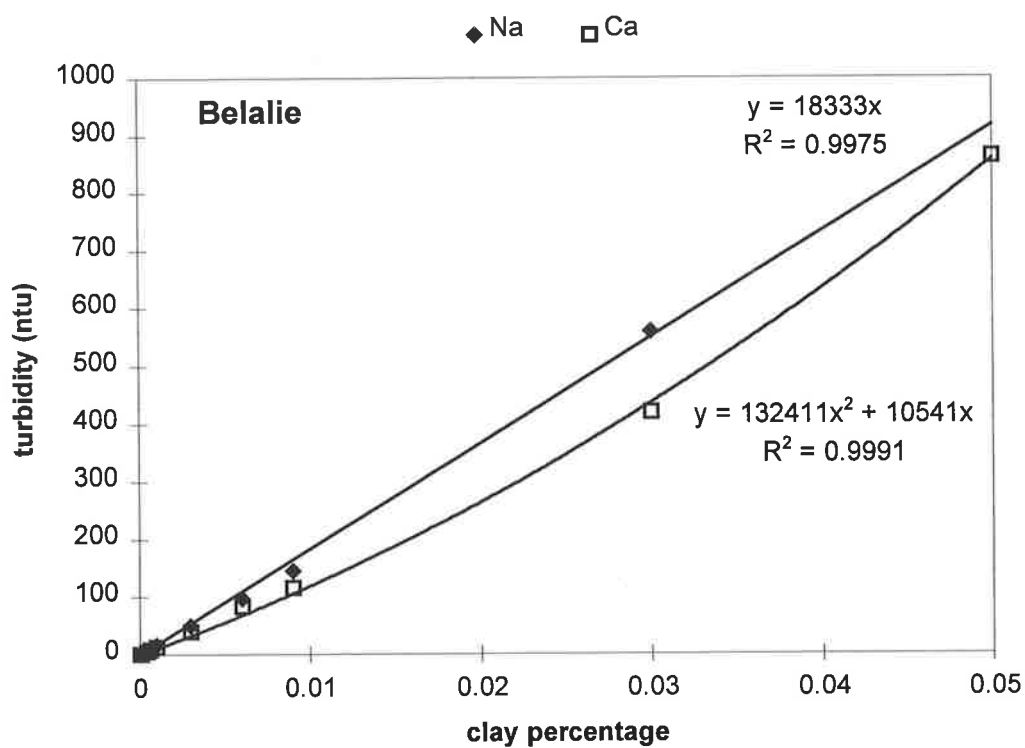


Figure 3-6 The standard turbidity curves for calcium- and sodium-saturated illitic Belalie and Tatura soils.

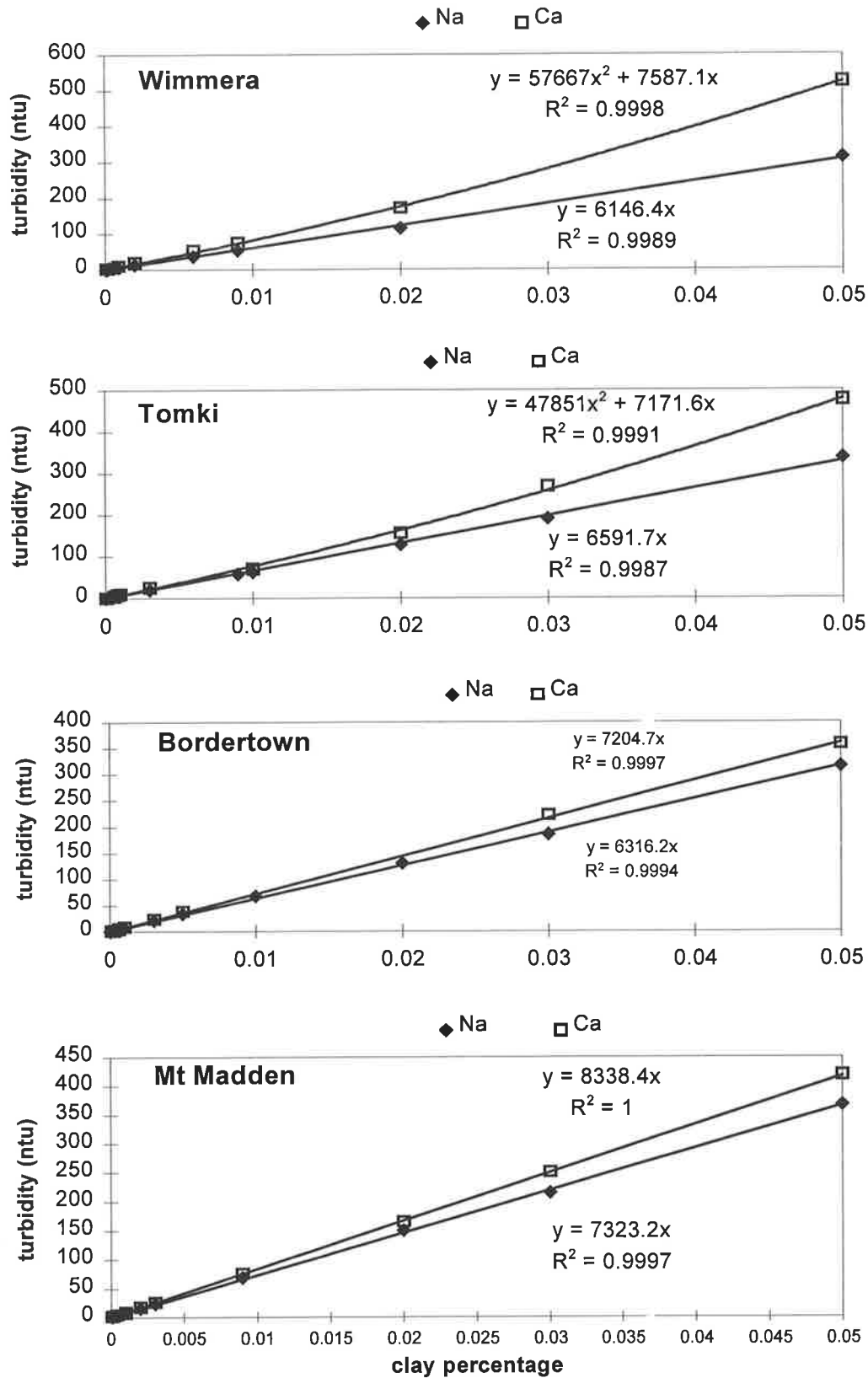


Figure 3-7 The standard turbidity curves for calcium- and sodium-saturated Wimmera, Tomki, Bordertown and Mt Madden soils.

problem with particles that contain a number of scattering centres is interference between the waves of light scattered from different parts of the same particle. As the size of the particle increases in relation to the wavelength, the complexity of the scattering relations increases (Orr & DallaValle, 1959). This results in non-linear relationships between turbidity and clay concentration. Keren & Klein (1995) observed that particle size does not appear to change significantly until ESP reaches 10-15, and dramatic changes were not observed until ESP was about 50. As the highest ESP in this study was twenty, the above suggests that the calcium-saturated clay standard curve could be used to estimate dispersed clay for all soils where the dominant exchangeable cation is divalent.

A 0.05% stock solution of each clay was made and then diluted to obtain the concentration range required for the standard curve. The turbidity of each solution was measured on a Hach turbidimeter.

3.12. Particle size measurement

Particle size of dispersed clay was measured using a Sunmicron Particle Sizer, model 370, Nicomp Particle Sizing Systems Santa Barbara California. The output was a Gaussian distribution with a summary of the mean particle diameter and standard deviation associated with the Gaussian fit. The Nicomp particle sizer employs photon correlation spectroscopy and calculates particle size using the Stokes-Einstein relation:

$$D = \frac{kT}{6\pi\eta R}$$

where D = diffusion coefficient
 k = Boltzmann constant
 T = temperature
 η = shear viscosity of solvent
 R = radius of particle

The diffusion coefficient, D, of uniform particles is the rate at which the particles move in suspension and is inversely related to the particle radius R, assuming the particles are spheres. The reliance of the particle size measurements on an assumed spherical uniform nature of the particles precludes accuracy in measuring the particle size of clay colloids, since they are not, by nature, either uniform or spheres. Therefore the results of the particle size measurements cannot be taken as the absolute size of dispersed particles, but instead indicate the fragmentation of the soil aggregates during a dispersion event. Due to the high standard deviations about the means, only the mean particle size has been included in the results reported in appendices 3, 4 6 and 7 to simplify the graphs and give a clearer picture of the outcome.

3.13. Induction of sodicity in natural aggregates

20 gms of 1-2 mm aggregates were sieved from the soils left in their natural state and placed on sintered glass funnels of porosity 4. Soils were wet slowly with 0.1 M calcium chloride at 100 cm suction for one week, then flooded with the solution and left overnight. The solution was mixed, left overnight again; then replaced by fresh calcium chloride solution. This procedure was repeated with fresh solution over three days, then the soils were drained and washed with

reverse osmosis water until the electrical conductivity was $< 20 \mu\text{S}/\text{cm}$. To induce the required ESP dilute solutions containing sodium chloride alone were added to the funnel, again flooding the soils. The required concentrations of sodium chloride were estimated by assuming a Gapon constant of $0.01 (\text{mmol}/\text{L})^{1/2}$ and solving a series of simultaneous equations that give the total sodium in solution and on clay surfaces. The premise of the calculations was that the soil was calcium-saturated and using the Gapon equation and conservation of calcium, sodium and exchange capacity, the concentration of sodium required to produce a target ESP was calculated (*pers. comm.* Murray and Mao, 1995). The salt solution was gently mixed morning and evening for three days then left to drain overnight. Soils were subjected to a final wash with reverse osmosis water and the electrical conductivity measured to calculate entrained salt. The ESP was determined by exchange with ammonium chloride (section 3.4). These soils were also subjected to the dispersion test described in section 3.8.

4. Effect of group II cations on the dispersion of soil

4.1. Introduction

As exchangeable cations, magnesium and calcium have long been considered to be equivalent in their effects when assessing sodicity in soil (US Salinity Laboratory Staff, 1954). However, many workers have reported that, although magnesium is a divalent cation, it may have an adverse effect on soil structure under certain conditions. When comparing the dispersion of soils containing magnesium/sodium and calcium/sodium, researchers (Rahman & Rowell, 1979; Yousaf *et al.*, 1987; Curtin *et al.*, 1994b) have found that soils with magnesium and sodium disperse to give either similar amounts or more clay than the calcium/sodium soil. Moreover, there seems to be mineralogical influences involved in the effect magnesium has on soil, with most reports of increased dispersion in the presence of magnesium occurring in illite-dominated soils and clays. It has been hypothesised that sodium competes more successfully for exchange sites with magnesium than with calcium (Rahman & Rowell, 1979; Hagnia & Pratt, 1988). At the same SAR, this results in the adsorption of more sodium ions, when exchangeable magnesium rather than calcium, is present in the soil solution. Hence there are two mechanisms which could contribute to the observed effect of magnesium on soil. One is termed a specific effect of exchangeable magnesium, which is similar in type to the effect exchangeable sodium has on soil (Curtin *et al.*, 1994b), and the other, an indirect or co-operative effect which results in higher ESP values in magnesium-dominated soils at a given SAR.

Most research has compared only the effects of magnesium and calcium on soil dispersion. As discussed in Chapter 2, there has been little investigation into the behaviour of soil when the group II, or alkaline earth cations, are present.

Comparison of the dispersion of soil when saturated with different group II cations (magnesium, calcium, strontium and barium) might enable better analysis of any effect of magnesium on dispersion as there are trends in chemical behaviour with progress down the group. It follows then that these trends may be translated into effects on soil dispersion. Such observations may indicate whether the degree of dispersion resulting from the presence of exchangeable magnesium, in relation to that arising from other Group II cations, is what might reasonably be expected from its position in group II. The aim of this experiment then, was to investigate the effects of group II cations on the dispersion of soils under sodic and non-sodic conditions.

4.2. Materials and Methods

Soils with ESP values of 0, 5, 10 and 20 were prepared using the method described in section 3.8. These soils were subjected to the spontaneous and mechanical dispersion experiments described in section 3.9 and 3.10. Mt Madden, as the first soil to be subjected to mechanical dispersion, was not exposed to the 2 hour shaking treatment; this was added later following analysis of the Mt Madden data. There were three replicates for each treatment. The results were expressed as the percentage clay dispersion; the percentage of clay that dispersed with respect to the percentage of clay obtained after 1 minute sonification. The results of each dispersion test were subjected to a one-way ANOVA test with three degrees of freedom, then subjected to a Tuckey's test.

This determined which of the treatments were significantly different from each other. The results obtained from the statistical analysis are displayed in Figures 4-1 to 4-8. Within an ESP, different letters indicate a significant difference in the percentage of clay dispersed.

4.3. Results

The measured pH range for each soil is in Table 4-1. Within this range few variable charge effects are generally observed. As the pH of a solution in contact with the surface of a clay mineral increases, the surface of the clay becomes increasingly negatively charged, but the extent of this change is affected by the concentration of salt in the solution. When clay minerals are exposed to low salt concentrations, changes in net surface charge with pH are smaller than those observed in high salt concentrations (Bowden *et al.*, 1980). Therefore, in a neutral solution with low salt concentrations the effects of variable charge are less than in a solution with high salt concentrations. In this study the clay minerals were exposed to solutions of low salt concentrations. Chorom *et al.* (1994) measured the dispersible clay from three soils over the pH range 3 - 10 and found that for an illitic and kaolinitic soil there was little change in dispersion when the pH was between 5.9 and 7.2 (neutral). Contrary to expectations, the montmorillonitic soil exhibited significantly more change in dispersion in this pH range. This soil contained about 3% organic matter, which can strongly affect the dispersion of a soil (Gupta *et al.*, 1984). In the absence of organic matter, it can be anticipated that soils with little variable charge show little effect of pH on dispersion. The montmorillonitic soils in the present study

are subsoils and organic carbon contents are very low ($< 0.5\%$), and so would not be expected to behave in a similar fashion to those used by Chorom *et al.* (1994).

Table 4-1 pH range of dispersed clay suspensions.

Soil	pH range
Wimmera	6.5 ± 0.5
Tomki	6.6 ± 0.6
Belalie	6.1 ± 0.2
Tatura	6.2 ± 0.2
Bordertown	6.2 ± 0.3

4.3.1. Mechanical Dispersion

Shaking twice end-over-end by hand

Dispersed clay measurements for this energy level are shown in Figure 4-1, with the dispersion results of Tomki and Bordertown at ESP 0 and 5 expanded in Figure 4-2.

ESP 0

From the ANOVA test, statistically significant differences in dispersion due to cations occurred in the Wimmera ($F = 16.03$, $P < 0.05$), Tomki ($F = 7.13$, $P < 0.05$) and Belalie ($F = 7.80$, $P < 0.05$) soils. However, neither of these soils exhibited differences in dispersion due to the presence of magnesium alone.

ESP 5 – 20

When the samples were sodic and subjected to this level of disturbance, other soils began to exhibit statistically significant differences in dispersion due to

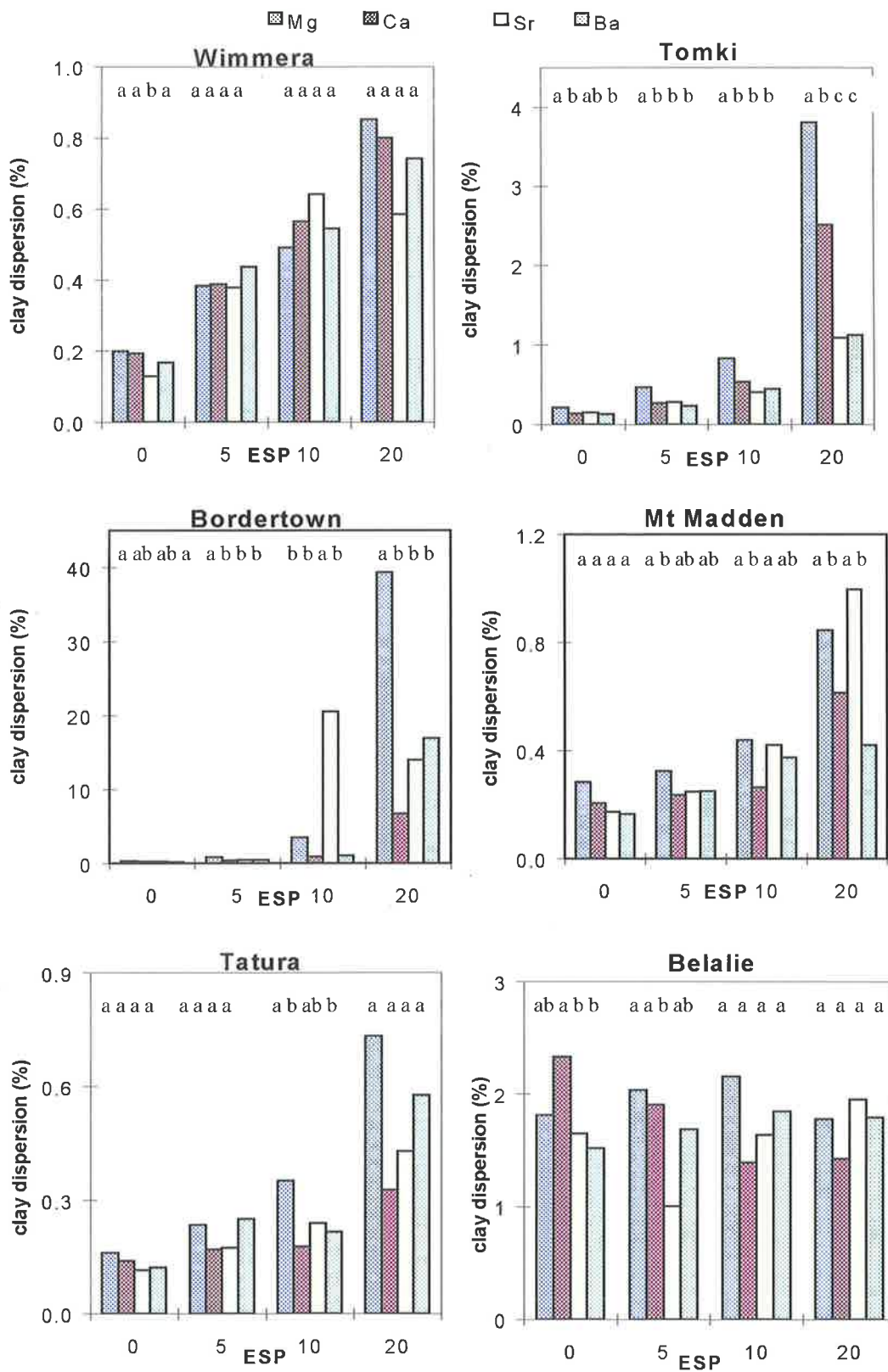


Figure 4-1 Average clay dispersion produced by end-over-end inversion of the soil suspension twice by hand, expressed as a percentage of that produced by 1 minute sonification.

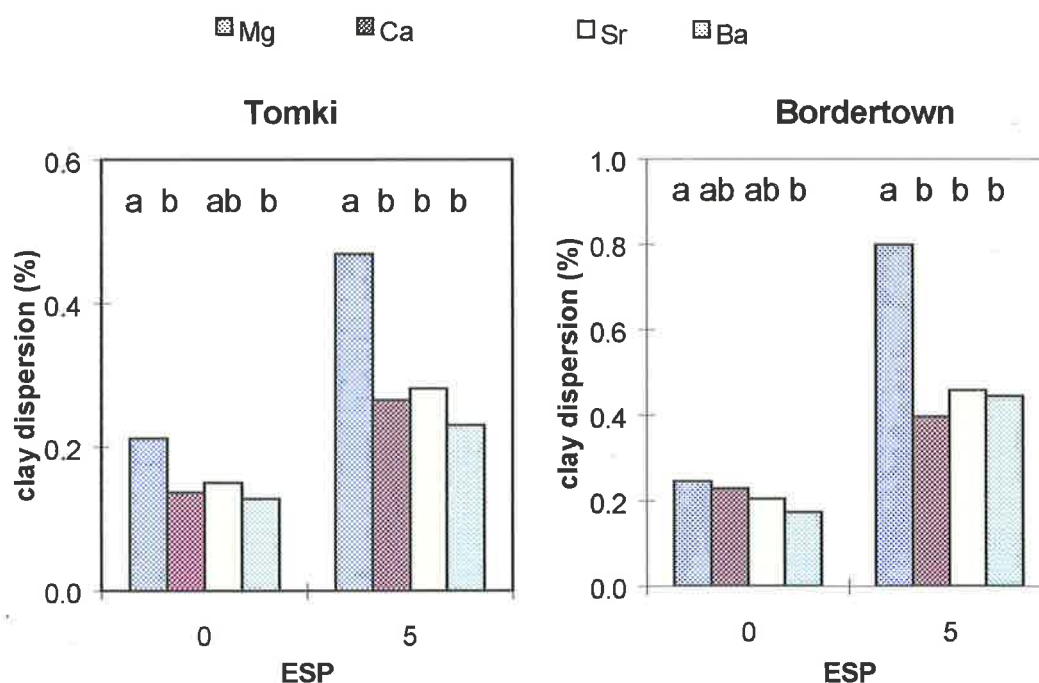


Figure 4-2 Average clay dispersion at ESP 0 and 5 produced from Tomki and Bordertown soils by end-over-end inversion of the soil suspension twice by hand and expressed as a ratio to that produced by 1 minute sonification.

exchangeable cations. At ESP 5, the Tomki soil exhibited a significant increase in dispersion when dominated by magnesium ($F = 15.36$, $P < 0.05$). The Bordertown soil with ESP 5 also exhibited significantly more dispersion when magnesium-dominated ($F = 13.09$, $P < 0.05$). The Mt Madden soil displayed a significant difference in dispersion between the magnesium- and calcium-dominated treatments ($F = 5.07$, $P < 0.05$), however there was a trend which suggests the magnesium-dominated soil dispersed more than the other treatments. The Belalie soil also exhibited significant differences in dispersion ($F = 6.13$, $P < 0.05$), but only between the strontium treatment (which dispersed less) and both the magnesium and calcium treatments.

As ESP increased to 10, the Tomki soil exhibited significantly more dispersion when magnesium-dominated, than the other three treatments ($F = 22.86$, $P < 0.05$, Figure 4-1). However, there were a variety of significant differences between treatments observed at ESP 10 for the Tatura, Mt Madden and Bordertown soils. Only the Tatura soil exhibited the trend of the magnesium-dominated soil dispersing more than the remaining treatments. The effects observed in the other two soils, especially Bordertown, were not expected. Why the strontium-dominated Bordertown dispersed to give more clay than the other treatments is unknown.

As the ESP increased to 20, the Tomki soil again exhibited significantly more dispersion when magnesium-dominated ($F = 22.63$, $P < 0.05$). The Bordertown soil displayed similar results ($F = 32.08$, $P < 0.05$). The Tomki soil exhibited significantly more dispersion when calcium-dominated, than when both strontium- and barium-dominated. The Mt Madden soil was the only other soil to display significant differences in dispersion, but the effects were not only due to magnesium ($F = 29.28$, $P < 0.05$). At this energy level Bordertown ESP 20 treatments exhibited higher percentages of dispersed clay compared with the other soils.

Tomki was the only soil to consistently disperse more when magnesium was the dominant cation at ESP 5, 10 and 20, while Bordertown dispersed significantly more at two ESP values when magnesium was the dominant cation. The Wimmera and Belalie soils displayed few effects of exchangeable divalent cations, but exhibited quite different responses to dispersion. As sodicity

increased, the Wimmera soil showed increased clay dispersion, while the Belalie soil displayed little effect of exchangeable cation and similar amounts of clay dispersed at all ESP values, regardless of the dominant divalent cation. It is important to note that this level of energy input is the lowest and that there may be considerable uncertainty in the energy imparted to the sample. These variations may be amplified for particularly unstable soils (eg Bordertown). Hence, few definite conclusions can be drawn from these results alone.

1 minute end-over-end shaking

Measurements of dispersed clay after this level of disturbance are shown in Figure 4-3, with the results for Tomki, Bordertown, Mt Madden and Tatura at ESP 0 and 5 enlarged in Figure 4-4.

ESP 0

Of the six soils, Tomki ($F = 13.08$, $P < 0.05$), Bordertown ($F = 32.0$, $P < 0.05$) and Mt Madden ($F = 17.88$, $P < 0.05$) all displayed significant increases in dispersion when magnesium was the divalent cation compared to the other ions. The remaining three soils (Wimmera, Tatura and Belalie) all displayed various treatments which exhibited significant differences in dispersion, but no trend was observed.

ESP 5-20

The Wimmera soil displayed a significant increase in dispersion when magnesium-dominated at ESP 20 ($F = 252$, $P < 0.05$). The calcium-dominated

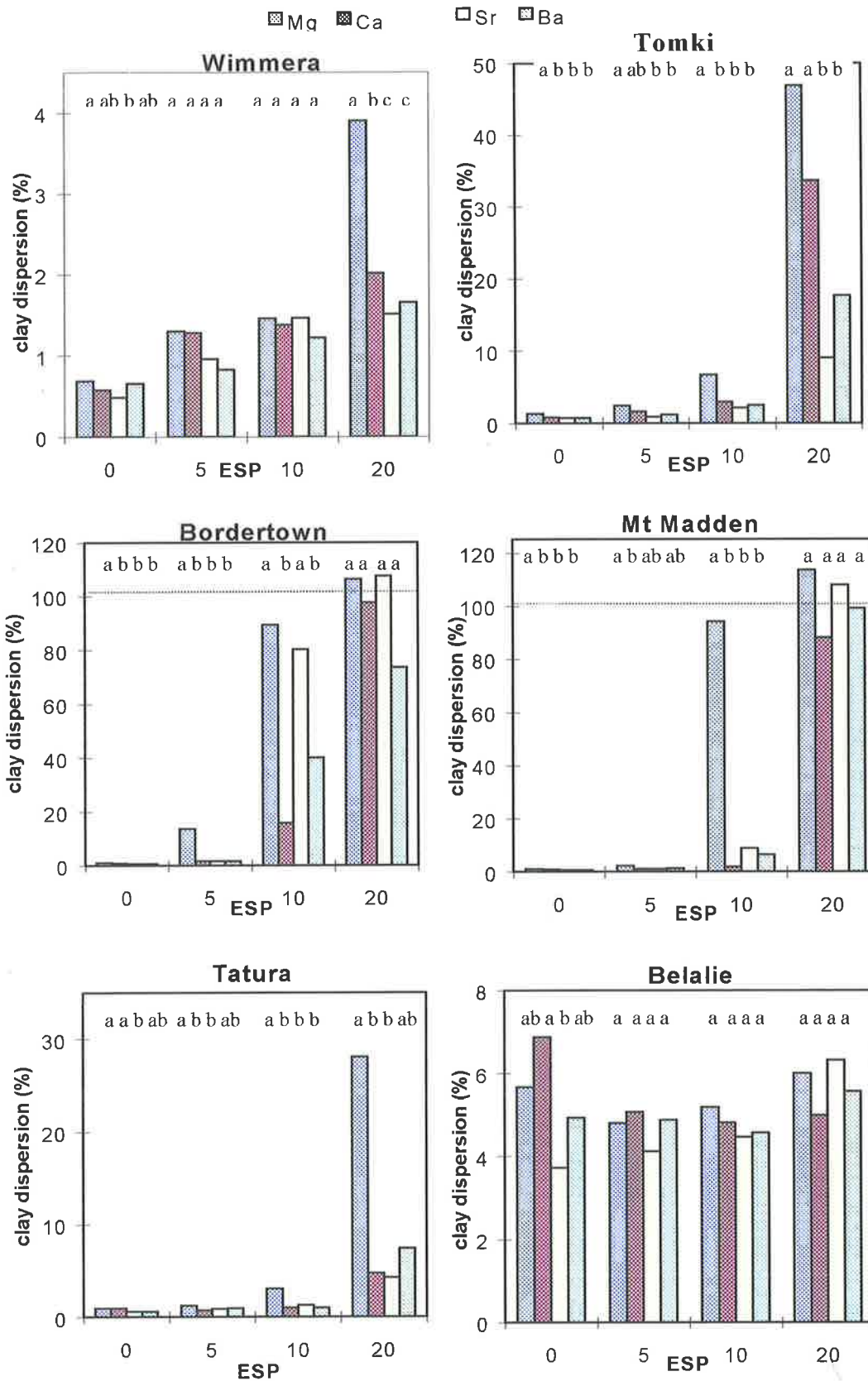


Figure 4-3 Clay dispersion produced by 1 minute end-over-end shaking expressed as a percentage of that produced by 1 minute sonification.

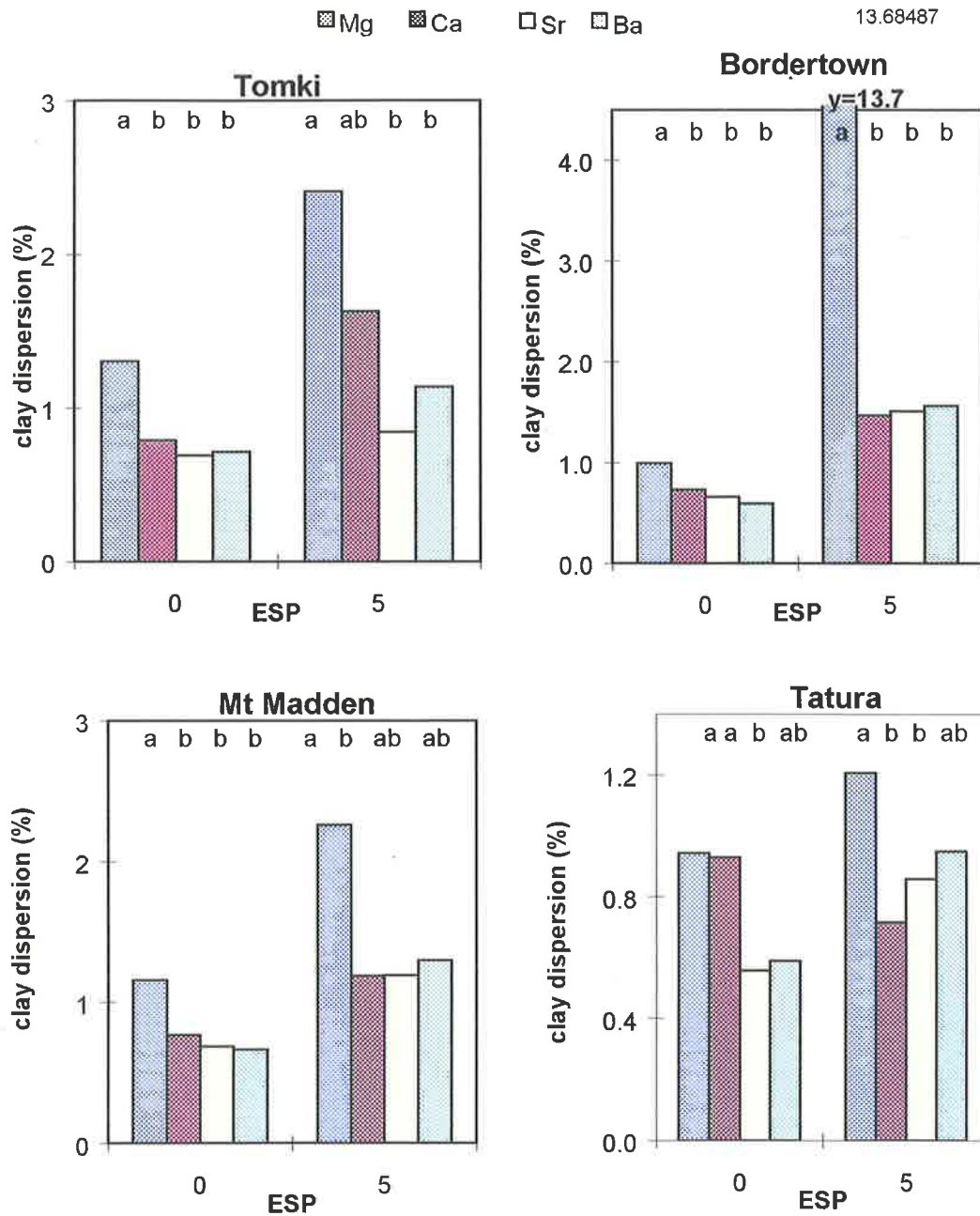


Figure 4-4 Clay dispersion of Tomki, Bordertown, Mt Madden and Tatura at ESP 0 and 5 produced by 1 minute end-over-end shaking and expressed as a percentage of that produced by 1 minute sonification.

treatment dispersed significantly more than both the barium- and strontium-dominated treatments at this ESP. Despite the relatively high level of exchangeable sodium present, the amount of clay dispersed at this energy level was still quite small (< 3%). This indicates the stability of the Wimmera soil, even at an ESP which is considered high (Northcote & Skene, 1972). The Tomki soil displayed a significant increase in dispersion when magnesium dominated at ESP 10 ($F = 32.86$, $P < 0.05$), but significant differences between treatments were also observed at ESP 5 and 20. For these two ESP values, the differences were mainly between magnesium treatments and the strontium and barium treatments. The Bordertown soil exhibited a significant increase in dispersion when dominated by magnesium at ESP 5. As the ESP increased to 10, differences were observed between the magnesium and strontium treatments on the one hand and the calcium and barium treatments on the other ($F = 38.86$, $P < 0.05$). The Mt Madden soil behaved similarly, except that the effect of magnesium on dispersion was observed at ESP 10 and not ESP 5 as in the Bordertown soil. The Tatura soil also displayed significant differences in dispersion due to exchangeable cations at ESP 5, 10 and 20. ESP 10 was the only ESP value where Tatura dispersed significantly more when magnesium-saturated ($F = 11.72$, $P < 0.05$). At ESP 5, the magnesium-saturated sample dispersed significantly more than the strontium- and calcium-saturated samples but not the barium-saturated sample ($F = 7.91$, $P < 0.05$); this was repeated at ESP 20 ($F = 5.46$, $P < 0.05$).

15 minutes end-over-end shaking

Results for the dispersion of soils after 15 minutes end-over-end shaking are displayed in Figure 4-5; Figure 4-6 shows dispersion of Bordertown, Mt Madden and Tatura at ESP 0 and 5. At this energy level, differences in dispersion due to exchangeable cation are more prevalent.

ESP 0

At this energy input there are four soils which exhibited a significant response to the exchangeable divalent cations. Two of these soils, Tomki ($F = 16.63$, $P < 0.05$) and Bordertown ($F = 16.82$, $P < 0.05$), displayed significantly more dispersion when dominated by magnesium. For Wimmera ($F = 9.08$, $P < 0.05$) and Mt Madden soils ($F = 12.90$, $P < 0.05$), the magnesium treatment dispersed significantly more clay than both the calcium and barium treatments, but not the strontium treatment.

ESP 5-20

When sodic, the Wimmera soil exhibited significantly more dispersion when dominated by magnesium at ESP 10 ($F = 11.22$, $P < 0.05$) and ESP 20 ($F = 158.43$, $P < 0.05$), but not ESP 5. Nevertheless, the amount of clay dispersed by Wimmera at this energy level was still quite low overall when compared to the other soils, especially at ESP 20. The Tomki soil exhibited similar behaviour to the Wimmera soil, where treatments at ESP 5 showed no effect of exchangeable cation. At ESP 10 and 20, the magnesium treatment dispersed significantly more clay than the other treatments ($F = 10.89$, $P < 0.05$ and $F = 27.46$, $P < 0.05$ respectively). At ESP 20 there was also a significant difference between the

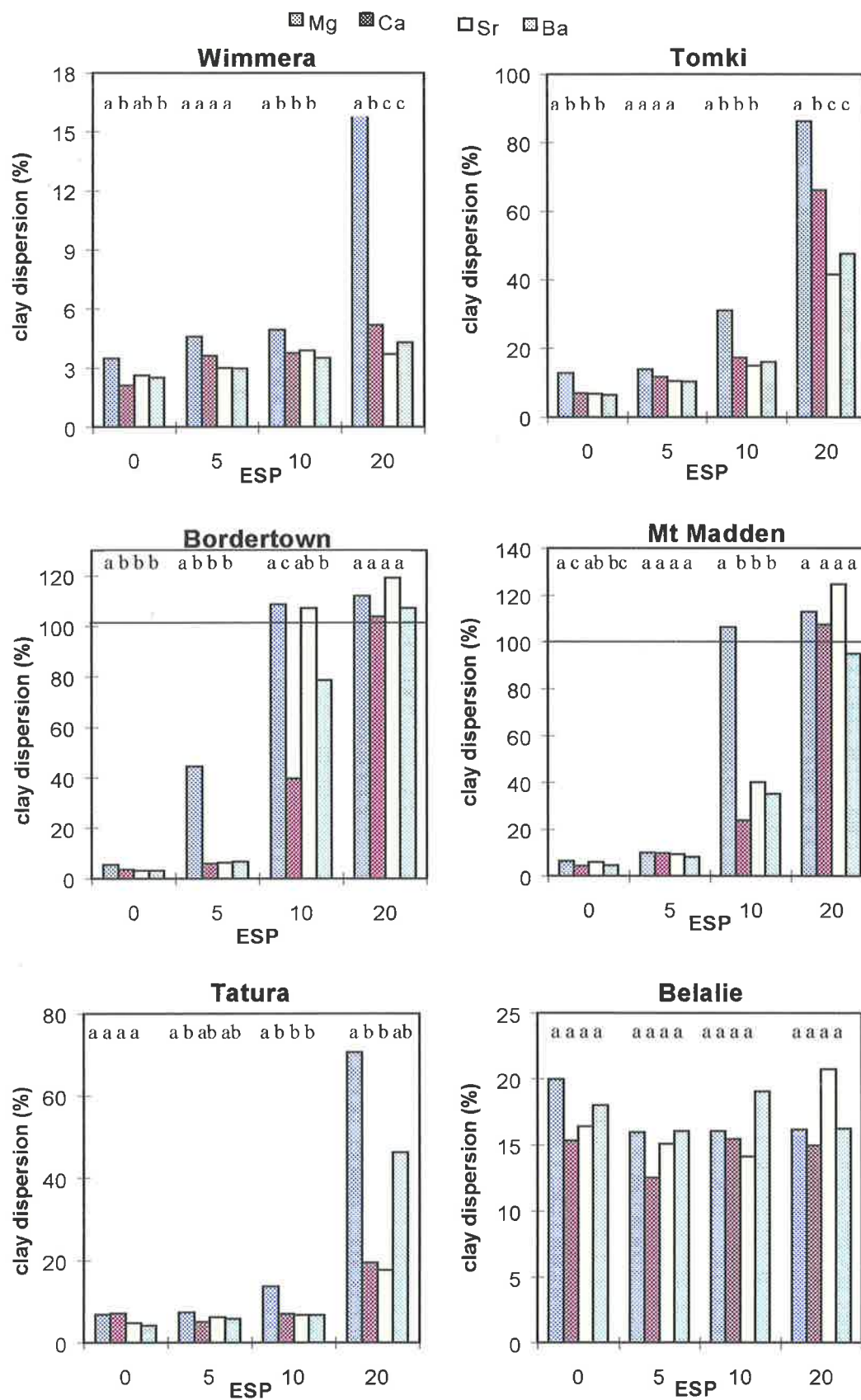


Figure 4-5 Average clay dispersion produced by 15 minutes end-over-end shaking, expressed as a percentage of clay produced by 1 minute sonification.

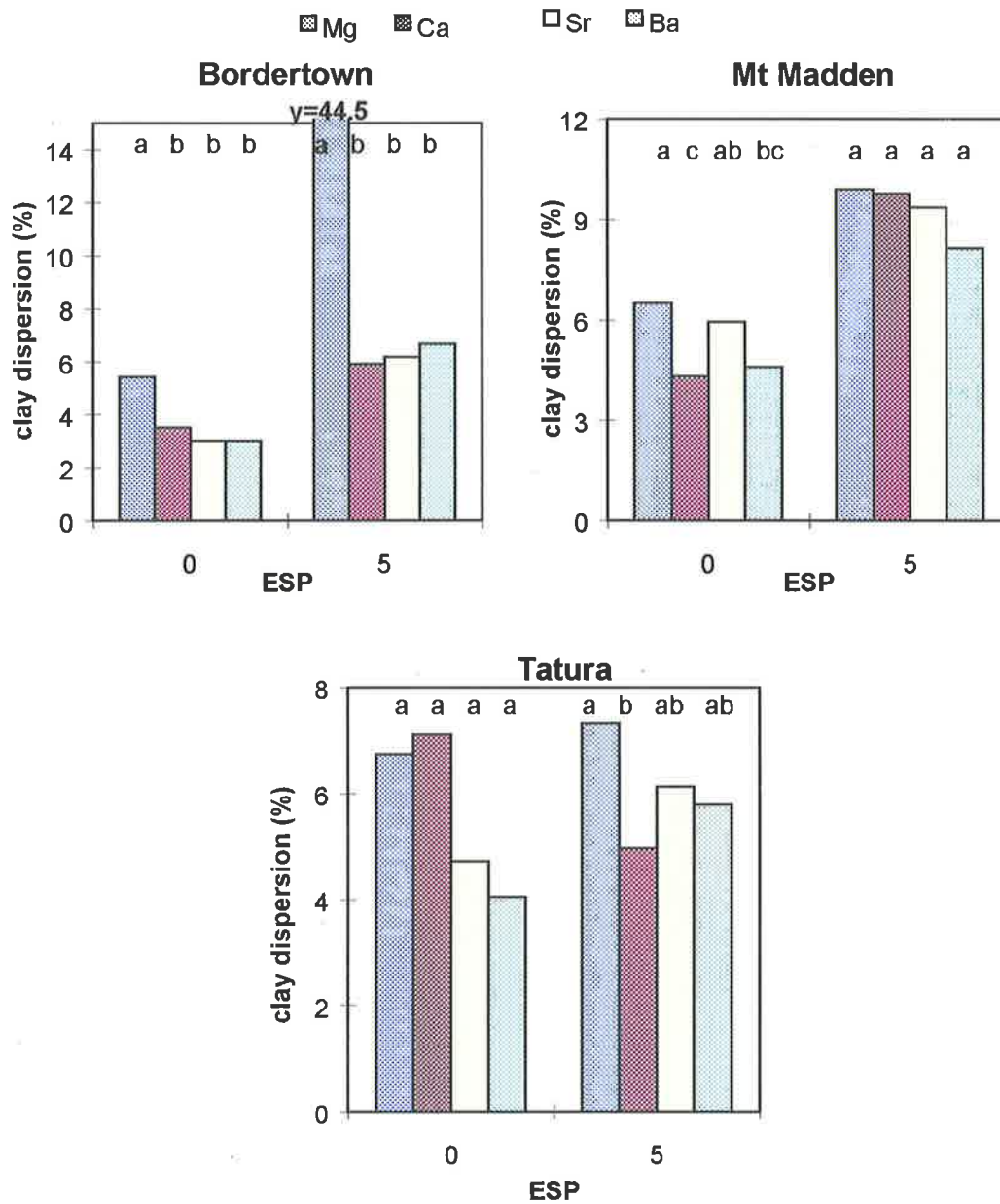


Figure 4-6 Average clay dispersion produced by Bordertown and Tatura ESP 0 and 5 at 15 minutes end-over-end shaking expressed as a percentage of that produced by 1 minute sonification.

calcium treatment and both the strontium and barium treatments. The Bordertown, Mt Madden and Tatura soil all exhibited one ESP where the magnesium treatment dispersed significantly more clay than the other treatments. For the Bordertown soil this was at ESP 5 ($F = 31.13$, $P < 0.05$), and for both Mt Madden ($F = 63.32$, $P < 0.05$) and Tatura samples ($F = 5.21$, $P < 0.05$) it occurred at ESP 10. The remaining ESP values for Mt Madden exhibited no significant cation dependence, while for the Bordertown and Tatura soils, various significant differences were observed but no trend was evident. The Belalie soil again dispersed to give similar amounts of clay for all ESP values and displayed no significant effect of the different exchangeable cations.

The dispersion of ESP 20 Bordertown and Mt Madden soils was essentially complete. At ESP 10, the magnesium-dominated treatment for Mt Madden also dispersed completely but not the other treatments. The Bordertown soil at ESP 10 had two exchangeable cation treatments that resulted in complete dispersion (magnesium and strontium).

2 hours end-over-end shaking

The results for the 2 hour shaking energy input are displayed in Figure 4-7. As noted earlier, there is no data for the Mt Madden soil at this level of disturbance.

ESP 0

At this energy level the Tomki ($F = 14.95$, $P < 0.05$), Bordertown ($F = 8.53$, $P < 0.05$) and Tatura ($F = 24.94$, $P < 0.05$) soils all dispersed significantly more

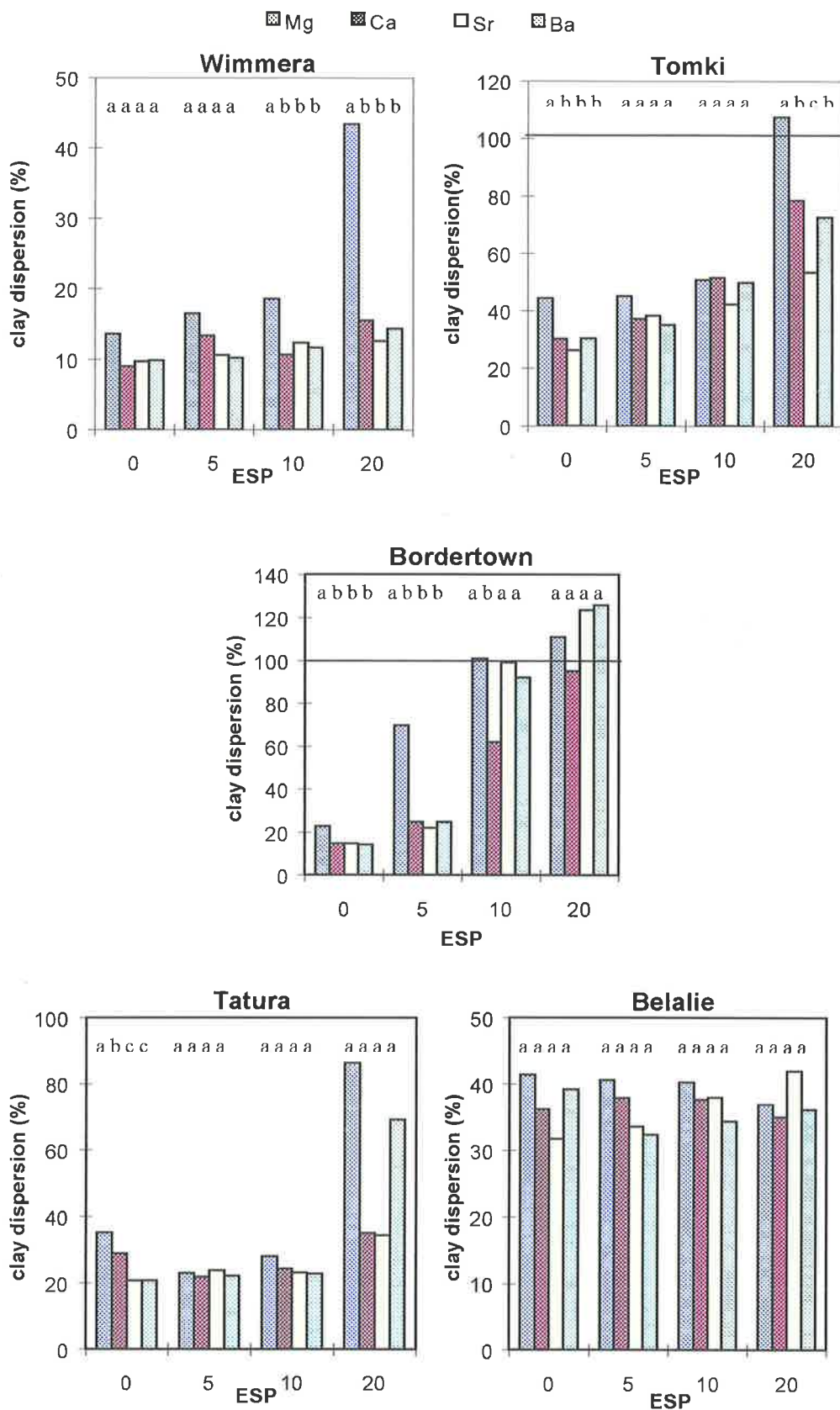


Figure 4-7 Average clay dispersion produced by 2 hours end-over-end shaking expressed as a percentage of that produced from 1 minute sonification.

when magnesium saturated. The Belalie and Tomki soil displayed no significant differences in the effects of exchangeable cations on dispersion.

ESP 5-20

At ESP 5, only the Bordertown soil exhibited a significant increase in dispersion when magnesium dominated ($F = 67.5$, $P < 0.05$). At ESP 10, the Wimmera soil was the only one to exhibit significantly more dispersion when magnesium-dominated ($F = 12.03$, $P < 0.05$). The Bordertown soil showed significantly less dispersion when calcium-dominated ($F = 12.92$, $P < 0.05$). When the ESP was 20, the Wimmera ($F = 61.49$, $P < 0.05$) and Tomki ($F = 69.47$, $P < 0.05$) soils dispersed significantly more when magnesium-dominated. The Tomki soil dispersed significantly less when dominated by strontium at ESP 20. The Tatura magnesium- and barium-dominated treatment dispersed significantly more than both the calcium- and strontium-dominated treatments ($F = 18.5$, $P < 0.05$).

16 hours end-over-end shaking

Results from shaking end-over-end for 16 hours are presented in Figure 4-8.

ESP 0

At this energy level, no soils exhibited significantly more dispersion when dominated by magnesium. There were various treatments that exhibited significant effects of a particular exchangeable cation on dispersion, but no trend in these results was observed.

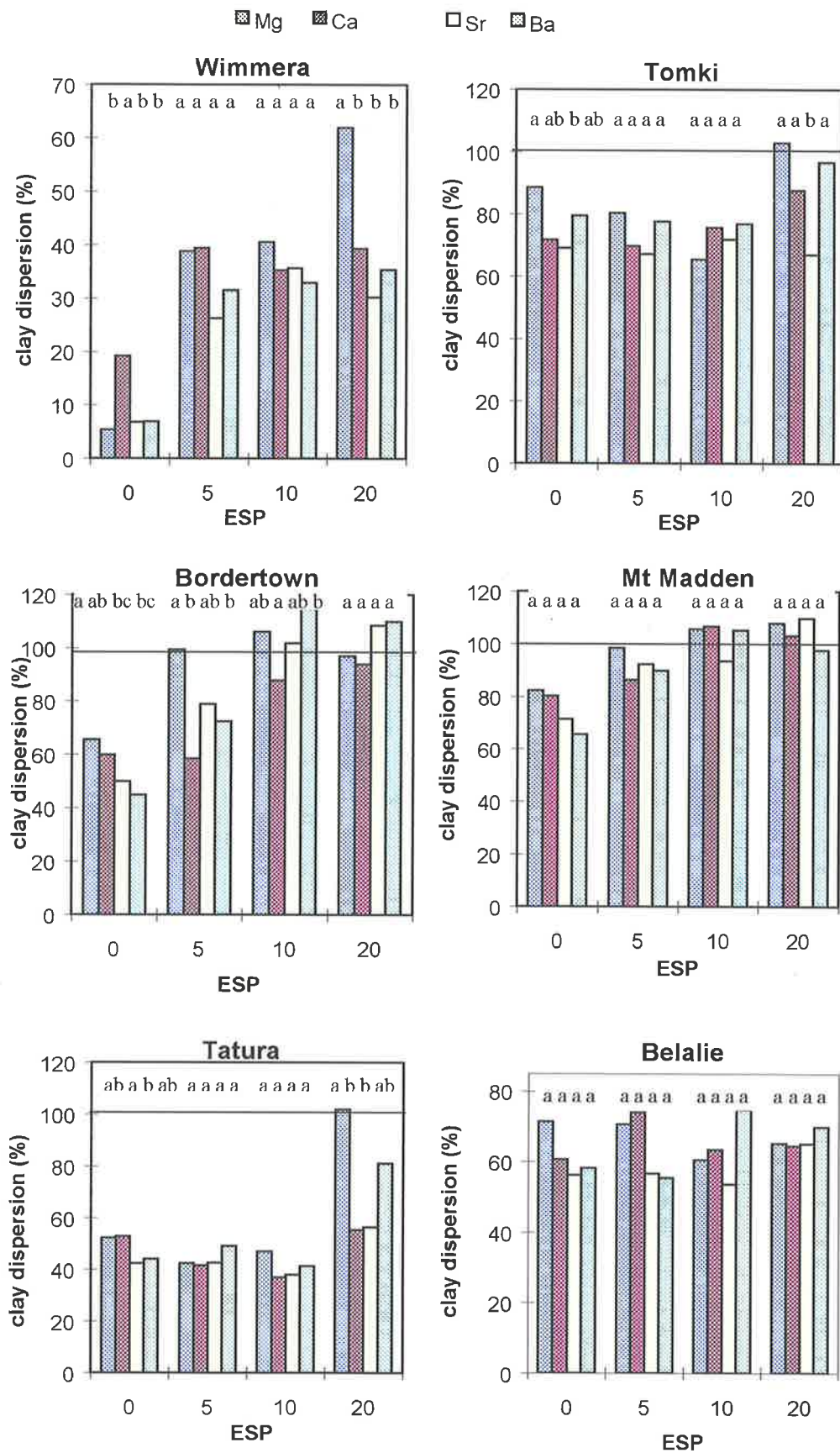


Figure 4-8 Average clay dispersion produced by 16 hours end-over-end shaking expressed as a percentage of that produced from 1 minute sonification.

ESP 5-20

Only the Bordertown soil exhibited any significant differences in dispersion at ESP 5. The magnesium-dominated treatment dispersed significantly more than both the calcium and barium treatments. ($F = 8.82$, $P < 0.05$). The Bordertown soil was also the only soil which exhibited significant differences in dispersion for ESP 10; this was between the barium- and calcium-dominated treatments only ($F = 6.06$, $P < 0.05$). At ESP 20 more soils displayed differences due to exchangeable cations. At this energy level and ESP it would be expected that the effects of the divalent exchangeable cations might be minimal due to the high exchangeable sodium and large amount of energy imparted to the system. It was expected that these conditions would produce complete dispersion in most soils. The Wimmera soil exhibited significantly more dispersion when magnesium-dominated ($F = 69.47$, $P < 0.05$). The Tomki soil when strontium-dominated dispersed significantly less than the other treatments at ESP 20 ($F = 15.99$, $P < 0.05$). The only other soil that displayed a response to exchangeable cations was Tatura. The treatment dominated by magnesium dispersed significantly more than both the strontium- and calcium-dominated treatments ($F = 14.69$, $P < 0.05$). The Bordertown and Mt Madden soils dispersed almost completely at ESP 10 and 20, and the Belalie soil exhibited no significant differences in dispersion between any treatments at this energy level.

4.3.2. Particle size

Particle size results are shown in Appendix 3. The Mt Madden soil was the first soil tested and no data for particle size was measured at that stage. There is a lack of data points for some of the other samples because the concentration of

dispersed clay was below the detection limits of the particle sizer. Some problems associated with measuring particle size are discussed in detail in section 3.12. The accuracy of particle size measurements is compromised if a few large particles are present. These large particles dominate light scattering and obscure the mean particle size of the suspended colloids. Overall, the expectation for each soil is for particle size to reduce as energy input increases and then to converge to a single size for each soil after 1 minute sonification, as this is considered sufficient energy to break the soil aggregates into individual particles.

The Wimmera soil did not show particle size convergence after 1 minute sonification; instead a range of particle sizes was observed in most cases. This is probably due to the highly smectitic nature of Wimmera resulting in clay particles with surfaces still in intimate contact, even after 1 minute sonification. The particle size of the Wimmera samples varied over all the energy levels and there seemed to be no general trend with exchangeable cation. The samples with exchangeable magnesium seemed to vary as much in particle size as those with the other group II cations present. ESP also seemed to affect the particle size of dispersed Wimmera clay, with samples containing no sodium generally displaying larger particle sizes at most energy levels, especially after 1 minute sonification. The particle sizes of ESP 20 samples after 1 minute sonification (except the ESP 20 calcium-dominated sample) were similar. When saturated with barium at different ESP values, an effect of ESP on particle size was observed after 16 hours end-over-end shaking; the sample saturated with barium,

but containing no sodium, dispersed to give the largest particle size, which decreased as ESP increased.

Tomki, the other smectitic soil, displayed some similarities to Wimmera in its particle size results. The range of particle sizes over all the mechanical energy inputs was greater than in the Wimmera soil. However there was an overall weak trend towards decreased particle size as energy input increased which was not evident in the Wimmera soil. The influence of the divalent cations on particle size seems to be less in the Tomki soil as the range of particle sizes after 1 minute sonification was smaller and all divalent cation treatments showed similar particle size ranges. Other than a general decrease, there did not seem to be any trends in the particle size with increasing ESP. As Tomki contains smectitic material, there are likely to be particles with surfaces still in intimate contact, which could cause the range of particle sizes observed after 1 minute sonification.

Of the illitic soils, Tatura displayed the expected decrease in particle size as energy input increased, with excellent convergence of particle size after 1 minute sonification. There seemed to be little effect of ESP and divalent cation on the dispersed particle size. Except for a few outliers, which could be the result of larger fragments breaking off the aggregates, the spread of particle sizes for Tatura soil was quite small over all the levels of mechanical energy input. The illitic Belalie soil exhibited distinct decrease in particle size as energy input increased and converged to a more or less common size on sonification.

The kaolinitic Bordertown soil gave the expected convergence of particle size after 16 hours end-over-end shaking, indicating that, after this level of energy input, neither the nature of the divalent cations nor the ESP have any effect on the particle size of dispersed clay. Even before the convergence of particle sizes there were no clear trends in the effect of ESP and/or divalent cations on micro-aggregate breakdown, suggesting that the cohesion of this soil is largely determined by other factors.

4.3.3. Spontaneous dispersion

Not all the samples prepared were assessed for spontaneous dispersion. The turbidimeter used was very sensitive to slight changes in turbidity and as spontaneous dispersion was very slow, the approach to "equilibrium" was also very slow. Samples saturated with magnesium or at ESP 5 that appeared to disperse spontaneously were measured in triplicate. Due to the lack of replicates for some samples it is difficult to conclude if any of the responses observed are significant.

ESP 0

When the soils had no exchangeable sodium (Figure 4-9), only the kaolinitic soils (Bordertown and Mt Madden) dispersed spontaneously to give more clay when magnesium, rather than calcium, was present as the dominant exchangeable cation. The difference in the percentage of clay dispersed from the kaolinitic samples saturated with magnesium and those with the other group II cations was quite dramatic. But, overall, the total percentage of clay dispersed spontaneously was quite small. For the illitic soils the calcium-saturated

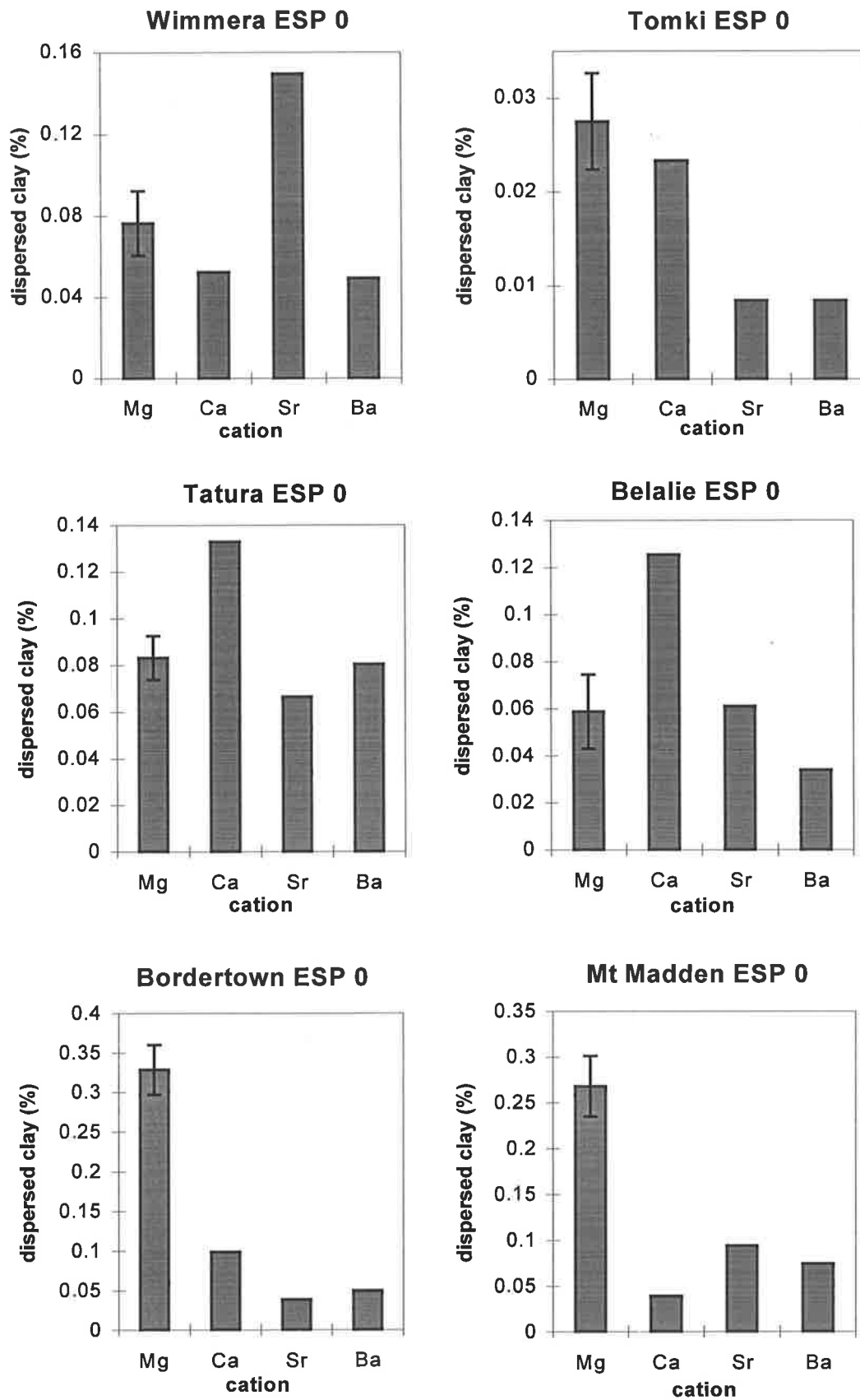


Figure 4-9 Percentage of clay spontaneously dispersed from soils with ESP 0. Error bars are standard deviations of average clay dispersion.

samples seemed to disperse more than the other samples with divalent cations, but since only one replicate was measured it is difficult to draw any conclusions. The remaining samples dispersed to give similar amounts of clay. For the Wimmera soil, it was the strontium-saturated soil that appeared to disperse the most, but again, since only one replicate was measured, it was difficult to draw conclusions from this result. With Tomki both the magnesium- and calcium-saturated treatments dispersed to give more clay than the strontium- and barium-saturated treatments. While only one replicate of calcium-saturated Tomki was measured, the dispersion of this sample was more than three times that produced by strontium- and barium-saturated treatments.

Only two of the soils, Tomki and Mt Madden (Figure 4-10) were assessed for spontaneous dispersion when sodic. Spontaneous dispersion measurements were made on Mt Madden soil with ESP 5, 10 and 20. Only samples with ESP 10 seemed to exhibit more dispersion when magnesium was present. At ESP 5 the calcium-saturated treatment appeared to disperse more. At ESP 20, all the Mt Madden samples tested dispersed to yield similar amounts of clay, indicating that the ESP and not divalent exchangeable cations was controlling dispersion. Only Tomki samples with ESP 10 and 20 dispersed spontaneously. At ESP 10 and 20, the magnesium-saturated soil dispersed significantly more than the other samples, with the differences for ESP 10 being especially marked.

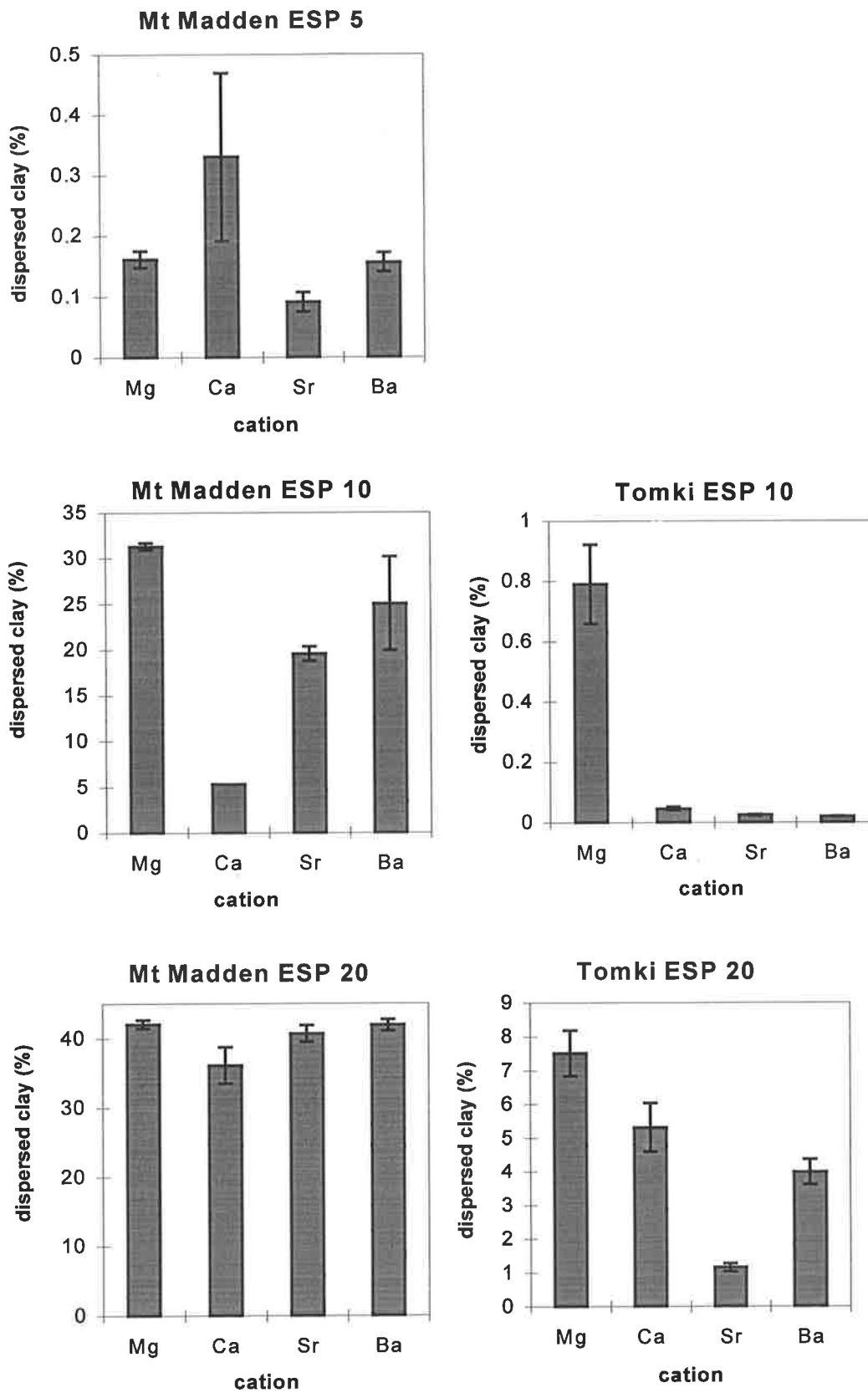


Figure 4-10 Percentage of clay spontaneously dispersed from Mt Madden ESP 5,10 and 20 and Tomki ESP 10 and 20. Error bars are standard errors of average clay dispersion.

4.4. Discussion

The turbidity measurements were transformed to clay percentages using a calibration curve determined on sonified clay which therefore had particles of very similar size. When the soils are dispersed the resulting clay suspension contains clay particles with different sizes that may influence turbidity results. This in turn will affect the calculation of percentage clay dispersed and may account for some of the anomalous results observed. Rayleigh theory indicates that particle size influences turbidity (section 3.11).

4.4.1. Mechanical dispersion

A summary of the results of dispersion events for each treatment is displayed in Table 4-2. The shaded areas indicate treatments that dispersed significantly more clay when magnesium was the dominant cation. The Tomki soil exhibited the greatest number of treatments that dispersed significantly more when magnesium was present as the dominant exchangeable cation. There appeared to be no trend in the nature of the treatments that displayed this effect. All ESP values and energy levels produced treatments that responded to exchangeable magnesium by dispersing significantly more than the treatments saturated with the other group II cations; this will be referred to hereafter as a "magnesium effect". There appears to be little connection between the magnesium effect and particle size. This indicates that for the Tomki soil, the particle size had little connection with the dispersion resulting from each treatment. Where a magnesium effect was observed, there was no corresponding decrease in the particle size dispersed from that soil. The Wimmera soil generally required higher levels of energy and sodium for the magnesium effect to occur.

Table 4-2 Summary of results for mechanical dispersion of six soils saturated with magnesium, calcium, strontium and barium, each with ESP values of 0 - 20.

Soils	ESP	2 EOE	1 minute	15 minutes	2 hours	16 hours
Wimmera (S,K)	0			Yellow	Yellow	
	5			Yellow	Yellow	
	10			Blue	Blue	Yellow
	20	Yellow	Blue	Blue	Blue	Blue
Tomki (RIM >> I,K)	0	Yellow	Blue	Blue	Blue	Yellow
	5	Blue	Yellow	Yellow	Yellow	Yellow
	10	Blue	Blue	Blue	White	White
	20	Blue	Yellow	Blue	Blue	Yellow
Bordertown (K,RIM,I)	0	Yellow	Blue	Blue	Blue	Yellow
	5	Blue	Blue	Blue	Blue	Yellow
	10	White	Yellow	Yellow	White	White
	20	Blue	White	White	White	White
Mt Madden (K >> RIM,I)	0		Blue		not measured	Yellow
	5	Yellow	Yellow			Yellow
	10		Blue	Blue		White
	20					White
Tatura (I > K,RIM)	0	Yellow			Blue	White
	5		Yellow	Yellow	White	White
	10	Yellow	Blue	Blue	Yellow	Yellow
	20	Yellow	White	Yellow	White	Yellow
Belalie (I >> K,RIM)	0			Yellow	Yellow	Yellow
	5				Yellow	White
	10	Yellow	Yellow		Yellow	White
	20					White

Blue squares are samples that exhibit significantly more dispersion when dominated by exchangeable magnesium than the other group II cations. Yellow squares are samples where magnesium dispersed to give more clay than the other group II cations, but the differences were not significant. Clay mineralogy of each soil is in brackets under soil name.

For this soil the total amount of clay dispersed after 16 hours of shaking was also the least in all the soils. This is an indication of the stability of the soil to mechanical disruption; most of the other soils dispersed completely at this point. In contrast to Wimmera, the Bordertown soil displayed the greatest effect of magnesium on dispersion at low ESP values for most energy levels. Conclusions about the effects of exchangeable magnesium on Mt Madden are more difficult to formulate due to the absence of results at 2 hours end-over-end shaking. There is no particular effect of magnesium at ESP 20 in the Mt Madden soil since, except for shaking end-over-end twice by hand, complete dispersion occurred for all treatments. In this case ESP was controlling the amount of dispersion and not the accompanying divalent exchangeable cations. The Tatura soil also displayed few magnesium effects, mainly when sodic. The remaining soil, Belalie, exhibited no significant effect of exchangeable magnesium, when compared to the other cations, during mechanical dispersion.

Since smectites are commonly thought to be quite dispersive (Frenkel *et al.*, 1978; Stern *et al.*, 1991), the relative stability of Wimmera to mechanical dispersion seems out of character. However, if the average density of surface charge is calculated (Table 4-3) for Wimmera and Tomki (both smectitic soils), a significant difference is observed. It has been shown previously that density of surface charge of smectites can have an important impact on the stability of soil. Shainberg *et al.* (1987) found the hydraulic conductivity of soil with a high charge density was not sensitive to the range of exchangeable potassium that might be found in cultivated soils. In contrast, montmorillonitic soil with a low surface charge density displayed increased dispersion and a decrease in the

Table 4-3 Charge properties of the soils used in the study.

Soil	CEC (meq/100g)	SSA _T (m ² /g) ^a	Charge density (meq/m ² x 10 ³)
Wimmera	52	410	1.3
Tomki	50	620	0.8
Belalie	20	120	1.7
Tatura	30	300	1.0
Bordertown	39	740	0.5
Mt Madden	29	560	0.5

^a Total specific surface area (ie “internal” and “external”) calculated from sums of the surface areas measured by N₂ and H₂O adsorption (Mooney *et al.*, 1952)

hydraulic conductivity with about 6% potassium. Results similar to those observed by Shainberg *et al.* (1987) were detected in the same soils but with sodium as the exchangeable cation instead of potassium (Alperovitch *et al.*, 1985). Surface density of charge also affects clay swelling in salt solutions; montmorillonitic clays with a high density of surface charge display limited swelling (Slade *et al.*, 1991). The same study also found that the origin of the surface charge in the structure was also important.

The calculated density of surface charge values shown in Table 4-3 are approximations as they are calculated from the sums of the total specific surface areas (ie “internal” and “external”) measured by water and nitrogen adsorption. The specific surface area calculated from water adsorption is only an estimate of the surface area since differences in interactions of water molecules with various surfaces and exchangeable cations means that water vapour retention cannot be easily transformed into specific surface area (Newman, 1983; Churchman *et al.*,

1991). Water is a polar solvent that is attracted to exchangeable cations and clusters around them instead of forming a monolayer on the clay surfaces (Quirk, 1955). Nevertheless, surface charge densities of soils calculated from surface areas obtained by the same procedure may be compared to indicate differences in behaviour, particularly when the soils have similar clay mineralogies and hence similar surfaces for water uptake.

The effect of differences in the surface charge density of clays can also be observed in the water content at 100 cm suction by calcium- and sodium-saturated soils (Table 4-4). Large differences in water content between the calcium- and sodium-saturated samples of a soil may indicate the presence of smectite. The work of Slade *et al.*, (1991) suggested that where smectite is present, the water content of the sodium-saturated sample relative to that of the calcium-saturated sample reflected the density of surface charge of the clay mineral. The greater the difference between the water content for sodium- and for calcium-saturated samples, the more liable is the smectite to swell. This is a reflection of its lower charge density and its lower stability. Therefore the water content and average density of surface charge data presented indicate that Wimmera is likely to be more stable than Tomki to the effects of mechanical dispersion and magnesium because it has a higher charge density. Illites have irregular surfaces which contribute to poor contact between crystals and so are generally more dispersive than kaolinites (Emerson & Chi, 1977; Levy, *et al.*, 1993a). The increase in dispersion observed in some samples of Tatura when dominated by magnesium is consistent with the findings of Emerson & Chi (1977) and Rahman & Rowell (1979) for illitic soils. The difference in water

Table 4-4 Water adsorption at 100 cm suction of soils used in this study.

Soil	Water adsorbed at 100 cm suction (g/g)	
	Calcium-saturated	Sodium-saturated
Wimmera	0.8	1.7
Tomki	0.6	3.4
Belalie	0.1	0.2
Tatura	0.5	1.0
Bordertown	0.3	0.9
Mt Madden	0.4	0.6

content between sodium- and calcium-saturated Tatura at 100 cm suction (Table 4-4) indicates the possible presence of smectitic material. The large increase in water content in the Tatura soil when sodium-saturated implies that the smectitic material may influence its stability quite significantly. The Tatura soil displayed only three treatments in which the presence of exchangeable magnesium resulted in significantly more dispersion.

Pore size distribution data (Appendix 2) indicated that the illitic soils (Belalie and Tatura) contain particles with a relatively wide range of thickness. The generally thicker particles within these soil clays predispose them to mechanical dispersion. The illitic soils displayed similar behaviour towards mechanical dispersion, with any differences probably attributable to differences in mineralogy. The Belalie soil was almost completely illitic, while the Tatura soil contained appreciable amounts of kaolinite and RIM. The higher smectite content of the Tatura soil (from RIM) may account for the magnesium effect observed, as it can have a destabilising effect on soil (Frenkel *et al.*, 1978).

Despite illitic soils being considered relatively unstable, the dispersion occurring after 16 hours of end-over-end shaking was not complete, as would be expected for an unstable soil. For Tatura only 60% of the clay dispersed, except for the magnesium-dominated ESP 20 sample that dispersed completely. For Belalie, the dispersion was variable and ranged from about 60 to 80%. Both illitic soils are red-brown in colour which indicates the presence of iron oxides (Williams, 1981). Iron oxides have been shown to increase the stability of soils (Alperovitch *et al.*, 1985; Goldberg *et al.*, 1990), but stability may not be entirely dependent on their presence (Deshpande *et al.*, 1964). It is possible that the domains were bound into larger entities by iron oxide that if dispersed would not appear in the $< 2 \mu\text{m}$ fraction sampled.

The kaolinitic soils used in this study were very dispersive, with complete dispersion of clay occurring more easily in Bordertown and Mt Madden than in any of the other soils studied. The kaolinitic soils each have different mineralogical characteristics, which may account for the differences observed in each soil's response to the presence of exchangeable magnesium. The Bordertown soil contains a large amount of smectitic material, as shown by the difference in water content between the calcium- and sodium-saturated soil at 100 cm suction (Table 4-3). The Bordertown soil seemed to behave more like a smectitic soil with respect to its stability, with the number of treatments that displayed a magnesium effect similar to that observed in the Tomki soil. The similarity between the water content of sodium- and calcium-saturated Mt Madden at 100 cm suction (Table 4-4) indicates the possible presence of a small amount of smectite. The dispersive behaviour of each of the kaolinitic soils is

probably due to different causes. The Bordertown soil contains equivalent amounts of kaolinite and smectite minerals, and previous studies have shown that the presence of montmorillonites in a kaolinitic soil can increase the dispersive behaviour of that soil (Frenkel *et al.*, 1978). In contrast, Mt Madden is largely kaolinite and so should be more stable than Bordertown. The highly dispersive behaviour of Mt Madden could be due to the coarse nature of the clay particles in the soil. Coarse particles do not fit together as well as fine particles making them more susceptible to disruption and dispersion from mechanical energy.

For each soil there seems to be a level of disturbance beyond which many treatments show a magnesium effect. The amount of energy required to produce a magnesium effect is an indication of the stability of that soil to mechanical dispersion. The Wimmera soil required quite a high level of energy before any effect of magnesium was observed. Both 15 minutes and 2 hours end-over-end shaking produced the most uniform magnesium response. In contrast, Tomki seemed to be particularly susceptible to the presence of magnesium. The lowest energy input, twice end-over-end by hand, produced the most extensive magnesium effect.

The response of Bordertown is completely different to that observed for the previous two soils. There seems to be no particular energy at which more treatments exhibited a magnesium response; instead all energy inputs have similar responses. Energy input may not be a controlling factor in the response of the Bordertown soil to the presence of magnesium; it is probable that mineralogy controls the magnesium response of this soil. The Mt Madden and

Tatura soils showed very few treatments that displayed a magnesium effect. The treatments, which did exhibit a magnesium effect, did not seem to follow any trend. Exchangeable magnesium probably has little effect on the dispersion of both soils. The Belalie soil exhibited no significant effect of exchangeable magnesium on dispersion, and the effects of all exchangeable cations were limited.

For each soil an effect of magnesium in significantly increasing dispersion when compared to the other group II cations, was shown only for certain samples with the trends within soils discussed previously. If the summary of results in Table 4-2 is analysed, there seems to be a common factor in some of the soils that exhibited a magnesium effect (where magnesium results in significantly more dispersion than that observed in calcium, strontium and barium). The soils are placed in order of decreasing numbers of treatments displaying a magnesium response. The three soils with the most treatments showing a magnesium effect are Wimmera, Tomki and Bordertown. The common factor in these soils is the presence of significant amounts of smectite. For Tomki and Bordertown the smectite is in the form of randomly interstratified minerals (RIM). The RIM probably consists of kaolinite/smectite layers (from XRD analysis, Appendix 1). From the XRD of the whole clay there appears to be no RIM present in the Wimmera soil. Subsequent XRD analysis of the fine clay fraction (Appendix 1) indicated that there is RIM in this fraction of the Wimmera soil. Therefore both the smectites and RIM present in the soil contribute to the response of Wimmera to exchangeable magnesium in certain samples. The Tomki soil clay fraction is dominated by RIM and is the most susceptible to the presence of exchangeable

magnesium, with more treatments exhibiting a magnesium effect at the lowest energy levels. The Bordertown soil contains significant amounts of RIM and has a correspondingly high number of treatments that exhibit a magnesium response.

Randomly interstratified minerals are thought to be more dispersive because of differences between their crystal structures and those of simple mixtures of kaolinite and smectite. With RIM, the smectite and kaolinite layers are in intimate contact within crystals. These differences may translate into differing particle geometries. Smectites are often thin flexible particles that can adsorb mechanical energy instead of breaking apart. The pore size distribution data of Wimmera shows that particles are generally composed of less than four lamellae, which is similar to the Vertisols studied by Murray *et al.* (1985). Who suggested that the Vertisols investigated contained clay lamellae that continuously overlapped resulting in long-range order in the clay structure. As the Wimmera soil has a similar pore size distribution and mineralogy to the Vertisols, it is possible that its clay lamellae are ordered in a similar way. This would also contribute to the increased stability the Wimmera soil exhibits against mechanical disruption compared to other soils investigated. According to transmission electron micrographs (Churchman *et al.*, 1994), interstratified kaolin/smectite mineral particles are usually poorly defined, have curved edges and vary in thickness. The nature of interstratification also appeared to be random, as there was no long-range order in the stacking sequence evident in the micrographs. The poor structure of interstratified layers was also evident in mixed-layer soils from Mexico, where the mixed layer kaolinite-montmorillonite crystals were nearly round (Schultz *et al.*, 1971). This poorly defined nature of

the RIM particles would make them more susceptible to dispersion as they are not packed together well and the bonds between the particles would be easier to break. While the pore size distribution of Tomki indicates that most particles are around 2 - 3 nm thick with little variation in thickness, the low density of surface charge of the smectite, which dominates the fine clay fraction, is likely to predispose it to dispersion when subjected to mechanical energy.

4.4.2. Particle size

The results of particle size measurements provide general information on aggregate breakdown, but it is difficult to draw definite conclusions about particle size due to limitations in the method. Particle size measurements of the kind described here assume that the colloids have a uniform spherical nature. Clay colloids are not spherical in nature, therefore the mathematics used to derive particle size are not entirely appropriate. The particle size data does, however, indicate that the breakdown of the aggregate is occurring much as expected; generally the dispersed clay particles become smaller as the energy input is increased. While the actual sizes measured may not be accurate, they do give some idea of the dimensions of the particles being dispersed and of the differences between soils. The differences in dispersed clay particle sizes observed at each energy level are possibly an indication of the extent of fragmentation of soil aggregates. When the aggregates are subjected to a small amount of energy, small fragments break off the original aggregate and disperse. As the energy input increases it is possible that the size of the fragments breaking off increases in some cases, and in the others these fragments themselves are broken into smaller particles. Most soils dispersed particles of a

size less than $2\mu\text{m}$. Only the Tomki soil appeared to disperse particles of a larger size (in comparison), especially at the lower levels of mechanical disturbance.

4.4.3. Spontaneous dispersion

Spontaneous dispersion arises from the repulsive forces between clay particles acting to overcome energy barriers due to attractive forces and causing them to detach from each other. Soils which spontaneously disperse when placed in water are generally considered to be structurally poor, with mobile clay particles (Sumner, 1993). Due to the lack of complete data and replicates for spontaneous dispersion measurements it is difficult to draw conclusions. Only the nominally kaolinitic soils displayed a trend in results for spontaneous dispersion. This could be attributed to the presence of kaolinite, although the Bordertown soil also contains considerable smectite. It is possible that the clay that dispersed was the kaolinite fraction, but this would have been very difficult to demonstrate. There is also the possibility that the spontaneous dispersion is probably not controlled purely by mineralogy. When both kaolinitic soils were observed in the field, they were both quite dispersive (as observed when natural soil is wet up slowly on a porous funnel, spontaneous dispersion occurs), and so when saturated with divalent cations, the underlying natural instability of the soils may still prevail.

The increase in dispersion observed in sodic Tomki samples that were magnesium-saturated is interesting and could be due to the dominance of RIM. There are some indications from the mechanical dispersion data that RIM could

enhance dispersion in the presence of exchangeable magnesium. Nevertheless, the Tomki ESP 0 sample saturated with exchangeable magnesium did not spontaneously disperse significantly more than the other treatments. However, the extent of spontaneous dispersion of the Tomki ESP 0 sample is so low as to be practically negligible. Since the other soils, which contain significant amounts of RIM, were not assessed for spontaneous dispersion, the suggestion that RIM enhances spontaneous dispersion when magnesium was present must remain tentative.

4.5. Conclusions

The effect of the group II cations (magnesium, calcium, strontium and barium) on the dispersion of six Australian soils was investigated. It was expected that the presence of exchangeable magnesium would result either in increased or similar dispersion when compared to the dispersion of the soil with the other group II cations. The results indicate that in many samples the presence of exchangeable magnesium produced significantly more dispersion than obtained with other divalent cations. Although this was observed in many treatments, no trend that could be applied to all soils was observed. Samples dominated by calcium, strontium and barium generally produced similar amounts of dispersed clay. This indicates that there is little difference in the way these cations affect soil stability. There was no consistent difference in the response of sodic and non-sodic soils to magnesium. The magnesium effect on the dispersion of soil does not appear to depend on the presence of exchangeable sodium; some magnesium-saturated (100% magnesium) treatments dispersed significantly more than calcium-saturated ones as was seen in Figure 4-3 for the Tomki, Bordertown

and Mt Madden soils with ESP 0. Hence, exchangeable magnesium has a specific effect (similar to the effect of sodium) as well as a possible influence on the uptake of sodium on exchange sites which was not observed here as each treatment had a specific amount of exchangeable sodium present.

There was also an expectation that clay mineralogy would dictate dispersive behaviour, and soils with similar mineralogies would behave alike. The results indicated that soils, which were considered to have similar mineralogies, based on their major clay mineral components, did not produce similar results. The two smectitic soils displayed quite different behaviour in the presence of exchangeable magnesium and this may be related to the different densities of surface charge and the specific clay minerals present in the soils. The two illites displayed similar behaviour despite some differences in mineralogy. The two kaolinites displayed quite different responses to the presence of exchangeable magnesium possibly because of both mineralogy and particle size and shape. Despite the differences in dispersion in the presence of exchangeable magnesium within a mineralogical group, a mineralogical trend for all soils was observed. The presence of randomly interstratified minerals (RIM) in a soil seemed to predispose it to enhanced dispersion when exchangeable magnesium was present. Other studies (Norrish & Pickering, 1983; Churchman *et al.*, 1994) have suggested that RIM is very widespread in Australian soils and the results of this study indicate that soils containing this type of mineral may be more susceptible to increased dispersion in the presence of exchangeable magnesium.

In conclusion, exchangeable magnesium, when dominant, caused significantly more dispersion in most, but not in all, soils. There was no clear pattern in the

samples that dispersed significantly more when magnesium dominated the exchange sites. The response of the soil to magnesium appeared to be enhanced by the presence of RIM, but could not be attributed to any one of the main types of clay minerals studied (kaolinite, illite or smectite).

5. Dispersion of soil in a mixed calcium-magnesium-sodium system

5.1. Introduction

In the field, calcium, magnesium, sodium and potassium ions are all frequently present in the soil solution and on the exchange sites of clay. However, the majority of work on the effect of magnesium on sodic soils has been undertaken with systems containing only two cations, generally only sodium with either calcium or magnesium. It is possible that the adverse effects of magnesium on sodic soil stability have been exaggerated as most conclusions have been drawn from studies of systems not representative of the field. In the few studies of mixed cation systems conducted, the conclusions drawn were contradictory. Curtin *et al.* (1994b) observed the effect of a calcium:magnesium:sodium (mixed cation) system (SAR 10 and 20) on the hydraulic conductivity of a smectitic soil. They noted that magnesium seems to have a relatively small effect on hydraulic conductivity. The hydraulic conductivity of the mixed cation system was very similar to that of the calcium-sodium system. Two calcium:magnesium ratios were investigated (1:2 and 2:1) and there appeared to be little difference in hydraulic conductivity between them. Rengasamy *et al.* (1986) observed the dispersion of sodic red-brown earths ($ESP > 6$) and found an increase in dispersion when the calcium:magnesium ratio was between 0.8 and 1.2. It can be seen that investigations into the effects of the calcium:magnesium ratio have been limited, both in respect to soil type and the calcium:magnesium ratios used. Hence the aim of the present study was to investigate the effect of different calcium:magnesium ratios on the dispersion of several soils over the ESP range 0-20.

5.2. Materials and Methods

A range of treatments was prepared using the method described in section 3.8. Treatments were prepared with the exchangeable cation percentages listed in Table 5-1. The final column in Table 5.1 is the labelling system for the treatments. The first number is the exchangeable sodium percentage (ESP), and the second number is the exchangeable magnesium percentage (EMgP). The remaining exchange capacity is occupied by calcium.

The results of each dispersion event were subjected to analysis of variance (ANOVA) with three degrees of freedom. A comparison of means (Tuckey's test) was then made for each ESP. The results of the Tuckey's test are shown on the results figures for this chapter as letters of the alphabet. Where the letters are different within an ESP, this indicates a significant difference in dispersion between treatments with the same ESP for each soil.

Electrophoretic mobility was measured on a Malvern Zetamaster and zeta potential was calculated using the Smoluchowski equation. The clay suspension used resulted from the 1 minute sonification treatment on which turbidity was measured (section 3.9). After 1 minute sonification, 0.5 ml of the $< 2 \mu\text{m}$ suspension was diluted to 30 ml with distilled water. The treatments labelled as pH 6.5 were not altered in any way before the zeta potential was measured.

Table 5-1 The exchangeable cations present in each treatment

ESP	EMgP	ECaP	ESP/EMgP
0	0	100	0/0
0	100	0	0/100
3	0	97	3/0
3	50	47	3/50
3	97	0	3/97
5	0	95	5/0
5	30	65	5/30
5	60	35	5/60
5	95	0	5/95
7	0	93	7/0
7	25	68	7/25
7	50	43	7/50
7	75	18	7/75
7	93	0	7/93
10	0	90	10/0
10	25	65	10/25
10	50	40	10/50
10	75	15	10/75
10	90	0	10/90
20	0	80	20/0
20	20	60	20/20
20	40	40	20/40
20	60	20	20/60
20	80	0	20/80

The pH of these treatments was the natural pH of the suspensions (6.5 ± 0.3). To obtain treatments with pH 5, 0.01 M HCl was added to the suspension until the pH remained constant. To increase the pH to 8, a basic solution of concentration 0.01 M, specific for each cation (see below), was added until the pH remained constant. During adjustment, the pH of each solution was maintained as close as possible to the target pH and was generally within 0.2 pH units. The basic solutions used were sodium hydroxide for sodium-saturated treatments, calcium hydroxide for calcium-saturated treatments and magnesium carbonate for magnesium-saturated treatments. Magnesium carbonate was used due to the low

solubility of magnesium hydroxide. The treatments were stirred continuously during adjustment of pH and zeta potential was measured almost immediately after pH stabilised.

5.3 Results

The pH of the dispersed treatments was again in the range where the effects of variable charge on dispersion appear to be minimal. A recent study of the dispersion of clay over the pH range 3 - 10 found increases in dispersible clay of less than two percent when the pH was between 5.9 and 7.2 for an illitic and a kaolinitic soil (Chorom *et al.*, 1994). A study by Goldberg and Forster (1990) found that with reference and soil clays the change in critical coagulation concentration (CCC) was minimal between pH 6 (lower limit of pH investigated) and pH 8. As the SAR of the solution rose the changes in CCC also increased, but ESP 20 was the upper limit used in this study and the results of Goldberg and Forster (1990) indicate that below SAR 20 the effects of sodium on CCC are minimal. Chorom *et al.* (1994) found quite significant increases in the dispersion of a montmorillonitic soil in the same pH range. Since montmorillonites contain little variable charge, other factors must be influencing the dispersion of this soil. It has been observed that the presence of organic matter can result in substantially more dispersion than occurs in the same soil without organic matter (Gupta *et al.*, 1984). Hence, organic matter may result in increased dispersion over this range. Since the subsoils used in this study contained < 1% organic matter, its effects are expected to be minimal and so the smectitic soils would probably show little change in dispersion over the range 5.9 - 7.2.

5.3.1 Mechanical dispersion

For ease of data analysis, results of the dispersion events were divided into non-sodic (ESP < 6) and sodic (ESP > 6) soils, according to the definition of Northcote & Skene (1972).

Shaking twice end-over-end by hand

The results of the dispersion of non-sodic treatments (ESP < 6) are displayed in Figure 5-1. No significant differences in dispersion due to magnesium were observed in the Wimmera soil. There was a difference between the amount of clay dispersed from treatments with sodium (ESP 3 and 5) and those without (ESP 0). Even at this low level of energy input, a small amount of sodium appears to make a difference in the amount of clay dispersed from the Wimmera soil. The results for Tomki under the same conditions are quite different to those observed with Wimmera. The magnesium-saturated ESP 0 treatment dispersed significantly more than the calcium-saturated ESP 0 treatment ($F = 23.81$, $P < 0.05$). At ESP 3 there was a significant increase in dispersion from the 3/0 treatment to the 3/50 treatment ($F = 7.76$, $P < 0.05$), but no statistical difference in dispersion was observed between the treatments with ESP 5. The illitic soils exhibited no significant differences in dispersion with changes in the calcium:magnesium ratio when non-sodic, but Belalie dispersed to give ten times more clay than Tatura at this energy level.

The two kaolinitic soils displayed quite different responses at this energy level. The Bordertown soil showed no significant differences in dispersion when non-sodic and no trend with increasing magnesium percentage was observed. In contrast the non-sodic treatments for Mt Madden exhibited significant

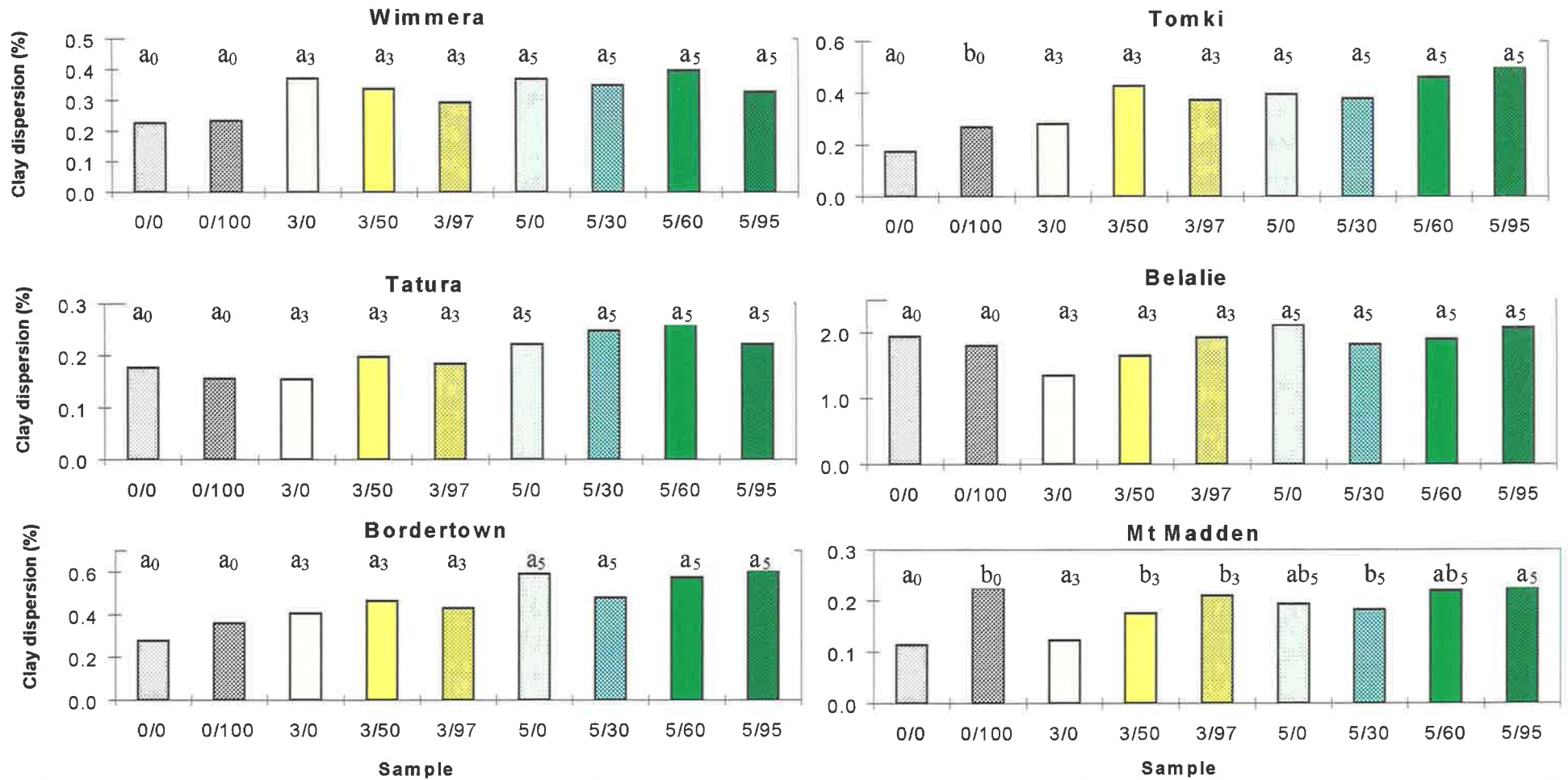


Figure 5-1 Clay dispersion from non-sodic soil treatments (ESP/EMgP) produced by end-over-end shaking twice and expressed as a percentage of that produced by 1 minute sonification. Letters indicate the results of a Tuckey's test for each ESP. The letters indicate statistically significant differences between the means of each treatment *with the same ESP*.

differences in dispersion due to magnesium at all non-sodic ESP values. At ESP 0 the magnesium-saturated treatment dispersed significantly more than the calcium-saturated treatment ($F = 686.09$, $P < 0.05$). When the ESP was 3, a significant difference was observed when exchangeable magnesium was present ($F = 25.44$, $P < 0.05$). At ESP 5 the 5/95 treatment dispersed significantly more than the 5/30 treatment ($F = 5.93$, $P < 0.05$), however no significant increases in dispersion were observed as the magnesium percentage increased.

When the soil treatments were sodic (Figure 5-2) and exposed to shaking twice end-over-end by hand, there was an overall increase in the total amount of clay dispersed compared to the non-sodic treatments. There was no effect of magnesium within each ESP on the dispersion of the Wimmera soil. For the Tomki soil, some differences are observed with ESP values of 7 and 10 (Figure 5-3), but no significant differences at ESP 20. At ESP 7 and 10, generally the treatments which were dominated by magnesium (7/75 and 7/93, and 10/90) displayed significantly more dispersion (ESP 7, $F = 9.60$, $P < 0.05$ and ESP 10, $F = 10.74$, $P < 0.05$). Both Tomki and Wimmera have similar patterns of dispersion, but the total amounts of clay that are dispersed are quite different for each soil. Even at this low level of energy disturbance, the Wimmera soil displayed more stability against the effects of mechanical energy than the Tomki soil.

For the illitic soils some significant differences in dispersion started to appear when the soils were sodic compared to when they were non-sodic. The Tatura soil showed a significant increase in dispersion at ESP 7 and 10 between only the calcium-dominated and magnesium-dominated treatments (ESP 7, $F = 4.09$, $P < 0.05$ and ESP 10, $F = 3.37$, $P < 0.05$). The sodic Belalie treatments exhibited a

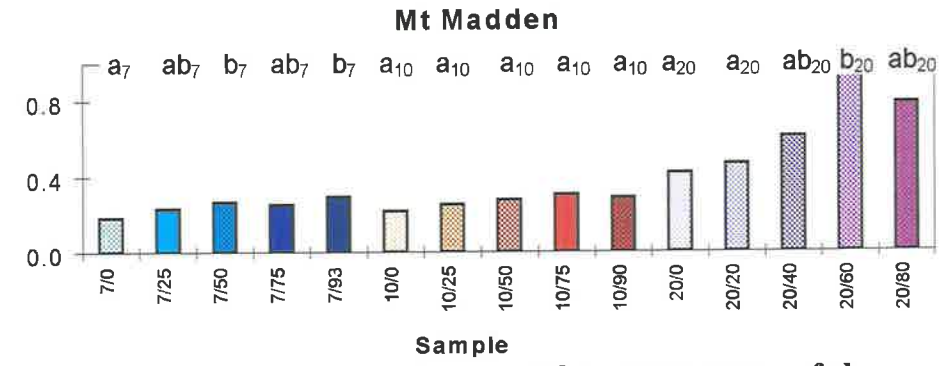
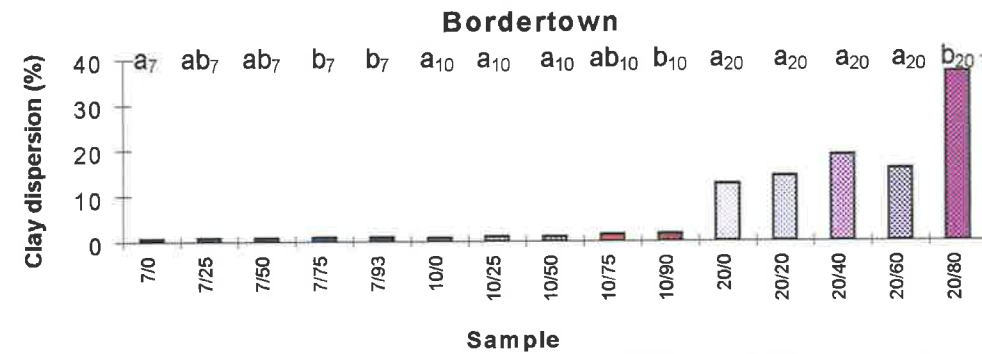
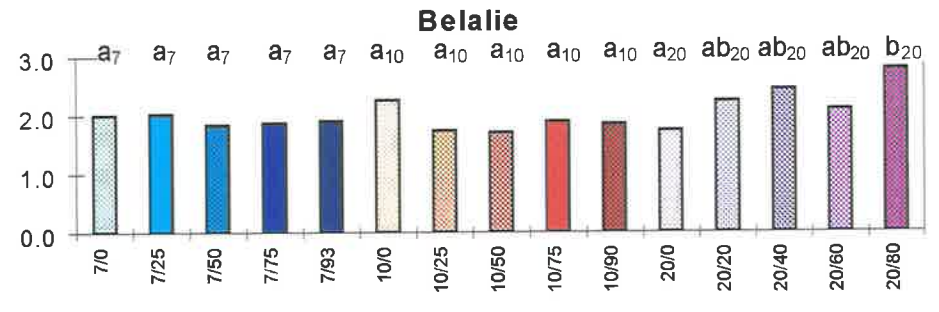
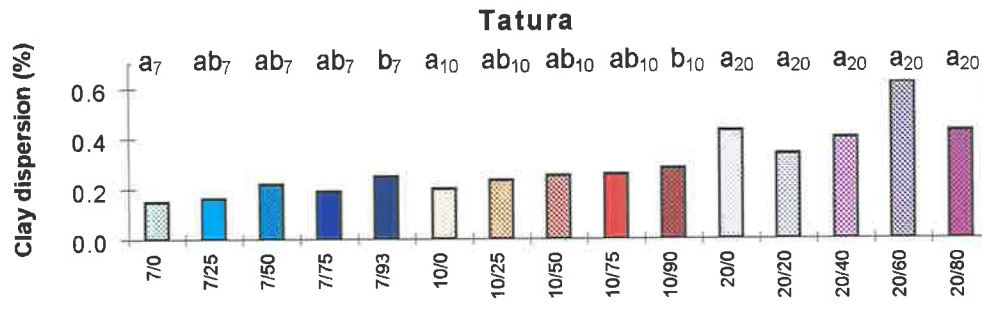
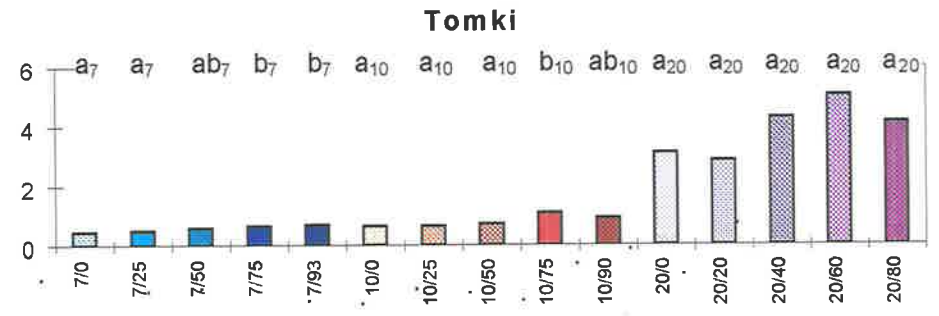
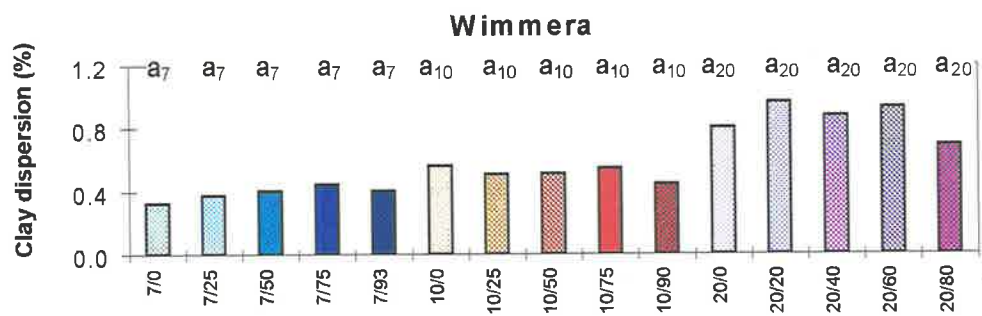


Figure 5-2 Clay dispersion of sodic soil treatments (ESP/EMgP) produced by end-over-end shaking twice and expressed as a percentage of clay produced by 1 minute sonification. Letters indicate the results of a Tuckey's test for each ESP. The letters indicate statistically significant differences between the means of each treatment *with the same* ESP.

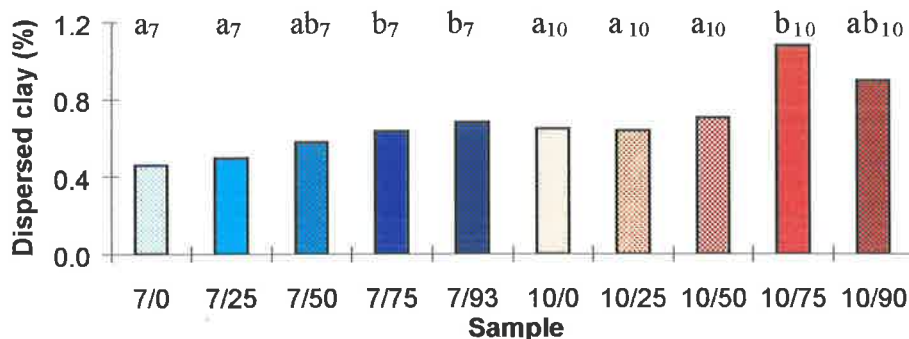


Figure 5-3 Clay dispersion of Tomki ESP 7 and 10 treatments produced by end-over-end shaking twice and expressed as a percentage of clay dispersed by 1 minute sonification. Letters indicate the results of a Tuckey's test for each ESP. The letters indicate statistically significant differences between the means of each treatment *with the same ESP*.

significant increase in dispersion between only the 20/0 and the 20/80 treatments ($F = 6.65$, $P < 0.05$). The Belalie and Tatura soils exhibit quite different patterns of dispersion despite both soils being illitic in nature. The Belalie soil exhibited little response to the effect of increasing sodium, the amount of clay dispersed from the soil was similar regardless of ESP. That Tatura soil, in contrast, dispersed to give more clay as the ESP increased.

The dispersion results for the Bordertown soil with ESP 7 and 10 are expanded in Figure 5-4. The sodic kaolinitic soils behaved differently to the soils previously mentioned. The Bordertown soil expressed significant differences in dispersion at all sodic ESP values, again, generally when magnesium-dominated compared with calcium-dominated (ESP 7, $F = 6.30$, $P < 0.05$, ESP 10 $F = 8.93$, $P < 0.05$ and ESP 20 $F = 10.22$, $P < 0.05$). The Mt Madden soil with ESP 7 exhibited slightly variable results, with the 7/50 and 7/93 treatments dispersing significantly more than the 7/0 treatment, but not the 7/75 treatment ($F = 5.54$, $P < 0.05$).

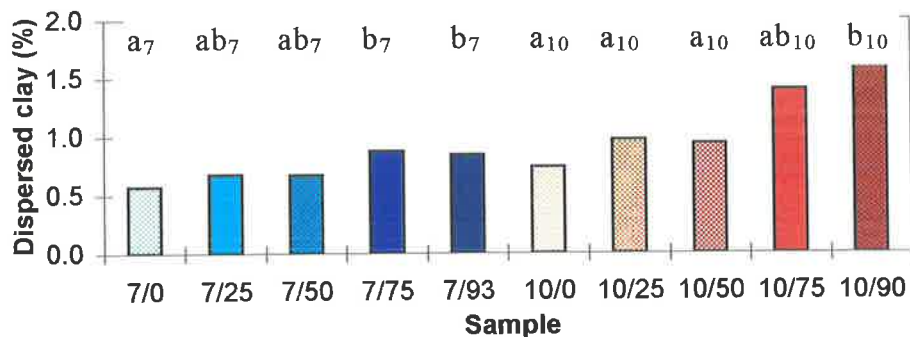


Figure 5-4 Clay dispersion of Bordertown ESP 7 and 10 treatments produced by end-over-end shaking twice and expressed as a percentage of clay produced by 1 minute sonification. Letters indicate the results of a Tuckey's test for each ESP. The letters indicate statistically significant differences between the means of each treatment with the same ESP.

There were no significant differences in dispersion observed at ESP 10, but at ESP 20 the 20/60 treatment dispersed significantly more than the 0/20 and 20/20 treatments ($F = 7.20$, $P < 0.05$).

Comparison of the results for all ESP values (ESP 0 - 20) for each soil at this energy level indicates;

- 1) Wimmera treatments did not show any trends with increasing exchangeable magnesium percentage over the ESP range used.
- 2) Tomki displayed a definite trend of increasing clay dispersion as the percentage of magnesium increased, at virtually all ESP values.
- 3) The illitic soils showed a similar but weaker trend with magnesium at ESP 3, but not at other ESP values and
- 4) The kaolinitic soils displayed the most similarities between two soils with similar clay mineralogies, and also exhibited a weak effect of magnesium on dispersion.

1 minute end-over-end shaking

The results for the non-sodic treatments at this energy level are presented in Figure 5-5. Differences in dispersion due to the presence of exchangeable magnesium in the Wimmera soil became apparent at this energy level. At ESP 0 and 3 the magnesium-dominated treatments dispersed significantly more than the calcium-dominated treatment (ESP 0, $F = 13.16$, $P < 0.05$ and ESP 3, $F = 5.93$, $P < 0.05$). The Tomki soil behaved similarly to the Wimmera soil, with the magnesium-dominated treatments dispersing significantly more than the calcium-dominated treatments (ESP 0, $F = 13.77$, $P < 0.05$ and ESP 3, $F = 5.31$, $P < 0.05$). At ESP 5, the results are slightly different, where the 5/30 treatment dispersed to give significantly less clay than the 5/95 treatment ($F = 4.81$, $P < 0.05$). The increase in energy input into the soil did not result in any significant differences between treatments being observed in the non-sodic Tatura samples, but Figure 5-5 indicates that as sodium percentage increased the dispersion increased. For the Belalie soil there appeared to be little difference in dispersion due to the sodium percentage, as was observed in the previous energy level. However, there was a significant difference in dispersion observed at ESP 3 between the 3/0 and 3/97 treatments ($F = 6.55$, $P < 0.05$).

The kaolinitic soils behaved quite differently at this level of energy input. the Bordertown soil exhibited a significant difference in dispersion only at ESP 5 when dominated by magnesium ($F = 25.04$, $P < 0.05$). In contrast, the Mt Madden soil displayed significant differences in dispersion at all ESP values when magnesium-dominated (ESP 0, $F = 24.10$, $P < 0.05$, ESP 3, $F = 12.30$, $P < 0.05$ and ESP 5, $F = 33.83$, $P < 0.05$).

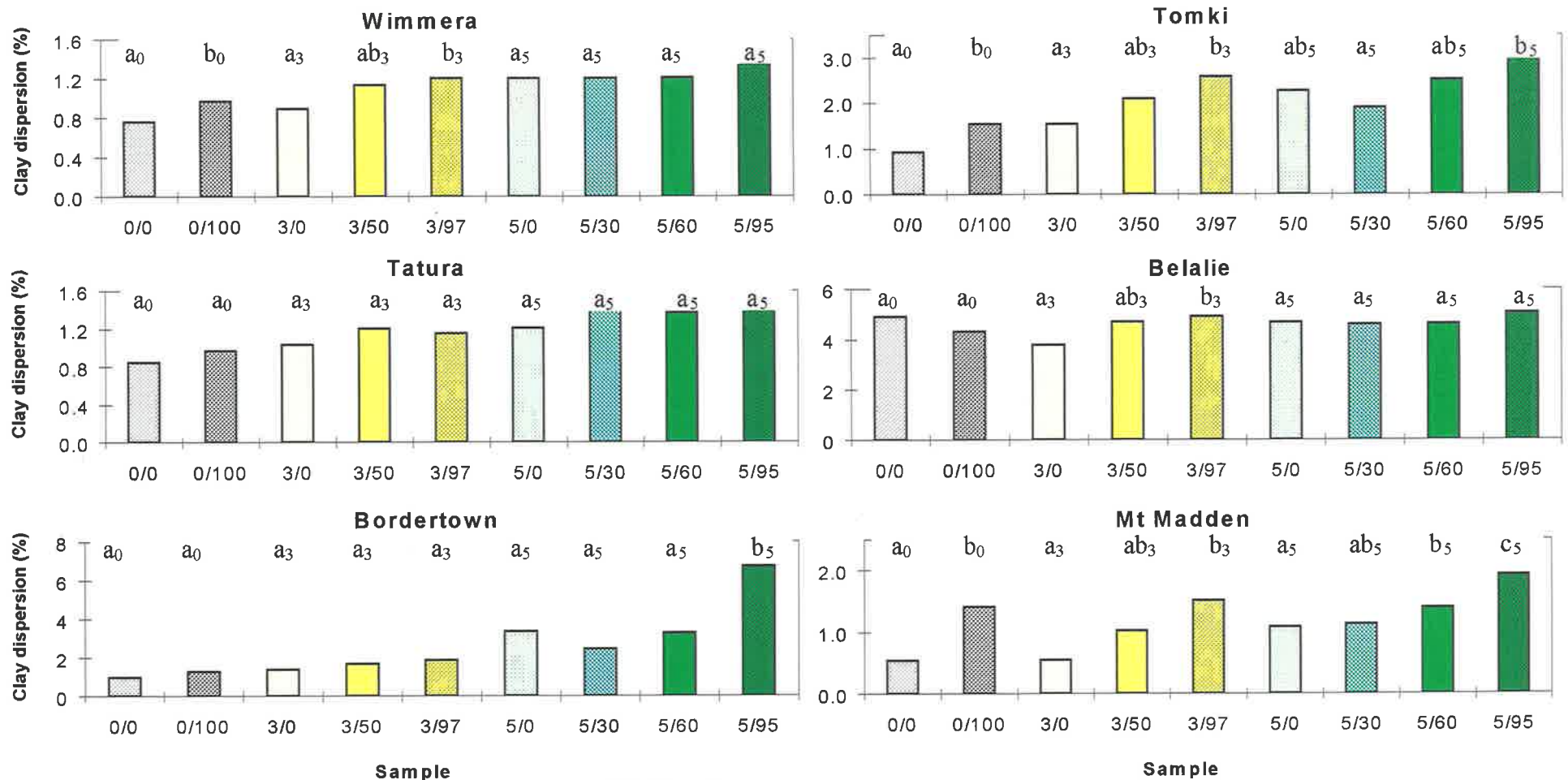


Figure 5-5 Clay dispersion from non-sodic soil treatments (ESP/EMgP) produced by 1 minute end-over-end shaking and expressed as a percentage of clay produced by 1 minute sonification. Letters indicate the results of a Tuckey's test for each ESP. The letters indicate statistically significant differences between the means of each treatment *with the same ESP*.

As the treatments became sodic (Figure 5-6), the Wimmera soil exhibited significant differences in dispersion only at ESP 20 ($F = 4.90$, $P < 0.05$). The sodic Tomki soil displayed opposite results, with the ESP 20 treatments exhibiting no significant differences in dispersion, but significant differences were observed at ESP 7 and 10 (Figure 5-7). At ESP 7, the magnesium-dominated treatment (7/93) dispersed significantly more than the 7/0 and the 7/25 treatments ($F = 9.80$, $P < 0.05$). When ESP increased to 10, a significant increase in dispersion was observed when the magnesium percentage reached 75 and 90. ($F = 9.47$, $P < 0.05$). The trend of increasing dispersion with increasing magnesium percentage is obvious in the Tomki treatments at ESP 7 and 10 (Figure 5-7). The results for the dispersion of the Tatura soil at ESP 7 and 10 are enlarged in Figure 5-8. The Tatura soil exhibited significant increases in dispersion when magnesium dominated the exchange phase at ESP 7 ($F = 6.99$, $P < 0.05$). When calcium and magnesium were present in nearly equivalent amounts the dispersion of that treatment was not significantly different from any other treatment with ESP 7. At ESP 10 the clay dispersed was significantly higher in the 10/90 treatment than the 10/0 and 10/25 treatments ($F = 6.43$, $P < 0.05$). A trend of increasing dispersion with increasing magnesium percentage was apparent in the Tatura soil at ESP 7 and 10. At ESP 20 there was no significant difference in dispersion between the treatments observed, despite the seemingly large differences in dispersion that can be observed on the graph. The error bars for this set of data were large. The sodic Belalie soils at this level displayed no significant differences in dispersion between treatments at all ESP. There again seemed to be little influence of sodium on the dispersion of the Belalie soil as most treatments exhibited similar amounts of clay dispersion

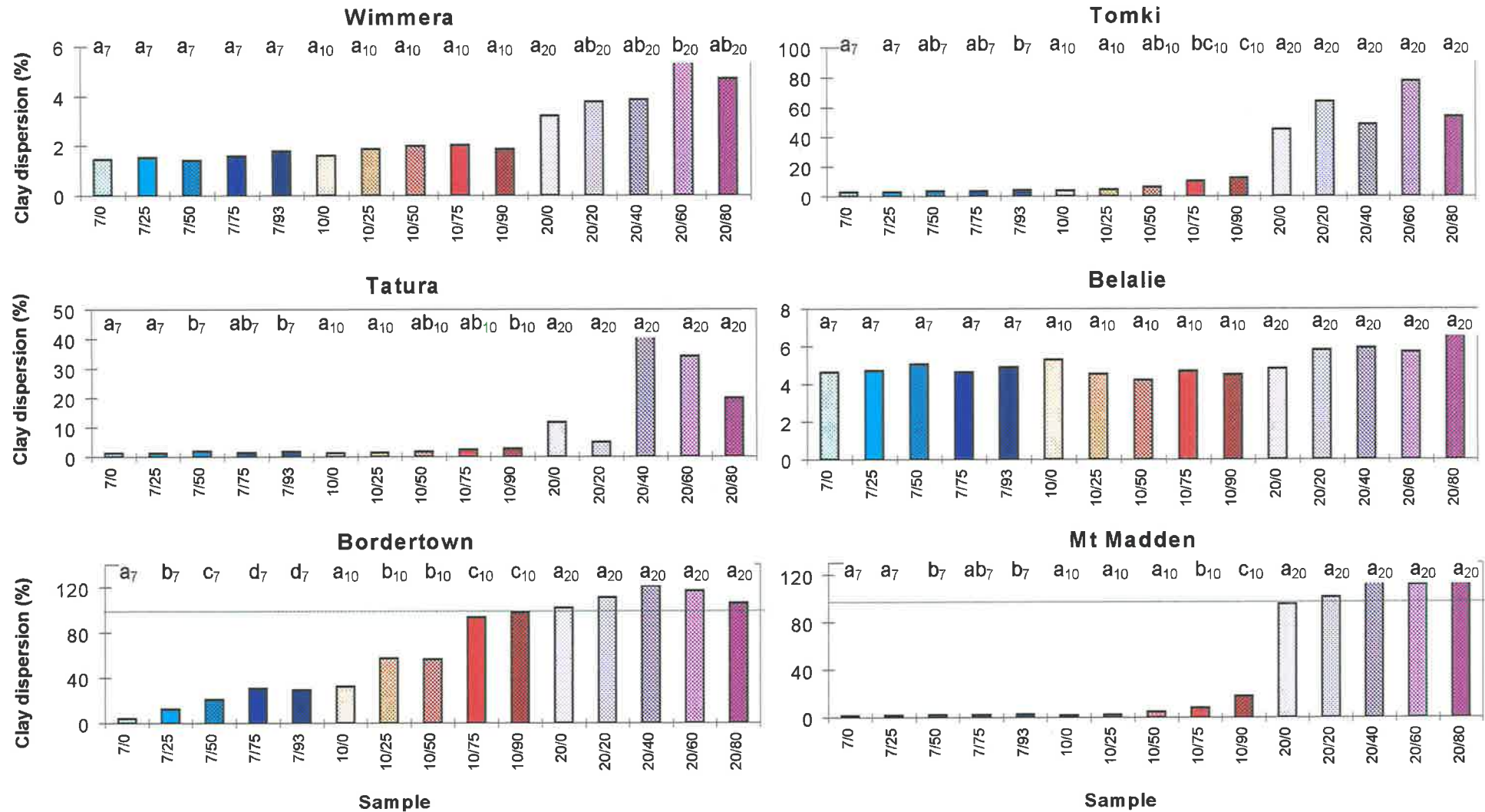


Figure 5-6 Clay dispersion from sodic soil treatments (ESP/EMgP) produced by 1 minute end-over-end shaking and expressed as a percentage of clay produced by 1 minute sonification. Letters indicate the results of a Tukey's test for each ESP. The letters indicate statistically significant differences between the means of each treatment *with the same ESP*.

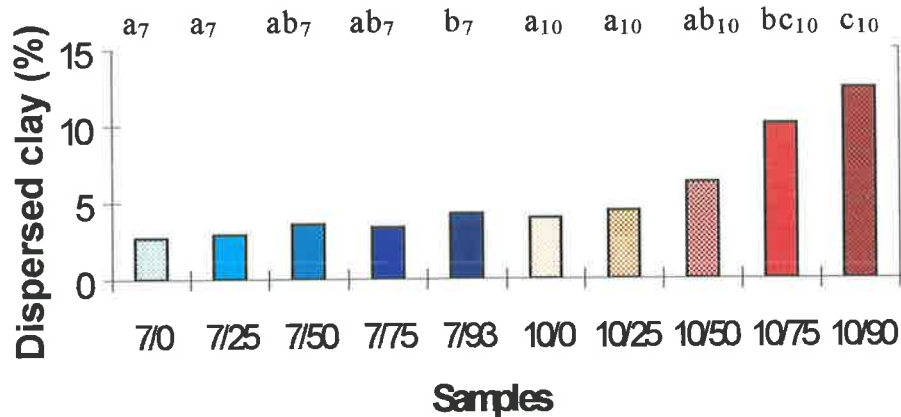


Figure 5-7 Clay dispersion of Tomki ESP 7 and 10 treatments (ESP/EMgP) produced by 1 minute end-over-end shaking and expressed as a percentage of clay produced by 1 minute sonification. Letters indicate the results of a Tuckey's test for each ESP. The letters indicate statistically significant differences between the means of each treatment *with the same ESP*.

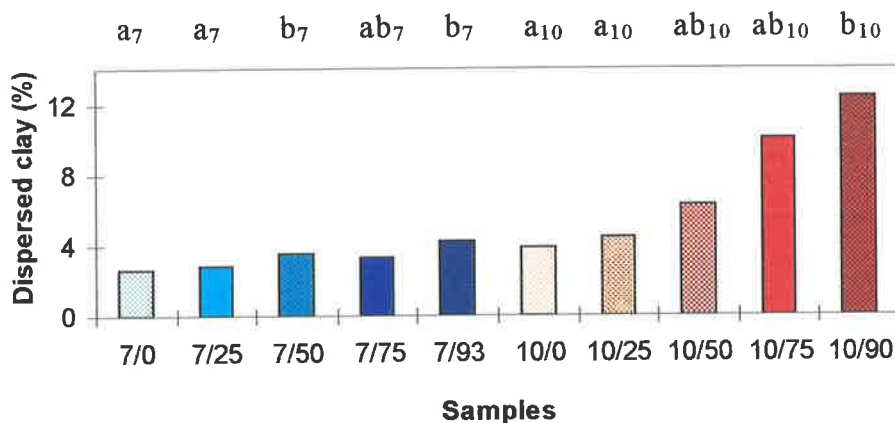


Figure 5-8 Clay dispersion of Tatura ESP 7 and 10 treatments (ESP/EMgP) produced by 1 minute end-over-end shaking and expressed as a percentage of clay produced by 1 minute sonification. Letters indicate the results of a Tuckey's test for each ESP. The letters indicate statistically significant differences between the means of each treatment *with the same ESP*.

regardless of ESP. The pattern of clay dispersed from these two soils was similar to that observed in the previous energy level, with the Belalie soil exhibiting little effects of both sodium and magnesium on dispersion. The Tatura soil, on the other hand exhibited generally increasing dispersion as the sodium and magnesium percentage increased.

The sodic Bordertown treatments exhibited dispersion that was affected by most increases in magnesium percentage at ESP 7 ($F = 45.73$, $P < 0.05$) and ESP 10 ($F = 30.42$, $P < 0.05$). For both the Mt Madden and Bordertown soils at ESP 20, all treatments essentially dispersed completely. The Mt Madden soil at ESP 7 and 10 (Figure 5-9) exhibited significant differences in dispersion between treatments which were dominated by magnesium and those which were dominated by calcium (ESP 7, $F = 21.95$, $P < 0.05$; ESP 10, $F = 84.46$, $P < 0.05$).

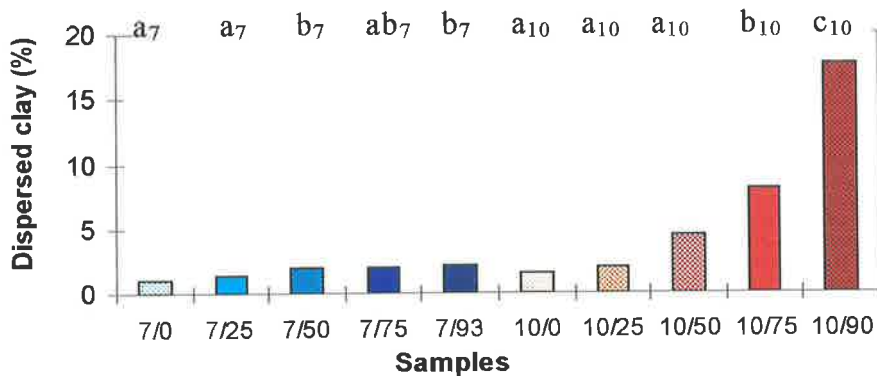


Figure 5-9 Clay dispersion of Mt Madden ESP 7 and 10 treatments (ESP/EMgP) produced by 1 minute end-over-end shaking and expressed as a percentage of clay produced by 1 minute sonification. Letters indicate the results of a Tuckey's test for each ESP. The letters indicate statistically significant differences between the means of each treatment *with the same ESP*.

A comparison of all soils over the complete ESP range used indicates;

- 1) The Wimmera soil exhibited an effect of magnesium on dispersion at ESP 0 and 3 only.
- 2) For the Tomki soil a weak magnesium effect was generally observed, especially when magnesium dominated the exchange capacity.
- 3) There was generally no effect of magnesium on dispersion observed in the illitic soils.

- 4) The kaolinitic soils exhibited a weak magnesium effect on dispersion, generally when sodic ($ESP > 6$).

15 minutes end-over-end shaking

As the energy input increased to 15 minutes end-over-end shaking (Figure 5-10) the Wimmera soil dispersed to give significantly more clay when magnesium-dominated and non-sodic. The Tomki soil at this energy level displayed no significant differences in dispersion except when the calcium-saturated and magnesium-saturated treatments were compared ($F = 26.83, P < 0.05$); however a trend of increased dispersion as magnesium percentage increased was observed.

For the illitic soils at this energy level only the Tatura samples at ESP 0 exhibited significant differences in dispersion due to the presence of magnesium ($F = 12.36, P < 0.05$). The remaining treatments all appeared to display little effect on the amount of clay dispersed from the soil due to magnesium or sodium.

When the Bordertown soil was non-sodic, magnesium had a significant effect on dispersion at ESP 5 only when it dominated the exchange capacity ($F = 33.88, P < 0.05$). The Mt Madden soil exhibited significant differences in dispersion at all non-sodic ESP values when dominated by magnesium (ESP 0, $F = 106.16, P < 0.05$, ESP 3, $F = 14.69, P < 0.05$ and ESP 5, $F = 12.0, P < 0.05$).

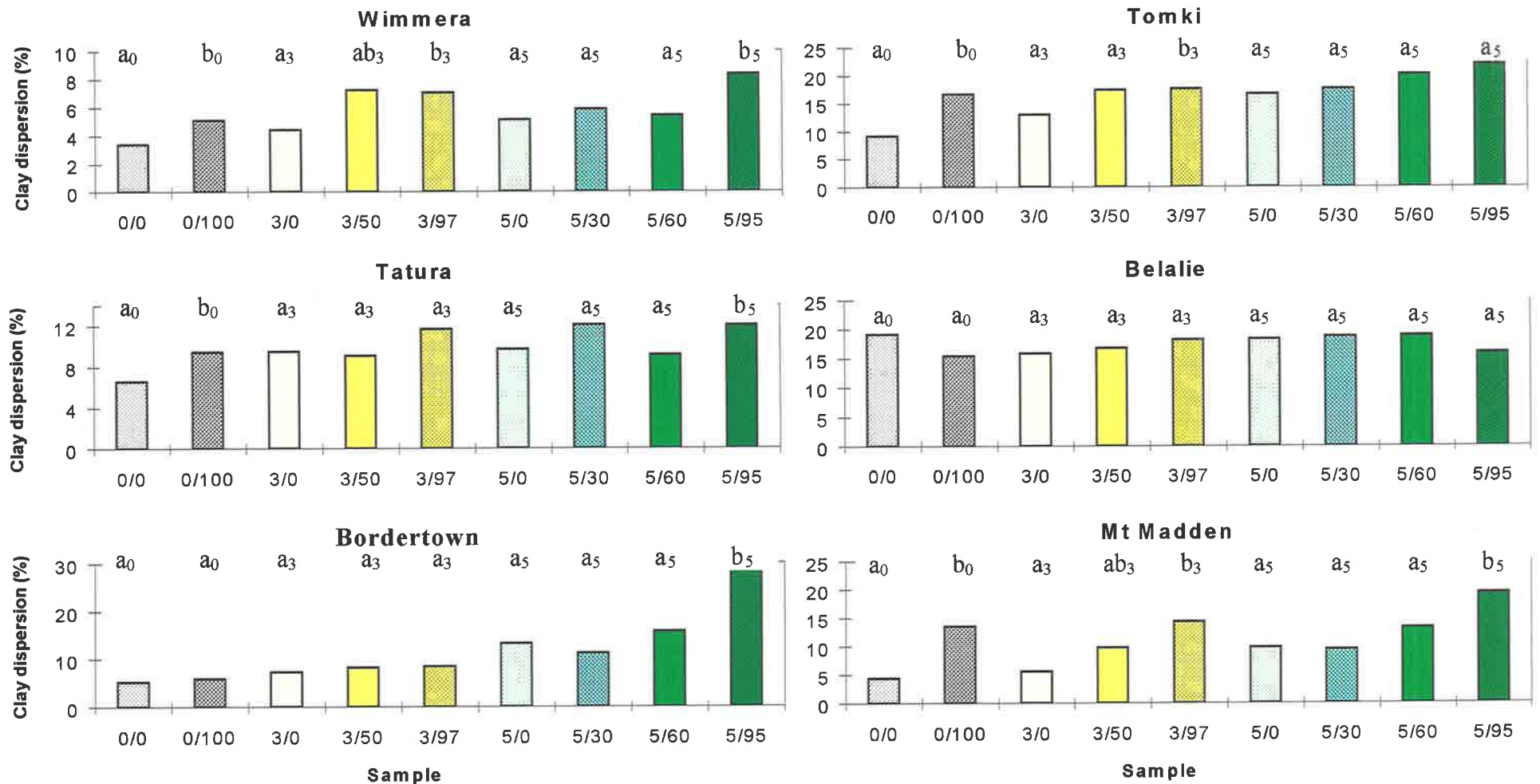


Figure 5-10 Clay dispersion of non-sodic soil treatments (ESP/EMgP) produced by 15 minutes end-over-end shaking and expressed as a percentage of clay produced by 1 minute sonification. Letters indicate the results of a Tukey's test for each ESP. The letters indicate statistically significant differences between the means of each treatment *with the same ESP*

Once the soils were sodic ($ESP > 6$) at this energy level (Figure 5-11), the results observed were similar to those reported at the previous energy level. The Wimmera soil generally exhibited significantly more dispersion when magnesium-dominated and sodic ($ESP 7, F = 6.15, P < 0.05$ and $ESP 10, F = 6.11, < 0.05$). There also appeared to be little effect of sodium on the dispersion at $ESP 7$ and 10 , as the amount of dispersed clay was similar. Once the ESP increased to 20 there was a substantial increase in the amount of clay dispersed from the soil. The Tomki soil also exhibited significant differences in dispersion at $ESP 7$ and 10 when magnesium dominated the exchange phase, but not at $ESP 20$. There also appeared to be little effect on the amount of clay dispersed as the ESP increased from 7 to 10 , but a significant increase in dispersion once the ESP reached 20 .

For the illitic soils, only Tatura with $ESP 20$ displayed any significant differences in dispersion due to the presence of magnesium, however these results were not as expected because the treatment with equivalent amounts of calcium and magnesium dispersed significantly more than the other treatments, ($F = 5.27, P < 0.05$). There seemed to be a weak trend of increasing dispersion with increasing magnesium percentage at $ESP 10$ in the Tatura soil. The Belalie soil exhibited no significant differences in dispersion due to magnesium and there also appeared to be little impact from the ESP on dispersion.

The two kaolinitic soils with an ESP of 20 again completely dispersed at this energy level. Both soils exhibited increases in dispersion with the increase in magnesium percentage at $ESP 7$ (Bordertown, $F = 36.0, P < 0.05$ and Mt

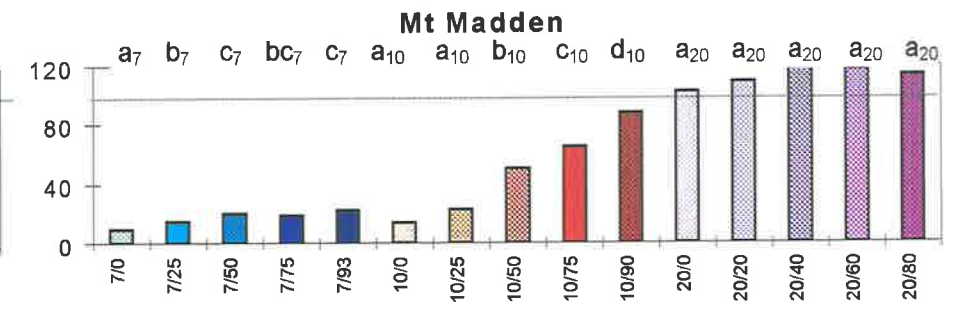
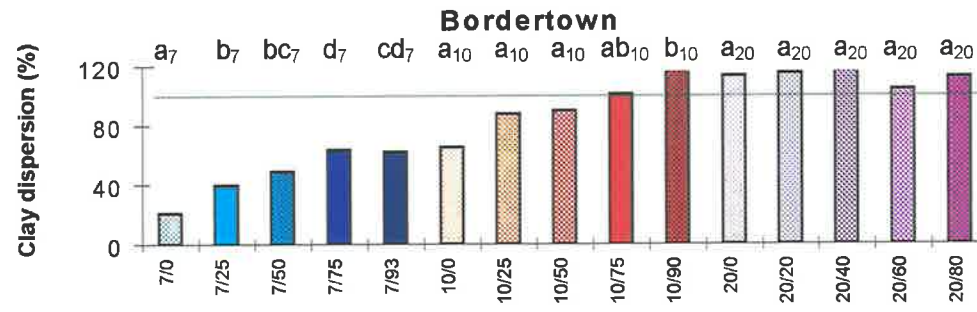
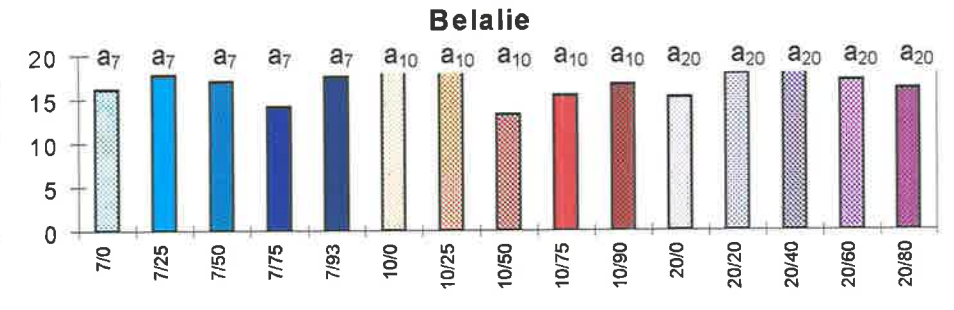
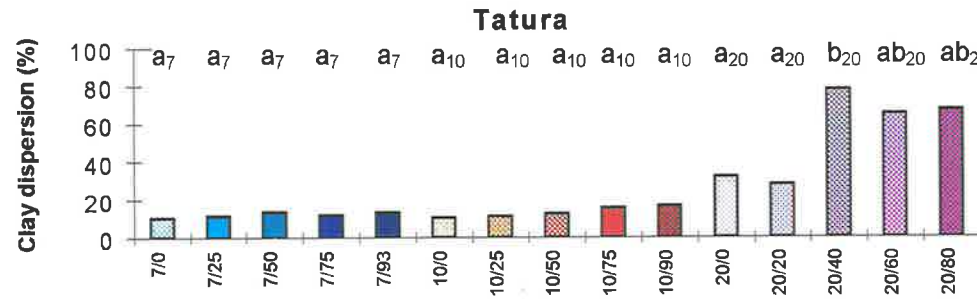
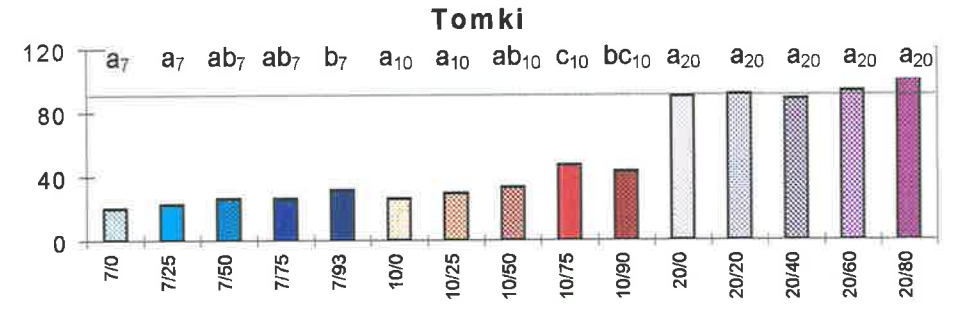
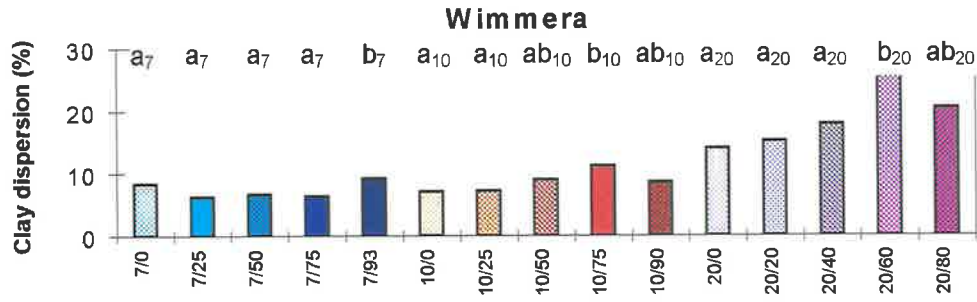


Figure 5-11 Clay dispersion of sodic soil treatments (ESP/EMgP) produced by 15 minute end-over-end shaking and expressed as a percentage of clay produced by 1 minute sonification. Letters indicate the results of a Tuckey's test for each ESP. The letters indicate statistically significant differences between the means of each treatment *with the same* ESP.

Madden, $F = 21.87$, $P < 0.05$). At ESP 10 the Mt Madden soil exhibited increased dispersion with increasing magnesium percentage ($F = 147.50$, $P < 0.05$), but the Bordertown soil at ESP 10 showed significant differences in dispersion only when magnesium-dominated ($F = 13.0$, $P < 0.05$). The response of the Mt Madden soil with ESP 10 to increasing magnesium levels at this energy level is quite clear-cut. Starting at 25%, each increase in magnesium percentage resulted in a significant increase in clay dispersed.

The results of clay dispersed from each soil over the ESP range tested after 15 minutes of end-over-end shaking can be summarised as:

- 1) The Wimmera soil exhibited an effect on dispersion of magnesium when the exchange phase was dominated by magnesium.
- 2) The Tomki soil exhibited a weak magnesium effect, generally when sodic.
- 3) The illitic soils exhibited generally little effect of magnesium on dispersion.
- 4) The kaolinitic soils displayed a magnesium effect when sodic ($ESP > 6$), except at ESP 20 where dispersion was essentially complete.

2 hours end-over-end shaking

When the energy level was increased to 2 hours end-over-end shaking for the non-sodic Wimmera soil (Figure 5-12), the results were similar to those observed within the previous energy level. At ESP 0 and 5 a magnesium effect is observed when magnesium dominates the exchange capacity (ESP 0, $F = 9.89$, $P < 0.05$ and ESP 5, $F = 8.18$, $P < 0.05$). The behaviour of the Tomki soil at this energy level was also similar to that at the previous energy level with only the

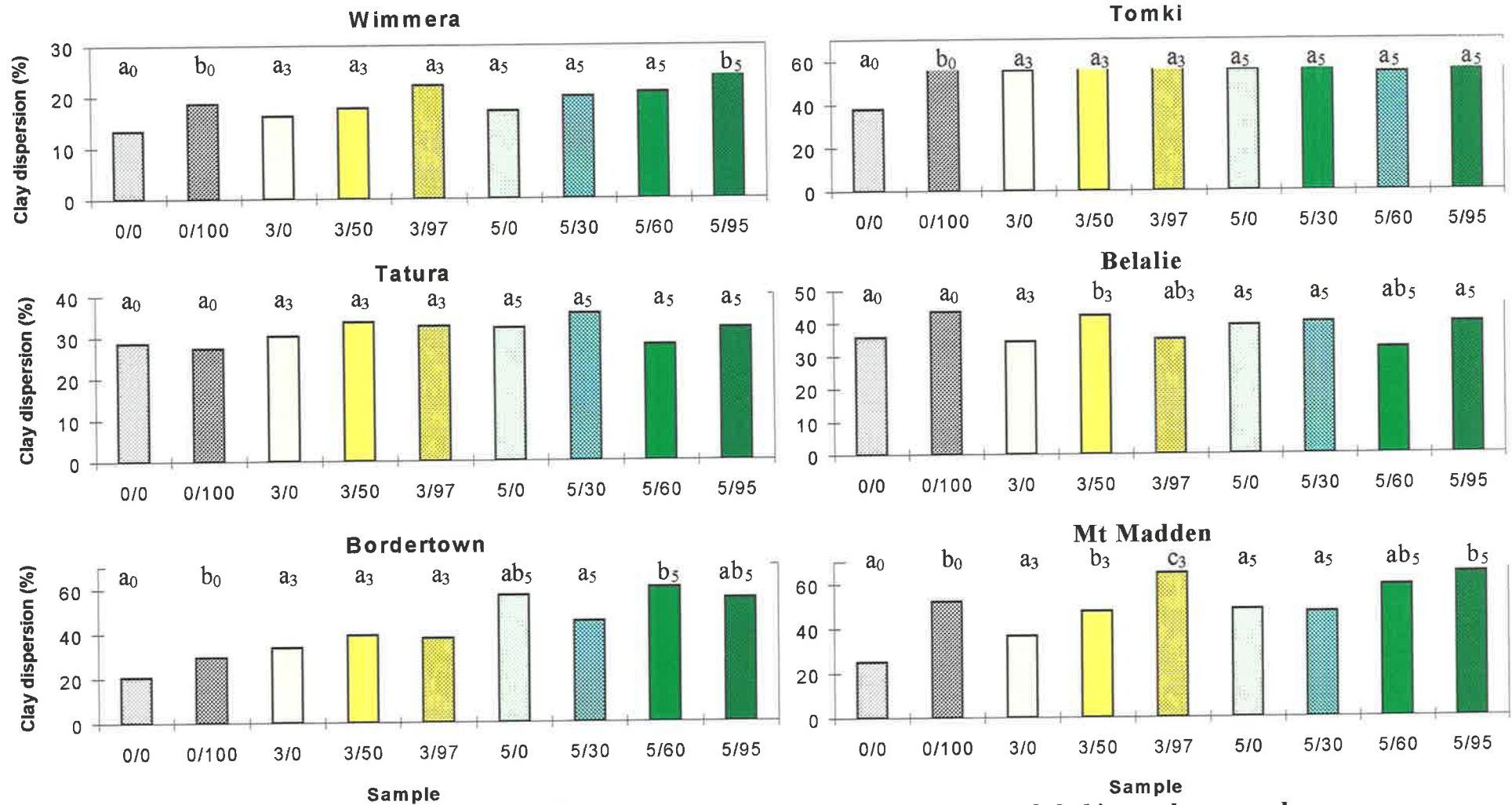


Figure 5-12 Clay dispersion of non-sodic soil treatments (ESP/EMgP) produced by 2 hrs end-over-end shaking and expressed as a percentage of clay produced by 1 minute sonification. Letters indicate the results of a Tuckey's test for each ESP. The letters indicate statistically significant differences between the means of each treatment *with the same ESP*.

ESP 0 treatments exhibiting a magnesium effect ($F = 16.62$, $P < 0.05$). There also appears to be little effect of increasing the ESP from 3 to 5 on the amount of clay dispersed from the Tomki soil at this energy level. The illitic soil generally exhibited no magnesium effect, only the Belalie ESP 3 samples showed differences in dispersion due to magnesium ($F = 5.80$, $P < 0.05$). However, the differences due to magnesium were shown between the 3/0 and 3/50 treatments. It appears that for both soils the energy input has more of an impact on dispersion than the exchangeable cations after 2 hours of end-over-end shaking.

The kaolinitic soils did not exhibit similar behaviour at this energy level. The Mt Madden soil displayed a magnesium effect at all non-sodic ESP values (ESP 0, $F = 49.57$, $P < 0.05$, ESP 3, $F = 47.93$, $P < 0.05$ and ESP 5, $F = 5.87$, $P < 0.05$). The Bordertown soil exhibited a magnesium effect at ESP 0 ($F = 13.18$, $P < 0.05$), but not at ESP 3. An interesting result occurred at ESP 5 where there is a significant difference in dispersion between the 5/60 and 5/30 treatments ($F = 5.69$, $P < 0.05$). If differences were to be observed it would be expected to be between the treatments containing no or low magnesium percentages and those containing high magnesium percentages, not between two treatments which fell in the middle of the treatment scheme. It seems likely that the reason for the differences observed might be due to variability in replicates within each treatment. Even though there is a significant difference, it may not be substantial considering the remaining two treatments (5/0 and 5/95) display similar dispersion results to each other and the 5/30 and 5/60 treatments. A greater number of replicates within each treatment may have clarified this issue.

When the soils were sodic (Figure 5-13), the smectitic and illitic soils all exhibited no effect of magnesium on dispersion within each ESP value after 2 hours end-over –end shaking. The Wimmera, Tomki and Tatura soils all exhibited an increase in the amount of clay that was dispersed from the soil when the ESP increased from 10 to 20. All three soils dispersed similar amounts of clay at ESP 7 and 10, indicating that this slight increase in sodium percentage has a minimal impact on the stability of these soils to mechanical energy. The Belalie soil showed no effect of either magnesium or sodium on clay dispersion, as observed at previous energy inputs. The amount of energy seems to impact more on the amount of clay dispersed rather than the exchangeable cations, as is observed in the other soils.

In the kaolinitic soils at this energy level the magnesium effect seems reduced. In the previous level increases in the amount of clay dispersed with each increase in magnesium percentage was observed. At this level of energy input this is no longer observed. For the Bordertown soil, only at ESP 7 ($F = 6.8$, $P < 0.05$) are effects of magnesium observed, and then when it dominates the exchange phase. The Mt Madden soil exhibited a magnesium effect at ESP 7 and 10, again generally when magnesium dominated the exchange phase (ESP 7, $F = 8.45$, $P < 0.05$, ESP 10, $F = 7.99$, $P < 0.05$).

Comparison of the results for the whole ESP range for each soil indicate;

- 1) The montmorillonitic and illitic soils generally exhibited no magnesium effect on dispersion.

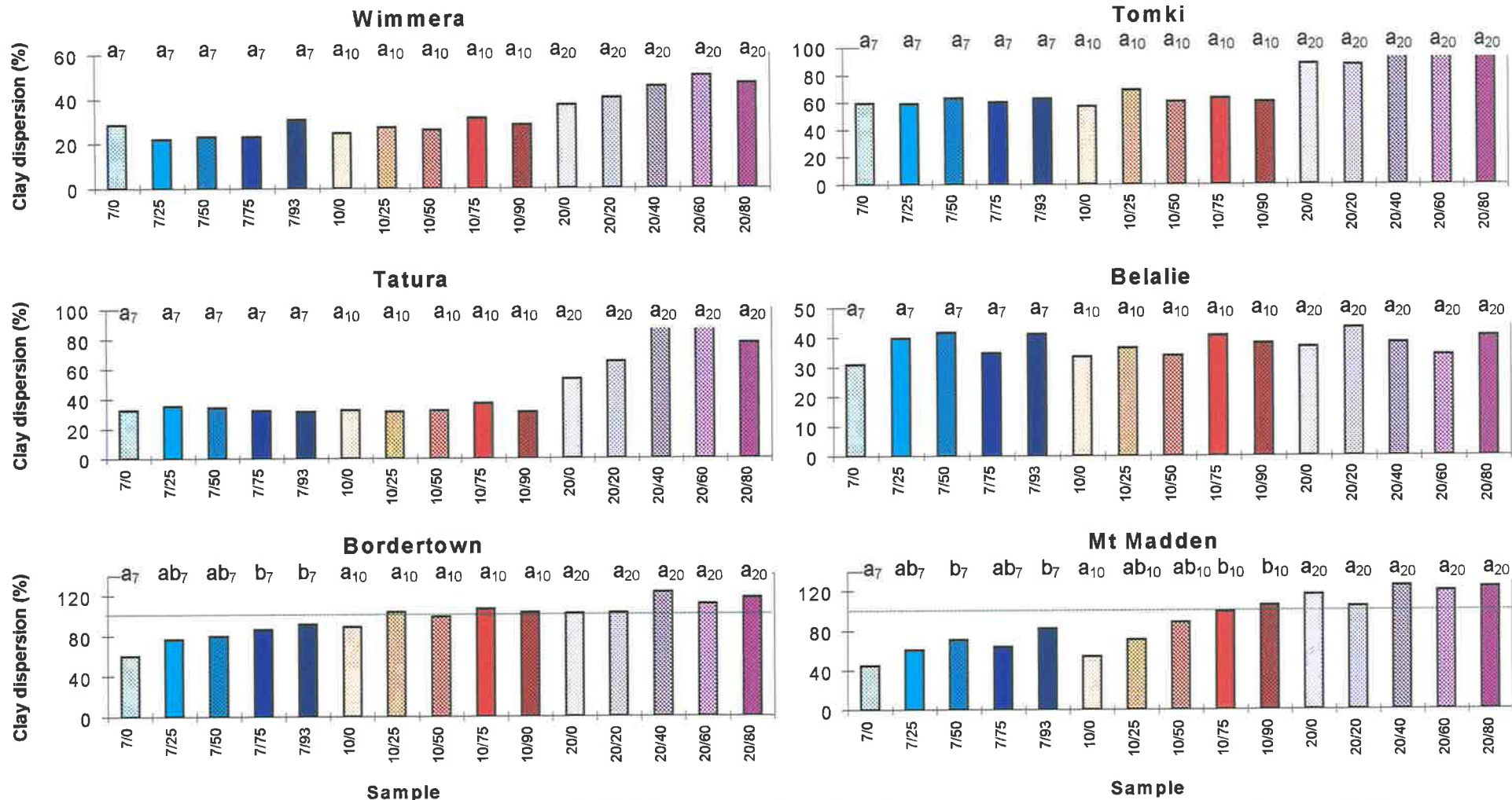


Figure 5-13 Clay dispersion of sodic soil treatments (ESP/EMgP) produced by 2 hrs end-over-end shaking and expressed as a percentage of clay produced by 1 minute sonification. Letters indicate the results of a Tukey's test for each ESP. The letters indicate statistically significant differences between the means of each treatment *with the same ESP*

- 2) There was a weak magnesium effect observed in the kaolinitic soils, especially when non-sodic ($ESP < 6$).

16 hours end-over-end shaking

The data for the dispersion of non-sodic soils after 16 hours end-over-end shaking are shown in Figure 5-14. The montmorillonitic soils exhibited no magnesium effect on dispersion. There were some samples that had replicates flocculate resulting in decreased values for the amount of clay dispersed. It is likely that these samples flocculated due to the release of salts from the soil as prolonged contact with solution may have dissolved some of the more insoluble salts contained in soils.

The remaining four soils, Tatura, Belalie, Bordertown and Mt Madden all displayed no significant effects of exchangeable magnesium on dispersion, with non-sodic treatments of Bordertown and Mt Madden completely dispersed when subjected to end-over-end shaking for 16 hours.

When the six soils were sodic and exposed to the 16 hour shaking period (Figure 5-15), there was no significant difference in the dispersion of all soils attributable to the presence of exchangeable magnesium. The Bordertown and Mt Madden soils dispersed completely, the ESP 20 treatments of Tomki and Tatura were also completely dispersed. The remaining treatments and soils dispersed about 60% of the dispersible clay. The Tatura and Tomki soils still apparently exhibited some response to exchangeable sodium, with the dispersion of clay increasing as the ESP increased from 10 to 20.

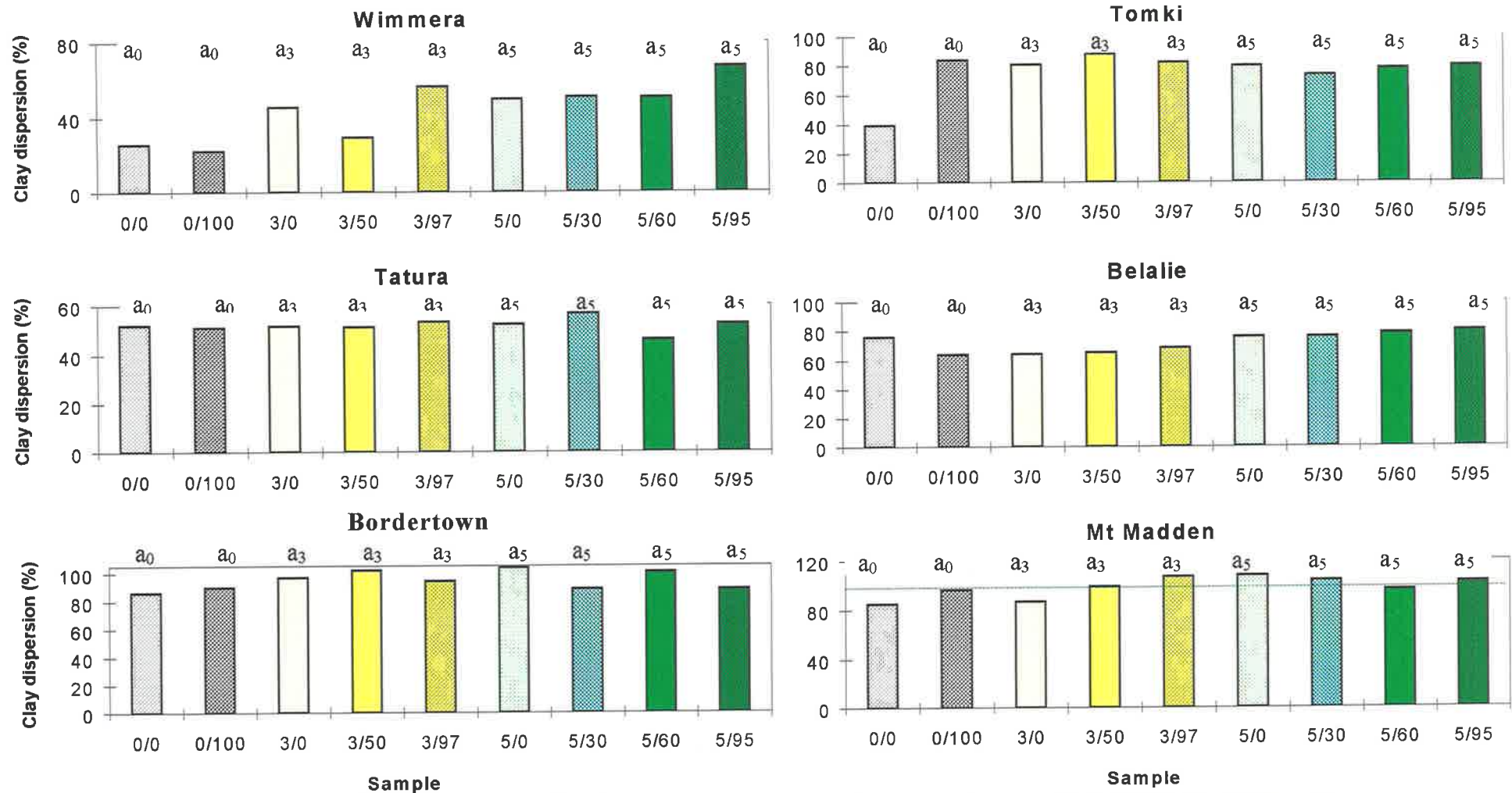
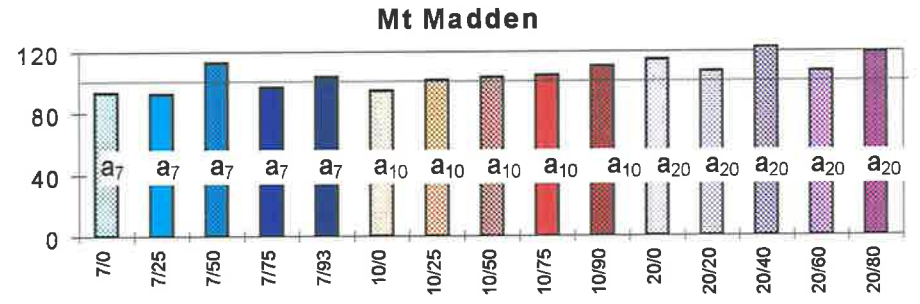
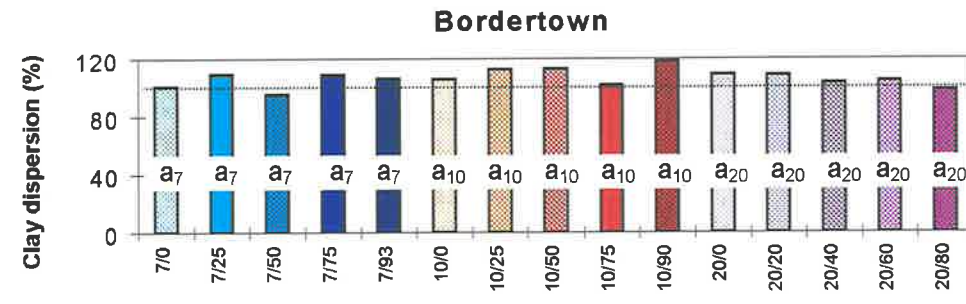
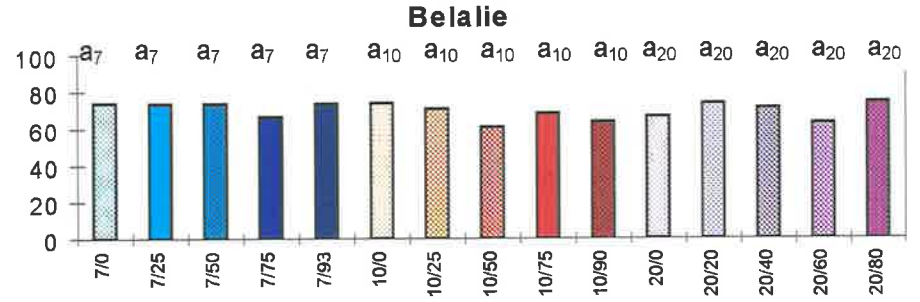
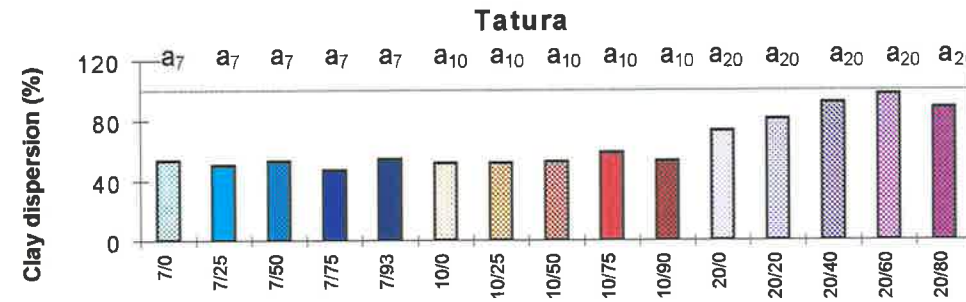
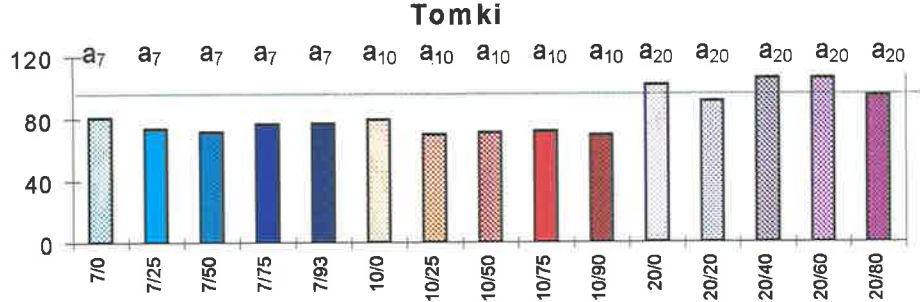
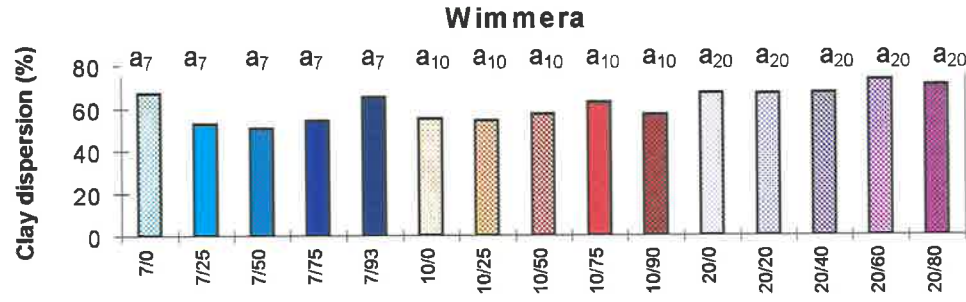


Figure 5-14 Clay dispersion of non-sodic soil treatments (ESP/EMgP) produced by 16 hours end-over-end shaking and expressed as a percentage of clay produced by 1 minute sonification. Letters indicate the results of a Tuckey's test for each ESP. The letters indicate statistically significant differences between the means of each treatment with the same ESP.



Sample

Figure 5-15 Clay dispersion of sodic soil treatments (ESP/EMgP) produced by 16 hours end-over-end shaking and expressed as a percentage of clay produced by 1 minute sonification. Letters indicate the results of a Tuckey's test for each ESP. The letters indicate statistically significant differences between the means of each treatment *with the same ESP*

Summary of dispersive behaviour

For each soil the influence of exchangeable sodium and mechanical energy inputs resulted in distinctive behaviour. The Wimmera soil exposed to energy levels up to 15 minutes end-over-end shaking required an ESP of 20 to exhibit a significant increase in dispersion. The treatments with ESP values < 20 appeared to disperse to give similar amounts of clay. After 2 hours end-over-end shaking the effects of exchangeable magnesium started to impact on the dispersion of Wimmera. The non-sodic treatments (ESP 3 and 5) both dispersed to give similar amounts of clay, hence exchangeable sodium resulted in little difference in dispersion at this level. Even the amount of clay dispersed from the calcium-saturated (ESP 0) treatment was similar to that dispersed from the ESP 3 and 5 treatments. This indicates that the dispersion of Wimmera, when non-sodic, is controlled by mechanical forces and not exchangeable sodium until the ESP reaches 7. Differences in dispersion of the Wimmera soil at low energy levels, required a high ESP. As the energy level increased, the sodium percentage where increases in dispersion occurred, decreased. The threshold ESP (taken as six in this study) above which a soil is considered sodic may overestimate the area of land which would exhibit adverse effects of sodicity in the case of Wimmera soil.

The response of non-sodic Tomki treatments to dispersion exhibited some differences to those observed in Wimmera. As the energy level increased the clay dispersion increased with the increase in ESP; this became dramatic at ESP 20. This indicates that dispersion generally increases as a continuum rather than through large increases at a certain ESP. The Tatura soil with ESP 3-10 generally dispersed to give similar amounts of clay, but the dispersion increased

at ESP 20. The Belalie soil displayed very little response to exchangeable cations with the amount of clay dispersed only changing with energy input.

For the kaolinitic soils, the response of non-sodic treatments to mechanical dispersion seemed to depend on the energy imparted to the system. In the Bordertown soil at the lower energy inputs, dispersion increased as the ESP increased to 3, then the treatments with ESP 5 and 7 appeared to disperse to give similar amounts of clay. The clay dispersion then increased again as the ESP increased further. As the energy input increased to 2 hours end-over-end shaking, the dispersion increased in each step as ESP increased. Hence the amount of exchangeable sodium in Bordertown dramatically affected the dispersion at this energy input.

The behaviour of Mt Madden was slightly different to that observed in Bordertown, as would be expected due to differences in mineralogy. The behaviour of the Mt Madden soil was similar up to 2 hours end-over-end shaking. Clay dispersion increased with ESP until the sodium percentage was five. Then the amount of clay dispersed was similar in the ESP range 5-10, but increased again at ESP 20.

5.3.2 Particle size

Particle sizes of the dispersed clay measured by a Nicomp particle sizer (section 3-12) followed a general trend of decreasing particle size as the energy input increased (Appendix 4). When particle sizes were considered in relation to soil ESP the ratio of calcium to magnesium did not appear to influence particle size;

the treatments with the same ESP all had very similar particle sizes. For Wimmera, ESP seemed to have little effect on the particle size of the dispersed clay, except when the soil was sodium-saturated and when the ESP 3 treatments were subjected to twice end-over-end shaking. When the soils were sodium-saturated, their particle sizes were consistently smaller than particle sizes of the treatments dominated by divalent cations. The ESP 3 treatments, after shaking twice end-over-end, had variable particle sizes that were generally higher than observed for treatments with other ESP values. This variability may be due to a few larger particles fragmenting from the aggregate which interfered with measurement by the particle sizer. This can result in higher than expected particle sizes. It is unusual that only the ESP 3 treatment exhibited this result for the Wimmera soil. This increase in particle size did not appear to impact on the clay dispersion result (ie no more clay dispersed than expected). As the energy input increased, for all ESP values there was a slight decrease in particle size with all treatments. The exception was the sodium-saturated soil, which had a fairly consistent particle size over the whole energy input range. It was expected that the particle size of all treatments after the final dispersion event (1 minute sonification) would be very similar because the clay had been broken down into the smallest particles encountered in this study.

In contrast to the Wimmera soil, the particle size of dispersed clay from the Tomki soil after twice end-over-end shaking at all ESP values was quite variable, except at ESP 20,. This variability may be due to the differences in energy input that occur from shaking twice end-over-end by hand. Different levels of energy input may result in different sized particles breaking off the

aggregates. At ESP 20 the effect of sodium on stability probably overcomes any of the structural effects observed at the lower ESP values and the particle sizes dispersed after shaking twice end-over-end by hand are more uniform in nature. Tomki displayed a definite trend of decreasing particle size as the mechanical energy increased. The particle size of dispersed sodium-saturated Tomki clay was again smaller than the treatments that contained divalent exchangeable cations. The particle sizes of all Tomki treatments after 1 minute sonification were very similar.

The particle size of the dispersed Tatura and Belalie clay decreased as the mechanical energy increased regardless of ESP. There seemed to be little difference in the particle size between all ESP values, and the particle sizes after 1 minute sonification were fairly uniform. The Belalie sodium-saturated soil is interesting in that there appears to be no difference in the size of these particles when compared to the magnesium- and calcium-saturated treatments. Most other soils exhibited smaller dispersed particles when sodium-saturated. The response of Belalie to a range of ESP values indicated that sodium percentage had minimal impact on the amount of clay dispersed, hence it would follow that the impact on the size of the dispersed clay would also be minimal. Exchangeable cations also had little impact on the dispersion of Belalie. This is confirmed by the particle size of the dispersed clay, only the mechanical energy imparted into the system had any effect on dispersion. As the mechanical energy increased the particle size decreased.

The Bordertown soil differs from the other soils as some treatments exhibited a very slight trend towards increased particle size as the energy input increased from 1 minute to 2 hours end-over-end, before decreasing again at higher levels of disturbance. This was probably due to small, mobile particles of the aggregate breaking away initially. As the energy input increased and the aggregates themselves started to break up, the particle size of the dispersed clay was slightly larger than the small initial mobile particles, hence the increase in particle size. The higher energy inputs disrupted the micro-aggregates, which reduced the mean particle size once again. The Bordertown soil did not display different particle sizes for changes in the calcium:magnesium ratio within a single ESP, and the particle sizes, after 1 minute sonification, were also very similar within each ESP. The Mt Madden soil displayed the most variation in particle size within an ESP, however this variation was not significant. The particle size of dispersed Mt Madden generally decreased as the energy input increased, and the exchangeable calcium:magnesium ratio appeared to have little influence on the size of the clay particles dispersed.

5.3.3 Zeta potential

Zeta potential is the potential at the shear plane, which is commonly considered to be at the boundary of the Stern and Gouy (diffuse) layers. As such it measures the surface charge and extent of ion dissociation into the Gouy layer, which may indicate the dispersive behaviour of the clay.

There were some limitations on measuring the zeta potential of dispersed clay that may affect the data. Zeta potential was measured on suspensions with extremely low clay contents. In such suspensions the number of exchangeable

cations may be dwarfed by those cations present as impurities in the water. Clays in such dilute suspensions may have many of their exchangeable cations replaced by H^+ ions or contaminating cations in the distilled water. The composition of the exchange capacity under these conditions is virtually impossible to define. Hence, if rapid, free exchange occurred, each soil may show no difference in zeta potential between the calcium- and sodium-saturated treatments. However, as the results indicate (Appendix 5) there are quite distinct differences in the zeta potentials of calcium- and sodium-saturated treatments, and some differences which could be due to pH. Since these differences are observed it is possible that the time taken for the transition of cations from the Stern layer to the bulk solution to occur is relatively long. This ensures that the clays still retain their exchange cations and produce differences in zeta potential.

Measurements of treatments containing various calcium:magnesium combinations were not included, as addition of the calcium and magnesium salts in the exact amounts required to maintain a particular exchangeable calcium:magnesium ratio, were considered impractical. Consequently, only the zeta potentials of treatments with sodium and only calcium or only magnesium as the dominant cation, and the ESP 0 treatments were considered. The volume of basic or acidic solution required to produce the change in pH was soil specific, resulting in different electrical conductivities of the solutions measured for zeta potential. The electrical conductivity of the solutions after pH adjustment was not measured. However the electrical conductivity of the solution has been reported to affect zeta potential measurements (Horikawa *et al.*, 1988), and this may account for some of the results observed.

There were no trends observed in the zeta potential measurements of all soils and with all cations, in fact, some results were contrary to the published literature. Despite the problems associated with the measurement of zeta potential, some interesting results were observed. Only Wimmera did not exhibit less negative zeta potentials at pH 8 when magnesium was the dominant cation compared to calcium. This exception to the general trend was possibly due to the higher concentration of calcium hydroxide required to change the pH of the Wimmera suspension than those of the other soils. This could have increased the electrical conductivity of the solution and resulted in a less negative zeta potential (Delgado *et al.*, 1986). The zeta potentials measured for the Tomki soil exhibited few differences with pH, except when it was sodium-saturated. At pH 6.5, as ESP increased, the zeta potentials of the magnesium-dominated suspensions became more negative than the calcium dominated suspensions. The zeta potential at pH 6.5 was measured on suspensions where no pH adjustment was made; this indicates the real effect exchangeable divalent cations have on zeta potential. If the zeta potentials of the magnesium-dominated samples were more negative than the calcium-dominated samples this would imply that the magnesium-dominated samples have the potential to be more dispersive.

The Tatura soil displayed marked differences in zeta potential at pH 8 compared with lower pH values. The effects of electrical conductivity probably contributed to the results observed. The zeta potentials at pH 8 were less negative than at the other pH's, which conflicts with previous reports (Delgado *et al.*, 1986). The zeta potential of Tatura became slightly more negative as ESP increased and moved closer to the zeta potentials observed for the sodium-

saturated clay. There seemed to be no effect of pH on the zeta potential of Belalie, except when sodium-saturated, and no effect of calcium or magnesium. However, magnesium-saturated suspensions at pH 8 were consistently less negative than the other suspensions, again, possibly due to the effects of electrolyte concentration. Even the zeta potentials observed for the sodium-saturated suspensions were not vastly different to those observed when calcium- or magnesium-saturated. These results correspond with the dispersion results observed, where exchangeable cation had little impact on the amount of clay dispersed. It appears that exchangeable cations also have little impact on the zeta potential. This suggests that surface charge may have a very small influence on the behaviour of the Belalie soil.

The Bordertown soil also possibly exhibited some effects of electrical conductivity on zeta potential. The addition of salts to the suspensions to obtain pH 8 and 5 probably resulted in the measured zeta potentials being less negative than the zeta potential at pH 6.5, where no salt additions were made. When the soil was sodium-saturated, the zeta potential of Bordertown became slightly less negative as the pH decreased as previously observed (Delgado *et al.*, 1986). There were also differences in the zeta potential of Bordertown when calcium- and magnesium-saturated, probably due to the differences in the electrical conductivity of the two solutions. Mt Madden clay exhibited a slight trend towards a more negative zeta potential as ESP increased, but no real differences in zeta potential with pH or when calcium- or magnesium-dominated.

5.4 Discussion

5.4.1 Mechanical Dispersion

Table 5-2 provides a general overview of the response of the six soils to the different calcium:magnesium ratios, when exposed to a range of mechanical energy inputs.

- Squares left blank (white) indicate ESP values with which no significant difference in clay dispersion was observed.
- Black squares indicate ESP values where a significant increase in dispersion occurred, as the magnesium percentage increased, in three or more treatments. The ESP 0 treatments where the magnesium-saturated sample dispersed significantly more than the calcium-saturated sample were also included in this group.
- The blue squares indicate a non-significant trend of increasing dispersion as the calcium:magnesium ratio decreased.
- The yellow squares with the letter A indicate ESP values where the calcium- dominated treatments dispersed to give significantly more clay than the magnesium-dominated treatments. All other treatments with the same ESP value dispersed similar amounts of clay to either the magnesium- or the calcium- saturated samples
- The yellow squares with the letter B indicate that the magnesium-dominated treatment dispersed to give significantly more clay than all other treatments with the same ESP.

Table 5-2 Summary of results for mechanical dispersion of six soils with differing calcium and magnesium ratios and ESP values ranging from 0 to 20.

Soil		2 eoe	1 min	15 min	2 hrs	16 hrs
Wimmera smectite, kaolinite	ESP 0					
	ESP 3		A	A		
	ESP 5				B	
	ESP 7			B	B	
	ESP 10					
	ESP 20					
Tomki RIM >> illite, kaolinite	ESP 0					
	ESP 3		A			
	ESP 5					
	ESP 7					
	ESP 10					
	ESP 20					
Tatura Illite > kaolinite, RIM	ESP 0					
	ESP 3		A			
	ESP 5					
	ESP 7	A				
	ESP 10	A				
	ESP 20					
Belalie Illite >> kaolinite, RIM	ESP 0					
	ESP 3					
	ESP 5					
	ESP 7					
	ESP 10					
	ESP 20	A				
Bordertown Kaolinite, RIM, illite	ESP 0					
	ESP 3					
	ESP 5		B	B		
	ESP 7					
	ESP 10					
	ESP 20	B				
Mt Madden Kaolinite >> RIM, illite	ESP 0					
	ESP 3		A	A		
	ESP 5			B		
	ESP 7					
	ESP 10					
	ESP 20					

Black squares - Significant increase in dispersion as magnesium percentage increases, between three treatments with same ESP, except at ESP 0 where a significant increase occurs between the calcium- and magnesium-saturated treatments.

Blue squares - Non-significant trend of increasing dispersion with increasing magnesium percentage

Yellow square, A - Significant difference between calcium-dominated treatment and magnesium-dominated treatment only.

Yellow square, B - Magnesium-dominated treatment dispersed significantly more than other treatments with same ESP.

The results show that despite the differences in their detailed mineralogy, the soils appear to fall quite well into the three original groups identified initially when selecting soils. These groups comprised two smectitic, two illitic and two kaolinitic soils. Table 5-2 indicated that Wimmera and Tomki (smectites) both exhibit similar effects of magnesium, Tatura and Belalie (illites) exhibited the least effect on dispersion due to the presence of magnesium, while the kaolinitic Bordertown and Mt Madden showed quite obvious effects of magnesium on dispersion. However, mineralogy does not adequately explain possible reasons for the behaviour of four soils (Wimmera, Tomki, Bordertown and Mt Madden) which displayed obvious significant effects from the presence of magnesium.

The previous chapter and the results of treatments with ESP 0 in the current chapter indicate that exchangeable magnesium can result in significant increases in the amount of clay dispersed. This coupled with the suggested lower stability of a smectite/kaolinite soil (Frenkel *et al.*, 1978) suggests that Wimmera might be expected to exhibit more effects of exchangeable magnesium on dispersion, when sodic, than it does. This implies that the Wimmera soil has a higher stability towards the effects of exchangeable magnesium on dispersion. Further investigation indicates that the density of surface charge of the Wimmera clay is comparatively higher than of the other soils. Alperovitch *et al.* (1985), Shainberg *et al.* (1987) and Slade *et al.* (1991) have all shown that a higher density of surface charge decreases the opportunity for swelling which decreases the opportunity for dispersion, as swelling may be the first step towards dispersion. This increases the general stability of the Wimmera soil, and reduces some of the effects of exchangeable magnesium on dispersion. The effect of

surface charge density on swelling is confirmed when a comparison of the surface charge densities and swelling abilities of Wimmera and Tomki are compared (Table 5-3).

Table 5-3 Comparison of some features of the Wimmera and Tomki soils.

Soil	Water adsorbed at 100 cm suction (g/g)		Density of surface charge (meq/m ² x 10 ³)
	Calcium-saturated	Sodium-saturated	
Wimmera	0.8	1.7	1.3
Tomki	0.6	3.4	0.8

The difference in the amount of water adsorbed by the calcium- and sodium-saturated forms of the Tomki and Wimmera soils indicate that the Tomki soil adsorbs much more water when sodium-saturated, than the Wimmera soil. Since the swelling ability of a soil is an indication of its dispersive potential then the fact that the Wimmera soil swells less means that the opportunity for dispersion, especially at the lowers energy inputs, is less.

There were four treatments of sodic Wimmera where significant differences occurred when magnesium dominated the exchange phase. This tends to indicate that the Wimmera soil is not as susceptible to changes in the calcium:magnesium ratio as other soils appeared to be. Again the stability of the Wimmera soil against the effects of exchangeable magnesium seems to insure it against dispersive effects of changes in the calcium:magnesium ratio until magnesium completely dominates the exchange phase.

The Tomki soil contrasts with the Wimmera in that it exhibited more treatments with a non-significant trend of increased dispersion as the calcium:magnesium ratio decreased. The Tomki soil had a comparably lower density of surface charge (Table 5-3) which contributed to a decrease in its stability. This translates to an increased susceptibility to the presence of exchangeable magnesium resulting in an increase in the amount of clay dispersed. This is observed at ESP 0 where most energy inputs resulted in more clay being dispersed from the magnesium-saturated soil than the calcium-saturated soil. The water adsorption of Tomki (Table 5-3) indicated that the sodium-saturated soil swells four times more than the calcium-saturated version. This suggests the opportunity for dispersion in the Tomki soil was much greater. The effect of both sodium and magnesium on Tomki had resulted in generally increasing dispersion as the calcium:magnesium ratio decreased. Even though this trend was non-significant, it did suggest that Tomki is vulnerable to decreases in the calcium content of its exchange phase.

The two illitic soils (Belalie and Tatura) showed very few effects of exchangeable magnesium on dispersion. The Tatura soil had a few more treatments that exhibited a response to the presence of magnesium than the Belalie soil. As illites generally have irregular surfaces in poor contact with each other, the impact of exchangeable cations on the soil could be reduced because the surfaces are mismatched. This is pronounced in the Belalie soil where the influence of all exchangeable cations (even sodium) is minimal. This was indicated by all treatments, regardless of ESP, dispersing to give similar amounts of clay. The Belalie soil also has a relatively wide distribution of pore

sizes (Appendix 2), which also reduces the packing ability and the structural stability of the soil. The low clay content of the Belalie soil also minimises the effect of changes in clay properties such as exchangeable ion contents on soil behaviour. The Tatura soil, on the other hand, had a few treatments where differences due to exchangeable cations were observed. The difference in water adsorbed at 100 cm suction between the calcium-saturated and sodium-saturated forms of Tatura (calcium-saturated = 0.5 g/g, sodium-saturated = 1.0 g/g) indicate a possible reason for this. The difference in water content between the calcium- and sodium-saturated forms indicated that there may be some influence of smectitic material on the soil. The smectitic material contains surfaces that fit closer together than those in illite and would have more of an impact on the response of the soil to changes in the exchangeable cations. The water adsorbed by the Belalie soil in the same situation (calcium-saturated = 0.1 g/g, sodium-saturated = 0.2 g/g) indicated that there was almost no swelling of this soil and that any smectitic material present had no influence on the response of this soil to exchangeable.

Despite the coarse nature of both soils, neither the Tatura nor the Belalie soil completely dispersed after 16 hours end-over-end shaking. It is thought that cementing agents such as iron and aluminium oxides and organic matter contributed to their stability. Emerson & Bakker (1973) found that for Lemnos loam (similar to the Tatura soil) calcium-aggregates with 6% free iron oxide, an ESP of 5 was required to initiate dispersion. The ESP required to initiate dispersion increased to 12 for a fine grained illite (Willalooka, Emerson, 1967). Similar observations were made if appreciable exchangeable aluminium was

present (Emerson & Bakker, 1973). Additions of iron have also been shown to stabilise the slaking of sodium-Willalooka illite (El-Swaify & Emerson, 1975). It has been suggested that iron interacting with organic matter can increase the porosity of soils (McIntyre, 1956). The organic matter contents of both soils was low, but may be present as organic matter-iron oxide complexes which could increase the stability of the finer fraction of both soils and hinder complete dispersion after 16 hours end-over-end shaking.

The Bordertown soil exhibited a mixture of responses to the changes in calcium:magnesium ratio. One difference between this soil and the other three soils (Mt Madden, Tomki and Wimmera) which exhibited major responses to changes in the exchangeable cations, was the lack of response to exchangeable magnesium at ESP 0. Only one of the samples with ESP 0 dispersed to give more clay when magnesium-saturated. This would tend to indicate that exchangeable magnesium had little influence on the response of the soil to dispersion. However, at ESP 7 and 10 the Bordertown soil exhibited treatments where a significant increase in dispersion occurred as the calcium:magnesium ratio decreased. Despite the lack of significant differences between the calcium- and magnesium-saturated samples at ESP 0, the response of the soil at ESP 7 and 10 tends to indicate that when sodium is present, Bordertown was more susceptible to changes in the amount of calcium present in the soil. The Bordertown soil also exhibited the non-significant trend of increasing dispersion with decreasing calcium:magnesium ratio that had been observed previously. This was a further indication that this soil is more sensitive to the effects of exchangeable magnesium when sodium was present in the soil. The

susceptibility of Bordertown to the effects of exchangeable cations is probably due to its mineralogy. It contains equivalent amounts of kaolinite and smectite, and as discussed previously, the presence of smectite in a kaolinitic soil can result in a decrease in stability (Frenkel *et al.*, 1978). The smectitic material in the Bordertown soil would have some influence on its behaviour, as there was an obvious difference in swelling abilities of the sodium-saturated (0.9 g/g water at 100 cm suction) and calcium-saturated (0.6 g/g water at 100 cm suction) soil. However similar differences in swelling behaviour were observed in the Wimmera soil, yet it did not exhibit similar behaviour to the Bordertown soil. If the density of surface charge of the two soils is compared ($0.5 \text{ meq/m}^2 \times 10^3$ for Bordertown and $1.3 \text{ meq/m}^2 \times 10^3$ for Wimmera) it is likely that this has influenced the behaviour of these two soils. The Bordertown soil has a relatively low density of surface charge which corresponds to a low stability for the soil (Alperovitch *et al.*, 1985; Shainberg *et al.*, 1987; Slade *et al.*, 1991). Hence the effect of smectite on the packing structure of kaolinite and the influence of the low density of surface charge of the smectitic material resulted in an increased sensitivity of Bordertown to changes in calcium:magnesium ratio.

The final soil, Mt Madden, seemed to exhibit the greatest number of treatments where significant differences or a non-significant trend occurred. The Mt Madden soil displayed a majority of samples with ESP 0 where the magnesium-saturated treatment dispersed to give significantly more clay than the calcium-saturated treatment. As discussed before, this is generally taken as an indication that the soil is susceptible to the effects of exchangeable magnesium on stability. There were also some sodic samples where significant increases in dispersion

occurred as the calcium:magnesium ratio decreased within an ESP. This occurred at a range of ESP values, indicating that sodium does not need to be present in any "threshold" amount before a significant response is observed. The Mt Madden soil contains a small amount of RIM (smectitic material), but the adsorption of water at 100 cm suction for the calcium-saturated (0.4 g/g) and the sodium-saturated soil (0.6 g/g) indicates that it has very little influence on the behaviour of the soil. The response of Mt Madden to changes in the calcium:magnesium ratio was probably due to the coarse nature of the particles found in Mt Madden as implied by the particle size distribution (Appendix 2). The coarseness of the particles suggests that the Mt Madden soil does not pack together well and so structurally is not especially stable. This means the bonds between particles are weaker and so more susceptible to slight changes in the exchangeable cations, especially calcium. Therefore, slight changes in the calcium:magnesium ratio, decreasing the calcium percentage, can result in significant increases in the amount of clay dispersed from the soil. The high number of treatments where the non-significant trend of increasing dispersion as the calcium:magnesium ratio decreases was another indication of the susceptibility of this soil to changes in the exchange phase. This trend occurred over all ESP values and energy levels and therefore must be considered as being an important indicator of the stability of the soil to dispersion. The Mt Madden soil was observed to be the most naturally dispersive soil during the course of all investigations, and this is further highlighted by the results obtained from this experiment.

5.4.2 Particle size and zeta potential

It can be concluded from particle size data that the calcium:magnesium ratio had little effect on the size of particles produced during a dispersion event, but sodium percentage and the mechanical energy input did affect particle size. The variable nature of the measured particle sizes suggests that the initial size of dispersed clay particle could be dominated more by aggregate structure than exchangeable cations. As the energy input and ESP increased, both impacted on the soil and resulted in smaller particle sizes.

It is difficult to draw conclusions from the zeta potential measurements of each soil due to the problems associated with these measurements. The effects of pH on zeta potential are masked by the effects of electrolyte concentration, due to the addition of salts to change pH. There was also no consistent difference in the zeta potentials of suspensions with pH 6.5; these were the only suspensions unaltered for zeta potential measurements.

5.5 Conclusion

It has been suggested that the calcium:magnesium ratio determined the effects of magnesium on soil stability (Rengasamy *et al.*, 1986). However, Curtin *et al.*, (1994b) found that soils with a calcium:magnesium ratio of 1:2 and 2:1 behaved more like a calcium-sodium soil than a magnesium-sodium soil. The results of this present work indicate that there is no particular calcium:magnesium ratio that always resulted in increased dispersion, especially when exposed to a range of energy inputs. Instead, each soil has an individual response to changes in the calcium:magnesium ratio. Most soils that contained smectitic material exhibited a consistent non-significant trend of increasing dispersion with decreasing

calcium:magnesium ratio. Where smectites were present and this did not occur, there were other mineralogical influences that could explain the results. Despite the lack of significant differences between treatments with different calcium:magnesium ratios at the same ESP, the trend observed was persistent enough to indicate that changes in the calcium:magnesium ratio do affect the stability of most soils. The results also indicated that there was no threshold magnesium percentage above which increases in dispersion become significant, and no obvious critical sodium percentage at which the effect of magnesium became more prevalent. However, the effects of magnesium on dispersion were slightly more prevalent in the treatments that were, by definition, sodic (Northcote & Skene, 1972). This indicates that the reduction in soil stability associated with sodium provides the opportunity for the slight effects of magnesium on dispersion to become more obvious.

The treatments that showed the greatest increase in dispersion usually contained 75% or more magnesium. Few agricultural soils contain magnesium percentages in this range so the effect of magnesium at this level has little relevance to land management. It is also probable that any effects of magnesium when present as < 75% of the exchange capacity would be counteracted in the course of amelioration for sodic soils. The traditional methods of sodic soil amelioration are gypsum application and organic matter retention.

The selectivity of soils for calcium over magnesium seems subject to some controversy. The selectivity is probably soil specific and the application of gypsum could have limited utilisation in replacing the exchangeable magnesium

in soils with calcium. However, the increase in electrolyte concentration from the dissolution of gypsum would help improve soil stability by increasing the electrolyte concentration. There also seems to be little work on the effects of magnesium and organic matter on soils and further investigation of its influence on soil stability would be beneficial.

Mineralogical similarities in the results were observed in a general way, but when it came to discussing the results in detail, the response to exchangeable magnesium and mechanical dispersion was specific to each soil. The two illitic soils displayed the most similar behaviour, and similarities in illites have been observed before (Emerson & Bakker, 1973; Emerson & Chi, 1977).

In summary, there seems to be no particular calcium:magnesium ratio that resulted in more clay dispersed, but a majority of soils did exhibit a non-significant trend of increased clay dispersion as the calcium:magnesium ratio decreased. The soils seemed to exhibit some mineralogical effects, especially for the illites and those soils containing RIM.

6. A method for inducing sodicity in soil with minimal structural disturbance

6.1. Introduction

Most methods used to impose a known ESP on soil involve either significant disruption of the aggregate structure (Rahman & Rowell, 1979; Rengasamy, 1983; Tucker, 1985) or else percolation of a solution with known SAR through the aggregates (Astaraei & Chauhan, 1992). The effects of aggregate disruption from percolation of solutions on the soil structure and subsequent clay dispersion are unknown. There is also some doubt as to whether equilibrium is reached when solutions are percolated through the soils. Hence the results obtained from soils produced in this way may not give a reliable indication of the behaviour of the soil in the field. There is a lack of precise methods for inducing sodicity in soil with minimal disruption of aggregate structure, and so such a method was developed for use in this work. The quantity of dispersed clay produced by these samples was then compared to that produced by the remoulded aggregates used in the experiments discussed in the previous two chapters. This comparison may indicate applicability of results from samples disturbed during preparation to the behaviour of soil in the field.

6.2. A method for inducing sodicity in soil with minimal structural disturbance

6.2.1. Materials and methods

Samples were prepared using the method described in section 3.13. Sodic conditions were imposed on aggregates of 1-2 mm diameter. During method development the continual removal of this size fraction reduces the viability of

the bulk sample. To make maximum use of the available bulk soil sample, method development was carried out on the same set of 1-2 mm aggregates. Once the method was perfected, it was repeated on fresh 1-2 mm aggregates removed from the bulk sample. The aggregates labelled as Set A in the results could not be considered truly undisturbed samples as they were those used to develop the method and were in contact with solutions of low concentration for extended periods of time.

6.2.2. Analysis of the method

Most methods aim to produce salt-free samples with known ESP values. This may be done by using solutions of the same SAR, but decreasing the salt concentrations (Curtin *et al.*, 1994b). One problem with this approach is the numerous solutions required to reduce the electrical conductivity, as well as some disturbance of the soil structure from solutions that are continually flowing through the sample. The initial method used in this study to induce a known ESP on soil was a modification of this approach. Two solutions with the same SAR but different concentrations were used. The initial solution had a total cation concentration high enough to exchange the cations and overcome the effects of any salt that may be present in the soil. The second solution was of very low total cation concentration and required continual changing to produce a soil with a very low electrical conductivity. This method was abandoned due to problems with reproducibility.

The method finally used is described in section 3-13. This method resulted in soils with the final ESP values listed in Table 6-1. Although the preparation was

only repeated once, the resulting soils had quite reproducible ESP values that were generally in the neighbourhood of the target sodium values of 2 and 6. The only soil in which ESP values were quite different from the target ESP was Belalie; the final ESP obtained was higher than expected. It is possible that the Gapon constant used ($0.01 \text{ (mmol/L)}^{-1/2}$) to calculate the concentration of salt required to obtain the target ESP was not correct for the Belalie soil; calculation of the Gapon constant from the measured ESP for Belalie with ESP 2 indicated a value double that expected. Using the electrical conductivity and ESP results of the soils prepared from the estimated Gapon constant, the actual Gapon constant of the six soils could be calculated. The calculated Gapon constant could then be put into the model instead of the estimated value and further samples prepared. The resulting ESP of these samples would reflect the accuracy of the calculated Gapon constant. This iterative approach was not tested due to time constraints, but would provide further validation of the method.

Table 6-1 Final ESP of samples produced using a method for achieving target ESP values of 2 and 6, which involved minimal disturbance of the soil structure.

Soil	Set A		Set B	
	ESP 2	ESP 6	ESP 2	ESP 6
Wimmera	1.2	7.8	2.1	9.7
Tomki	2.2	6.0	2.2	4.5
Belalie	6	11	5.2	10.7
Tatura	3.8	7.2	3.5	6.5
Bordertown	3.6	6.4	3.5	8.1
Mt Madden	3.2	6.7	3.2	8.0

This method is limited to producing samples with low sodium percentages. At high ESP values the soils dispersed spontaneously on the funnels during the distilled water wash. This caused slaking, disruption of aggregates and loss of

clay from the samples, resulting in soils which were altered from the bulk or undisturbed samples.

The Gapon constants for each soil were calculated from the measured ESP and electrical conductivities of the soils and found to be in the range 0.0055 - 0.021 (Table 6-2). The kaolinitic and illitic soils had Gapon constants which were similar to one another, regardless of ESP; the differences appear to be insignificant. The Gapon constants for the smectitic soils changed more than for the other soils with changes in ESP. The Gapon constant for the Wimmera soil increased as the ESP increased whereas for the Tomki soil the Gapon constant decreased as ESP increased. Girdhar (1996) found that at a given electrical conductivity the Gapon constant increased with an increase in SAR in a Haplustalf containing calcium, magnesium and sodium cations. This was attributed to a preference of the soil for calcium and magnesium over sodium. It is possible that the changes in Gapon constants observed in this experiment also correspond to soil preferences for calcium or sodium. Where there is little difference between the Gapon constants at both ESP values, no preference for either calcium or sodium would be observed. For the Wimmera soil the Gapon constant increased with ESP indicating a preference for calcium over sodium, however, for the Tomki soil the Gapon constant decreased indicating a preference for sodium over calcium. The presence of clay domains in montmorillonitic soils results in more effect on the Gapon constant than in the illitic and kaolinitic soils. The presence of internal surfaces in the montmorillonitic clay can cause the affinity of the clay for calcium to increase with increasing exchangeable calcium concentrations (Shainberg *et al.*, 1980).

However, the lack of further investigation and experimental work into the validity of these calculated Gapon constant, results in it being difficult to make satisfactory conclusions about these values.

Table 6-2 Calculated Gapon constants for each target ESP of the six soils.

Soils	ESP 2	ESP 6
Wimmera	0.0069	0.018
Tomki	0.0084	0.0055
Belalie	0.021	0.016
Tatura	0.013	0.008
Bordertown	0.016	0.013
Mt Madden	0.012	0.011

Average Gapon constants for American soils have been calculated as 0.015 (US Salinity Laboratory Staff, 1954), while for Israeli soils they have been observed to be in the range 0.0072 - 0.0169 (Shainberg & Oster, 1972). The values calculated for these six Australian soils appear to be largely within the range of published values.

6.2.3. Results

The soils used to produce the results of set A in table 6-1 could not be considered truly undisturbed as they were used to develop the method for inducing ESP with minimal disturbance. Comparisons between these samples and those that were truly undisturbed are not possible. Hence only the soils which produced the results labelled set B in Table 6-1 are discussed here. These soils were exposed to the same mechanical energy regime as the treatments discussed in the previous two chapters. The pH of the dispersed samples was in the range 5.9 - 7.2. As has been discussed in chapter 4 and 5, there are few effects of variable charge on the dispersion of clay minerals in this pH range.

The particle size measurements are in Appendix 6. There is generally little difference between the particle sizes of both treatments for all soils. Also, most particles are less than 2 μ m, which was the target size sampled for after each dispersion event.

Error bars indicate the standard error from three replicates; the dispersion results were not statistically analysed any further. The results for shaking twice end-over-end by hand are displayed in Figure 6-1. Except for Belalie all soils indicate a general trend of increased dispersion as the ESP increased. For the Wimmera, Bordertown and Mt Madden soils, these differences appeared to be significant. The Belalie soil exhibited less dispersion when the ESP was higher, however, results discussed earlier have indicated that exchangeable cations generally have little effect on the amount of clay dispersed from this soil. The clay dispersed after shaking end-over-end by hand is governed by mechanical energy. Since the energy imparted into the system is difficult to keep consistent, it is possible that slight differences in the small energy input involved could have resulted in the differences observed in the Belalie soil. There is also the possibility that the sample with higher ESP slaked into larger fragments than the ESP 5.2 sample. This could result in less clay being dispersed from the ESP 10.7 sample as the surface area exposed was less, and so the clay had less opportunity to move out of the aggregates.

With 1 minute end-over-end shaking (Figure 6-2), the effects of mechanical energy on soil with different ESP values became more obvious. The Belalie soil exhibited its peculiar behaviour, with no differences observed in the amount of

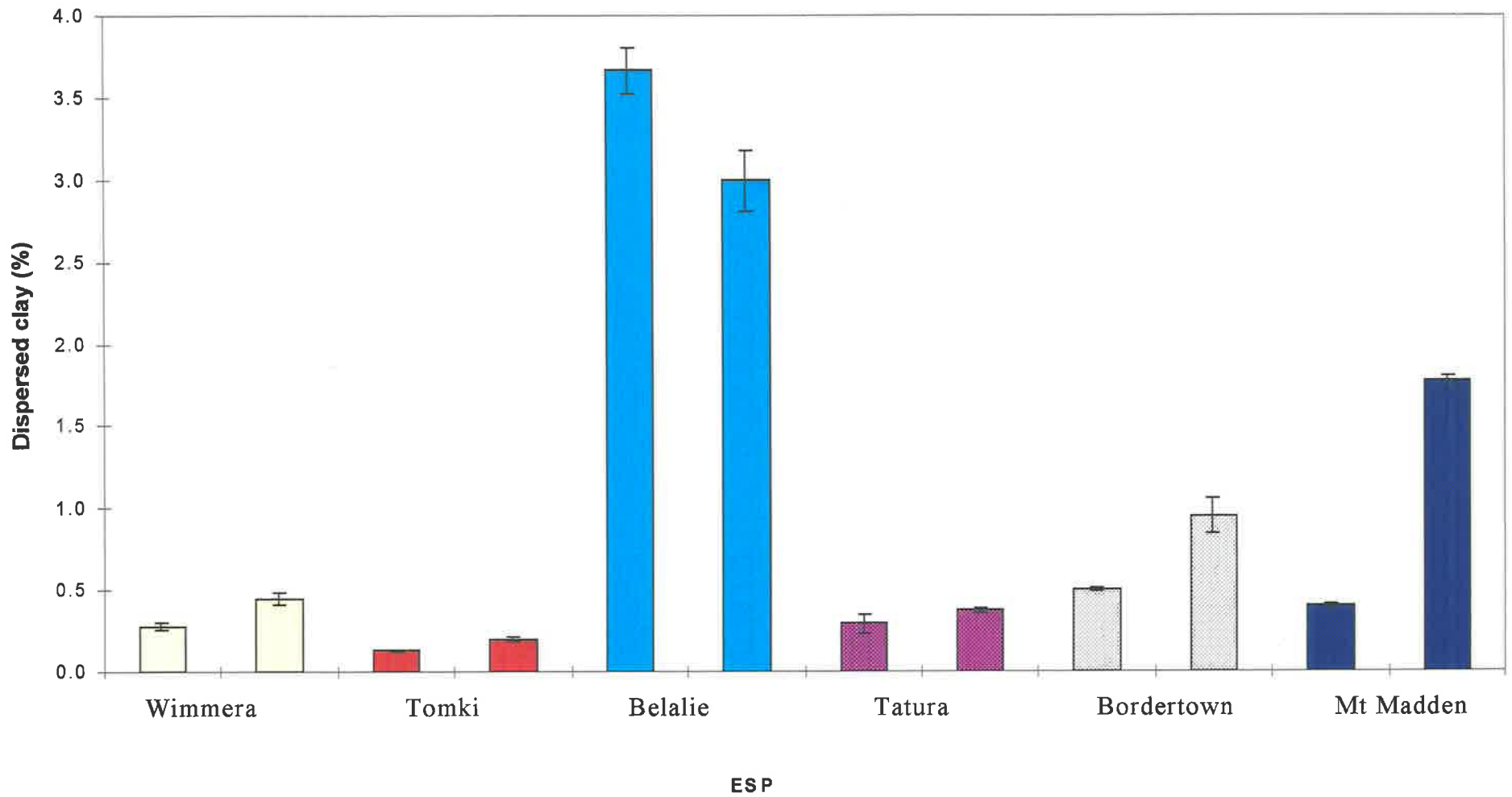


Figure 6-1 Clay dispersed from six soils that were minimally disturbed during sample preparation as a percentage of that produced by sonification. Samples were exposed to shaking twice end-over-end by hand. Error bars indicate the standard error of three replicates.

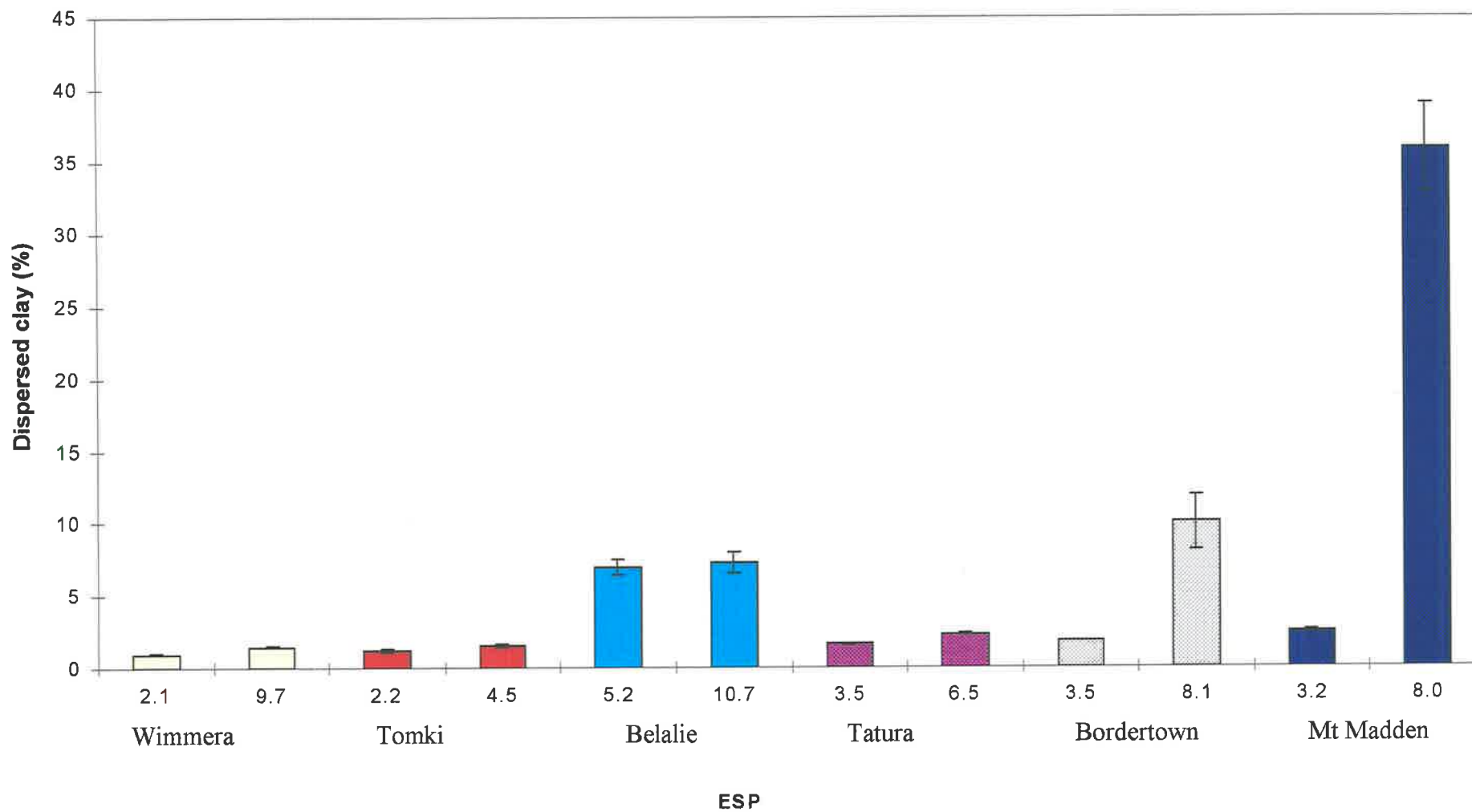


Figure 6-2 Clay dispersed from six soils that were minimally disturbed during sample preparation as a percentage of that produced by sonification. Samples were exposed to 1 minute end-over-end shaking. Error bars indicate the standard error of three replicates

clay dispersed at different ESP values. The total amount of clay dispersed from Belalie is also greater than in most other soils. The remaining soils exhibited generally greater amounts of clay dispersed when the ESP value was higher; however, Mt Madden and Bordertown exhibited the largest differences in clay dispersed between the sodic and non-sodic samples. The Mt Madden soil at ESP 8 produced 7 to 10 times more clay by dispersion than the other soils at similar ESP values. This is an indication of the susceptibility of these soils to sodicity and mechanical disturbance.

After 15 minutes end-over-end shaking (Figure 6-3) the differences between the clay dispersed from each soil at the two ESP values have all but disappeared, except for the kaolinitic soils. The kaolinitic soils continue to exhibit a far stronger response to high ESP values. Comparisons of the amount of clay dispersed from all soils at this energy level begin to indicate the stability of each to mechanical energy. The Wimmera, Tomki and Tatura soils all dispersed to give similar amounts of clay regardless of ESP. The Belalie soil dispersed to give more clay but again no effect of exchangeable cation on dispersion was observed. Only the kaolinites showed differences with the lower ESP treatments giving similar amounts of clay as the other soils upon dispersion, while the treatments with higher ESP values (especially Mt Madden) dispersed to give more clay.

The greater stability of the Wimmera soil to the effects of mechanical energy becomes more apparent after 2 hours end-over-end shaking (Figure 6-4).

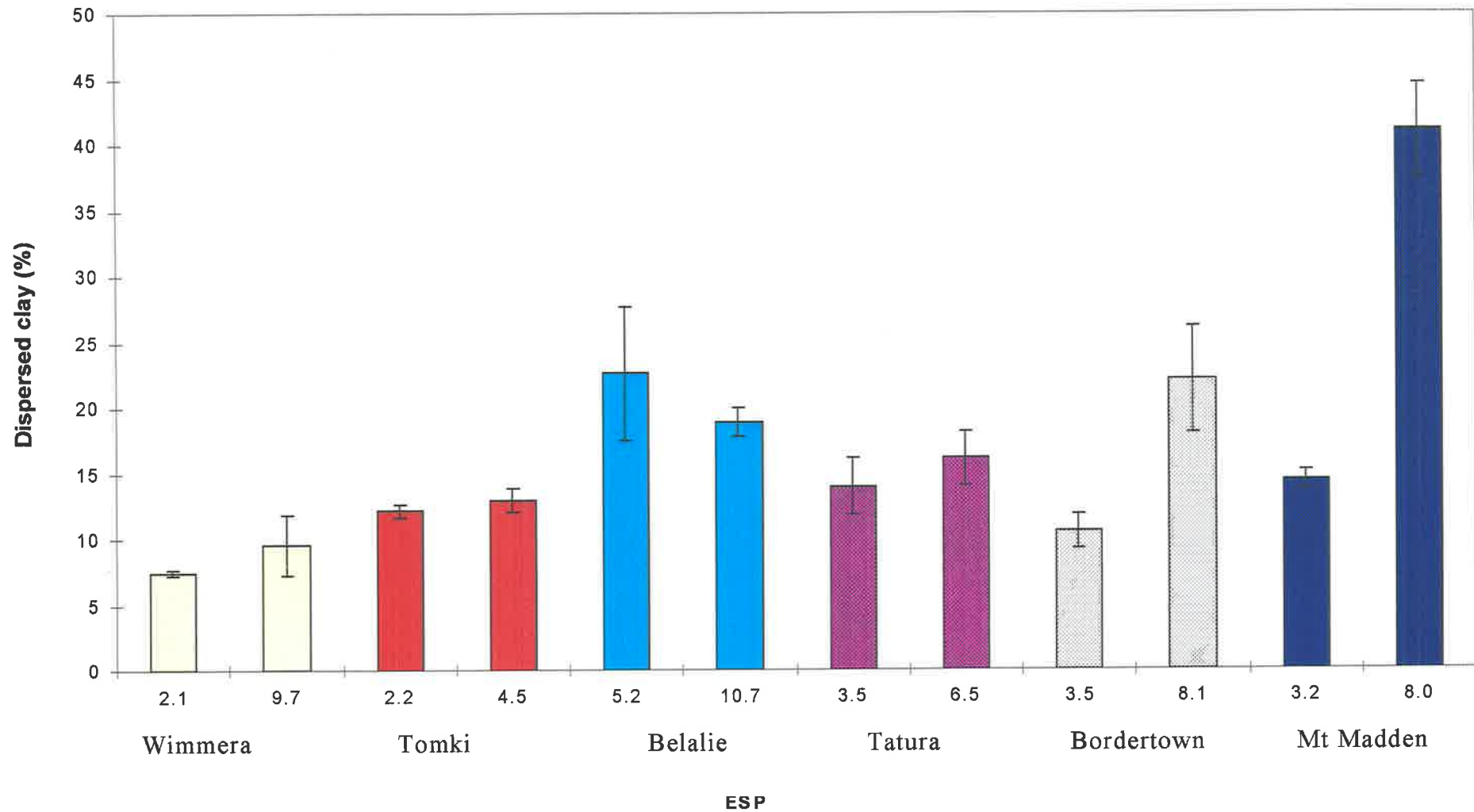


Figure 6-3 Clay dispersed from six soils that were minimally disturbed during sample preparation as a percentage of that produced by sonification. Samples were exposed to 15 minutes end-over-end shaking. Error bars indicate the standard error of three replicates.

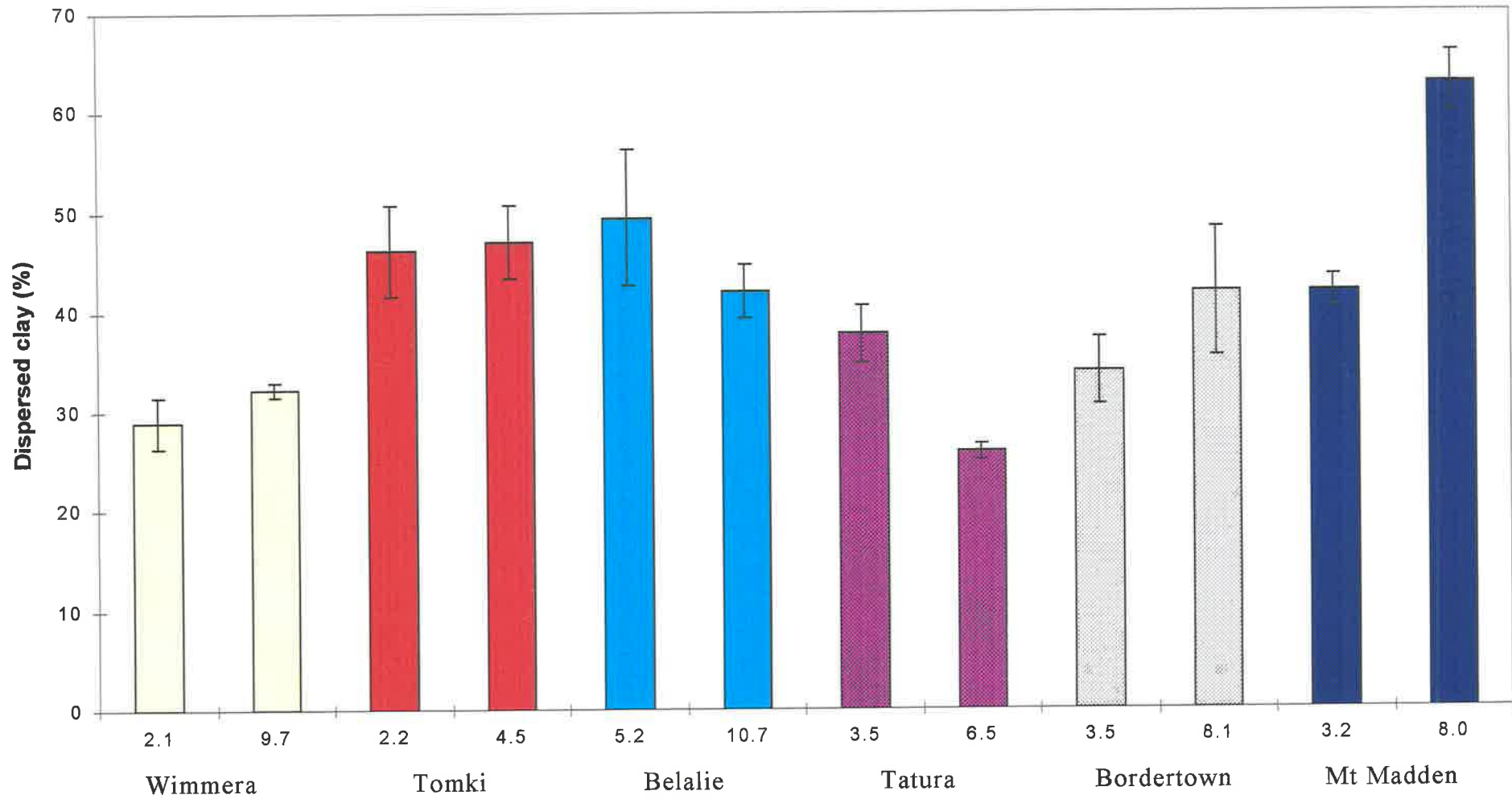


Figure 6-4 Clay dispersed from six soils that were minimally disturbed during sample preparation as a percentage of that produced by sonification. Samples were exposed to 2 hours end-over-end shaking. Error bars indicate the standard error of three replicates.

Compared with the other five soils, Wimmera dispersed generally less clay. Also at this energy level only the Mt Madden soil continued to exhibit significant differences in dispersion between the high ESP value and the low ESP value. For all other soils the effects of mechanical energy on dispersion seemed to out-weigh any effects due to exchangeable cations.

The dispersion of the Tatura soil with high ESP was low compared to the sample with ESP 3.5. The lower amount of dispersion was also observed after 16 hours end-over-end shaking (Figure 6-5). It is possible that there was partial flocculation which was not visible, reducing the clay in suspension and hence the turbidity. This partial flocculation may have resulted from a release of salts in the sample after the extended period (2 hours) of contact with the solution. The Wimmera soil with ESP 2.1 also exhibited a lower percentage of dispersed clay after 2 hours end-over-end shaking than after 15 minutes end-over-end shaking. Some of the colloids may have flocculated in this soil similar to the Tatura soil. Flocculation of clay probably resulted from the release of salts from the soil after prolonged contact with the soil, even though not visible to the eye. The samples of soils used were from "natural" soils, which had minimal mechanical disturbance during preparation. It is probable that the variation in aggregates in these samples would be higher than any variations in the remoulded aggregates. As these aggregates have not been in contact with high quality water for extended periods of time, unlike the remoulded aggregates, the cementing agents within these soils may be more intact. This may also account for the higher stability (decreased dispersion) of some of the samples. Again natural variations in aggregates within soil may account for why some samples exhibit

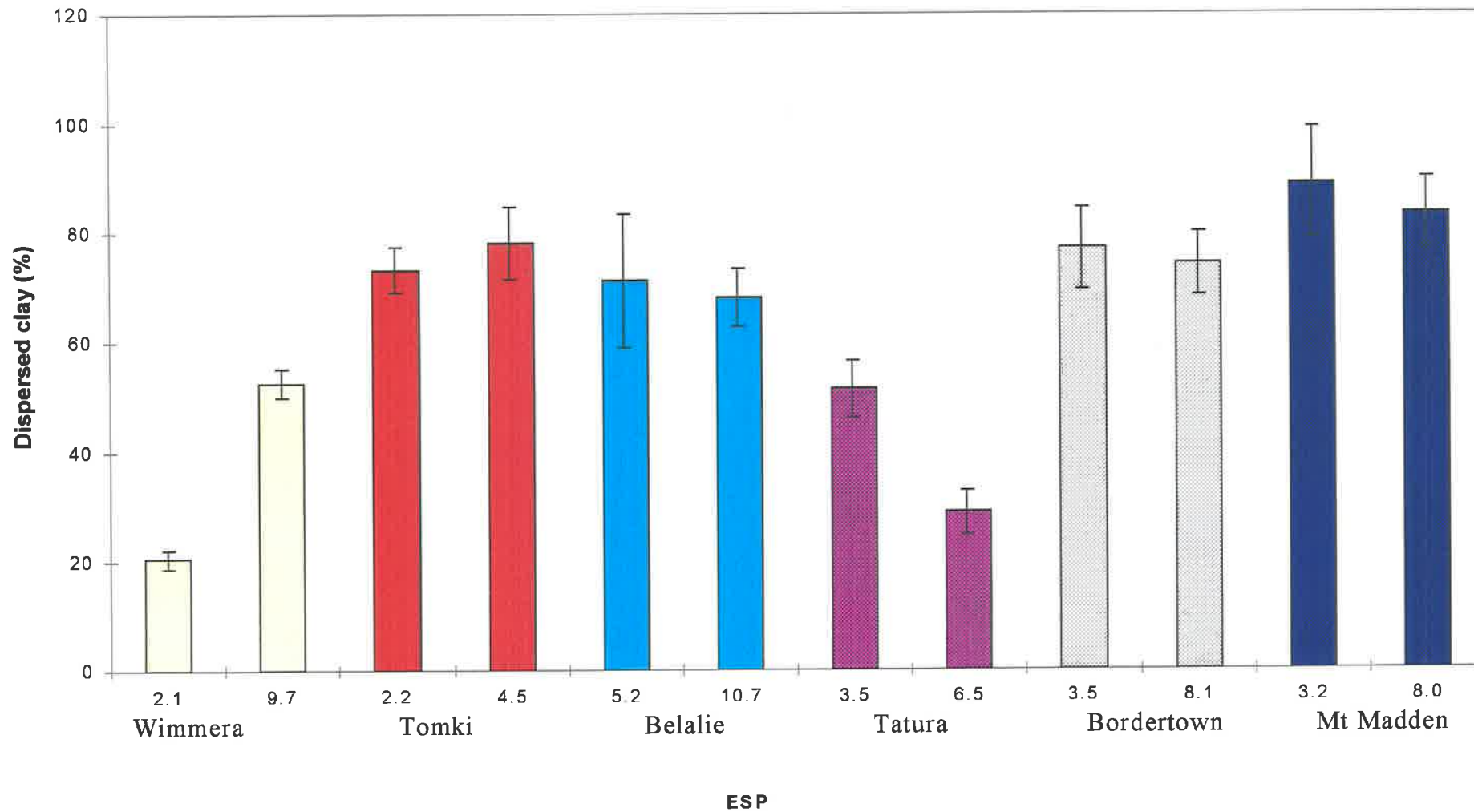


Figure 6-5 Clay dispersed from six soils that were minimally disturbed during sample preparation as a percentage of that produced by sonification. Samples were exposed to 16 hours end-over-end shaking. Error bars indicate the standard error of three replicates.

less dispersion than others do. The remaining soils exhibited no differences in dispersion due to ESP, and so the mechanical input has most control on the amount of clay dispersed. The Mt Madden soil dispersed almost completely.

6.2.4. Discussion and conclusions

The effect of mechanical energy on all six soils at all energy levels was generally as expected. The pattern of dispersion from mechanical energy of these undisturbed soils is very similar to that observed when the soils were remoulded. The Wimmera soil yielded the lowest amount of clay on dispersion, which when compared to other soils, as was observed previously. This resulted from the higher stability Wimmera exhibits, as discussed in the previous two chapters. The Tomki soil yielded more clay by dispersion than the Wimmera soil, as observed in other treatments and discussed previously. The Belalie soil again exhibited no effects of exchangeable cation on the amount of clay dispersed. The kaolinitic soils displayed the most sensitivity to the effects of exchangeable sodium, as had also been observed in the previous experiments.

The method developed to induce a target sodicity in undisturbed soil appears to have some potential, however further development and validation of the procedure is required. The pattern of clay dispersion from these undisturbed soils appeared similar to that observed when the soils were remoulded and dispersed. A comparison of the clay dispersed from each of the two methods, remoulded and undisturbed, will provide indication of any differences in clay dispersion with the method of preparation.

6.3. Comparison of the clay dispersed by samples prepared by remoulding and with minimal disturbance

6.3.1. Materials and methods

The clay dispersed from aggregates prepared using the method developed and discussed previously in this chapter (hereafter referred to as “natural” aggregates – those prepared with minimal disturbance, 1-2 mm) was compared with that from aggregates with similar ESP values, prepared by remoulding (hereafter referred to as “synthetic aggregates – those prepared by remoulding, 1-2 mm). The results of dispersion of remoulded aggregates are taken from the experiments discussed in Chapters 4 and 5.

6.3.2. Results

Some of the treatments prepared without disturbing the aggregate structure have a different ESP value to the remoulded treatment which makes a statistical analysis of results not possible.

A comparison of the particle sizes from both methods of sample preparation is in Appendix 7. The legend for the particle size results is as follows; U indicates a sample prepared with minimal disturbance, R indicates the remoulding method of preparation. The numbers after the letter U or R indicates the ESP of the sample. For the remoulded samples, ESP 3 and 5 results come from the experiment discussed in Chapter 5 and the ESP 5(2) results come from the experiment discussed in Chapter 4. The particle sizes for the Wimmera and Mt Madden soils appeared to display two distinct groupings, one for the treatments prepared with minimal disturbance and one for the remoulded aggregates. This

distinction in particle size became more obvious as the energy input increased. This may not be significant. The treatments prepared with minimal disturbance also appeared to show less variability in particle size at each energy input. The Tomki soil exhibited a similar trend, although the minimally disturbed aggregates decreased in dispersed particle size as the energy level increased. For the Belalie, Tatura and Bordertown soils there appeared to be little difference that could be attributed to the method of preparation. In general, where the method of preparation appeared to influence the particle size of dispersed clay, the particle sizes from treatments prepared with minimal disturbance were always larger than the particles dispersed from remoulded aggregates. It would be expected that differences in particle size between the two preparation methods would be observed. The remoulding method involved destroying the structure of the samples and making a more uniform sample. This could reduce the size of clay particles within the aggregates and result in smaller particles being dispersed.

The comparison of clay dispersed from aggregates prepared using two different methods is displayed in Figures 6-6 to 6-11. The treatments labelled ESP 3 and 5 result from the experiment discussed in chapter 5. The treatment labelled ESP 5(2) resulted from the experiment discussed in chapter 4. Each of these treatments contains only sodium and calcium.

For the Wimmera soil, the difference in preparation methods did not seem to affect the percentage of clay dispersed at the two lower energy levels (shaking twice end-over-end by hand and 1 minute, Figure 6-6). The dispersion increased

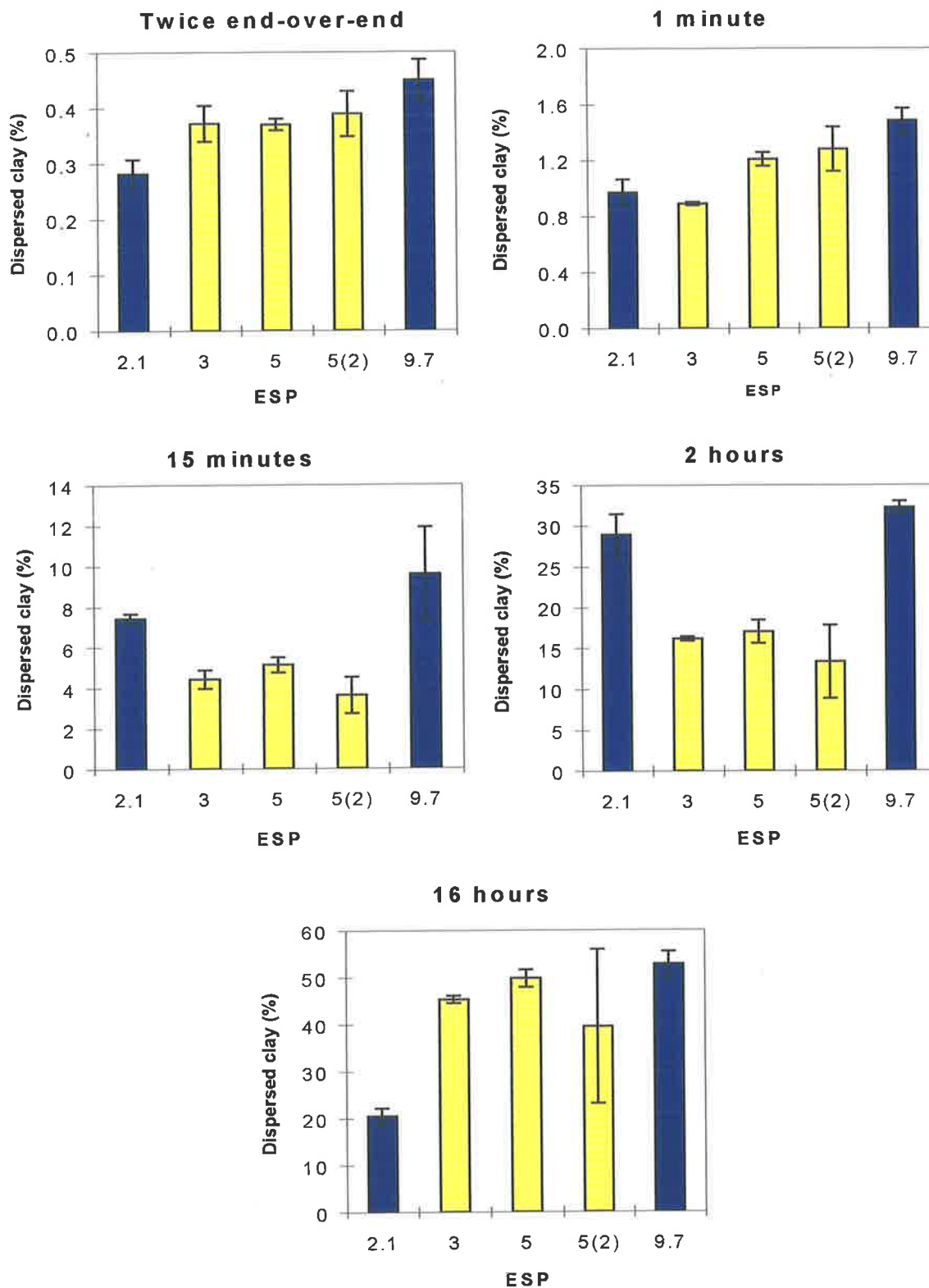


Figure 6-6 Comparison of the average dispersion of three replicates of Wimmera soil prepared using two methods. Error bars are the standard error of the average dispersion. Dark bars are the “natural” aggregates and the light bars are the “synthetic” aggregates.

sensibly with increasing ESP, which suggests that the method of aggregate preparation did not strongly influence dispersion. At the middle two energy levels (15 minutes and 2 hours end-over-end shaking), however, there were distinct differences in the amount of clay dispersed between the two methods. The “natural” aggregates dispersed to give considerably more clay than the “synthetic” aggregates. This indicated that the method of preparation may influence the amount of clay dispersed in Wimmera, but it was dependent on the energy input. As the energy input was increased to 16 hours end-over-end shaking, the treatments again produced similar amounts of dispersed clay. For the Tomki soil, the pattern is different (Figure 6-7). There appears to be little difference between the clay dispersed from the “natural” aggregates and the “synthetic” aggregates from chapter 5. However, the “synthetic” aggregates labelled ESP 5(2) consistently dispersed to give less clay than the other samples treated. The ESP 5(2) samples were the first ones to be remoulded and the samples for the experiment discussed in Chapter 5 were remoulded separately. It is possible that the differences in remoulding time for both or the length of time each soil was exposed to the wetting and drying cycles may have had some effect on dispersion. However, if the soils were so sensitive to differences in remoulding time or the length of the wetting and drying cycles, the results for all soils and treatments would be much more variable. After exposure to three wetting and drying cycles, the micro-structure of remoulded soils returns to essentially pre-remoulding status (*pers comm.* Dr R S Murray, 1997). In contrast, the macro-structure of these remoulded samples may be affected differently. This is because the fine pores could fill completely during the wet cycle while the large pores would not. When exposed to the drying cycle the finer pores would be

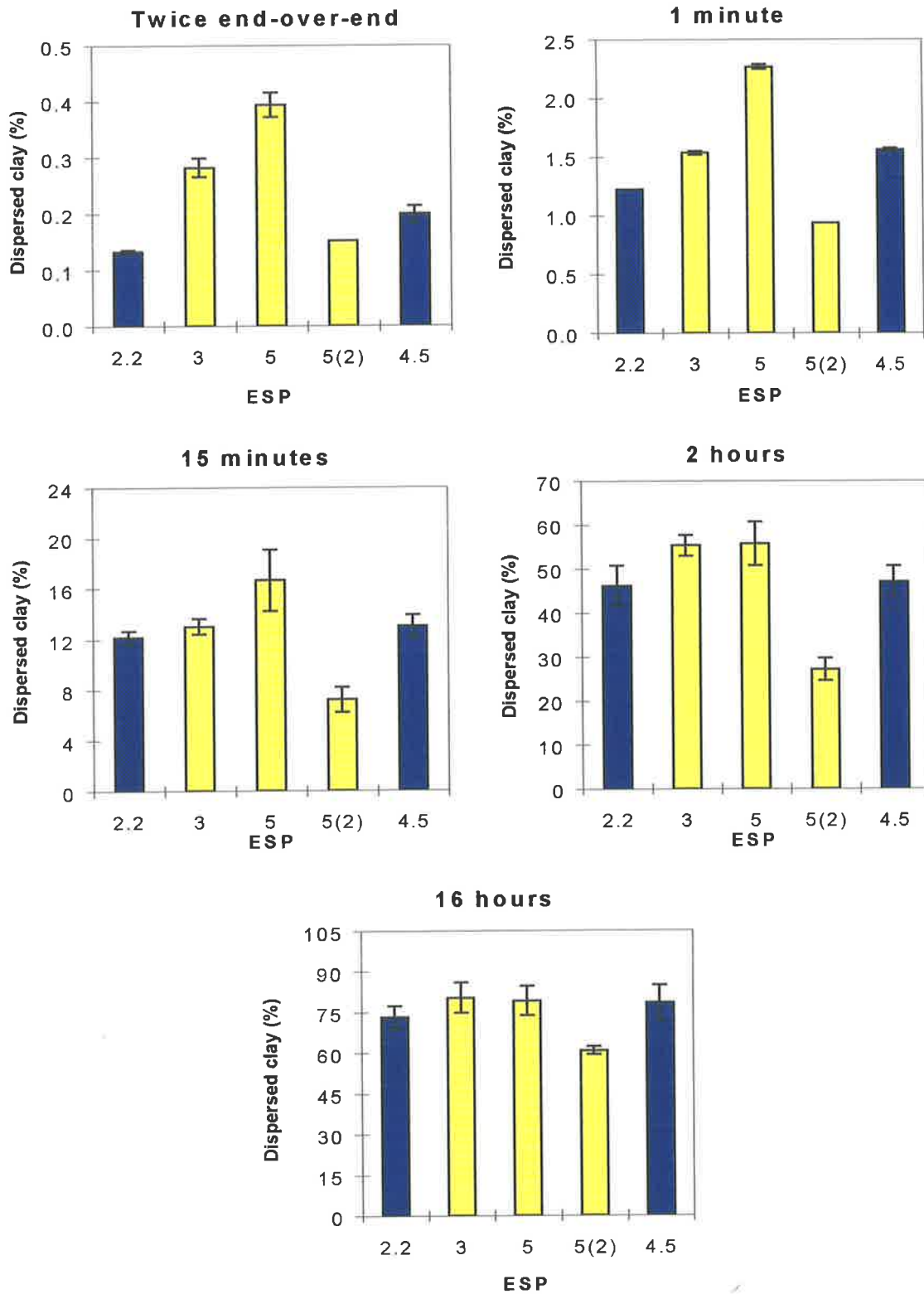


Figure 6-7 Comparison of the average dispersion of three replicates of Tomki soil prepared using two methods. Error bars are the standard error of the average dispersion. Dark bars are the “natural” aggregates and the light bars are the ‘synthetic’ aggregates.

placed under more stress than the larger pores because they would be full of water. These stresses result in the smaller pores returning to their pre-remoulding structure, while the larger pores may not. There would be some changes in the macro-structure but they would not be uniform. This may translate to differences in the slaking of each sample, which in turn impacts on the subsequent dispersion of that sample.

The Tatura (Figure 6-8) and Belalie soil (Figure 6-9) both exhibited similar results. At the lower energy levels (shaking end-over-end twice and for 1 minute) the aggregates prepared with minimal disturbance seemed to produce more clay. As the energy input increased the amount of clay dispersed from all samples was generally similar. There were also significant differences in clay dispersion between the 5 and 5(2) treatments with both the illitic soils. However unlike the Tomki soil where the differences were consistent, for the illitic soils differences were only observed at some energy levels. They also seemed to occur more in the Tatura soil than the Belalie soil. This is consistent with previous observations of the Belalie soil, which indicated that mechanical energy has the highest impact on the amount of dispersed clay. Any differences observed in the Belalie soil disappear once the energy level increased to 2 hours end-over-end shaking. For the Tatura soil, the ESP 6.5 "natural" aggregates after 2 hours end-over-end shaking dispersed to give a clay percentage yield which was much lower than expected, as was the case for 15 minutes end-over-end shaking. This may have been due to the occurrence of some flocculation of the clay which was not visible (discussed earlier). It is unlikely the lower dispersion would be attributable to problems with the sonification as this would

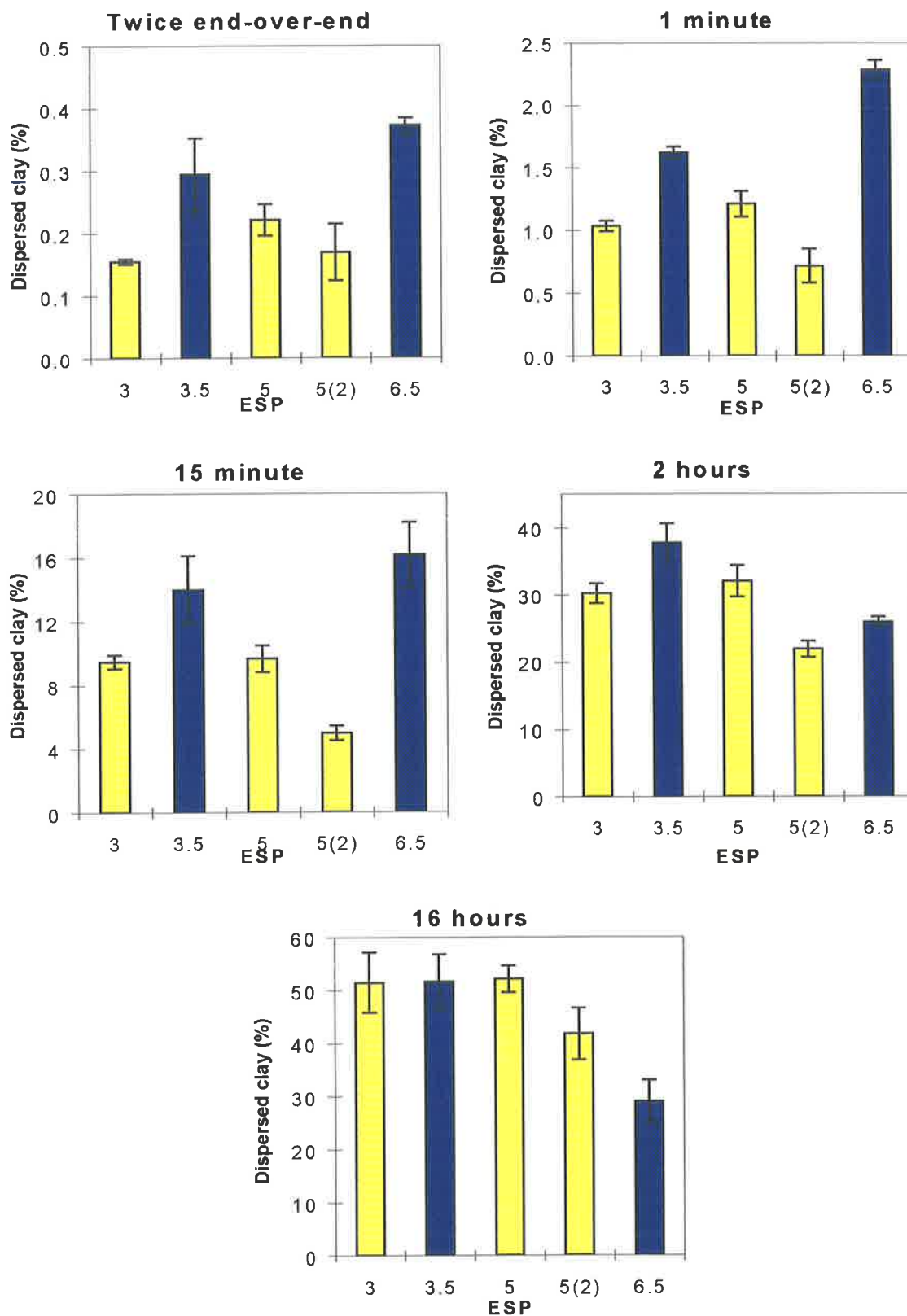


Figure 6-8 Comparison of the average dispersion of three replicates of Tatura soil prepared using two methods. Error bars are the standard error of the average dispersion. Dark bars are the “natural” aggregates and the light bars are the “synthetic” aggregates.

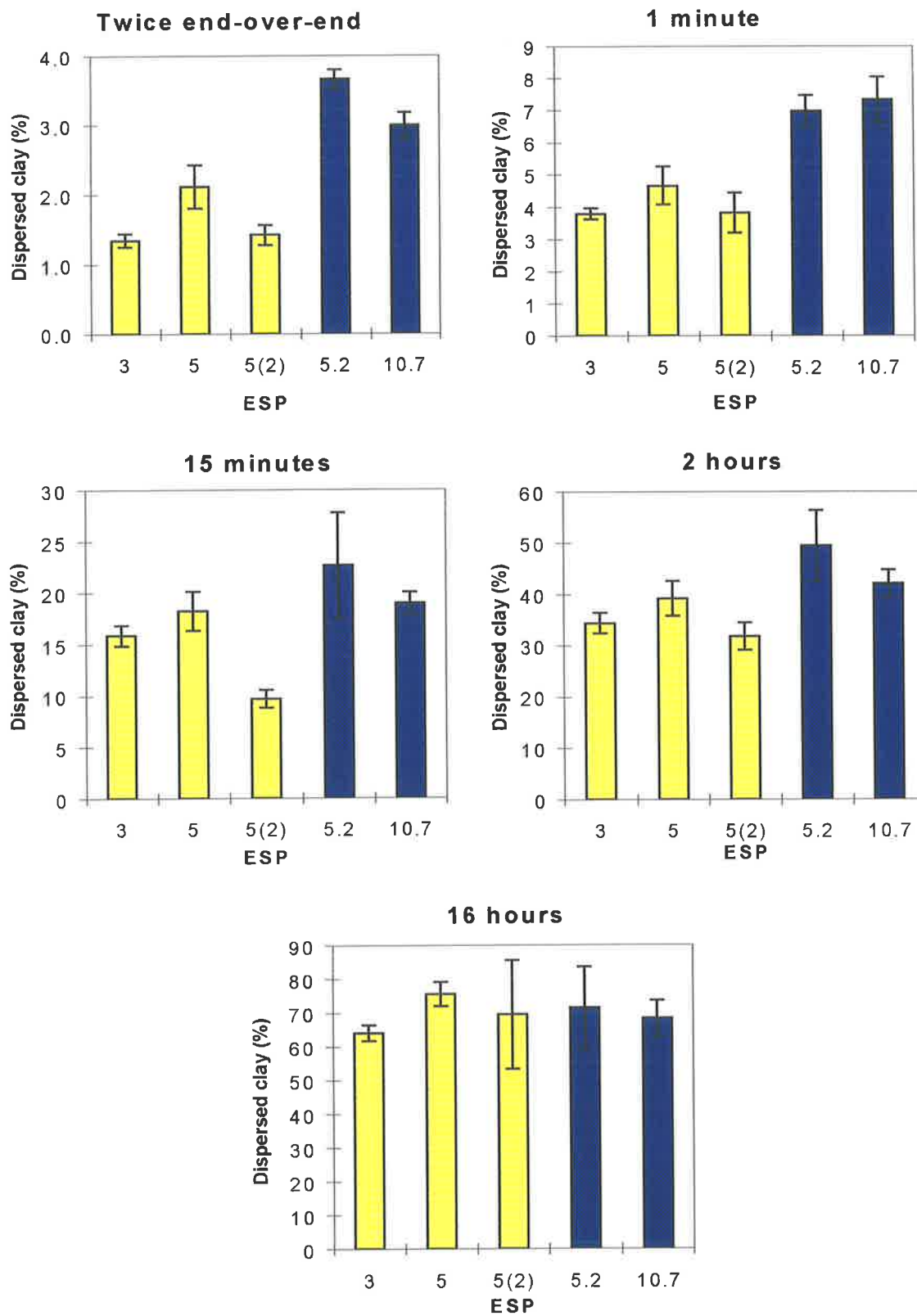


Figure 6-9 Comparison of the average dispersion of three replicates of Belalie soil prepared using two methods. Error bars are the standard error of the average dispersion. Dark bars are the “natural” aggregates and the light bars are the “synthetic” aggregates.

have resulted in a larger error and it would also have been reflected in the results for other soils, as all replicates were treated at the same time. Hence, with the illitic soils, the method of sample preparation may only be important at lower energy inputs. At higher levels of mechanical disturbance, the method of preparation appears to have minimal impact, as might be expected from previous observations.

The Bordertown soil (Figure 6-10) displayed quite variable results. It appeared that ESP was the most important factor influencing dispersion at the lower energy levels as the sample with the highest ESP dispersed to give the most clay. However, a difference in dispersion between the ESP 5 and ESP 5(2) treatments was again observed for the Bordertown soil. It was evident in all energy levels and the ESP 5(2) treatment did not ever disperse completely as “synthetic” aggregates with other ESP levels appeared to do. With 16 hours end-over-end shaking both the ESP 3 and 5 treatments dispersed completely, but the “natural” aggregates did not. It is possible that the remoulding process disrupted the bonds between micro-aggregates, weakening them to the forces of sonification. In the “natural” treatments the micro-aggregate bonds were not affected and so withstood the forces of sonification better. For the Mt Madden soil (Figure 6-11) there was a tendency for the “natural” aggregates to disperse to give more clay than the artificial aggregates at the three lowest energy input levels. The treatment with ESP 8 dispersed considerably more clay than the other treatments but this would be expected because of its high sodium percentage. As the energy input increased to 2 hours end-over-end shaking and higher, all the samples gave similar amounts of clay in dispersion. Hence, the dispersion of the Mt Madden

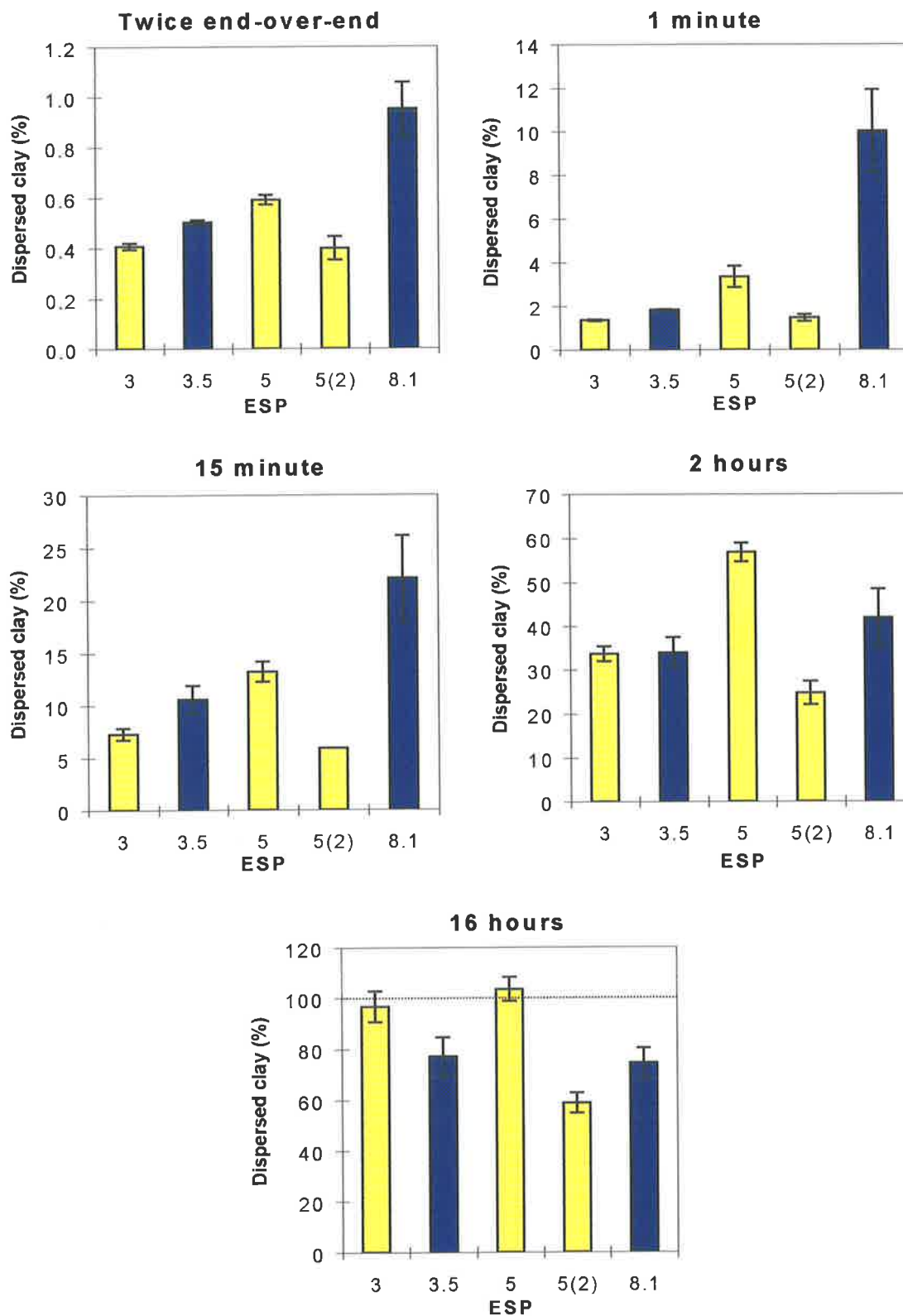


Figure 6-10 Comparison of the average dispersion of three replicates of Bordertown soil prepared using two methods. Error bars are the standard error of the average dispersion. Dark bars are the “natural” aggregates and the light bars are the “synthetic” aggregates.

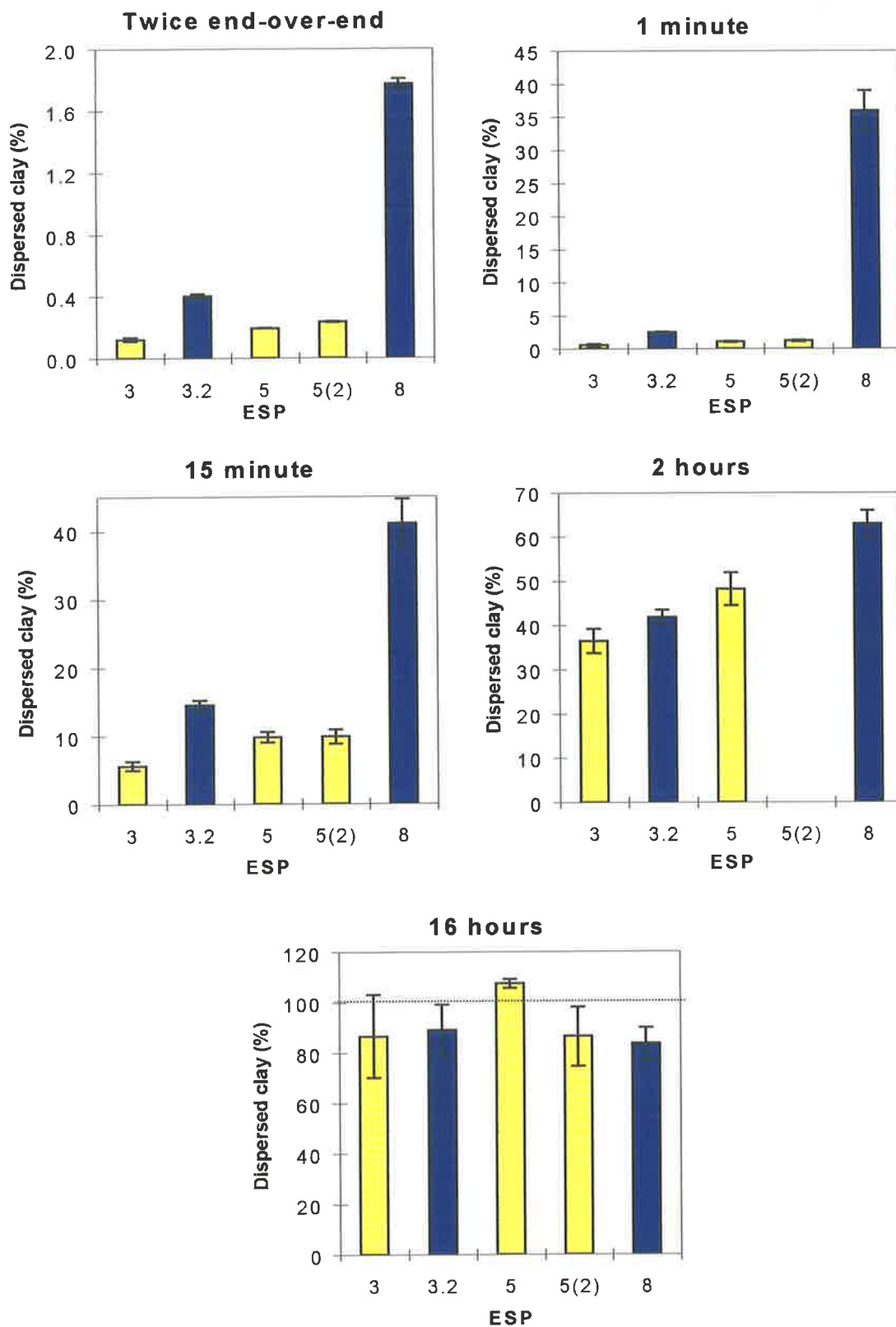


Figure 6-11 Comparison of the average dispersion of three replicates of Mt Madden soil prepared using two methods. Error bars are the standard error of the average dispersion. Dark bars are the “natural” aggregates and the light bars are the “synthetic” aggregates.

soil may be governed at low energy levels by the preparation method, but not at higher levels, where mechanical energy and ESP tend to dominate clay dispersion.

6.3.3. Discussion

The comparison of preparation methods did not produce consistent results for all soils. Only the Bordertown soil showed no differences in dispersion with preparation method while the Tomki soil dispersed more when remoulded than when undisturbed. The remaining soils all dispersed to give more clay when prepared with minimal disturbance than when remoulded.

The process of remoulding involves the destruction of structure to ensure complete mixing of the soil and brings clay particles closer together (Emerson, 1983). The micro-structure (< 50 nm) of the remoulded soil appears to be essentially returned to pre-remoulded status after three wetting and drying cycles (*pers comm.* Dr R S Murray, 1997). Therefore, there is probably little difference in the micro-structure of samples resulting from the methods of preparation. Differences in dispersion between samples could be due to differences in macro-aggregate structure as this may not be so easily returned after remoulding. This suggests that slaking would be more pronounced in the remoulded samples (Emerson, 1989) and so should enhance opportunities for dispersion.

Both the Tomki and Bordertown soils behaved differently from the other soils. These two soils are also those which appear to have the ability to swell the most. The water adsorption data of the calcium- and sodium-saturated forms of the

Bordertown and Tomki soils and also their surface charge densities indicate that both can swell more than the remaining soils. The presence of RIM with low surface charge may contribute to the increased swelling behaviour of the Tomki and Bordertown soils, but there is not enough known about the behaviour of RIM in soils to enable a firm prediction to be made about its contribution to swelling. Most work on RIM has been limited to descriptions of its nature (Schultz et al, 1971 and Churchman et al, 1994). There appears to have been little or no studies of the behaviour of RIM or its effects on soil structural stability.

The method used to produce samples for remoulding involved extended contact with high quality water to produce essentially salt-free soils. This long contact with water could result in the dissolution of cementing agents within the soil. This could have two outcomes; one would be an increase in clay dispersion as the cementing agents no longer help to hold the clay particles together (El-Swaify & Emerson, 1975; Goldberg *et al.*, 1990); this could have occurred in the Wimmera, Tatura, Belalie and Mt Madden soils. The other would be the opportunity, presented by the removal of cementing agents and other materials between clay particles, for the further intimate contact of clay particles during remoulding and drying; this could have occurred in the Tomki soil. A more ordered clay structure without interfering amorphous material to disrupt the particle associations could result, producing a more stable soil aggregate.

6.4. Conclusions

The method developed to induce low levels of sodicity in samples without disturbing aggregate structure produced samples which gave ESP values

generally close to those sought. The method is reasonably simple and although it takes about six weeks to complete, is not labour intensive. A by-product of the method was the ability to calculate Gapon constants for each soil. These Gapon constants could be used in further work by inserting them into the model, which would enable more accurate calculations, and probably result in final soil ESP values closer to those targeted.

Comparisons of the amounts of dispersed clay from samples prepared using the different methods showed that the remoulding method, somewhat surprisingly, may under-estimate the total clay that will be dispersed from undisturbed aggregates after mechanical input. This may possibly be due to differences in macrostructure, the strength of bonds in aggregates or the loss of cementing agents. The process of producing saturated soil samples and remoulding these samples appears to have a strong influence on the behaviour of most soils when they are subsequently exposed to mechanical energy. Further investigation into the behaviour of the essentially undisturbed samples is required; especially if they can be produced with ESP values the same as the remoulded samples. This would allow a more rigorous analysis of the results.

The method of sample preparation may not be important if a comparison of soil responses is all that is required. However, if the results of laboratory experiments are to be related to field conditions, there needs to be awareness of the effects that can result from preparation methods.

7. General discussion and conclusions.

7.1. Discussion

7.1.1. Introduction

The impact of sodicity on the management and sustainability of land is an increasing problem in Australia. As much as 25% of the land area of Australian soils includes sodic soils (Rengasamy & Olsson, 1991), with more under the threat of becoming sodic. A review of the work previously done on sodic soils and the effect sodicity has on soil structure is documented in chapter 2. It was concluded that there has been limited investigation into the behaviour of soils with $ESP < 6$, and little agreement in the results of investigations into the effects of exchangeable magnesium on sodic soils. The effect of magnesium on soil stability is of particular relevance to Australia where many subsoils contain high amounts of exchangeable magnesium (Isbell, 1986). Hence the aims of this work were:

1. To observe the response of six Australian soils with a range of exchangeable sodium values, when exposed to various levels of mechanical energy.
2. To investigate the effect of magnesium on the dispersion of six Australian soils exposed to various levels of mechanical energy.
3. To determine any mineralogical influences upon the response of the six Australian soils exposed to the various conditions in the first and second aims, and
4. To develop a method for inducing sodicity in soils that does not vigorously disrupt the aggregate structure and to then use these soils to compare the applicability of results from more artificially manipulated soils to those in the field.

7.1.2. Relevance of a sodium percentage to define a sodic soil

Traditionally in Australia a soil is considered sodic when it has an ESP > 6 (Northcote & Skene, 1972). The relevance of a specific ESP to define sodic soils has been questioned by some researchers who found soils with ESP values below six that displayed adverse behaviour (Bakker & Emerson, 1973; Rengasamy *et al.*, 1984b). Crescimanno *et al.*, (1995) suggested that the soil behaviour as ESP increased appeared to be a continuum, with no critical threshold evident, and that at low cation concentrations, predictions of soil quality can be forecast in the ESP 2 to 5 range. Rengasamy *et al.*, (1984b) inferred that a non-sodic soil is potentially dispersive under the appropriate conditions, further promoting the observation of whole soil behaviour over a range of conditions before determining management strategies. Abundant evidence was observed in this study to indicate that, over a range of mechanical inputs, no threshold ESP was apparent at which soil suddenly became more dispersive in a calcium/sodium system. Crescimanno *et al.*, (1995) investigated the effects of a range of ESP values (2, 5, 10, 15) on the hydraulic conductivity of two kaolinite/illite soils and found a linear relationship between the increase in ESP and the decrease in hydraulic conductivity. However, a similar relationship between ESP and percentage of clay dispersed was not observed in the six soils investigated in this study. With only exchangeable calcium and sodium, the majority of soils exhibited only slight increases in the amount of clay dispersed in the ESP range 3 – 10 when exposed to a range of energy inputs. A few soils displayed “threshold” energy inputs where the increase in dispersion with ESP was more obvious, but this was mainly at higher energy inputs. The only soil to exhibit generally increasing clay dispersion with increasing ESP was the Bordertown soil. For all soils, except Belalie, once the ESP reached 20 in a

calcium-sodium system the amount of clay dispersed significantly increased. The Belalie soil exhibited little variations in response to different exchangeable cations and dispersed to give similar amounts of clay regardless of exchangeable cation.

The small differences in dispersion generally observed from samples with ESP values ranging from 3 - 10 may be due to the presence of quasi-crystals. Smectitic soils with ESP values < 15 form particle arrangements of near parallel alignment of the crystals. These particle arrangements are referred to as quasi-crystals, and behave as a single entity in clay-water systems (Quirk & Aylmore, 1971). The exchangeable cation arrangement in these particles indicates that the exchangeable calcium resided on the inner surfaces of the quasi-crystal and the exchangeable sodium ion on the outer surface (Shainberg & Kemper, 1966a; Shainberg & Otoh, 1968). The presence of the exchangeable calcium ions on the inner surfaces of the quasi-crystals contributes to their stability and results in only the slight increases observed in the amount of clay dispersed from the six soils. When exchangeable sodium concentrations increase to about 20% of the exchange phase, sodium begins to replace some of the exchangeable calcium ions on the inner surfaces of the quasi-crystals. This provides the quasi-crystals with the ability to break into smaller pieces, increasing the amount of observed dispersed clay. It has been observed that as the ESP of soils reaches 50 – 60 % the quasi-crystals may become individual clay particles (Bar On *et al.*, 1970). From the results observed, it appears that at ESP values from 0-15 the clay quasi-crystals remain relatively intact. Any increases in the amount of clay dispersed could possibly reflect the amount of energy imparted to the system

only. Hence, similar percentages of clay dispersed over this ESP range at lower inputs of energy. When these aggregates are exposed to higher energy levels the forces imparted to the system are enough to break the bonds within the quasi-crystals, so dispersion may occur from the internal surfaces. When the ESP increases to 20, the presence of sodium on the internal surfaces of the aggregates reduces the strength of the bonds between particles. Smaller energy inputs will result in higher percentages of dispersed clay when compared with the same treatment of aggregates with $ESP \leq 15$. Similar influences of domains have been observed in illitic soils (Lebron *et al.*, 1993), where the domains start to break down after the addition of 13-18% sodium.

Effects due to domains have not been observed in kaolinitic soils. For the kaolinitic soils used in this current study, (Bordertown and Mt Madden) there was a more obvious increase in the dispersion of clay with the increase in ESP. As domains have not been shown to form in these soils there is a high probability that sodium ions are present on all the surfaces of the aggregates at low ESP values. This will make these soils more susceptible to the destabilising effects of sodium on soil structure, as each increase in sodium percentage enhances the dispersion of soil within the low ESP range. Shainberg *et al.* (1987) found surface charge density to have a marked effect on the hydraulic conductivity of smectitic soils. Hydraulic conductivity and dispersion was found to decrease more in soils with low density of surface charge than soils with high density of surface charge, at the same ESP (Shainberg *et al.*, 1987). The Bordertown soil contains significant amounts of smectitic material in the form of RIM. It has been shown that smectitic material further destabilises the stability

of a kaolinitic soil by interfering in the edge-to-face bonds (Frenkel *et al.*, 1978). As a result, the Bordertown soil may be particularly unstable towards applied mechanical energy.

7.1.3. The effect of magnesium on soil stability

When exchangeable magnesium is added to the soil system, the effect of increasing ESP on the dispersion of clay can be quite dramatic. Since much of the earlier research on the effects of magnesium gave contradictory results, a comparison of the effects of the group II cations on dispersion seemed logical. Overall, when comparing a two cation system, (sodium and a divalent cation from the group II series) the presence of exchangeable magnesium resulted in significant increases in the amount of dispersed clay, compared to the amount of clay dispersed when a soil was dominated by calcium, strontium or barium.

It has been suggested that there are two possible effects of magnesium on the dispersion of soil (Rahman & Rowell, 1979). The first is that magnesium has a specific effect similar, but of a smaller magnitude, to that produced by the presence of sodium. Hence the presence of the magnesium ion is enough to result in spontaneous dispersion. Alperovitch *et al.*, (1981) found a specific effect of magnesium on hydraulic conductivity when soils were leached with a magnesium/sodium solution. They suggested that the susceptibility of soils to the presence of magnesium was due to the exchangeable magnesium stabilising the structure and preventing dissolution of the clay minerals. Hence the electrical conductivity would be lower in these soils than those leached with a calcium/sodium solution and so dispersion would occur more readily. This may

have occurred in the experiments conducted in this study. This would have been confirmed with measurements of the electrical conductivity of the suspensions of calcium and magnesium dominated samples. However, problems in maintaining the sample integrity precluded measuring the electrical conductivity of the dispersed clay suspension before sampling for turbidity measurements.

Therefore it is difficult to indicate whether differences in electrical conductivity occurred and hence, whether differences in chemical stability may have occurred. However, a specific effect of magnesium did occur in most soils in which magnesium-saturated sample (no sodium present) dispersed more than the calcium-saturated sample (no sodium present).

The second reason given for the effect of magnesium on soil stability is an indirect effect, where the presence of magnesium, rather than calcium, results in increased adsorption of sodium onto the exchange phase. This produces a higher ESP in the soil and results in increased dispersion (Rahman & Rowell, 1979). This occurs because sodium competes more successfully with magnesium for exchange sites than it does with calcium. Hagnia & Pratt, (1988) found that as the magnesium/calcium ratio increased the exchangeable sodium percentage increased. The samples in this study were prepared in a way that a fixed amount of sodium was present. This prevents the possibility of more sodium being adsorbed onto the clay surfaces as might occur in sample preparation using solutions with determined SAR values.

The results of this present study indicate that there is definitely a specific effect of magnesium on clay dispersion. The magnesium-saturated samples of most

soils generally dispersed to give more clay than the calcium-saturated soils. The reasons given in the literature for the observed effect of magnesium on soil stability are many and varied. They range from differences in the adsorption strength of the two cations (Emerson & Chi, 1977) to the size of the hydrated ion (Bakker *et al.*, 1973). Keren (1991) proposed that magnesium ions were present on the external surfaces of clay tactoids due to their wider hydration shell, and so exhibit similar behaviour to clays with sodium on the external surface. If this was the case then all soils investigated would have shown quite dramatic responses to the presence of magnesium at most energy levels, similar to that of sodium. The results of the experiment discussed in chapter 4 indicate that only a few soils exhibited a magnesium response over the energy input investigated. All soils, except Belalie, which displayed no effects of exchangeable cation, exhibited an effect from the presence of sodium. Hence, it would be expected that if magnesium behaved in a way similar to sodium, then all soils would exhibit more of a response to the presence of magnesium than was observed.

It seems possible that the reason for differences in stability between soils with exchangeable calcium and magnesium may be due to differences in the cohesion each cation imposes on soil. Calcium ions possibly result in stronger bonds between particles that could be more difficult to break. When the calcium ions are replaced by magnesium, the bonds between the clay particles may become weaker and so break more easily resulting in less stable soils. The difference in cation and hydration size probably account for the differences in cohesion observed between the two cations.

There does not appear to be a threshold magnesium percentage after which dispersion increased dramatically. This is further evidence that the effects of exchangeable magnesium are probably due to differences in bond strength between magnesium and the clay. If magnesium behaved similarly to sodium with respect to the formation of domains, it would be expected that at some point the dispersion would increase dramatically. This did not occur in samples where the magnesium percentage was increased incrementally. When differing calcium/magnesium ratios were investigated, there was an overwhelming steady trend of increased dispersion as the magnesium percentage increased in all soils except Belalie. In some cases the increases were significant. The continuum approach towards defining a sodic soil discussed previously can also be applied to the effects of exchangeable magnesium.

Generally when the presence of magnesium resulted in significant increases in dispersion it dominated the exchange capacity. Very few top soils in Australia are dominated by exchangeable magnesium, and in most soils the amelioration of sodicity by adding gypsum and increasing organic matter would also tend to counter any effects of the presence of exchangeable magnesium. Improvements to soil structural stability will also benefit soils which contain exchangeable magnesium. The incorporation of organic matter and gypsum application, both promote structural stability in soil (McNeal & Coleman, 1966; Robbins, 1986; Shainberg *et al.*, 1989).

7.1.4. *The influence of mineralogy on soil stability*

Initial soil choice was based on various criteria, one of which was mineralogy. The aim was to have two soils whose clay fractions were dominated by each of the three main clay minerals. One of the two soils was to be dominant in that particular mineral and the other soil was to contain mainly that clay mineral, but in a mixture with others. This would enable observations of mineralogical trends if they were present.

There were only weak mineralogical effects on dispersion when only calcium and sodium were present on the exchange sites. The two illitic soils (Belalie and Tatura) generally exhibited little effect of exchangeable sodium on dispersion in a calcium-sodium system. The exception was the Tatura soil at ESP 20. The Tatura soil at relatively high sodium levels produced quite distinct increases in the dispersion of clay. Since this does not occur at lower sodium levels, the presence of smectitic material does not explain the observed results. Smectites have been shown to increase the clay dispersion of kaolinitic soils (Frenkel *et al.*, 1978) and it is possible that similar effects occur in the illitic soil. However, it is likely that domains of illitic material have formed, and that dispersion only increases dramatically when the ESP is 20. At this point sodium begins to reside on the internal surfaces of the illite domains and break up the domains. Increased dispersion has been shown to occur at between 13-18% of exchangeable sodium for illites (Lebron *et al.*, 1993). The significant smectitic content of the Tatura soil may contribute to increases in dispersion occurring at ESP 20. Smectitic domains normally start to break down at ESP values > 15 (Shainberg & Otoh, 1968). The Belalie soil exhibited generally very little response to the exchangeable cations regardless of type. The dispersion of clay

from the Belalie soil was generally a result only of the mechanical energy imparted to the system. The low clay content and low cation exchange capacity of the clay may have contributed to this behaviour. Neither of the illitic soils completely dispersed after 16 hours end-over-end shaking. This was unusual as both contained coarse particles (Appendix 3) which generally decrease the structural stability of a soil. Coarse particles do not pack together well and so the bonds between the particles are weaker. Both soils were red-brown earths, which generally contain iron oxides (Williams, 1981). It is proposed that the iron oxides were behaving as cementing agents stabilising the clay against the impacts of mechanical dispersion. The effect of iron oxides on soil stability is still under some dispute, and difficulties in determining the actual effect of iron oxides present in the soil prevent a resolution of the issue. Research has shown iron oxides variously to have no effect on soil stability and to increase soil stability (McIntyre, 1956; Emerson, 1967; Emerson & Bakker, 1973; El-Swaify & Emerson, 1975).

The two kaolinitic soils (Mt Madden and Bordertown) behaved contrary to expectations from published literature. Generally kaolinites are considered to be quite stable towards dispersion (Velasco-Molina *et al.*, 1971; Frenkel *et al.*, 1978), but in this case both soils proved to be quite susceptible to the effects of both mechanical energy and exchangeable sodium. The Mt Madden soil was dominantly kaolinitic, but the clay fraction was quite coarse. This would contribute to the instability observed and increase its susceptibility to the effects of exchangeable sodium. The Bordertown soil contained equivalent amounts of smectitic and kaolinitic material. The presence of smectites has been shown to

decrease the stability of a soil. Frenkel *et al.*, (1978) found that the smectitic material interfered with the edge-to-face bonds of the kaolinitic material. This decreased the strength of the bonds between particles and increased its susceptibility to the effects of sodium and mechanical energy.

The two smectitic soils contained different types of 2:1 mineral layers, with the Tomki soil dominated by randomly interstratified minerals (RIM), while the Wimmera soil was mainly montmorillonite as the smectitic material. The Wimmera soil also contained similar amounts of kaolinitic material to the amount of smectitic present. This may be part of the reason the behaviour of both soils is quite different. The Tomki soil generally reacted to increased mechanical energy and ESP by an increase in the amount of dispersed clay. The Tomki soil dispersed completely after 16 hours of end-over-end shaking. In contrast the Wimmera soil proved to be relatively stable to the effects of mechanical energy and exchangeable sodium. The Wimmera soil was fairly resistant to the effects of sodium at low energy levels and did not disperse completely after 16 hours end-over-end shaking. As well as mineralogical differences, the density of surface charge for the clays in each soil also contributed to the different results observed. Clays with high density of surface charge display limited swelling (Slade *et al.*, 1991) and are able to withstand higher ESP values before the hydraulic conductivity is affected (Alperovitch *et al.*, 1985). Clays in the Wimmera soil had a higher surface charge density than those in the Tomki soil and this may have contributed to the increased stability observed for this soil. The mineralogical trends observed in a magnesium/sodium system were slightly different to those observed in a

calcium/sodium system. Contrary to previously published results, this current study found little effect of exchangeable magnesium on the behaviour of illitic soils. Some effects of magnesium were observed, but were not significant. Chi *et al.*, (1977) and Emerson & Chi, (1977) found that magnesium had a specific effect on illitic soils. The illites studied by Chi *et al.*, (1977) and Emerson & Chi, (1977) were both fine and coarse grained, with one illite having a higher density of surface charge than the rest. Despite this, all three illites studied by Chi *et al.*, (1977) and Emerson & Chi, (1977) appeared to disperse more when magnesium rather than calcium was present as the dominant exchangeable cation. This was observed from spontaneous dispersion of the soils and measured by eye with no replication of treatments. Hence it is possible that the differences observed were not significant. In this study, the amount of clay that actually dispersed spontaneously was so small as to be undetectable to the naked eye at ESP 0. Hence detection and categorisation of the effect of exchangeable magnesium on illitic soils was difficult. Despite the similarities in the soil used by Chi *et al.*, (1977) and Emerson & Chi, (1977) and those used in this study, it is difficult to compare the results due to methodology differences. In contrast to the published literature, overall it could be said that the effect of magnesium on the dispersion of the illitic soils used in this study was minimal.

The most conspicuous mineralogical trend observed in the effect of magnesium on soil was for soils that contained significant quantities of smectitic material. This includes the Bordertown soil as well as the Tomki and Wimmera soils. The soils that contained significant amounts of smectitic material (Wimmera, Tomki and Bordertown) displayed the largest effect of magnesium on dispersion and

soil stability. The presence of smectitic material as a percentage of the clay fraction has been shown previously to affect soil erodibility, but no emphasis was placed on the presence of exchangeable magnesium (Young & Mutchler, 1977). In this study the presence of RIM also seemed to influence the response of a soil to the presence of exchangeable magnesium. The Tomki soil contained the most RIM and exhibited the largest response to the presence of exchangeable magnesium. RIM is thought to be more dispersive partly due to the particle geometry of the material. Churchman *et al.* (1994) found interstratified minerals to be poorly defined with curved edges that varied in thickness. Poorly structured interstratified layers were also found in soils from Mexico, where the mixed layer crystals were nearly round (Schultz *et al.*, 1971). This particle geometry would result in poor contact between particles producing a soil that is more unstable towards dispersion. Considering the prevalence of RIM in soils around the world (Churchman *et al.*, 1994), the lack of investigation into the properties of this mineral and its influence on soil stability is surprising. The Wimmera soil contains some RIM, but is mainly montmorillonitic. This soil exhibited a response to magnesium but generally at the higher ESP values. It is possible that the higher density of surface charge of the montmorillonitic material had a greater influence in soil stability than the effects of RIM.

The mineralogical trends observed in the two cation magnesium-sodium system were not so obvious in the three cation magnesium-calcium-sodium system. While the majority of soils exhibited, at a given ESP, a trend of increasing dispersion as the magnesium percentage increased, there was a lack of statistically significant differences in the data. The two kaolinitic soils

(Bordertown and Mt Madden) displayed the most treatments where there were significant differences in dispersion as the magnesium percentage increased within a particular ESP value. Both kaolinitic soils were highly dispersive and hence likely to be especially sensitive to factors causing increased dispersion, such as exchangeable magnesium. The percentage of the dispersible clay in soil has been shown to control the physical condition of the soil (Shanmuganathan & Oades, 1982) and both kaolinitic soils appear to have a high percentage of dispersible clay. The nature of both soils in the field also indicates that the amount of organic matter present to stabilise both the macro- and micro-aggregate structure is minimal. The high sand content of both soils may also contribute to their general instability to dispersion. Sand particles have no charge and so do not contribute to the forces between particles that result in aggregates stable to mechanical forces. Hence soils with high sand contents have less clay, which does contribute to the forces between particles, and so are likely to be less stable than soils with higher clay contents. The Mt Madden soil comes from a salt scald where vegetation is nil, and the Bordertown soil is a clay sodic subsoil below non-wetting sand, used for broadacre cropping. The massive nature of the clay subsoil limits the penetration of roots due to lack of pores and poor aeration and nutrient supply.

The two smectitic soils, Wimmera and Tomki, appeared to behave quite differently with the three cation system. The Wimmera soil exhibited very few effects of changing the exchangeable calcium and magnesium ratios. The Wimmera soil displays more observable effects of magnesium when only exchangeable sodium and magnesium are present. Once exchangeable calcium

was added, the strength of calcium in maintaining the bonds between particles overcame many of the effects of magnesium that were observed previously. When calcium was added, the Tomki soil still exhibited a considerable effect of magnesium on dispersion. The particle geometry of the RIM in Tomki possibly results in weaker bonds between particles in this soil, so that slight changes in the calcium percentage have greater impact than expected. Hence the Tomki soil was more significantly affected by changes in the calcium/magnesium ratios than the Wimmera soil.

The illitic soils exhibited similar behaviour in the two cation magnesium/sodium system as in the three cation system. There seemed to be little effect of exchangeable magnesium on the dispersive behaviour of the illitic soils. This tends to confirm that the exchangeable cations of the Belalie and Tatura soils have a minimal effect on the stability of the soils. Hence the mineralogical trend observed when the soils were saturated with the group II cations, was not as strong in the three cation system.

The illitic soils exhibited behaviour that was generally consistent between the experiments discussed in chapters 4 and 5. The trend observed for smectitic material was not as strong in the three cation system, but the two soils most dominant in RIM continued to exhibit a magnesium effect. The kaolinitic soils showed quite a strong response to changing the magnesium/calcium ratio. When comparing the results of the kaolinitic soils from chapters 4 and 5, it can be observed that the Mt Madden soil exhibited no magnesium effect when the group II cations were compared. In contrast, when the calcium/magnesium ratio

changed the Mt Madden soil exhibited quite a strong magnesium effect.

However, the Bordertown soil, which is influenced by both kaolinite and RIM, exhibited a significant dispersive effect of magnesium in the three cation system as it had shown when the group II cations were compared.

The results of this work indicate that soil behaviour cannot be predicted from single factors like dominant clay mineralogy alone. There were some mineralogical effects observed in the kaolinitic and illitic soils, but other soil factors also came into play. Predicting soil behaviour involves knowledge of the particle size, detailed mineralogy, cation exchange capacity, surface area and density of surface charge. A total soil characterisation needs to be detailed, and behaviour cannot be predicted from one or two factors. Although not investigated in this work, organic matter also greatly influences the behaviour of soils (Emerson, 1983; Durgin & Chaney, 1984; Gupta *et al.*, 1984; Chaney & Swift, 1986; Nelson & Oades, 1996).

7.1.5. Evaluation and comparison of methods used to produce samples with particular ESP values

A method for inducing sodicity in soils with minimal disturbance of the soil structure was developed. Samples with low ESP values only were able to be produced using this method due to problems with spontaneous dispersion. Spontaneous dispersion resulted in slaking, loss of clay and clogging of the porous sinter of the funnel. The method requires further validation, but has the potential to produce soil samples with specific ESP values that have been subjected to minimal disturbance.

Comparisons were made of the clay produced from dispersing samples prepared using both the remoulding and the minimal disturbance method. Only two soils (Bordertown and Tomki) exhibited no difference between the two methods of preparation in the amount of clay dispersed. These two soils exhibit the most potential for swelling, compared to the other soils. This can be inferred from the differences in the amount of water absorbed between the calcium- and sodium-saturated clays. The potential of a soil to swell can be an indication of the amount of smectitic material present. Both Tomki and Bordertown contain mainly smectites as the dominant minerals. The shape and size of smectitic minerals generally result many surfaces coming into contact when they are exposed to wetting and drying. This makes them more resistant to the effects of dispersion. Since the "natural" aggregates would have been exposed to wetting and drying in the field they would naturally have a greater stability towards mechanical energy. The "synthetic" aggregates were exposed to wetting and drying cycles and may develop this close packing of particles, resulting in greater stability towards dispersion. The remaining soils contained quantities of illitic and kaolinitic material which hinder the ability of the particles to pack closely. With less surfaces in close contact, the soils may be less stable to the influences of dispersion.

Many methods for determining the dispersibility of soil have been used over the years. Most include spontaneous dispersion of samples, exposure to mechanical energy at one or more levels (Velasco-Molina *et al.*, 1971; Oster & Schroder, 1979; Shanmuganathan & Oades, 1982) or determining the salt concentration required to flocculate dispersed clay (Goldberg & Forster, 1990). The commonly

used method involves exposing soils to end-over-end shaking for a set time period. It has been suggested that this method strongly disturbs the soil and so only remotely resembles the conditions soils are exposed to in the field (Singer *et al.*, 1994). However, Dong *et al.*, (1983) found that a 4-hour shaking treatment simulated the onset of soil erosion conditions in the field. They investigated dispersion at frequent intervals and felt that shorter shaking times more accurately simulated dispersibility under field conditions, as factors such as viscosity of the suspension may affect dispersibility after extended periods of shaking. The use of distilled water when testing soils for stability was considered by Rengasamy *et al.*, (1984b) to be qualitatively indicative of field dispersibility of bare soil during a rainfall event. Gupta *et al.*, (1984) found that the method of wetting aggregates before dispersion tests affected the relevance of results to field conditions. Measurements of aggregate breakdown under rainfall wetting were stated to be more realistic than tests based on immersion and tension wetting. The use of rainfall simulators can be cumbersome and is complicated by water application rates and drop sizes used. The method of end-over-end shaking is generally simpler to use, efficient and requires less equipment.

Since the results of end-over-end shaking are dependent on the specific methodology used, So *et al.* (1997) investigated the effects of various parameters (period of shaking, suspension concentration, container size and air-gap above suspension, temperature and texture) and recommended a standard methodology to enable comparisons between results of different workers. Their method required larger soil and solution volumes than used here and demands larger

amounts of soil than are sometimes available. So *et al.* (1997) found that the percentage of clay dispersed from the sample increased as a proportion of the total soil weight, which is not surprising as there would be more collisions between aggregates during shaking and so more clay would be dispersed. The method recommended by So *et al.* (1997) also used only one level of energy input, which is the standard for most researchers who use end-over-end shaking to determine soil stability. The length of shaking time was different in most methods summarised by So *et al.*, (1997), with only one author, Dong *et al.*, (1983), using multiple levels of energy input. This current study has shown that the behaviour of a soil can alter quite dramatically over a range of energy inputs. The Wimmera soil is one example where, at the lower energy levels, dispersion is minimal. Only after subjecting this soil to higher levels of energy does the soil exhibit significant dispersion. Hence management strategies for this soil when wet would depend on the level of disturbance the soil experienced. The method used in this study was a slight modification of the method developed by Churchman & Foster (1994) and enabled comparisons of soil behaviour to be made between the soils.

7.2. Conclusions

In conclusion, the validity of proposing ESP 6 to define a sodic soil is questionable. The behaviour of soils with exchangeable sodium should be considered more as a continuum. Other soil factors also affect the response of a soil to sodic conditions and need to be taken into consideration.

Exchangeable magnesium does affect the stability of a soil, both when sodium is present and when magnesium is the only exchangeable cation. There appears to be both a specific and an indirect effect due to magnesium, with samples containing only exchangeable magnesium and those containing both exchangeable magnesium and sodium exhibiting increased dispersion that can be attributed to the presence of magnesium. It may be that the presence of magnesium results in more dispersion due to the lower binding power it has within a soil. Soils that contain mainly calcium have stronger bonds between the cation and the clay and so are more stable to the effects of dispersion.

There were mineralogical trends observed in the behaviour of the six soils when exposed to various conditions. These trends were not always as published previously in the literature. The illitic soils exhibited generally little response to the presence of exchangeable cations. The kaolinitic soils both behaved in a similar way when they contained all three cations, but in the two cation system exhibited differences in behaviour. The smectitic soils behaved a similar way in the two cation system, but behaved quite differently in the three cation system. The presence of RIM in soils seemed to lead to a stronger response to the presence of magnesium when sodium was the only other cation but seemed to have less influence when the soils contained three cations.

The management of soils with high levels of exchangeable magnesium would require strategies similar to those utilised in sodic soils. Improving the soil structure by the incorporation of organic matter and the addition of gypsum will help improve soil structural stability. This will negate the effects of magnesium

on soil structure. Further study into the spontaneous dispersion of the soils used in this study would be of benefit.

A simple method for inducing sodicity in soils with minimal disturbance of the soil structure was developed. Further fine tuning of the method is required, but initial tests indicate that it is fairly successful, and enables calculations of the Gapon constants to be made. The comparisons of dispersed clay from samples prepared using this method and remoulding indicated that method of preparation may affect results. Soils that have the ability to swell extensively are less vulnerable to the effects of preparation method. Remoulded samples produce results which can be compared, but may not be completely relevant to field situations. When determining the method of preparation for samples the application of the results need to be considered. Further development of the method involving minimal disturbance of samples is required, as well as further investigation into the relationship between the behaviour of remoulded soils and those in the field.

8. References

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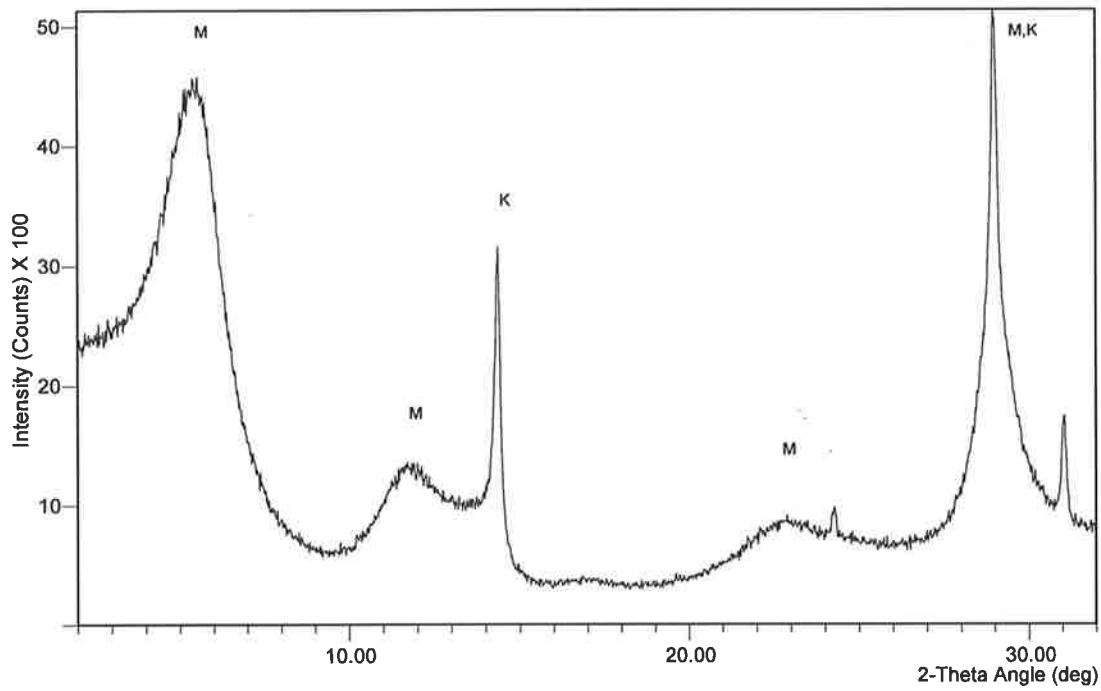
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9. Appendices

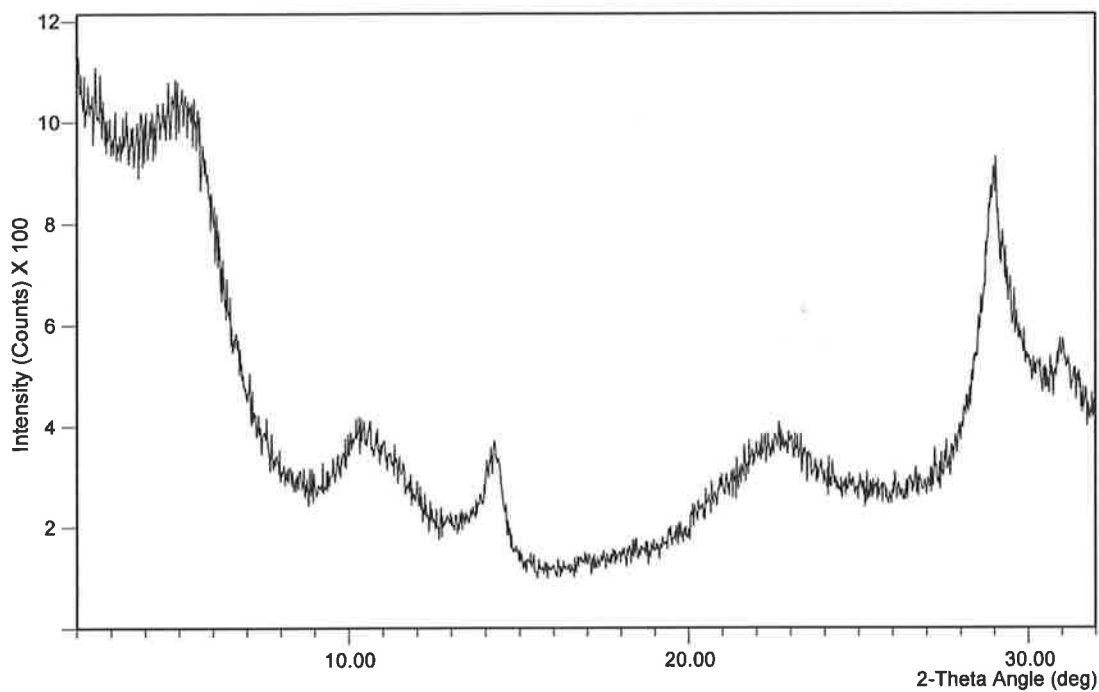
Appendix 1 Xray diffraction patterns for whole and fine clay of the six soils characterised.

Wimmera whole clay



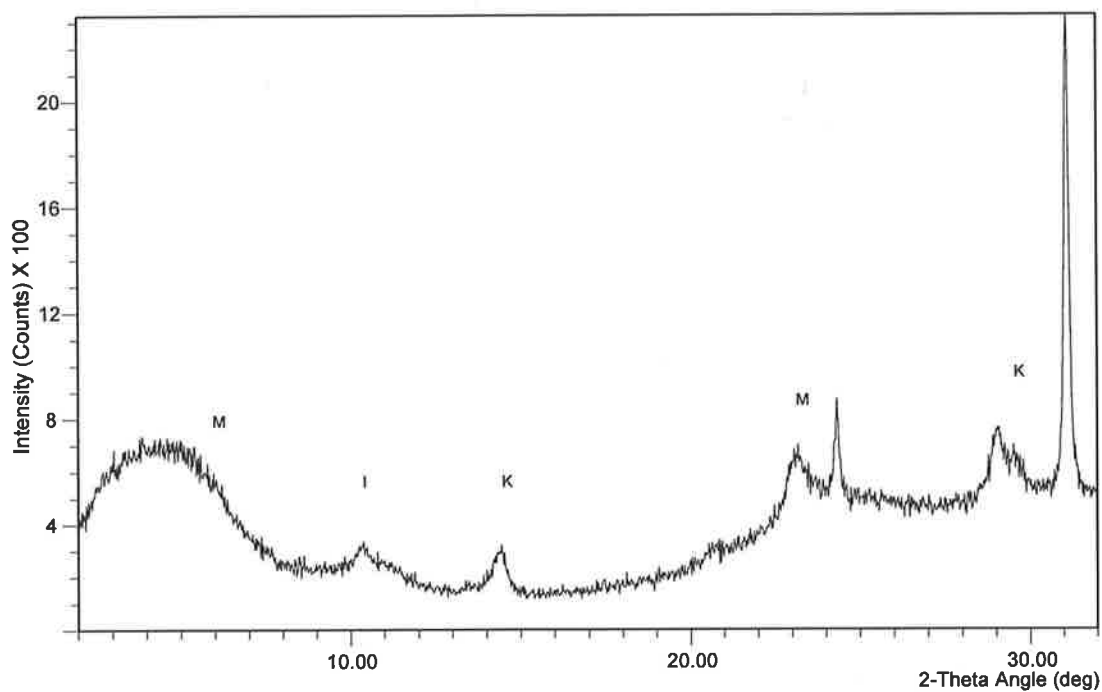
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Wimmera fine clay



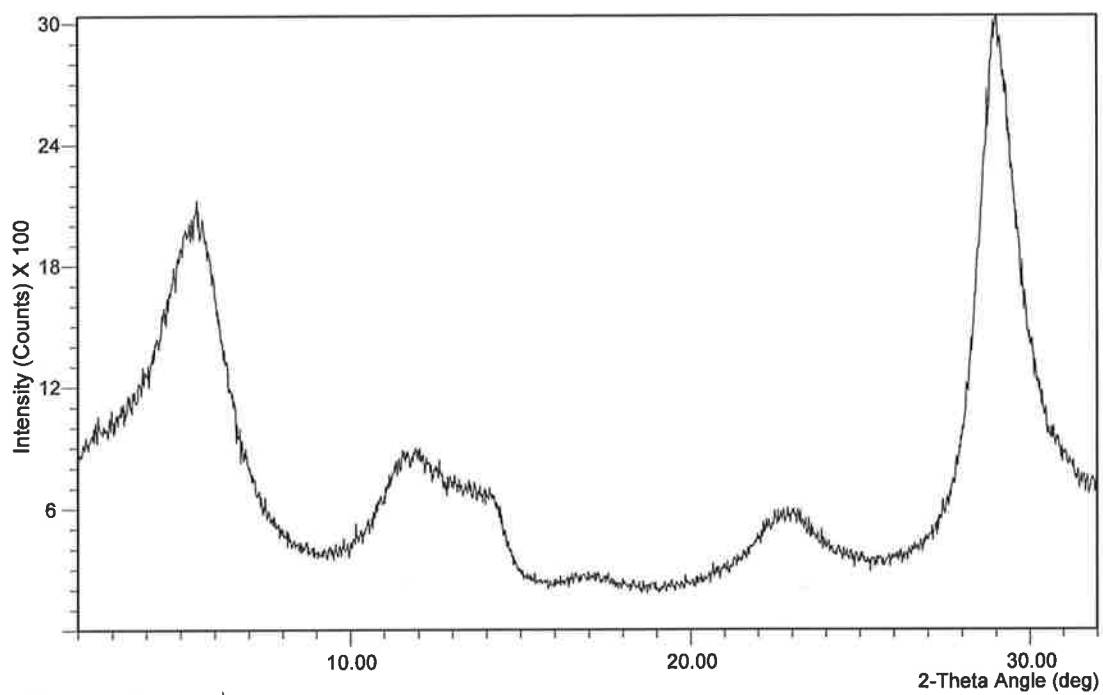
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Tomki whole clay



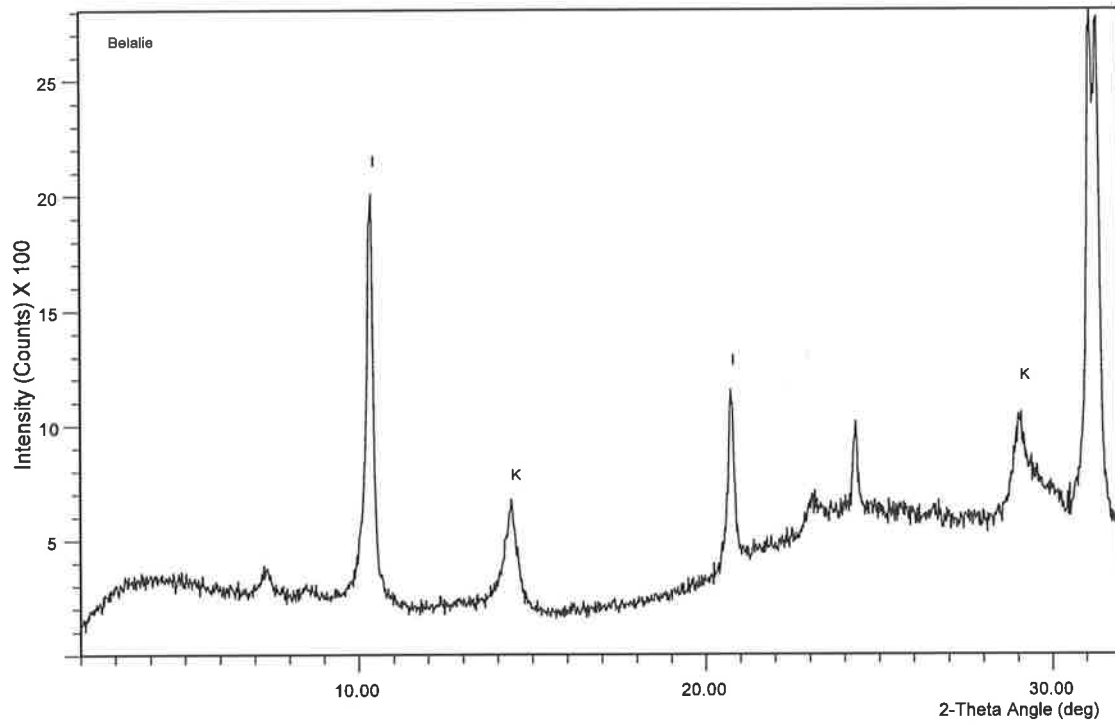
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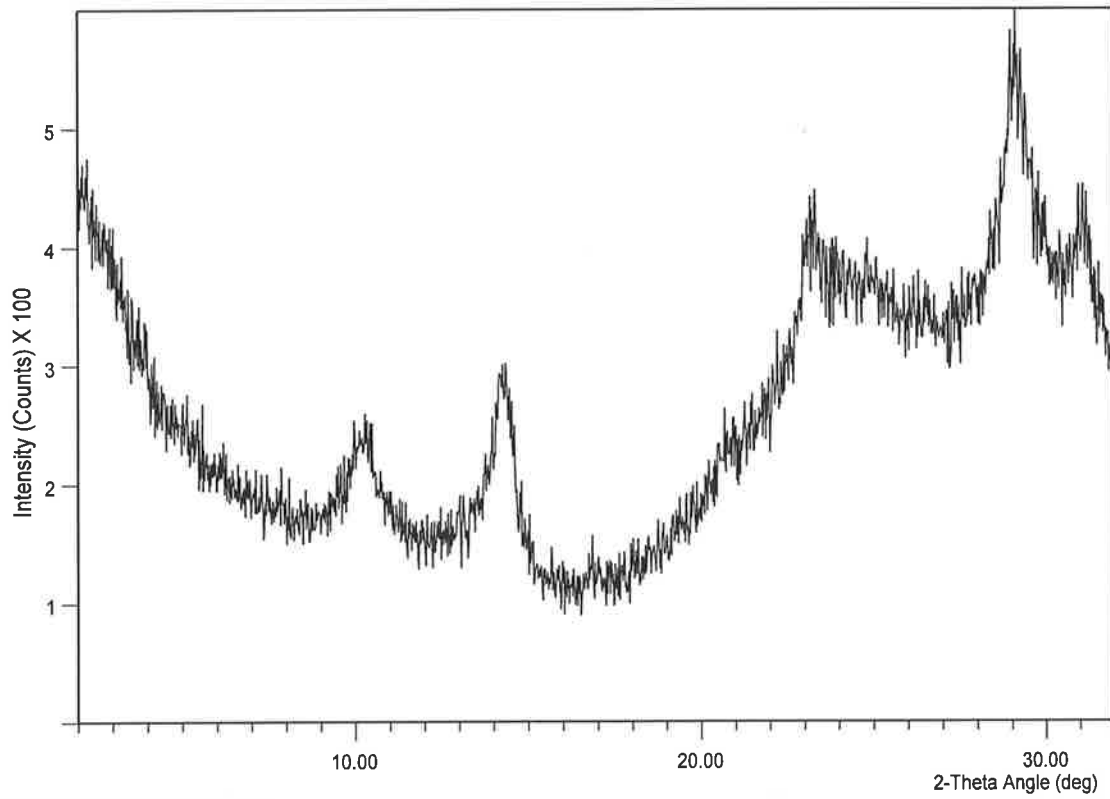
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Belalie whole clay



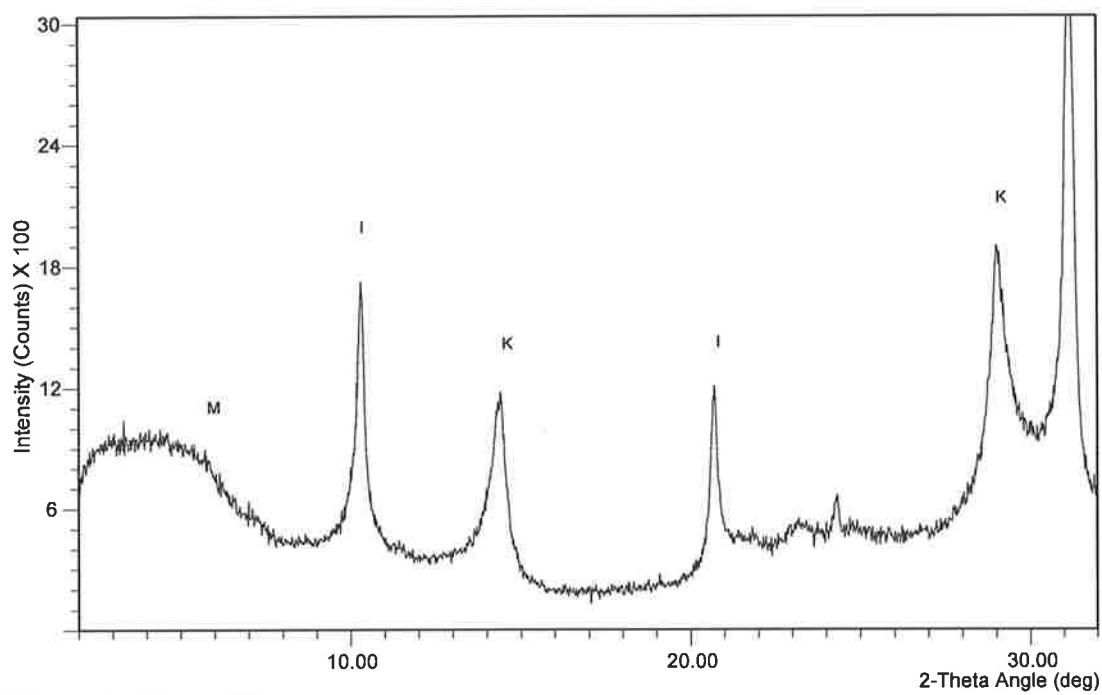
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Belalie fine clay

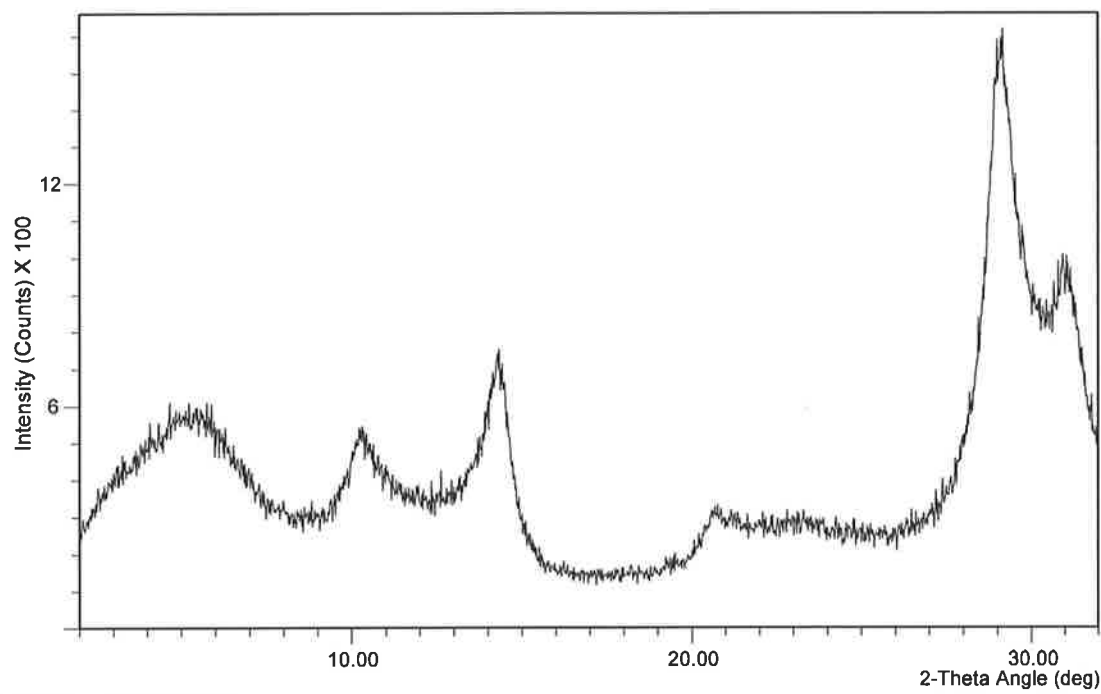


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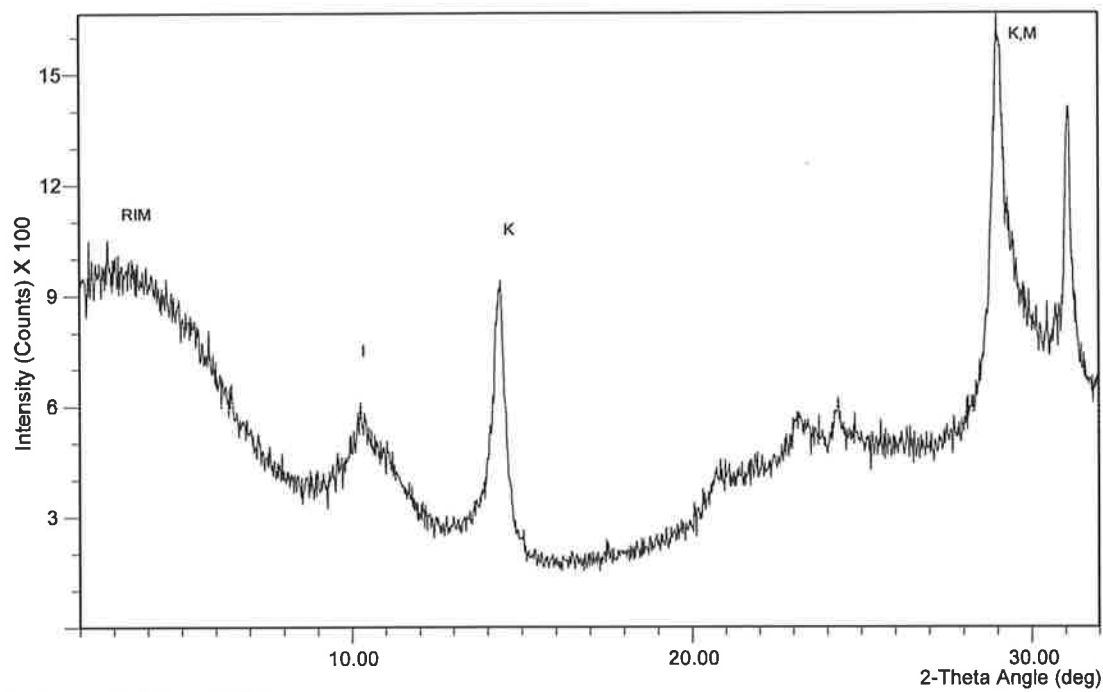
Tatura whole clay



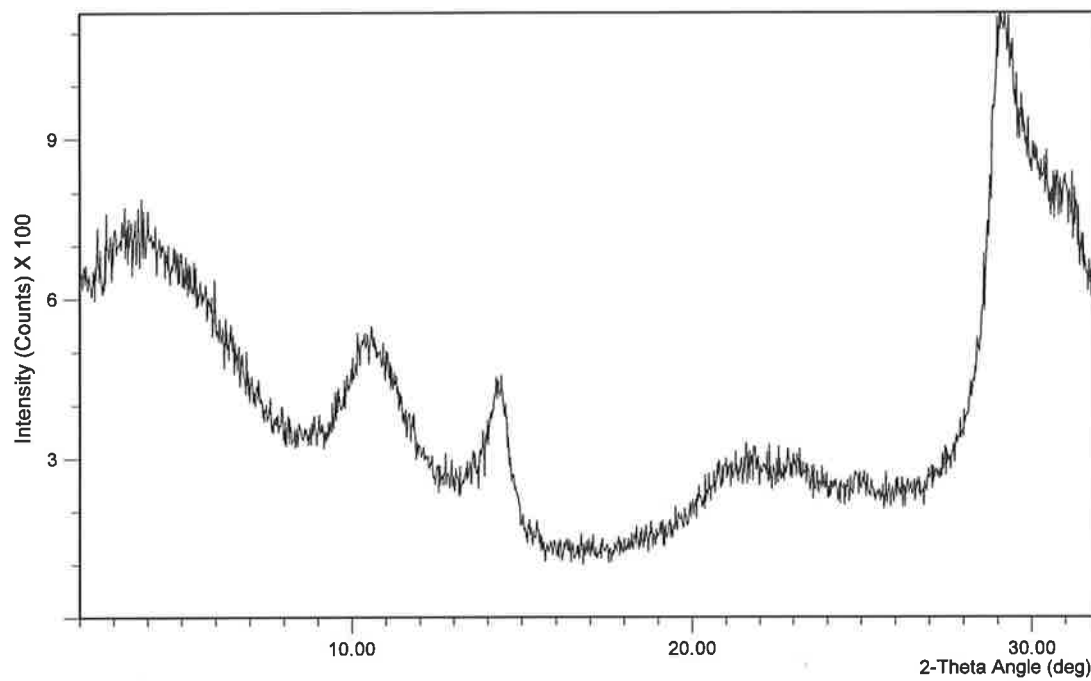
Tatura fine clay



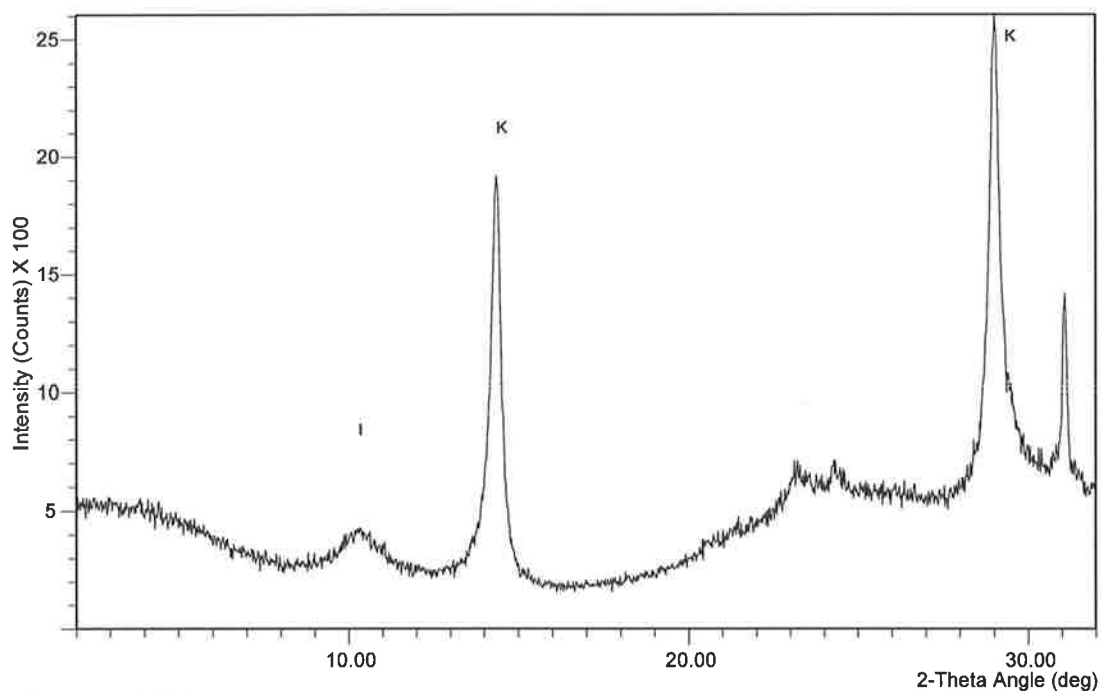
Bordertown whole clay



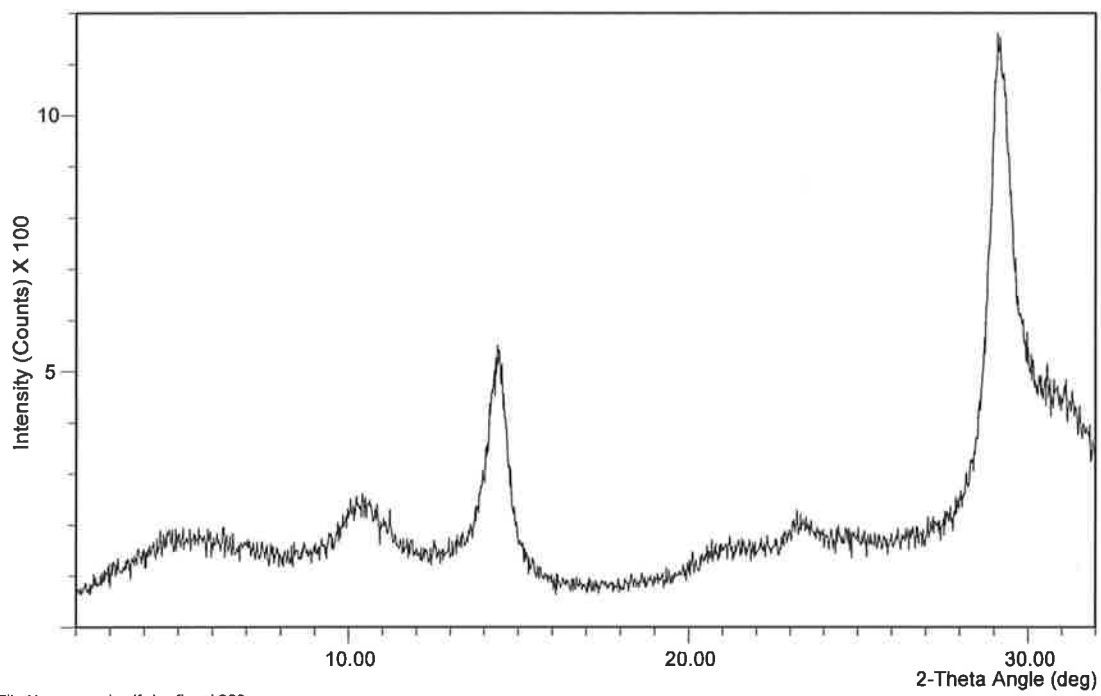
Bordertown fine clay



Mt Madden whole clay

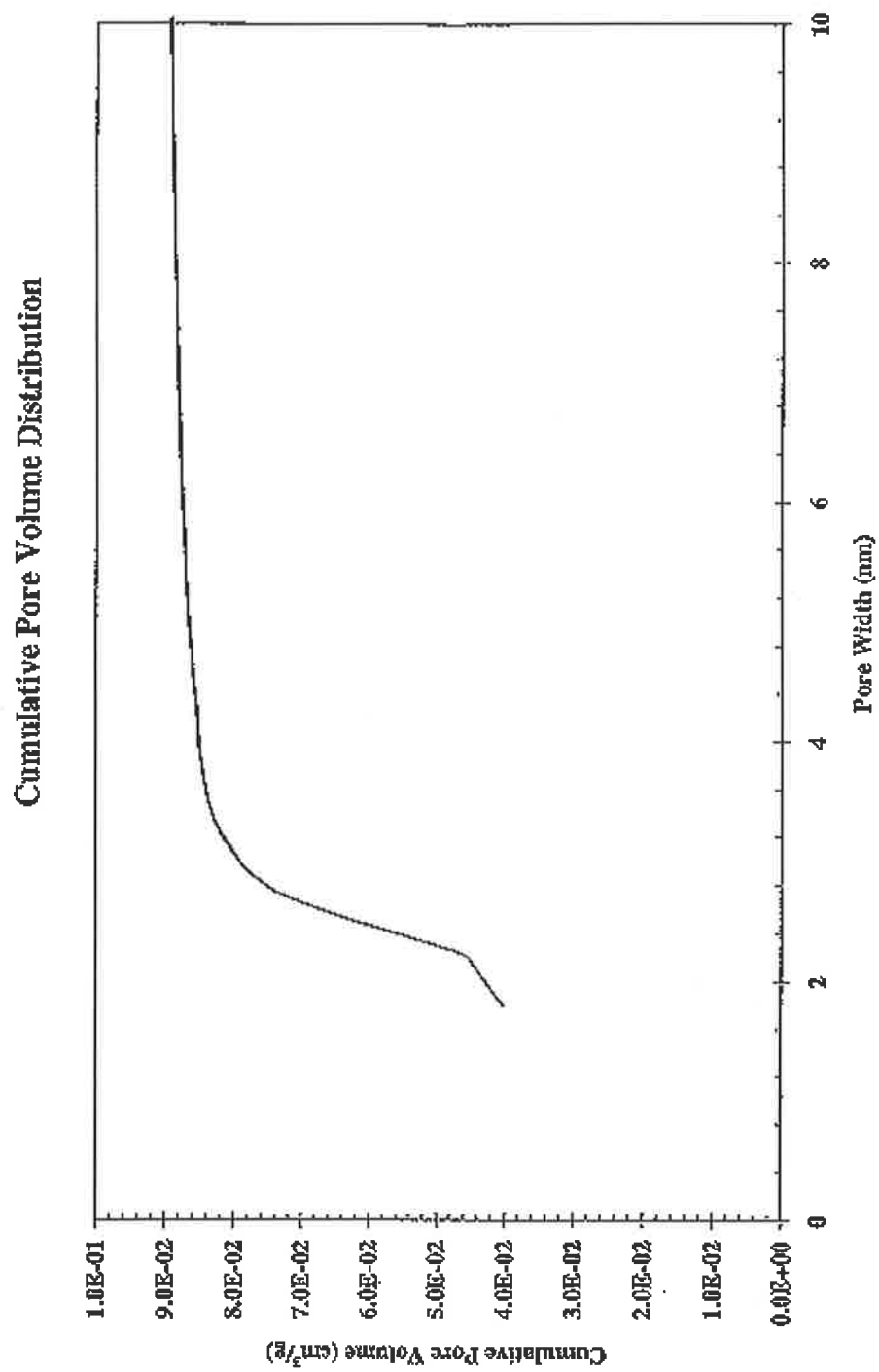


Mt Madden fine clay

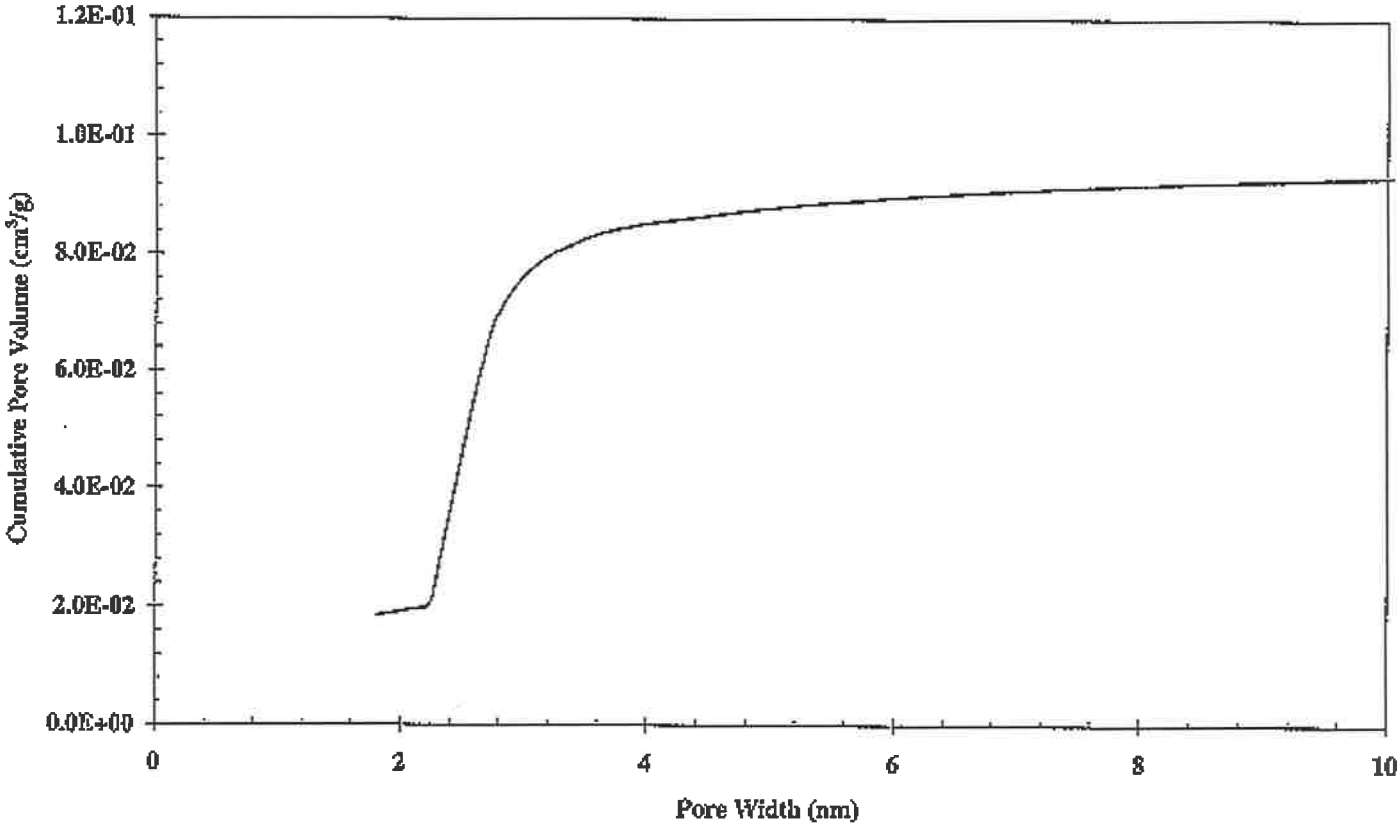


Appendix 2 Pore size distribution data of whole natural soil (1-2 mm aggregates) for the six soils characterised.

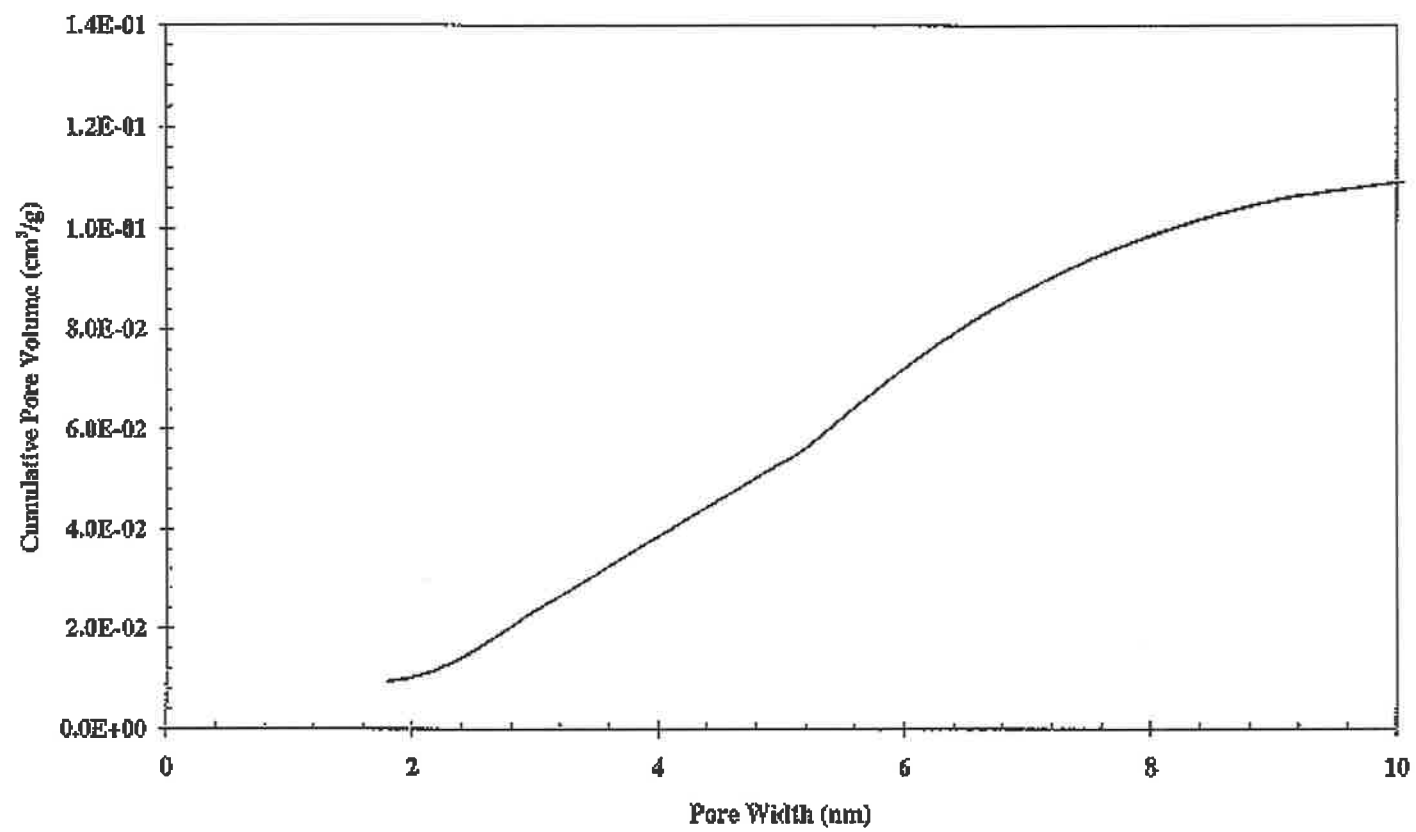
Wimmera



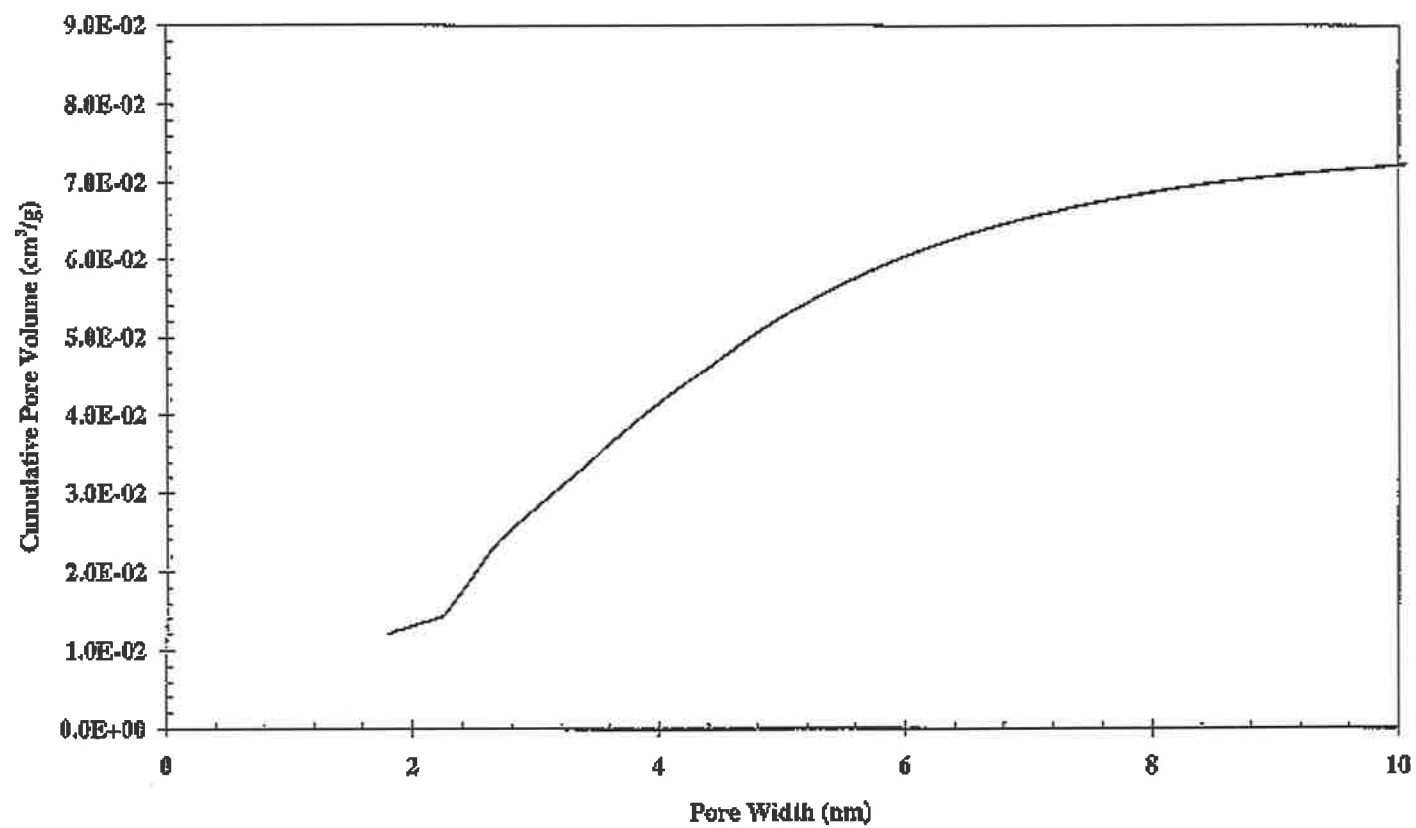
Cumulative Pore Volume Distribution



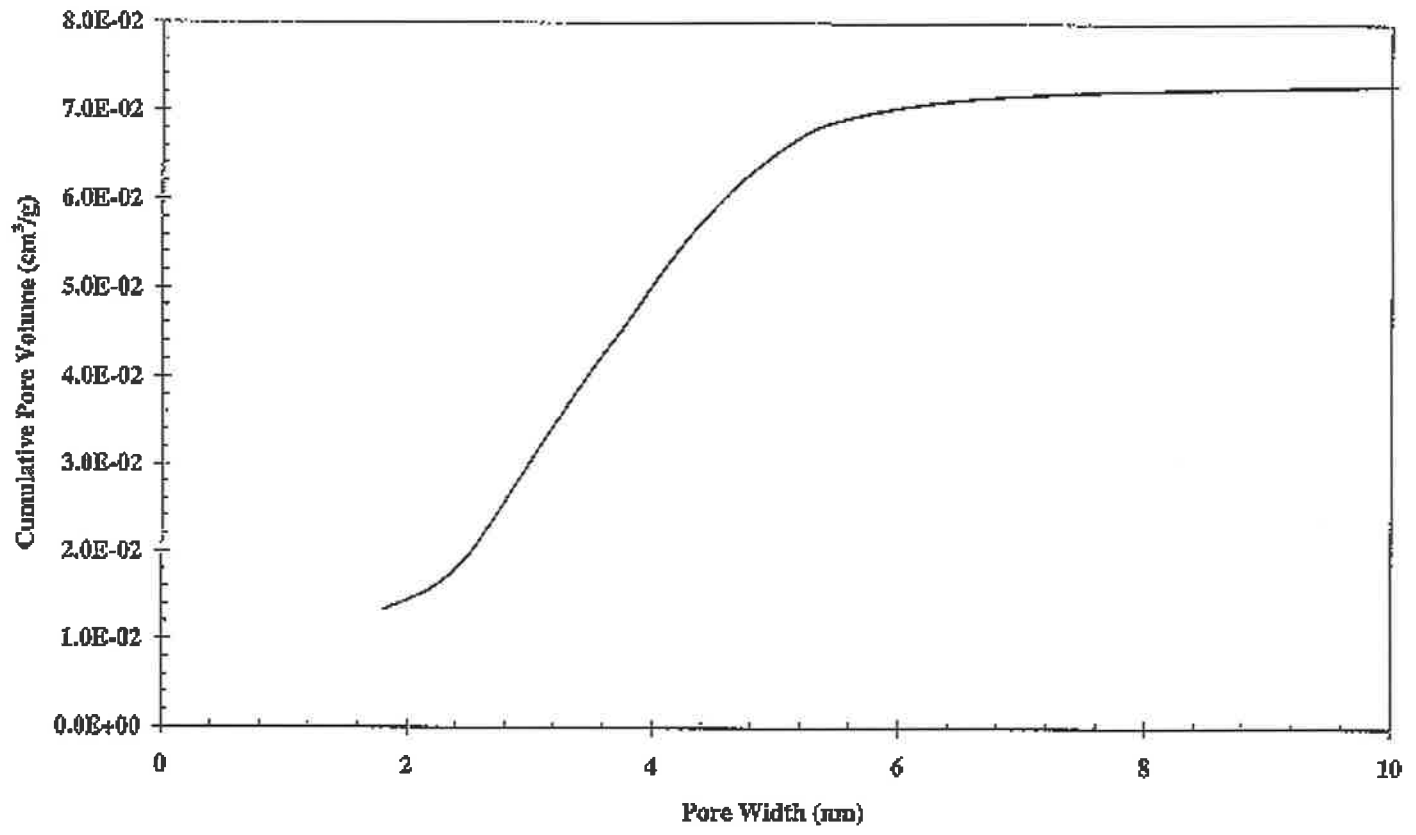
Cumulative Pore Volume Distribution



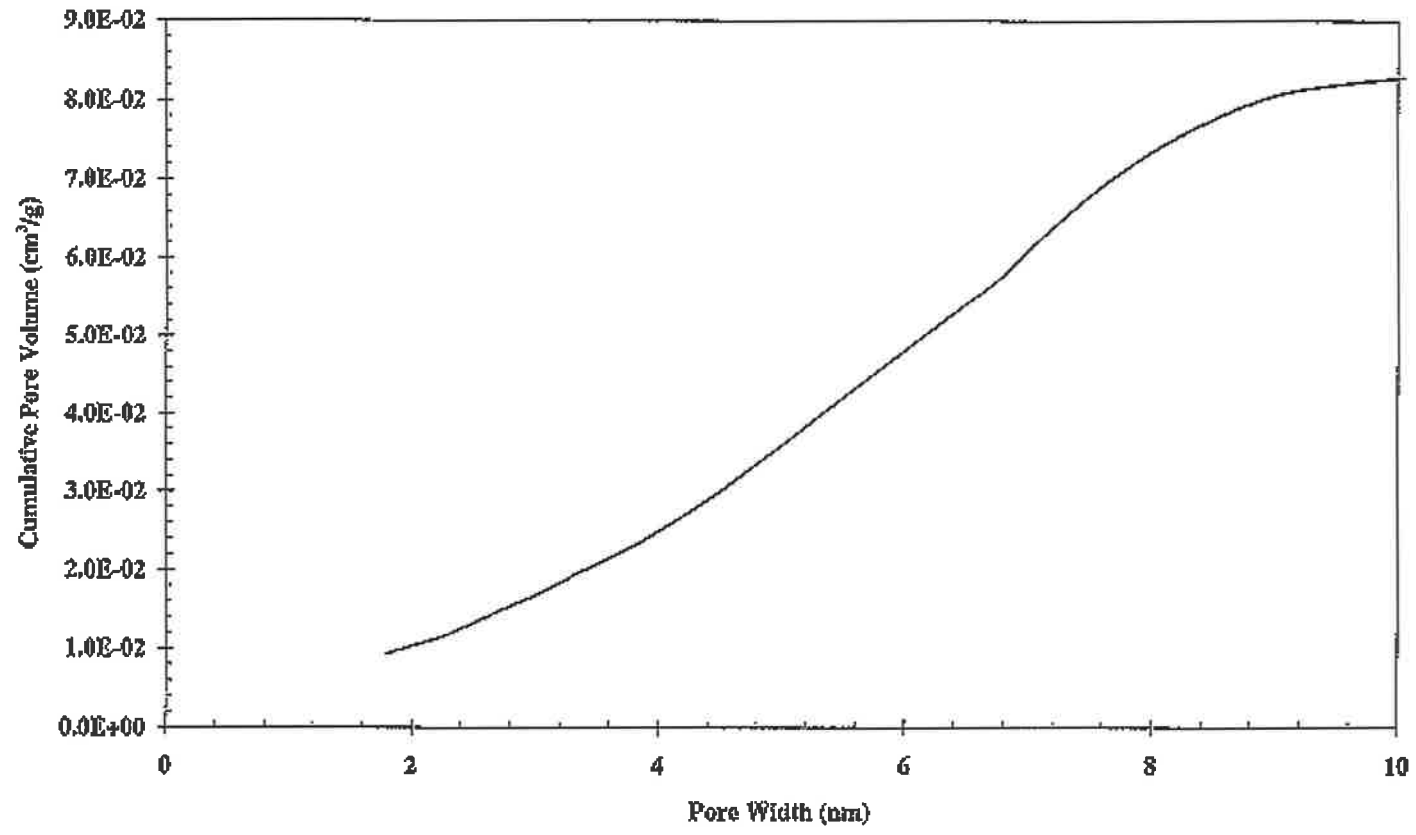
Cumulative Pore Volume Distribution



Cumulative Pore Volume Distribution

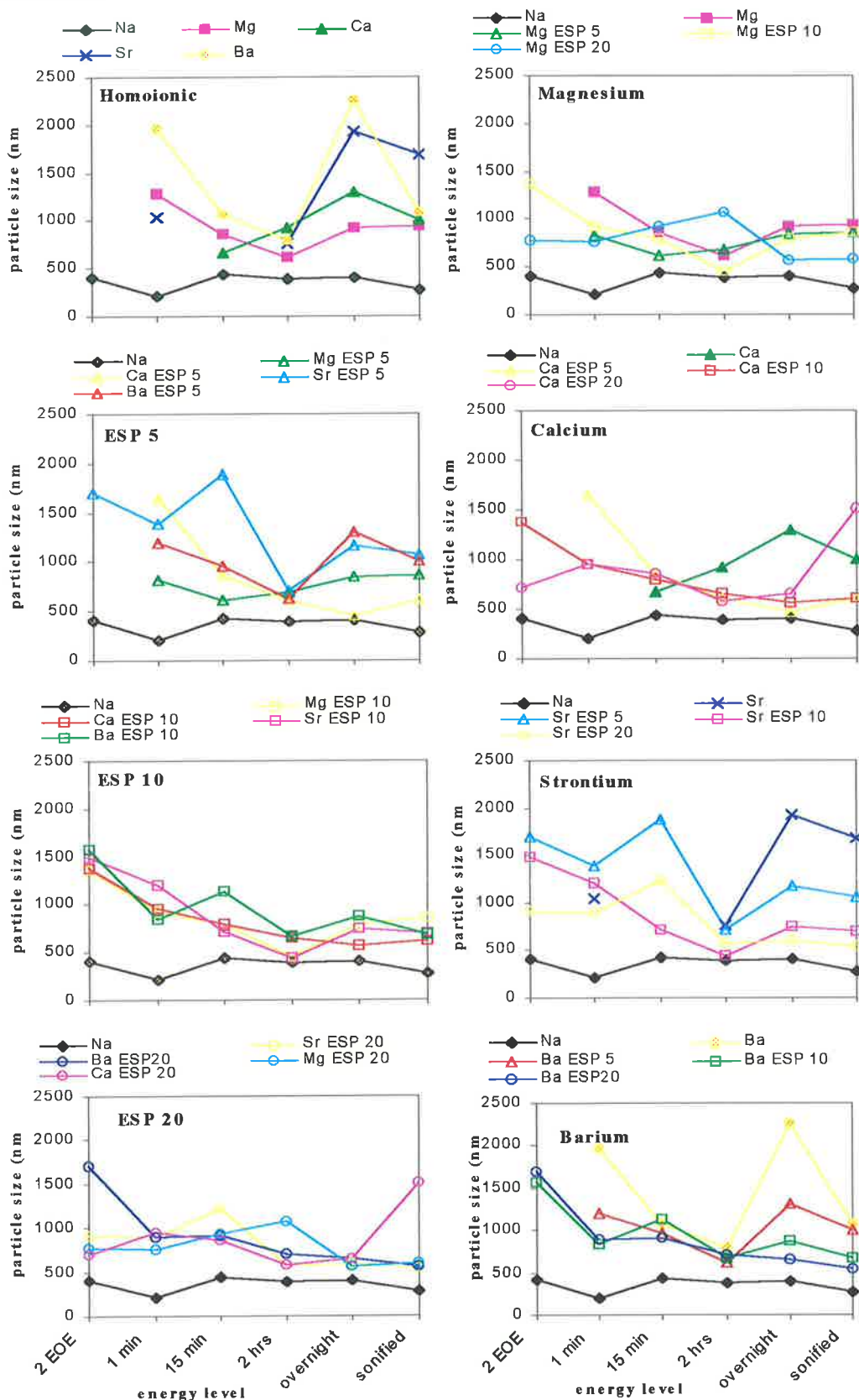


Cumulative Pore Volume Distribution

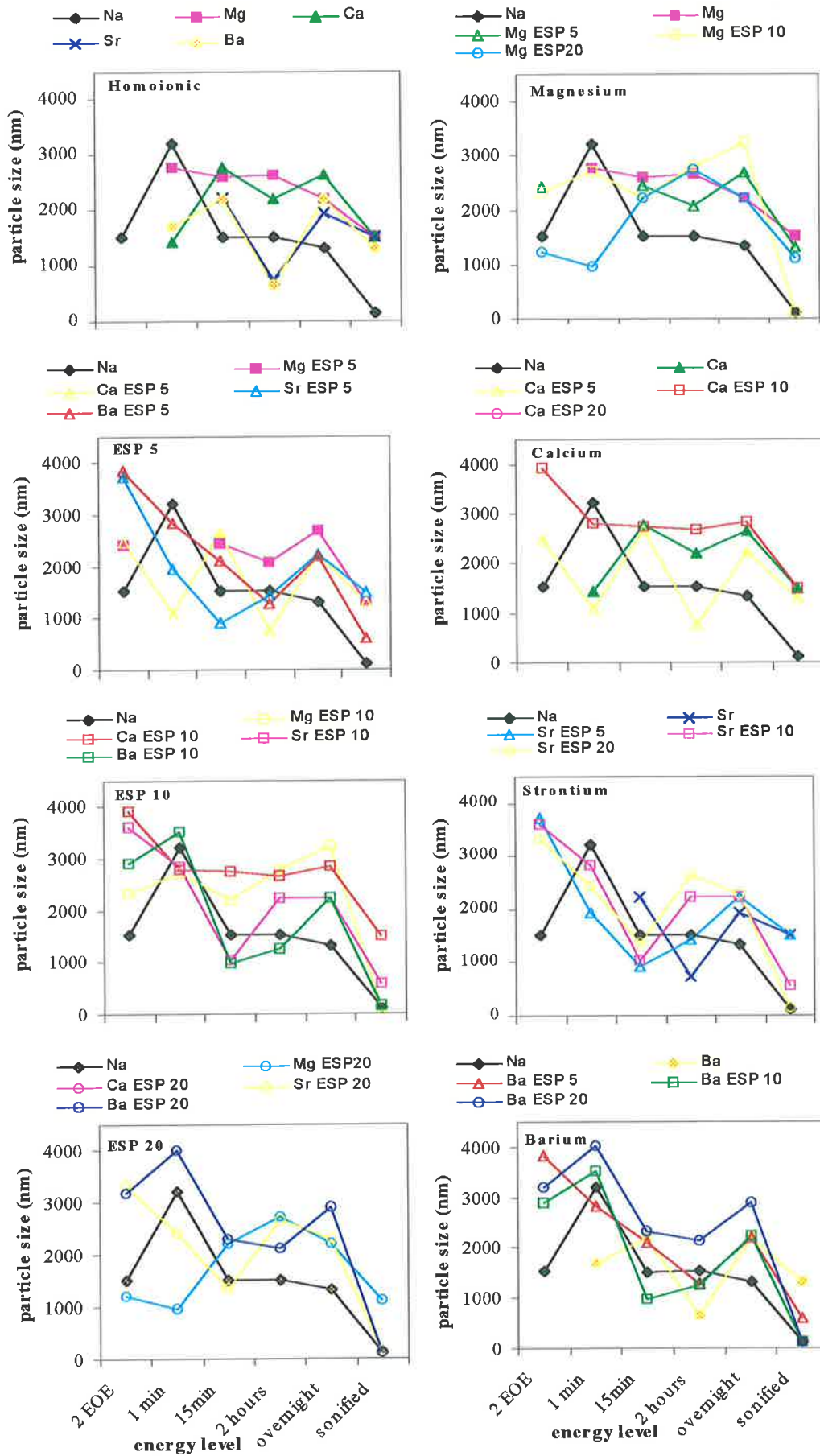


Appendix 3 Mean particle size distribution of dispersed clay from samples with various ESP values and the exchange complex completed from the group II cations.

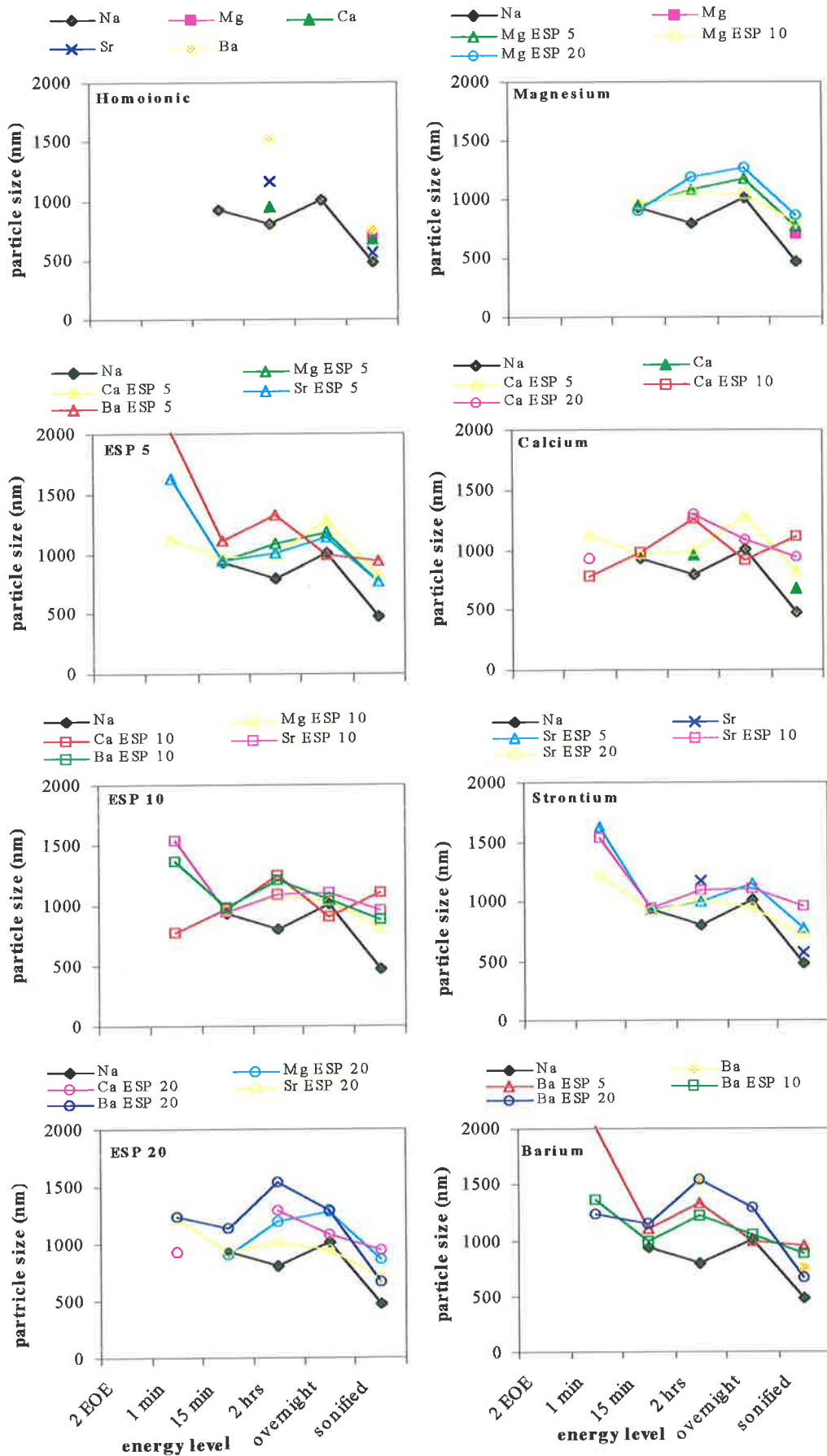
Wimmera



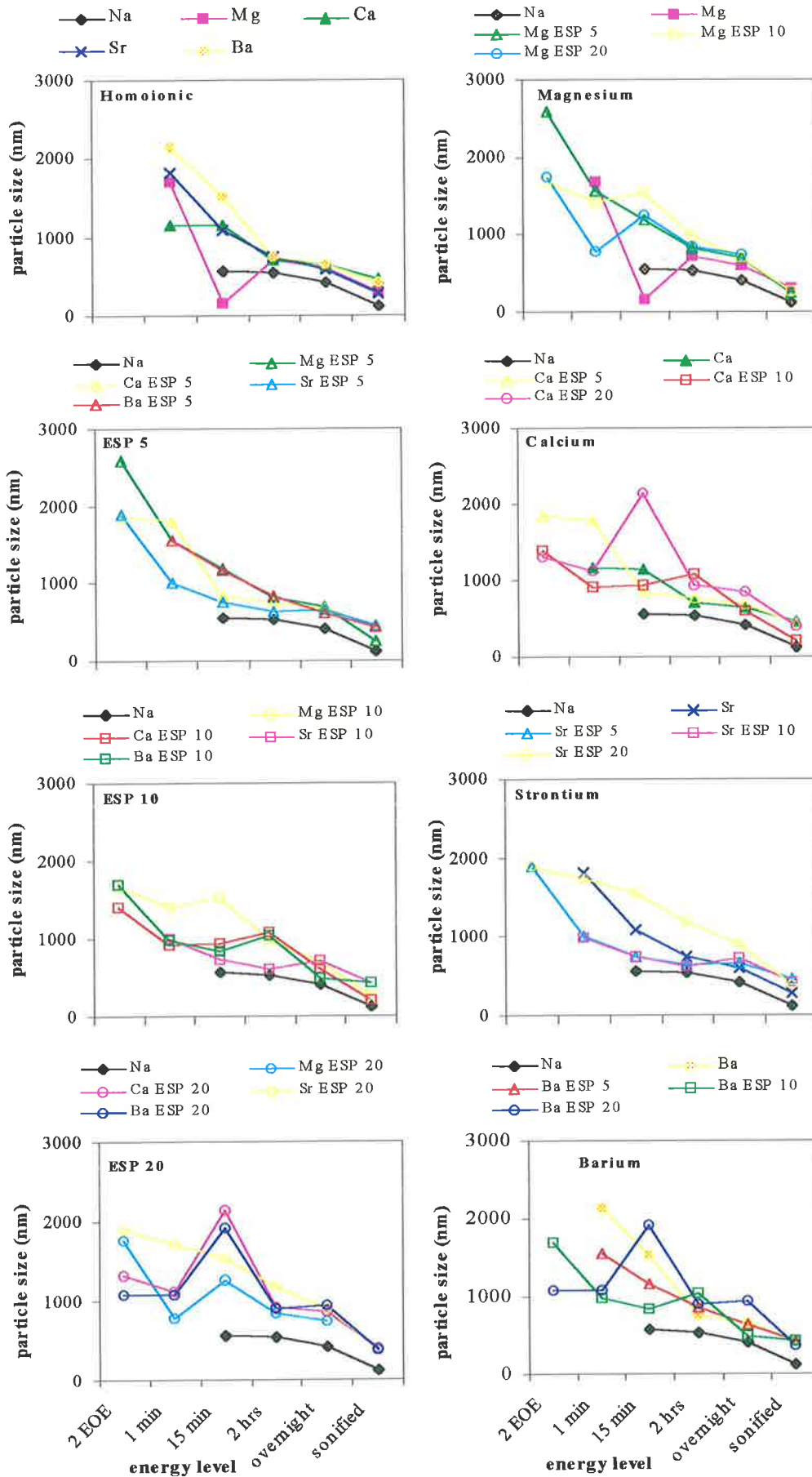
Tomki



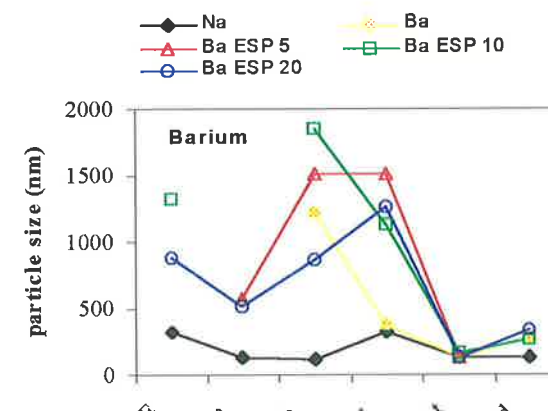
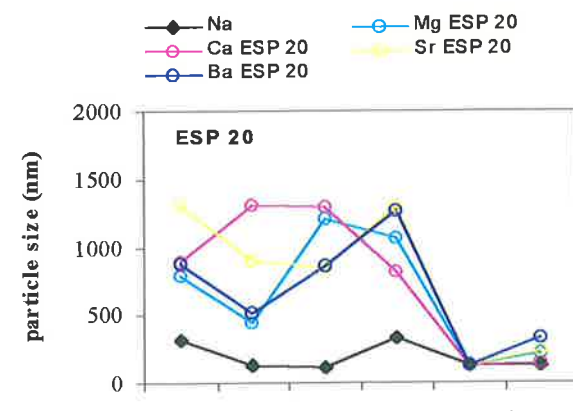
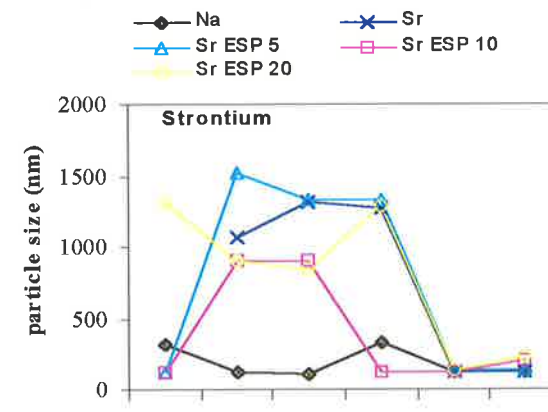
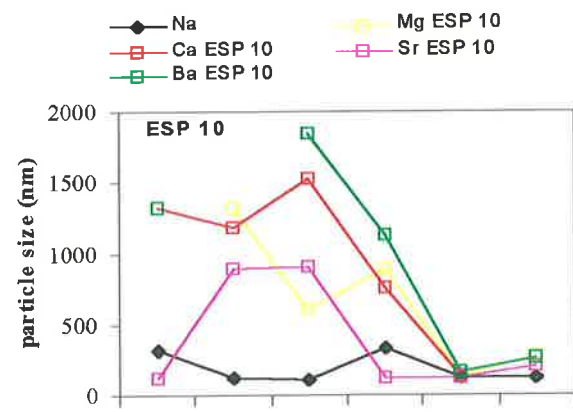
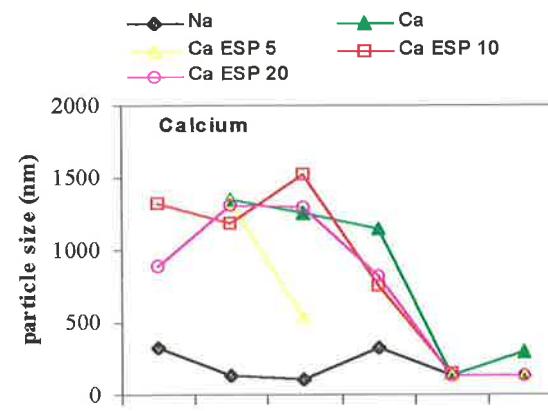
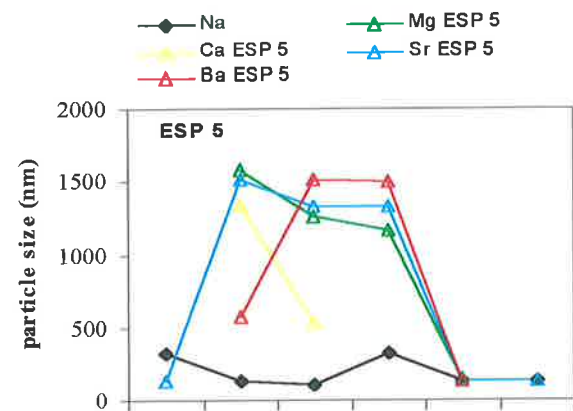
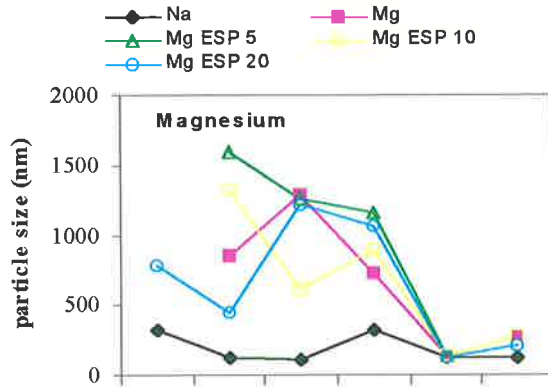
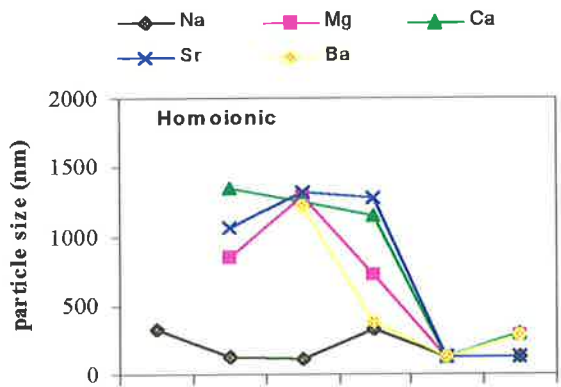
Belalie



Tatura



Bordertown

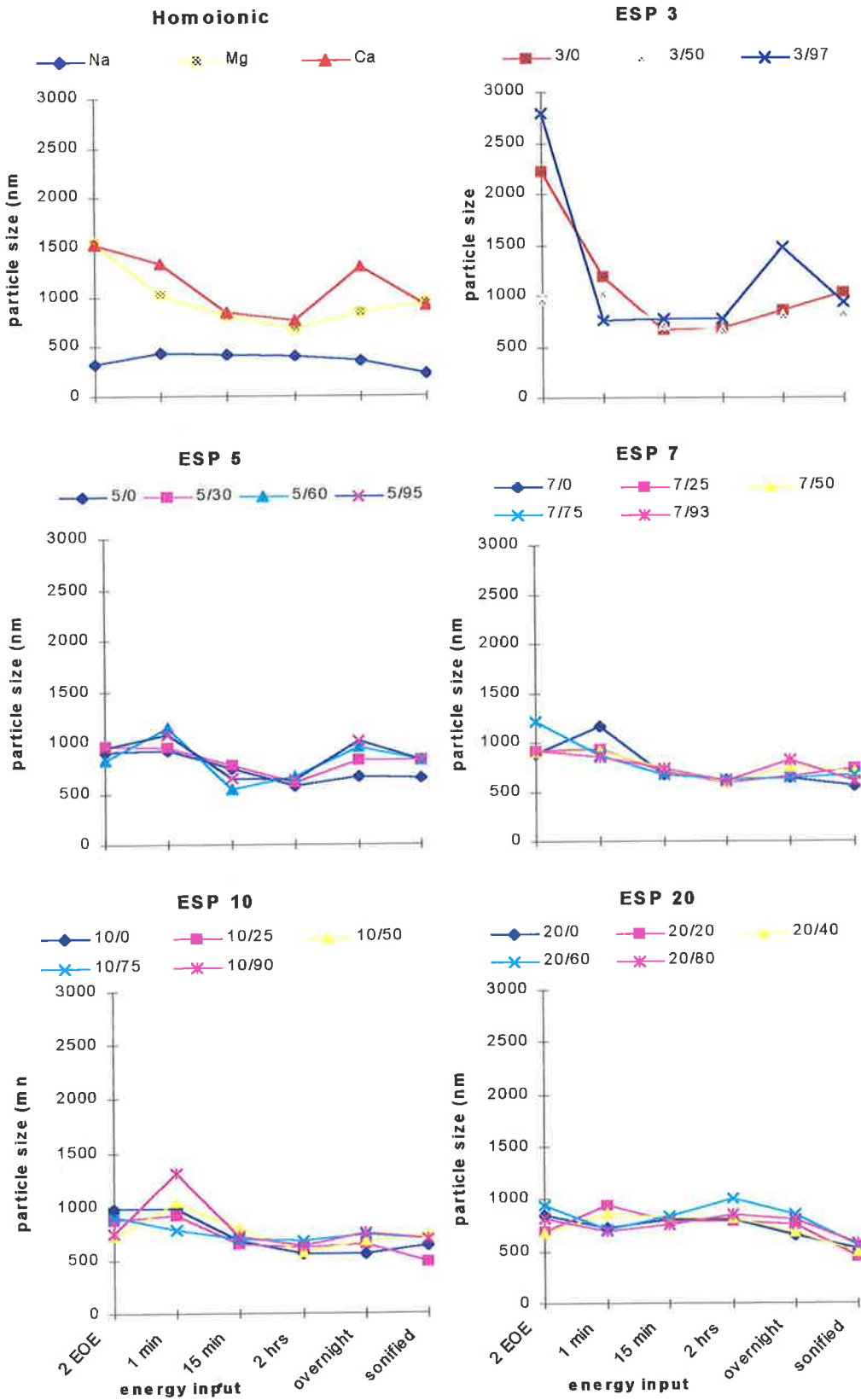


energy level

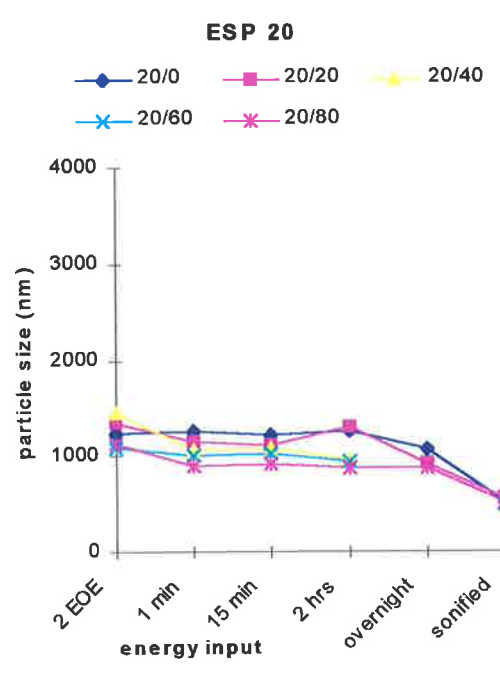
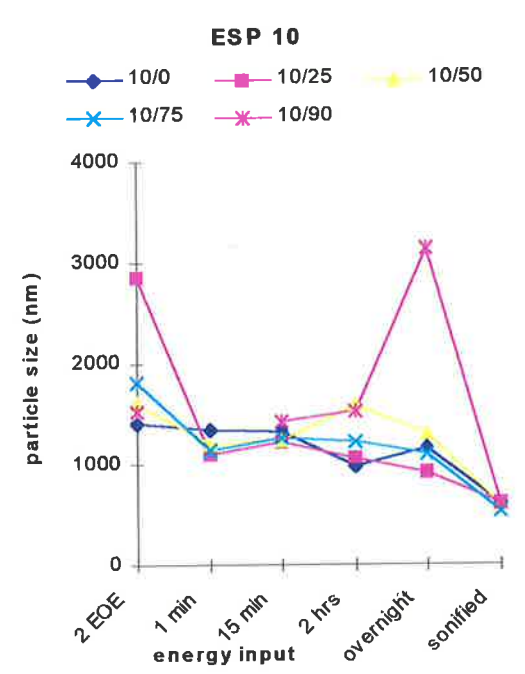
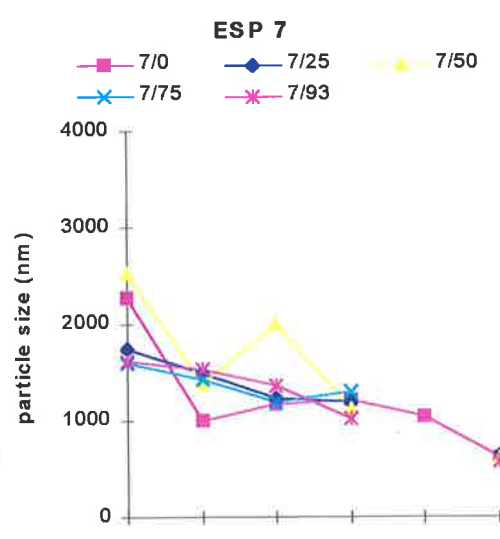
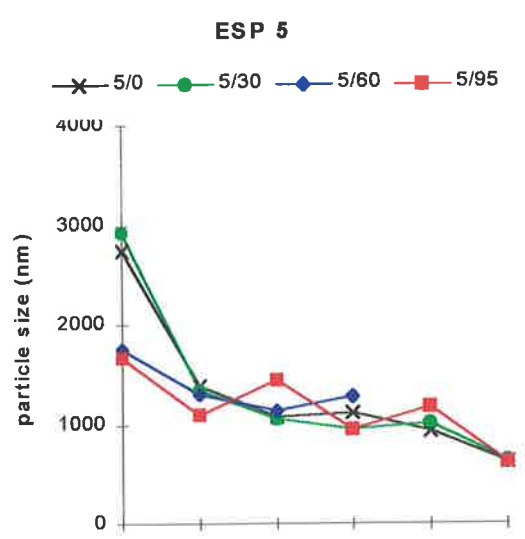
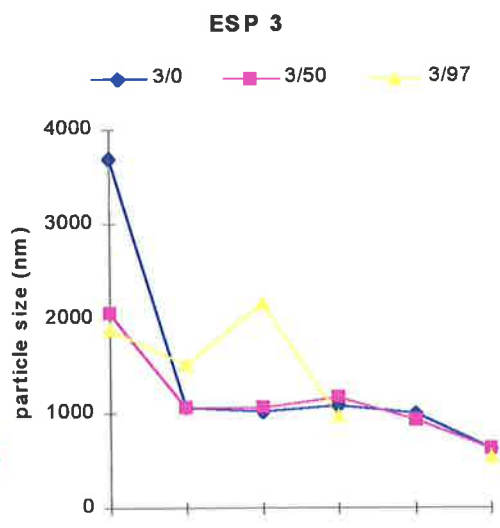
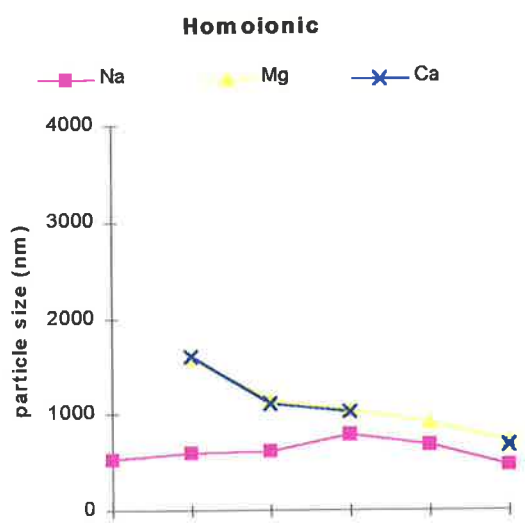
energy level

Appendix 4 Mean particle size of clay dispersed from treatments with different calcium:magnesium ratios and ESP values.

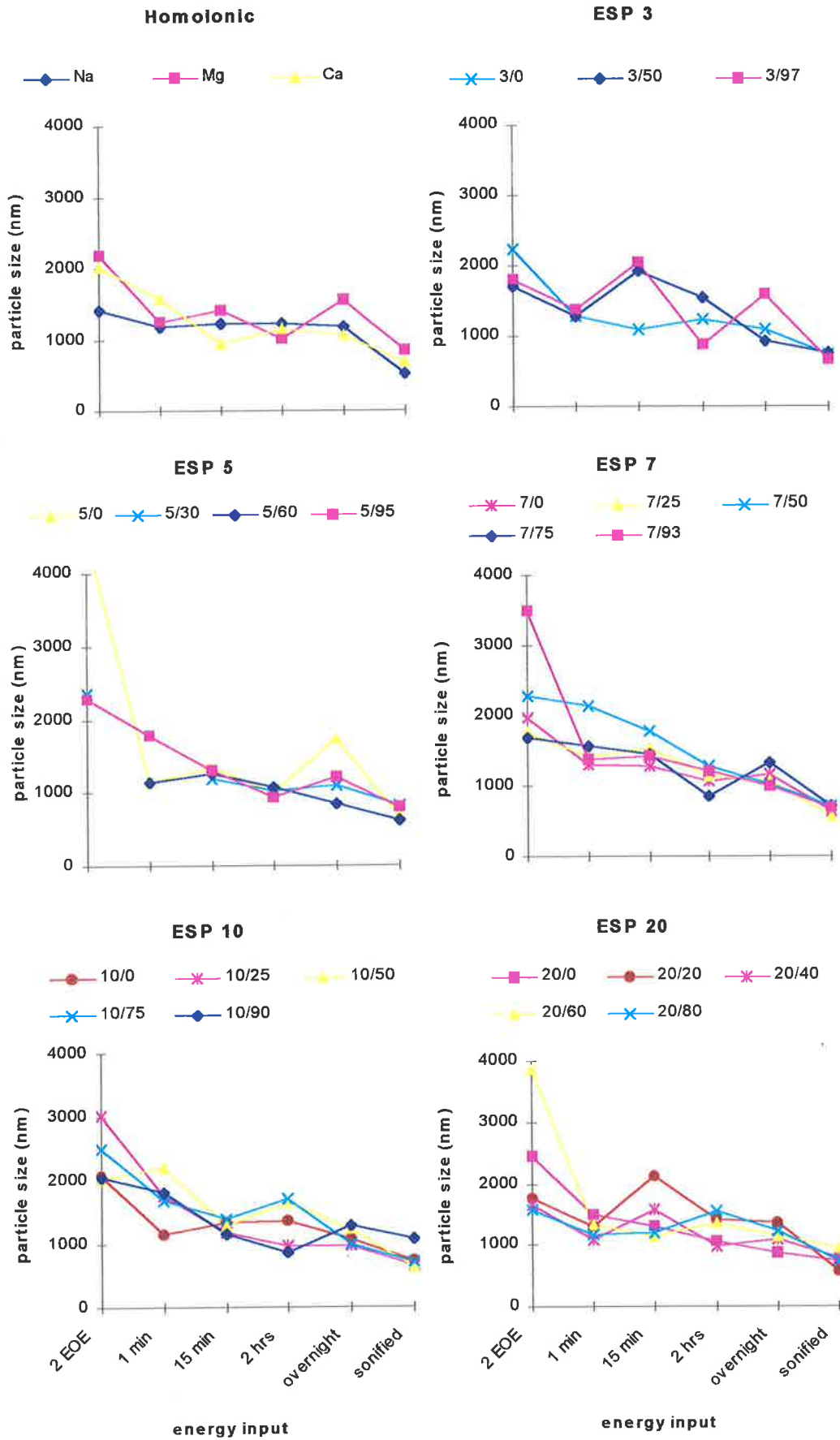
Wimmera



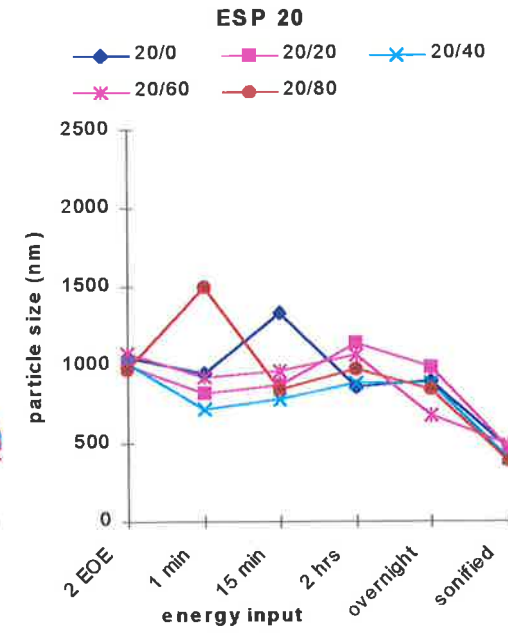
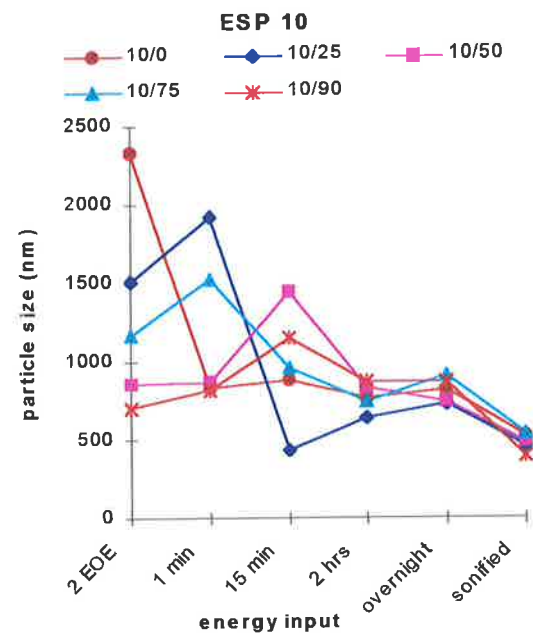
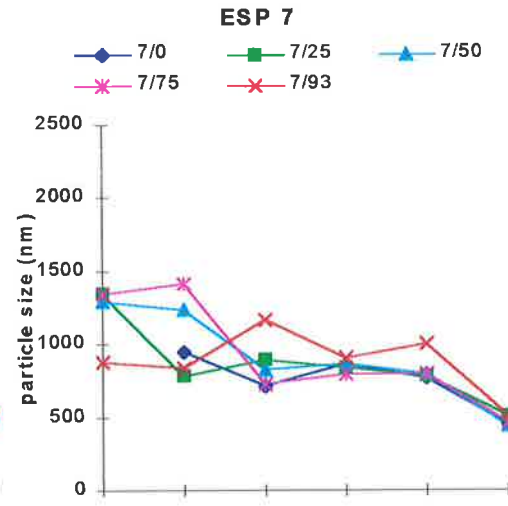
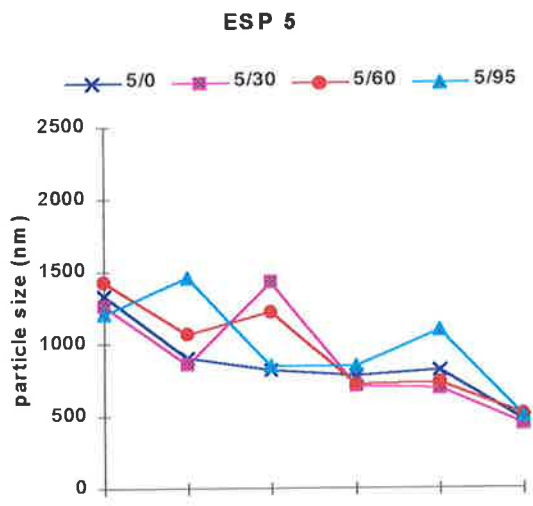
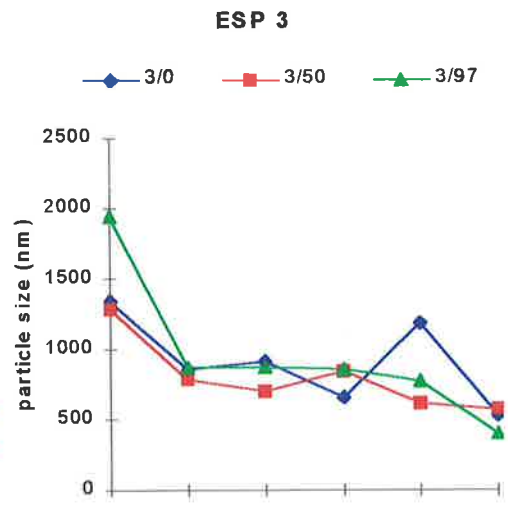
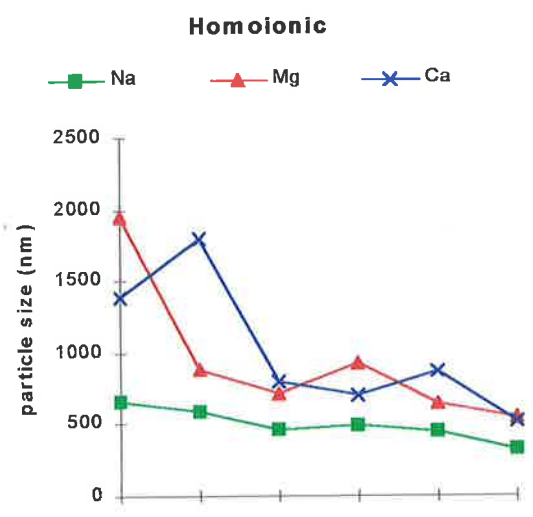
Tomki



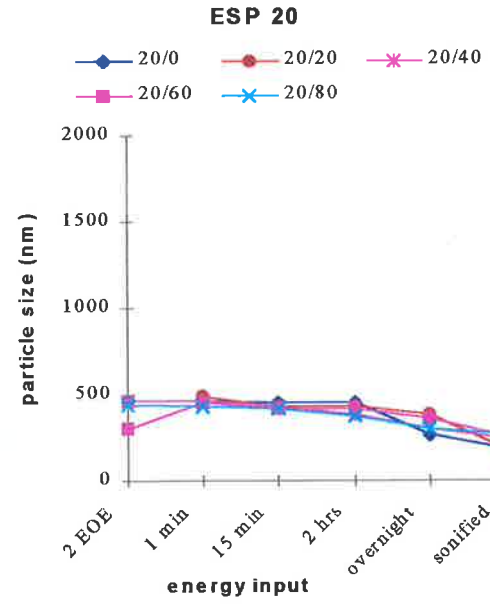
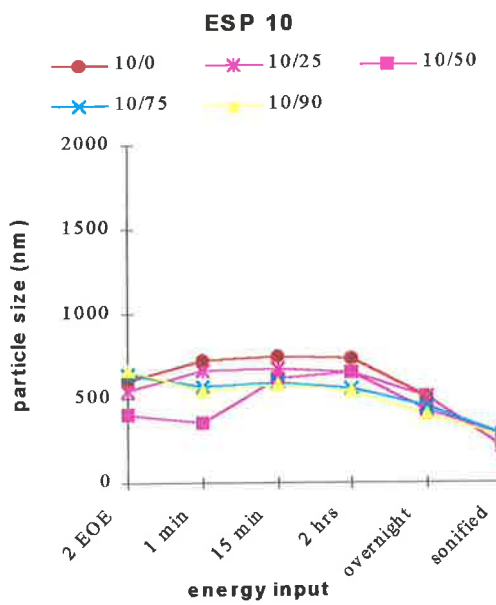
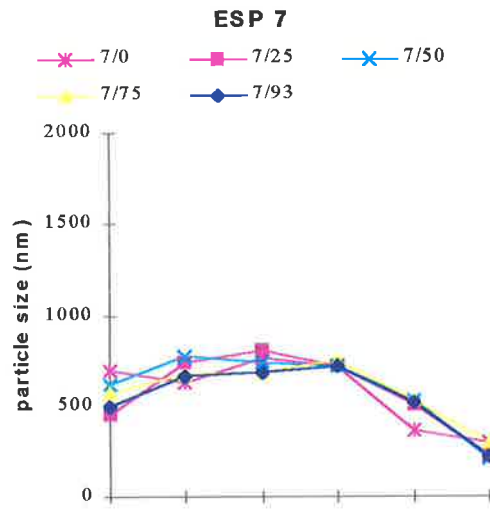
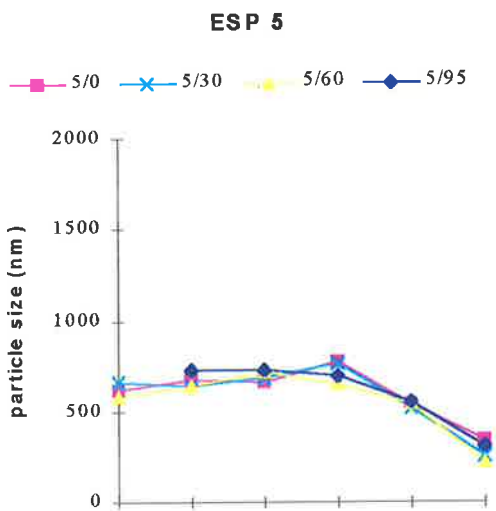
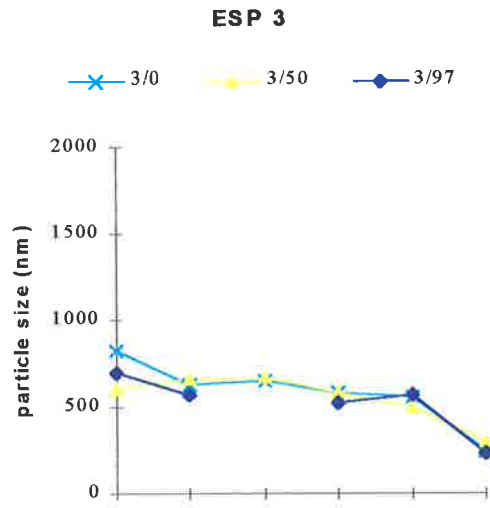
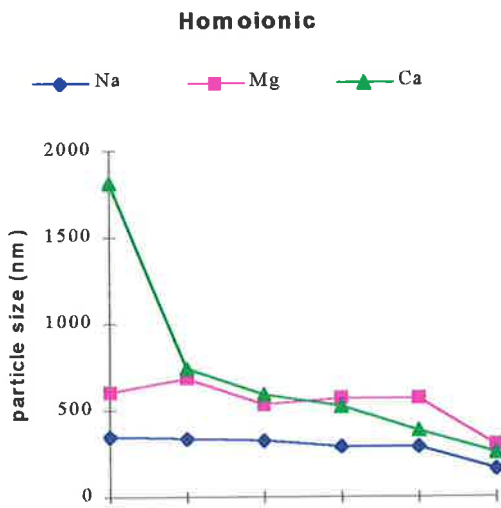
Belalie



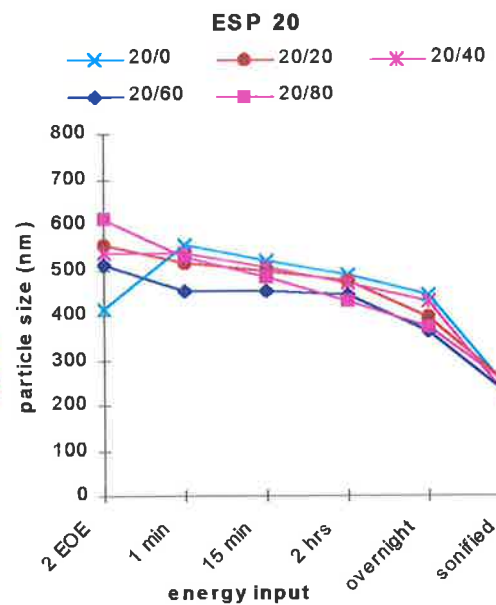
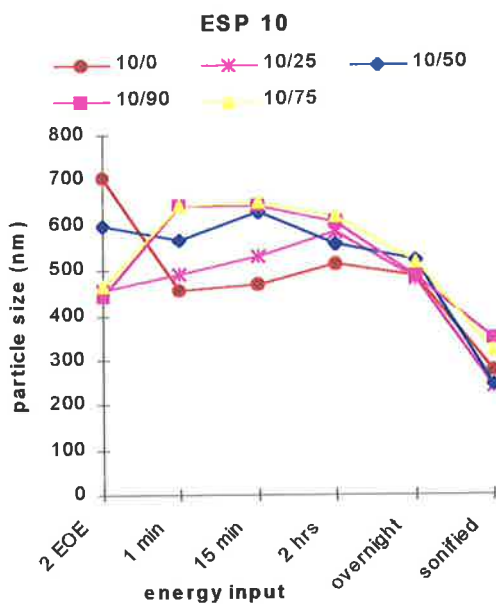
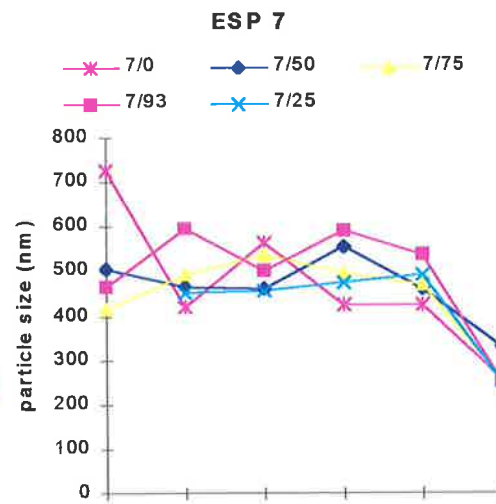
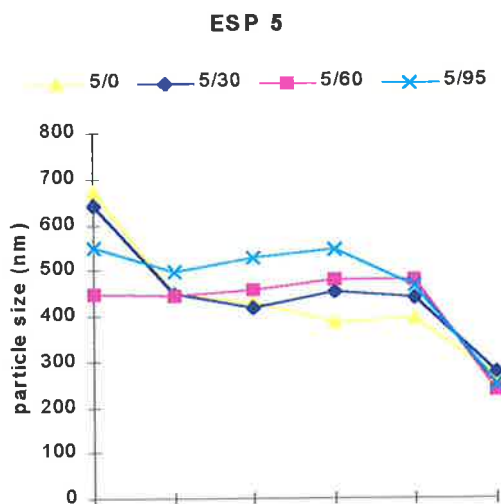
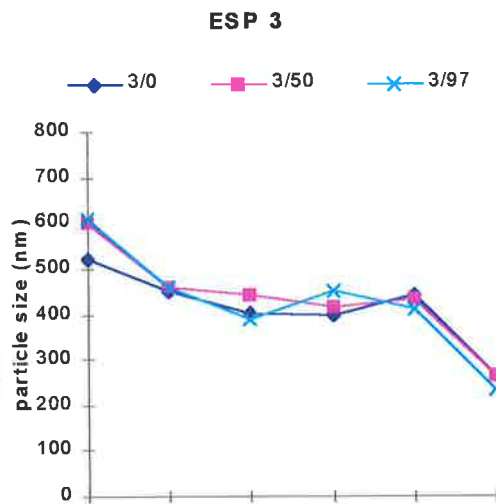
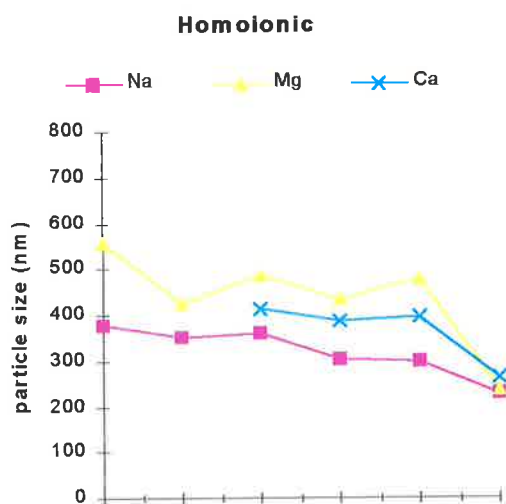
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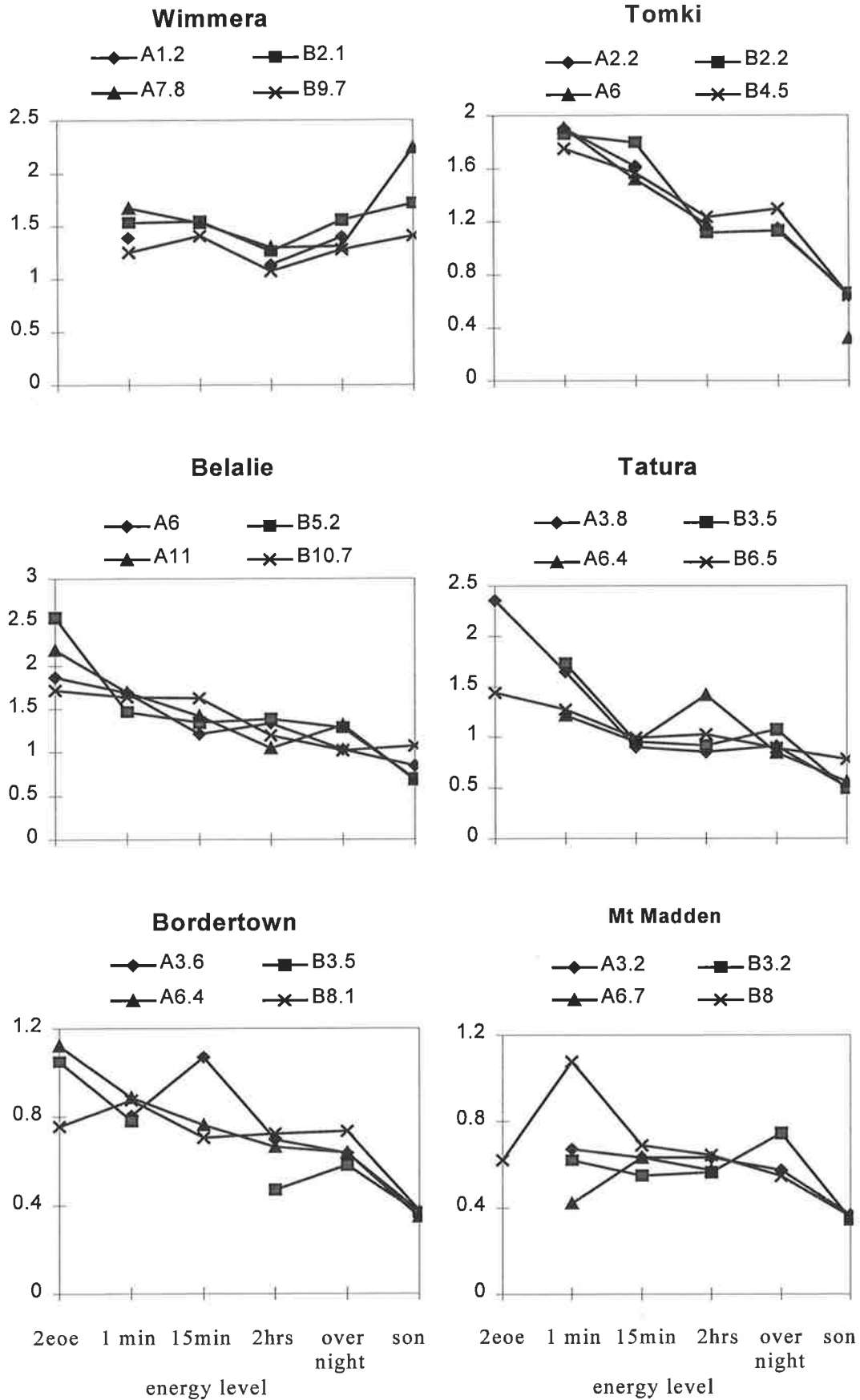
Mt Madden



Appendix 5 Zeta potential measurements of dispersed soil samples calcium or magnesium dominated and with various ESP values.

Soil	ESP	Sodium (mV)			Magnesium (mV)			Calcium (mV)		
		pH 5	pH 6.5	pH 8	pH 5	pH 6.5	pH 8	pH 5	pH 6.5	pH 8
WIMMERA	0				-21	-18	-19	-21	-19	-22
	3				-20	-20	-20	-21	-19	-16
	5				-21	-19	-18	-16	-20	-13
	7				-18	-20	-17	-18	-20	-16
	10				-17	-21	-16	-22	-21	-14
	20				-18	-23	-17	-21	-24.5	-16
	100	-36	-40	-37.5						
TOMKI	0				-26	-27	-26	-26	-27	-32.5
	3				-26	-27	-26	-28	-28	-28
	5				-26	-26	-27	-27	-28	-26
	7				-26	-32	-25	-26	-26	-27
	10				-29	-36	-24	-27	-31	-28
	20				-31	-35	-30	-27	-29	-29
	100	-42	-38	-45						
BELALIE	0				-33	-36	-24	-34	-35.5	-36
	3				-33	-35	-32	-33	-36.5	-36
	5				-32	-37	-30	-32	-36	-35
	7				-31	-35	-26	-33	-36	-33.5
	10				-32	-37	-29	-31	-34	-34
	20				-30.5	-34	-28	-30.5	-35	-34
	100	-35	-39	-40.5						
TATURA	0				-29	-30	-20	-28	-28	-24
	3				-28	-28	-18	-28	-27	-24
	5				-28	-27	-16	-28	-28	-21
	7				-28	-27.5	-19	-27	-28	-20.5
	10				-29	-29	-18	-27	-28	-23
	20				-30	-34	-24	-31	-34	-23
	100	-37	-38	-41						
BORDER-TOWN	0				-32	-35	-25	-30	-32	-27
	3				-30	-33	-22	-29.5	-32	-26
	5				-28	-35	-22	-29	-33	-27
	7				-33	-35	-27	-30	-33	-28
	10				-28	-40	-28	-30	-34	-30
	20				-31	-40	-27.5	-34.5	-41	-32
	100	-41	-42	-47						
MT MADDEN	0				-31	-36	-32	-31	-31	-34
	3				-34	-33	-28	-31	-30	-31
	5				-35	-33	-28	-31	-32	-35
	7				-28	-38	-32	-28	-36	-34
	10				-31	-34	-36	-34.5	-37	-31
	20				31	-39	-35	-34	-40	-39.5
	100	-43	-44	-51						

Appendix 6 Mean particle size measurements of dispersed clay from replicate “natural” aggregate samples prepared with minimal disturbance to aggregate structure.



Appendix 7 Comparison of mean particle sizes of dispersed clay samples prepared by remoulding (“synthetic”) and with minimal disturbance (“natural”) to aggregate structure.

