5. FIELD STUDY TO ASSESS SEASONAL INFLUENCES ON SOIL pH, NITRATE AND AMMONIUM

5.1 Introduction

Long-term effects of pasture management on soil acidification, for a range of soils across the NSW Northern Tablelands, were assessed in the paired-sites survey (Chapter 4). The issue of seasonal variation of soil parameters was raised in the discussion of that study. As the paired-sites study captured data at one time only, it did not provide information about the short-term and seasonal changes in the soil chemical properties of managed pastures. Thus the field study described in this chapter was developed to monitor volatile soil chemical properties that relate to soil acidification: soil pH, ammonium and nitrate. Drought effects on the nitrogen cycle were also considered.

A series of sites was set up at *Newholme* Research Station, a University of New England (UNE) property just north of Armidale. Sampling was undertaken every four weeks at these sites. The experiment ran for fourteen months, from May 2002 to May 2003, during weather that was atypical to predictions based on long-term climate averages. A repeated-measures analysis was carried out to determine the influence of rainfall and temperature on soil pH, electrical conductivity, nitrate-N and ammonium-N over the seasons of a year.

5.1.1 Background

Soil acidification processes in relation to grazing land have been described previously in Section 2.4. Generally, the production of organic acids from a buildup of soil organic matter, nitrification of ammonium fertilizers, loss of nitrate produced by nitrification in leaching or runoff, and export of organic anions with product removal are the principal soil acidification processes under exotic, fertilized pasture (Helyar and Porter 1989). Nitrate leaching is a major soil acidifying process in parts of southern NSW and northern Victoria (Helyar and Porter 1989). In the temperate climate of that area, the nitrate pool builds up during the dry, warm months and before it can be used by plants, it is leached by winter rain.

On the Northern Tablelands of NSW, also with a temperate climate, rainfall generally prevails in spring and summer. It is the timing of this rainfall when pasture plants are actively growing that suggests nitrogen recycling (Crocker and Holford 1991). As the paired-sites study provided results at only one point in time, more information was needed on nitrate leaching and nitrate uptake by plants to assess the nitrification process further.

5.1.2 Objectives

- To assess the effects of rainfall and temperature on soil chemical properties relating to soil acidification.
- To gain an insight into temporal variations of soil chemical properties.
- To seek evidence of soil acidification processes, such as nitrate leaching, if they existed.

Acidification processes, in particular nitrogen cycling, were reviewed in relation to the objectives and the field trial was developed. Site selection, the experimental design, soil sampling and analyses, weather records and statistical analyses are described in the next section. Results from the trial are then given. A discussion of the results completes the chapter.

5.2 Sites and Procedures

UNE's rural property, *Newholme* Research Station, was used for this exercise. As sampling took place every four weeks, the property was ideal for travel logistics as it was only 30 km north of the university. In addition, *Newholme* offered a variety of sampling locations by way of paddocks with different management regimes, and detailed management records. Five paddocks, each differently managed, were selected for sampling (Figure 5.1). Variations in soil chemical properties within each site were statistically analysed. Between-site variation was considered, but lack of duplication between paddock management types meant this could not be statistically tested.

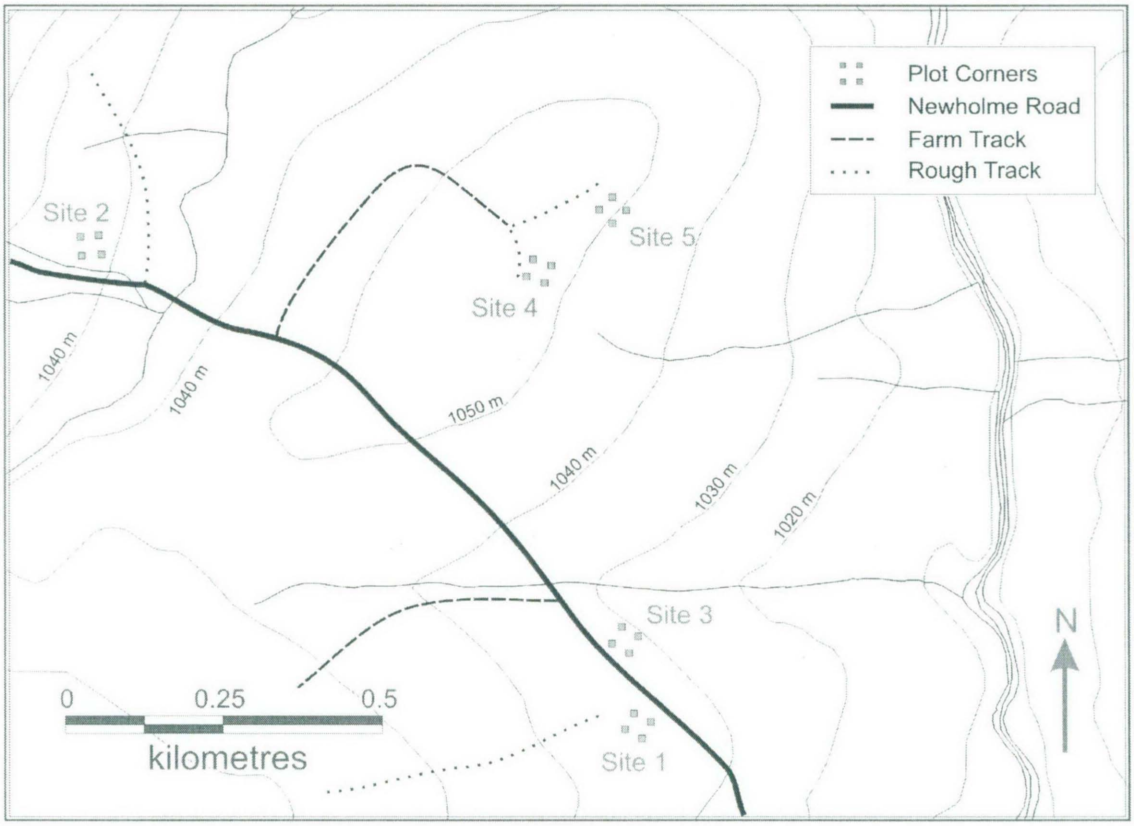

Figure 5.1 Site map and plot locations at *Newholme*.

Earlier field studies, which assessed measurements over time were reviewed for this study some of which will be critiqued in the discussion (Section 5.4). These included Coleman *et al.* (1974), Smith and Johns (1975), Smith and Stephens (1976), Friesen *et al.* (1985) and Chen *et al.* (1999) in the Northern Tablelands region, and Slattery and Ronnfeldt (1992) and Conyers *et al.* (1997) in other areas. The study reported here was developed for the sites and specific objectives and was not modelled on any previous study.

5.2.1 Selection and Description of Sites

Five sites were selected for their different land management attributes (Table 5.1), similar landscapes and accessibility. A full management history was obtained for each paddock.

Table 5.1 Summary of paddock management of *Newholme* sites since 1963

Site No.	Amendment	Groundcover	Grazed
1	superphosphate at 125 kg / ha plus other high analysis fertilizers every second year since 2000	exotic pasture of Demeter fescue, ryegrass, cocksfoot and mixed clovers, plus rat's tail fescue (*Vulpia* sp.)	sheep and cattle
2	superphosphate at 125 kg / ha on average, irregularly, every 5 years	native pasture of slender rat's tail grass (*Sporobolus creber*), paddock lovegrass (*Eragrostis leptostachya*), hairy panic (*Panicum effusum*) and tussocky poa (*Poa sieberiana*)	sheep and cattle
3	nil	native pasture of slender rat's tail grass, hairy panic, purple wire grass (*Aristida ramosa*)	sheep and cattle
4	nil	native pasture of paddock love grass, slender rat's tail grass, hairly panic	not stocked [2]
5	nil	sparse[1] tree cover of yellow box (*Eucalyptus melliodora*), Blakely's red gum (*E. blakelyi*), groundcover of weeping rice grass (*Microlaena stipoides*), slender rat's tail grass	not stocked [2]

[1] Specht *et al.* (1974) in McDonald *et al.* (1990)

[2] Paddocks occasionally grazed by kangaroos

Within each paddock a plot, 30 m by 30 m, was marked out. McKenzie *et al.* (2000) recommended that a plot size be > 400 m^2, and the *Newholme* plots met these criteria. Plot sites were selected from uniform and representative sections of the paddocks. Sites had to be away from any drainage lines or gullies, ridges and any other disturbance such as animal camps, rabbit warrens and former experimental sites. The plots were marked by a steel fencepost in each corner and coordinates were taken using GPS. Table 5.2 lists site attributes.

Table 5.2 Summary of paddock landscape attributes of *Newholme* sites

Site No.	Slope (%)	Elevation (m)	Aspect	Position in landscape[1]	Soil type[2]
1	3.8%	1034	NE	Simple slope, gently inclined	Yellow Chromosol
2	3.8%	1040	E	Waning lower slope, gently inclined	Yellow Chromosol
3	1.9%	1030	NE	Waning lower slope, very gently inclined	Yellow Chromosol
4	3.8%	1049	ESE	Simple slope, gently inclined	Yellow Chromosol
5	5.7%	1050	SE	Crest to simple slope, gently inclined	Yellow Chromosol

[1] Speight (1967, 1971) in McDonald *et al.* (1990), [2] Isbell (1996)

Plate 5.1 Site 1, grazed, fertilized, exotic pasture at *Newholme*.

Plate 5.2 Site 3, grazed, native pasture at *Newholme*. And technicians Dave (on the left) and Trac.

Plate 5.3 **Looking down to Site 1 (on right) and Site 3 over the road at *Newholme.***

Plate 5.4 **Site 5, trees in paddock at *Newholme.***

5.2.2 Sampling Design

At four-weekly intervals for 14 months, soil was sampled from the plots in each of the five paddocks. A stratified random sampling design was developed for the soil sampling. Results from the *Kirby* trial (Appendix 2) found soil pH increased downslope, and this was considered when developing the design. Accordingly, the plots were divided into four equal blocks down the slope and into three equal sections across the slope. Thus each plot was divided into twelve block-sections (Figure 5.2). At each sampling, one soil core was taken from each block-section. Core positions were located using random number coordinates. Additional coordinates were available for each block-section to provide alternative sampling locations should a randomly-selected location be unsuitable because of disturbance, and to allow the plots to be used again for future experiments.

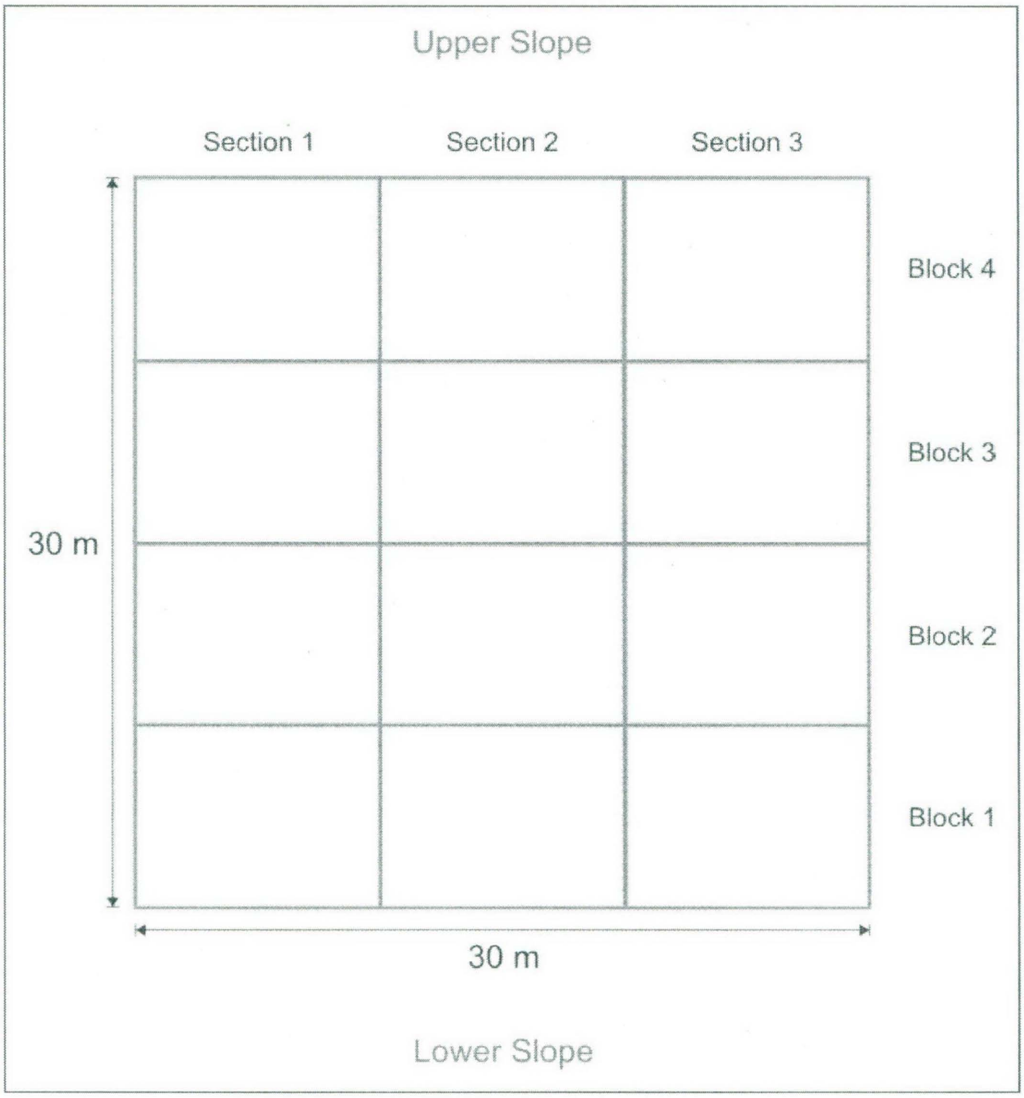

Figure 5.2 Subdivision of *Newholme* plots into sampling block-sections

Sampling-location coordinates for each plot were obtained from a sheet of randomly-generated numbers (Figure 5.3), which corresponded to the stage of sampling program. Thus, at Time 9, each core position would be selected from those squares numbered nine on the random-number sheet. If a core position was unsuitable because of some obstruction such as a tree, rock, ants' nest or rabbit hole, it was replaced by that random number plus 40. Thus for the ninth sampling, nine would be replaced by 49 for that coordinate. Core positions were marked by a coloured peg. An optical square, survey ropes and a survey pole were used to facilitate the procedure. A different colour was used for each block, three pegs to a block.

Site 1

Time: 9
Date: 13 Feburary 2003

Rainfall: mm

Top of Slope

		1	2	3	4	5	6	7	8	9	11	12	13	14	15	16	17	18	19	21	22	23	24	25	26	27	28	29	
	29	45	44	34	11	47	7	58	13	46	43	59	53	62	44	29	40	1	11	5	9	50	57	38	35	23	44	6	29
	28	20	55	10	43	36	12	28	60	15	12	32	37	58	39	49	34	30	54	58	4	56	10	0	47	46	8	3	28
	27	17	6	33	52	5	1	23	30	31	31	46	35	33	45	14	5	9	48	29	20	55	21	16	61	42	41	52	27
Block 4	26	8	39	41	26	57	18	62	4	56	10	18	52	8	61	24	2	4	21	59	14	36	30	26	27	39	60	18	26
	25	50	42	2	14	22	9	54	38	59	26	51	16	60	17	19	27	28	6	37	7	62	15	17	48	31	54	34	25
	24	40	27	51	35	49	0	21	37	61	15	22	3	38	47	20	7	0	55	1	25	28	19	49	11	53	32	12	24
	23	53	24	19	3	25	48	29	32	16	36	56	13	42	41	25	57	50	23	13	43	24	51	45	40	33	2	22	23
	22	38	29	10	54	31	19	7	8	61	23	21	6	9	57	29	60	55	38	29	26	59	8	60	32	15	50	23	22
	21	22	11	14	15	44	4	32	42	27	24	36	26	10	34	51	44	20	58	27	62	52	16	11	6	2	17	49	21
	20	56	13	62	41	18	23	1	39	6	17	39	7	27	25	4	13	56	40	56	39	31	37	44	54	10	22	61	20
Block 3	19	28	12	0	53	57	25	35	17	2	12	32	59	15	30	54	53	3	41	12	9	19	51	45	1	40	55	24	19
	18	9	45	21	3	49	24	20	33	26	37	45	11	62	16	48	5	46	8	33	14	18	35	36	5	38	53	21	18
	17	40	55	46	48	37	47	30	52	16	52	19	61	22	31	42	28	18	49	30	4	28	41	43	0	13	58	47	17
	16	60	5	59	50	34	43	36	58	51	0	35	33	50	14	2	43	1	47	34	25	48	57	3	42	46	7	20	16
	14	13	33	58	22	17	49	19	25	39	19	17	7	50	59	2	44	62	40	36	50	29	61	47	42	32	11	26	14
	13	12	56	31	4	48	50	41	51	42	54	56	52	22	13	35	36	28	29	35	40	37	46	24	34	60	53	13	13
	12	8	1	54	34	27	11	52	9	5	26	6	49	5	39	15	55	60	51	18	23	45	20	21	22	7	19	31	12
Block 2	11	60	61	7	10	35	57	37	45	59	14	46	58	12	10	41	1	3	25	62	54	10	16	59	3	49	15	27	11
	10	2	38	16	23	20	26	53	36	15	18	20	9	11	33	57	38	34	24	14	39	1	9	55	0	52	28	5	10
	9	32	43	46	62	18	3	30	6	47	30	23	32	37	8	53	47	27	4	12	2	43	51	44	38	57	4	6	9
	8	40	21	28	0	44	29	24	55	14	45	0	43	31	42	61	21	16	48	56	8	48	58	41	25	17	33	30	8
	7	6	25	28	24	42	48	10	59	11	48	58	24	50	45	34	28	27	19	33	54	61	6	39	1	56	34	59	7
	6	54	2	37	5	49	45	15	44	13	40	3	2	36	4	43	51	38	13	11	47	0	2	29	42	15	23	48	6
	5	33	50	26	52	40	17	1	35	27	62	31	44	12	59	25	39	5	61	9	37	26	22	30	38	12	49	5	5
Block 1	4	19	12	32	38	51	21	46	9	57	17	32	10	49	23	6	21	54	22	19	40	46	24	27	25	7	10	55	4
	3	22	61	23	29	34	58	3	41	20	7	9	33	15	8	55	60	41	18	43	21	35	8	3	58	14	44	28	3
	2	60	7	62	47	14	53	31	43	55	29	16	53	20	35	1	11	46	37	17	16	62	31	32	4	18	57	50	2
	1	18	56	39	36	8	16	30	0	4	26	57	56	14	0	52	47	42	30	53	52	20	60	51	45	36	41	13	1
		1	2	3	4	5	6	7	8	9	11	12	13	14	15	16	17	18	19	21	22	23	24	25	26	27	28	29	

Section 1 Section 2 Section 3

Notes:

Figure 5.3 Schematic of random-number coordinate field sheet
Each square represents and area 1 m x 1 m within the plot.

5.2.3 *Soil Sampling*

Soil cores, 50 mm in diameter, were sampled using a hand-held soil corer, driven to a depth of 50 cm with a posthole rammer and donger. A wallaby jack was used to extract the corers. Extruded cores in sets of three, one set from each block, were laid on a sheet of polyester roofing and cut into sample depth intervals of 0-5, 5-10, 10-20, 20-30, 30-40 and 40-50cm. Depth samples from each set of three cores were bulked in the field, and each bulked sample was placed in a labelled airtight clip-seal plastic bag (Figure 5.4). Thus from each paddock, four sets of six depth samples were retrieved, one from each block.

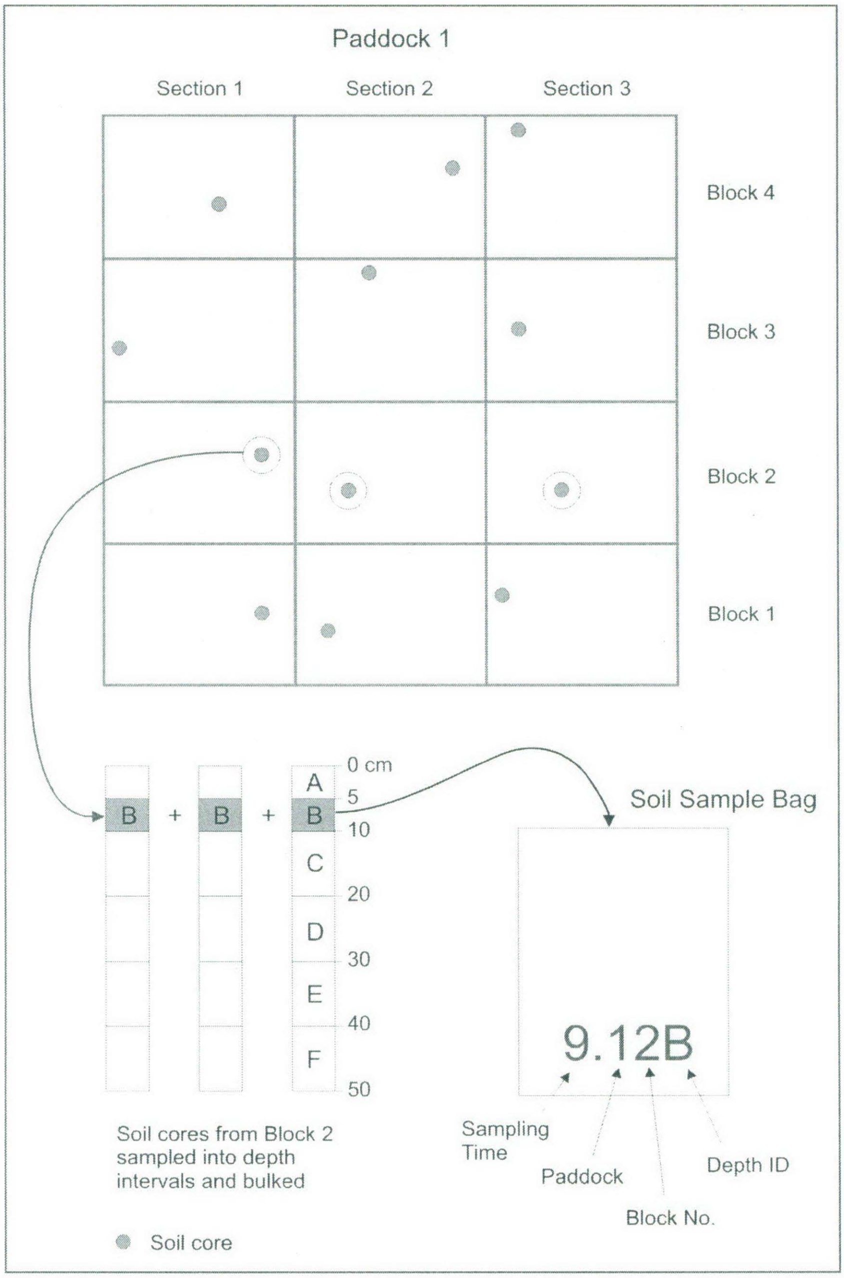

Figure 5.4 Soil cores from *Newholme* plots sampled by depth intervals, bulked and labelled

5.2.4 Laboratory Analyses

All bagged samples were immediately transferred to an esky and kept cool with ice packs. The samples were taken to the laboratory within 5 hours of the first sampling.

For Times 0 and 13 the soil samples were airfreighted to the former commercial Incitec laboratory at Gibson Island, Queensland. Samples of a UNE reference soil, Kirby 7, were also included as a quality control procedure to check laboratory standards. Tests included soil pH_W, pH_{Ca}, $EC_{1:5}$, ECEC, organic carbon, ammonium-N, and nitrate-N. Incitec test procedures are provided in Table 5.3.

Table 5.3 Methods of Incitec Soil Analyses[1]

All soil samples dried (40°C) and ground (<2mm)

pH (1:5 Water)	1:5 soil to water suspension, tumbled 1 hour, read using a combination electrode (*as per Method 4A1* (Rayment and Higginson 1992))[2]
pH (1:5 $CaCl_2$)	1:5 soil to water suspension, tumbled 1 hour, stood 1 hour, read using a combination electrode (*as per Method 4B1*)
Electrical Conductivity (dS/m)	1:5 soil to water suspension, tumbled 1 hour, solution measured for electrical conductivity (*Method 3A1*)
Ammonium-Nitrogen (mg/kg)	1:5 soil to 2M KCl solution ratio, shaken end-over-end for 1 hour, centrifuged and measured colorimetrically in a segmented flow analyser using the Berthelot indo-phenol blue reaction at a wavelength of 630 nm (*Method 7C2*)
Nitrate-Nitrogen (mg/kg)	1:5 soil/water suspension, intermittently stirred for 1 hour, centrifuged, nitrate measured in a segmented flow analyser at 520 nm (*Method 7B1*)

1 Adapted from Soil Analysis Report, Incitec Analysis Systems, Form No. 805 (Rev. 5), with additional information from Paul Kennelly, Incitec Pivot Laboratory, Werribee (pers.comm. 2006).

2 Methods in italics are methods prescribed by Rayment and Higginson (1992) and sourced by the Incitec Pivot Laboratory.

Soil samples for Times 1 to 12 were air dried, sieved to < 2 mm and analysed in the laboratory at Agronomy and Soil Science, UNE. Analyses were soil pH_W (1:5 soil:water suspension), pH_{Ca} (1:5 soil:0.01 M $CaCl_2$ suspension), $EC_{1:5}$ (1:5 soil:water suspension), ammonium-N and nitrate-N. For ammonium-N and nitrate-N, each sample was extracted with 30 mL of 2M KCl and the jars were tumbled end-over-end (15 revs/minute) for 1 hour. The contents were filtered using *Whatman* No. 42 filter paper and the filtrate read by a *Technicon* auto analyser using a dual-channel system. Ammonium ions were measured using the Adamsen *et al.* (1985) indophenol blue method with nitrate-N being reduced to ammonium-N via a cadmium column. The Kirby 7 reference soil and two reference secondary-standard soils with a soil pH_{Ca} of 4.6 and 5.1, Proficiency Samples 30 and 50 produced by the Australian Soil and Plant Analysis

Council (ASPAC), were included within every set of samples analysed as a quality check.

5.2.5 *The Weather*

At the same time as the soil was sampled, precipitation collected in rain gauges over the preceding four weeks was measured, recorded and the gauges emptied. One rain gauge was situated between Paddocks 1 and 3. A second gauge was at Paddock 2 and a third gauge was between Paddocks 4 and 5. Rainfall and temperature data for Armidale UNE meteorological station were provided on request from the BoM. As 30 km separates the station and *Newholme*, some differences in the weather would occur. However, it was accepted that temperature data from BoM would be reliable. Rainfall data as collected from *Newholme* were used. If any errors existed, they would be relative across the five sites.

5.2.6 *Statistical Tests*

A repeated measures analysis of variance was undertaken for each soil chemical variate in each of the five paddocks, across six depths, for fourteen, temporally dependent, four-weekly sampling times. Soil chemical variables assessed were soil pH_{Ca}, soil pH_W, $EC_{1:5}$, ammonium-N and nitrate-N. As each paddock had a different management practice, it was treated as an independent unit. The paddocks were not replicated because they were selected for the sequence of different treatments, rather than comparative treatments. Statistical analyses were performed on data from within a paddock; interpretation was restricted to that paddock on that farm and could not be extrapolated to another area.

Observed means for each soil chemical variable, at each depth for each paddock were plotted against time and smoothing splines were fitted for each data set. Correlations between field rainfall data, BoM temperature data and the five soil chemical variables, for each depth for each paddock were carried out using the CORREL function in *Microsoft* EXCEL.

5.3 Results

5.3.1 Rainfall and Temperature

The fourteen-month sampling period, May 2002 to May 2003 was atypical compared with long-term climate expectations due to the prevailing drought. Spring and summer rainfall between October 2002 and February 2003, on average 45 mm per month, was below the long-term average. Then above-average rain fell in autumn (March, April and May 2003) with extremely heavy falls totalling 160 mm in March 2003. Rainfall measured at *Newholme* was similar to that recorded by the Meteorological Station at UNE, provided by BoM (Figure 5.5).

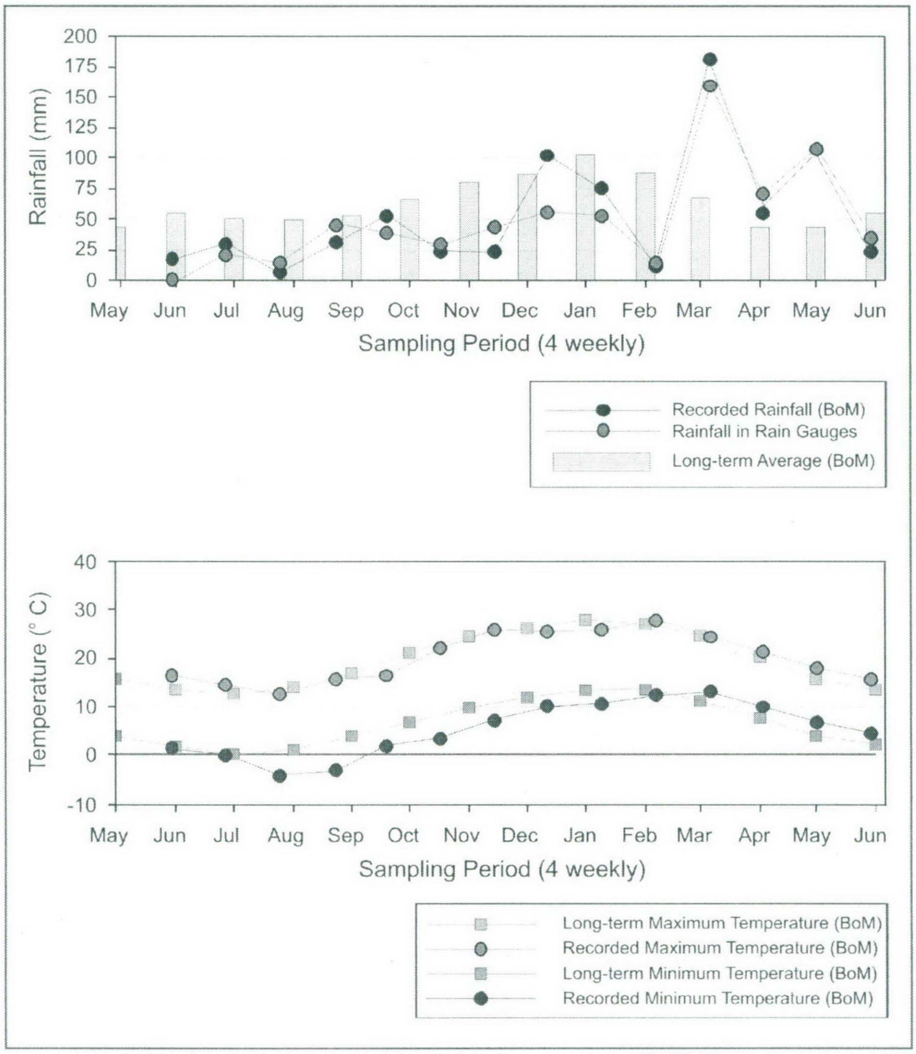

Figure 5.5 Rainfall and temperature data for study period at *Newholme* compared with long-term averages (BoM)
Field data reflects date of reading and as such is offset from BoM long-term monthly averages.

5.3.2 Soil Chemical Data

Results from the analyses of each of the chemical variables are given in Appendix 5.1.

5.3.3 Statistical Analyses

Results from the analysis of variance are summarised in Table 5.4. In addition, the correlation between ammonium and nitrate was tested (Table 5.4). Details of the statistical analyses are provided in Appendix 5.2.

Table 5.4 Analysis of variance of *Newholme* soil chemical properties over time, and correlation between ammonium and nitrate

Figures in bold type denote effects at the 5% level. N/A, no result.

Paddock	Depth	pH_w	pH_{Ca}	$EC_{1:5}$ (dS/m)	NH_4^+-N (mg/kg)	NO_3^--N (mg/kg)	Correlation NH_4^+ vs NO_3^-
1	0-5	**<0.001**	0.354	0.270	0.667	0.078	0.34
1	5-10	**0.003**	0.622	0.543	0.871	0.105	0.43
1	10-20	**<0.001**	0.887	0.930	0.317	**0.013**	0.15
1	20-30	0.177	0.172	**<0.001**	0.297	**0.008**	-0.07
1	30-40	**0.002**	0.138	**<0.001**	0.929	**0.018**	0.53
1	40-50	**0.003**	**0.031**	**<0.001**	0.619	**0.030**	0.48
2	0-5	0.083	0.073	0.386	0.374	**0.016**	0.63
2	5-10	0.510	0.772	**<0.001**	0.572	**0.005**	0.57
2	10-20	**0.030**	0.322	0.126	0.442	**0.002**	-0.46
2	20-30	**<0.001**	0.095	0.622	**0.015**	**0.006**	-0.12
2	30-40	**0.007**	**0.002**	0.435	0.197	**0.011**	-0.05
2	40-50	0.247	0.380	**0.041**	0.391	**<0.001**	0.47
3	0-5	0.481	0.175	0.794	0.368	**0.002**	0.40
3	5-10	**0.038**	0.714	0.456	0.150	0.410	0.34
3	10-20	**0.002**	0.404	0.540	**0.044**	0.239	0.19
3	20-30	**<0.001**	0.480	0.157	0.344	**0.022**	0.26
3	30-40	**<0.001**	0.694	N/A	0.138	**0.001**	0.21
3	40-50	**0.009**	0.813	N/A	0.478	0.175	**0.73**
4	0-5	**0.009**	0.861	**0.004**	0.933	**0.048**	-0.11
4	5-10	**0.018**	0.673	0.244	**0.022**	**0.026**	-0.26
4	10-20	**0.009**	0.744	**0.012**	**0.033**	**0.042**	-0.28
4	20-30	**0.026**	0.730	**<0.001**	**<0.001**	**0.024**	-0.38
4	30-40	0.335	0.247	**0.003**	**<0.001**	0.051	-0.08
4	40-50	**0.008**	0.198	**<0.001**	0.078	0.626	**0.91**
5	0-5	**<0.001**	0.160	**0.010**	0.227	**0.011**	0.56
5	5-10	**0.005**	0.326	0.055	0.237	**0.020**	-0.53
5	10-20	**0.014**	0.902	**0.021**	0.691	**0.014**	-0.59
5	20-30	**<0.001**	0.906	**0.007**	0.809	0.120	-0.08
5	30-40	0.147	0.715	**<0.001**	**0.002**	**0.029**	-0.23
5	40-50	**0.040**	0.822	**<0.001**	0.274	**0.024**	0.30

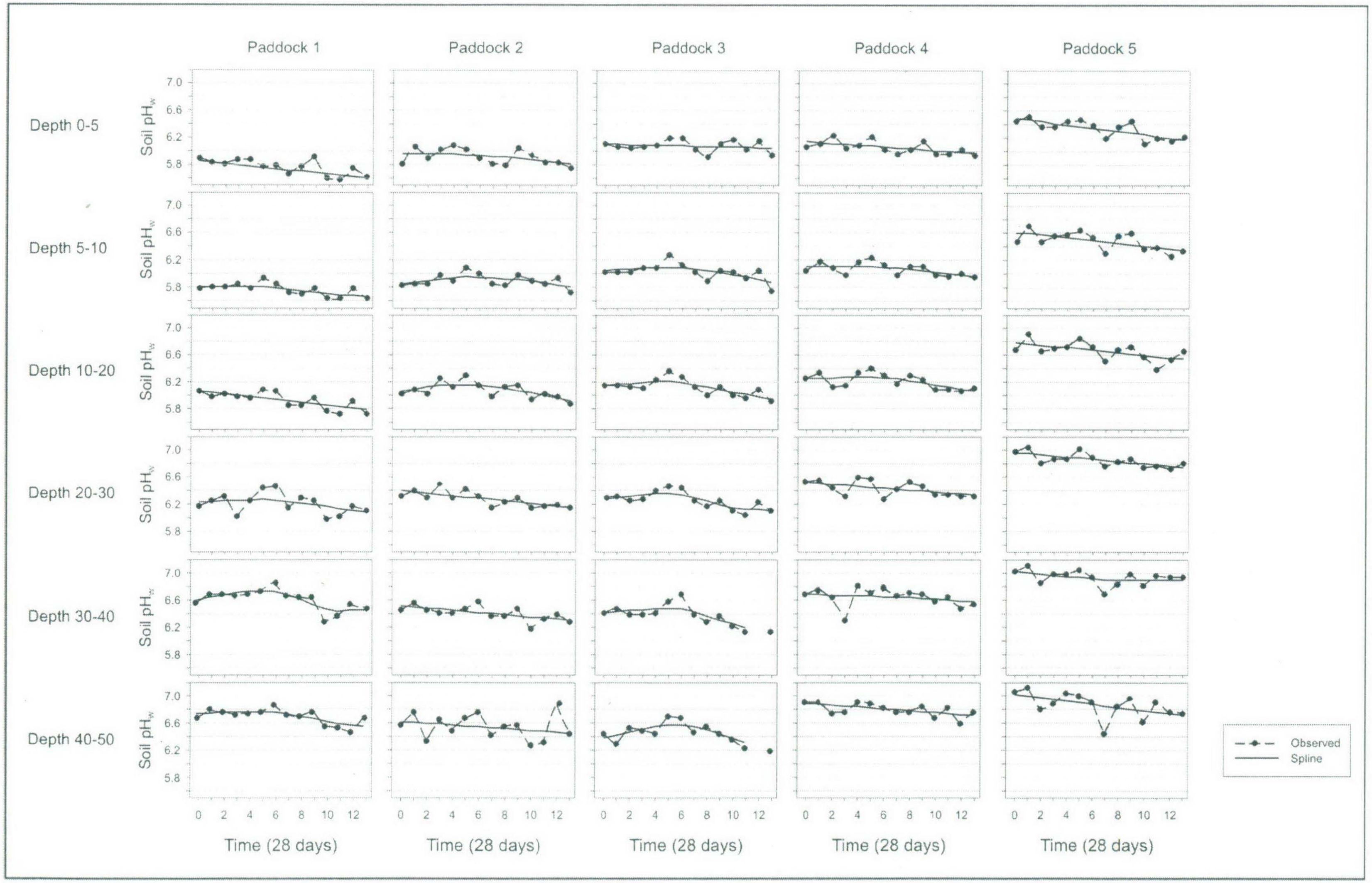

Figure 5.6 Observed means and smoothing splines for soil pH$_W$ over depth and time for each *Newholme* paddock

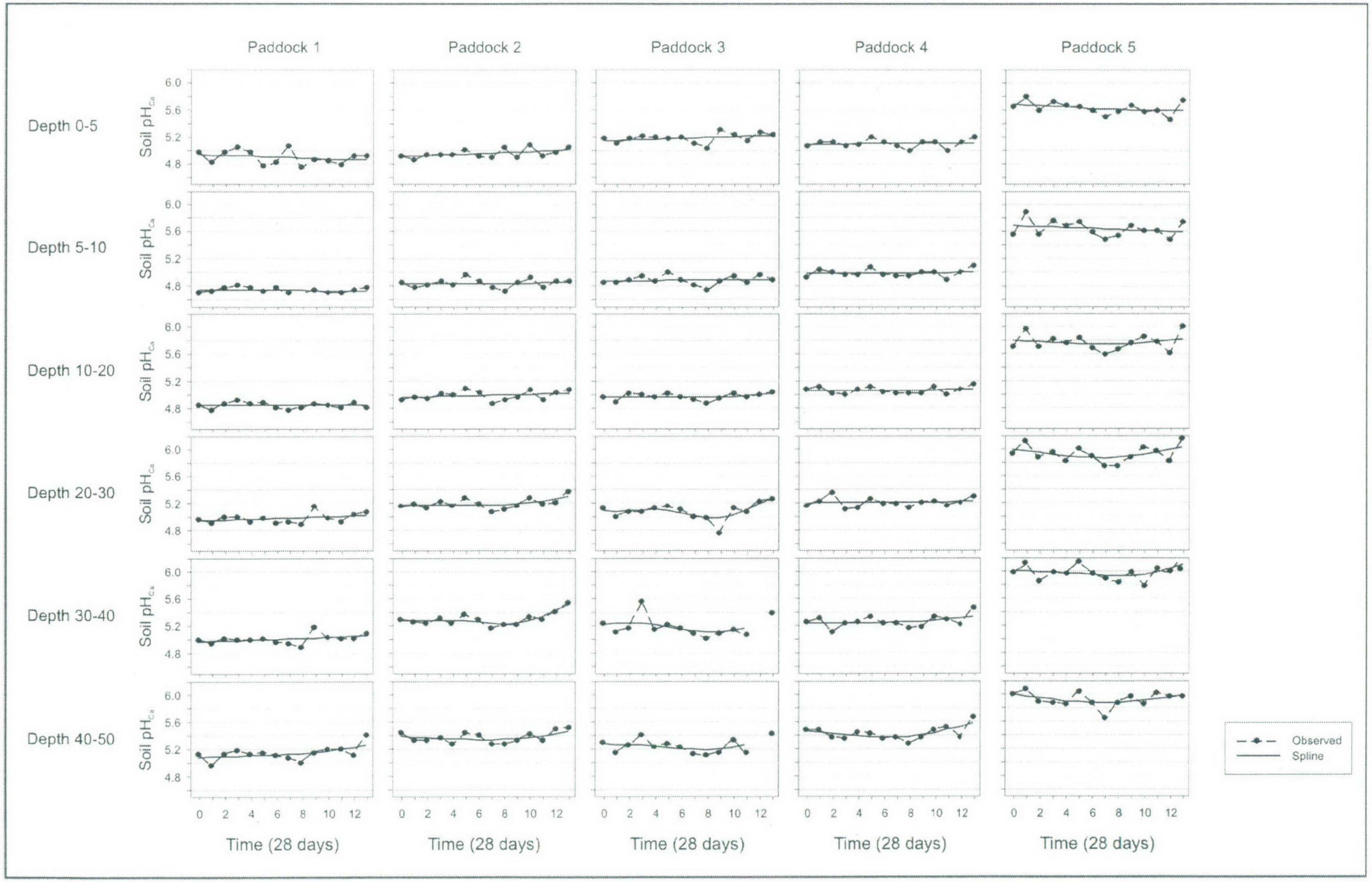

Figure 5.7 Observed means and smoothing splines for soil pH$_{Ca}$ over depth and time for each *Newholme* paddock

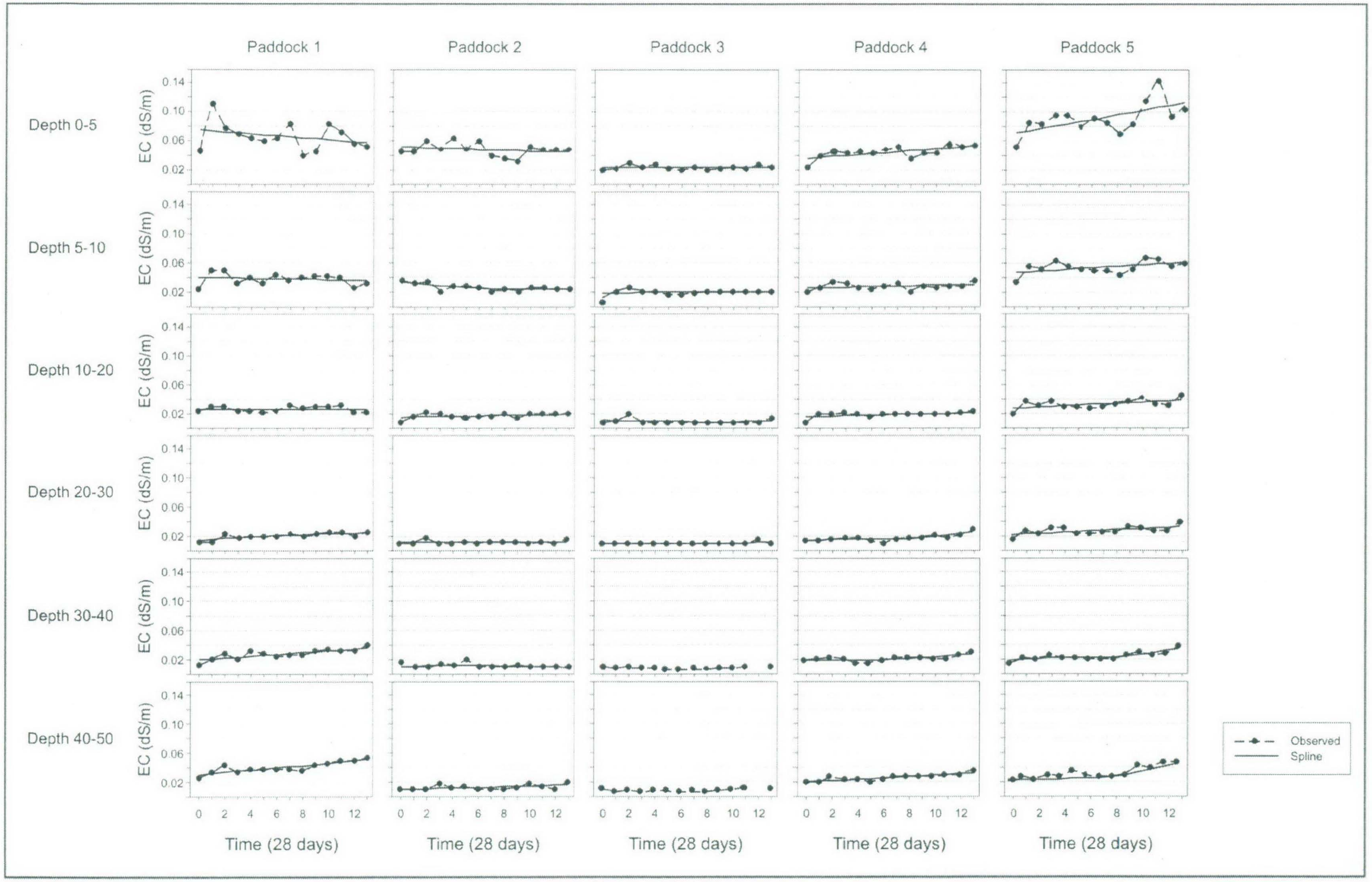

Figure 5.8 Observed means and smoothing splines for soil $EC_{1:5}$ over depth and time for *Newholme* paddocks

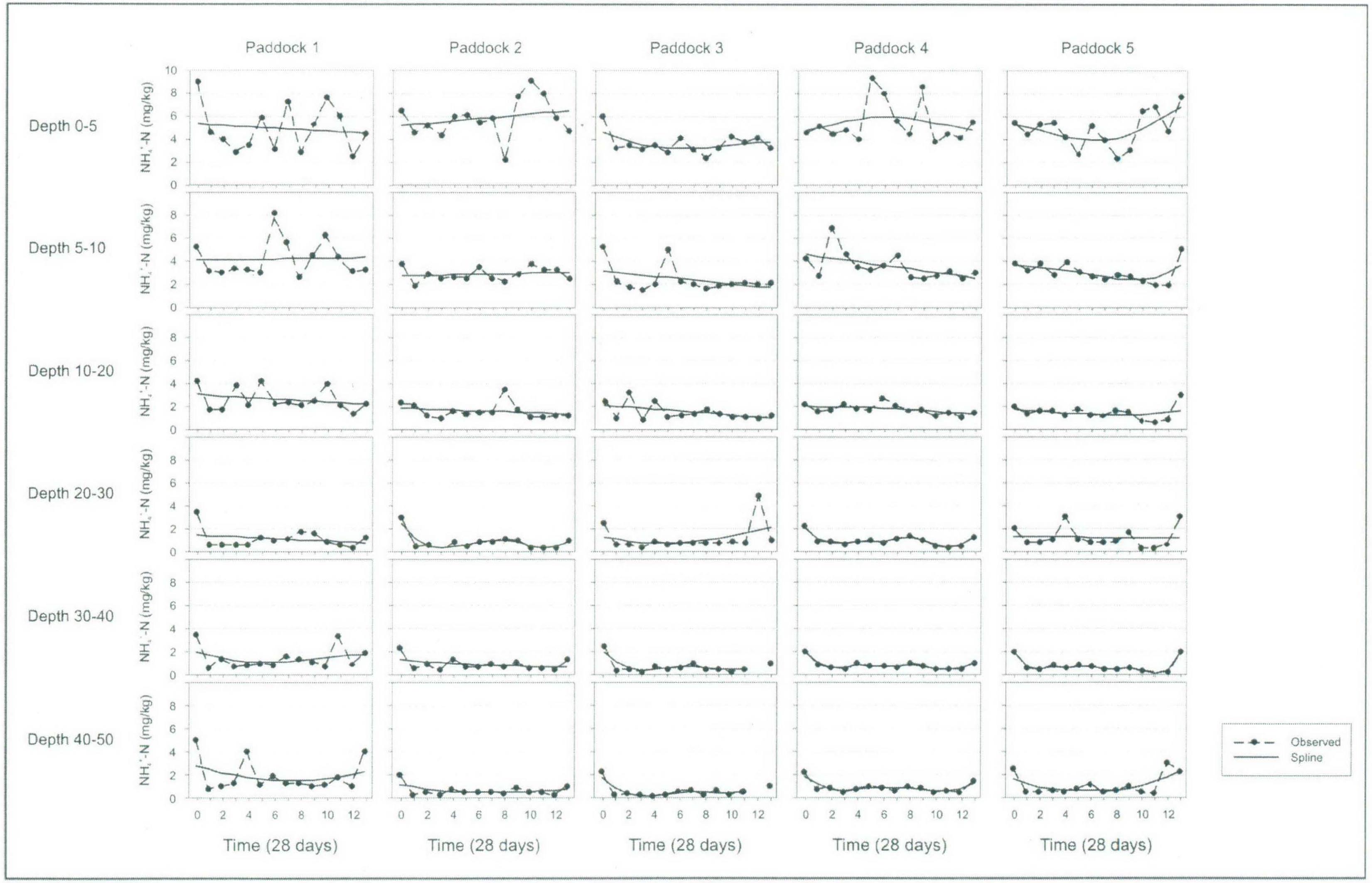

Figure 5.9 Observed means and smoothing splines for ammonium-nitrogen over depth and time for *Newholme* paddocks

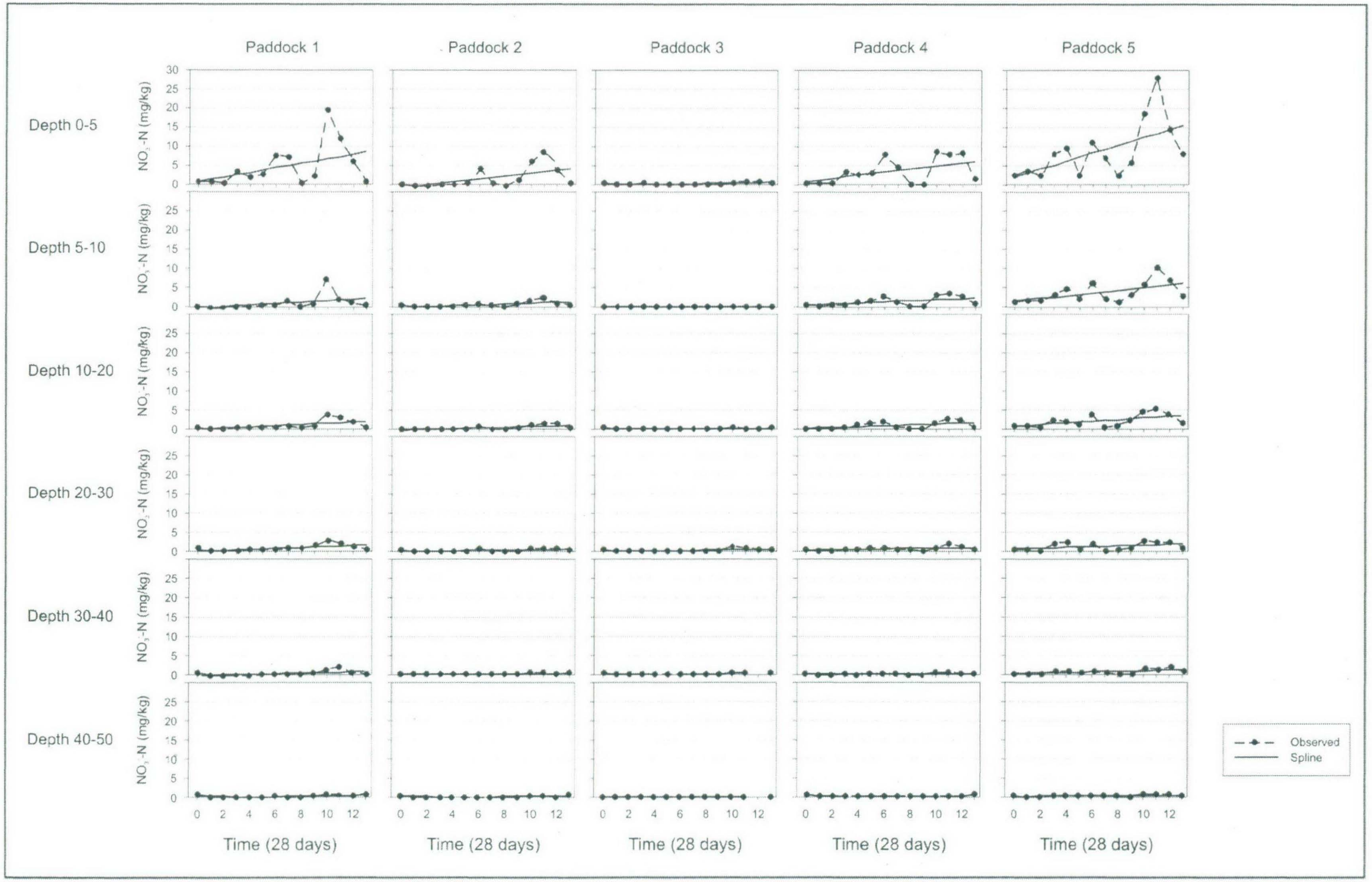

Figure 5.10 Observed means and smoothing splines for nitrate-nitrogen over depth for each *Newholme* paddock

Graphs of fitted time responses, spline curves, for each soil chemical variable, for each of the six depths, for each of the five paddocks are given (Figures 5.6 to 5.10). These fitted responses are either spline curves or linear in shape. A spline suggests consistency of change in data. On the other hand, if a graph has a "curve" that is linear, this reflects either very little, or no, consistency of change.

The fitted responses for soil pH_W over depth, against time (Figure 5.6) tended to have negative trends and this indicated that pH_W decreased over time. Most observations for soil pH_W (Table 5.4) were significant ($P \leq 0.05$) and indicated that pH_W fluctuated over time and this can be clearly seen in Figure 5.6. Soil pH_W was negatively correlated ($P \leq 0.005$) with rainfall for most depths in Paddocks 1 and 5 (Table 5.5) and for some depths in Paddocks 2, 3 and 4. Any spikes for soil pH_W tended to be at a time of low rainfall and any dips corresponded with high rainfall. No correlation with temperature was observed (Table 5.6).

Overall soil pH_{Ca} did not change over time for any depth in any paddock (Table 5.4, Figure 5.7). Fluctuations in soil pH_{Ca} were not consistent with rainfall across the paddocks. For example, pH_{Ca} in Paddocks 1 and 2 peaked with high rainfall while Paddock 5 peaked with low rainfall. Apparent spikes were only 0.2 to 0.3 pH units in magnitude and could have been the result of field variability or laboratory error. Any significant effects for soil pH_{Ca} (Paddock 1 for 40-50 cm and 30-40 cm in Paddock 2) were statistically due to chance. Soil pH_{Ca} was not correlated with rainfall (Table 5.5) apart from Paddock 5 ($P \leq 0.05$) for 0-5 cm and 30-40 cm. Soil pH_{Ca} was not correlated with temperature (Table 5.6) with one exception at 20-30 cm in Paddock 3 ($P \leq 0.05$).

The summary statistics (as graphed) for both soil pH_W (Figure 5.6), and to a certain extent for soil pH_{Ca} (Figure 5.7), show a change in soil pH, over all depths, that may be the result of the different management regimes. Paddock 1, the most intensively-managed paddock, a grazed, fertilized exotic pasture had quite low values of around the pH_{Ca} threshold of 4.8. Soil pH_{Ca} values were also low in Paddocks 2, 3 and 4. Soil pH was higher for Paddock 5 compared with the other paddocks.

For most depths in Paddocks 4 and 5 (Figure 5.8, Table 5.4) $EC_{1:5}$ increased significantly ($P<0.05$) over the time. However, the $EC_{1:5}$ values for all sites were very low. These data were converted to EC_{se} as per Section 4.4 using a suitable multiplicative factor, in this case

20, correlated for field capacity and percentage saturation for a sandy loam (Hazelton and Murphy 1992; Taylor 1996). The highest resulting value was <0.2 dS/m, which was negligible (Hazelton and Murphy 1992) and showed that the sites were not saline. Because the sites were not saline, any increase or decrease for $EC_{1:5}$ was negligible. No correlation with rainfall (Table 5.5) or temperature (Table 5.6) was observed, apart from one exception.

Ammonium-N (Figure 5.9) varied considerably over time but no consistent pattern was apparent between the paddocks. Ammonium-N concentrations in Paddock 4 declined ($P \leq 0.05$) over the 5-40 cm depths (Figure 5.9; Table 5.4). The data analyses showed no statistical correlation against rainfall or temperature (Tables 5.5 and 5.6). The only exceptions were negative correlations in Paddock 5 ($P \leq 0.05$) for the 5-10 and 10-20 cm depths.

Nitrate-N concentrations also fluctuated over time, particularly in the 0-5 cm layers (Figure 5.10) possibly in response to rainfall. Significant positive correlations ($P \leq 0.05$) were apparent over most depths for all paddocks (Table 5.4). These fluctuations were more variable compared with ammonium-N if significant differences are considered. The graphed summary statistics (Figure 5.10) show nitrate-N values were very low in Paddock 3, the grazed, native pasture, for all times. In the other paddocks the values were very low until autumn (March, April and May) when increases were observed for the 0-5 cm depths. For these depths, an increase occurred in Paddocks 1 and 4 at Time10. In Paddock 2, the increase coincided with Time 11. For Paddock 5, the increase at Time 10 peaked at Time 11. These increases coincided with the heavy rainfall at that time. However, correlations against rainfall (Table 5.5) were only significant ($P \leq 0.01$) in Paddock 1 for the 0-5, 5-10, 10-20 and 20-30 cm depths, and Paddock 3 for 20-30cm. Other correlations ($P \leq 0.05$) were observed in Paddock 4 (0-5 and 5-10 cm) and Paddock 5 (30-40 and 40-50 cm). No apparent increases of nitrate-N, as compared with the surface peaks, were observed down any profile of any paddock following rainfall. Smaller peaks of nitrate-N observed at depth for Paddocks 1, 2, 4 and 5 were concurrent or slightly delayed compared with the surface peaks in time.

At Time 8, nitrate-N was low for all paddocks for all depths. This followed low rain periods in December and January and coincided with high temperatures at that time. It was observed that a flush of pasture growth also occurred at this time. Normally, pasture growth peaks in December and January but during this sampling season it was delayed with lack of adequate rainfall. No pasture measurements were taken during this trial.

Table 5.5 Rainfall correlations against soil chemical variables for each depth over all paddocks

Correlation coefficient > 0.661 significant at 1% in bold type
Correlation coefficient > 0.532 significant at 5% in italics and bold type

Paddock	Depth	pH_W	pH_{Ca}	$EC_{1:5}$ (dS/m)	NH_4^+-N (mg/kg)	NO_3^--N (mg/kg)
1	0-5	***-0.62***	-0.01	0.24	0.22	**0.78**
1	5-10	-0.46	-0.31	-0.02	0.23	**0.84**
1	10-20	***-0.58***	-0.05	0.30	0.05	**0.78**
1	20-30	-0.50	-0.30	0.40	-0.29	**0.70**
1	30-40	***-0.65***	-0.19	0.23	-0.19	0.50
1	40-50	**-0.67**	-0.09	0.32	-0.25	0.26
2	0-5	-0.14	0.33	-0.05	0.35	0.52
2	5-10	-0.13	-0.02	-0.43	0.28	0.45
2	10-20	-0.44	0.13	-0.02	-0.13	0.53
2	20-30	***-0.59***	0.03	-0.18	-0.28	0.41
2	30-40	**-0.76**	0.02	0.01	-0.32	0.45
2	40-50	-0.30	0.07	0.14	-0.27	0.19
3	0-5	0.06	-0.13	0.09	0.04	0.50
3	5-10	-0.16	0.02	-0.05	-0.28	0.24
3	10-20	-0.38	-0.07	-0.16	-0.37	0.30
3	20-30	-0.46	0.17	0.22	0.23	**0.72**
3	30-40	-0.40	-0.29	-0.07	-0.22	0.35
3	40-50	-0.24	-0.01	0.20	-0.24	-0.05
4	0-5	***-0.57***	-0.24	0.16	-0.47	***0.62***
4	5-10	-0.42	-0.15	-0.15	-0.33	***0.55***
4	10-20	-0.42	0.07	0.18	-0.50	0.43
4	20-30	-0.24	-0.20	0.26	-0.37	0.36
4	30-40	-0.20	0.12	0.25	-0.36	0.41
4	40-50	***-0.62***	-0.01	0.42	-0.46	-0.30
5	0-5	**-0.71**	***-0.60***	0.34	0.11	0.52
5	5-10	***-0.59***	-0.43	0.36	***-0.53***	0.37
5	10-20	-0.51	-0.28	0.22	***-0.56***	0.44
5	20-30	***-0.56***	-0.14	0.17	-0.41	0.48
5	30-40	***-0.59***	***-0.57***	0.24	-0.42	***0.58***
5	40-50	**-0.67**	-0.48	0.41	-0.11	**0.68**

The most significant correlation ($P \leq 0.01$) with rainfall was for nitrate-N in Paddock 1 over the 0-5, 5-10, 10-20 and 20-30 cm depths. Soil pH_W was negatively correlated with rainfall ($P \leq 0.05$) for depths 0-5, 10-20, 30-40 and 40-50 cm for Paddock 1 and all depths except 10-20 cm for Paddock 5. Other minor correlations ($P \leq 0.05$) occurred in Paddock 2 and Paddock 4. Soil pH_{Ca} was correlated with rainfall ($P \leq 0.05$) in Paddock 5 for two depths. Ammonium-N ($P \leq 0.05$) and rainfall were correlated over two depths in Paddock 5.

Table 5.6 Temperature correlations against soil chemical variables

Correlation coefficient > 0.532 significant at 5% in italics and bold type

Paddock	Depth	pH_w	pH_{Ca}	$EC_{(1:5)}$ (dsS/m)	NH_4^+-N (mg/kg)	NO_3^-N (mg/kg)
1	0-5	-0.19	-0.40	-0.29	0.13	0.41
1	5-10	-0.07	-0.50	0.11	0.52	0.35
1	10-20	-0.15	-0.23	0.23	0.06	0.32
1	20-30	0.23	-0.08	0.37	0.09	0.50
1	30-40	0.05	0.04	0.11	-0.14	0.28
1	40-50	0.01	-0.21	0.07	-0.34	-0.04
2	0-5	-0.06	0.09	-0.44	0.23	0.34
2	5-10	0.34	-0.10	***-0.54***	0.22	0.30
2	10-20	0.13	-0.03	-0.15	0.17	0.23
2	20-30	-0.26	-0.31	0.02	-0.01	0.22
2	30-40	-0.11	-0.36	0.20	-0.16	-0.03
2	40-50	-0.05	-0.32	-0.20	-0.09	-0.16
3	0-5	0.10	-0.09	-0.43	-0.19	-0.09
3	5-10	0.07	-0.30	-0.32	-0.11	-0.18
3	10-20	0.07	-0.38	-0.32	-0.41	-0.26
3	20-30	-0.07	***-0.54***	-0.25	-0.20	0.10
3	30-40	0.14	-0.53	-0.42	-0.19	-0.10
3	40-50	0.32	-0.48	-0.11	-0.07	-0.28
4	0-5	-0.24	-0.28	0.05	0.45	0.30
4	5-10	0.04	-0.29	-0.46	-0.44	0.24
4	10-20	0.11	-0.18	-0.06	-0.09	0.21
4	20-30	-0.14	-0.37	-0.16	-0.20	0.16
4	30-40	0.30	-0.17	-0.04	-0.18	-0.02
4	40-50	-0.09	-0.37	0.02	-0.28	-0.36
5	0-5	-0.15	-0.48	0.01	-0.43	0.17
5	5-10	-0.03	-0.36	-0.14	**-0.56**	0.19
5	10-20	-0.18	-0.38	-0.05	-0.35	0.28
5	20-30	-0.21	-0.34	-0.09	-0.34	0.05
5	30-40	-0.37	-0.40	-0.14	-0.36	-0.03
5	40-50	-0.28	-0.33	-0.01	-0.26	0.11

Temperature was not significantly correlated with most of the soil chemical variables over all depths and all sites

5.4 Discussion

This discussion is divided into two sections. Seasonal factors and the differences between the effects for soil pH_W and pH_{Ca} are assessed in Section 5.4.1. Then, in Section 5.4.2, seasonal effects on nitrogen cycling are discussed.

5.4.1 Soil pH in Relation to Rainfall and Temperature

Fluctuations in soil pH_W were negatively correlated with rainfall in Paddocks 1 and 5. For all paddocks, soil pH_W decreased over time, a decrease possibly related to increased rainfall late in the sampling period. Rainfall in March, April and May at the end of the sampling period was much higher than the long-term average. Paddock 1 had very short ground cover because of the drought and grazing intensity and moisture infiltration through the profile could have increased. For Paddock 5, an increase of moisture in the profile, surplus to the requirements of the trees on that site, could have occurred. Field observations while soil sampling support this notion. Early in the sampling the soil was very dry and most often the soil core comprised loose soil below 10 or 20 cm. Following rain in March, coherent soil cores were obtained. No correlation with temperature was observed for soil pH_W.

These results differ from those of Friesen *et al.* (1985) who monitored soil test phosphorus, potassium and soil pH monthly for two years on permanent pastures at *Chiswick*, at the CSIRO Pastoral Research Laboratory, south of Armidale. They found that soil pH_W was positively correlated to the soil moisture index and negatively correlated with temperature. A prolonged drought during the second year of that study severely limited pasture growth, soil moisture declined and soil pH_W also declined. Friesen *et al.* (1985) concluded that this was consistent with the effect of soil moisture on the concentration in the sampling zone of soluble salts that would be expected to rise during dry periods and decline in wet periods.

The decrease in soil pH_W with an increase in rainfall at *Newholme* also differed with the results of Slattery and Ronnfeldt (1992). In that study four sites in northeast Victoria were sampled over a period of three years to investigate the source of soil test variation in soil pH_W and soil pH_{Ca}, aluminium and manganese. Slattery and Ronnfeldt (1992) found that soil pH_W increased after rainfall in autumn, then decreased slowly over spring and summer to a low in late summer. They concluded rainfall would lower the salt to soil moisture ratio and the effective decrease in salt content would tend to increase soil pH_W.

Friesen *et al.* (1985) and Slattery and Ronnfeldt (1992) both stated that the decrease in the concentration of salt with an increase in soil moisture was the reason for the increase in soil pH_W. In the *Newholme* study, no evidence for a decrease or increase in salt concentration was evident from the $EC_{1:5}$ statistical tests. Friesen *et al.* (1985) also found that soil pH_W declined with an increase in temperature. They concluded that the influence of soil temperature on soil pH_W was possibly due to increased soil microbial activity and root activity with a rise in temperature and subsequent expected depression of pH_W values. Dry conditions over spring and summer at *Newholme* suppressed expected nitrate-N production over that time. Thus, soil pH_W was not influenced by temperature.

Table 5.4 suggested that soil pH_{Ca} did not change over the sampling period. This result differs from the findings of Conyers *et al.* (1997) in an investigation of temporal variation in soil pH_{Ca} at four unfertilized, uncropped sites within 50 km of Wagga Wagga. Like the *Newholme* study, Conyers *et al.* (1997) used smoothing splines (Verbyla *et al.* 1999) to model the long-term and smooth the short-term fluctuations in soil properties but with fewer sites and fewer variables. Conyers *et al.* (1997) found temporal variation in soil pH_{Ca} of up to 0.45 units, a variation that was less than the spatial variability at the sites but greater than the long-term acidification rate of 0.1 pH per annum proposed by Helyar *et al.* (1990). However, the smooth short-term trends or spikes could be either temporal variation in the soil pH_{Ca} from short-term processes such as temperature or moisture fluctuations, or sampling and laboratory error (Conyers *et al.* 1997).

Although from Figure 5.7, soil pH_{Ca} data for all sites in the *Newholme* study appeared to show variation with rainfall over the study period this was not consistent across the paddocks. Rainfall had no statistical effect soil pH_{Ca} apart from Paddock 5 ($P<0.05$) for the 0-5 and 30-40 cm depths. Even the more extreme conditions with higher than average rainfall at the end of the sampling period, did not result in a significant decline in soil pH_{Ca}. Temperature also did not influence soil pH_{Ca}. These results differ from Conyers *et al.* (1997) but agree with those of Slattery and Ronnfeldt (1992). Conyers *et al.* (1997) found that during the first year of their study, soil pH_{Ca} generally decreased following rain after a long dry summer, before becoming more cyclic for the next two years. They concluded that the temporal variation in soil pH_{Ca} was dominated by specific periods of more extreme seasonal conditions than average, rather than the general cyclic pattern of soil water content and temperature. Slattery and Ronnfeldt (1992) found no significant seasonal variation in soil pH_{Ca}, and concluded that because of the uniform ionic strength of this test, these measurements were less sensitive to variations compared with soil pH_W. The *Newholme* results also suggest that soil pH_{Ca} is the more robust measure and this supports the findings in the paired-sites survey of Chapter 4. The results are also consistent with those of Schofield and Taylor (1955); Helyar and Porter (1989) and Slattery *et al.* (1999).

5.4.2 Ammonium and Nitrate in Relation to Rainfall and Temperature

Ammonium-N concentrations fluctuated over the sampling time for all paddocks but no correlation was found between ammonium-N and rainfall or temperature. This result differs from that of Chen *et al.* (1999) in a pasture experiment at *Chiswick* where selected areas were labelled with ^{34}S-enriched elemental sulfur and ^{15}N-enriched NH_4Cl solution. Here it was found that ammonium-N in the 0-5 cm layer was significantly higher in autumn and winter. Chen *et al.* (1999) concluded that the rate of nitrification was affected by seasonal changes in soil temperature and moisture, that pasture growth was synchronized with mineralization and nitrification, and that ammonium domination of the soil nitrogen system prevented the leaching of nitrate in that environment.

At *Newholme*, nitrate-N showed more variation compared with ammonium-N and nitrate-N fluctuated over time, probably in response to rainfall. Figure 5.10 shows nitrate-N values were very low in Paddock 3, the grazed, native pasture, for all times. In the other paddocks the values were comparatively low until Times 10 and 11 when increases occurred in Paddocks 1 and 5. Increases were also observed about the same time in Paddocks 2 and 4. These increases coincided with the heavy rainfall at the same time. However, the correlation against rainfall was only significant in Paddock 1 for the depths 0-30 cm and in Paddock 4 at 0-10 cm. Other correlations occurred at depth (20-30 cm) in Paddock 2 and 30-50 cm in Paddock 5. Thus, for Paddocks 1 and 4, changes in nitrate-N are consistent with differences in rainfall. This implies that nitrification in excess of plant uptake of nitrate was occurring as a result of rainfall for these paddocks. The influence of temperature could have confounded the issue here. Some rain fell in December and January, and this together with the high temperatures of January and February assisted pasture growth that was observed but not measured in this survey. This coincided with very low nitrate-N concentrations over all depths and across all paddocks.

Small increases in nitrate-N over the 5-10, 10-20, 20-30 and 30-40 cm depths were apparent for Paddocks 1, 2, 4 and 5 and this suggested that some nitrate movement had occurred down the profile. However, this movement was only to 40 cm and within the root zone. A B2 clay horizon at 40 to 55 cm was observed at each site and this coincides with the field textures. No large increases of nitrate-N down any profile of any paddock were observed following rainfall. That some nitrate leaching had occurred was evident from small increases in nitrate-N at depth. This observation agrees with that of Chen *et al.* (1999) who found limited nitrate-N in their study at *Chiswick* and suggested that nitrogen dynamics differed between climates with winter rainfall and those with summer rainfall. It has been suggested (Chen *et al.* 1999; Friesen *et al.* 1985) that if pasture growth is synchronized with rainfall, then plant uptake of nitrate counters the acidifying effect of nitrate leaching. With the *Newholme* study, however, the rainfall pattern differed from the long-term average. As mentioned in the previous paragraph, pasture growth coincided with high temperatures in the months following some rainfall, but this was later than normal. Then unseasonable heavy rainfalls came at a time when pasture plants were not actively growing.

It is suggested that nitrification had slowed at *Newholme* because of the dry conditions with drought during the first part of the study. Precipitation was higher than the long-term average occurring in autumn, and with these rainfall events nitrate-N concentrations increased. It might be expected that ammonium-N concentrations would decrease and nitrate-N concentrations might increase as ammonium-N is mineralized to nitrate. However, ammonium-N and nitrate-N were not correlated (Table 5.4). The ratio of nitrate to ammonium was 0.8 and was consistent in the surface (0-5 cm soils). Nitrate-N concentrations increased (> 20 mg/kg) at times, but ammonium-N concentrations went only as high as 10 mg/kg.

5.5 Conclusion

One main feature from the results is that soil pH_W and pH_{Ca} are not correlated because marked differences in the variability between the two variates existed. A correlation would normally be expected between soil pH_W and pH_{Ca} with soil pH_W values being higher than pH_{Ca} values. However, as found in the paired-site study (Chapter 4), if salt in the form of fertilizers were added then the soil pH_W could be lower than expected. It was suggested in that chapter that pH_{Ca} was the more robust measurement of soil pH as it was not affected by changes in moisture or by salts in the soil. Soil pH_W decreased significantly for all paddocks over time and was negatively correlated with rainfall with significant correlations in Paddocks 1 and 5. This decrease in soil pH_W could have been related to an increase in nitrate-N. Electrical conductivity was not seasonally influenced. Electrical conductivity values were very low for all sites.

No correlation between nitrate-N and ammonium-N values was found. Ammonium-N fluctuated over time but no statistical correlation existed between ammonium-N and rainfall and temperature. Nitrate-N values also fluctuated over time and tended to increase with rainfall at the end of the sampling period. However, this increase was only significantly correlated with rainfall for surface layers in Paddocks 1 and 4 and at depth in Paddock 5. A small amount of nitrate-N movement down the profiles was detected. Low nitrate-N concentrations in January and February were probably the result of some rainfall in the preceding months, high temperatures at the time, and a flush of pasture growth that utilized the store of nitrate-N.

Drought had an effect on the study. Rainfall on the Northern Tablelands prevails during spring and summer. However, for this study rainfall from October to February was lower than the long-term average. Then rain fell with higher than average falls during March, April and May. When rainfall was low, no clear patterns were evident. After heavy rain, a clear response was observed for nitrate-N and this suggested that nitrification had slowed during the drier times. The response to rainfall of the chemical variants may have been different had rainfall been seasonal according to the long-term predictions.

One question raised from this study was why the response of nitrate to rainfall was limited to some management regimes (Paddocks 1 and 4 only). It might be expected that microbial activity was higher in Paddock 1 with pasture improvement. Paddock 4, a non-grazed native pasture, had a considerable nitrate-N response to rainfall compared with that of Paddock 3, the grazed native pasture. The data from this study did show that seasonal changes may have been missed in the paired-site study of Chapter 4. However, no clear patterns of seasonal variation in nitrate and ammonium concentrations emerged, apart from the response in some paddocks of nitrate to rainfall. To assist in the interpretation of these results, two incubation experiments (Chapter 6) were designed to further assess management, temperature and moisture effects on soils of the Northern Tablelands.