

AN ABSTRACT OF THE THESIS OF

Richard J. Roseberg for the degree of Master of Science in
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Rate and Soil Solution Constituents.

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Abstract approved: _____

Thomas L. Jackson

Chloride containing fertilizers are used to reduce the severity of take-all root rot of wheat in western Oregon and appear to reduce nitrification in moderately acid soils. Objectives of this study were to determine if nitrification is inhibited by the Cl ion, increasing soil solution ionic strength, or changes in pH. Soil incubation experiments were designed to measure inhibition of nitrification by Cl in soils having a pH gradient, a soil solution ionic strength gradient, or being of a different soil series. In addition to comparing nitrification rates resulting from salt amendments, soil solutions were recovered in order to evaluate

differences in soil solution constituents resulting from the added salt type, amount, and background soil pH. Overall nitrification was inhibited by Cl salts compared to SO_4 salts at equal soil solution ionic strength. Cl inhibition of nitrification disappeared as soil pH approached neutral. Nitrification rate increased as pH increased. Cl salt additions resulted in higher soil solution ionic strength than SO_4 additions. Soil solution constituents changed as salt additions increased, with higher concentrations of cations in solution when higher rates of salt were added. Levels of Ca and SO_4 were high enough to suspect CaSO_4 precipitation in samples where high rates of K_2SO_4 were added.

Chloride Fertilizer and Soil pH Effects on
Nitrification Rate and Soil Solution Constituents

by

Richard J. Roseberg

A THESIS

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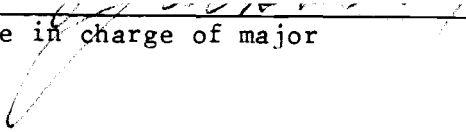
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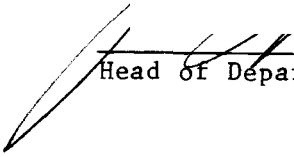
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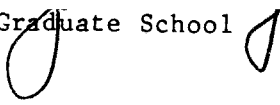
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CHLORIDE FERTILIZER AND SOIL PH EFFECTS ON NITRIFICATION
RATE AND SOIL SOLUTION CONSTITUENTS

INTRODUCTION

Literature Review

Application of chloride (Cl) containing fertilizers can increase grain yield in winter wheat (Triticum aestivum L.) subject to Take-all root rot, caused by Gaeumannomyces graminis var. tritici (Christensen et al., 1981; Christensen et al., 1982; Christensen and Brett, 1985; Taylor et al., 1983). Ammonium (NH_4) suppresses the fungus more than nitrate (NO_3) (Christensen and Brett, 1985; Macnish and Speijers, 1981; Smiley and Cook, 1973; Smiley, 1974; Taylor et al., 1983). Plants obtaining sufficient levels of NO_3 have lower disease severity compared to plants experiencing nitrogen (N) deficiency (Huber et al., 1968). Inhibition of nitrification with nitrapyrin enhanced NH_4 suppression of take-all (Huber et al., 1980). Liming moderately acid soils increases take-all severity, which may be due to increased nitrification (Christensen and Brett, 1985; Garrett, 1936; Taylor et al., 1983; Walker, 1975). Studies have suggested that addition of Cl inhibits nitrification as compared to SO_4 and that Cl additions release more NH_4 -N from the soil than SO_4 additions (Agarwal et al., 1971; Broadbent, 1965; Christensen and Brett, 1985; Hahn et al., 1942; Heilman, 1975). Ryan (1971)

indicated that KCl decreased ammonification compared to KH_2PO_4 or NaH_2PO_4 , and increased salt levels also decreased ammonification. He did not compare KCl to K_2SO_4 , however, and in his study differences in ammonification disappeared over time regardless of salt type or concentration. On an allophanic soil in Hawaii, NH_4 -N release was a direct function of salt concentration and length of incubation for a group of Cl salts (Singh et al., 1969). One report was found where KCl was used to reduce nitrification in a field production situation (Golden et al., 1979).

Objectives

Therefore, a series of laboratory and field studies were conducted with the following objectives:

1. To characterize nitrification rate in several soils amended with Cl or SO_4 salts.
2. To measure any interaction between soil pH and Cl inhibition of nitrification.
3. To characterize soil solution constituents from two soils treated differentially with Cl and SO_4 salts.

4. To compare differences among soil solution constituents in the two soils, relating these differences to differences in nitrification.
5. To determine if inhibition of nitrification is a specific Cl effect, a soil solution ionic strength effect, or both.

Objectives 1, 2, and 5 will be dealt with in the first article, while objectives 3 and 4 will be dealt with in the second article.

CHLORIDE SALT INHIBITION OF NITRIFICATION

ABSTRACT

Chloride (Cl) containing fertilizers (NH_4Cl , KCl) appear to reduce nitrification in moderately acid (pH 5.3-5.8) soils in western Oregon and are used to reduce the severity of take-all root rot of wheat. Objectives of this study were to determine if nitrification is reduced by the Cl ion, increasing soil solution ionic strength, changes in pH, changes in Mo availability, or a combination of the above. In every experiment, 100 ug $\text{NH}_4\text{-N/g}$ soil was added to 50g soil samples brought to 10 kPa matric potential and incubated for four weeks at 25°C. Samples were analyzed for 2M KCl extractable NH_4 , NO_3 , and NO_2 after 0, 3, 9, 14, and 28 days incubation. Cl ion and ionic strength effects on nitrification were evaluated by amending Woodburn pH 5.3 (Aquultic Argixeroll) and Nekia pH 4.8 (Xeric Haplohumult) soil samples with solutions of $\text{NH}_4\text{Cl} + \text{KCl}$ or $(\text{NH}_4)_2\text{SO}_4 + \text{K}_2\text{SO}_4$ having ionic strengths of 36, 73, 145, and 291 mM. In a duplicate experiment, soil solutions were recovered by centrifugation, ionic strength and pH were determined, and solutions were analyzed for NH_4 , NO_3 , Ca, Mg, K, SO_4 , Cl, P, Mo, Al, and Na. Nitrification rate was reduced by increasing ionic strength of the added solution for both Cl and SO_4 salts. Soil solution ionic strengths were higher where Cl salts were applied. Ca and SO_4 concentrations in soil solution indicate that the solubility product of CaSO_4 was exceeded with the more concentrated

$(\text{NH}_4)_2\text{SO}_4 + \text{K}_2\text{SO}_4$ solutions. At equivalent ionic strength in the recovered soil solution Cl salts inhibited nitrification more than SO_4 salts. Added Cl solutions having ionic strengths of 145 and 291 mM/L were as effective in inhibiting nitrification as the addition of 2 ug nitrapyrin/g soil. Interaction between added Cl and soil pH was assessed by measuring Cl effects in three soils. Woodburn (pH 5.3 to 6.7), Nekia (pH 4.8 to 6.5), and Willamette (Pachic Ultic Argixeroll, pH 5.5-6.2) soil samples were amended with Cl and SO_4 solutions (36 mM/L). Below a pH of 5.8-6.0, nitrification was inhibited by Cl salts. Above pH 6.0, nitrification rates were the same in Cl and SO_4 treated samples. Nitrification rates increased as pH increased. The addition of 1 ug Mo/g soil to the Woodburn pH 5.3 soil did not alter nitrification for samples receiving the eight Cl or SO_4 salt treatments. Addition of nitrapyrin (2 ug/g) stopped nitrification in all cases. Addition of dicyandiamid (DCD) to contribute 10% of added N slowed nitrification, but did not stop it. The decrease in nitrification with DCD was more pronounced at the higher soil pH.

LITERATURE REVIEW

Application of Cl fertilizer can reduce the severity of take-all root rot of wheat (Gaeumannomyces graminis var. tritici) (Christensen et al., 1981; Christensen et al., 1982; Christensen and Brett, 1985; Taylor et al., 1983). If Cl does inhibit nitrification, it would alter levels of NH_4 and NO_3 in the soil. A change in the NH_4/NO_3 ratio would alter the rhizosphere environment (Smiley, 1974). This change of rhizosphere environment could be altering the fungus' virulence or the plant's vigor and/or resistance to disease.

Previous studies have been conducted in which the nitrification and/or mineralization rate of Cl vs SO_4 amended soils were compared. Agarwal (1971), found that Cl salts of Na, K, and Ca were more effective than corresponding SO_4 salts in releasing $\text{NH}_4\text{-N}$ from an allophanic soil not receiving N additions. The comparisons were made for added Cl and SO_4 salt solutions at equal molar concentrations. Increasing salt solution molar concentration increased $\text{NH}_4\text{-N}$ levels, but decreased NO_3 levels. SO_4 salts promoted nitrification compared to Cl salts at equal molar concentrations of added salt. Broadbent (1971) found that increasing salt concentration increased mineralization in one

soil, but no definite trend occurred in two other soils. He also noted that additions of NH_4 salts increased mineralization to a much higher level than any of the other salts. Nitrification effects were not measured by Broadbent (1971).

In these studies, however, the composition of the soil solutions after addition of fertilizer salt solutions were not compared. Also, either ionic concentrations of the added Cl or SO_4 salt solutions were not equal, or else unequal amounts of N were added, both of which affect the mineralization rate and could alter the nitrification rate (Agarwal et al., 1971; Broadbent and Nakashima, 1965). Because take-all is suppressed in the presence of NH_4 vs NO_3 -N, (Christensen and Brett, 1985; Huber et al., 1980; MacNish and Speijers, 1981; Smiley and Cook, 1973; Smiley, 1974; Taylor et al., 1983) and is promoted in neutral vs acid pH soils, (Christensen and Brett, 1985; Garrett, 1936; Taylor et al., 1983; Walker, 1975) these reports suggest that application of Cl fertilizers may suppress take-all by inhibiting nitrification, resulting in a root environment with more NH_4 and less NO_3 .

One possible explanation for the increased nitrification with SO_4 as compared to Cl salt addition is the similarity in SO_4 and MoO_4 reactions with soil clays. It was postulated that added SO_4 exchanged with MoO_4 , increasing the level of available Mo in the solution. Little work has been done to quantify the

micronutrient requirements of nitrifying bacteria. However, it was recently determined that a nitrogen fixing bacteria, Rhizobium meliloti, infecting alfalfa on a moderately acid western Oregon agricultural soil (Woodburn series) responded to application of 1 ug Mo/ g soil (Doerge et al., 1985). If nitrifying bacteria also respond to added Mo, perhaps adding SO_4 is simply increasing Mo availability and alleviating a Mo deficiency experienced by the nitrifying organisms.

A series of experiments were designed to try to resolve the unknown effects of salt additions on nitrification. The objectives of these studies were as follows:

1. To characterize nitrification rate in several soils amended with Cl or SO_4 salts.
2. To determine if inhibition of nitrification is a specific Cl effect, a soil solution ionic strength effect, or both.
3. To measure any interaction between soil pH and Cl inhibition of nitrification.
4. To determine if application of Mo alters Cl or SO_4 salt effects on nitrification.

MATERIALS AND METHODS

Ionic Strength Comparisons

A laboratory soil incubation experiment was conducted using samples of unfertilized Woodburn silt loam (fine-silty, mixed, mesic Aquultic Argixeroll), pH 5.5, and recently fertilized Nekia silty clay loam (clayey, mixed, mesic Xeric Haplohumult), pH 4.8. Soil samples (50g) were placed into Nalgene 125ml LPE plastic bottles and amended with NH_4Cl or $(\text{NH}_4)_2\text{SO}_4$ salt solutions to provide 100 ug $\text{NH}_4\text{-N/g}$. Treatments were designed so that added solutions had equal ionic strength at four levels. This was achieved by adding KCl or K_2SO_4 to the NH_4Cl or $(\text{NH}_4)_2\text{SO}_4$ solutions, respectively as shown in Table 1.

Solution ionic strengths were calculated using the van't-Hoff equation and verified using a Wescor vapor pressure osmometer (Model 5100C). The experiment was repeated with addition of 1 ug Mo/g soil to all treatments, a level found to stimulate microorganisms in N fixation studies (Doerge et al., 1985).

All treatments were replicated, maintained at 10 kPa matric potential, and incubated at 25° C. Samples were sacrificed at 0, 3, 9, 14, and 28 days, extracted with 75 ml of 2M KCl solution, filtered, and analyzed for NH_4 , NO_3 , and NO_2 colorimetrically using an autoanalyzer (Scientific Instruments Corp., Pleasantville,

NY.) Nitrate was measured after reduction to NO_2 by cadmium reduction column and NH_4 was measured using sodium salicylate and nitroprusside.

Table 1. Composition and ionic strength of added salt solutions giving four rates of Cl or SO_4 salts, all containing equivalent amounts of $\text{NH}_4\text{-N}$.

Added solution ionic strength mM/L	Contribution to ionic strength mM/L	
Total	$\text{NH}_4\text{Cl} + \text{KCl}$	$(\text{NH}_4)_2\text{SO}_4 + \text{K}_2\text{SO}_4$
36.4	36.4 + 0	27.5 + 8.9
72.7	36.4 + 36.4	27.5 + 45.2
145.4	36.4 + 109.0	27.5 + 117.9
290.8	36.4 + 254.4	27.5 + 263.3

In order to analyze the soil solution itself, a separate experiment was conducted in which the Woodburn pH 5.3 and Nekia pH 4.8 soil samples were subjected to the same eight treatments, both with and without Mo, and incubated for 15 days. Soil solutions were then recovered by centrifugation, as follows: Acid washed pyrex wool filters were placed in the bottom of 10 ml plastic, porous bottom test tubes. Soils were then packed into the test tubes, and the test tubes were placed into centrifugation tubes. Tubes were centrifuged for 50 minutes at 15,000 RPM, which resulted in 2-4 ml solution collecting in the bottom of each tube. This method was

similar to one used in a previous soil solution study (Reynolds, 1984). Solution pH was immediately determined with a glass electrode, and samples from a given treatment were bulked for analysis of ionic strength and constituent ions. Ionic strength was determined with a Wescor vapor pressure osmometer (Model 5100C).

Data were subjected to statistical analysis, and NO_3 accumulation was regressed on time and fitted to the following regression model (Engelstad 1968):

$$Y = a + b_1 t_1 + b_2 t_2 + b_n t_n$$

Linear regression coefficients and incubation time for a particular N source - ionic strength combination are represented by b_i and t_i , respectively. Regression coefficients represent net rate of nitrification, measured as $\mu\text{g NO}_3\text{-N/ g soil * day}$. NH_4 levels were measured to compute accumulation of inorganic N in the various samples.

Soil pH- N Source Interactions.

Three soil series which had a variable pH due to past liming treatments were chosen to evaluate Cl effects on nitrification with changing pH. The soils used were the Woodburn silt loam (pH 5.4, 5.8, 6.3, 6.7); Nekia silty clay loam (pH 4.8, 5.5, 6.5) and Willamette silt loam (fine-silty, mixed, mesic Pachic Ultic Argixeroll, pH 5.5, 5.8, 6.2). Soils were amended with the lowest

level of NH_4Cl and $(\text{NH}_4)_2\text{SO}_4$ salts (36 mM), incubated, extracted with KCl, and analyzed for NH_4 and NO_3 as described earlier. Because of the rapid rate of nitrification found in some of these soils, NH_4 sometimes became limiting, resulting in curvilinear NO_3 accumulation with time. These responses were fitted to a quadratic function of the form:

$$Y = a + b_{1i}t_{1i} + b_{11i}t_{1i}^2 + b_{nn}t_n + b_{nnt_n}^2$$

Linear and quadratic regression coefficients and time are represented by b_{1i} , b_{11i} , and t_{1i} , respectively. Statistical comparison of curved lines was done using the Bonferroni joint interval estimate, which gives simultaneous confidence intervals for the b_{1i} and b_{11i} coefficients in the quadratic equation (Neter, et al., 1983).

Because the nitrification rate was linear in some soils and curvilinear in others, comparison between soils was made during the time period that the nitrification rate was linear. Thus, Cl, pH, and Cl X pH interaction effects could be compared for different soils during a period when NH_4 was not limiting.

Series Nitrification Rate Characterization.

In addition to the three soils which had a range in soil pH, two other soils which are commonly used for wheat production were

treated with the 36 mM level of added Cl and SO₄ salts to determine if Cl inhibited nitrification. These were samples of a Newberg fine sandy loam (coarse-loamy, mixed, mesic Fluventic Ultic Haploxeroll, pH 6.2) and Cloquato silt loam (coarse-silty, mixed, mesic Cumulic Ultic Haploxeroll, pH 6.4). Results from these soils were subjected to the quadratic statistical analysis shown above.

Commercial Nitrification Inhibitor Comparison

In a concurrent experiment, 2 mg nitrapyrin/100 mg added N (2 ug nitrapyrin/g soil) was added to the Woodburn pH 5.3 soil samples receiving Cl or SO₄ salt amendments at four ionic strengths. This was done to compare the relative effectiveness of any inhibition of nitrification due to the fertilizer treatments with that of a commercial nitrification inhibitor. Another nitrification inhibitor, dicyandiamide, [H₂NC(NH)NHCN, DCD], was added to Nekia pH 4.8, 5.5, 6.5, and Woodburn pH 5.3, 5.8, 6.3, and 6.7 samples treated with (NH₄)₂SO₄. DCD was applied at a rate of 10% of added N as DCD, to compare any effects on nitrification between the salts and the commercial inhibitor. Due to the low solubility of the pure DCD material, warming and vigorous swirling for 30 minutes was needed to dissolve the material.

RESULTS AND DISCUSSION

Ionic Strength Comparisons.

Differences in rates of nitrification between Cl and SO₄ salt amendments were found for both soils as shown in Fig. 1 and 2 and Table 2. Nitrification rates for Cl treatments were lower than rates for comparable SO₄ treatments at all levels of added salt for both soils. Within the Cl or SO₄ treatments, nitrification rates decreased with increased ionic strength of the added salt solution. No stimulation of nitrification was observed due to added Mo in this experiment.

As ionic strength of added solutions increased, the difference between soil solution ionic strength and added solution ionic strength became larger and larger, especially in the case of the SO₄ salts (Table 3). Although Cl salts inhibited nitrification more than SO₄ salts at equal added ionic strength, soil solution ionic strength at equilibrium was also much greater for Cl than SO₄ salts. This suggested that the inhibition of nitrification by Cl salts could have been due strictly to the higher soil solution ionic strength resulting when Cl salts were applied. To separate ionic strength effects from specific Cl effects, the measured soil solution ionic strengths were plotted against rate of nitrification (Fig. 3 and 4). If the inhibition of nitrification were due strictly to ionic strength of the soil

solution, the points describing nitrification rates for SO_4 and Cl salt amendments should all have fallen along the same line. Because they do not fall along the same line for either soil, it can be seen that at any given soil solution ionic strength, Cl salts resulted in a lower rate of nitrification than SO_4 salts. Within either the Cl or SO_4 salts, nitrification rate decreased as ionic strength increased.

For two widely different soils, increasing rates of Cl or SO_4 salts decreased the nitrification rate, and the effect was due to both the increasing salt concentration and a specific effect of the Cl ion inhibiting nitrification even where soil solution ionic strength was equal to that of SO_4 treated samples.

Measurements of NH_4 during the incubations indicated that mineralization was occurring to a small degree. Total inorganic N levels increased only slightly with increased salt levels, the most extreme case being the Woodburn soil amended with Cl salts, where total inorganic N increased roughly 15% from the 36mM to 291mM added salt rate. Inorganic N increases for the other cases were much less. High levels of inorganic N in the Nekia soil by the end of the incubation period were probably due to the fact that the field from which this soil was taken had just previously received a large application of nitrogen. This added N, though not measured as inorganic N ($\text{NH}_4 + \text{NO}_3$) by KCl extraction at the start of the study, could easily become mineralized by microbial activity, adding a large dose of inorganic N to the system during incubation.

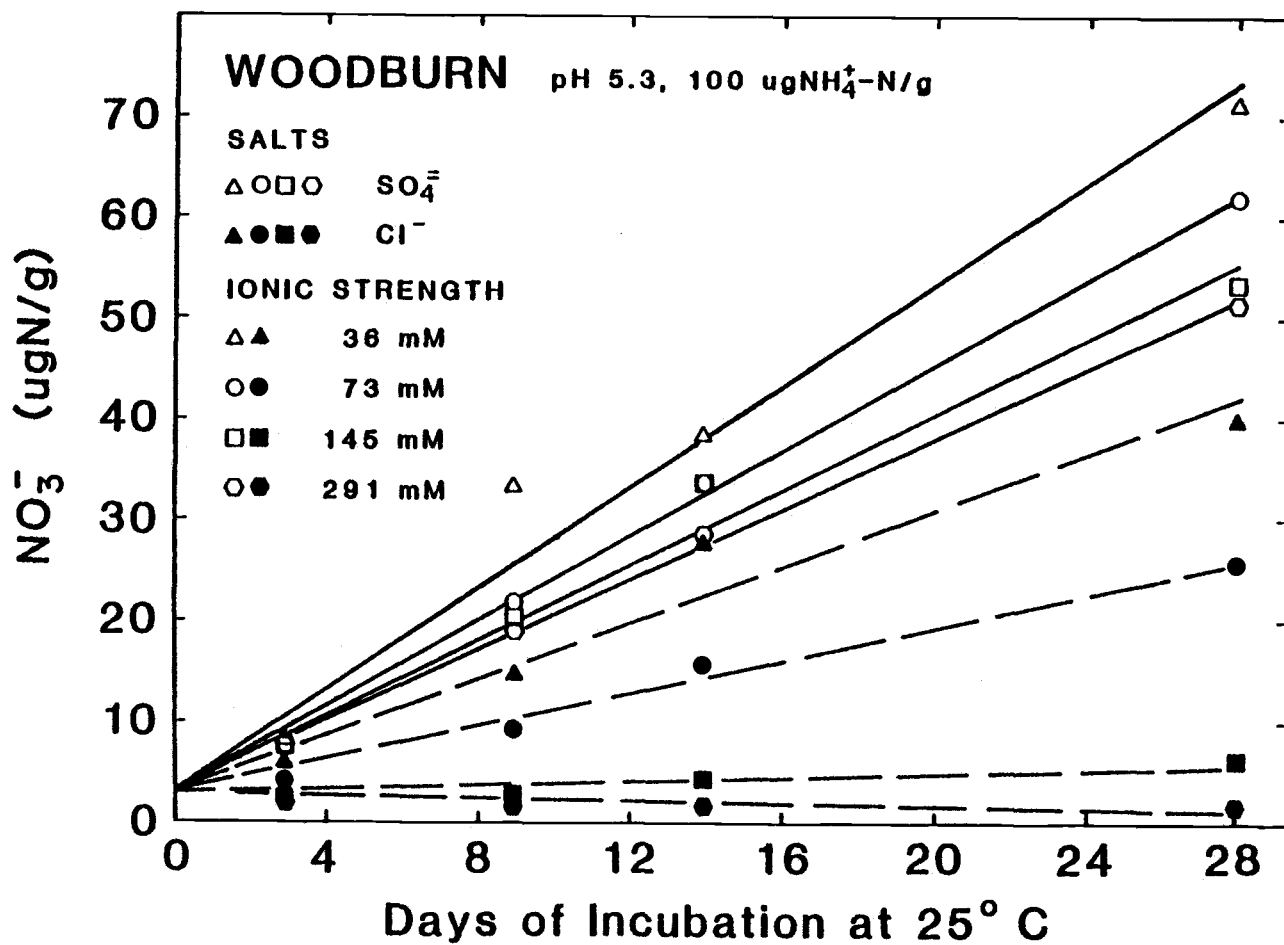


Figure 1. Effects of Cl or SO_4 salts at four ionic strengths on nitrification rate in Woodburn silt loam samples, pH 5.3.

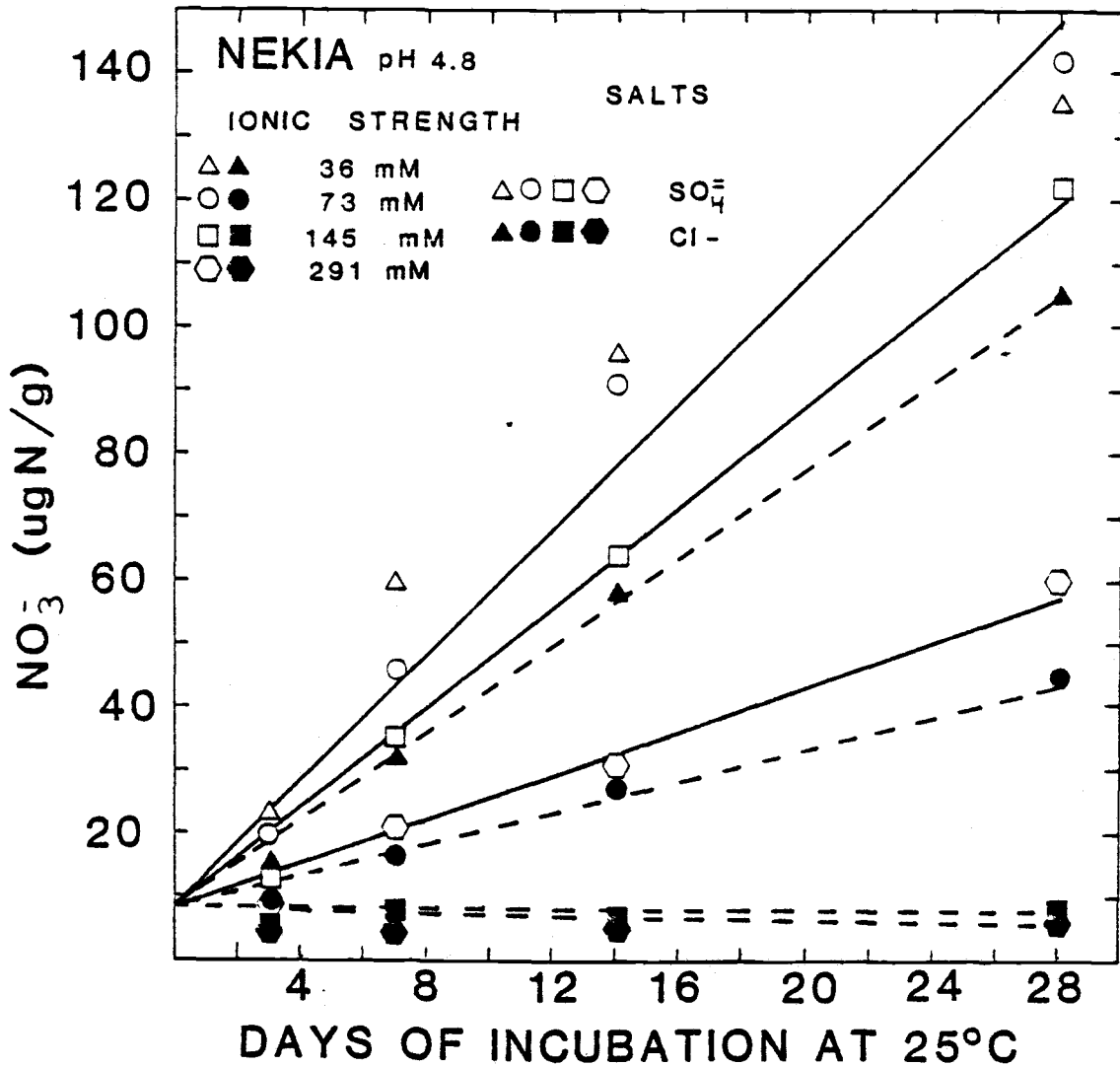


Figure 2. Effects of Cl or SO₄ salts at four ionic strengths on nitrification rate in Nekia silty clay loam samples, pH 4.8.

Table 2. Nitrification rates as affected by Cl and SO₄ salt amendments.

Added solution ionic strength (mMol/L)	$\Delta \text{NO}_3 / \Delta t$ (b _i) ug N/g soil * day			
	Woodburn pH 5.3		Nekia pH 4.8	
	Cl	SO ₄	Cl	SO ₄
36.4	1.40	2.52	3.43	4.94
72.7	0.82	2.12	1.27	4.95
145.4	0.10	1.88	-0.06	3.96
290.8	-0.07	1.75	-0.17	1.73
Constant =	2.815		9.286	
R ² =	0.98		0.98	
MSE =	8.728		33.685	
SED =	9.032 * 10 ⁻²		0.18015	
LSD(.001) =	0.31		0.62	
LSD(.01) =	0.24		0.48	
LSD(.05) =	0.18		0.36	

Table 3. Soil solution ionic strength as influenced by Cl and SO₄ salt amendments.

Added solution ionic strength (mMol/L)	Soil solution ionic strength (mMol/L)			
	Woodburn		Nekia	
	Cl	SO ₄	Cl	SO ₄
36.4	36	31	56	50
72.7	51	39	59	48
145.4	91	54	101	58
290.8	185	82	173	89

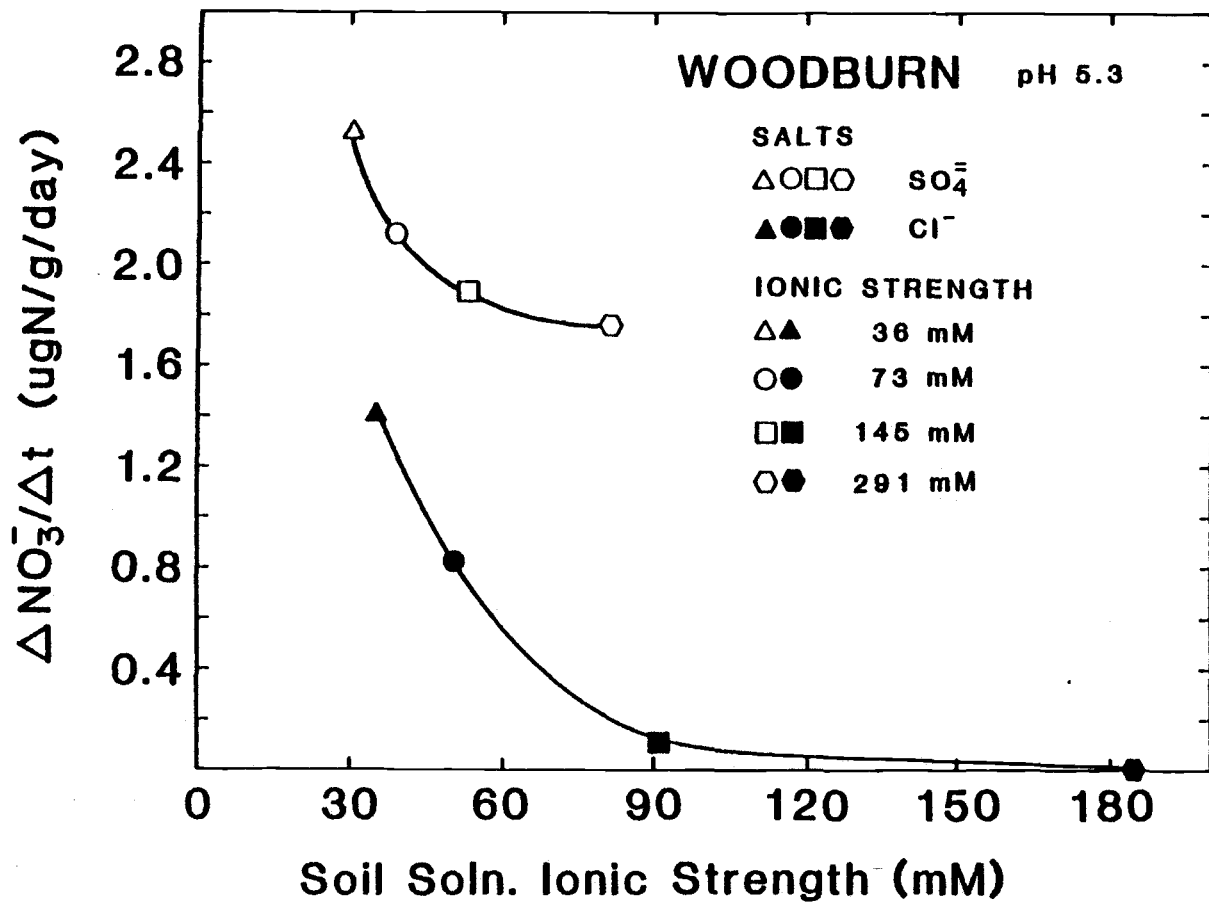


Figure 3. Nitrification rates in Woodburn silt loam samples as influenced by soil solution ionic strength resulting from Cl and SO₄ treatments.

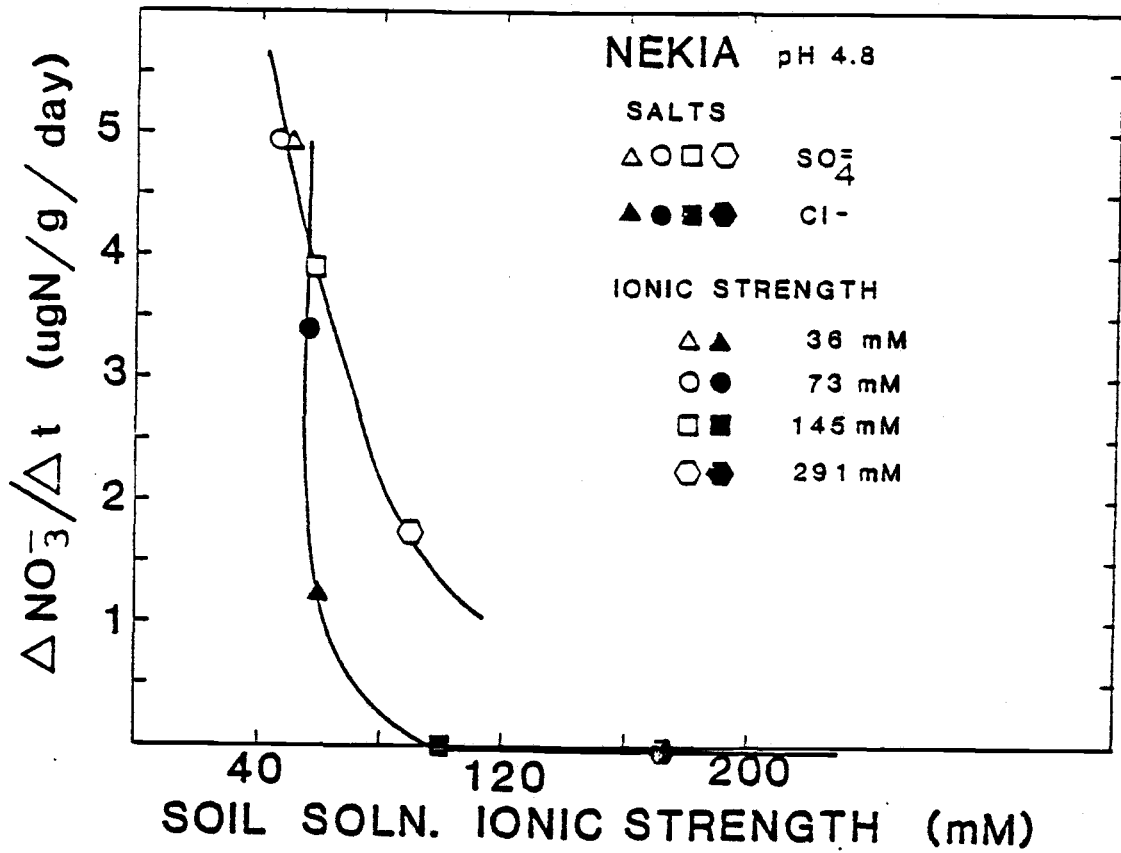


Figure 4. Nitrification rates in Nekia silty clay loam as influenced by soil solution ionic strength resulting from Cl and SO₄ treatments.

Soil pH-N Source Interactions

Nitrification rates for the three soils with pH gradients (Woodburn, Nekia, Willamette) are shown in Fig. 5, 6, and 7. Statistical comparisons were made for the entire incubation period, which sometimes resulted in a curvilinear response, and for the linear portion of the incubation, that is, during the period when NH_4 was not limiting (Table 4, 5, and 6). In each case the rate of nitrification in NH_4Cl amended soils was less than or equal to the rate in $(\text{NH}_4)_2\text{SO}_4$ amended soils. For all three soils there was no difference in nitrification rate between NH_4Cl and $(\text{NH}_4)_2\text{SO}_4$ amendments when the pH was 5.8 or above for the curvilinear response curves. Linear portion comparisons showed inhibition of nitrification by Cl salts when soil pH was less than 5.8 for Woodburn and Willamette soils, but Cl salts inhibited nitrification for the entire pH range in Nekia soils. As anticipated, nitrification rate increased with increasing soil pH.

Because NH_4 levels were measured throughout the incubation period, total levels of inorganic N could be determined. Overall, changes in pH had little effect on amount of inorganic N present, indicating that pH did not greatly influence mineralization rate.

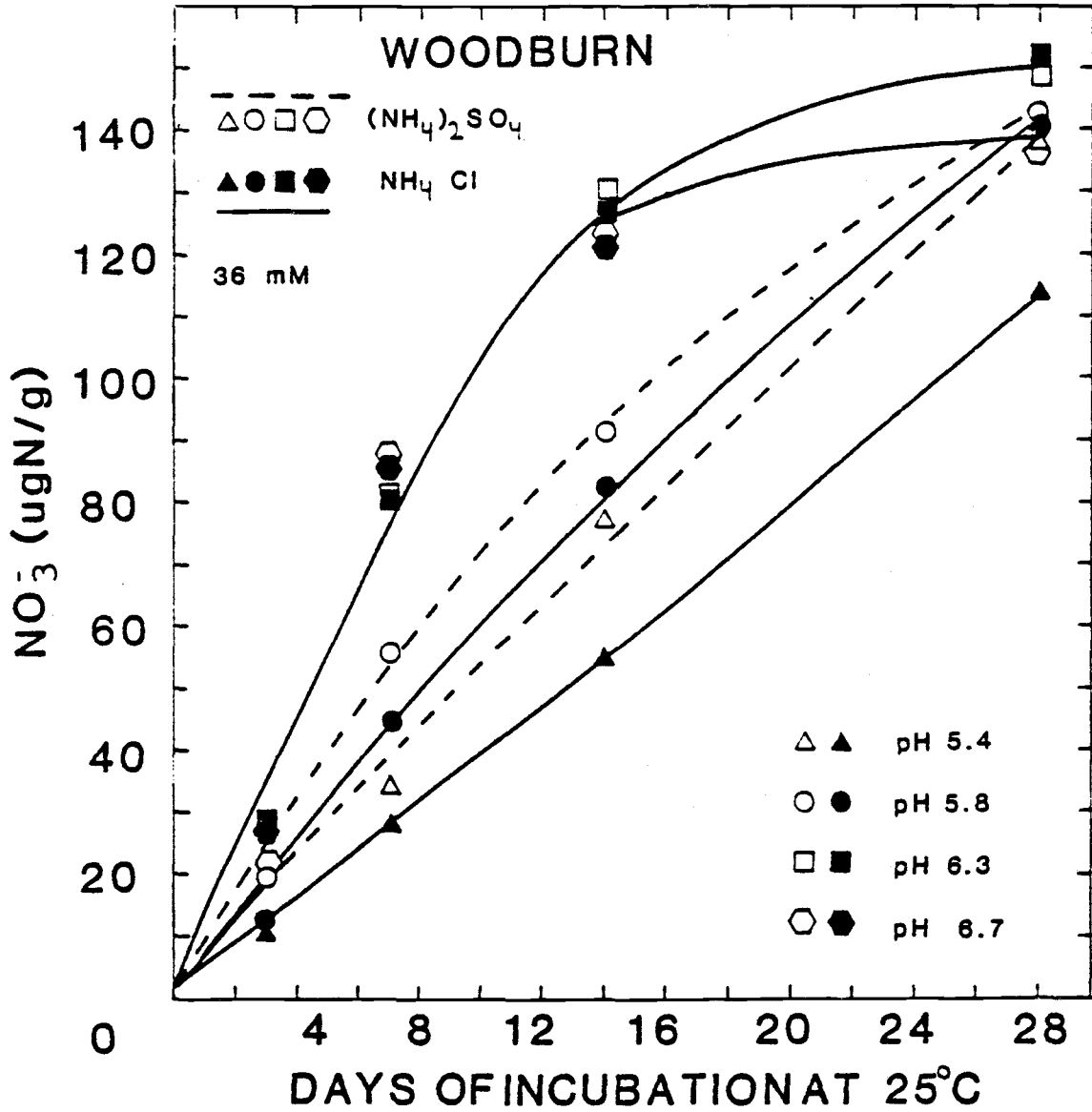


Figure 5. Effects of pH on nitrification rate in Woodburn silt loam samples amended with 36 mM/L Cl or SO₄ salt solutions.

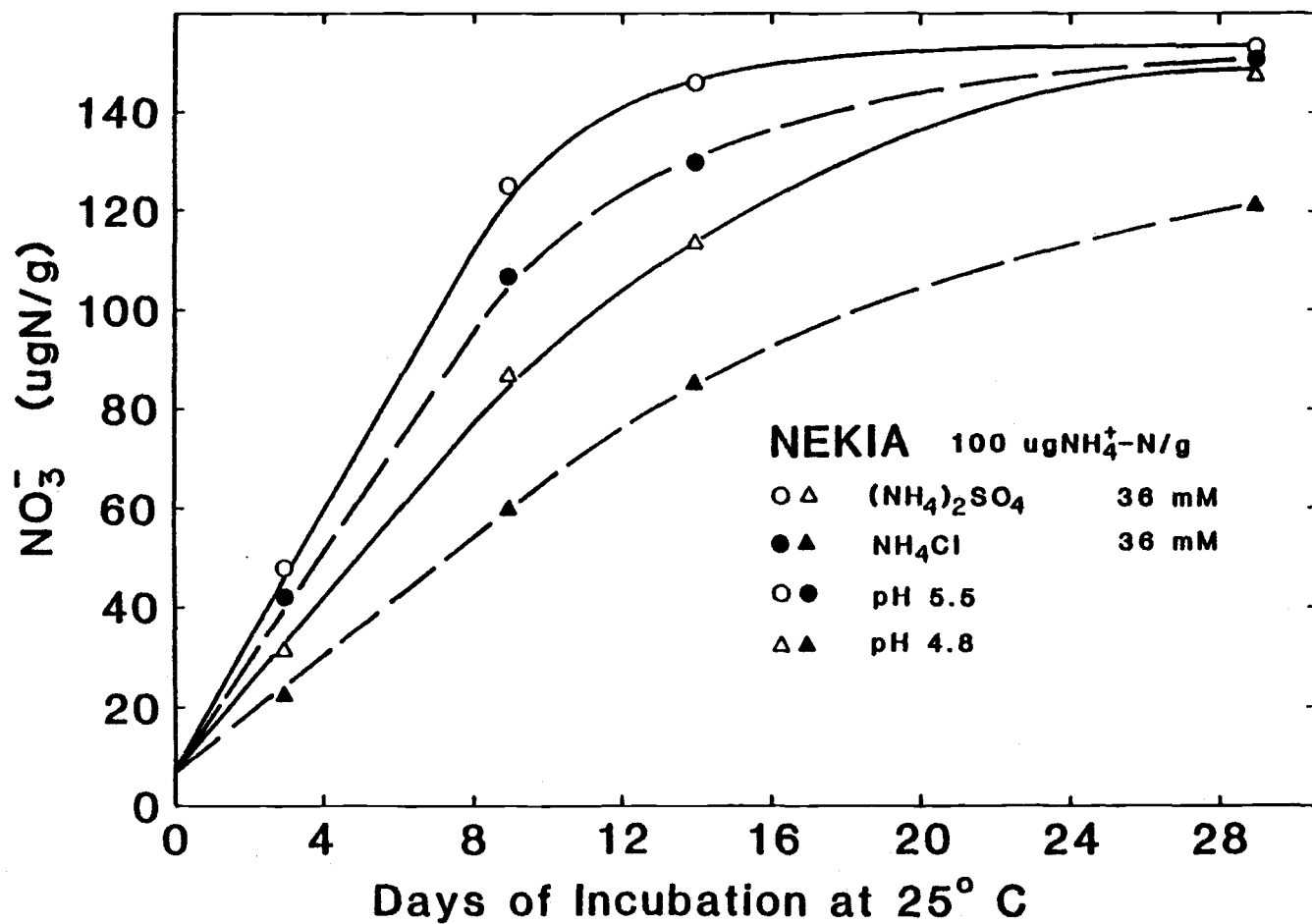


Figure 6. Effects of pH on nitrification rate in Nekia silty clay loam samples amended with the 36 mM/L Cl or SO_4 salt solutions.

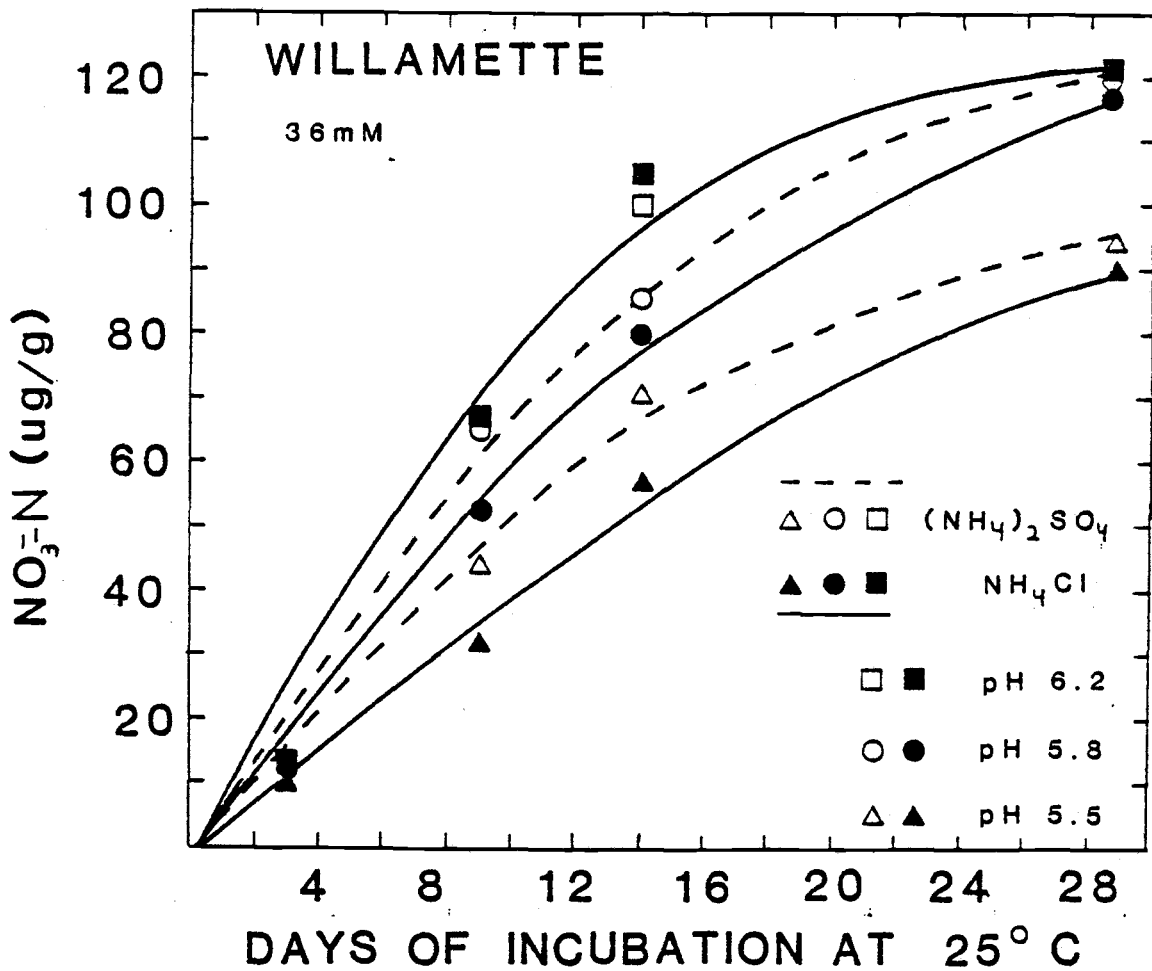


Figure 7. Effects of pH on nitrification rate in Willamette silt loam samples amended with the 36 mM/L Cl or SO_4 salt solutions.

Table 4. Nitrification rate as affected by N-source and soil pH combinations, Woodburn silt loam.

Soil pH	Anion	Quadratic Regression Terms*			Sign.®
		a	+ b _i t	+ b _{ii} t ²	
5.4	Cl	2.6	3.44	0.0196	a
5.4	SO ₄	2.6	5.18	-0.0116	a
5.8	Cl	2.6	6.23	-0.0445	ab
5.8	SO ₄	2.6	7.86	-0.1017	b
6.3	Cl	2.6	12.39	-0.2518	c
6.3	SO ₄	2.6	12.77	-0.2689	c
6.7	Cl	2.6	12.51	-0.2733	c
6.7	SO ₄	2.6	12.71	-0.2836	c

Soil pH	Anion	Linear Regression Terms#		Significance\$
		a	+ b _i t	
5.4	Cl	5.8	3.40	a
5.4	SO ₄	5.8	4.83	b
5.8	Cl	5.8	5.43	bc
5.8	SO ₄	5.8	6.31	c
6.3	Cl	5.8	9.02	d
6.3	SO ₄	5.8	9.23	d
6.7	Cl	5.8	8.82	d
6.7	SO ₄	5.8	8.93	d

* $R^2 = 0.99$ for multiple quadratic regression lines having a common intercept.

@ Treatments followed by different letters have significantly different nitrification response curves by the Bonferroni joint interval estimate method at $p = 0.01$.

$R^2 = 0.97$ for multiple linear regression lines having a common intercept and covering only the linear portion of the response curve.

\$ Treatments followed by different letters have significantly different nitrification rates for the linear portion of the response curve at $p = 0.01$.

Table 5. Nitrification rate as affected by N-source and soil pH combinations, Nekia silty clay loam.

Soil pH	Anion	Quadratic Regression Terms*			Sign.®
		a	+ b _i t	+ b _{ii} t ²	
4.8	Cl	34.9	6.84	-0.1000	a
4.8	SO ₄	34.9	10.26	-0.1865	b
5.5	Cl	34.9	12.99	-0.2784	c
5.5	SO ₄	34.9	15.54	-0.3687	d
6.5	Cl	34.9	15.31	-0.3550	d
6.5	SO ₄	34.9	16.47	-0.3946	d
		Linear Regression#		Significance\$	
		a	+ b _i t		
4.8	Cl	6.5	5.81	a	
4.8	SO ₄	6.5	8.78	b	
5.5	Cl	6.5	11.18	c	
5.5	SO ₄	6.5	13.19	d	
6.5	Cl	6.5	13.83	e	
6.5	SO ₄	6.5	14.40	f	

* R² = 0.99 for multiple quadratic regression lines having a common intercept.

@ Treatments followed by different letters have significantly different nitrification response curves by the Bonferroni joint interval estimate method at p = 0.01 .

R² = 0.99 for multiple linear regression lines having a common intercept and covering only the linear portion of the response curve.

\$ Treatments followed by different letters have significantly different nitrification rates for the linear portion of the response curve at p = 0.01.

Table 6. Nitrification rate as affected by N- source and soil pH combinations, Willamette silt loam.

Soil pH	Anion	Quadratic Terms*			Sign.®
		a	+ $b_i t$	+ $b_{ii} t^2$	
5.5	Cl	-2.0	4.64	-0.0513	a
5.5	SO ₄	-2.0	6.35	-0.1037	a
5.8	Cl	-2.0	7.09	-0.1026	ab
5.8	SO ₄	-2.0	8.27	-0.1397	b
6.2	Cl	-2.0	9.77	-0.1892	b
6.2	SO ₄	-2.0	9.37	-0.1766	b

Soil pH	Anion	Linear Regression#		Significance\$
		a	+ $b_i t$	
5.5	Cl	-2.4	3.90	a
5.5	SO ₄	-2.4	4.99	b
5.8	Cl	-2.4	5.73	bc
5.8	SO ₄	-2.4	6.43	cd
6.2	Cl	-2.4	7.43	d
6.2	SO ₄	-2.4	7.15	d

* $R^2 = 0.97$ for multiple quadratic regression lines having a common intercept.

® Treatments followed by different letters have significantly different nitrification response curves by the Bonferroni joint interval estimate method at $p = 0.01$.

$R^2 = 0.97$ for multiple linear regression lines having a common intercept and covering only the linear portion of the response curve.

\$ Treatments followed by different letters have significantly different nitrification rates for the linear portion of the response curve at $p = 0.01$.

These results indicate that in some manner, at moderately acid soil pH, Cl was exerting a detrimental influence upon the nitrifying organisms. Because this specific Cl effect usually disappeared as the pH approached neutrality, the change in soil environment due to pH rise must be favorable enough to allow the nitrifying organisms to endure or avoid the conditions brought on by added Cl. The result that nitrification rate is the same at slightly acid pH regardless of whether Cl or SO_4 is applied could explain the observation that take-all root rot is not affected by Cl additions in slightly acid soils, only in moderately acid soils (Christensen and Brett, 1985; Taylor et al., 1983). This would lend credence to the idea that Cl application does not directly affect the take-all fungus, but sometimes alters the form of N in the soil, which in turn affects the environment at the root surface, the site of fungus invasion.

In addition, any use of Cl fertilizers strictly for inhibition of nitrification in cropping situations where take-all is not a problem would have to be carefully considered, realizing that soil pH and salt concentration would have a large influence on the success of such an application. In moderately acid soils, and especially if the fertilizer is banded, application of NH_4Cl could prove beneficial where loss of N through NO_3 leaching or denitrification is a problem.

Series Nitrification Rate Characterization

Nitrification results for the Newberg and Cloquato soil samples are shown in Fig. 8 and Table 7. Both of these soils were above pH 6.0, and although the nitrification rate tended to be lower with NH_4Cl , there was no significant difference between treatments in either soil for either the entire response curve or the linear portion. This lack of inhibition at these pH's is consistent with results for Woodburn and Willamette soils above pH 6.0. Further study on samples with a pH gradient would be necessary to determine the pH at which nitrification is inhibited by Cl in these soils.

The five soils exhibited a consistent trend in Cl effects on nitrification rate where a pH gradient existed. In general, nitrification rate increased as pH increased. Nitrification rate in Cl salt amended soils was less than or equal to the rate in SO_4 amended soils. The magnitude of nitrification inhibition by Cl salts decreased as pH increased.

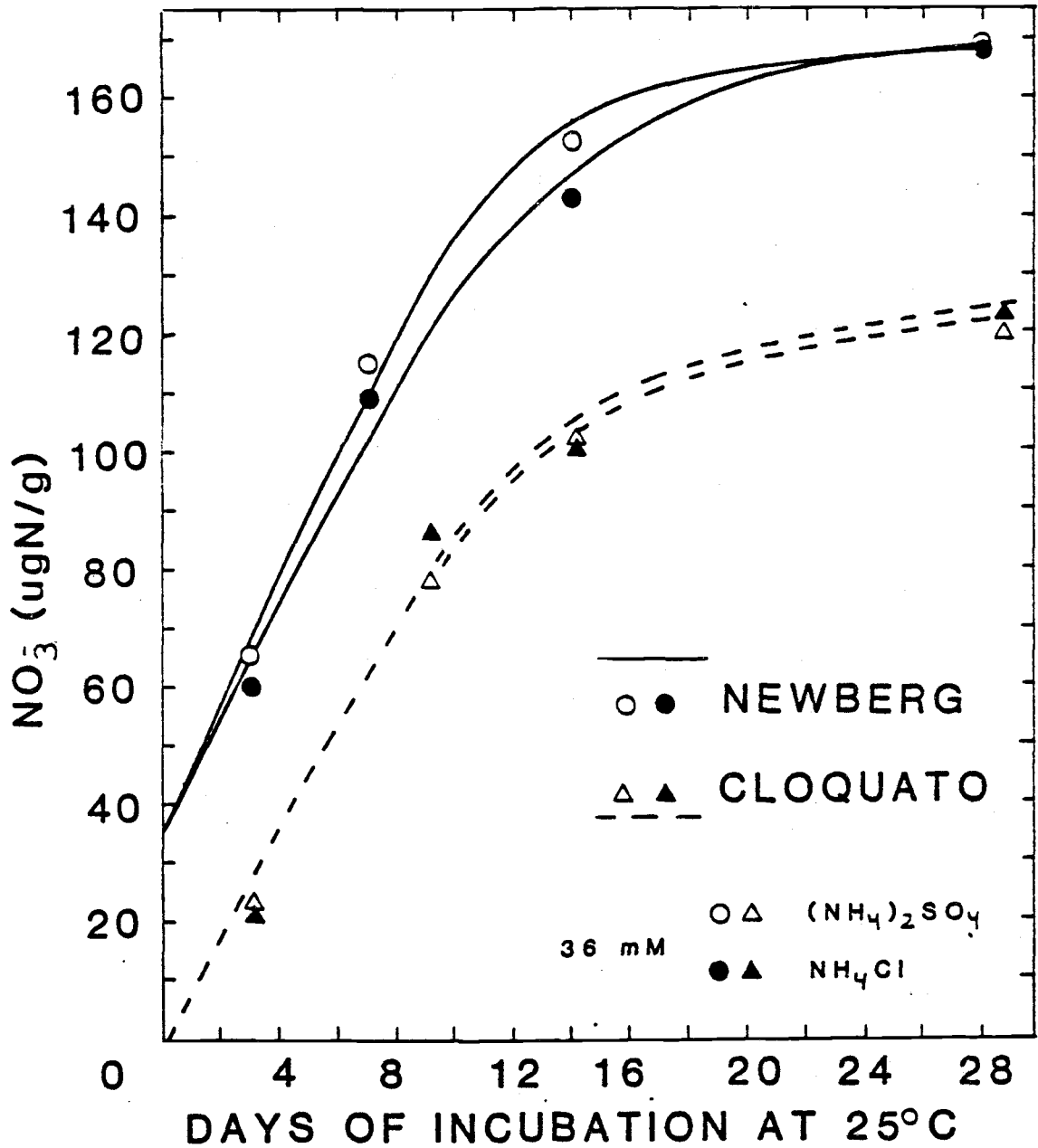


Figure 8. Nitrification rate for Newberg fine sandy loam and Cloquato silt loam soil samples amended with 36 mM/L Cl or SO₄ salt solutions.

Table 7. Nitrification rate as affected by N-source and soil series combinations.

Soil Series	Anion	Quadratic Regression Terms*			Sign. @
		a	+ $b_i t$	+ $b_{ii} t^2$	
Newberg pH 6.2	Cl	33.8	11.34	-0.2344	a
"	SO ₄	33.8	12.65	-0.2805	a
Cloquato pH 6.4	Cl	-2.0	10.77	-0.2232	a
"	SO ₄	-2.0	10.53	-0.2180	a
		Linear Regression #			
		a	+ $b_i t$		Significance \$
Newberg pH 6.2	Cl	32.7	10.65		a
"	SO ₄	32.7	11.61		a
Cloquato pH 6.4	Cl	5.4	7.33		a
"	SO ₄	5.4	7.20		a

* $R^2 = 0.99$ (Newberg) and 0.97 (Cloquato) for multiple quadratic regression lines having a common intercept for each soil.

@ Treatments followed by different letters have significantly different nitrification response curves by the Bonferroni joint interval estimate method at $p = 0.01$ (Comparing within soils only).

$R^2 = 0.99$ (Newberg) and 0.95 (Cloquato) for multiple linear regression lines having a common intercept for each soil and covering only the linear portion of the response curve.

\$ Treatments followed by different letters have significantly different nitrification rates ($p=0.01$) for the linear portion of the response curve (Comparing within soils only).

Commercial Nitrification Inhibitor Comparison

Dicyandiamide (DCD) effects on nitrification in Woodburn and Nekia soils having a pH gradient is shown in Fig. 9 and 10. Response curves for samples not receiving DCD were reproduced from Fig. 5 and 6 to compare the effect of added DCD. Nitrification rate in Woodburn and Nekia samples during the linear portion of the response curve (when NH_4 was not limiting) is shown in Table 8. The nitrification rate for DCD treated samples was significantly lower at $p = 0.01$ than untreated samples in all cases in both soils. DCD treatment did not stop nitrification, but it did slow it down. In contrast to Cl treatments, the inhibitory effect was most pronounced at the higher pH's. Nitrapyrin stopped nitrification completely for all samples for the duration of the experiment.

In this experiment, DCD did not inhibit nitrification as effectively as nitrapyrin. However, the heating and mixing of the DCD solution prior to mixing with fertilizer solution in the soil could have had a detrimental effect which would not be realized in commercial situations where DCD would be prilled with urea or applied in suspension with urea and $(\text{NH}_4)_2\text{SO}_4$. As the pH increased, DCD became more effective. Therefore, its benefit may be in slowing down nitrification in situations where high nitrification rates are expected. Given the relative ineffectiveness of Cl inhibition of nitrification and Cl suppression of take-all at pH 6.5 (Christensen and Brett, 1985), DCD may prove to be effective in suppressing take-all in slightly acid soils.

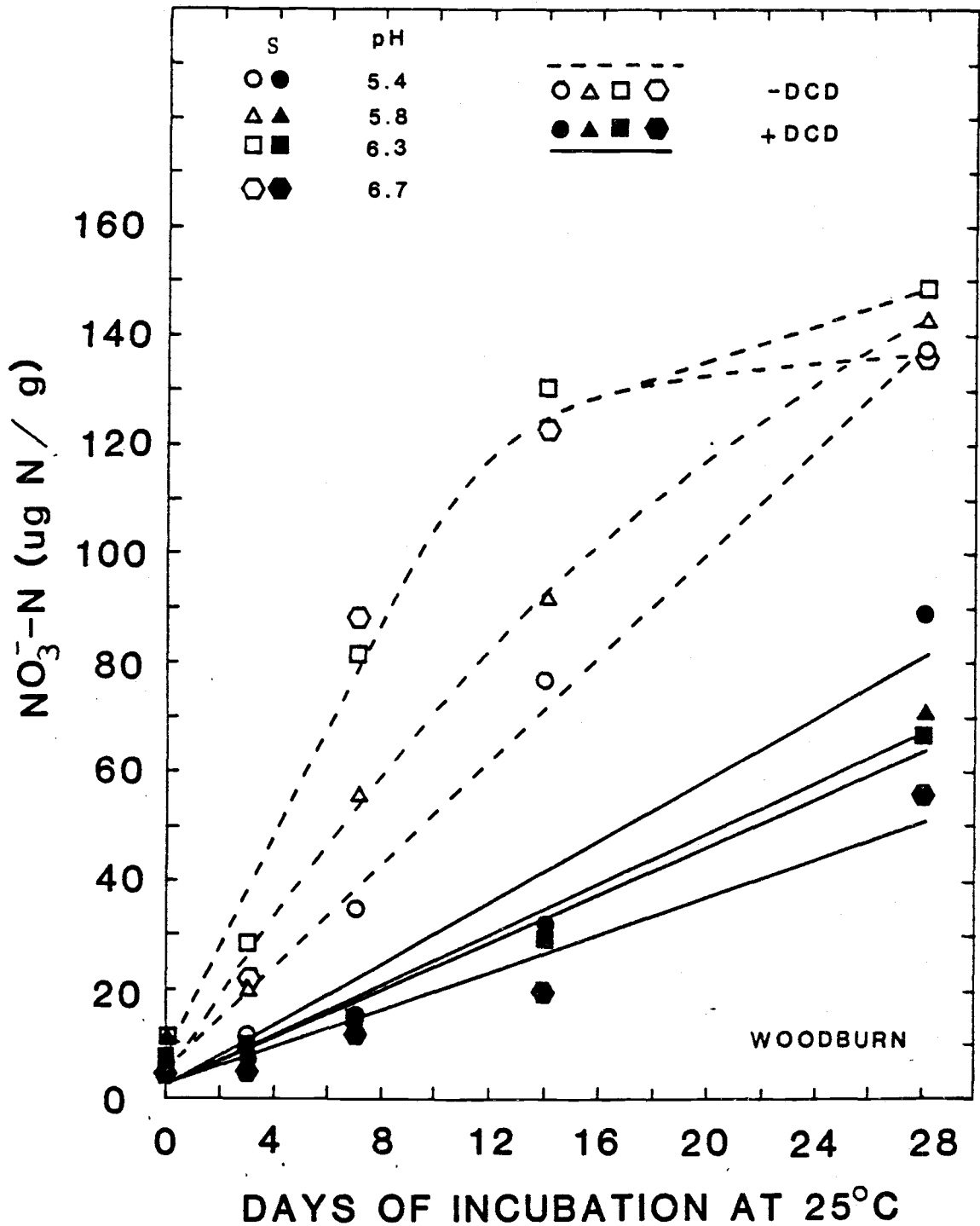


Figure 9. Effect of DCD and soil pH on nitrification rate in Woodburn silt loam samples amended with the 36 mM/L SO_4 salt solution.

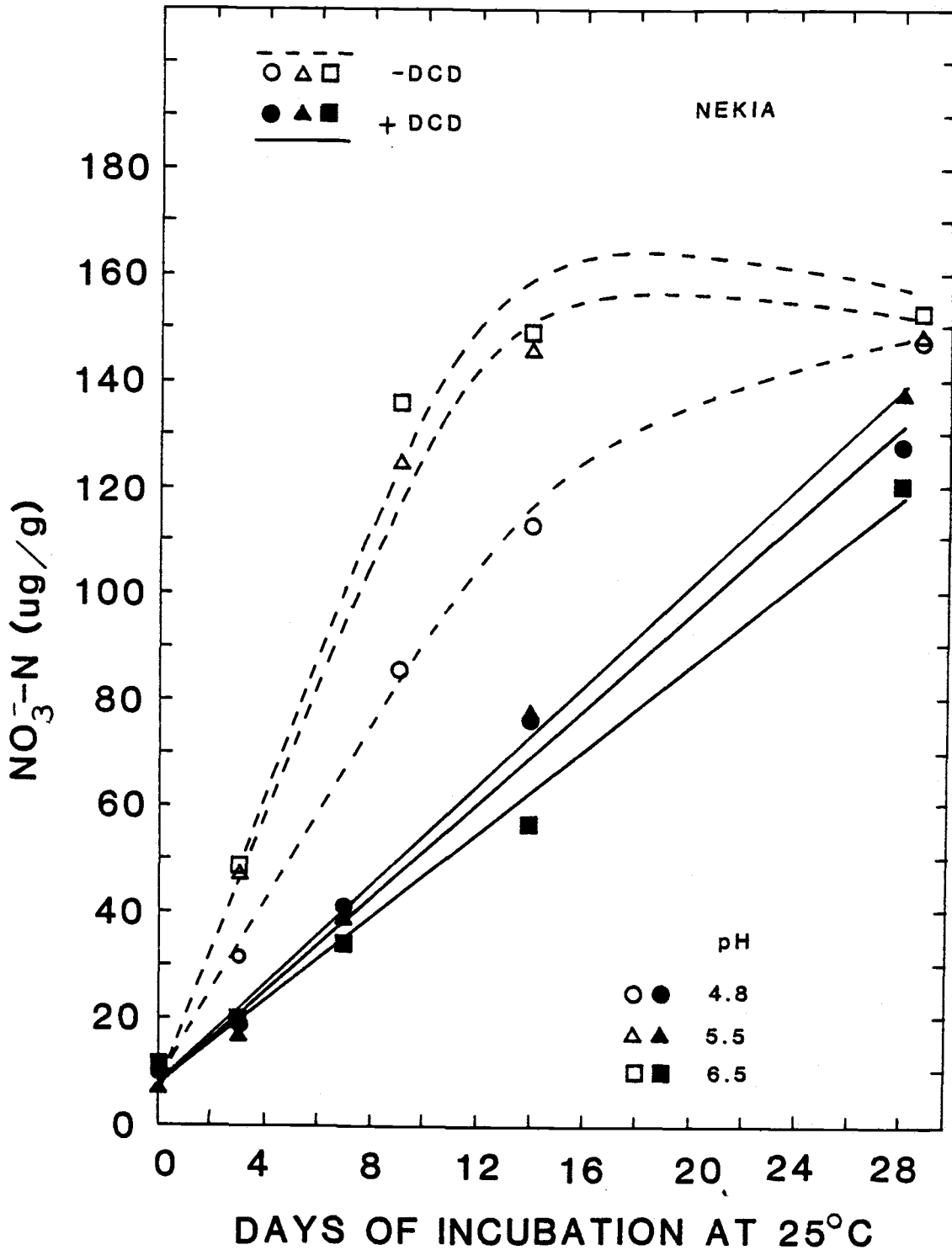


Figure 10. Effect of DCD and soil pH on nitrification rate in Nekia silty clay loam samples amended with the 36 mM/L SO₄ salt solution.

Table 8. Dicyandiamide effects on nitrification rates in Nekia and Woodburn soils having a pH gradient and amended with SO_4 salt solutions at 36 mM/L concentration.

Soil	pH	ug $\text{NO}_3\text{-N/g soil * day (b}_i\text{)}$	
		$(\text{NH}_4)_2\text{SO}_4 + \text{DCD}$	$(\text{NH}_4)_2\text{SO}_4$
Nekia	4.8	4.41	8.58
"	5.5	4.66	12.97
"	6.5	3.91	14.20
Woodburn	5.4	2.79	5.08
"	5.8	2.28	6.57
"	6.3	2.19	9.48
"	6.7	1.72	9.18

Linear Regression Values		
	Nekia	Woodburn
R^2	0.99	0.96
Constant	8.09	3.17
MSE	11.70	51.78
SED	0.376	0.223
LSD(.01) =	1.02	0.59
LSD(.05) =	0.76	0.45

SOIL SOLUTION CONSTITUENTS FOLLOWING APPLICATION
OF CHLORIDE OR SULFATE SALTS

ABSTRACT

Incubation experiments in which soil samples received equal additions of N as NH_4Cl or $(\text{NH}_4)_2\text{SO}_4$ and increasing rates of KCl or K_2SO_4 , respectively, showed that nitrification was inhibited by increasing ionic strength, and that Cl inhibited nitrification more than SO_4 at a given soil solution ionic strength. Therefore, it was desirable to examine and compare the soil solution constituents resulting from these treatments. Three incubations were conducted. In every case 100g of air dried topsoil was placed in a glass beaker along with the appropriate treatment. All samples received 100 ug $\text{NH}_4\text{-N/g}$ soil as either NH_4Cl or $(\text{NH}_4)_2\text{SO}_4$. In the first incubation, pH 5.4 Woodburn silt loam samples received 35.5 ml of NH_4Cl or $(\text{NH}_4)_2\text{SO}_4$ solutions to which KCl or K_2SO_4 had been added, respectively, to bring ionic strength to 36, 73, 145, or 291 mM/L. The second incubation duplicated the first, using pH 4.8 Nekia silty clay loam samples. The third incubation used samples of Woodburn pH 6.3 and Nekia pH 6.5 soil, each receiving only the 36 mM Cl and SO_4 treatment. Soil solutions were recovered by centrifugation, as follows: Acid washed pyrex wool filters were placed in the bottom of 10 ml plastic, porous bottom test tubes. Soils were then packed into the test tubes, and the test tubes were placed into centrifugation tubes. Tubes were centrifuged for 50 minutes at 15,000 RPM, which resulted in 2-4 ml solution collecting in the bottom of each tube.

Increasing ionic strength of added solutions decreased NO_3 and increased NH_4 in solution, with Cl salts accentuating this effect. Concentrations of Ca, Mg, K, Na, and Mn in solution increased as ionic strength increased, probably due to exchange between the added K and exchangeable cations. Ionic strength of soil solutions were less where SO_4 was added as compared to Cl. An ion speciation computer program was used to calculate activity coefficients and species activities of the ions in solution (Hickey and Peek, 1985). Levels of Ca and SO_4 in solution indicated that CaSO_4 could have precipitated in the four SO_4 treatments for Woodburn pH 5.3 and for the 145 and 291 mM SO_4 treatments in Nekia pH 4.8, which could explain the discrepancy in ionic strength between Cl and SO_4 treatments. No Mo or P was measured in any of the soil solutions, while Al was found only in the Nekia pH 4.8 soil solutions. Recovery of added Cl was high for all soils. K recovery increased as K-salt rates increased. Recovery of SO_4 was higher in Woodburn than Nekia. Recovery of added N was higher in Nekia, probably due to a higher nitrification rate resulting in more N in the NO_3 form. Woodburn pH 6.3 had more Ca, less Mn, and about the same Mg, K, and Na levels as Woodburn pH 5.3. Nekia pH 6.5 had more Ca, Mg, K, and Na, and less Mn and Al than Nekia pH 4.8. Cation-anion balance in solution almost always had a discrepancy of less than 10% for the Nekia pH 4.8 and Woodburn pH 5.3 solutions, but errors were larger for the Nekia pH 6.5 and Woodburn pH 6.3 solutions. Solution activity coefficients decreased slightly with increasing ionic strength of soil solution.

LITERATURE REVIEW

The phenomenon of cation exchange capacity was first studied and documented over 130 years ago (Way, 1850; Thompson, 1850). Early on it was theorized that cation exchange was a stoichiometric reaction. Later studies showed that certain cations, such as divalent and trivalent ions, are held more tightly, and readily replace other ions on the colloid (Jenny, 1935). Additional studies gave rise to mathematical equations to describe these reactions. A review by Marshall (1964) describes these equations, along with their limitations.

A method has been devised to compare the activity of an ion in solution vs its concentration in solution. Ion activity is often lower than concentration due to ion pairing, hydrolysis, or dissociation. Adams (1971) described the following procedure for correcting measured soil solution ion concentration to actual ion activities. This procedure was used to determine the effects of added NH_4 and KCl or K_2SO_4 treatments on equilibrium soil solutions in two western Oregon soils.

Pertinent Equations:

Ionic strength of a solution is defined as follows:

$$[1] \quad u = (0.5) \left(\sum C_i Z_i^2 \right) \quad u = \text{ionic strength}$$

C_i = molar concentration
of
each ion
 Z_i = each ion's valence

Ionic activity for a particular ion is found by:

$$[2] \quad a_i = f_i C_i \quad a_i = \text{ionic activity}$$

C_i = ionic concentration
 f_i = activity coefficient

Activity coefficients are calculated by :

$$[3] \quad -\log f_i = A Z_i^2 (u)^{0.5} / [1 + B a_i' (u)^{0.5}]$$

A and B are temperature dependant constants. At 25°C, A = 0.509 and B = 0.329. a_i' is an ion size parameter taken from a table (Kielland, 1937).

Ion pair equilibrium constants must be known for ion pairs which are likely to form in solution. In this study CaSO_4 is the only likely pair. The thermodynamic equilibrium expression is:

$$(4) \quad K = (\text{Ca}^{2+}) (\text{SO}_4^{2-}) / \text{CaSO}_4, \text{ where } K = 5.25 \times 10^{-3}$$

(Tabled value)(Davies, 1962; Sillen and Martell, 1964).

Calculating ion concentrations, ion pair concentrations, and ionic activities is done by successive iterative estimates using the above four equations. The following steps are followed to find the ionic activities of the ions in solution:

1. Ionic strength. Making an estimate of the actual ion concentration, one calculates the ionic strength, u , using [1].
2. Activity coefficients. Coefficients, f_i , are calculated with [3], using u from step 1 and a tabled value for a_i' .
3. Ionic activities. Activities are calculated with [2], using f_i from step 2 and measured C_i values.
4. Ion pair concentrations. Concentrations are calculated with [4], using ionic activity from step 3 and a tabled ion pair equilibrium constant, (K) .
5. A second estimate of ion concentrations is calculated by subtracting the ion pair concentration estimate from the measured concentration.
6. A revised ionic strength is calculated using the ionic concentration from step 5 in [1] as in step 1.
7. A revised activity coefficient is calculated using the revised ionic strength from step 6 in [3] as in step 2.

8. New ionic activities are calculated with [2] using new estimates of ion concentration from step 5 along with the new activity coefficient from step 7.
9. Ion pair concentrations are then revised using the new ionic activities from step 8 with [4].
10. Steps 5-9 are repeated until successive calculations produce no change in the ionic concentration (C_i).

This procedure is applicable to complex soil solutions, but is extremely time consuming if done by hand. A computer program which will run on a microcomputer has been developed and will perform all the intermediate iterations (Hickey and Peek, 1985). At present this program only deals with solution equilibria, and not solid-solution equilibria. It does, however, allow comparisons between measured concentrations and actual activities, as well as showing changes in the activity coefficient (f_i) under different treatments.

MATERIALS AND METHODS

A laboratory soil incubation experiment was conducted using 100g samples of unfertilized Woodburn silt loam (fine-silty, mixed, mesic, Aquultic Argixeroll), pH 5.5, and recently fertilized Nekia silty clay loam (clayey, mixed, mesic, Xeric Haplohumult), pH 4.8. Soil samples were placed in glass beakers and amended with NH_4Cl or $(\text{NH}_4)_2\text{SO}_4$ salt solutions to provide 100 ug $\text{NH}_4\text{-N/g}$. Treatments were designed so that added solutions had equal ionic strength at four levels. This was achieved by adding KCl or K_2SO_4 to the NH_4Cl or $(\text{NH}_4)_2\text{SO}_4$ solutions, respectively, as shown in Table 9. Samples were covered to control evaporative loss, and incubated at 25° C for 15 days.

Soil solutions were recovered by centrifugation, as follows: Acid washed pyrex wool filters were placed in the bottom of 10 ml plastic, porous bottom test tubes. Soils were then packed into the test tubes, and the test tubes were placed into centrifugation tubes. Tubes were centrifuged for 50 minutes at 15,000 RPM, which resulted in 2-4 ml solution collecting in the bottom of each tube. This method was similar to one used in a previous soil solution study (Reynolds, 1984). Soil solution pH was determined with a glass electrode immediately after recovering soil solutions. Soil solution ionic strength was determined with a Wescor vapor pressure osmometer (Model 5100C). NH_4 , NO_3 and P were determined colorimetrically with an autoanalyzer (Scientific Instruments

Corp., Pleasantville, NY). Nitrate was measured after reduction to NO_2 by cadmium reduction column, NH_4 was measured using sodium salicylate and nitroprusside, and P was measured by the molybdate blue method using a dialysis membrane. Cl was determined by titration with AgNO_3 using a Cl ion electrode to detect the endpoint. S was determined turbidimetrically by precipitation with Ba to form BaSO_4 , with absorbance read on a Bausch-Lomb spectrophotometer at 500nm (Tabatabai and Bremner, 1970). Al, Ca, Mg, K, Na, Mn, and Mo were determined on a Perkin-Elmer model 4000 atomic absorption spectrophotometer.

In order to measure any soil pH related differences in Cl and SO_4 salt effects on soil solution, the incubation procedure was repeated using soil samples from limed plots. The samples used were a Nekia pH 6.5 and Woodburn pH 6.3. Only the 36 mM/L Cl or SO_4 salt treatment was applied. (Treatments 1 and 5).

Table 9. Composition and ionic strength of added salt solutions giving four rates of Cl or SO_4 salts, all containing equivalent amounts of NH_4 -N.

Added solution ionic strength mM/L	Contribution to ionic strength mM/L		
	$\text{NH}_4\text{Cl} + \text{KCl}$	$(\text{NH}_4)_2\text{SO}_4 + \text{K}_2\text{SO}_4$	
Total			
36.4	(1) 36.4 + 0	(5) 27.5	+ 8.9
72.7	(2) 36.4 + 36.4	(6) 27.5	+ 45.2
145.4	(3) 36.4 + 109.0	(7) 27.5	+ 117.9
290.8	(4) 36.4 + 254.4	(8) 27.5	+ 263.3

Treatments were assigned a number, one through eight, in parenthesis above, to facilitate discussion.

RESULTS AND DISCUSSION

Woodburn pH 5.3 and Nekia pH 4.8

The results of the analyses of the Woodburn pH 5.3 and Nekia pH 4.8 samples are shown in Table 10 and 11. One method to examine the fate of added salts, as well as to check analytical procedures, is to compare the levels of cations and anions in solution under different treatments. Because added solutions are balanced between cations and anions on a mmol_c/L basis, and any cation or anion exchange should be stoichiometric, the solutions should have a rough balance between cations and anions (although absolute concentrations will be different between treatments). Table 10 and 11 are balance sheets for totalling cations and anions in the two soils.

For both soils, the NH_4 concentration increased with each salt addition. This may have been due to increased cation exchange, with K substituting for NH_4 on the colloid. The fact that nitrification is slower at higher salt additions also contributes to this effect, with more NH_4 available to exchange when nitrification rate is low. Nitrification inhibition also accounts for the observation that NH_4 levels are higher for Cl salts (Treatments 1-4) than SO_4 salts (Treatments 5-8). This corresponds well with the observation that NO_3 concentrations decrease with added salt, and are lower with added Cl than SO_4 .

Table 10. Cation-Anion balance in soil solution for Woodburn pH 5.3.

	Ion Concentration (mmol _c /L)							
	Treatment							
	1	2	3	4	5	6	7	8
Cations								
NH ₄	1.2	2.6	5.0	8.0	1.3	2.0	3.3	5.0
Ca	13.4	20.2	36.6	65.6	11.3	19.3	26.4	21.5
Mg	3.2	4.7	8.4	13.5	3.0	4.4	6.3	8.9
K	0.5	3.0	11.8	42.5	1.2	4.2	14.4	43.8
Na	0.7	0.8	1.0	1.1	0.8	0.8	0.8	1.0
Mn	0.2	0.3	0.6	1.0	0.1	0.2	0.5	1.0
Sum	19.2	31.6	63.4	131.7	17.7	30.9	51.7	81.2
Anions								
Cl	14.1	30.4	63.4	125.5	0.4	0.4	0.6	0.3
SO ₄	0.1	0.2	0.3	0.3	9.6	26.8	54.3	83.6
NO ₃	4.1	2.1	0.6	0.1	7.7	5.2	5.0	3.2
Sum	18.3	32.7	64.3	125.9	17.7	32.4	59.9	87.1
Cation - Anion	0.9	-1.1	-0.9	5.8	0	-1.5	-8.2	-5.9
Ionic Strength mM/L								
	37.0	53.0	95.1	193.1	32.0	40.8	56.0	85.0
pH	6.24	6.58	5.74	5.10	6.93	6.82	6.56	6.41
No Mo, Al, or P was measured.								

Table 11. Cation-Anion balance in soil solution for *Nekia* pH 4.8

		Ion Concentration (mmol _c /L)							
Cations	Treatment								
	1	2	3	4	5	6	7	8	
NH ₄	2.9	5.2	8.0	12.2	1.1	1.6	2.5	5.9	
Ca	14.9	15.5	24.0	26.4	10.9	8.9	9.4	14.8	
Mg	2.2	1.3	3.0	1.4	1.6	0.8	1.4	2.1	
K	2.0	4.3	15.9	61.1	2.6	5.2	11.3	58.1	
Na	1.5	1.4	1.5	1.6	1.4	1.4	1.2	1.5	
Mn	2.5	2.8	4.3	5.5	1.4	1.4	1.4	2.3	
Al	0.4	0.4	3.2	6.0	1.2	0.7	0.9	0.9	
Sum	26.4	30.9	59.9	114.2	20.2	20.0	28.0	85.6	
Anions									
Cl	12.7	26.6	59.5	128.2	1.0	0.9	1.0	1.0	
SO ₄	0	0	0	0	0.4	1.4	12.5	69.8	
NO ₃	8.9	4.6	1.2	1.4	10.5	13.9	9.7	6.5	
Sum	21.6	31.2	60.7	129.6	11.9	16.2	23.2	77.3	
Cation - Anion	4.8	-0.3	-0.8	15.4	8.1	3.8	4.8	8.3	
Ionic Strength mM/L	55.8	58.9	100.9	173.1	50.2	48.0	58.0	89.2	
pH	4.13	4.23	4.23	4.22	4.28	4.39	4.59	4.54	
No Mo or P was measured.									

Ca, Mg, Na, and Mn all increased in Woodburn pH 5.3 as added Cl and SO_4 salt levels increased. This is probably due to a straight cation exchange reaction, with increasing amounts of added K replacing these cations on the colloid. The increases in Na and Mn were about equal between added Cl or SO_4 , but Ca and Mg levels were higher with added Cl than SO_4 . This may have been due to the higher ion concentrations in Cl treated soils which would tend to displace more of the divalent cations into solution. K, Cl, and SO_4 all increased where they were added as KCl or K_2SO_4 , as would be expected.

For Nekia pH 4.8, as Cl salt levels increased, Ca, Al, and Mn levels increased, probably due to exchange reactions with the added K as was suggested for the Woodburn pH 5.3 soil. Ca, Al, and Mn levels were variable for the SO_4 salts. Mg and Na were variable for all eight treatments, with little change throughout. The formation of CaSO_4 in the high SO_4 salt additions could account for some confusing cation exchange results. The Nekia soil has additional complications due to its pH and its mineralogy. At pH 4.8, much Al is found in the $\text{Al}(\text{OH})_2^{2+}$ and $\text{Al}(\text{OH})_2^+$ forms (Lathwell and Peach, 1964). These ions are able to form complexes with soils colloids as well as anions such as SO_4 , thus reducing their activity (Chao et al., 1962a; Mattson, 1927). The iron (Fe) and Al oxides which are prevalent in this soil retain SO_4 strongly, changing the activity of SO_4 in solution.

As added salt level increased, pH decreased for Woodburn pH 5.3, probably due to more K exchanging with H^+ on the colloid. Because H^+ ions tend to be in higher concentration near the colloid, and the solution which is centrifuged out of the soil is mainly that which is not tightly held by the colloid, the pH of the centrifuged solution could be higher than that of 2:1 water to soil pH measurement. Cl treatments resulted in lower pH than SO_4 , which would be reasonable due to the higher ion concentration found in the Cl treated soil solution. The good overall cation/anion balance, considering the number of determinations made, suggests that lab technique was good, and that no major ions were overlooked in this soil solution. In contrast to the Woodburn soil, the solution pH in the Nekia soil samples varied little from treatment to treatment, and was slightly lower than the 2:1 water to soil pH. A drop in pH would be expected where K was added due to K exchange with H held on the colloid. The fact that little pH difference occurs between treatments might be due to the low pH. At such a low soil pH, very little of the pH dependant cation exchange capacity is left for added K to occupy, thus the K ions face strong competition for limited sites from abundant H ions in solution, lowering the rate of K displacing H from the colloid.

A direct method to determine the fate of added ions is to compare the amount added with the amount measured in the resulting soil solution. This was done and is summarized in Tables 12, 13, 14, and 15 for the four added ions (NH_4^+ , K^+ , Cl^- , SO_4^-) in Woodburn pH 5.3 and Nekia pH 4.8 soils. In the cases

of Cl, SO_4 , and K, where at least one sample received no added ion, the background level of that particular ion was subtracted from the ion concentration in soil solution to give a corrected percent recovery.

Recovery of N was determined to be the NH_4 concentration plus the NO_3 concentration, due to the nitrification which occurred during the incubation. Recovery levels of added N in both soils were similar within the SO_4 salt treatments (5-8). Recovery increased with increasing salt concentration for the Cl salts in Woodburn pH 5.3. Recovery tends to be higher in the SO_4 treated soils. This result could be due to the higher nitrification rate in SO_4 treated soils, resulting in more NO_3 and less NH_4 in the system. SO_4 additions could also exchange with any NO_3 held on anion exchange sites.

As was shown previously, the nitrification rate was higher in the SO_4 treated soils. Thus, more NH_4 remained sorbed on the colloid, out of solution, in the Cl treated soils, whereas the large amount of NO_3 found in the SO_4 treated soils would be more easily extractable in the soil solution. Hence, the lower N recovery for the Cl treatments. Within the Cl treatments, where nitrification was slower, the increasing levels of added KCl exchanged more NH_4 into solution, resulting in more N recovery for the higher salt additions within the Cl treatments. This is especially true for Woodburn pH 5.3, where increased salts increased mineralization.

Table 12. Recovery of N (as $\text{NH}_4 + \text{NO}_3$) in Woodburn pH 5.3 and Nekia pH 4.8 soil solution as compared to added NH_4 levels.

Treatment	mmol /L added	mmol /L in solution		% N recovered	
		Woodburn	Nekia	Woodburn	Nekia
1	18.4	5.3	11.8	28.8	63.8
2	18.4	4.7	9.8	25.3	53.0
3	18.4	5.7	9.2	30.7	49.5
4	18.4	8.1	13.5	43.8	73.3
5	18.4	9.0	11.6	48.9	62.6
6	18.4	7.2	15.5	39.0	83.9
7	18.4	8.3	12.2	44.8	66.1
8	18.4	8.2	12.4	44.7	67.5

Recovery levels were higher for Nekia pH 4.8 than Woodburn pH 5.3. This is probably due to Nekia's higher nitrification rate, putting more N into the NO_3 form, which is more easily recovered in the soil solution. For Cl additions, N recovery decreased until the highest salt addition. As salt was added, nitrification decreased, leaving less N in the easily recoverable NO_3 form. At the highest rate, however, the large amount of added K could have exchanged with a large amount of the NH_4 , putting a higher percentage of it into solution. For the SO_4 salts, the first, third, and fourth rate all gave similar recoveries. This could have been due to a rough balance between the decrease in NO_3 levels as

salt was increased (due to lower nitrification), and the increase in NH_4 levels as K was added (due to cation exchange). The second SO_4 salt treatment had a similar nitrification rate to the first SO_4 treatment, thus similar NO_3 levels. The added K salt, however, could have resulted in greater NH_4 exchange, giving the higher N recovery rate.

Table 13. Recovery of K in Woodburn pH 5.3 and Nekia pH 4.8 soil solution as compared to added K levels.

Treatment	mmol _c /L added	mmol _c /L in solution		% K recovered ¹	
		Woodburn	Nekia	Woodburn	Nekia
1	0	0.5	2.0	(background)	
2	18.4	3.0	4.3	13.6	12.4
3	55.3	11.8	15.9	20.5	10.8
4	129.0	42.5	61.1	32.6	45.8
5	6.1	1.2	2.6	19.1	9.3
6	30.7	4.2	5.2	13.7	10.5
7	79.8	14.4	11.3	18.1	11.7
8	178.1	43.8	58.1	24.6	31.5

¹ After subtracting background level.

For the Cl treatments, increased levels of added K increased K recovery. This could have been due to simple exchange, with higher K levels overloading the exchange sites, and thus more and more remaining in solution. For the SO_4 treatments, added K did not clearly increase K recovery until the highest salt addition.

If the high levels of added K were not found in solution, perhaps more of the added K was attaching to the colloid than was occurring in the Cl treatments. If CaSO_4 was precipitating in the SO_4 treatments as was suggested by Table 16, the K would have more opportunity to compete for the sites vacated by Ca, thus remaining out of solution. The data indicate that most of the K was not in solution for any of the treatments, with 32.6% the highest recovery for Woodburn and 45.8% the highest recovery for Nekia. K recovery on Nekia pH 4.8 was lower than Woodburn pH 5.3 until the highest salt rate was applied for both Cl and SO_4 salt additions. Less Ca and Mg in the Nekia would give less competition to added K for the exchange sites at the lower salt additions. The Nekia, having a higher clay content, could provide more surface area for K to sorb onto. The clays in the Nekia are mainly 1:1, along with Fe and Al oxides. Thus there would be little K being "fixed" between 2:1 sheets in the Nekia, but more opportunity for K to become sorbed in coordination with metal oxides on the edge of the colloid.

Because the Cl ion is negatively charged, one would expect a large portion of added Cl to be found in solution, and such is the case. Higher additions of KCl resulted in higher Cl recoveries, suggesting that the limited anion exchange sites were quickly occupied by the first Cl addition, leaving the remainder to stay in solution. Although recovery was lower for Nekia than Woodburn on the lower KCl additions, the recovery rate increased rapidly in

Nekia, so that the recovery at the highest salt addition was slightly higher than that of the Woodburn soil. Possibly there was less opportunity for Cl anion exchange or ion retention in the Nekia soil, resulting in a more rapid increase in recovery as more Cl was added.

Table 14. Recovery of Cl in Woodburn pH 5.3 and Nekia pH 4.8 soil solution as compared to added Cl levels.

Treatment	mmol /L added	mmol _c /L in solution		% Cl recovered ¹	
		Woodburn	Nekia	Woodburn	Nekia
1	18.4	14.1	12.7	74.0	63.6
2	36.9	30.4	26.6	81.1	69.6
3	73.7	63.4	59.5	85.5	79.4
4	147.4	125.5	128.2	84.8	86.3
5	0	0.4	1.0	(background)	
6	0	0.4	0.9	"	
7	0	0.6	1.0	"	
8	0	0.3	1.0	"	

¹ After subtracting background level.

As added SO_4 increased, SO_4 recovery increased until the highest rate, where SO_4 recovery decreased for Woodburn pH 5.3 only. The absolute concentration always increased with each addition of SO_4 . Thus, for the highest rate of added SO_4 salts, an increased percentage of the added SO_4 was not being recovered in solution for the Woodburn soil. If CaSO_4 was precipitating, as

suggested by Table 16, then the last SO_4 addition could have been going mostly to CaSO_4 , with little remaining in solution, giving a lower recovery than the previous salt additions.

Concentrations and recoveries of SO_4 are lower for Nekia than for Woodburn in all cases. The fact that the CaSO_4 solubility product is not reached in the Nekia soil until the third rate of added K_2SO_4 (Table 16) indicates that while SO_4 is not remaining in solution in the Nekia soil receiving treatments 5 and 6, it is not precipitating as CaSO_4 either.

Possibly SO_4 sorption is tying up most of the added SO_4 until the highest amounts are added. The Nekia soil fits the pattern of soils which would be expected to have a high SO_4 retaining ability (Chao et al, 1962a). The factors which contribute to SO_4 retention include low soil pH, high organic matter content, large amounts of Fe and Al oxides, and presence of K. A soil which is quite similar to the Nekia was found to retain high levels of SO_4 , while a soil similar to the Woodburn was found to be poor at retaining SO_4 (Chao et al., 1962a).

The results in Tables 10 and 11 show that the ionic strength in SO_4 amended soils was far less than that of Cl amended soils. Two methods were used to determine if ion pairing or salt precipitation was causing the discrepancy. The only sparingly soluble salt likely in this system would be CaSO_4 . By comparing the concentrations of Ca and SO_4 with the solubility product of CaSO_4 , one can determine if the levels of Ca and SO_4 are high

Table 15. Recovery of SO_4 in Woodburn pH 5.3 and Nekia pH 4.8 soil solution as compared to added SO_4 levels.

Treatment	mmol _c /L added	mmol _c /L in solution		% SO_4 recovered ¹	
		Woodburn	Nekia	Woodburn	Nekia
1	0	0.1	0	(background)	
2	0	0.2	0	"	
3	0	0.3	0	"	
4	0	0.3	0	"	
5	24.6	9.6	0.4	38.2	1.5
6	49.2	26.8	1.4	54.2	2.8
7	98.3	54.3	12.5	55.0	12.7
8	196.6	83.6	70.0	42.4	35.6

¹ After subtracting background level.

enough to cause precipitation. The solubility product is the product of molar concentrations of two ions which can combine to form a sparingly soluble salt at the point where precipitation begins (Weast, 1972). The products of Ca and SO_4 concentrations for the eight treatments for both Woodburn pH 5.3 and Nekia pH 4.8 soils are shown in Table 16.

From these results, it appears that CaSO_4 could be precipitating in treatments 5-8 (the four cases where K_2SO_4 was added) for Woodburn, and treatments 7-8 for Nekia. Precipitation would not be found in treatments 1-4 for either soil.

The second method to determine if ions were precipitating involves calculation of the ionic activities, as described in the literature review section. Using the computer program described, the activities of all ions and salts were calculated, along with activity coefficients (f_i) for each treatment. The resulting effect on f_i for each treatment is shown in Table 17 and 18.

Table 16. Product of Ca and SO_4 ion concentrations in soil solutions from Woodburn pH 5.3⁴ and Nekia pH 4.8 soil samples.

Treatment	[Ca] X [SO ₄] (M/L)		Product
	Woodburn	Nekia	
1	3.34×10^{-7}		1.86×10^{-7}
2	8.80×10^{-7}		0
3	2.40×10^{-6}		0
4	4.71×10^{-6}		1.73×10^{-7}
5	2.71×10^{-5}		1.02×10^{-6}
6	1.29×10^{-4}		3.08×10^{-6}
7	3.58×10^{-4}		2.94×10^{-5}
8	4.49×10^{-4}		2.59×10^{-4}

$CaSO_4$ solubility product at 25°C = 2.45×10^{-5} .

Table 17. Activity coefficients for ions of valence state 0 to 3 in soil solutions extracted from Woodburn pH 5.3 soil samples receiving the eight Cl or SO₄ salt treatments.

Treatment	Activity Coefficient (f_i)			
	0	Ion valence number		
		1	2	3
1	1.00	0.84	0.49	0.20
2	1.00	0.82	0.45	0.16
3	1.00	0.78	0.38	0.11
4	1.00	0.75	0.31	0.07
5	1.00	0.85	0.51	0.22
6	1.00	0.83	0.48	0.19
7	1.00	0.81	0.44	0.16
8	1.00	0.79	0.39	0.12

Table 18. Activity coefficients for ions of valence state 0 to 3 in soil solutions extracted from Nekia pH 4.8 soil samples receiving the eight Cl and SO₄ salt treatments.

Treatment	Activity Coefficient (f_i)			
	0	Ion valence number		
		1	2	3
1	1.00	0.81	0.44	0.16
2	1.00	0.81	0.43	0.15
3	1.00	0.78	0.37	0.11
4	1.00	0.75	0.32	0.08
5	1.00	0.82	0.45	0.17
6	1.00	0.82	0.46	0.17
7	1.00	0.81	0.44	0.15
8	1.00	0.79	0.38	0.12

For all cases, the calculated concentrations of the ions were not markedly different from the measured concentrations.

Solid-aqueous phase equilibria were not determinable by this program. Table 17 shows that increasing salt concentrations did influence the activity of ions by slightly decreasing the activity coefficients (f_i). The f_i for the SO_4 treatments were slightly higher than in the Cl treatments, indicating slightly fewer ions in solution. This is compatible with the ionic strength values for these treatments shown in Table 10.

The activity coefficients decreased with each Cl or SO_4 salt addition, indicating that the solutions behave less ideally as salt is added. SO_4 treatments had higher f_i than Cl, reflecting their lower ionic strength. This result is the same as occurred in the Woodburn pH 5.4 samples.

Woodburn pH 6.3 and Nekia pH 6.5

Ion concentrations were measured in the two soil solutions as was done in the previous section. Results are shown in Table 19.

The NH_4 and NO_3 levels in Woodburn pH 6.3 were similar to those in pH 5.3 with one exception: NO_3 levels were higher in pH 6.3 for SO_4 amended soils. In Nekia soils NH_4 levels were not too different between pH's, but NO_3 levels were higher in pH 6.5 than pH 4.8 for both Cl and SO_4 amended soils. This is probably

Table 19. Soil solution cation-anion balance for Woodburn pH 6.3 and Nekia pH 6.5 soil samples, each receiving the 36 mM/L Cl and SO₄ treatment.

Cations	Ion concentration (mmol _c /L)			
	Woodburn		Nekia	
	Cl	SO ₄	Cl	SO ₄
NH ₄	0.5	0.2	0.5	0.1
Ca	35.1	35.8	44.9	6.7
Mg	4.2	4.9	0.9	0.9
K	1.5	1.7	1.2	1.7
Na	1.4	1.2	1.1	0.8
Mn	0	0	0	0
SUM	42.7	43.8	48.6	10.3
Anions				
Cl	20.6	0.7	15.8	0.7
SO ₄	0.1	10.2	0	1.3
NO ₃	3.5	20.3	17.8	40.3
SUM	24.2	31.2	33.6	42.3
Cation - Anion	18.5	12.6	15.0	-32.0
Ionic Strength mM/L	54	39	51	37
pH	6.4	6.6	6.5	6.5

No Al, Mo, or P was measured.

due to the higher rate of nitrification in the higher pH soils. NO_3 was higher and NH_4 lower for the SO_4 salts as compared to Cl for both the Woodburn and Nekia soils, due to the higher nitrification rate observed with SO_4 salt additions.

For the Woodburn 6.3 soil, Ca, Mg, K, Na, Mn concentration and pH were similar for the Cl and SO_4 treatments, indicating little difference in the exchange reactions in this soil. Comparing Woodburn pH 6.3 with 5.4 (Table 19 vs 10), the higher pH soil had higher levels of Ca, Mg, and Na, while Mn decreased. These results are often observed in limed soils. The pH of the solution was little different between Cl and SO_4 , again pointing to similarity in ion exchange.

For Nekia pH 6.5 soil, levels of Mg, K, Na, and Mn were similar between Cl and SO_4 treated soils. Mg, Na, Mn, and Al all decreased as pH increased from 4.8 to 6.5 (Table 19 vs 11). This decrease in solubility of Al and Mn when the pH is increased was expected, due to their low solubility in neutral soils. Ca levels increased in Cl treated pH 6.5 soils as compared to pH 4.8, but decreased slightly in SO_4 treatments. The increase is expected when soils are limed. The lack of Ca concentration increase in SO_4 treated samples could indicate less exchanged Ca due to less competition from H, Mn, and Al at the higher pH. Greater Ca sorption could occur due to the ultisol's tendency to sorb Ca and SO_4 , a simultaneous adsorption phenomena studied by Chao et al. (1962).

The cation/anion balance was not as good as was found in the lower pH soils. The large negative balance in Nekia where SO_4 was applied could be due larger amounts of SO_4 being loosely attached to the colloid, which would give an overestimate of SO_4 in solution under equilibrium conditions. This effect could occur to a lesser degree in the Woodburn soil, and in fact the Woodburn with SO_4 treatment gives the best balance. The large positive balance where Cl was applied could be due to an overestimation of Ca content. Because these soils are near neutral pH, perhaps some CaCO_3 was in solution before the K was added, giving a higher than expected Ca reading. Also possible is an increase in Ca salt solubility brought about by the addition of salt solutions. Underestimation of total anions would account for the large positive imbalance in three of the four solutions in Table 19. Because these soils are near neutral pH, ions such as HCO_3^- and $\text{CO}_3^{=}$ could be present in high concentrations. Concentrations of these ions were not measured, leaving their contribution to ion balance in these solutions unknown.

Recovery of added N, K, Cl, and SO_4 was calculated for Woodburn pH 6.3 and Nekia pH 6.5 soils as had been done for the Woodburn pH 5.3 and Nekia pH 4.8 soils. Results are shown in Table 20, 21, 22, and 23.

Table 20. Recovery of N (as $\text{NH}_4 + \text{NO}_3$) in soil solution as compared to added NH_4 levels in Woodburn pH 6.3 and Nekia pH 6.5 soil samples.

Treatment	mmol _c /L added	mmol _c /L in solution	% N recovered
Woodburn Cl	18.4	4.0	21.6
" SO ₄	18.4	20.4	110.8
Nekia Cl	18.4	18.3	99.0
" SO ₄	18.4	40.4	219.1

Table 21. Recovery of K in soil solution as compared to added K levels in Woodburn pH 6.3 and Nekia pH 6.5 soil samples.

Treatment	mmol _c /L added	mmol _c /L in solution	% K recovered ¹
Woodburn Cl	0	1.5	(background)
" SO ₄	6.1	1.7	3.3
Nekia Cl	0	1.2	(background)
" SO ₄	6.1	1.7	8.5

¹ After subtracting background level.

The levels and recovery of N were much higher in the Nekia pH 6.5 than pH 4.8 for both Cl and SO_4 . Recovery in Woodburn pH 6.3 was higher than pH 5.3 where SO_4 salts were applied. The high nitrification rate at higher pH would result in more N in the NO_3 form, which is more easily recoverable by the method employed. Because increased mineralization can occur when $\text{NH}_4\text{-N}$ is added to a system (Broadbent, 1965), more NH_4 would be available than was added, resulting in more $\text{NO}_3\text{-N}$ in solution than was added when nitrification rates are high, as was the case here.

Similar levels of K recovery were observed between Nekia pH 4.8 and 6.5 soils. K recovery was higher for Woodburn pH 5.3 than 6.3. At pH 6.3, especially with the SO_4 salt, the higher nitrification rate results in almost all the N being in the NO_3 form. Thus, less NH_4 would provide less competition for exchange of added K, giving a lower recovery in solution.

The level of Cl recovery was higher for both Woodburn and Nekia at pH 6.3 and 6.5 than at pH 5.4 and 4.8, respectively. Perhaps the higher levels of OH^- could displace Cl^- from any anion exchange sites, putting more Cl into solution.

Woodburn pH 6.3 SO_4 recovery levels were similar to those found in pH 5.4 soil. Nekia pH 6.5 SO_4 recovery was higher than that of pH 4.8. As was suggested for Cl, perhaps the higher levels of OH^- at the higher pH displaced more SO_4 into solution from anion exchange sites, or less pH dependant anion exchange sites were available at the higher pH.

Table 22. Recovery of Cl in soil solution as compared to added Cl levels in Woodburn pH 6.3 and Nekia pH 6.5 soil samples.

Treatment	mmol _c /L added	mmol _c /L in solution	% Cl recovered ¹
Woodburn Cl	18.4	20.6	107.9
" SO ₄	0	0.7	(background)
Nekia Cl	18.4	15.8	81.5
" SO ₄	0	0.7	(background)

¹ After subtracting background level.

Table 23. Recovery of SO₄ in soil solution as compared to added SO₄ levels in Woodburn pH 6.3 and Nekia pH 6.5 soil samples.

Treatment	mmol _c /L added	mmol _c /L in solution	% SO ₄ recovered ¹
Woodburn Cl	0	0.1	(background)
" SO ₄	24.6	10.2	41.2
Nekia Cl	0	0	(background)
" SO ₄	24.6	1.3	5.2

¹ After subtracting background level.

The concentrations of Ca and SO_4 in the solutions indicated that CaSO_4 could have been precipitating in the Woodburn pH 6.3 soil which was treated with SO_4 , but not where Cl was applied or in either case for the Nekia pH 6.5 soil (Table 24). These results matched those found when Ca and SO_4 levels were examined for the low pH Woodburn and Nekia soils. Sorption of SO_4 in the Nekia as described earlier could account for the lower SO_4 in solution, thus the greater amount which must be added to cause CaSO_4 precipitation.

As was done with results from the Woodburn pH 5.3 and Nekia pH 4.8 incubations, the microcomputer program was used to calculate activity coefficients and ion activities for the Woodburn pH 6.3 and Nekia pH 6.5 soil solutions. Calculated concentrations were not markedly different from measured concentrations. Activity coefficients changed as shown in Table 25.

Table 24. Product of Ca and SO_4 ion concentrations in soil solutions from Woodburn pH 6.3⁴ and Nekia pH 6.5 soil samples.

Treatment	[Ca] X (Mole/L)	[SO_4] Product
Woodburn	Cl	6.60×10^{-7}
"	SO_4	9.13×10^{-5}
Nekia	Cl	0
"	SO_4	2.20×10^{-6}

CaSO_4 solubility product at $25^\circ\text{C} = 2.45 \times 10^{-5}$.

Table 25. Activity coefficients for ions of valence state 0 to 3 in soil solutions extracted from Woodburn pH 6.3 and Nekia pH 6.5 soil solutions resulting from the 36 mM/L SO_4 salt treatment.

		Activity Coefficient (f_i)			
Treatment		Ion valence number			
		0	1	2	3
Woodburn	Cl	1.00	0.82	0.44	0.16
"	SO_4	1.00	0.84	0.49	0.20
Nekia	Cl	1.00	0.82	0.45	0.17
"	SO_4	1.00	0.84	0.49	0.20

CONCLUSIONS

Inhibition of nitrification by addition of salts was related to several factors, each of which may determine the nitrification rate under specific conditions. Using several soils from western Oregon, it was seen that nitrification was inhibited as rate of added salt increased. Nitrification was inhibited more by Cl than SO_4 salts at a given soil solution ionic strength where equal rates of $\text{NH}_4\text{-N}$ were added. The addition of Cl salts would prove beneficial if reducing nitrification rate is the objective, such as in a wheat crop where take-all root rot infection is expected. The effect would be accentuated by high ionic strength, such as would occur in a fertilizer band. Because nitrification rate increases with soil pH and Cl inhibition of nitrification decreases as soil pH increases, the benefit of using Cl to inhibit nitrification in soils above pH 6.0 would probably not justify the cost. DCD could prove useful in inhibiting nitrification in slightly acid soils, where it was more effective than in moderately acid soils.

Although the specific microbiological effect of Cl on the nitrifying organisms was not determined by this study, it seems certain that Cl does inhibit their metabolism in some manner in moderately acid soil regimes. This reduction of nitrification, altering the soil solution constituents and most importantly the NH_4/NO_3 ratio, would appear to be the manner in which Cl reduces the severity of infection by the take-all fungus.

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