Solution, exchangeable and clay-fixed ammonium in south coast British Columbia soils

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Kowalenko, C. G. and Yu, S. 1996. **Solution, exchangeable and clay-fixed ammonium in south coast British Columbia soils.** Can. J. Soil Sci. **76**: 473–483. Solution, exchangeable and clay-fixed ammonium were measured in a variety of south coast British Columbia soils in the laboratory using extraction, equilibration and leaching procedures, and with and without ammonium amendments in order to evaluate the relative significance of adsorption and fixation processes on nitrogen behavior. Non-amended soils contained from 59 to 224 g N g^{-1} of fixed ammonium and these amounts were correlated with clay (positive) and sand (negative) contents. The amount of native fixed ammonium in the soils was influenced by management history. Recovery of ammonium added to eight selected samples by a small volume of solution followed by air drying was the same with 1 and 2 M KCl extractions, but less was extracted by 0.1 M KCl and even less by water. This showed that both 1 and 2 M KCl had sufficient K^+ to displace the NH_4^+ present (inherent and added) on the exchange sites without an apparent effect on fixed ammonium. Up to 68% of the ammonium added was not extracted by 2 M KCl and assumed to have been fixed in the clay lattice. The proportion of the added ammonium that was adsorbed onto the exchange sites was linear up to 200 µg N g^{-1} application, but the amount fixed by the clays was linear to only about 100 µg N g^{-1} application rate. Data from studies where soil columns were leached with NH_4NO_3 provided only limited information on the relative importance of exchange versus fixation processes to the adsorption of ammonium. Leaching columns with a limited number of batches of NH_4NO_3 followed by water (short cycle) were useful for comparing the ability of different soils to adsorb and retain ammonium, but the relative importance of exchange versus fixation could not be determined. In the 18 samples of this study, the amount of NH_4^+ adsorbed ranged from 84 to 25% during short cycle column leachings. Different patterns of adsorption occurred among the four soil samples that were leached with a large number of batches of ammonium (long cycle), but it could not be determined whether or not these patterns were related to differences in proportions of fixation relative to exchange. Measurements showed that ammonium was fixed in the soils during the long cycle leachings but that the amounts of fixed ammonium measured were influenced by air drying the sample before analysis. Several studies with and without toluene additions showed that microbial activity must be controlled during these measurements. It was concluded that south coastal soils contained significant amounts of fixed ammonium and can fix additional ammonium. The amount of ammonium in the clay fixed pool and the potential to fix added ammonium was different in relation to the soil type, their previous management, and wetting and drying cycles. The biological significance of fixed ammonium and the fixation process must not be discounted in any nitrogen studies of these soils for proper interpretation of data.

Key words: Ammonium fixation, equilibration, column leaching, microbial/enzyme inhibition, extractant concentration

Kowalenko, C. G. et Yu, S. 1996. **Ammonium en solution, sous forme échangeable et sous forme fixée sur argile dans les sols côtiers du sud de la Colombie-Britannique.** Can. J. Soil Sci. **76**: 473–483. Nous avons mesuré en laboratoire, au moyen de méthodes d'extraction, d'équilibrage et de percolation, les concentrations de $NH4^+$ en solution, échangeable et fixé par l'argile dans divers sols du littoral sud de la Colombie-Britannique, avec et sans apports complémentaires de NH_4NO_3. L'objet était d'évaluer l'importance relative des processus d'adsorption et de fixation pour le comportement de l'azote. Les sols non fertilisés contenaient de 59 à 224 µg N g^{-1} d'ammonium fixé et ces valeurs étaient corrélées positivement à la proportion d'argile dans le sol et négativement à sa proportion de sable. Les quantités d'ammonium d'ammonium fixé d'origine dans le sol variaient selon les antécédents culturaux. Dans un essai d'apport de N ammoniacal en solution sur 8 échantillons de sol, suivi de séchage à l'air du sol, la quantité de N ammonical de fumure récupérée était la même par extraction dans des solutions 1 et 2 M de KCl, mais elle était plus basse en solution 0,1 M et encore davantage dans l'eau seule. Les solutions 1 et 2 M de KCl contenaient donc assez de K pour déplacer les ions NH_4^+ présents (d'origine et de fumure) sur les sites d'échange, sans effet apparent sur les quantités de NH_4 fixé. Jusqu'à 68% du NH_4 de fumure n'était pas extrait dans KCl 2 M, perte imputé à la fixation sur l'argile. La proportion de NH_4 de fumure absorbé sur les sites d'échange était linéaire jusqu'à la dose d'apport de 200 µg N g^{-1} de sol et la quantité fixée sur les particules d'argile ne l'était que jusqu'à la dose d'environ 100 µg N g^{-1}. Les données obtenues par percolation de NH_4NO_3 sur des colonnes de sol n'apportaient que peu d'éclairage complémentaire sur l'importance relative des processus d'échange et de fixation dans l'absorption de l'ammonium. La percolation n'impliquant qu'un petit nombre d'apports de NH_4NO_3 suivie par délavage à l'eau (cycle court) se révélait utile pour comparer l'aptitude des divers sols à adsorber et à retenir l'ammonium, sauf qu'elle ne permettait pas d'établir l'importance relative de l'échange par rapport à celui de la fixation. Dans les 18 échantillons de sol étudiés, la quantité de NH_4^+ adsorbé allait de 84 à 25%. Dans le traitement de percolation comportant un nombre élevé d'apports d'ammonium (cycle long), la quantité de NH_4 adsorbé différait parmi les quatre échantillons de sol utilisés, mais il était impossible de conclure si ce comportement était lié à l'importance relative de la fixation par rapport à l'échange. Il ressort de ces observations qu'une partie de l'ammonium était fixée durant la percolation, mais que les quantités fixées étaient influencées par le séchage à l'air du sol préalablement à l'analyse. Plusieurs expériences effectuées avec ou sans apport de toluène ont fait ressortir l'importance de maîtriser l'activité microbienne dans ce genre d'analyse de l'azote. La conclusion qui ressort de ces travaux est que les sols du littoral sud de la Colombie-Britannique contiennent d'importantes quantités d'ammonium sous forme fixée, mais qu'elles peuvent en fixer encore davantage. La quantité d'ammonium originellement fixée dans l'argile et l'aptitude du sol à en fixer davantage différaient selon le type de sol, selon les antécédents culturaux et selon les cycles d'humectation et de séchage. Pour être valide, l'interprétation des résultats des études sur l'azote dans ces sols doit donc absolument prendre en compte l'importance biologique de l'ammonium fixé et des mécanismes de fixation.

Mots clés: Fixation de l'ammonium, mise à l'équilibre, percolation sur colonnes, inhibition des enzymes microbiennes, concentration de l'extractif

Ammonium fixed in the lattice of clays has been shown to occur in soils throughout the world (Young and Aldag 1982) and many places in Canada (Hinman 1964; Moore 1965; Sowden et al 1978). Clay fixation has been shown to influence the amount of ammonium that is in the soil solution and on cation exchange sites (Kowalenko and Cameron 1976), and hence influenced the amount of nitrate released during laboratory incubations (van Schreven 1968; Cameron and Kowalenko 1976), under field fallow conditions (Kowalenko and Ross 1980), when immobilization was favored by carbon amendments (Kowalenko 1981) and in the presence of plant growth (Kowalenko and Cameron 1978; Preston 1982; Saha and Mukhopadhyay 1986; Wehrmann and Eschenhoff 1986; Scherer and Weimar 1993).

Despite the large amount of information that has shown the significance of clay fixation of ammonium in soils, only recently have measurements of this nitrogen fraction been reported for south coast British Columbia soils (Kowalenko 1987, 1989). These studies examined fixed ammonium in only one soil type in the Fraser Valley even though mineralogical reports indicate that clays that are known to fix ammonium (vermiculites, smectites) are present in south coast soils (Theisen et al 1959; Mackintosh and Gardner 1966; Luttmerding 1981). Also, the moderate climate and large applications of manure and fertilizer nitrogen in south coast British Columbia provides an excellent milieu in which to study nitrogen reactions in soils. More data on south coast soils will provide both general and regional information on the theoretical and practical importance of clay fixed ammonium for nitrogen management.

The objective of this study was to measure the quantity of clay-fixed ammonium inherent in samples that represent many different soil types and management histories, to determine the relationship among solution, exchangeable and fixed ammonium, and to examine the dynamics of the fixation and release of inherent and added ammonium. Although the method for quantifying the amount of fixed ammonium in soils is relatively widely accepted (Keeney and Nelson 1982), methods for studying the relationships and dynamics of ammonium fractions are not well defined or widely used. For example, fixed ammonium has been operationally defined as the ammonium that is not extracted by 1 M KCl (Keeney and Nelson 1982). This definition assumes that 1 M KCl extracts all solution and exchangeable ammonium present without extracting any fixed ammonium. However, 2 M KCl is most commonly used to extract solution plus exchangeable ammonium (Maynard and Kalra 1993). In the absence of widely accepted methods for determining relationships and dynamics of various fractions of ammonium in soils, several were used and critically evaluated. The methods included were: extractions after amending soils with ammonium; classical equilibrations using large solution-to-soil ratios; and leaching columns of samples with ammonium-solutions and water. Special evaluation was made on the influence of KCl extractant concentration, of wetting and drying the sample and of enzyme or microbial activity. Keeney and Nelson (1982) and Kowalenko and Yu (1996) concluded that enzyme or microbial activity was responsible for significant changes in inorganic nitrogen after relatively short times when inorganic nitrogen was added to and extracted from soils. Knowledge about quantities, interrelationships, and dynamics of soil ammonium fractions, and critical evaluation of methods used to make those measurements are essential for the proper understanding and practical management of the nitrogen cycle.

MATERIALS AND METHODS

Soil Samples

Samples used for this study were obtained at various locations from Ladner to Agassiz areas representing a wide range of soil types and management histories that occur in the Lower Fraser Valley. Some details of their characteristics have been included in a report on nitrate adsorption (Kowalenko and Yu 1996). The 18 samples included 11 different soils and several management histories. Soils sampled that had different management histories were: Deas and Richmond (manured and unmanured), Hatzic (zero and high lime with standard cropping inputs, and no lime with minimal cropping inputs), Monroe (0–15 and 60–75 cm depths), Marble Hill (in treed shelterbelt and in raspberry plantings), and Buckerfield (gully and ridge areas). The samples had a wide range of chemical and physical characteristics (Table 1). They included sandy loams to silty clays, a range of organic carbon and cation contents, and **cation exchange capacities (CEC)**. Sampling was done by shovel at one small location in a specific area of the field that had been visually judged to represent the desired soil series and management practice. The sampling sites were selected to provide a wide range of characteristics, therefore, only one large bulk sample was taken similar to that for soil survey profile characterization purposes.

Native Fixed and 2 M KCl Extractable Ammonium

Clay fixed or nonexchangeable ammonium was measured on finely ground air-dried soil samples using the method of Keeney and Nelson (1982). The method involves removal of soluble and exchangeable ammonium and organic nitrogen by a hot solution of alkaline potassium hypobromite. After washing with KCl, the residue is dissolved in an hydrofluo-

Table 1. Comparison of clay fixed and 2 M KCl-extractable ammonium in selected Fraser Valley soil samples with selected physical and chemical measurements

Soil	Clay fixed NH_4	2 M KCl extractable NH_4	CEC	Ca	Mg	K	Na	Organic carbon	Texture
	(μg N g^{-1})		(meq 100 g^{-1})					(%)	
Deas-a	169	8	26	11	2.3	1.1	0.4	3.3	SiL
Deas-b	160	9	26	11	1.8	0.5	0.6	3.4	SiL
Richmond-a	175	7	50	13	2.4	0.9	0.4	16.1	SiCL
Richmond-b	169	6	46	13	2.0	1.1	0.3	12.5	SiCL
Vye	193	4	27	15	2.2	0.2	0.4	2.6	SiC
Dixon	142	2	10	6	1.4	0.2	0.3	1.0	SL
Fairfield	201	4	24	12	1.1	0.6	0.3	3.2	SiCL
Hatzic-a	164	2	24	10	0.8	0.2	0.3	3.2	SiCL
Hatzic-b	167	2	26	18	0.6	0.3	0.3	2.9	SiCL
Hatzic-c	168	12	26	10	1.1	0.2	0.3	3.9	SiC
Monroe-a	127	3	20	7	1.4	0.4	0.2	2.7	SL
Monroe-b	115	5	11	2	0.3	0.2	0.3	1.1	SiL
Ladner	221	31	20	13	2.4	1.0	1.1	3.0	SiL
Westham	171	5	22	11	1.0	0.9	0.3	3.6	SiCL
Marble Hill-a	59	12	31	4	0.4	0.3	0.5	6.8	SiL
Marble Hill-b	77	2	16	17	0.2	0.3	0.2	4.1	SiL
Buckerfield-a	197	6	26	8	1.6	0.8	0.2	3.6	SiC
Buckerfield-b	224	5	24	10	1.4	0.4	0.3	3.3	SiCL
LSD	9	1	NA[z]	NA	NA	NA	NA	0.4	

[z] NA = not applicable; only one analysis conducted.

ric-hydrochloric acid mixture in preparation for fixed ammonium quantification by an alkaline steam distillation procedure.

Extractable (soluble plus exchangeable) ammonium was determined by shaking a 1:10 soil weight to 2 M KCl solution volume for 1 h, filtering and measuring the ammonium in the extract solutions by an automated flow injection analyzer (Tecator). The filter papers used in the extractions were pre-washed with 2 M KCl and a small amount of the soil extract before the extract was collected for analysis to minimize contamination (Scharf and Alley 1988). The analyzer involved the reaction of the sample with sodium hydroxide so that ammonia was diffused through a teflon membrane into an acid containing a pH sensitive indicator. The amount of ammonium in this solution was determined colorimetrically.

Extraction after Wetting and Drying Amendment

Fifty grams (sufficient for triplicate extractions by each of four different extraction solutions) of selected air-dry soil samples were wetted and thoroughly mixed with 25 mL of either water or solutions of ammonium nitrate, spread out to air dry, and then sieved through a 2-mm mesh screen. The ammonium nitrate solutions contained sufficient total nitrogen (ammonium and nitrate) to result in 100 and 200 μg N g^{-1} air-dry soil. Air-dry water contents were determined on subsamples to enable calculation of the N rate treatments on an oven-dry basis. Two batches of soil samples were treated in this way; one batch was used for water/KCl extraction with no toluene added and another where several drops of toluene were added to the solutions before extraction. The toluene was added to minimize microbial activity. The extract solutions were 0 (water), 0.1, 1, and 2 M KCl solutions at 1:10 soil to solution ratio and 1 h shaking time. Both ammonium and nitrate were measured in the extracts by flow injection analysis. Nitrate was determined by cadmium reduction (Kowalenko and Yu 1996) and ammonium as described in the previous section. The effectiveness of KCl concentration to extract ammonium from different soils containing different amounts of ammonium was determined by analysis of variance with presence and absence of toluene in the extracting solutions treated as a split plot. Recovery of added ammonium and nitrate were calculated by subtracting the mean of the three triplicate extractions of samples that had no nitrogen added to them from the means of the triplicates of nitrogen-treated samples of each soil.

Equilibration

The proportions of soluble and soluble-plus-exchangeable ammonium were determined in the same equilibrations as used to determine soluble and adsorbed nitrate (Kowalenko and Yu 1996) using triplicate ammonium nitrate treatments of 0, 25, 50, 100, and 200 μg NH_4-N g^{-1} and 1 h shaking. After the equilibration, the treatment solution was removed by centrifuging and the soil was extracted with 2 M KCl to determine exchangeable ammonium content. Fixed ammonium was assumed to be the added ammonium that was not recovered in the equilibrium solution and KCl extraction. Corrections were made for carryover of ammonium between equilibration and extraction steps by weighing the containers to determine solution volumes and using measured ammonium concentrations. Linear regression was used to determine the proportion of added ammonium that was adsorbed on exchange sites or fixed in clay lattices. Linearity was assessed by visual inspection of graphed data and comparisons of the magnitudes of the regression coefficients when different treatment ranges (0 to 200 or 0 to 100 μg NH_4-N g^{-1}) were examined. Equilibrations with the

Table 2. Influence of a wetting (with toluene added to minimize microbial activity) and drying treatment of air-dry soil on 2 M KCl extractable ammonium and nitrate

	NH_4 (μg N g^{-1})		NO_3 (μg N g^{-1})	
Soil	Before	After	Before	After
Richmond-b	6	16	66	68
Vye	4	13	64	69
Dixon	2	8	61	56
Buckerfield-b	5	11	3	9
Ladner	31	29	262	233
Marble Hill-b	2	10	2	4
Hatzic-a	2	9	2	6
Monroe-a	3	14	3	5
Mean	7	14	58	56

AOV[z]	P value for NH_4	P value for NO_3
Replicate	0.46	0.28
Soil	0.00	0.00
Treatment	0.00	0.14
Soil X Trt.	0.00	0.00

[z] AOV = Analysis of variance with treatment as split plot.

addition of toluene were accepted as the best data, although six samples were run without addition of toluene to evaluate the influence of microbial activity during the equilibrations.

Column Leaching

The adsorption of added ammonium and subsequent removal by water was measured in "short-cycle" column leachings used for nitrate adsorption (Kowalenko and Yu 1996). The columns were 10 g of air-dry soil in 22 × 85 mm extraction thimbles flushed with 10-mL batches of 50 μg NH_4-N mL^{-1} solution or of water. Adsorption was assumed to be the proportion of ammonium added that was not recovered during ammonium nitrate leaching. All calculations were on a gram oven-dry soil basis. Adjustments were made for the ammonium in the first pore volume of the leaching and first pore volume of the subsequent water leaching.

Table 3. Influence of toluene in KCl extracting solutions of various concentrations on the extraction of ammonium and nitrate from soils that had been treated with various amounts of ammonium nitrate

Source of variation	NH_4	NO_3	$NH_4 + NO_3$
	(μg N g^{-1})		
Toluene	9[z]	7[y]	16
KCl concentration × toluene			
0	7	12	18
0.1 M	10	8	19
1 M	10	5	15
2 M	10	3	13
NH_4NO_3 treatment × toluene			
0	5	3	8
100 μg N g^{-1}	7	9	18
200 μg N g^{-1}	16	9	25
Soil × toluene			
Richmond-b	1	2	3
Vye	15	9	24
Dixon	8	8	16
Buckerfield-b	12	6	19
Ladner	12	17	29
Marble Hill-b	8	4	13
Hatzic-a	7	4	12
Monroe-a	9	7	16
	P value		
Toluene (Tol.)[x]	0.00	0.00	0.00
Tol. × KCl concentration (Conc.)	0.00	0.00	0.24
Tol. × S × Conc.	0.00	1.00	1.00
Tol. × Ntrt. × Conc.	0.00	0.89	0.96
Tol. × S × Ntrt.	0.00	0.44	0.16
Tol. × Conc. × S × Ntrt.	0.01	1.00	1.00

[z] Soil concentration values shown = value with minus values without toluene.

[y] Recovery of added NO_3 with and without toluene averaged 96 and 86%, respectively.

[x] Only analysis of variance results for treatments that involve toluene shown.

In addition to the "short cycle" leachings of 10-mL portions of water, ammonium nitrate and then water, additional duplicate columns of four selected samples that had previously been flushed with water to remove initial soluble inorganic N by leaching six times with 5 mL water (approximately five to six pore volumes), and 42 times with 10 mL portions 50 μg NH_4-N mL^{-1} of ammonium nitrate solutions. These long cycle leachings attempted to differentiate adsorption on the exchange sites from fixation within the clay particles. The graph of ammonium leached from each column during NH_4NO_3 application was examined and two different sigmoid type of curves were noted. For three soils, there was complete adsorption of ammonium for a short time, followed by a time when the amount of applied ammonium that was not adsorbed decreased rapidly and then a period when the decease in adsorption was more gradual. The pattern for the fourth sample was similar to the other three soils except that there was never a period when there was complete adsorption of applied ammonium. Different regression equations were fitted to the two phases of the curve where ammonium retention was changing in relation to the logarithm of pore volumes of ammonium applied to each soil by examination of moving-average results of adsorption data and iteration to derive best fit as shown by the regression coefficient. Application of the logarithm of the accumulated pore volumes leached was required to linearize the results.

At the end of each long cycle leaching, the soil was removed from each column and split into two approximately equal portions. One of these portions was air dried and the other left undried. Fixed ammonium was determined on both the air-dried and undried portions. Fixed ammonium was also determined on unground samples that had not been leached to compare and evaluate the influence of fine grinding on the measurement.

Statistical Procedures

Standard statistical procedures such as correlations, regressions, and analyses of variance were used with triplicate analyses of each sample as the basis of replication rather than replicate soil samplings since an evaluation of the variability of the method of analysis was given priority over the variability of the soil sample. It was assumed that the large homogenized sample from each site provided adequate representation of the soil type and its management history. All measurements (each replicate of each treatment) were used for regressions in order to include measurement variability

Table 4. Increased extraction of ammonium by presence of toluene (values with minus without) by water and 2 M KCl solutions from soils that had previously been treated with various amounts of ammonium as ammonium nitrate

		$\mu g\ NH_4\text{-}N\ g^{-1}$ added		
KCl concentration	Soil	0	53	106
		$(\mu g\ NH_4^{-1}\ N\ g^{-1})$		
0	Richmond-b	3[z]	1	–2
	Vye	6	5	6
	Dixon	4	5	8
	Buckerfield-b	5	5	9
	Ladner	6	7	16
	Marble Hill-b	5	6	14
	Hatzic-a	6	5	7
	Monroe-a	5	5	13
2 M	Richmond-b	4	–1	–1
	Vye	7	15	37
	Dixon	5	8	14
	Buckerfield-b	5	11	35
	Ladner	9	17	13
	Marble Hill-b	4	2	14
	Hatzic-a	4	3	11
	Monroe-a	5	5	10

[z]Soil concentration value shown = with toluene minus without toluene.

along with the treatments. In this way, both variability due to the replication of the analysis and of the treatment could be evaluated on the same basis by visual inspection of plotted data. A 95% confidence interval was used as the minimum throughout the study to consider an effect to be significant.

RESULTS AND DISCUSSION

Native Fixed and 2 M KCl Extractable Ammonium

Fixed ammonium in the 18 Fraser Valley soil samples of this study was considerably higher than 2 M KCl extractable ammonium (Table 1) but the amounts of these fractions were not correlated with each other. The amount of fixed ammonium in these samples was directly correlated with clay content ($R^2 = 0.56$), inversely correlated with sand content ($R^2 = -0.40$) but not correlated with silt content. This shows that most of the fixed ammonium was present in the clay fraction. Kowalenko and Ross (1980) did show, however, that small amounts of fixed ammonium were measured in silt and sand fractions in Bainsville soil of Ontario. Fixed ammonium was not correlated with CEC, exchangeable Ca, K, and Na, pH nor Walkley-Black organic carbon, but was correlated with exchangeable Mg ($R^2 = 0.39$). These correlations, and lack of correlations, might be expected since ammonium fixation is dependent on the type of clay, and amount and type of other cations that can compete for fixation sites (Sowden et al. 1978).

According to an analysis of variance (determined on a subset of two soils that had either manure or no manure), Deas soil contained less fixed ammonium than Richmond soil (164 compared with 173 $\mu g\ N\ g^{-1}$ soil main effect means, respectively) and for both soils there was consistently less fixed ammonium in the manured locations than in the control locations (164 compared with 172 $\mu g\ N\ g^{-1}$ manure main effect means, respectively). The interaction effect between soil and manure was not significant. A similar statistical analysis comparison showed that samples from the manured and control areas of these two soils had similar (no treatment or interaction effects) and low KCl extractable ammonium contents (Table 1). Organic or inorganic (especially potassium) constituents in the manure may have influenced the fixation or removal of ammonium and hence the consistent manure effect on fixed ammonium at the two locations; however, a more rigorous study having replicated treatments and samplings at each location would be required to confirm this preliminary observation.

Table 5. Analysis of variance of effects of soil and ammonium additions on the extraction of ammonium by KCl of different molarities with toluene added

Source of variation	df	sum of squares	*P*
Replicate	1	275	0.00
Soil (S)	7	27525	0.00
Extraction concentration (Conc.)	3	44475	0.00
0 vs. 0.1, 1, 2 M	1	43500	0.00
0.1 vs. 1, 2 M	1	993	0.00
1.0 vs. 2 M	1	14	0.52
NH_4 treatment (Ntrt.)	2	178900	0.00
S × Conc.	21	3929	0.00
S × Ntrt.	14	10772	0.00
Conc. × Ntrt.	6	24695	0.00
S × Conc. × Ntrt.	42	2378	0.00
Error	95	588	

The Buckerfield-b sample, which was from a ridge area of a field, contained 27 $\mu g\ N\ g^{-1}$ more fixed ammonium than Buckerfield-a sample, which came from a gully area of the same field, but KCl-extractable ammonium contents did not differ (Table 1). Fixed ammonium in the three samples of Hatzic soil did not differ, but KCl-extractable ammonium was greater in the border location (Hatzic-c) than for the two lime treatments (Hatzic-a and -b). Although there were relatively large differences in fixed ammonium for the samples of different crop history (Marble Hill samples) and depth of sampling (Monroe samples), they were not significantly different due to relatively large within-sample variability. The sample from the shelterbelt (Marble Hill-a) area of one location of the same soil had considerably more KCl extractable ammonium (10 $\mu g\ N\ g^{-1}$) than from an area that had grown raspberries for a number of years (Marble Hill-b).

Although differences were measured in the amounts of extractable and fixed ammonium in the samples of this study, specific relationships to soil type or management could not be derived due to the limited numbers and types of samples of this study. However, the results suggest that both soil type and management have effects on these inorganic ammonium fractions.

Extraction after Wetting and Drying Amendment

The inclusion of toluene in the water during the wetting and drying of the soil samples during N treatment did not entirely stop changes in extractable inorganic N (Table 2). It was concluded that the changes were predominantly the result of non-biological (physical-chemical) processes because there were relatively greater changes of ammonium-N than of

Table 6. Recovery of ammonium added to selected Fraser Valley soil samples by water and 2 M KCl extracting solutions with toluene added

	Water extraction		2 M KCl extraction	
Soil	53 µg N g^{-1} added	106 µg N g^{-1}added	53 µg N g^{-1} added	106 µg N g^{-1}added
	% recovery of added			
Richmond-b	17	23	92	106
Vye	11	14	72	87
Dixon	13	16	32	38
Buckerfield-b	13	17	60	86
Ladner	30	43	92	97
Marble Hill-b	25	41	74	100
Hatzic-a	13	20	72	95
Monroe-a	19	29	85	104
Mean	18	25	72	89

Table 7. Effect of toluene in one hour water equilibration on the subsequent 2 M KCl extraction of ammonium from selected Fraser Valley soil samples

Soil	With toluene	No toluene
	(µg N g^{1})	
Richmond-a	13	6
Vye	13	2
Ladner	18	16
Marble Hill-a	12	24
Monroe-a	8	9
Monroe-b	3	3

Source of error	df	Sum of squares	*P*
Replicate	2	0.3	0.73
Soil (S)	5	948.3	0.00
Toluene (T)	1	13.6	0.00
S × T	5	451.0	0.00
Error	22	8.6	

nitrate-N. However, we could not determine whether the additional extractable ammonium was derived from the native clay-fixed or the organic pool of soil N.

Addition of toluene to extracting solutions of various KCl concentrations generally increased the amounts of both ammonium and nitrate extracted compared with when toluene was not added to the solutions (Table 3). The effect of toluene was more complex for ammonium than for nitrate. For ammonium measurement, interactions among KCl concentrations, amount of inorganic N added to the soil, and soil type were observed, but only an interaction between toluene addition and KCl concentration occurred for nitrate measurements. There was a tendency for greater ammonium extraction with increasing KCl concentration whereas there was a smaller increase in nitrate extracted such that when both ammonium and nitrate extractable N were considered together, there was no toluene × KCl concentration interaction effect. This opposite influence of toluene on ammonium and nitrate extraction with different KCl concentrations may have been due to the dominance of physical-chemical processes on ammonium but microbial-enzyme processes on nitrate changes. High concentrations of KCl without toluene addition appeared to arrest microbial-enzyme activity in a nitrate extraction study (Kowalenko and Yu 1996). An increasing concentration of KCl would be expected to result in increased extraction of exchangeable ammonium. The toluene × KCl concentration × soil × N treatment interaction also probably reflects the different influences of adsorption and fixation on ammonium extraction in the presence versus absence of toluene in different soils (Table 4).

Analysis of variance of the extraction of native and added ammonium results for eight soils studied was complex with many significant interaction effects (Table 5). The complexity resulted from the relatively large differences that the soils had to adsorb and fix the added ammonium. However, contrast analyses of the extraction-concentration main effect supports the conclusion that 1 and 2 M KCl extract essentially the same amount of ammonium from the soils, but greater quantities than with 0.1 M KCl and water. Water, then, is assumed to extract only soluble ammonium whereas KCl at concentrations equal to or greater than one molarity extract both soluble and exchangeable ammonium. A KCl solution of 0.1 M would extract all of the soluble ammonium in the soil but only a fraction of all the exchangeable present. This confirms observations by Bremner (1965) on Iowa soils, but it may be necessary to re-examine the influence of KCl concentration for extracting exchangeable ammonium in soils that have large pools of native fixed ammonium and/or that can fix large proportions of added ammonium.

Recovery of added ammonium with water extraction (soil solution or non-adsorbed) and with 2 M KCl extraction (soil solution plus exchangeable) ammonium varied from soil to soil. The proportion of ammonium recovered increased as the amount of ammonium added increased (Table 6). Recovery of added ammonium in the soil solution (water extraction) ranged from 11% (6 µg N g^{-1} for Vye soil with 53 µg N g^{-1} added) to 43% (46 µg N g^{-1} for Ladner soil with 106 µg N g^{-1} added). There was considerable added ammonium that was not recovered by 2 M KCl extraction from Dixon soil (62 to 68% or 33 to 72 µg N g^{-1}), whereas, there was greater to essentially complete recovery from the other soil samples.

Equilibration

The addition of toluene influenced ammonium results during equilibrations, which was similar to that found for equilibration and extraction studies on nitrate (Kowalenko and Yu 1996). In a preliminary evaluation of six soil samples, the amount of ammonium extracted by KCl after equilibra-

Table 8. Exchangeable ammonium calculated by linear regression on 2 M KCl extractions after equilibration with 0 to 200 μg NH_4- N g^{-1} and comparison to 2 M KCl extraction of non-equilibrated samples for a range of soil samples from the Fraser Valley

Soil	Regression equation: Slope	Constant	Difference between regression constant and standard 2 M KCl extraction
Hatzic-b	0.60*a*	6.8*ghij*	4.4*bcd*
Hatzic-a	0.59*a*	5.3*jk*	3.4*cde*
Buckerfield-b	0.55*b*	7.6*fghi*	2.8*cdef*
Buckerfield-a	0.53*bc*	8.5*fgh*	2.3*cdef*
Hatzic-c	0.53*bcd*	14.0*b*	2.5*cdef*
Richmond-b	0.52*cde*	8.8*efg*	3.1*cdef*
Vye	0.52*cde*	11.9*c*	8.0*a*
Richmond-a	0.51*de*	11.1*cd*	4.3*bcd*
Fairfield	0.51*e*	10.9*cd*	6.9*ab*
Deas-a	0.51*e*	7.6*fghi*	–0.7*g*
Deas-b	0.50*ef*	9.4*def*	0.8*efg*
Westham	0.48*f*	6.5*hij*	1.7*defg*
Monroe-a	0.42*g*	10.5*cde*	7.6*a*
Ladner	0.40*g*	16.8*a*	--14.4*h*
Marble Hill-a	0.34*h*	12.4*bc*	0.2*fg*
Dixon	0.30*i*	3.8*k*	1.4*defg*
Marble Hill-b	0.29*ij*	6.9*ghij*	5.1*abc*
Monroe-b	0.27*j*	6.4*ij*	1.2*efg*

*a–k*Values within columns followed by the same letter not different ($P <$ 0.05) according to Tukey's multiple range test.

Table 9. Fixation of ammonium calculated by linear regression on ammonium not recovered by 2 M KCl extractions after equilibration with 0 to 100 μg NH_4- N g^{-1} for a range of soil samples from the Fraser Valley

Soil	Regression equation: Slope	Constant	R^2
Vye	0.19*a*	–12.1*g*	0.94*abc*
Monroe-a	0.18*ab*	–7.5*def*	0.95*abc*
Monroe-b	0.18*abc*	–2.6*ab*	0.98*ab*
Richmond-a	0.17*abc*	–12.5*g*	0.87*cde*
Dixon	0.16*abcd*	–2.3*a*	0.99*a*
Marble Hill-a	0.16*abcd*	–13.8*g*	0.93*abcd*
Ladner	0.14*bcde*	–28.4*h*	0.90*abcde*
Buckerfield-a	0.13*cdef*	–7.3*def*	0.98*ab*
Buckerfield-b	0.12*def*	–5.0*bcd*	0.96*ab*
Deas-b	0.12*def*	–8.4*f*	0.98*ab*
Westham	0.10*efg*	–5.7*cde*	0.99*a*
Deas-a	0.10*efg*	–7.1*def*	0.94*abcd*
Fairfield	0.09*efg*	–8.1*ef*	0.85*de*
Marble Hill-b	0.09*efg*	–2.0*a*	0.96*abc*
Richmond-b	0.09*fg*	–8.9*f*	0.89*bcde*
Hatzic-c	0.08*fg*	–13.8*g*	0.95*abc*
Hatzic-b	0.07*g*	–4.4*abc*	0.90*abcde*
Hatzic-a	0.06*g*	–2.7*ab*	0.83*e*

*a–h*Values within columns followed by the same letter not different ($P <$ 0.05) according to Tukey's multiple range test.

tion in the presence of toluene was from 10.7 μg N g^{-1} greater to 12.1 μg N g^{-1} smaller than when no toluene was present (Table 7). Likewise, the regression relationship of ammonium measured in solution to that applied in equilibrations having 0 to 200 μg NH_4-N g^{-1} amendments differed for each soil when toluene was added compared with when it was not (data not shown). With toluene added the regression equation constant was 12.4 μg N g^{-1} greater to 19.9 μg N g^{-1} smaller and slope 0.1 greater with than without toluene. There was also a slightly better overall fit for the regression when toluene was present (R^2 = 0.99 to 1.00) than when it was not present (R^2 = 0.90 to 1.00). It was concluded that there was variable microbial activity during the equilibrations and an inhibitor such as toluene is required to derive more correct data for evaluating physical-chemical reactions of inorganic nitrogen in soils.

Visual inspection of plots of the amount of ammonium extracted with 2 M KCl after equilibration of soil samples with 0 to 200 μg NH_4-N g^{-1} and toluene suggested a good linear fit with the possibility of a slight decrease in exchangeable ammonium at the highest treatment rate (data not shown). Regression coefficients (R^2) ranged from 0.993 to 1.000. Regressions for 0 to 100 μg NH_4-N g^{-1} treatments were essentially the same but coefficients were slightly poorer (R^2 from 0.989 to 1.000). It was concluded that adsorption of ammonium by these soil samples was acceptably linear to additions of up to 200 μg NH_4-N g^{-1}. The slope of the regression equation would show the fraction of added ammonium that was adsorbed and the constant would be the amount of exchangeable ammonium already present in the sample (Table 8). Adsorption of added ammonium on exchange sites of the study samples, therefore, ranged from 27 to 60%. Adsorption was the same for the manured and control sites of Deas and Richmond soils and for gully and ridge locations of Buckerfield soil. The soil sample from the shelterbelt area (Marble Hill-a) was able to adsorb slightly more ammonium than the area that had a history of raspberry management (Marble Hill-b). Application of lime did not influence adsorption capacity (Hatzic-a and -b), but both samples of this soil had a slightly higher capacity than the sample from the area that had minimal crop management (Hatzic-c). The subsurface of one soil (Monroe-b sample) adsorbed considerably less ammonium than the corresponding surface sample (Monroe-a). The amount of ammonium initially present in the soil samples calculated by the regression equation (constant of the equation) ranged from 3.8 to 14.0 μg NH_4-N g^{-1} and differed from that extracted by 2 M KCl without prior equilibration. The difference between these two values was not consistent from sample to sample.

Linear regressions between 0 and 200 μg NH_4-N g^{-1} treatment and ammonium not recovered (i.e., clay fixed) by 2 M KCl extraction after equilibration were quite poor (R^2 from –0.09 to 0.91), but visual inspection suggested that the proportion of fixation decreased at the 200 μg NH_4-N g^{-1} treatment rate in essentially all samples (data not shown). Recalculation using 0 to 100 μg NH_4-N g^{-1} treatments resulted in quite good linear fit (R^2 from 0.83 to 0.99). Although a curvilinear relationship would best fit all the data, it was concluded that a linear fit to 100 μg NH_4-N g^{-1} was adequate and simpler for comparative purposes. Variability was relatively large, probably because the fixed ammonium is calculated as unrecovered ammonium and not directly measured, but still provides a good measure of the relative fixation potential of these soils when moderate amounts (0 to 100 μg N g^{-1}) of ammonium are added. From 6 to 19% of the added ammonium was fixed by the soil samples of this study (Table 9). In all of the samples, the constant of the regression equation was negative. Theoretically, the constant of the regression relationship should be essentially zero or within the variability of zero because fixed ammonium should not be extracted by water or KCl solutions. Although analytical and random error could account for a portion of these values being negative, some of this negative occurrence may be that measurement of adsorption by cation exchange involved an operational assumption (i.e., extraction with KCl at a specific concentration and soil:solution ratio). There could also have been simultaneous extraction of native fixed and fixation of added ammonium during the equilibration and KCl extraction steps of the procedure. Kowalenko and Ross (1980) observed, with isotopically labelled ammonium, that some "exchange" of fixed ammonium can occur in some soils. On the other hand, the negative constant may indicate that there needs to be a threshold quantity of extractable ammonium before fixation will occur. Constants of the regression equations for fixation were relatively closely correlated with constants for equations for adsorption by exchange sites ($R^2 = 0.83$). This supports the theory that the negative constants for the fixation regression are a function of KCl extraction more than analytical error. The regression equation relating the constants from the fixed ammonium regression (FXCONST) with that for extractable ammonium (EXCONST) was:

$$\text{FXCONST} = 7.3 - 1.7\ \text{EXCONST}.$$

The slopes of the regression equations for ammonium fixation (Table 9) were not correlated ($R^2 = 0.22$) with the slopes for the regression equations for the exchange ammonium (Table 8), showing that added ammonium that was fixed by the clay was not proportional to adsorption of added ammonium by the exchange sites. Fixation potential in samples from manured and unmanured soils were not consistent (no difference for Deas soil but less fixation potential for manured location than control for Richmond soil) but they were consistent (no differences within each soil) for adsorption on exchange sites. The potential for exchange was less for the soil that had limited management input (Hatzic-c) than both limed or unlimed plot areas (Hatzic-b and -c), but fixation potential was similar for all samples of this soil. Fixation potential was the same for surface and subsurface samples of Monroe soil, but exchange potential was greater in the surface than in the subsurface.

The potential for fixation of added ammonium, as determined by this method, was correlated neither with native fixed ammonium ($R^2 = -0.02$, $n = 18$) nor with clay content ($R^2 = -0.13$). However, the potential for adsorption of ammonium on exchange sites was correlated with clay content ($R^2 = 0.83$) and also native fixed ammonium ($R^2 = 0.47$). It is probable that the significant correlation occurred because initially there was little exchangeable ammonium in the samples, and the lack of correlations is due to the fixed ammonium already present in the samples.

Column Leaching

The proportion of ammonium that was adsorbed during a short duration (approximately 11 pore volumes) of NH_4NO_3 leaching ranged from 84 to 25% of the approximately 500 µg NH_4-N applied to each column of soil (Table 10). Retention of the applied ammonium that was adsorbed against water leaching was generally greater than adsorption during ammonium leaching, and ranged from 97 to 68%. This suggests that adsorbed ammonium is held quite strongly. Correlation between the initial adsorption and subsequent retention was poor ($R^2 = 0.59$) and the regression relationship had a large negative constant (–86) and small slope (+1.7).

Table 10. Comparison of the proportion of ammonium adsorbed during NH_4NO_3 leaching (10 portions of approximately 500 µg NH_4-N to each column) and retention of that adsorbed ammonium against 11 pore volumes of water leaching for 18 Fraser Valley soil samples

Soil	Adsorption (%)	Retention (%)
Hatzic-b[z]	84	97
Deas-a	81*a*	93*a*
Ladner[z]	80	86
Vye[z]	80	90.3
Richmond-a	79*ab*	92*a*
Deas-b	79*ab*	93*a*
Richmond-b	76*ab*	92*a*
Hatzic-a	73*ab*	93*a*
Westham[z]	73	95
Buckerfield-b[z]	72	90.4
Buckerfield-a	72*ab*	89*ab*
Fairfield	69*ab*	89*ab*
Hatzic-c	63*ab*	90.0*ab*
Monroe-a	54*bc*	90.4*a*
Dixon	47*bc*	85*ab*
Marble Hill-a	40*bc*	68*b*
Monroe-b	28*d*	77*ab*
Marble Hill-b[z]	25	51

[z]Single analysis only.

a–*d*Values followed by the same letter for each of adsorption and retention not different ($P < 0.05$) by Tukey multiple range test.

Despite numerous measurements (50 portions of NH_4NO_3 added) required during the long cycle NH_4NO_3 leaching, the soil columns appeared to remain physically stable, and reproducibility of results between duplicates was very good. For example, correlations of accumulated number of pore volume leached between duplicates of each soil were excellent ($R^2 = 1.00$). This suggests consistent or negligible change in soil packing in each column as leaching progressed.

The pattern of adsorption of ammonium from the NH_4NO_3 added during long cycle leaching differed among the four soil samples tested (Table 11). The Marble Hill-b sample never completely adsorbed the added ammonium, whereas the other three soils adsorbed all ammonium added, at least for a short period. The period of essentially complete adsorption for Vye, Buckerfield-b and Ladner soil samples ranged from 7 to 3 pore volumes and hence from 284 to 130 µg N g^{-1}. In all four samples there were two different stages in the rate at which added ammonium was consistently adsorbed, but at a progressively decreasing rate. The first stage of decreasing adsorption (second phase of leaching), the amount of ammonium adsorbed was high, but it declined rapidly with each extra pore volume leached. In the second stage of decreasing adsorption (third phase of leaching), the amounts of ammonium adsorbed were much smaller than in the first stage of decreasing adsorption, and they declined more slowly with each extra pore volume leached. In the

Table 11. The pattern and overall adsorption of ammonium (mean of duplicates) during leaching of soil-filled columns with an NH_4NO_3 solution

Measurement	Soil sample			
	Vye	Buckerfield-b	Ladner	Marble Hill-b
First phase of leaching (when complete adsorption occurred)				
Pore volumes of leaching (number)	4*b*	3*c*	7*a*	NA[z]
Ammonium applied (μg N g^{-1})	208*b*	130*c*	284*a*	NA
Adsorption of applied (%)	98*ab*	100*a*	96*b*	NA
Second phase of leaching (when rapid decreasing rate of adsorption occurred)				
Pore volumes of leaching (number)	8*c*	10*b*	10*b*	14*a*
Ammonium applied (μg N g^{-1})	417*c*	470*b*	413*c*	522*a*
Adsorption of applied (%)	58*a*	62*a*	55*a*	25*b*
Regression equation[y]				
Constant	193*b*	172*b*	267*a*	76*c*
Slope	–150*b*	–125*b*	–194*c*	–64*a*
Coefficient (R^2)	1.00*a*	0.98*ab*	0.98*ab*	0.96*c*
Third phase of leaching (when slow decreasing rate of adsorption occurred)				
Pore volumes of leaching (number)	36*c*	39*bc*	45*b*	56*a*
Ammonium applied (μg N g^{-1})	1838*a*	1899*b*	1817*c*	965*a*
Adsorption (%) of applied relative to				
First elution of third phase	32*a*	30*a*	28*a*	13*b*
All elutions of third phase	15*a*	14*a*	12*a*	4*b*
Regression equation[y]				
Constant	90*a*	80*ab*	80*ab*	15*b*
Slope	–50*c*	–34*b*	–34*b*	–7*a*
Coefficient (R^2)	0.84*a*	0.77*a*	0.76*a*	0.24*a*
Over whole leaching period				
Adsorption of applied				
μg N g^{-1}	722*a*	681*a*	720*a*	207*b*
%	29*a*	27*a*	28*a*	8*b*
Fixation of applied[x] when				
Fresh sample analyzed (μg N g^{-1})	26*a*	32*a*	28*a*	17*a*
Air-dried sample analyzed (μg N g^{-1})	123*a*	95*b*	55*c*	14*d*

a–*d*Values within rows followed by the same letter are not different ($P < 0.05$) according to Tukey's multiple range test.

[z] NA = not applicable, complete adsorption of applied ammonium did not occur in this sample.

[y] Regression equation: % NH_4-N adsorbed = constant + slope × (logarithm of pore volume leached).

[x] Difference between initial analysis of soil and after leaching (both on 2-mm mesh sample).

second phase of leaching where there was the rapid decline of adsorption, the Marble Hill-b sample was also considerably different (i.e., smaller rate of decline in adsorption as shown by the slope of the regression equation between adsorbed ammonium and log of pore volumes leached, and there was proportionately less overall adsorption of ammonium added) than the other three soils. Although Vye, Buckerfield, and Marble Hill-b samples adsorbed similar proportions of added ammonium, the rate of change of adsorption was greatest in the Ladner sample. Similarly, for the third phase of the leaching, the pattern of adsorption for the Marble Hill-b sample was considerably different from the other three samples, and the pattern of adsorption among those three samples differed much less.

Despite some differences in the pattern of adsorption of added ammonium among Vye, Buckerfield-b, and Ladner samples, the proportions of adsorption (27 to 29%) and total amounts adsorbed per unit mass of soil (680 to 720 μg N g^{-1}) were quite similar and considerably greater than for the Marble Hill-b sample (Table 11). Although the change in measurable fixed ammonium in all four fresh samples ranged from 17 to 32 μg NH_4^+-N g^{-1}, the differences among the samples were not statistically different. This shows that there was considerable variability of analyses, possibly related to poor reproduction of sampling a moist sample, that the measurement of fixed ammonium had to be done on a coarse rather than a finely ground sample or a combination of these factors. Air drying the samples after the leaching was completed, however, had a variable effect on the difference in fixed ammonium measured, with large differences for the Vye, Buckerfield-b and Ladner samples, but no effect on the Marble Hill-b sample.

Fixed ammonium in the Vye, Buckerfield-b, Ladner, and Marble Hill-b samples was consistently greater (significant sample and grinding main effect but not of the interaction of the two factor by analysis of variance) when measured on samples that were finely (200 mesh) ground samples (172 μg N g^{-1}) compared with unground (2 mm) samples (160 μg N g^{-1}) (data not shown). The ratio of coarse to fine analyses ranged from 85 to 96%. It was assumed that although fixed ammonium analyses are not as complete on coarsely as compared with finely ground samples, comparisons of fresh unground with dried unground sample analysis were acceptable for determining ammonium fixation during the leaching studies.

GENERAL DISCUSSION AND CONCLUSIONS

Fixed ammonium was found in all of the soil samples collected for this study. The amounts of fixed ammonium (59 to 224 μg N g^{-1}) were similar to those reported for other North American soils (Young and Aldag 1982), and were correlated with the amount of clay in the soil. There was some indication that sample history also influenced that amount, but more analyses of samples of varying history would be required to determine those that have the greatest influence.

Two molar KCl extraction of applied ammonium by wetting and drying, equilibration, and column leaching methods showed that the soils were capable of fixing applied ammonium, and that all methods were limited in their ability to quantify potential fixation. The limitation was partially related to the fact that it was difficult to distinguish adsorption by cation exchange on soil surfaces from ammonium fixation within the clay lattice. The measurement of ammonium fixation as that not recovered by 2 M KCl after amendment involved wetting and drying of the sample. This wetting and drying resulted in some physical-chemical changes in soluble and exchangeable ammonium pools and probably the fixed ammonium pool and fixation process. The proportion of fixed ammonium measured by this method decreased as the amount of ammonium increased. From 8 to 68% of 53 μg N g^{-1} added and 0 to 62% of 106 μg N g^{-1} added was not recovered by 2 M KCl from eight samples studied by this method.

The equilibration approach showed that adsorption on cation exchange sites was the dominant process for removing ammonium from solution, but fixation by clays was also important. Adsorption by the exchange mechanism was linearly related to concentration to at least 200 μg NH_4-N g^{-1} added, but the proportion of ammonium fixed by clays started to decrease at around 100 μg NH_4-N g^{-1} application.

Column leaching, which may provide information that is closer to actual field conditions because of a narrower soil to solution ratio, was more difficult to do and the results difficult to fully interpret. Only four soil samples were leached with sufficient ammonium to observe the pattern of adsorption, but differentiation between exchange and fixation could not be determined from the patterns that occurred and direct analysis of fixed ammonium was necessary. However, air drying the samples changed the amount of fixed ammonium determined in three of the four samples. In the three samples where air drying had an effect, the magnitude of the effect was different among the soils. This observation on the effect of air drying confirms observations from a field study of a Fraser Valley soil (Kowalenko 1989), and studies at other locations (Sucha and Siranova 1991; Thompson and Blackmer 1993). It is possible that there may be different types of ammonium fixation. Lumbanraja and Evangelou (1994) speculated from observations in their studies that fixation did not require "physical entrapment by a collapsed interlayer" of the soil clay.

Short cycle leaching involving adsorption and then desorption showed that retention of ammonium was not directly related to adsorption of added ammonium, supporting the observation that fixation and exchange occurred simultaneously but were not necessarily proportional. Long cycle leaching showed that the adsorption pattern varied among soils; therefore, short cycle leachings may not have proceeded to a similar point with respect to ammonium saturation of adsorption sites and comparisons among soils would have limited meaning. Since the soils examined by long leachings adsorbed from 200 to 720 μg NH_4-N g^{-1}, it is evident that large amounts of ammonium over short periods or small amounts over long periods need to be applied to the soils to approach saturation of fixing and exchange sites. It is possible that the pattern of ammonium leaching (i.e., a period of high rate of adsorption of added ammonium followed by a low rate of adsorption) may have indicated periods when exchange or fixation was the dominant adsorption process. Direct measurement of fixed ammonium at various stages during ammonium leaching would be required to determine if that was the case. Isotope tracer may be required, as Kowalenko and Ross (1980) showed that added ammonium can replace native fixed ammonium without changing the total amount of fixed ammonium.

This laboratory study has shown that Fraser Valley soils contain significant but varying amounts of clay-fixed ammonium and were capable of fixing ammonium added to them. Fixed ammonium and the fixation process should not be ignored when interpreting nitrogen research data and incorporated into computer simulation models. Fixation of ammonium apparently has not been incorporated into deterministic nitrogen models (Styczen and Storm 1995) and, if this process is included in these models, they should also incorporate a relationship to soluble and exchangeable ammonium. Unfortunately, measurement of fixed ammonium is not convenient for routine analyses and further work is required to develop methods to improve studies of the fixation process.

ACKNOWLEDGMENT

This study was funded by the Canada – British Columbia Soil Conservation Program. The authors thank Orlando Schmidt (Program Coordinator of the Dairy Producers' Conservation Group) and Dr. Art Bomke (Soil Science Department, The University of British Columbia), who assisted in the selection of some of the sites where the soils were sampled.

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