

AN ABSTRACT OF THE THESIS OF

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(Name) (Degree) (Major)

Date thesis is presented August 9, 1965

Title INFLUENCE OF ANHYDROUS AMMONIA ON THE
SOLUBILITY OF SOIL ORGANIC MATTER

Abstract approved [REDACTED]
(Major professor)

Four surface and three subsurface horizons of agriculturally important Oregon soils were exposed to excessive volumes of anhydrous ammonia and reequilibrated with the atmosphere for several time periods prior to extraction with water. The carbon solubilized was determined by a modified wet combustion technique. Nitrogen in the soils, extracts, and residues was determined by a micro-Kjeldahl procedure.

About three to ten % of the indigenous carbon was extracted. The actual amount of carbon solubilized was proportional to the original soil carbon contents. This amount of carbon approximated that solubilized during extraction of soils with 0.15 N NH_4OH . The soil moisture content at ammoniation time appeared to have little influence on the quantity of carbon solubilized. With an increase in reequilibration time with the atmosphere there was only a slight decrease in the amount of carbon extracted.

Anhydrous ammonia application and subsequent aeration increased nitrogen contents over the indigenous values about twice as much in the C horizons as in the A horizons. Within three days 20 to 50% of the initially retained nitrogen was lost to the atmosphere. The pH values of the soils and extracts corresponded to the nitrogen values and decreased with the length of time elapsing prior to extraction.

Assuming that the laboratory treatments and extracting methods were much more severe and effective in solubilizing organic matter than would be expected under field conditions, it is suggested that soil structural changes due to organic matter solubilization after anhydrous ammonia application would be minor. Changes in structural stability may be more related to phenomena accompanying large pH changes than to dissolution and redistribution of the organic fraction.

INFLUENCE OF ANHYDROUS AMMONIA ON THE
SOLUBILITY OF SOIL ORGANIC MATTER

by

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A THESIS

submitted to

OREGON STATE UNIVERSITY

in partial fulfillment of
the requirements for the
degree of

MASTER OF SCIENCE

June 1966

APPROVED:



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Date thesis is presented August 9, 1965

Typed by Opal Grossnicklaus

ACKNOWLEDGMENTS

The author gratefully acknowledges the thoughtful suggestions and patient guidance of Dr. J Lowell Young throughout the research and preparation of this manuscript. Appreciation is also extended to Dr. H. Aft for his valuable advice and useful ideas.

The support of the project by Phillips Petroleum Company, the Agriculture Research Service, and Oregon State University is greatly appreciated.

The encouragement and moral support of my friends and the understanding and patience of my family have remained utmost in importance to me throughout this study.

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INFLUENCE OF ANHYDROUS AMMONIA ON THE SOLUBILITY OF SOIL ORGANIC MATTER

INTRODUCTION AND LITERATURE REVIEW

Anhydrous ammonia is the most alkaline source of fertilizer nitrogen and upon reacting with soil moisture has been assumed to form ammonium hydroxide (13, 26, 27, 44). Like alkalies that are often used to dissolve soil organic matter, ammonia applied to soil may act as a solvent for certain soil organic fractions (5, 19, 33, 37, 41, 45). Several researchers have noted organic matter in water extracts of ammoniated soils as indicated by brown-colored extracts (6, 19, 20, 30, 33, 48). Violanda (48) found nitrogen added to a muck soil as ammonia was uniformly distributed in the organic matter. Ammoniation not only increased the nitrogen content but also the solubility of the soil organic matter.

Changes in soil structural stability after anhydrous ammonia application have been blamed or credited, in part, to induced changes in organic matter solubility (5, 6, 20, 41). For instance, some farmers have complained of degraded tilth after applying anhydrous or aqua ammonia, while Anderson (5) claimed that with subsequent decreases in pH, solubilized soil organic matter redistributes and precipitates on the mineral soil particles forming more water-stable aggregates than were present prior to ammoniation.

Reactions Occurring With Anhydrous Ammonia Application

In practical application, anhydrous ammonia is injected into the soil as a liquefied gas which instantly vaporizes and diffuses about four inches radially. A cylindrical zone of high ammonia or ammonium concentration, or both, is created with pH values as high as 9.5 (5, 6, 20, 27, 30, 34, 44). Problems are encountered in anhydrous ammonia application differing from those peculiar to solid and liquid fertilizer materials (44). This recognizes that nitrogen sources and soil components influence the chemical reactions occurring in the soil (16, 33). Sohn and Peach (43) found more nitrogen fixed¹ by the soil, for example, when the nitrogen source was an ammonia rather than an ammonium fertilizer. This ammonia fixation may be due, in part, to reactions of ammonia directly with soil organic matter with the formation of organic nitrogenous compounds containing little exchangeable ammonium. Although some investigators feel ammonia reacts only slightly with soil organic materials (3, 17), other researchers have shown organic matter to have a high affinity for ammonia (16, 31, 43). Reactions of ammonia with soil organic matter may account for at least 50% of the

¹"Fixed ammonia" is considered here as the added anhydrous ammonia held by the mineral and organic soil fractions against extraction with 0.5 N KCl.

ammonia fixed by surface soils (16, 43). Increases in ammonia fixation with soil depth have also been attributed to ammonia reactions with soil organic matter (2, 3, 7, 11, 18, 28, 32, 33, 34, 40).

Effect of Moisture on Ammonia Retention²

Diverse opinions exist concerning the role of soil moisture on ammonia retention. As ammonia and water are highly soluble in one another, soil moisture could serve as a short-time carrier until the ammonia reacted with the soil clay and organic particles. Stanley (44) reported optimum ammonia retention at 15 to 18% moisture in a Putman silt loam. He felt that the air-dry soil (2% moisture) contained too little water with which the ammonia could react and be held while at higher soil moisture contents approximating field capacity (25% moisture), less ammonia was retained because the ammonia was unable to move radially as readily from the injection point. Supporting Stanley's observations, McDowell (30) found that an air-dry soil (Putman silt loam) retained less ammonia than did a moist soil (17% moisture). Blue and Eno (9, 10) reported a high degree of correlation between the soil moisture content and ammonia retention in a sandy soil.

² Ammonia retention is considered as the difference between the total nitrogen content of an ammoniated soil and that of a corresponding non-ammoniated control soil.

Other investigators conclude that for practical purposes soil moisture has a negligible effect on ammonia retention (23, 25, 41). After ammoniating soils at two moisture contents, Nommik (34) found the more moist soil retained more ammonia while the ammonia traveled further radially in the less moist soil. Later, due to a higher nitrification rate in the soil containing the higher moisture content, he found no difference in ammonia retention between the two soils and concluded that moisture was not a decisive factor in ammonia retention.

McDowell (30) found that a moist sandy soil lost more ammonia than did an air-dry silt loam or clay. This suggests that factors other than soil moisture (within the range encountered practically) contribute considerably to ammonia retention. For example, pronounced effects on ammonia retention have been related or attributed to such factors as exchange capacity, organic matter, type of clay, and the greater specific surfaces afforded by medium and heavy-textured soils (21, 23, 25, 30, 50).

Objectives

Although soil organic matter solubilization after anhydrous ammonia application has been noted, primarily in terms of the color of soil extracts, the amount of organic carbon solubilized has not been measured. It is difficult to evaluate the significance

of the solubilization without knowing the quantity of organic matter solubilized. The objective of the present study was to determine the extent to which anhydrous ammonia application and subsequent water extraction influenced the solubility of soil organic matter by evaluating the carbon and nitrogen contents of the soils and extracts

- 1) With relation to the time elapsing between ammoniation and water extraction.
- 2) With relation to the soil moisture content at the time of ammoniation.

EXPERIMENTAL METHODS

Soils

The surface and one subsurface horizon of four widely different soils were studied. The soils were:

- 1) Chehalis silt loam, an alluvial soil found on the flood plain of the Willamette Valley. It is used extensively for the growth of inter-tilled crops and represents one of the better agricultural soils in the Willamette Valley.
- 2) Nehalem silt loam, an alluvial soil developed from recent alluvium and found in coastal areas of Oregon. Due to the short growing season, it is used dominantly for pasture and production of forage crops.
- 3) Walla Walla silt loam, a Chestnut soil developed from loess and found in the 12 to 16-inch rainfall areas throughout the Columbia basin. It is used extensively for wheat farming.
- 4) Quillayute silt loam, an Ando-like soil developed on old alluvium in the coastal areas of Oregon. It is subject to cold, wet seasonal limitations and is used for the growth of pasture in the dairy country surrounding Tillamook.

The soils are some for which characterization data were available from a previous study of ammonium and ammonia fixation (51).

They were sampled from profiles of agriculturally important soils in Oregon and represent wide ranges in great soil groups, parent materials, annual rainfall and organic matter contents. Profile descriptions are included in the appendix.

Laboratory Procedures

Soil Moisture Contents at Ammoniation

The A and C horizons of the Chehalis, Nehalem, Walla Walla, and the A horizon of the Quillayute soils were ammoniated at two moisture contents. Moisture 1 was the air-dry moisture content of the soil. Since soils have different moisture constants, it was felt more comparable moisture contents would be attained by equilibrating the samples over water for one week rather than imposing a particular moisture content on all the soils. Thus, moisture 2 was that attained by equilibrating approximately 20 g of air-dry soil (in a petri dish) over water in a desiccator (100% relative humidity) for seven days prior to ammoniation (8). After equilibration, moisture 2 contents more than doubled the moisture 1 contents (Col. 2, Table 1).

Sample Ammoniation

Approximately 20 g of the soil sample were placed in a polyethylene tube six inches long and 3/4 inches in diameter. Anhydrous

ammonia under a slight pressure was passed slowly through the sample for one-half hour at approximately 10 ml/min, an exaggerated treatment. One end of the polyethylene tube was connected to the anhydrous ammonia tank while the other end was open to the atmosphere. A simple flowmeter consisting of a plastic bead in glass tubing was inserted into the system as a visual check on the ammonia flow rate.

Aeration and Reequilibration after Ammoniation

Extraction 1 was made immediately after sample ammoniation and prior to passing air from the laboratory line through it for 30 min to help remove a major portion of the loosely-held excess ammonia. Extraction 2 was made immediately following sample ammoniation and a 30 min aeration. Extractions 3 and 4 were made three and ten days after ammoniation and aeration.

Extraction of Ammoniated Samples

Four-gram subsamples of each ammoniated-aerated soil sample were immediately weighed into 50 ml bottles and stored exposed to the atmosphere until they were extracted with water. The subsamples were extracted with water after each of the several time periods of reequilibration with the atmosphere. Twenty ml of distilled water were added and the sample was shaken continuously for

15 min on a mechanical shaker. The contents of the bottle were then filtered through a Whatman No. 5 filter paper in a Buchner funnel and washed with two additional 10 ml aliquots of distilled water. The extracts were stored briefly in a refrigerator until they were analyzed for carbon and nitrogen. The soil residues were air-dried before storing in closed bottles.

Ammonia Retention and Distribution

One-half gram of the soil, extracted residue, or 4 ml of the extract was placed into a semi-micro-Kjeldahl flask immediately after ammoniation-aeration or extraction with water. Total nitrogen was determined by a semi-micro-Kjeldahl procedure using 8 ml of concentrated sulfuric acid containing salicylic acid (for nitrates) and a copper sulfate-selenium (5:1) catalyst for digestion. About 15 ml of 20 N NaOH were added and the ammonia was distilled into a 2 % boric acid solution containing a mixed indicator. The ammonium in the distillate was titrated with standardized 0.015 N HCl.

Extraction of Samples with Ammonium Hydroxide

Four grams of air-dry soil were weighed into a 50 ml bottle. Twenty ml of ammonium hydroxide were added and the bottle was shaken continuously for 15 min on a mechanical shaker. The contents were then filtered through a Whatman No. 5 filter paper in a

Buchner funnel and washed with two 10 ml aliquots of distilled water. Chehalis A, Nehalem A, Walla Walla A, and Quillayute A soils were extracted with 0.015, 0.15, 0.75, 1.5, and 7.5 N NH_4OH . Since dispersion complicated filtering of some of the soils at the higher normalities of ammonium hydroxide, recovery of some of the extracts was aided by centrifugation prior to filtering. The soil organic matter solubilized by the ammonium hydroxide was determined by the same wet combustion procedure that was used to analyze the extracts from the anhydrous ammonia-treated samples.

Carbon Determinations

Soil organic matter determination procedures are numerous (1, 12, 24, 39, 42, 45, 47, 50). Part of the problem leading to proliferation and choice of methods is that the percentage of carbon in soil organic materials is not uniform or constant (15, 35, 38, 42). To avoid conversion factors between soil organic matter and carbon contents, it was considered desirable to report organic matter changes in terms of carbon changes in the soils, residues, and extracts. As it turned out, considerable effort was consumed in arriving at the two carbon procedures finally adopted.

A rapid dry combustion technique yielding quantitative total carbon was developed (52) partly for such work. The brown color of extracts plus reported solubilization of copious quantities of

organic materials from ammoniated samples suggested considerable amounts of carbon in the extracts. Moreover, the presence of non-colored organic materials in the extract would tend to invalidate the density of the extract color as a reliable index of organic matter solubilized. The amount of carbon, however, in 2 ml of extract, the capacity of the ceramic boat used in the dry combustion method, turned out to be insufficient for a satisfactory determination. The blank associated with the dry combustion procedure approximated 1 mg, which approached the amount of carbon in 2 ml of extract. Considerable sample preconcentration, or repeated pipetting and drying of several aliquots in the combustion boats, was necessary to obtain an adequate amount of carbon from an extract for combustion; either alternative was considered undesirable.

Wet combustion techniques were then investigated. A modification of a bioassay for detecting small amounts of antifungal substances in soils looked promising (29). The procedure is similar to the Walkley-Black (49) method, i. e. being dependent on spontaneous heating of dilution and the reduction of chromic acid. Less heat was available and less organic matter was oxidized as compared with Schollenberger's (39) application of external heat. Discrimination between the active and less active forms of carbon is claimed (24, p. 219). Although soils contain chloride, ferrous, and manganese compounds capable of complicating analytical procedures (24),

Bremner (12) considered these compounds present in too small amounts in soils to affect the procedure. Reduction of chromic acid was measured by colorimetry rather than by titration as with several procedures (22, 46).

This procedure, as modified, gave consistent results and followed Beer's law within the 0 to 1.25 mg C range, well encompassing the quantity of carbon present in 1 ml of soil extract. The amount of dichromate present is sufficient for oxidizing 3.7 mg organic matter.

Wet Combustion Technique for Carbon in Extracts. One ml of extract was pipetted into a 10 ml test tube. One ml of distilled water was added followed by the addition of 4 ml of $K_2Cr_2O_7-H_2SO_4$ (1.27 g $K_2Cr_2O_7$ in 200 ml conc. H_2SO_4). The extract and reagents were mixed immediately and transmittance read 20 min later with the colorimeter set at 645 m μ . The blank consisted of 2 ml distilled water and 4 ml $K_2Cr_2O_7-H_2SO_4$. Glucose was used as a standard.

Dry combustion Procedure. Total carbon of the untreated air-dry soils was determined by dry combustion using a high-frequency induction furnace (52). With this technique $\frac{1}{2}$ g of soil was placed in a ceramic boat. Two grams of iron chips and 1 g of granulated tin were spread on top of the soil sample. A 60-sec ignitor preheat and a 120-sec combustion in a stream of oxygen with no additional oxygen flush was used. The carbon was weighed as carbon dioxide collected in a flask of caroxite. Total carbon was also determined on the

air-dried residues after ammoniation and leaching, as described above, to see if the carbon solubilized could be more conveniently determined by difference. The results, though possibly a little low³, showed the difference method by dry combustion to be less accurate than the wet-combustion technique.

Paper Chromatography

Water extracts of the ammoniated soils were spotted near the end of a strip of Whatman No. 5 paper. The solvent butanol-acetic acid-water (6:2:1 v/v) was used in the descending technique of chromatogram development. After air drying, the papers were observed under an ultraviolet lamp to detect fluorescent compounds and treated with iodine and ninhydrin to detect possible nitrogenous compounds.

Thin-layer Chromatography

Small amounts of the extracts were spotted on glass plates coated with a thin layer of silica gel G. The plate was placed in a tank with one edge in the solvent ethylmethyl ketone-formic acid-acetone-water (40:1:2:6 v/v). The plates were air-dried and observed under ultraviolet light and after iodine and ninhydrin

³Inadvertently, the ignitor was not preheated as it should have been and incomplete combustion of some organic components might have occurred (52).

treatments.

Acid-insoluble organic material was precipitated by acidifying four drops of the extract with one drop of 10% HCl. Paper and thin-layer chromatography techniques were repeated on aliquots of the supernatant as described, again using ultraviolet light, iodine, and ninhydrin treatments for detection of reactive components.

RESULTS AND DISCUSSION

Carbon Solubilized During Water Extraction of Anhydrous Ammonia-Treated Soils

"Copious" quantities of soil organic matter have been observed in extracts of ammoniated soil samples but specific quantities have not been reported. Table 1 shows the milligrams of carbon per gram of soil (mg C/g soil) that were solubilized and the percent of the total indigenous carbon this represented in each case. Between 0 and 5 mg C/g soil were measured in the extracts, except for the Quillayute which yielded about 13 mg C/g soil. The carbon solubilized represented 3 to 10% of the total carbon in all the samples, but the absolute amounts in lbs/A varied markedly and were directly related to the original soil carbon contents. The extraction 2 ($\frac{1}{2}$ hr) extracts of the air-dry surface horizons are illustrated in Fig. 2, row 2 (p. 35).

Carbon Solubilized in Relation to Moisture Content at Ammoniation Time

From Table 1 it is apparent that under the experimental conditions employed the amount of moisture present at the time of ammoniation had little influence on the amount of carbon solubilized (See discussion under ammonia retention).

Table 1. Carbon Measured in Water Extracts of Soils Treated with Anhydrous Ammonia and Reequilibrated with the Atmosphere for Varying Time Periods

Soil	% H ₂ O	% C	Time Period Reequilibrated	Carbon Solubilized		
				mg C/g soil	% Indigenous C	
Chehalis A	4.9	4.10	C*	0.7	2	
			0	2.3	6	
			$\frac{1}{2}$	2.6	6	
			3	1.8	4	
			10	2.2	5	
	11.5	3.83	C	0.5	1	
			$\frac{1}{2}$	2.1	5	
			3	2.1	5	
			10	2.1	5	
	Chehalis C	4.1	1.18	C	0.4	3
$\frac{1}{2}$				0.8	7	
3				0.4	3	
10				0.8	6	
9.0				1.12	C	0.1
		$\frac{1}{2}$	0.5		4	
		3	0.5		4	
		10	0.7		7	
		Nehalem A	7.7		4.92	C
0				5.0		10
$\frac{1}{2}$	4.5			9		
3	3.6			7		
10	3.5			7		
15.5	4.53		C	0.7	2	
			$\frac{1}{2}$	4.9	10	
			3	3.1	7	
			10	2.2	5	

Table 1 (Continued) Carbon Measured in Water Extracts of Soils Treated with Anhydrous Ammonia and Reequilibrated with the Atmosphere for Varying Time Periods

Soil	%H ₂ O	% C	Time Period Reequilibrated	Carbon Solubilized	
				mg C/g soil	% Indigenous C
Nehalem C	7.5	2.14	C	0.2	0
			$\frac{1}{2}$	1.1	5
			3	1.2	6
			10	1.3	6
	12.6	2.03	C	0.4	2
			$\frac{1}{2}$	1.6	8
			3	1.5	7
			10	0.7	4
Walla Walla A	1.6	.98	C	0.0	0
			0	0.4	4
			$\frac{1}{2}$	0.5	5
			3	0.5	5
			10	0.4	4
	3.9	.96	C	0.0	0
			$\frac{1}{2}$	0.1	1
			3	0.0	0
			12	0.0	0
Walla Walla C	1.6	.42	C	0.0	0
			$\frac{1}{2}$	0.1	3
			3	0.0	0
			10	0.4	9
	4.3	.41	C	0.0	0
			$\frac{1}{2}$	0.0	0
			3	0.0	0
			12	0.0	0

Table 1 (Continued) Carbon Measured in Water Extracts of Soils Treated with Anhydrous Ammonia and Reequilibrated with the Atmosphere for Varying Time Periods

Soil	% H ₂ O	% C	Time Period Reequilibrated	Carbon Solubilized	
				mg C/g soil	% Indigenous C
Quillayute A	9.2	13.88	C	0.0	0
			0	13.4	10
			$\frac{1}{2}$	10.9	8
			5	6.1	5
			10	5.8	4
	19.6	12.92	C	0.0	0
			$\frac{1}{2}$	12.8	10
			5	6.0	5
			10	6.4	5

*

- C = Control
 0 = Extraction immediately following ammoniation
 $\frac{1}{2}$ = Extraction following ammoniation and 30 minute aeration
 3 = Extraction 3 days following ammoniation and aeration
 10 = Extraction 10 days following ammoniation and aeration

Carbon Solubilized in Relation to Time of Atmospheric Reequilibration

Table 1 shows the carbon extracted by water after the anhydrous ammonia-treated samples had been exposed to the atmosphere for various time periods. The amount of carbon solubilized did not vary greatly with the length of reequilibration with the atmosphere. As one might expect, the trend was for less carbon to be solubilized after several days reequilibration than was solubilized immediately after ammoniation.

Ammonia Retention and Distribution

Changes in ammonia retention⁴ after ammoniation-aeration were measured to help evaluate the role of ammonia in solubilizing soil organic matter. Table 2 shows the total nitrogen values of the samples prior to ammoniation, after ammoniation (of air-dry surface soils), and preceding each water extraction. Table 2 also includes total nitrogen values of the extracts immediately following extraction. The data show that like the carbon solubilized the ammonia retention differed only slightly for the two moisture levels established in the soil prior to ammoniation (Table 2 and Fig. 1).

Some investigators (10, 44) have reported moisture as a

⁴See page 3 for definition.

Table 2. Total Nitrogen Values of Ammoniated Soils and Water Extracts Following Several Periods of Time for Reequilibration with the Atmosphere

Soil (% C)	% H ₂ O	Soil pH	Time Period Reequilibrated	Soil N Before Extraction me/100 g	Extract N me/100 g	Extract pH	
Chehalis A (4.10)	4.9	5.8	C*	21.3	0.7	6.8	
		10.4	0	101.5	62.6	10.2	
		10.0	$\frac{1}{2}$	69.8	33.8	9.6	
		8.6	3	48.1	9.3	8.5	
		8.4**	10	46.6	8.3	8.8	
	11.5			C	19.9	1.5	7.1
				$\frac{1}{2}$	66.2	38.7	10.0
				3	51.0	7.9	8.8
				10	46.4	6.3	8.8
Chehalis C (1.18)	4.1	6.2	C	7.4	1.9	6.7	
			$\frac{1}{2}$	45.2	24.8	9.7	
			3	30.2	7.3	9.0	
			10	29.0	9.8	8.9	
	9.0			C	7.0	1.2	7.6
				$\frac{1}{2}$	46.9	38.8	10.3
				3	28.3	5.8	9.0
				10	25.8	5.8	9.0
Nehalem A (4.92)	7.7	5.4	C	29.7	0.4	5.5	
		10.5	0	159.0	66.5	10.0	
		10.1	$\frac{1}{2}$	107.0	64.2	9.9	
		8.4	3	85.3	13.5	8.9	
		8.0**	10	74.2	11.1	8.7	
	15.6			C	27.2	2.0	6.3
				$\frac{1}{2}$	89.4	58.2	10.0
				3	78.0	10.9	8.9
				10	70.9	8.3	8.5

Table 2 (Continued) Total Nitrogen Values of Ammoniated Soils and Water Extracts Following Several Periods of Time for Re-equilibration with the Atmosphere

Soil (% C)	% H ₂ O	Soil pH	Time Period Reequilibrated	Soil N Before Extraction me/100 g	Extract N me/100 g	Extract pH				
Nehalem C (2.14)	7.5	5.7	C	12.4	0.3	7.1				
			$\frac{1}{2}$	82.7	37.9	9.9				
			3	64.5	9.6	9.0				
			10	57.0	7.8	8.8				
	12.6			C	11.8	1.3	6.6			
				$\frac{1}{2}$	73.1	43.8	10.0			
				3	57.4	7.9	8.9			
				10	53.9	7.1	8.7			
				Walla Walla A (0.98)	1.6	6.6	C	5.7	0.7	6.5
							0	28.1	16.6	10.2
$\frac{1}{2}$	19.6	10.3	9.9							
3	13.6	5.0	9.2							
10	11.9	2.6	9.1							
8.6**										
3.9			C	5.5	1.6	6.6				
			$\frac{1}{2}$	15.1	6.0	9.6				
			3	13.2	3.3	8.7				
			12	11.9	2.8	9.1				
			Walla Walla C (0.42)	1.6	7.0	C	2.8	1.2	6.7	
$\frac{1}{2}$	16.4	10.7				9.9				
3	9.6	4.1				9.2				
10	9.4	3.3				9.1				
4.2				C	2.7	1.3	6.8			
				$\frac{1}{2}$	10.3	5.9	9.7			
				3	10.4	3.5	9.1			
				12	9.2	2.7	9.2			

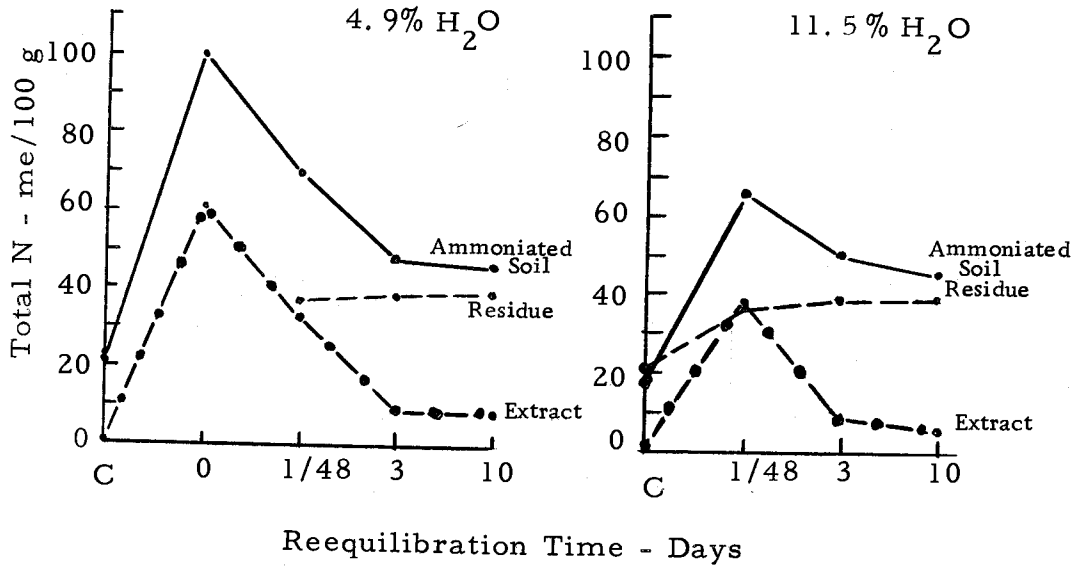
Table 2 (Continued) Total Nitrogen Values of Ammoniated Soils and Water Extracts Following Several Periods of Time for Re-equilibration with the Atmosphere

Soil (% C)	%H ₂ O	Soil pH	Time Period Reequilibrated	Soil N Before Extraction me/100 g	Extract N me/100 g	Extract pH	
Quillayute A (13.88)	9.2	4.8	C	66.0	1.5	5.9	
		10.1	0	264.7	30.0	9.8	
		9.9	$\frac{1}{2}$	197.0	39.8	9.4	
		8.4	5	141.7	21.4	8.9	
		7.9**	10	132.7	19.8	8.7	
	19.6			C	59.0	2.0	6.6
				$\frac{1}{2}$	190.7	44.9	9.7
				5	154.7	15.8	8.8
				10	146.4	15.0	8.6

* See footnote p. 18.

**14 days.

CHEHALIS A



CHEHALIS C

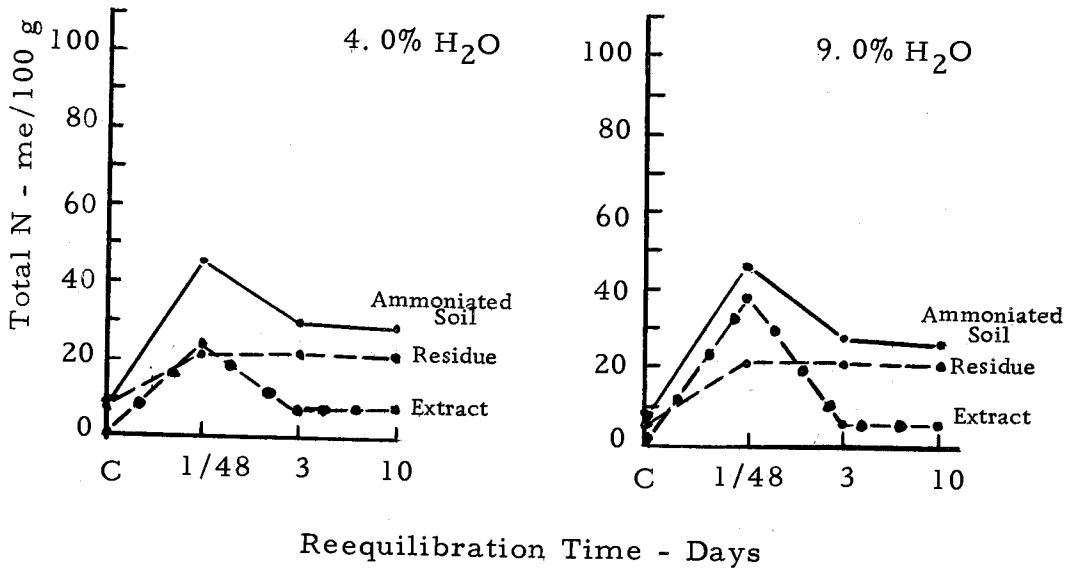


Figure 1. Nitrogen values of soils (ammoniated), extracts, and residues related to length of reequilibration time and soil moisture at ammoniation time.

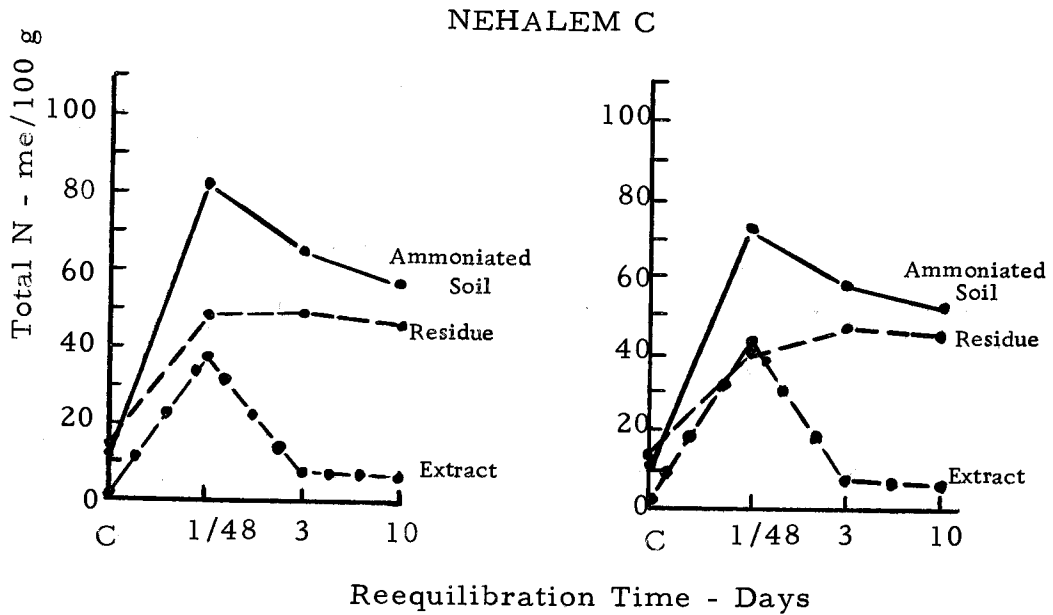
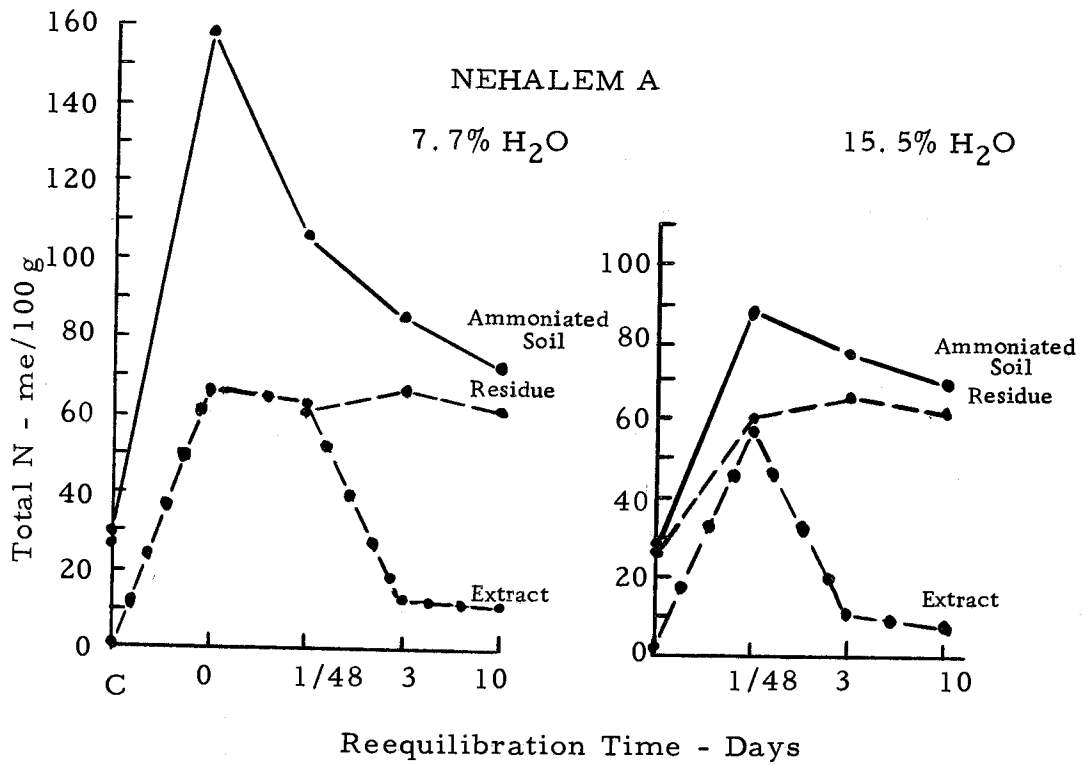
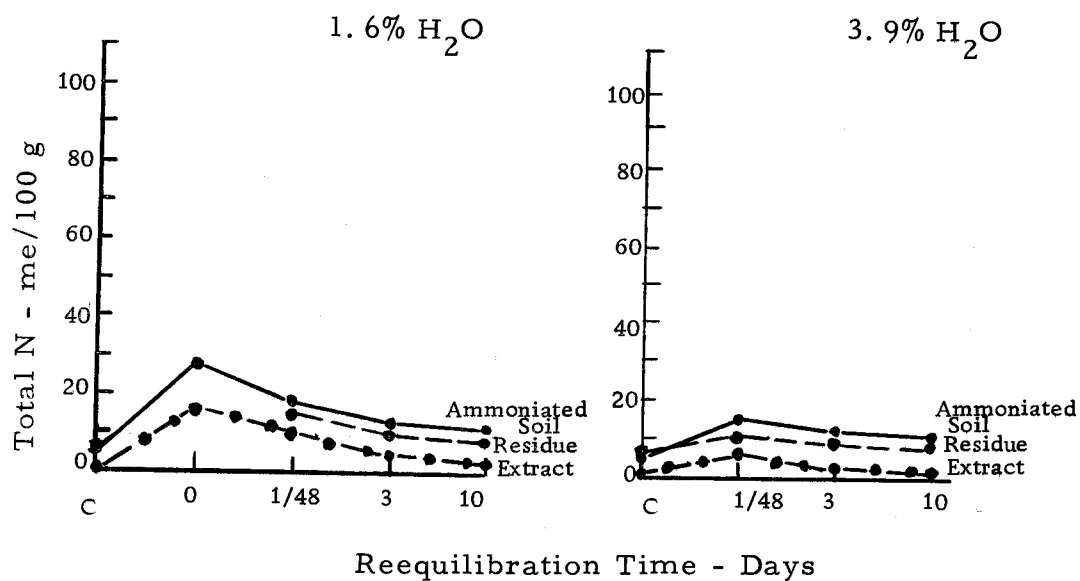


Figure 1 (Continued). Nitrogen values of soils (ammoniated), extracts, and residues related to length of reequilibration time and soil moisture at ammoniation time.

WALLA WALLA A



WALLA WALLA C

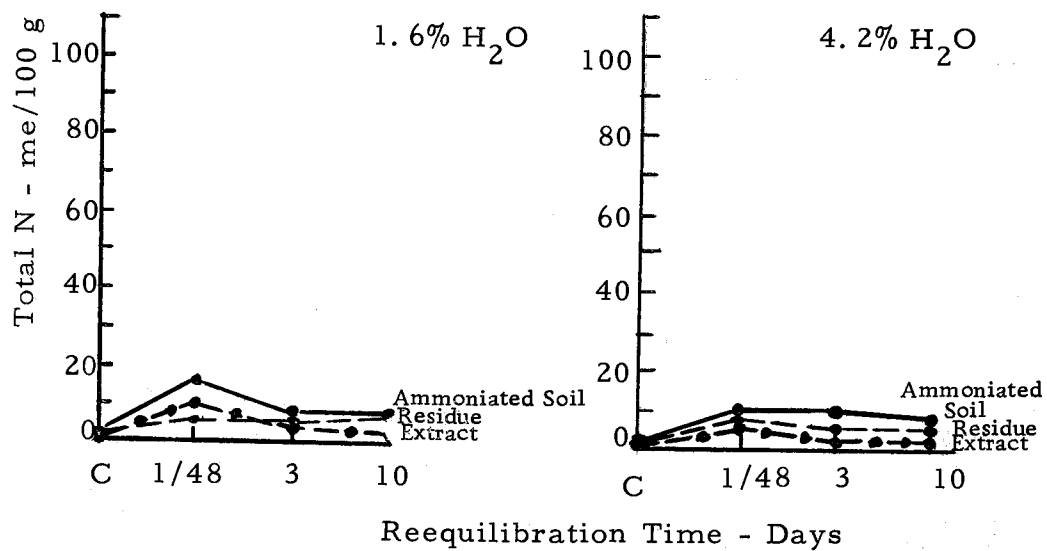


Figure 1 (Continued). Nitrogen values of soils (ammoniated), extracts, and residues related to length of reequilibration time and soil moisture at ammoniation time.

QUILLAYUTE A

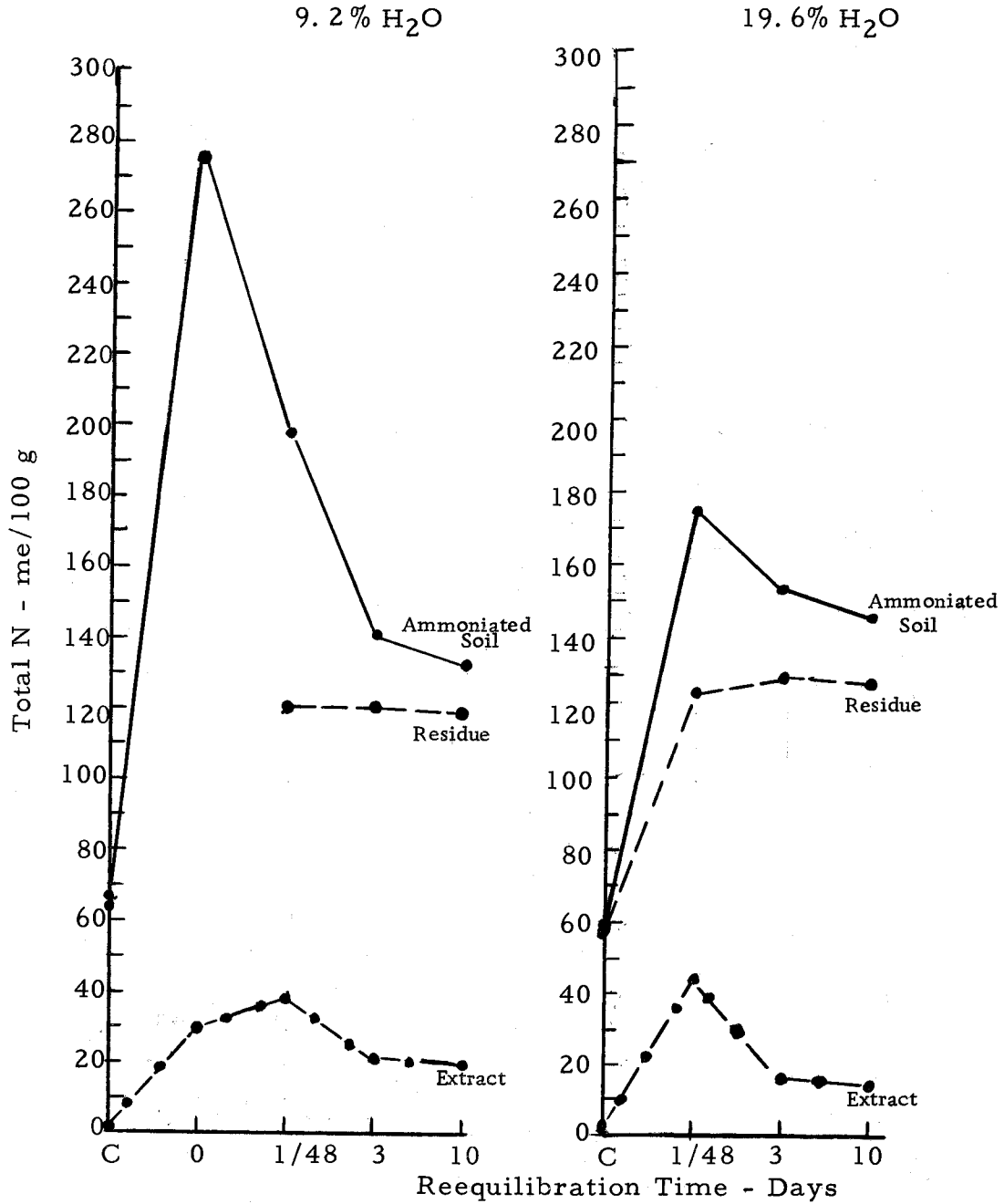


Figure 1 (Continued). Nitrogen values of soils (ammoniated), extracts, and residues related to length of reequilibration time and soil moisture at ammoniation time.

major factor influencing ammonia retention by soils while others believe it to be of little significance under field conditions (25, 34, 41). Ammoniation procedures vary according to experiments and therefore probably achieve different ammoniation results. Water vapor and ammonia sorption interactions have been indicated (53). Brown and Bartholomew (13) postulated that aqueous vapor and gaseous ammonia compete for sorption sites in moist clay systems and they cited changes in the appearance of the clay during ammoniation as evidence of water vapor and ammonia interactions. Similar phenomena were noticed in the present study. As soon as ammonia was introduced into the system, a wetting front moved through the cylinder of soil. The soil became darker and droplets of moisture appeared on the inside of the polyethylene tube. The front passed completely through the cylinder within five minutes and not until then could ammonia be detected passing from the system. During ammoniation, soil temperatures increased as much as 25 degrees C. This heat of reaction of the ammonia with the soil components and moisture would help account for moisture loss during ammoniation.

In retrospect, the adopted ammoniation aeration procedure could have changed both the air-dry and moist soils to nearly the same moisture level, thus explaining why no great change in ammonia retention or solubilization of soil organic matter was

measured. Because of this displacement "competition" between ammonia and water vapor, it would be difficult to achieve saturation exposure of ammonia at a preset specified soil moisture.

With respect to nitrogen distribution, Table 2 and Fig. 1 showing total nitrogen values of the soils and extracts indicate that ammoniation treatments increased the nitrogen content of the soils over the indigenous nitrogen values about twice as much in the C horizons as in the A horizons. This trend held for all atmospheric exposure times. However, a substantial and rapid nitrogen loss of 20 to 50 % occurred within three days and an additional 3 to 15% was lost between the three and ten-day extractions. Table 3 shows that at the end of ten days 30 to 55% of the ammonia nitrogen retained at the $\frac{1}{2}$ hr analysis time had been lost to the atmosphere. Cattani (16) used different ammoniation and degassing procedures on the same samples and reported ammonia retention values which agreed very closely with those determined in the present study after ten days of reequilibration (see Appendix).

Table 2 and Fig. 1 indicate that ammonia retention had approached an asymptotic equilibrium level by three days. As previously shown, however, ammonia may continue to be lost to the atmosphere for months after ammoniation (53).

Fig. 1 shows that the longer ammonia was allowed to remain in the soil before it was extracted with water, the more nitrogen

Table 3. Changes in Ammonia Retention of the Soil with Time of Exposure to Atmosphere

Soil (%C)	% H ₂ O	Total N Indigenous meN/100g	NH ₃ -N $\frac{1}{2}$ hr meN/100g	% inc. over Ind.	NH ₃ -N 3 days me N/100 g	% dec. from $\frac{1}{2}$ hr	NH ₃ -N 10 days me N/100 g	% dec. from $\frac{1}{2}$ hr
Chehalis A (4.10) A	4.9 11.5	21.3 19.9	48.5 46.2	227 232	26.8 31.0	45 33	25.3 26.4	48 43
Chehalis C (1.18) C	4.1 9.0	7.4 7.0	37.8 39.9	512 569	22.8 21.3	40 47	21.5 18.7	43 53
Nehalem A (4.92) A	7.7 15.6	29.7 27.2	77.3 62.1	261 228	55.6 50.7	28 18	44.5 43.7	42 30
Nehalem C (2.14) C	7.5 12.6	12.4 11.8	70.3 61.3	567 521	52.1 45.7	26 26	44.6 42.2	37 31
Walla Walla A (.98) A	1.6 3.9	5.7 5.5	14.0 9.6	246 174	7.9 7.6	43 20	6.2 6.3**	56 34
Walla Walla C (.42) C	1.6 4.3	2.8 2.7	13.6 7.6	484 278	6.7 7.7	50 0	6.6 6.5**	51 15
Quillayute A (13.88) A	9.2 19.6	66.0 59.0	130.9 131.8	198 235	75.7* 95.7*	42 31	66.7 87.4	49 37

*

5 days

** 12 days

appeared to resist extraction. Nommik (16, p. 15) reported that the longer an ammonium source of nitrogen remained in contact with a soil before leaching it with KCl, the more ammonium was fixed by the soil. Young (53) observed that with time, mineral-fixed ammonia increased in certain soils although there was a marked decrease in total ammonia retention.

The time of atmospheric reequilibration greatly affected the amount of nitrogen extracted by water. From two to six times more nitrogen was extracted after $\frac{1}{2}$ hr of reequilibration than after three days reequilibration. Although 30 minutes of aeration was highly effective in removing nitrogen from the ammoniated Chehalis and Walla Walla soils, it appeared to have little effect on the Nehalem sample. In the Quillayute soil less nitrogen was measured in the extract prior to than after a $\frac{1}{2}$ hr aeration. (No good explanation for the latter result has been found.) There was only a slight drop in nitrogen values between the three and ten-day reequilibrations. More nitrogen was present in the extracts of the ammoniated moist samples than was determined in the air-dry soils, excepting from the Nehalem A and Walla Walla A and C soils. In the three and ten-day extracts, however, more nitrogen was determined in the ammoniated air-dry soil than in the corresponding moist soil. In part, the data seem to support Stanley's (44) work indicating that water present in the soil acts as a temporary carrier for ammonia prior to ammonia

reactions with the soil organic and mineral fractions.

Incidentally, Table 2 shows that the extracts of the moist controls have a slightly higher pH than that of the corresponding air-dry controls, excepting the Nehalem C and Quillayute A. More nitrogen was leached from the moist controls (five times more in the Nehalem A) than was leached from the air-dry controls in all the samples except the Chehalis C. Microbial release of nitrogen during equilibration over water may have accounted, in part, for the additional nitrogen in the moist controls.

Table 2 shows that the differences in the pH of the extracts paralleled the nitrogen values. The pH of the extracts from the samples ammoniated and aerated $\frac{1}{2}$ hr were typically three pH units higher than the pH of the control extracts. Those extracts obtained immediately following ammoniation from non-aerated samples had pH values as high as 10.2. The pH values of the extracts from soils exposed for three days to the atmosphere dropped sharply compared with the $\frac{1}{2}$ hr values but dropped only a few tenths of a pH unit more within the three to ten-day period.

In discussing the influence of moisture on ammonia retention the time elapsing after ammoniation should be given. The nitrogen values of the extracts (Table 2) indicate that a moist soil ammoniated and immediately leached with water may retain less ammonia against water extraction than an air-dry soil ammoniated and

immediately leached. Drying the soil contributes to ammonium fixation by contraction of the mineral lattices and subsequent entrapment of ammonium (16). In an air-dry soil, more ammonia may also react directly with the clay and organic matter rather than dissolving first in the soil moisture and forming ammonium hydroxide. This may help explain the slightly greater ammonia retention against water extraction following exposure to the atmosphere of the air-dry soils as compared with the moist soils.

Extraction of Soils with Ammonium Hydroxide

Ammonium hydroxide may be formed when anhydrous ammonia reacts with soil moisture (44). To get a better idea of possible concentrations of ammonium hydroxide formed during anhydrous ammonia treatments, several soils were extracted with a series of known concentrations of ammonium hydroxide.

Table 4 shows that the amount of carbon solubilized increased as the soils were extracted with higher normalities of ammonium hydroxide. The amount of carbon solubilized during water extraction of an ammoniated soil was, presumably, related to the strength of ammonium hydroxide formed by the reaction of anhydrous ammonia with soil moisture. After comparing the data in Tables 4 and 1, it may be concluded that the concentration of ammonium hydroxide formed during the ammoniation treatment approximated 0.15 N.

Table 4. Percentage of Indigenous Carbon Extracted with Various Normalities of NH_4OH

Soil	% H_2O	% C	Normality of NH_4OH (pH)				
			0.015 (10.3)	0.5 (11.0)	0.75 (--)	1.5 (11.7)	7.5 (12.5)
			% C	% C	% C	% C	% C
Chehalis A	4.9	4.10	2.4 (7.2)	4.6 (9.9)	5.6 (--)	6.3 (11.0)	8.5* (11.7)
Nehalem A	7.7	4.92	3.5 (8.8)	6.1 (9.4)	11.5 (--)	15.6 (10.5)	18.6* (11.6)
Walla Walla A	1.6	0.98	1.0 (9.3)	3.0 (10.5)	2.8 (--)	3.0 (11.2)	6.0 (11.7)
Quillayute A	9.2	13.88	1.6 (8.9)	8.9 (9.4)	36.5 (--)	48.2* (10.7)	50.7* (11.4)

* Samples were centrifuged and extracts filtered

Fig. 2 shows how the extracts of the surface horizons of the Chehalis, Walla Walla, Nehalem, and Quillayute that had been treated with anhydrous ammonia compare with those obtained from soils with various concentrations of ammonium hydroxide. As with anhydrous ammonia-treated samples the amount of carbon solubilized was directly proportional to the indigenous carbon in the soils. The largest amount of carbon was extracted, of course, from the Quillayute soil which contained 13.9 % carbon.

Fig. 3 illustrates the effect of the ammoniation and subsequent extraction on the appearance of the soil residue after air drying. It may be seen that as the ammonia concentration became greater, the soil residue became more dispersed. One-half hour of ammoniation followed by water extraction had about the same effect as extraction with 0.15 N NH_4OH on the appearance of the soil.

Chromatography

It was of interest to consider in an exploratory way whether different compounds as well as different quantities of organic matter were solubilized from the different soils as a result of ammoniation. Preliminary trials with paper and thin-layer chromatography were made as possible aids in identification of the organic matter fractions solubilized.

No migration of the compounds of the water extracts was

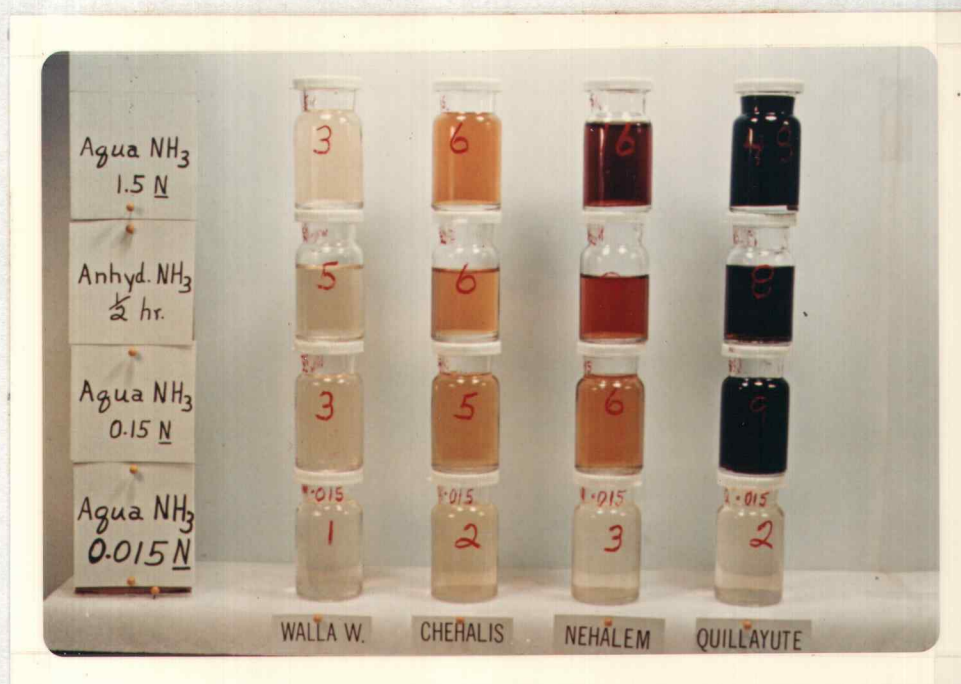


Figure 2. Extracts from surface horizons of soils treated with anhydrous ammonia and various normalities of aqua ammonia.



Figure 3. Soil residues after extraction and subsequent air-drying.

observed on paper or thin-layer chromatographs. Ultraviolet light, iodine, and ninhydrin were used as detecting agents.

The same solvents and procedures were used to detect compounds of acidified extracts from which acid precipitable organic matter had been removed. No migration was detected using the iodine and ninhydrin reagents. When the acidified extracts were chromatographed and viewed under an ultraviolet light several components were visible slightly separated from their original spots. They were not identified. Apparently, simple nitrogenous compounds were not extracted in sufficient concentration to be detected with the sample concentration, reagents, and solvents used. Further work in elucidating the solubilized compounds utilizing the newer methods of thin-layer chromatography in conjunction with extract concentration and selective hydrolysis might prove more satisfactory.

GENERAL DISCUSSION

The carbon solubilized during water extraction of anhydrous ammonia-treated soils in this study ranged from three to ten % of the total indigenous soil carbon. Because the laboratory ammonia-tion and extraction methods were much more disruptive than the anhydrous ammonia injection would be in the field, they should be more effective in solubilizing organic matter. On this basis anhydrous ammonia might be expected to solubilize less organic matter from these soils under field conditions.

Although the carbon solubilized during water extraction followed trends similar to those of the nitrogen values, the amount of carbon extracted did not differ nearly as greatly with length of re-equilibration as did the ammonia nitrogen values. The changes in pH with reequilibration time corresponded closely with the nitrogen changes. It is possible that alteration of structural stability may be related more directly to dispersion of the soil mineral fractions due to the large pH changes than to the solubilization and redistribution of the soil organic fraction per se.

Some qualitative observations which lend support to this contention have accrued from subsequent work by colleagues involving a number of surface soils besides those included in this study. For example, when some ammoniated soils were put in a glass column

and leached with water, they sealed off completely. This was not only true of the Quillayute but also of the Jory, a Reddish-Brown Lateritic representative containing minimal amounts of expanding-lattice clays. It was also observed that twice as much organic matter was solubilized from ammoniated-aerated samples leached in a column as from ammoniated-aerated samples shaken for 15 minutes. It is significant that the amount of carbon solubilized when the extractant was 0.5 N KCl or either 0.15 N KOH or NaOH adjusted with HCl to pH 11 approximated the carbon in the water-extracted controls. (See Fig. 4 and 5, Appendix).

A number of unanswered questions have arisen and the study could be extended to systematically evaluate many parameters under a range of controlled artificial conditions. Available resources precluded efforts to simulate field conditions in the laboratory and thus to approximate and study the reactions that occur when anhydrous ammonia is injected into large volumes of soil. Despite the number of uncontrollable variables encountered, the extent to which ammonia may solubilize soil organic matter and the possible influence this may have on soil structure needs to be examined for a broad range of conditions in soils actually ammoniated in the field.

SUMMARY

The carbon solubilized from four surface and three subsurface ammonia-treated soils, whether extracted immediately or following several lengths of time for reequilibration with the atmosphere, ranged from 0 to 5 mg C/g soil except for the Quillayute which yielded 13 mg C/g soil. These amounts represented three to ten % of the total indigenous carbon and were proportional to the original carbon contents of the soils.

The moisture content of the soil at the time of ammoniation appeared to have little influence on the amount of carbon solubilized under the experimental conditions of the study. With time of re-equilibration with the atmosphere, there was a slight reduction of carbon solubilized.

Preliminary investigations with chromatography were made for a possible indication as to the nature of the organic fractions solubilized. No simple nitrogenous compounds could be detected with the sample concentrations, solvents, and reagents used.

Extraction of the soils with ammonium hydroxide showed that the percent of indigenous carbon solubilized was proportional to the normality of the ammonium hydroxide used although ammonium hydroxide was not an equally effective extractant in all of the soils.

The percentage of carbon solubilized by extraction with 0.15 $\underline{\text{N}}$ NH_4OH

approximated the amount of carbon measured in the water extract of the anhydrous ammonia-treated soils.

Anhydrous ammonia application and subsequent aeration increased the nitrogen contents of the soils over the indigenous nitrogen about twice as much in the C horizons as in the A horizons. For example, the indigenous nitrogen contents of the Chehalis A and C horizons were 21.3 and 7.4 me/100 g soil respectively. After ammoniation and aeration for one-half hour, nitrogen values were respectively 64.8 and 45.7 me/100 g soil. Within three days 20 to 50% of the initially-retained nitrogen was lost to the atmosphere. There was a small increase in the nitrogen content of the residues with increase of time prior to water extraction. The pH values of the soils and extracts corresponded to the nitrogen values and decreased with the length of time elapsing prior to extraction.

In comparing the slight differences in ammonia retention of the soils that were ammoniated at different moisture contents, moisture appeared to act as a temporary ammonia carrier before soil organic and mineral fractions could fix and retain ammonia. When discussing moisture influences on ammonia retention the time elapsing after ammoniation should be given. Due to displacement "competition" between ammonia and water vapor, it is difficult to see how saturation exposure to ammonia can be accomplished at a pre-set specified soil moisture content. During ammoniation and

aeration the moisture status of both the air-dry and moist soil could have been changed until they were nearly identical. This helps to explain why little differences in ammonia retention and carbon solubilization were detected.

The carbon solubilized followed trends similar to that of the nitrogen values of the extracts but they were not as pronounced or intensive. There was, at most, only a five % drop in carbon solubilized as compared with a 50% loss in nitrogen within ten days. Because the laboratory treatment and extracting methods were much more disruptive, hence presumably more effective in solubilizing organic matter than the leaching encountered under field conditions, extrapolation would suggest that soil structural changes due to organic matter solubilization after anhydrous ammonia application would generally be minor. Changes noticed in structural stability of soils after injection of anhydrous ammonia may be more related to dispersion of the soil mineral fraction or other phenomena accompanying large pH changes than to dissolution and redistribution of the organic fraction per se.

BIBLIOGRAPHY

1. Alexander, L. T. and H. G. Byers. A critical laboratory review of methods of determining organic matter and carbonates in soil. Washington, 1932. 26 p. (U. S. Dept. of Agriculture. Technical Bulletin no. 317)
2. Allison, F. E., M. Kefauver, and E. M. Roller. Ammonium fixation in soils. *Soil Science Society of America Proceedings* 17:107-110. 1953.
3. Allison, F. E. Fixed ammonia in soils and its availability to crops. *Agricultural Ammonia News* 8:19-20, 43. 1958.
4. Allison, L. E. Organic soil carbon by reduction of chronic acid. *Soil Science* 40:311-320. 1935.
5. Anderson, O. E. Effects of anhydrous ammonia on some soils and crops of New Jersey. Ph. D. thesis. New Brunswick, Rutgers University, 1955. 120 numb. leaves. (Abstracted in *Dissertation Abstracts* 15:1691. 1955)
6. Andrews, W. B. Anhydrous ammonia as a nitrogenous fertilizer. *Advances in Agronomy* 8:61-125. 1956.
7. Axley, J. H. and J. O. Legg. Ammonium fixation in soils and the influence of potassium on nitrogen availability from nitrate and ammonium sources. *Soil Science* 90:151-156. 1960.
8. Baver, L. D. *Soil physics*. 3d ed. New York, Wiley, 1961. 487 p.
9. Blue, W. G. and C. F. Eno. Distribution and retention of anhydrous ammonia in sandy soils. *Soil Science Society of America Proceedings* 18:420-424. 1954.
10. _____ Some aspects of the use of anhydrous ammonia on sandy soils. *Soil Science Society of Florida Proceedings* 12:157-164. 1952.
11. Bremner, J. M. Determination of fixed ammonium in soil. *Journal of Agricultural Science* 52:147-160. 1959.

12. Bremner, J. M. and D. S. Jenkinson. Determination of organic carbon in soil. *Journal of Soil Science* 11:394-401. 1960.
13. Brown, J. M. and W. V. Bartholomew. Sorption of anhydrous ammonia by dry clay systems. *Soil Science Society of America Proceedings* 26:258-302. 1962
14. _____ Sorption of gaseous ammonia by clay minerals as influenced by sorbed aqueous vapor and exchangeable cations. *Soil Science Society of America Proceedings* 27:160-164. 1963.
15. Browning, G. M. A comparison of the dry combustion and the rapid dichromate titration methods for determining organic matter in soil. *Soil Science Society of America Proceedings* 3:158-161. 1938.
16. Cattani, R. A. Ammonium and ammonia fixation in some Oregon soils. Master's thesis. Corvallis, Oregon State College, 1960. 77 numb. leaves.
17. Coffee, Roy Clifford. Sorption and volatilization processes of ammoniacal nitrogen in plant residues and in soils. Ph. D. thesis. Raleigh, North Carolina State College, 1961. 177 numb. leaves. (Abstracted in *Dissertation Abstracts* 22:3832. 1962)
18. Dhariwal, A. P. S. and F. J. Stevenson. Determination of fixed ammonium in soils. *Soil Science* 86:343-349. 1958.
19. Fraps, G. S. and N. C. Hamner. Studies of the ammonia-soluble organic matter in the soil. College Station, 1910. 49 p. (Texas Agricultural Experiment Station. Bulletin no. 129)
20. Gifford, R. O. and E. Strickling. Effect of anhydrous ammonia on water stability of soil aggregates. *Soil Science Society of America Proceedings* 22:209-212. 1958.
21. Goring, Martin. Diffusion and sorption of aqua ammonia injected in soils. *Soil Science* 88:336-341. 1959.
22. Graham, E. R. Determination of soil organic matter by means of a photoelectric colorimeter. *Soil Science* 65:181-183. 1948.

23. Hagin, J. and S. Manzur. Retention of anhydrous ammonia by soils of different texture and moisture contents. *Bulletin of the Research Council of Israel Section Technology* 10:177-182. 1962. (Abstracted in *Biological Abstracts* 38:1554. 1962)
24. Jackson, M. L. *Soil chemical analysis*. 3d ed. Englewood Cliffs, N. J., Prentice-Hall, 1962. 498 p.
25. Jackson, M. L. and S. C. Chang. Anhydrous ammonia retention as influenced by depth of application, soil texture, moisture content, pH value, and tilth. *Journal of the American Society of Agronomy* 39:623-633. 1947.
26. Jewitt, T. N. Loss of ammonia from ammonium sulfate applied to alkaline soils. *Soil Science* 54:401-409. 1942.
27. Johnson, Donald. Transformations of ammonia in soils. *Agricultural Ammonia News* 7:31-32. 1957.
28. Legg, J. O. and F. E. Allison. Recovery of N^{15} -tagged nitrogen from ammonium-fixing soils. *Soil Science Society of America Proceedings* 23:131-134. 1959.
29. Lu, K. C., J. E. Dawson and M. Alexander. A microchemical method for detecting antifungal substances. *Archiv fur Mikrobiologie* 33:182-185. 1959.
30. McDowell, L. L. and G. E. Smith. The retention and reactions of anhydrous ammonia on different soil types. *Soil Science Society of America Proceedings* 22:38-42. 1958.
31. McIntosh, T. H. Fixation of added ammonium by clay and organic fractions of soil. Ph. D. thesis. Ames, Iowa State University, 1962. 155 numb. leaves. (Abstracted in *Dissertation Abstracts* 23:372. 1962)
32. Mattson, Sante and Elisaveta Koutler-Andersson. The acid-base condition in vegetation, litter, and humus. VI. Ammonia fixation and humus nitrogen. *Lantbrukshogskolans Annaler* 11:107-134. 1943.
33. Mela Mela, Pedro. Fixation of ammonium by clay minerals in relation to some probable effects on vegetative development of plants. *Soil Science* 92:189-194. 1961.

34. Mortland, M. M. Reactions of ammonia in soils. *Advances in Agronomy* 10:325-348. 1958.
35. Nommik, H. and K. O. Nilsson. Nitrification and movement of anhydrous ammonia in soil. *Acta Agriculturae Scandinavica* 13: 205-219. 1963.
36. Read, J. W. and R. H. Ridgell. On the use of the conventional carbon factor in estimating soil organic matter. *Soil Science* 13:1-6. 1922.
37. Russell, E. J. *Soil conditions and plant growth*. 9th ed. London, Longmans, 1961. 688 p.
38. Schollenberger, C. J. Determination of soil organic matter. *Soil Science* 59:53-56. 1945.
39. _____ A rapid approximate method for determining soil organic matter. *Soil Science* 24:65-68. 1927.
40. Smith, Arthur, Ammonia can become leach-proof. *Agricultural Ammonia News* 8:13, 15, 31. 1958.
41. _____ Anhydrous ammonia as a soil conditioner. *Agricultural Ammonia News* 4:57-58. 1954.
42. Smith, H. W. and M. D. Weldon. A comparison of some methods for determination of soil organic matter. *Soil Science Society of America Proceedings* 5:177-182. 1940.
43. Sohn, S. B. and M. Peech. Retention and fixation of ammonia by soils. *Soil Science* 85:1-9. 1958.
44. Stanley, F. A. and G. E. Smith. Effect of soil moisture and depth of application on retention of anhydrous ammonia. *Soil Science Society of America Proceedings* 20:557-561. 1956.
45. Tinsley, J. The determination of organic carbon in soils by dichromate mixtures. In: *Transactions of the Fourth International Congress of Soil Science, Amsterdam, 1950*. Vol. 1. Groningen, Hoitsema, 1950. p. 161-164.
46. Tsyplenkov, V. P. Rapid colorimetric method of determining humus in soils and soil solutions. *Pochvovedenie* 10:91-95. 1963.

47. Van Slyke, D. D. and J. Folch. Manometric carbon determinations. *Journal of Biochemistry* 136:509-541. 1940.
48. Violanda, A. T. Ammonia fixation by soil organic matter: some relationships between forms of nitrogen and components of soil organic matter. Ph. D. thesis. Ithaca, Cornell University, 1958. 93 numb. leaves. (Microfilm)
49. Walkley, A. A critical examination of a rapid method for determining organic carbon in soils--effect of variations in digestion conditions and of inorganic soil constituents. *Soil Science* 63: 251-264. 1947.
50. Walkley, A. and I. A. Black. An examination of the Degtjareff method for determining soil organic matter, and a proposed modification of the chromic acid titration method. *Soil Science* 37: 29-38. 1934.
51. Young, J. L. and R. A. Cattani. Mineral fixation of anhydrous ammonia by air-dry soils. *Soil Science Society of America Proceedings* 26:147-152. 1962.
52. Young, J. L. and B. L. McNeal. Ammonia and ammonium reactions with some layer-silicate minerals. *Soil Science Society of America Proceedings* 28:335-339. 1964.

APPENDIX

Profile Descriptions of Soils Used*

Chehalis silt loam (Alluvial soil)

Location: NW $\frac{1}{4}$, NE $\frac{1}{2}$, section 36, T. 11S, R. 5W Horticulture farm
Linn County, Oregon.

Description by: J. Pomerening, July 30, 1958.

Profile samples collected by: D. L. Carter, J. Pomerening and
B. McNeal, July 30, 1958.

Site: Maple, ash, poison oak; no slope; from post pleistocene alluvial mixture of igneous and sedimentary materials; well drained.

Horizon	Depth	Description
A ₁	0-11	Very dark brown (10YR 2/2) moist; silt loam; strong, fine and very fine sub-angular blocky structure; friable, slightly sticky, slightly plastic; numerous, fine (1-2mm.) roots, several large (1-2") tree roots; numerous earthworm holes and casts; distinct wavy horizon boundary.
A ₃	11-18	Very dark grayish brown (10YR3/2) moist; silt loam; moderate, fine and very fine sub-angular blocky structure; friable, slightly sticky, slightly plastic; common fine roots and numerous worm holes; clear, smooth horizon boundary.
C ₁	18-28	Very dark grayish brown (10YR 3/2) moist on ped surface, dark grayish brown (10YR 4/2) in peds; silt loam; weak, medium sub-angular blocky to moderate, very fine and fine sub-angular blocky structure; friable, slightly sticky, slightly plastic, common fine roots; numerous fine worm holes, common large vertical worm channels; clear, gradual horizon boundary.

*From reference 16 (excepting quillayute).

Horizon	Depth	Description
C	28-48	Very dark grayish brown (10YR 3/2) moist on ped surface, dark grayish brown (10YR 4/2) in peds; silt loam; weak, very fine and fine sub-angular blocky structure; friable, slightly sticky, slightly plastic (very smooth); common, large (2-5 mm) vertical worm holes; few, fine roots below 36".

Nehalem silt loam (Alluvial soil)

Location: NW 1/4, SW 1/4, section 5, T. 2S, R. 9W, SW corner of the enclosure of the Nehalem soil fertility plots established on the Tillamook Naval Air Base, Tillamook County, Oregon by T. L. Jackson, E. Jenne and others.

Description by: E. G. Knox, L. H. Robinson and C. Bowlsby, March 27, 1958.

Profile samples collected by: R. A. Cattani and L. H. Robinson, August 1958.

Site: Silt from recent silt alluvium on the flood plain of the Trask River. Well drained on less than 1% slope.

Horizon	Depth	Description
A _{1p}	0-9	Dark yellowish brown (10YR 3/4) moist, brown (10YR 5/3) dry; silt loam (but almost silty clay loam); strong, fine and very fine sub-angular blocky structure; friable, slightly sticky, slightly plastic; abundant roots; abundant, fine and very fine interstitial pores; lower boundary clear and smooth; pH 5. 2.
A ₁₂	9-17	Dark yellowish brown (10YR 3. 5/4 moist; silt loam (but almost silty clay loam); medium prismatic breaking to strong, fine sub-angular blocking structure; friable, slightly sticky, slightly plastic; abundant roots; abundant fine and tubular pores, few, medium and coarse tubular pores; coating on peds and pores are dark yellowish brown (10YR 3/4); lower boundary, gradual and smooth; pH 5. 4.

Horizon	Depth	Description
AC	17-36	Dark yellowish brown (10YR 3.5/4) moist; silty clay loam; moderate, coarse prismatic breaking to strong, medium sub-angular blocky structure; friable, plastic, sticky; common roots, abundant, fine tubular pores; lower boundary gradual and smooth; pH 5.6.
C ₃	36-54	Dark yellowish brown (10YR 3.5/4) moist; silty clay loam; weak, coarse prismatic breaking to moderate, fine and medium sub-angular blocky structure; friable, plastic, sticky; few roots; abundant, fine and very fine tubular pores, few medium and coarse tubular pores; few, faint fine mottles; pH 5.6.

Walla Walla silt loam (Chestnut soil)

Location: Section 20, T. 1S, R. 17E; 2 1/2 mi. S & E of Moro.

Description by: L. H. Robinson, August 1958.

Profile samples collected by: L. H. Robinson, R. A. Cattani, Aug. 1958.

Site: Crested wheatgrass, cheat and blue-bunch grass. Soil from loess, 8% NE slope, gently sloping upland, moderate permeability, well drained; semiarid climate, 13"/yr. moisture, 1800' elevation. Reduced iron around root channels, mycelia-shaped lime along root channels.

Horizon	Depth	Description
A _{1p}	0-7	Very dark grayish brown (10YR 3/2) moist; very fine sandy loam or loam; weak, medium platy structure; friable, slightly sticky, slightly plastic; abundant roots; abrupt, smooth lower boundary; pH 6.5.
A ₁₂	7-13	Very dark grayish brown (10YR 3/2) moist; very fine sandy loam or loam; weak, coarse prismatic structure; friable, slightly sticky, slightly plastic; abundant roots; abrupt, smooth lower boundary; pH 6.6.

Horizon	Depth	Description
AC	13-23	Dark brown (10YR 3.5/3) moist; silt loam; weak, coarse prismatic and weak, medium coarse sub-angular blocky structure; friable, slightly sticky, slightly plastic; plentiful roots; gradual, smooth lower boundary; pH 6.6.
AC ₂	23-47	Dark brown (10YR 4/3) moist; silt loam; same characteristics as AC except has many fine pores; pH 6.8.
C _{cal}	47-57	Dark brown (19YR 4/3) moist; silt loam; massive structure; friable, slightly sticky, slightly plastic; many fine pores; coarse, sand-size basalt fragments; diffuse, smooth lower boundary; pH 8.3.
C _{ca2}	57	Dark brown (10YR 4/3) moist; silt loam; same characteristics as horizon above except pH 8.2.

Quillayute silt loam (Ando-like soil)

Type Clallam County, Washington; located at a point 6 miles west of Forks; 1-3/4 miles east of Quillayute School and 75 feet southwest of logging railroad crossing over private road in the NE 1/4 SE 1/4 NE 1/4 Sec 9, T. 28N R. 14W. Described by A. O. Ness, August, 1960.

Site: Bracken fern, spruce, grasses. Soils formed in old valley fill materials of basic volcanic origin, nearly level or gently sloping terraces, well-drained, moderate permeability; cool humid climate, 90 to 120"/yr moisture, 35 to 100' elevation. The profile is very strongly acid in the A horizon and medium or strongly acid in the B and C horizons.

Horizon	Depth	Description
A ₁₁	0-8"	Black (10YR 2/1) silt loam, very dark gray (10YR 2/1) dry; strong fine granular structure; friable, plastic and slightly sticky; abundant roots, fern roots up to 1/2 inch diameter numerous; very strongly acid (pH 4.6); diffuse boundary. 6 to 10 inches thick.

Horizon	Depth	Description
A ₁₂	8-16"	Black (10YR 2/1) silt loam, very dark gray (10YR 3/1) dry; strong medium granular structure; friable, plastic and slightly sticky; abundant roots; very strongly acid (pH 4.8); gradual wavy boundary. 7 to 10 inches thick.
A ₁₃	16-32"	Very dark brown (10YR 2/2) silt loam, dark grayish brown (10YR 4/2) dry; moderate medium granular structure; friable, plastic and slightly sticky; plentiful roots; very strongly acid (pH 3.7); gradual wavy boundary, 14 to 21 inches thick.
B	32-48"	Brown (10YR 4/3) silt loam, pale brown (10YR 6/3) dry; weak to moderate fine subangular blocky structure; friable to firm, plastic and slightly sticky; few roots; many fine tubular pores; numerous krotovines; very thin patchy clay films in pores and along vertical fractures; medium acid (pH 5.9); diffuse wavy boundary. 15 to 20 inches thick.
C ₁	48-70"	Dark yellowish brown (10YR 4/4) silt loam; very pale brown (10YR 7/4) dry; massive with vertical partings 3 to 6 inches apart; firm, plastic and slightly sticky; few roots; common fine pores; colloidal staining on partings and in pores; few distinct (5YR 4/8) fine mottles on parting surface and in some root channels; numerous krotovines; medium acid (pH 5.9); diffuse wavy boundary. 20 to 40 inches thick.
C ₂	70-80"	Very similar to above horizon but fractures range from 3 to 12 inches apart; occasional pebbles 1/4 inch diameter; medium acid (pH 5.6); diffuse wavy boundary.
C ₃	80-96"+	Dark yellowish brown (10YR 4/4) silt loam, very pale brown (10YR 7/4) dry; massive, firm, slightly sticky and slightly plastic; very few roots; common fine pores; few krotovines; few distinct (5YR 4/8) fine mottles in root channels; occasional fine pebbles; pH 5.2.

Table 5. Laboratory Characterization Data of Soils (from Reference 16)

Soil	Horizon	Depth inches	Organic Matter % ¹	Clay % ²	Silt % ²	Sand % ²	CEC ³ me/100 g	Ex. Ca, Mg, K, Na me/100 g	Moisture air-dry %	pH
Chehalis	A1	0-11	6.65	35	62	3	38.7	32.3	4.9	5.8
	C1	18-28	1.70	30	57	13	29.0	26.1	4.1	6.2
Nehalem	Alp	0-9	8.34	38	57	5	53.7	35.0	7.7	5.4
	AC	17-36	3.52	35	58	5	48.7	35.7	7.5	5.7
Walla Walla	Alp	0-7	1.97	13	46	41	12.4	11.2	1.6	6.6
	AC	13-23	0.46	14	56	30	12.3	11.5	1.6	7.1
Quillayute	A1	0-7	20.50	39	47	14	54.2	8.7	-	5.5

¹Walkley, A. and I. A. Black. An examination of the Degtjareff method for determining soil organic matter, and a proposed modification of the chromic acid titration method. Soil Science 37:29-38. 1934.

²Kilmer, Victor J. and Lyle T. Alexander. Methods of making mechanical analyses of soils. Soil Science 68:15-24. 1949.

³Schollenberger, C. J. and R. H. Simon. Determination of exchange capacity and exchangeable bases in soils-ammonium acetate method. Soil Science 59:13-24. 1945.

Relation Between the Dry and Wet Combustion Techniques.

Since carbon extracted was to be designated as a percentage of the total soil carbon previously determined by dry combustion, correlation of the dry and wet combustion procedures was necessary. Carbon was determined on several concentrated water extracts of an ammoniated soil containing 4.85% carbon using both the proposed wet-combustion and dry combustion techniques. The modified wet-combustion method oxidized about 78% of the total carbon in the extracts as determined by the dry combustion method, indicating the wet-combustion procedure was reasonably precise though incomplete. The chromic acid reduction method has been reported as giving consistent recovery of carbon from all horizons despite the total amounts of organic matter present (50). The percentage of the total carbon measured by the wet-combustion technique used in this study was in accordance with that found by other people using similar or comparable wet-combustion methods (4, 15, 35, 39, 42, 50).

It can be seen from Table 6 comparing the milligrams of carbon measured using the two procedures that the wet combustion procedure was reasonably accurate at least throughout the limited range of carbon contents of interest here. The carbon values are directly proportional to one another. The extracts, though containing different amounts of carbon, were from one soil. Extracts from soils containing less organic matter contained too little carbon to conveniently

concentrate satisfactorily for dry combustion determinations.

Table 6. Carbon in Extracts as Measured by Dry and Wet Combustion Techniques

Run	Dry Combustion mg C	Wet Combustion mg C	% Recovery
1	.32	.22	69
2	.48	.36	75
3	.55	.44	80
4	.55	.44	80
5	.55	.44	80
6	1.12	.88	78
7	1.36	1.12	82
8	1.67	1.20	72
9	1.93	1.48	77
10	2.54	1.98	78
11	3.92	3.03	77
12	5.16	3.80	74

Comparison of Ammoniation Procedures

The ammonia retention values after ten days of reequilibration with the atmosphere were comparable to those reported by Cattani (16) for the same soil samples as shown in Table 6. He used a different ammoniation procedure (51) which for practical purposes he

assumed achieved ammonia saturation. Cattani degassed his ammoniated samples at room temperature (25 to 27 degrees C) for 12 hours under a vacuum created by a water aspirator. He felt such degassing would remove most of the physically-sorbed ammonia. Apparently, then, the 30-minute aeration with a stream of air used in the present study, though removing a considerable amount of nitrogen, was only slightly less effective than Cattani's degassing procedure.

Table 7. Comparison of Ammonia Retention* Values as Determined by Mangum and Cattani

Soil	Horizon	Cattani me N/100 g	Mangum (10 days) me N/100 g
Chehalis	A	23.3	25.3
	C	20.5	21.5
Nehalem	A	43.7	44.6
	C	40.1	44.6
Walla Walla	A	5.9	6.2
	C	6.0	6.6
Quillayute	A	65.6	66.7

* See page 3 for definition.

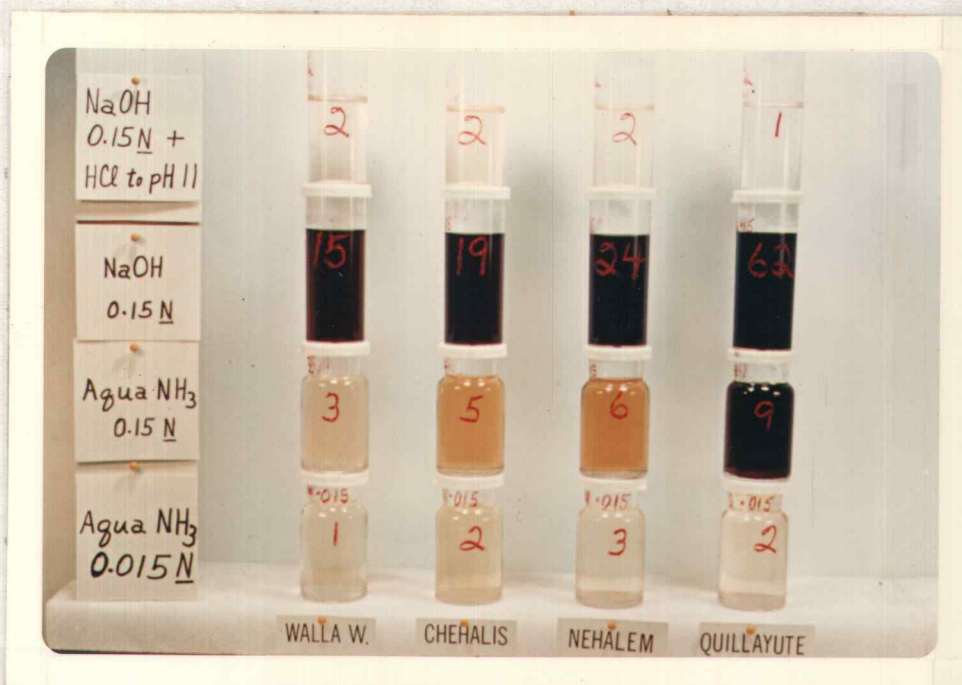


Figure 4. Extracts from surface soils extracted with 0.015 \underline{N} NH_4OH , 0.15 \underline{N} NH_4OH , 0.15 \underline{N} NaOH with pH lowered to pH 11 with HCl .



Figure 5. Air-dried residues of soils extracted with 0.015 \underline{N} NH_4OH , 0.15 \underline{N} NH_4OH , and 0.15 \underline{N} NaOH with pH lowered to pH 11 with HCl .