

AN ABSTRACT OF THE THESIS OF

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Title: Silicic Acid and Oxidizable Carbon Movement in a Walla Walla  
Silt Loam as Related to Long-Term Residue and Nitrogen  
Applications

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Intensive cultivation of Walla Walla silt loams (coarse silty, mixed, mesic, typic Haploxeroll) in eastern Oregon and Washington during the past 50 years, has decreased internal soil drainage in the 15 to 40 cm layer. However, no measurements have been made to determine the causes and corrective management for this internal drainage problem.

Gradual acidification of the plow layer, partially as a result of long-term use of nitrogen fertilizers in a summer-fallow management system may possibly have contributed to release of soil constituents that contribute to cementation of a high strength soil layer of variable thickness found at depths from 15 to 40 cm. Therefore, the potential for release, and possible interactions, of silicic acid, organic carbon, and major cations from the plow layer and subsequent movement through or desposition in layers below were evaluated.

The test soils came from selected plots subjected to residue and nitrogen addition treatments for a period of 50 years. Samples were taken from the four upper 15-cm layers of a Walla Walla silt loam, placed in a system of laboratory columns, and leached with distilled water. The columns were designed to simulate a leaching soil profile and to facilitate continuous collection of leachate for analysis.

Results indicate that soluble silica concentrations in Walla Walla soils are high in comparison to soils of the United States found outside of the Pacific Northwest. When no silica enters a layer (the 0 to 15-cm layer) silicic acid concentration in the leachate increases as original soil pH decreases. When the input fluid contained silicic acid, as in all layers below 15 cm, there was a smaller trend for increasing silicic acid concentration with decreasing soil pH.

Silicic acid release from the 0 to 15-cm layer was decreased 24% by addition of large amounts of organic material, and 32% by the addition of lime compared to other treatments with lower soil pH values. All management systems showed a net release of silicic acid from the 0 to 15-cm layer and a net gain in each 15 cm layer below to a depth of 60 cm. Maximum release was  $4.3 \times 10^{-2}$  mol  $\text{H}_4\text{SiO}_4/\text{m}$  of liquid depth and maximum gain was  $2.7 \times 10^{-2}$  mol  $\text{H}_4\text{SiO}_4/\text{m}$  of liquid depth, both in the plot treated with 45 kg N/ha·yr. Silicic acid concentration and transfer were each correlated ( $R^2 = 0.99$  and  $0.87$ , respectively) with both soil pH and long-term carbon additions to the soil surface.

Soluble carbon also gave a release and movement response with a maximum net release of  $1.3 \times 10^{-1}$  mol C/m of liquid depth and a maximum gain of  $7.2 \times 10^{-2}$  mol C/m of liquid depth. However, there were no significant correlations of either soluble organic carbon or major cations with silicic acid release or retention.

Silicic acid solubility increases with increasing soil acidity. More silicic acid leaves the plow layer thereby increasing the potential for adsorption or deposition in lower layers. Desorption, movement and sorption of silicic acid may affect such soil physical and chemical properties as hydraulic conductivity and cementation. Because silicic acid in soil solutions, and associated movement, is susceptible to changes in soil management, silica solubility effects on soil physical properties deserves more attention.

Silicic Acid and Oxidizable Carbon Movement in a Walla Walla Silt  
Loam as Related to Long-Term Residue and Nitrogen Applications

by

Clyde Lee Douglas, Jr.

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SILICIC ACID AND OXIDIZABLE CARBON MOVEMENT IN A  
WALLA WALLA SILT LOAM AS RELATED TO LONG-TERM  
RESIDUE AND NITROGEN APPLICATIONS

CHAPTER I

BACKGROUND AND NEED FOR STUDY

Water infiltration in the dryland areas of eastern Oregon and Washington is seriously slowed by restricted soil water movement in the upper 60 cm especially in the pressure pan (Appendix Table 1). Before cultivation started, approximately 100 years ago, internal drainage of the upper 60 cm of a Walla Walla silt loam was slower than in the 60 to 120-cm depth, but cultivation, normally at the 15 to 25-cm depth, has further decreased internal drainage in the upper 40 cm (Allmaras et al., 1982). Associated with these cultivation effects on water movement in the upper 40 cm is a modest increase in dry bulk density in the 15 to 30-cm zone and a soil pH decrease to depths as great as 45 cm.

A restricting layer for water movement occurs just below the maximum depth of tillage in Walla Walla silt loams (Appendix Table 1). This restricting layer reduces internal water flow rates and therefore increases runoff, and soil erosion, and also increases evaporation. This low water-conductivity layer has a high strength, especially when dry. A dry bulk density of  $1.4 \text{ Mg/m}^3$  or less indicates that strength of the layer is derived from some factor(s) other than soil compaction.

Clay and organic matter percentages tend to decrease with depth in a typical Walla Walla soil (Allmaras et al., 1977). Absence of

an increase in cation exchange capacity or clay at some depth in the profile rules out clay movement as a factor contributing to high dry strength.

The Pacific Northwest is unique in the U.S., in that approximately 70% (Sternes, 1966) of the annual precipitation occurs during the winter months (Appendix Table 2). Therefore, soils are moist when cold and dry when warm.

The major type of agriculture practiced in this area is a wheat-fallow system. Ammonium-type fertilizers have generally been used for the past 40 years, but anhydrous ammonia has been used more extensively than other N sources in the last 15 years because of its lower cost. Soil pH has been gradually reduced by the use of ammonium fertilizers, sometimes to a depth of 45 cm. Many surface layers have a pH as low as 4.9 (in 0.01 M  $\text{CaCl}_2$ ) while below 40 cm the pH may still be 6.0 or greater.

Walla Walla silt loam soils naturally support a high concentration of water-soluble silica (Leggett et al., 1959). Therefore, gradual acidification of the plow (Ap) layer and associated increases in soluble silica could cause cementation, formation of more tortuous pores, or both, in layers below 15 cm.

Movement of dissolved and suspended solids is one of the important processes in soil profile differentiation (McKeague and St. Arnaud, 1969; Buol et al., 1973). However, the possible influence of intensive agriculture on changes in the movement of soil constituents has received little attention. Rather than waiting until changes are fully developed in the field, long range conserva-

tion planning might be achieved better by projecting changes in soil horizon character that can be made from descriptions of the involved chemical, physical, and biological processes and their measured response to the agricultural ecosystem.

Based upon this circumstantial evidence, it was postulated that dissolved silica materials could collect in the area of high soil strength. The objectives of this study were: to determine the amount of silica, carbon and major cations that can be transferred downward in a Haploxeroll as influenced by management practices; to locate zones of silicic acid deposition; and to document whether or not soil pH decrease in the zone of anhydrous ammonia additions to the plow layer would increase silicic acid release and subsequent movement down through the soil.

## CHAPTER II

### LITERATURE REVIEW

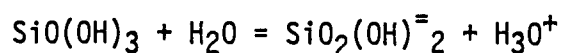
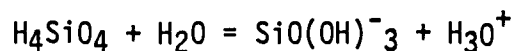
#### Introduction

Basic to the understanding of silica eluviation and subsequent illuviation in soils is an understanding of soil physical and chemical properties that, individually or collectively, affect silica solubility. This review will discuss some of these soil properties and their effects on silica.

#### Monosilicic Acid in Solutions

Most authors now agree that monomeric silicic acid is the main form of soluble silica in soil solutions, groundwaters, and streams. Alexander et al. (1954) outlined a simple procedure that determined the amount of monomeric silica in solution. At least 98% of the monosilicic acid present reacted with molybdic acid within two minutes. Disilicic acid reacted completely within 10 minutes and polysilicic acid reacted more slowly. Ihler (1955) distinguished soluble silica from colloidal silica because the latter would not react with molybdic acid to form the yellow silicomolybdate. He then found that silica exists in solution as a monomeric acid,  $H_4SiO_4$ , or as a silicate ion if the pH is above 9. McKeague and Cline (1963a) used the molybdic procedure of Alexander et al. (1954) and a color reaction time of 2.5 minutes or less to show that most of the dissolved silica in natural waters is in true solution as monosilicic acid. Jones and Handreck (1965) also used the method of Alexander et al. (1954) to show that silica in soil solutions is present entirely as

monosilicic acid and soil reserves are capable of maintaining a steady concentration in solution despite repeated withdrawals. Greenberg (1959) found pK's of 9.8 and 11.8, respectively, for the reactions:



which are consistent with uncharged silicic acid in soil solutions. Gifford and Frugoli (1964) determined silica source by determining heats of solution. Heats of solution, ranging from 4.2 to 5.2 kg cal/mole, for silica in extracts from 7 soils were in good agreement with a computed 4.5 kg cal/mole heat of solution for solid silicic acid.

#### pH Effects on Silica Reactions

Even though monosilicic acid is now considered to be the dominant form of silica in soil solutions, the effects of pH on silica solubility in soil solutions is still in question. Several authors show that the concentration of silicic acid in equilibrium with a solid phase in pure silica systems is not affected by pH (Ihler, 1955; Alexander et al., 1954).

Alexander et al. (1954), Ihler (1955), and Krauskopf (1956) reported that the solubility of amorphous silica in water is independent of pH over the pH range 1 to 9. After studying silica in hot-spring waters, White et al. (1956) concurred that silica solubility in natural water is most likely greater in acid than in weakly alkaline waters. Okamoto et al. (1957) also found that the

solubility of amorphous silica in natural waters did not increase with pH until pH was greater than 9. Furthermore, the optimum pH for precipitation of colloidal silica was approximately 4.5 and that of molecularly dispersed silica near 8.

Leggett et al. (1960) found that  $\text{SiO}_2$  concentration in a 1:1 soil to solution mixture was approximately four times more at pH 4.5 than at pH 8.3. In a 1:5 soil to solution mixture the difference was not so great; however, there was a continued increase in  $\text{SiO}_2$  concentration with decreasing pH. Apparently there is a silica containing compound in soils, whose solubility is affected by pH. Leggett et al. (1961) found that pH markedly affects leachable silica. Silica concentrations in the first 20 mL of effluent were sensitive to pH, whereas that of subsequent increments were not. They believe the silica-containing compound is not likely amorphous silica, since its solubility was not affected greatly by the pH range in their experiments. Jones and Handreck (1963) found that silica concentration in soil solutions decreased from 60 to 23 ppm as the pH increased from 5.5 to 7.2. They indicate that this decrease contrast with the solubility of amorphous silica in water, which is independent of pH over the pH range 1 to 9 as reported by Alexander et al. (1954), Ihler (1955), and Krauskopf (1956).

In review, D'Hoore and Coulter (1972) indicated that pH did not influence the solubility of silica in soils. Rather pH helped to regulate the equilibrium between free and adsorbed silica. For instance, silica is adsorbed by hydroxides of Fe and Al, when acidity is favorable for their formation, and not combined with or immobilized by these hydroxides. Raupach and Piper (1959) found that the



concentration of silica in saturated extracts of Australian soils decreased with increasing soil pH throughout the pH reaction range of 4 to 9.

As indicated above, McKeague and Cline (1963a) found lower concentrations of dissolved silica in soil-water mixtures at higher pH values, and increased silica adsorption as pH increased in the range 4.8 to 9.7 (1963b). However, because their results were consistent with the pH-dependent adsorption hypothesis, they did not project that appreciable deposition of silica would occur with an increase in pH in a soil profile. This projection contrasts with the results of Miller (1967) who leached soil cores with distilled water or 0.01 N HCl and found that solubility of silica in a soil solution is pH sensitive. He indicates that the presence of pans containing cementation by silica might be at least partially explained by changes in pH of soil profile layers. Beckwith and Reeve (1963) found that under neutral or slightly alkaline conditions silica equilibrium was rapidly established, but dilute or acidic conditions delayed the approach to equilibrium. Increased anion concentration caused very little change in  $H_4SiO_4$  concentration, therefore they decided that a decreased sorption under acid conditions was caused by pH effects rather than a larger concentration of anions. All 12 soils they tested showed an increased silica concentration in acidified soil solutions, but the changes varied widely among soils. Beckwith and Reeve (1964) found that when pH conditions favored sorption, i.e. a pH of 6.5 compared to 5.0, the smallest release of monosilicic acid by soils occurred. Moreover,

the large increase in extracted native silica under acid conditions was paralleled by decreased sorption of added monosilicic acid under the same conditions.

Acquaye and Tinsley (1965) indicate that the amount of silica dissolved by water from soils is likely to depend very much on pH of the solution. A pH increase of 0.5 pH units is enough to cause precipitation of some of the silica. They state "These results strongly reinforce the opinion of Raupach (1957) that a change from an acid to alkaline pH results in precipitation of silica from solution in a soil profile." Wada and Inoue (1974) found that adsorption of silica on volcanic ash soils increased with increased pH throughout the pH range 6 to 10. Adsorption equilibriums at pH 10 were obtained within a day and at pH 6 not within a week. Adsorption capacities were also much smaller at lower pH's. Hingston and Raupach (1967) determined the effect of pH on the adsorption of  $\text{SiO}_2$  by  $\text{Al}(\text{OH})_3$ . Adsorbed  $\text{SiO}_2$  was approximately 2.25 mg/g of  $\text{Al}(\text{OH})_3$  at pH 7.6 and 4.0 mg/g at pH 9.2 for the same solution.

Gramineous plant species contain 10 to 20 times more silica than leguminous species (Jones and Handreck, 1965). Silica concentration in both species decreases when soil pH increases, but mature plants grown in different soils of the same pH contain different proportions of silica. Decomposition of plant residues returns most of the silica in readily soluble form, but may also enhance liberation of soluble silica from adjoining weatherable minerals.

### Temperature and Evaporation Effects on Silica Solubility

Most authors agree that temperature affects silica reactions in soil solutions. Leggett et al. (1960) found approximately a 30% increase in solubility of  $H_4SiO_4$  in soil extracts when temperature increased from 17 to 30 C. McKeague and Cline (1963a) found silica concentration in soil solution to increase with increased temperature at the rate of approximately 0.2 to 0.3 mg/l/degree C. Hingston and Raupach (1967) found that the amount of silicic acid desorbed from soil samples increased from approximately 3 mg  $SiO_2$  adsorbed for each g of  $Al(OH)_3$  at 10 C to 6 mg at 35 C. Okamoto et al. (1957) found the solubility of amorphous silica to increase with increased temperature. At a solution pH of 7,  $SiO_2$  concentration in mg/l increased from 100 at 0 C to almost 500 at 90 C to 900 at 200 C. Krauskopf (1956) showed amorphous silica to reach quasi-equilibrium of 50 to 80, 100 to 140, or 360 to 420 mg/l at 0, 25, and 100 C, respectively. Ihler (1973) states that, at temperatures greater than room temperature, increased silica is dissolved but then redeposited when the solution is returned to room temperature. Therefore, cold weather during leaching will accelerate silica deposition in soils.

McKeague and Cline (1963b) suggested that, based on their results of some adsorbed silica at 100°C and none at 45°C, drying temperatures in soils would have little effect on subsequent desorption of silica. As water loss (evaporation) proceeds, total silica in solution decreases and only the monomeric form is present. This indicates that dissolved silica is being adsorbed at certain particle surfaces. However, silica concentration in solution does not increase in direct

proportion to the fraction of water evaporating as the soil dries. As water evaporates and the concentration of  $H_4SiO_4$  in soil solution rises,  $H_4SiO_4$  may be adsorbed to mineral particle surfaces to form amorphous coatings in soil (McKeague and Cline, 1963a). Miller (1967) found that soil temperature increases of  $25^{\circ}C$  increased silica concentrations between 15 and 100% (i.e. 4 to 15 mg/l in the leachate). He indicates that ageing and drying would aid the development of deposits of a nonreversible nature.

Addition of  $Na_2SiO_3$  to a layered system of different soil cores showed that the concentration of silica in the leachate changes gradually as the volume of leachate increases. When the cores are leached, dried, and leached again concentrations may either increase or decrease (Miller, 1967). Silica in the first effluents was characteristic of that expected from the bottom soil layer only and was independent of the composition of the upper layers. As leaching continued the upper soil layers influenced the effluent composition. The solubility of silica could fluctuate enormously in some profiles. Silica solubility can also differ in adjacent soil layers causing either deposition, or solution of silica.

#### Adsorption and Precipitation of Silica

Beckwith and Reeve (1963) found that much of the monosilicic acid dissolving from soils is derived from adsorbing surfaces rather than from amorphous silica or crystalline silicate mineral surfaces. Holt and King (1955) used  $H_4SiO_4$  labelled with  $Si^{31}$  to show that

silicic acid is adsorbed on quartz, and the adsorption increased with increased pH.

Dempster and Ritchie (1953), Gibb et al. (1953), and Bergman et al. (1961) all reported that there is a layer of amorphous character present on quartz surfaces, which is readily dissolved by water. Ihler (1955) reported that soluble silicates precipitate in the presence of salts. This precipitate redissolves upon dilution if the salt is of a monovalent metal, but is insoluble if precipitated by a salt of a polyvalent metal. Flach et al. (1974) report that duripans form in parent materials which readily release silica on weathering and in climates which provide enough water for weathering but not enough for intensive leaching of the soil profile in most years. Macromorphology and micromorphology strongly suggest duripans are genetic horizons formed through downward movement of silica in solution and precipitation of silica in the pan horizon.

## CHAPTER III

### METHODS AND MATERIALS

#### Test Soils

The Walla Walla silt loam used in this study (a coarse silty, mixed, mesic typic Haploxeroll) was sampled at 15-cm intervals to a depth of 60 cm, from various plots (referred to as "crop residue plots") in a long-term study, in existence since 1931. This field study consisted of nitrogen fertilizer rates and various crop residue handling methods including addition of manure. Selected characteristics of a typical Walla Walla silt loam and treatments imposed on the crop residue plots are given in Tables 1 and 2, respectively. This study is located on the Columbia Basin Agricultural Research Center, Pendleton, Oregon. All fertilization and residue was incorporated by moldboard plowing in the spring of the summerfallow year.

Soil samples were air dried, passed through a 2 mm sieve, and stored in closed non-metallic containers. Table 3 gives the laboratory treatments imposed on soils taken from the crop residue plots.

#### Leaching Procedure

A system of laboratory columns was constructed to simulate a leaching soil profile, and to facilitate continuous collection of leachate for analysis. All soils were air dry when placed into the columns. All materials in the leaching apparatus were selected to minimize silica contamination or sorption. The diameter of the

Table 1. Selected properties of the test Walla Walla silt loam.

Depth (cm)	Particle size distribution <sup>1/</sup>			Organic matter (%)	Cation exchange capacity <sup>2/</sup>	pH range <sup>3/</sup>
	sand	silt	clay			
0-15	12.5	67.8	19.6	1.8	0.189	4.5 - 6.2
15-30	11.8	70.8	17.4	1.5	0.193	5.4 - 6.4
30-45	12.2	72.2	15.6	1.0	0.202	6.0 - 6.3
45-60	12.4	72.9	14.7	0.8	0.193	6.2 - 6.4

<sup>1/</sup> Sand 2.0 to 0.053 mm; silt 0.053 to 0.002 mm; clay < 0.002 mm.

<sup>2/</sup> mol(NH<sub>4</sub>OAC)/kg

<sup>3/</sup> In 0.01 M CaCl<sub>2</sub>; pH in water is normally 0.7 units higher.

Table 2. Treatments (imposed since 1931) from which Walla Walla silt loam samples were obtained for laboratory leaching studies.

Treatment code	Residue incorporated or (other treatment) <sup>1/</sup>	N added	Range of C additions	Chemical properties in Ap layer		
				Total C	pH	C/N <sup>4/</sup>
		- - - kg/(ha·yr) - - -		(%)		
+N	Wheat straw	34(45) <sup>2/</sup>	900-1300	1.14	4.9	13.2
-N	Wheat straw	0	800-900	1.05	5.5	13.5
SM	Wheat straw plus 22 Mg/ha strawy manure	0	2000-2200	1.35	6.2	12.7
FB	Wheat straw burned in fall after wheat harvest	0	< 400 <sup>3/</sup>	1.02	5.5	14.2
PV	Wheat straw plus 2.3 Mg/ha dry pea vines	0	1500-1700	1.22	5.8	12.7

<sup>1/</sup>Pea vines or strawy manure incorporated in late March or early April when wheat straw was incorporated by moldboard plowing in spring of summerfallow year.

<sup>2/</sup>From 1931 to 1966, 34 kg of N/ha; from 1967 to the present, 45 kg of N/ha.

<sup>3/</sup>Projected on a basis that 35% of the C was volatilized during burning (Rasmussen et al., 1980).

<sup>4/</sup>From Rasmussen et al., 1980.



Table 3. Laboratory treatments imposed on soil samples from the crop residue plots described in Table 2.

Treatment code	Laboratory treatment imposed
-N2	Soil from the -N plot was first leached, then air dried in the leaching column and leached again.
SM2	Soil from the SM plot was first leached, then air dried in the leaching column and leached again.
SM-AN	Soil from the SM plot was saturated with anhydrous ammonia.
FB-AN	Soil from the FB plot was saturated with anhydrous ammonia.
+N+L	The 0 to 15-cm layer of soil from the +N plot was incubated, at 20% moisture by weight with an equivalent of $2.24 \times 10^3$ kg $\text{CaCO}_3$ /ha. Final pH was 6.8.

four columns, in a vertical arrangement, was determined such that the cross-sectional area of each column was approximately one-fourth that of the column above. A constant head of deionized water was introduced into the upper column. The percolate, from each column, was split so that approximately one-half was collected for analysis and one-half was directed into the column below. One-half and not one-fourth was allowed to flow through the columns to be sure flow continued through the lower columns, and that a head of liquid did not form. All percolate from the last column was collected for analysis. Measured percolate volume saved for analysis, deionized water volume introduced into the first column, head on the first column, and weight of water in each column all permitted an accounting of constituent transfer in the leaching flow. Appendix Figure 1 shows a cross-sectional drawing; an overall view of the leaching columns is shown in Appendix Figure 2. Examples of accounting procedures needed to determine constituent transfer are shown in Appendix Tables 3 and 4.

Percolate samples were centrifuged at 9200 times gravity (in a Sorvall SS-3 automatic superspeed centrifuge with a Sorvall type SS-34 head) to remove occasional small amounts of solids, and then refrigerated at 2 to 3°C until analyzed.

### Silica

Silica was determined as silicic acid ( $H_4SiO_4$ ) by a slightly modified heteropoly blue method as found in Rand et al. (1975). In this method ammonium molybdate, with an approximate pH of 2 reacts

with silica and any phosphate present to produce heteropoly acids. Molybdophosphoric acid, but not molybdosilicic acid, is destroyed by adding oxalic acid. The yellow molybdosilicic acid is reduced with aminonaphtholsulfonic acid to produce the heteropoly blue.

Color was developed by rapidly adding, to 50 mL of a prepared or untreated sample, in succession 1.0 mL of one-to-one HCl and 2.0 mL ammonium molybdate reagent. The sample was mixed and then not disturbed for 5 to 10 minutes. Then 1.5 mL oxalic acid solution was added and the sample mixed again. After at least 2 but not more than 15 minutes, 2.0 mL reducing agent (aminonaphthol-sulfonic acid) was added and the sample mixed again. After 2 minutes, the blue color was read photometrically at a wavelength of 815 m $\mu$  with a Bausch and Lomb Spectronic 20. The slight modification was the use of 0.03 M HCl instead of water where the original procedure indicated that one mL of the unknown sample was to be diluted to 50 mL. This modification decreased variability between duplicates (Personal communication, Glen Leggett, Snake River Conservation Research Center, ARS, USDA, Kimberly, Idaho).

#### Soluble Organic Carbon

Soluble organic carbon was determined on a Technicon auto-analyzer II using a 1976 Industrial Method (numbered 451-76W). In this method inorganic carbon is removed by entraining the sample stream, acidified with H<sub>2</sub>SO<sub>4</sub>, with a high velocity stream of air free of CO<sub>2</sub>. The sample is then transformed into a thin turbulent liquid film which is transported rapidly through a large-bore coil

to provide the necessary surface area for efficient CO<sub>2</sub> removal. Up to 500 mg of inorganic C could be removed. An aliquot of carbonate-free sample is then segmented, mixed with a stream of H<sub>2</sub>SO<sub>4</sub> and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, and subjected to UV radiation. CO<sub>2</sub> generated from the organic C present in the unknown is dialyzed through a silicone rubber membrane and reacted with a weakly buffered phenolphthalein indicator. The decrease in color of the indicator is proportional to the original C content. The detection limit is 0.20 mg of C/L.

### Cations

Cations were determined on a Perkin-Elmer 303 atomic absorption spectrophotometer using a hollow cathode light source. All cations were determined using an air-acetylene flame except for a nitrous oxide acetylene flame to determine Al. Instrument settings are shown in Appendix Table 5.

### Miscellaneous Soil Properties

Soil pH was measured, in a mixture (w/w) of 1 part soil in 2 parts of 0.01 M CaCl<sub>2</sub>, with a combination pH/reference electrode.

Particle size analysis was determined by first passing the bulk soil sample through a 2-mm sieve and then weighing a sample of 10 ± 0.01 g. Organic matter was removed by first adding, in a hood, 50 mL of distilled water and 5 mL of 30% H<sub>2</sub>O<sub>2</sub> plus two drops of glacial acetic acid to each beaker. The samples were heated to 90 C on a hot plate, treating with H<sub>2</sub>O<sub>2</sub> until organic matter appeared oxidized. Each sample was washed with 750 mL of distilled water and the

supernatant removed by applying vacuum to a Pasteur-Chamberlain filter of "F" fineness. The samples were stirred occasionally and back pressure was used to clean the filter periodically. Samples in beakers were dried overnight at 105°C, cooled, and weighed to the nearest 0.001 g. Ten mL of a dispersing agent (5% solution of Calgon) was added, after which the sample was allowed to heat at room temperature overnight. Approximately 250 mL of distilled water was used to wash the samples into a Bouyoucos cylinder. Samples were dispersed with an air jet for 5 minutes at 1.76 kg/cm<sup>2</sup>, then passed through a 0.053-mm sieve suspended in a funnel in the top of a Bouyoucos cylinder. Samples were washed to a volume of 1100 mL with distilled water. Sand-size material was washed from the sieve into a beaker and dried at 105°C, weighed and recorded. Material less than 0.053 mm was placed overnight in a constant temperature bath in a constant temperature room to reach equilibrium at 25°C. The cylinder was then shaken by completely inverting the cylinder 60 times; it was then again placed in the bath. At the correct settling time for silt and clay, 25 mL of samples were pipetted into a 100-mL beaker. The pipette was rinsed with 25 mL of distilled water which was also put into the same 100 mL beaker. The beakers and contents were dried overnight at 105°C and weighed. Times for sampling at 25 C were 4 minutes for particles 0.020 mm, and 415 minutes for particles 0.002 mm in diameter.

Material calculations for less than 0.002, 0.002 to 0.02, 0.02 to 0.05 mm and greater than 0.05 mm were as follows:

Pipetted fraction -  $(A-B)(K)(D)$ (% of pipetted fraction),

where A = weight in g of pipetted fraction,

B = weight correction for dispersing agent in g,

K = 1130/25, (25 is the volume contained by the pipette) and

D = 100/(organic-free oven dry weight of total sample).

Material in the 0.02 to 0.05 mm range was obtained by difference; material greater than 0.05 mm (sand) was obtained as the product of D and the weight (g) of the fraction on a sieve.

Organic matter was determined as 1.72 times the organic C found by combustion in a Leco furnace.

Cation exchange capacity was determined with a 1 M  $\text{NH}_4\text{OAc}$  (pH 7) extracting solution (Chapman, 1961).

### Physical Measurements

A modified Utah core (1.87-cm diameter) sampler was used to determine dry bulk density in soil increments of 2 cm to a depth of 48 cm. At least 13 cores were used to determine each mean dry bulk density. Penetrometer load was determined with a cone (30-degree cone with a 10-mm base diameter) penetrometer connected to a proving ring and a displacement dial. At least 10 penetrometer advances were used to determine each mean penetrometer load.

### Soil Exposure to Anhydrous Ammonia

Air dried, < 2-mm sieved soil from the 0 to 15 cm layer of the FB and SM treatments (Table 2) of the crop residue plots as saturated

with anhydrous ammonia. A schematic of the system used is shown in Appendix Figure 3. Approximately 3800 g of soil, adjusted to 20% (w/w) moisture was placed into a polyvinyl chloride column. Anhydrous ammonia was bled at a low ( $0.4 \text{ kg/cm}^2$ ) pressure into the bottom of each column until ammonia could be detected by smell at the top of the column. The amount of anhydrous injected into each column was not measured because the purpose was to obtain anhydrous ammonia saturation of each soil. After saturation the columns were covered with a PVC cap; however, they were not sealed. The columns then set for 10 days, after which time the soil was removed and spread out to air dry for five days. The soil was then passed through a 2-mm screen, and subjected to the leaching process described earlier. The soil pH in 0.01 M  $\text{CaCl}_2$ , and  $\text{NH}_4^+$  (with the Technicon Auto-analyzer, II) were determined before and after leaching.  $\text{H}_4\text{SiO}_4$ , soluble C, and cations were also determined as indicated previously.

## CHAPTER IV

### RESULTS AND DISCUSSION

#### pH and Temperature Effects on Silica Solubility

Because of the confusion in the literature a preliminary experiment was conducted to determine if pH might affect silica solubility in a Walla Walla silt loam. Two hundred g of Walla Walla silt loam was incubated at room temperature (20°C) for 3 months with either 1.1 g (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> or 0.4 g CaCO<sub>3</sub>. Ten g of this treated and incubated or untreated soil was weighed into each of 10 beakers and 50 mL of distilled water added. Beakers were neither shaken nor disturbed during the equilibration. Samples for silica analysis in the supernatant were taken at the times shown in Table 4. Low soil pH, relative to other treatments, increased silicic acid concentration. Incubation of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> with soil from the +N plot had no significant effect but the incubation with CaCO<sub>3</sub> reduced soluble silica after 3 hours of exposure. Soluble silica in the supernatant over soil from the SM plot was always less than over the soil receiving N fertilizer. The pH of the SM soil is approximately 0.9 units greater than the +N soil (Table 2); it also received large additions of organic matter.

A second experiment was conducted to determine the effect of temperature on silica solubility. Twenty g of Walla Walla silt loam was mixed with 60 mL of distilled water in a beaker and incubated for variable periods up to 32 days at either 10 or 20°C. An aliquot of 30 mL for silica analysis was removed periodically. After each



Table 4. Silicic acid solubility in the supernatant above a Walla Walla soil treated with long term management of nitrogen or strawy manure and then exposed to  $(\text{NH}_4)_2\text{SO}_4$  or  $\text{CaCO}_3$ .

Long term treatment of soil (treatment code)	Chemical added during incubation	Depth (cm)	Soil pH	Cumulative soluble silica after indicated hours of exposure					
				1.0	3.0	6.0	24.0	48.0	72.0
----- $10^2 \text{ mol/m}^3$ -----									
+N <sup>1/</sup>	0	0-15	4.9	14	22	23	39	56	59
		15-30	5.6	12	22	22	40	50	64
		30-45	6.0	10	17	20	37	58	64
		45-60	6.4	10	14	17	32	50	60
+N <sup>2/</sup>	$(\text{NH}_4)_2\text{SO}_4$	0-15	4.5	12	16	20	41	52	66
		15-30	4.5	14	19	24	54	76	86
		30-45	5.3	12	16	20	41	58	66
		45-60	5.1	14	28	40	51	44	74
+N	$\text{CaCO}_3$	0-15	6.8	13	14	18	24	40	48
		15-30	7.1	16	15	18	20	42	48
		30-45	7.5	14	16	20	30	42	54
		45-60	7.4	16	18	26	34	64	48
SM	0	0-15	6.2	08	12	16	35	46	51
		15-30	6.4	08	12	18	32	42	49
		30-45	6.3	06	13	15	32	40	48
		45-60	6.4	08	16	19	34	42	52

<sup>1/</sup>Only measurements on the +N treated soil were duplicated. Average  $\bar{s}_x$  for each column: 0-to-15 cm, 0.034; 15-to-30 cm, 0.043; 30-to-45 cm, 0.033; and 45-to-60 cm, 0.038  $\text{mol/m}^3$ . These  $\bar{s}_x$  were calculated by random difference between duplicates.

<sup>2/</sup>Definition of treatment code symbols given in Table 2.

aliquot was removed, water was added to the beaker to maintain the original weight. Each sample was shaken for 30 seconds each day.

Silicic acid solubility increased with time and was always about  $25 \times 10^{-4} \text{ mol/m}^3$  higher at 20 than at 10°C. The solubility change per degree C was  $2.7 \times 10^{-4} \text{ mol/m}^3 \cdot \text{deg}$  after 32 days of equilibration (Table 5).

These two preliminary experiments indicated that silicic acid concentration in a Walla Walla silt loam was sensitive to both pH and temperature changes.

#### Physical and Chemical Properties of a Cultivated Walla Walla Silt Loam

Selected physical properties of a typical cultivated Walla Walla silt loam (Figure 1) and the measurements in Appendix Table 1 collectively suggest water flow and plant root penetration problems in the 15- to 30-cm layer. The absence of clay accumulation or high cation exchange capacity (Table 1) rules out an argillic or duripan horizon as contributors to the high strength. The bulge of dry bulk density at 25 cm (Figure 1) identifies a pressure pan; however, the low dry bulk density (Figure 1), even in the pressure pan, provides little or no evidence that compaction and associated particle proximity should alone induce the high penetrometer load shown for the 21 to 42-cm layer in Figure 1. A peak of dry strength just below the peak of dry bulk density is suggestive but nonconclusive evidence for a cementing substance in the 24 to 30-cm zone. The respective

Table 5. Temperature effect on silicic acid solubility in the supernatant above a Walla Walla silt loam.

Time (Days)	Temp. (°C)	H <sub>4</sub> SiO <sub>4</sub> concentration <sup>1/</sup> (10 <sup>4</sup> mol/m <sup>3</sup> )	Temperature effect on solubility (10 <sup>4</sup> mol/m <sup>3</sup> ·°C)
10	10	61	2.7
	20	88	
20	10	75	3.0
	20	105	
32	10	84	4.3
	20	127	

<sup>1/</sup>The average standard error of  $2.5 \times 10^{-4}$  mol/m<sup>3</sup> was determined from disagreement between replicates.

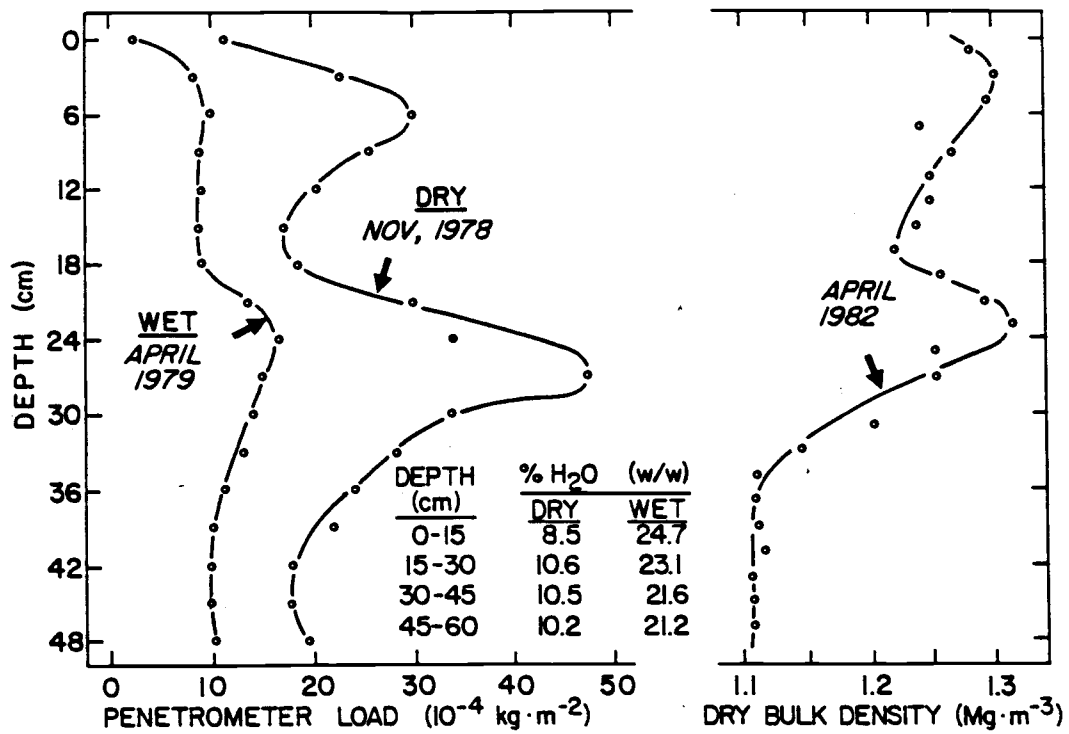


Figure 1. Typical penetrometer load and dry bulk density of Walla Walla silt loam under wheat-summerfallow culture.

average standard errors of the means for penetrometer load and dry bulk density were  $2.61 \times 10^{-4} \text{ Kg}\cdot\text{m}^{-2}$  and  $1.0 \times 10^{-3} \text{ Mg}\cdot\text{m}^{-3}$ , as determined by the residuals after drawing the curves in Figure 1. The saturated hydraulic conductivity (Appendix Table 1) does show slow internal drainage. The relatively low pH in the Ap layer suggests that ammonium type fertilizers have decreased pH somewhat (Allmaras et al., 1978).

#### Liquid Movement Through Soil Columns

A typical example of cumulative outflow from each soil layer as a function of elapsed time after the initiation of deionized water addition is shown in Figure 2. Each curve intercepts the time axis when drainage first started from the indicated layer. The time span between outflow for the layer in question and the superposed layer indicates the time interval for drainage through the layer in question. For example, 2.5 hours elapsed for flow through the 15 to 30-cm layer, because outflow from the 0 to 15 and 15 to 30-cm layers started at 1.0 and 3.5 hours, respectively. Because of soil packing variations, flow rates varied as much as 40% between replicated columns. All columns showed a decrease in liquid flow with time. Occasionally an experiment was terminated earlier than desired because flow through the 30 to 45-cm layer could not be sustained. Regression parameters of cumulative flow versus time (an exponential function of time) are shown in Appendix Table 6. Flow through soil from the high nitrogen-plus-lime (+N+L) plot was especially slow in this 30 to 45-cm layer (not shown). Possibly increased calcium in the

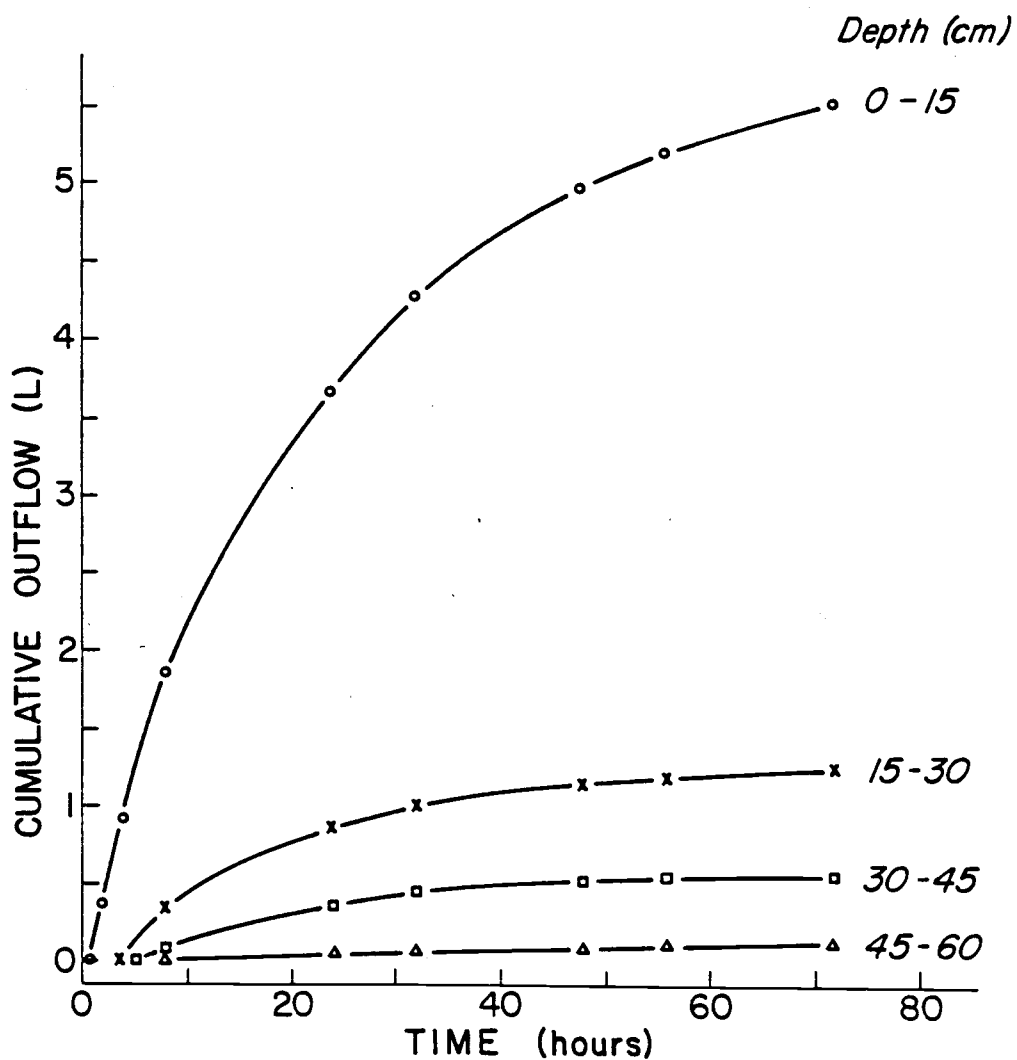


Figure 2. Cumulative outflow from four contiguous soil layers of the +N plot as a function of elapsed time after deionized water delivery to the 0- to 15-cm layer.

limed treatment reduced the proton activity which decreased the solubility of the silica source. However, when the soil in an intact leaching column was air dried and leached again after a prior run (i.e., -N and SM2), liquid flow was restricted even more than when lime was added before the first run (+N+L).

Treatment of the soil with anhydrous ammonia (FB-AN, SM-AN) increased liquid flow through soil from the fall burned plot (FB) but not through soil from the strawy-manure (SM) plot (not shown).

### Silicic Acid

Cumulative silicic acid outflow (Figure 3) was similar to cumulative fluid outflow (Figure 2). The large difference among depths in both fluid and silicic acid outflow was caused by the experimental design, because the next lower column always had 25% as much cross-sectional area. Similarity of cumulative fluid and silicic acid outflow was also produced because there were only minor changes of silicic acid concentration in the outflow as a function of fluid outflow (or elapsed time). This effect was analyzed by fitting a third order polynomial ( $y = a + bx + cx^2 + dx^3$ , where  $x =$  flow in ml and  $y =$  cumulative silicic acid) to the cumulative silicic acid outflow as a function of fluid flow. An average concentration was obtained by evaluating these equations at some specified cumulative flow, and then dividing by the cumulative fluid flow. Such evaluations made at both one-half and total cumulative fluid flow confirmed negligible changes in silicic acid concentration in outflows as a function of time (or fluid flow). Evaluation for the first one-half, second one-half, and total flow are shown in Appendix Table 7.

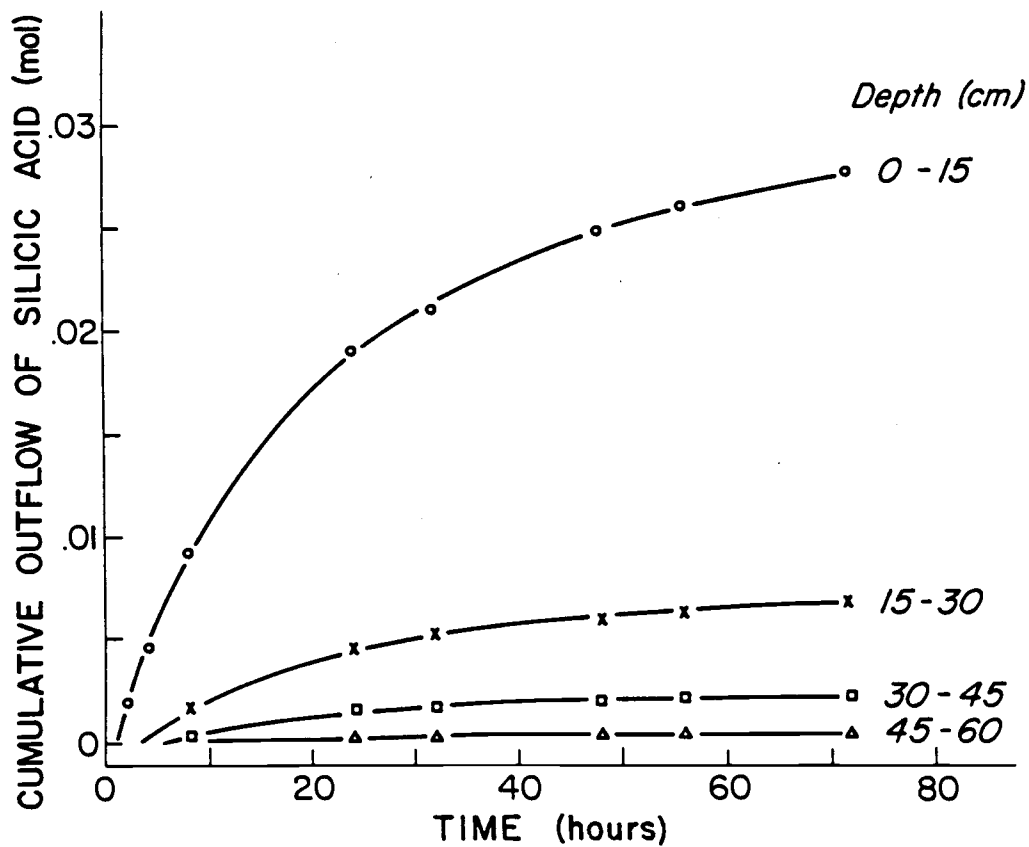


Figure 3. Cumulative outflow of silicic acid from four contiguous layers of the +N plot as a function of elapsed time after deionized water delivery to the 0- to 15-cm layer.



When no silica was entering the layer, i.e. the 0 to 15-cm layer, silicic acid concentration in the leachate increased as soil pH decreased (Table 6). When the input liquid contained silicic acid, as in all layers below 15 cm, there was a smaller trend for increased silicic acid concentration as the pH decreased. The large amount of organic matter added in the PV and SM treatments (Table 2), depressed soluble silica 24% in the leachates as compared to the fall burn (FB) and no nitrogen (-N) treatments in which pH was not changed significantly. Lime addition (+N+L treatment) reduced soluble silica 32%. Reduced proton activity must have decreased the solubility of the silica source. Beckwith and Reeve (1963) and Leggett et al. (1959) showed that solution concentration of anions or calcium had no effect. McKeague and Cline (1963b) also found no effect of salt concentration on release of sorbed silica.

Addition of anhydrous ammonia (Table 6) had practically no effect on silicic acid movement to a depth greater than 60 cm. Drying the soil in the intact column after a run tended to decrease the amount of silicic acid leaching below 60 cm (Table 6).

Table 7 gives the net transfer of silicic acid from each horizon. The transfer was calculated using equation [1] which expresses the net retention in the  $i^{\text{th}}$  soil layer as follows:

$$\text{NRI} = \text{AREA} [\text{SJ} - (\text{SJ} - \text{SJI}) - \text{SI}] / \text{FLOWI} \text{ - - - - - [1]}$$

where  $i$  indexes from 1 for the 0 to 15-cm layer to 4 for the 45 to 60-cm layer;

NRI is the net silicic acid (mol) per m of liquid effluent retained in the  $i^{\text{th}}$  soil layer;

Table 6. Mean silicic acid concentration in leachates from successive 15 cm soil layers of a Walla Walla silt loam as affected by long term N and residue treatments.

Treatment code <sup>1/</sup>	Silicic acid concentration (mol/m <sup>3</sup> ) and pH for indicated treatment and soil depth increments.							
	0-15 cm		15-30 cm		30-45 cm			
	pH	H <sub>4</sub> SiO <sub>4</sub>	ph	H <sub>4</sub> SiO <sub>4</sub>	pH	H <sub>4</sub> SiO <sub>4</sub>	pH	H <sub>4</sub> SiO <sub>4</sub>
+N	4.9	1.42 a <sup>2/</sup>	5.4	1.43 a	6.0	1.09	6.4	1.10
-N	5.5	1.33 ab	5.8	1.26 ab	6.1	1.18	6.2	1.16
+N+L	6.8	0.97 ab	6.4	1.21 ab	6.0	1.12	6.4	1.00
FB	5.5	1.36 ab	5.7	1.28 ab	6.1	1.07	6.2	1.17
SM	6.2	0.85 b	6.4	0.96 b	6.3	0.92	6.4	1.01
PV	5.8	0.97 ab	5.8	0.96 b	6.2	0.76	6.4	0.85
ave $s_{\bar{x}}$	0.142		0.123		0.134		0.174	
-N <sub>2</sub> <sup>3/</sup>	(5.5) <sup>3/</sup>	1.33	(5.8)	1.10	(6.1)	1.92	(6.2)	0.86
FB-AN	7.9	1.11	5.7	1.97	6.1	1.64	6.2	1.20
SM-AN	8.2	1.20	6.4	0.95	6.3	1.19	6.4	0.99
SM <sub>2</sub>	(6.2)	0.78	(6.4)	0.77	(6.3)	0.74	(6.4)	0.69

<sup>1/</sup> Definition of treatment code symbols given in Tables 2 and 3 (-N<sub>2</sub>, FB-AN, SM-AN, and SM<sub>2</sub> were not duplicated).

<sup>2/</sup> Value within each column of each depth increment followed by the same letter are not significantly different at  $p = 0.05$ . The  $s_{\bar{x}}$  were determined from disagreement between duplicate columns.

<sup>3/</sup> pH for -N<sub>2</sub> and SM<sub>2</sub> not measured but assumed the same as in column not air dried.

Table 7. Long-term N and residue management effects on silicic acid retention in the four shallowest 15-cm layers during leaching of a Walla Walla silt loam.

Treatment <sup>1/</sup> code	Silicic acid retention, 10 <sup>2</sup> mol/m of liquid depth, for indicated depth increment			
	0-15 cm	15-30 cm	30-45 cm	45-60 cm
+N	-4.33 <sup>2/</sup> / <sub>a</sub> <sup>3/</sup>	+ 2.69 a	+ 0.55 a	+ 0.14 ac
-N	-3.19 b	+ 0.94 b	+ 0.44 b	+ 0.16 ab
+N+L	-2.96 c	+ 0.89 b	+ 0.30 c	+ 0.20 b
FB	-3.80 d	+ 0.32 c	+ 0.55 a	+ 0.10 c
SM	-2.58 e	+ 0.80 b	+ 0.26 cd	+ 0.42 d
PV	-2.96 c	+ 1.31 d	+ 0.24 d	+ 0.04 e
ave $s_{\bar{x}}$	0.050	0.032	0.014	0.013
-N2	-2.35	-0.08	+ 0.21	+ 1.28
SM2	-2.32	+ 0.77	+ 0.03	+ 0.48
SM-AN	-3.65	+ 0.77	+ 0.78	+ 0.31
FB-AN	-3.38	+ 0.51	+ 0.52	+ 0.08

<sup>1/</sup> Definition of treatment code symbols given in Tables 2 and 3. The four treatments -N2, SM2, SM-AN, FB-AN were not duplicated.

<sup>2/</sup> A net loss from the layer is negative; a net gain in the layer is positive.

<sup>3/</sup> Values within a column followed by the same letter are not significantly different at  $p = 0.05$ . The average  $s_{\bar{x}}$  was determined from random difference between duplicate leaching columns.

AREA is the cross-sectional area ( $m^2$ ) of the  $i^{th}$  soil layer;  
 SJ is the cumulative silicic acid (mol) leaving the  $j^{th}$  soil layer ( $j = i-1$ );

SJI is the cumulative silicic acid (mol) leached from the  $j^{th}$  soil layer that entered the  $i^{th}$  soil layer, minus the silicic acid that did not have a chance to exit the  $i^{th}$  soil layer before leaching was terminated;

SI is the cumulative silicic acid (mol) leaving the  $i^{th}$  soil layer;

FLOWI is the total liquid flow ( $m^3$ ) from the  $i^{th}$  soil layer.

SJ and SJI are zero for the 0 to 15-cm layer. SJI was calculated by evaluating a polynomial equation (equations not shown) between the upper and lower limit of cumulative flow from the  $j^{th}$  soil layer. The upper limit was the total liquid flow from the  $j^{th}$  layer that entered the  $i^{th}$  soil layer; the lower limit was the upper limit minus the amount of liquid in the  $i^{th}$  layer at the end of the leaching run. The polynomial equation expressed mass transfer as a third order linear function of liquid flow.

Large net losses of silicic acid occurred in the first 15-cm increment. Net gains occurred in all subsequent increments (Table 7). The sums of transfers within the upper 60 cm are negative for all treatments indicating a significant upper profile loss of silicic acid controlled mainly by the loss from the first 15-cm layer. Loss of silicic acid from the 0 to 15-cm layer increased as soil pH decreased. Past carbon additions reduced the amount of silicic acid leaving the 0 to 15-cm layer.

Leachate concentrations (Table 6) and net silicic acid trans-

fers (Table 7) indicated that sorbed silica was the source for soluble silica as determined earlier by McKeague and Cline (1963a). Their studies showed that the source of silica could not be dissolution of a compound. Perfusions conducted by McKeague and Cline (1963a) had soil exposures to water similar to soils in this experiment. When a series of perfusions in their study were each initiated with distilled water the soluble silicic acid increased rapidly initially and then slowly thereafter. Each new perfusion produced a lower concentration of soluble silicic acid. This reaction is similar to the conditions and response in the 0 to 15-cm soil layer (Table 6 and associated discussion). When the perfusate from one soil sample was used to perfuse a new sample of the same soil, silicic acid concentration in solution increased gradually (McKeague and Cline, 1963a). The same type of response was observed in our lower three 15-cm soil layers (Table 6 and associated discussion).

Soluble silicic acid concentrations in Table 6 are at least three times greater than values reported in the review by McKeague and Cline (1963c). This general observation agrees with measurements of soluble silicic acid in solution extracts of 18 soils from the western United States (Leggett et al., 1959). Their Walla Walla silt loam had saturated solution silicic acid concentrations roughly 2 to 3 times greater than soils outside Washington and Idaho, and those shown by McKeague and Cline (1963a). The soluble silicic acid in Table 6 is still only about 50% of that in the presence of pure amorphous silica (McKeague and Cline, 1963a).

### Soluble Organic Carbon

Cumulative outflow of oxidizable organic carbon with time in the +N treatment (Figure 4) showed large differences among layers just as with silicic acid outflow (Figure 3). These large differences are experimentally related to the geometric reduction of column diameter. However, cumulative outflows of carbon for the lower layers are larger, relative to that from the upper layer, in the case of organic carbon compared to silicic acid. The curves in Figure 4 also plateau more than the curves for silicic acid outflow. Soluble carbon concentration (Table 8) was not significantly affected by soil pH. The +N plot had the highest carbon concentration. Liming decreased carbon concentrations by 50%. Drying intact soil columns and then renewing the leaching process decreased organic carbon concentration by an average of 25%. Anhydrous ammonia saturation produced large increases in leachate carbon concentrations (i.e. SM-AN vs SM and FB-AN vs FB, Table 8).

Soluble organic carbon concentration in all four 15-cm layers declined at least 50% during the leaching (Appendix Table 7) in all treatments except the +N+L treatment. However, as the fluid moved down through and out of each soil layer, carbon concentrations increased. Part of this increase may have occurred because the geometric reduction in flow cross-section accentuated the increase in concentration as leaching progressed from a given layer. These changes in carbon concentration, as flow from a given layer progressed, were not similar to silicic acid concentration changes. Concentrations of organic carbon in the first 15-cm layer of all leaching columns from soil with only field treatment (+N, -N, SM,

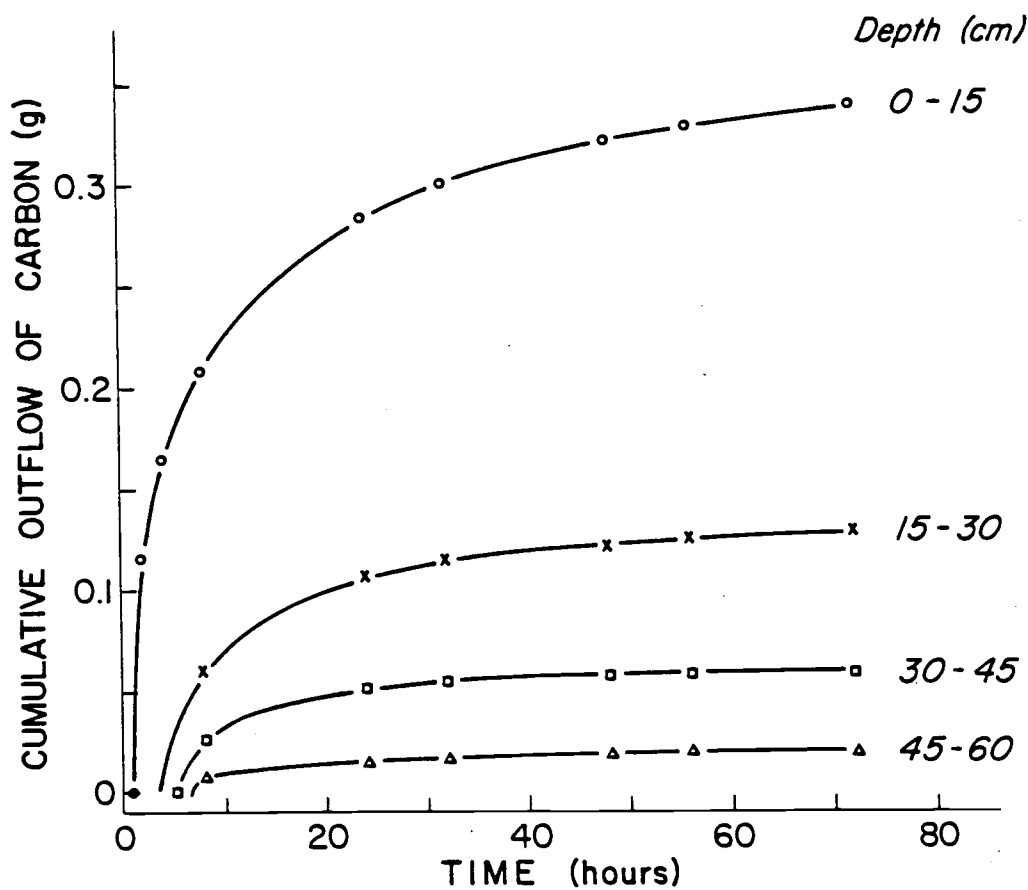


Figure 4. Cumulative outflow of soluble organic carbon from four contiguous soil layers of the +N plot as a function of elapsed time after deionized water delivery to the 0- to 15-cm layer.

Table 8. Mean soluble organic carbon concentration in leachates from successive 15-cm layers of a Walla Walla silt loam as affected by long-term N and residue treatments.

Treatment code	Soluble organic carbon concentration (mol/m <sup>3</sup> ) for indicated soil depth increments and treatment			
	0-15 cm	15-30 cm	30-45 cm	45-60 cm
+N <sup>1/</sup>	4.35 a <sup>2/</sup>	6.94 a	7.85 a	10.77
-N	1.59 b	1.98 b	2.92 b	3.29
+N+L	2.12 ab	3.42 ab	3.90 b	7.99
FB	2.32 ab	3.84 ab	5.35 ab	7.00
SM	2.37 ab	3.77 ab	3.69 b	6.33
PV	2.93 ab	3.67 ab	4.10 b	4.61
-----	-----	-----	-----	-----
s $\bar{x}$	0.690	1.050	0.940	2.650
-----	-----	-----	-----	-----
-N2	1.07	4.79	2.36	6.96
FB-AN	20.81	14.10	20.43	16.80
SM-AN	31.47	42.40	61.35	42.70
SM2	2.01	3.30	2.45	7.83

<sup>1/</sup> Definition of treatment code symbols given in Tables 2 and 3 (-N, FB-AN, SM-AN, and SM2 were not duplicated).

<sup>2/</sup> Values within each column of each depth increment followed by the same letter are not significantly different at  $p = 0.05$ . The  $s\bar{x}$  were determined from disagreement between duplicate columns.



FB, PV) increased somewhat as the C/N ratio (Rasmussen et al., 1980) decreased. Soil saturated with anhydrous ammonia released 10 times more soluble organic carbon than released from any of the other treatments (Table 9). Apparently the high pH, resulting from anhydrous ammonia, solubilized much of the water-insoluble organic compounds.

Drying the soil in the intact columns followed by another leaching had no significant effect on organic carbon solubility (Table 9).

There was a net carbon loss from the 0 to 15-cm layer and net gains in the layers below (Table 9). The greatest loss from the soils not tested with anhydrous ammonia was from the +N treatment. These net carbon transfers were computed using Equation [1] and carbon contents instead of silica contents.

Net gains in a layer of soil (Table 9), when leachate concentrations are increasing with depth (Table 8), can occur only when the soil is dry initially and gains in water content before the water stops flowing through the layer. That is, these columns are not steady-state with respect to fluid flow. The leaching column system of this study simulates the soil wetting in nature. As wetting of a dry soil proceeds, in winter, near saturation occurs in the upper part of the Walla Walla silt loam. As precipitation declines in the spring and early summer drainage creates a moisture content near field capacity, which then dries to near air-dry during the summer. The presence of a crop dries the soil more than if summer fallowed. Either way soil solution flow ceases. Thus some silica (or any solute) can enter and then not exit a soil layer, as is measured by the SJI term in Equation [1].

Table 9. Long-term nitrogen and residue management effects on soluble organic carbon movement in the four shallowest 15-cm layers during leaching of a Walla Walla silt loam.

Treatment code <sup>1/</sup>	Soluble organic carbon retention ( $10^2$ mol/m of liquid depth) for indicated depth increment.			
	0-15 cm	15-30 cm	30-45 cm	45-60 cm
+N	-13.25 <sup>2/</sup> a <sup>3/</sup>	+7.24 a	+1.97 a	+0.32 a
-N	-4.78 b	+1.30 b	+0.58 b	+0.37 b
+N+L	-6.44 c	+1.41 b	+0.71 c	+0.48 c
FB	-7.04 c	-0.38 c	+1.10 d	+0.28 a
SM	-6.92 c	+1.39 b	+1.10 d	+1.07 d
PV	-8.93 d	+3.45 d	+0.80 c	+0.28 a
----- $s_{\bar{x}}$	0.209	0.158	0.044	0.022
-----				
-N2	-3.26	-2.64	+2.20	-0.33
SM2	-6.12	+1.22	+0.28	-0.33
SM-AN	-95.73	+19.99	+21.58	-1.60
FB-AN	-63.30	+29.27	+1.85	-0.40

<sup>1/</sup> See Tables 2 and 3 for definition of treatment code symbols. This series of treatments (-N2, SM2, SM-AN, FB-AN) were not duplicated.

<sup>2/</sup> A net loss from the layer is negative; a net gain in the layer is positive.

<sup>3/</sup> Values within each column followed by the same letter are not significantly different at  $p = 0.05$ . The mean  $s_{\bar{x}}$  was determined by random disagreement between duplicate columns

Saturation with anhydrous ammonia perhaps occurs only in a small zone after normal field exposure. The treatment was intended to determine if soil organic carbon could be affected by anhydrous ammonia. As Tables 8 and 9 show, anhydrous ammonia solubilized organic carbon. The pH in the anhydrous ammonia treated soils increased from 5.5 to 7.9 for the FB soil, and from 6.2 to 8.2 in the SM soil. There are reports of soil pH values as high as 10.2 after addition of anhydrous ammonia (Mangum, 1965; Humbert and Ayers, 1957; Stanley and Smith, 1956). It is likely necessary for an extracting solution to have a pH above 8.5 if an acceptable yield of humic material is expected (Russell, 1961). Field application of anhydrous apparently creates localized areas of soil with a high pH. Many years of this activity may solubilize and move large amounts of organic material.

The large concentrations of soluble organic carbon (Table 9), and their failure to correlate significantly with silicic acid movement indicate that soluble organic carbon is not controlling solubilization of sorbed silica.

### Cations

All cation concentrations in the leachates (calcium, Table 10; magnesium, Table 11; sodium, Table 12) except potassium (Table 13) increased with depth. Potassium concentrations increased to a depth of 30 cm, and then decreased at greater depths. All cation concentrations in the leachates decreased with time (Appendix Tables 8 and 9). Liming increased the concentrations of all cations, except sodium, in the leachates. Drying soil in intact leached columns and anhydrous ammonia saturation in general increased concentrations of cations in the leachate.

Table 10. Calcium concentrations in leachates from four successive 15-cm layers of a Walla Walla silt loam.

Treatment code <sup>1/</sup>	Ca <sup>++</sup> concentration (mol/m <sup>3</sup> ) for indicated depth increments			
	0-15 cm	15-30 cm	30-45 cm	45-60 cm
+N	0.17 a <sup>2/</sup>	0.38 a	0.60 ab	0.88 a
-N	0.15 a	0.20 a	0.28 a	0.49 a
+N+L	0.77 b	0.76 b	1.08 b	2.24 b
FB	0.24 a	0.32 a	0.38 a	0.72 a
SM	0.20 a	0.32 a	0.41 a	1.22 a
PV	0.33 a	0.45 ab	0.46 a	0.60 a
-----				
s $\bar{x}$	0.074	0.095	0.154	0.261
-----				
-N2	0.30	0.64	0.31	1.06
SM2	0.26	0.42	0.40	1.08
SM-AN	0.67	1.24	2.06	2.37
FB-AN	0.50	1.08	1.15	1.02

<sup>1/</sup> Definition of treatment code symbols given in Tables 2 and 3. This section of treatments (-N2, SM2, SM-AN, FB-AN) were not duplicated.

<sup>2/</sup> Values within each column of each depth increment followed by the same letter are not significantly different at  $p = 0.05$ . The  $s\bar{x}$  were determined from disagreement between replicated columns.

Table 11. Magnesium concentrations in leachates from successive 15-cm layers of a Walla Walla silt loam.

Treatment Code <sup>1/</sup>	Mg <sup>+</sup> concentration (mol/m <sup>3</sup> ) for indicated depth increments			
	0-15 cm	15-30 cm	30-45 cm	45-60 cm
+N	0.09 a <sup>2/</sup>	0.22 a	0.36 ab	0.60 a
-N	0.08 a	0.13 a	0.16 a	0.33 a
+N+L	0.34 b	0.46 b	0.62 b	1.48 b
FB	0.14 ab	0.21 a	0.26 ab	0.54 a
SM	0.08 a	0.16 a	0.22 a	0.88 ab
PV	0.22 ab	0.27 ab	0.26 ab	0.52 a
-----				
$s_{\bar{x}}$	.063	0.078	0.114	0.229
-----				
-N2	0.24	0.51	0.28	0.82
SM2	0.18	0.28	0.24	0.70
SM-AN	0.09	0.58	1.12	1.22
FB-AN	0.12	0.52	0.63	0.51

<sup>1/</sup> Definition of treatment code symbols given in Tables 2 and 3. This section of treatments (-N2, SM2, SM-AN, FB-AN) were not duplicated.

<sup>2/</sup> Values within each column of each depth increment followed by the same letter are not significantly different at  $p = 0.05$ . The  $s_{\bar{x}}$  were determined from disagreement between replicated columns.

Table 12. Potassium concentrations in leachates from four successive 15-cm layers of a Walla Walla silt loam.

Treatment Code <sup>1/</sup>	K <sup>+</sup> concentration (mol/m <sup>3</sup> ) for indicated depth increments			
	0-15 cm	15-30 cm	30-45 cm	45-60 cm
+N	0.38	0.49 a <sup>2/</sup>	0.30	0.28
-N	0.88	0.51 a	0.44	0.46
+N+L	0.49	0.55 a	0.39	0.46
FB	0.31	0.42 a	0.34	0.37
SM	0.86	1.06 b	0.72	0.50
PV	0.64	0.58 a	0.42	0.30
-----				
$s_{\bar{x}}$	0.286	0.133	0.125	0.091
-----				
-N2	0.68	0.92	0.63	0.88
SM2	1.38	1.59	1.31	0.80
SM-AN	1.28	2.19	1.19	0.45
FB-AN	0.47	0.85	0.64	0.43

<sup>1/</sup> Definition of treatment code symbols given in Tables 2 and 3. This section of treatments (-N2, SM2, SM-AN, FB-AN) were not duplicated.

<sup>2/</sup> Values within each column of each depth increment followed by the same letter are not significantly different at  $p = 0.05$ . The  $s_{\bar{x}}$  were determined from disagreement between duplicated columns.

Table 13. Sodium concentrations in leachates from four successive 15-cm layers of a Walla Walla silt loam.

Treatment Code <sup>1/</sup>	Na <sup>+</sup> concentration (mol/m <sup>3</sup> ) for indicated depth increments			
	0-15 cm	15-30 cm	30-45 cm	45-60 cm
+N	0.17 a <sup>2/</sup>	0.18 ab	0.25 ab	0.34
-N	0.62 b	0.10 a	0.13 a	0.21
+N+L	0.15 a	0.22 b	0.33 b	0.55
FB	0.12 a	0.18 ab	0.22 ab	0.32
SM	0.07 a	0.15 ab	0.21 ab	0.54
PV	0.09 a	0.15 ab	0.18 a	0.20
-----				
$s_{\bar{x}}$	0.028	0.024	0.041	0.098
-----				
-N2	0.07	0.27	0.20	0.54
SM2	0.06	0.15	0.21	0.60
SM-AN	0.08	0.39	1.78	4.05
FB-AN	0.19	0.21	0.41	0.34

<sup>1/</sup> Definition of treatment code symbols given in Tables 2 and 3. This section of treatments (-N2, SM2, SM-AN, FB-AN) were not duplicated.

<sup>2/</sup> Values within each column of each depth increment followed by the same letter are not significantly different at  $p = 0.05$ . The  $s_{\bar{x}}$  were determined from disagreement between replicated columns.

Cation release or retention values are shown in Tables 14 through 17. All cations show a net release from the 0 to 15-cm layer and almost all give net retention values in lower layers. However, net release from the plow layer is greater than net retention in the layers below. In general, wetting and drying tends to release more cations from the surface as well as at greater depths. Anhydrous ammonia saturation of the 0 to 15-cm layer shows the same trend as wetting and drying. The effects of wetting and drying and anhydrous ammonia were more variable at lower soil depths. No correlation was noted between any cation(s) movement and the movement of silicic acid or carbon. Preliminary measurements indicate that soluble aluminum concentrations in the leachates were no more than  $3.7 \times 10^{-2} \text{ mol/m}^3$ . Leachate iron ( $\text{Fe}^{+3}$ ) concentrations in the leachates ranged from  $1.8 \times 10^{-2}$  to  $9.8 \times 10^{-2} \text{ mol/m}^3$  and showed no clear relationship to  $\text{H}_4\text{SiO}_4$  or C movement.

#### Silicic Acid and Organic C Interactions

Leachate concentrations (Table 6) and net silicic acid transfer (Table 7) from the 0 to 15-cm layer are both sensitive (as determined by multiple linear regression) to soil pH and carbon additions produced during the long-term management. Carbon additions were accomplished by N fertilization, manure additions, or burning to reduce residue. Transfers of silicic acid were more negative (i.e. more lost from the 0 to 15-cm layer) as long-term carbon addition and soil pH decreased. These multiple linear relationships (Table 18) collaborate the effect of decreasing silicic acid in solution with



Table 14. Calcium retention for four successive layers of a Walla Walla silt loam.

Treatment Code <sup>1/</sup>	Ca # retention ( $10^2 \text{ mol/m}^3$ ) for indicated depth increment			
	0-15 cm	15-30 cm	30-45 cm	45-60 cm
+N	-0.50 <sup>2/</sup> b <sup>3/</sup>	+0.20	+0.10	+0.07 b
-N	-0.44 b	+0.11	+0.04	+0.02 b
+N+L	-2.34 a	+0.94	+0.22	+0.08 b
FB	-0.71 b	+0.02	+0.13	+0.02 b
SM	-0.59 b	+0.12	+0.07	+0.12 a
PV	-0.99 b	+0.28	+0.58	+0.02 b
-----				
$s\bar{x}$	0.226	0.071	0.184	0.026
-----				
-N2	-0.92	-0.22	+0.30	+0.18
SM2	-0.78	+0.12	+0.02	+0.22
SM-AN	-2.04	-0.14	+0.92	+0.50
FB-AN	-1.51	+0.10	+0.23	+0.05

<sup>1/</sup> Definition of treatment code symbols given in Tables 2 and 3. This section of treatments (-N, SM2, SM-AN, FB-AN) were not duplicated.

<sup>2/</sup> A net loss from the layer is negative; a net gain is positive.

<sup>3/</sup> Values within each column of each depth increment followed by the same letter are not significantly different at  $p = 0.05$ . The  $s\bar{x}$  were determined from disagreement between duplicate columns.

Table 15. Magnesium retention for four successive 15-cm layers of a Walla Walla silt loam.

Treatment Code <sup>1/</sup>	Mg # retention ( $10^2$ mol/m <sup>3</sup> ) for indicated depth increments			
	0-15 cm	15-30 cm	30-45 cm	45-60 cm
+N	-0.28 <sup>2/</sup> b <sup>3/</sup>	+0.08 ab	+0.04	+0.01
-N	-0.25 b	-0.01 b	+0.03	+0.02
+N+L	-1.02 a	+0.30 a	+0.07	+0.03
FB	-0.43 ab	+0.01 b	+0.54	+0.01
SM	-0.26 b	+0.03 b	+0.03	+0.05
PV	-0.65 ab	+0.18 ab	+0.07	+0.00
-----				
$s_{\bar{x}}$	0.192	0.064	0.194	0.022
-----				
-N2	-0.73	-0.16	+0.23	+0.17
SM2	-0.53	+0.10	+0.02	+0.13
SM-AN	-0.28	-0.35	+0.39	+0.28
FB-AN	-0.37	-0.02	+0.09	+0.03

<sup>1/</sup> Definition of treatment code symbols given in Tables 2 and 3. This section of treatments (-N2, SM2, SM-AN, FB-AN) were not duplicated.

<sup>2/</sup> A net loss from the layer is negative; a net gain is positive.

<sup>3/</sup> Values within each column of each depth increment followed by the same letter are not significantly different at  $p = 0.05$ . The  $s_{\bar{x}}$  were determined from disagreement between duplicated columns.

Table 16. Potassium retention for four successive 15-cm layers of a Walla Walla silt loam.

Treatment Code <sup>1/</sup>	K <sup>+</sup> retention (10 <sup>2</sup> mol/m <sup>3</sup> ) for indicated depth increment			
	0-15 cm	15-30 cm	30-45 cm	45-60 cm
+N	-1.14 <sup>2/</sup>	+0.65	+0.20	+0.04
-N	-2.70	+1.40	+1.47	+0.07
+N+L	-1.51	+0.51	+0.17	+0.05
FB	-0.94	+0.02	+0.16	+0.18
SM	-2.63	+0.75	+0.34	+0.35
PV	-1.96	+0.83	+0.16	-0.00
-----				
$\bar{s}_x$	0.870	0.511	0.039	0.118
-----				
-N2	-2.08	-0.04	+0.36	+0.42
SM2	-4.21	+1.20	+0.10	+0.84
SM-AN	-3.89	-0.12	+2.12	+0.33
FB-AN	-1.44	+0.24	+0.23	+0.03

<sup>1/</sup> Definition of treatment code symbols given in Tables 2 and 3. This section of treatments (-N, SM2, SM-AN, FB-AN) were not duplicated.

<sup>2/</sup> A net loss from the layer is negative; a net gain is positive.

Table 17. Sodium retention for four successive 15-cm layers of a Walla Walla silt loam.

Treatment Code <sup>1/</sup>	Na <sup>+</sup> retention (10 <sup>2</sup> mol/m <sup>3</sup> ) for indicated depth increments			
	0-15 cm	15-30 cm	30-45 cm	45-60 cm
+N	-0.50 <sup>2/</sup> a <sup>3/</sup>	+0.47 a	+0.04	+0.03
-N	-0.21 ab	+0.05 b	+0.03	+0.01
+N+L	-0.45 ab	+0.01 b	+0.03	+0.03
FB	-0.15 b	-0.00 b	+0.05	+0.03
SM	-0.21 ab	+0.01 b	+0.03	+0.08
PV	-0.27 ab	+0.06 b	+0.03	+0.01
-----				
$s_{\bar{x}}$	0.083	0.067	0.011	0.022
-----				
-N2	-0.21	-0.14	+0.10	+0.12
SM2	-0.17	-0.02	-0.01	+0.12
SM-AN	-0.26	-0.20	+0.06	+0.19
FB-AN	-0.57	+0.09	+0.01	+0.02

<sup>1/</sup> Definition of treatment code symbols given in Tables 2 and 3. This section of treatments (-N2, SM2, SM-AN, FB-AN) were not duplicated.

<sup>2/</sup> A net loss from the layer is negative; a net gain is positive.

<sup>3/</sup> Values within each column of each depth increment followed by the same letter are not significantly different at  $p = 0.05$ . The  $s_{\bar{x}}$  were determined from disagreement between duplicate columns.

Table 18. Soil pH and carbon addition effects on silicic acid concentration and net silicic acid transfer from the 0 to 15-cm layer of a Walla Walla silt loam.

Dependent variable	Parameter estimates and statistics in multiple linear relation <sup>1/</sup>			
	R <sup>2</sup>	Intercept	coeff. of X <sub>1</sub>	coeff. of X <sub>2</sub>
[H <sub>4</sub> SiO <sub>4</sub> ] <sup>2/</sup>	0.99	3.43	-2.55 × 10 <sup>-4</sup>	-0.35
H <sub>4</sub> SiO <sub>4</sub> Transfer	0.87	9.79	-4.89 × 10 <sup>-4</sup>	-1.05

<sup>1/</sup> X<sub>1</sub> is carbon addition in kg/(ha·yr); treatment means obtained from ranges in Table 2; X<sub>2</sub> is pH; treatment values are shown in Table 6.

<sup>2/</sup> Units of [H<sub>4</sub>SiO<sub>4</sub>] and H<sub>4</sub>SiO<sub>4</sub> transfer are mol/m<sup>3</sup> and 10<sup>2</sup> mol/m, respectively. Transfer is the same as a negative retention.

decreasing soil acidity. They also indicate that solid-phase organic compounds affected silica release from the sorbed phase.

The large concentrations of soluble organic carbon (Table 8), and their failure to correlate significantly with silicic acid movement indicate that soluble organic carbon is not controlling solubilization of sorbed silica. Also, there was no correlation found between any cation(s) and silicic acid movement.

### Projected Silica Migration

The leaching columns in the laboratory demonstrated that silica movement is affected by management of soil pH and organic matter in a Walla Walla silt loam. Management treatments (Table 2) had been imposed for over 50 years during which adsorbed silica surfaces and their associated soluble silica could approach a characteristic of the treatment. It would be instructive to evaluate how the absolute magnitudes of movement in the leaching columns might relate to the field.

Silicic acid movement in a Walla Walla silt loam can be projected from hydrologic information and the leaching column information. When wheat and other related crops mature in the Pacific Northwest, soil in the upper 80 cm is usually drier than -30 bar water potential (Papendick et al., 1971). As winter approaches and the soil enters the recharge cycle of the hydrologic year, water and silicic acid movements should react similar to that in the leaching columns. As recharge progresses, soil moisture distribution gradually shifts to one dominated by the low saturated hydraulic conductivity of the pressure pan (Appendix Table 1). Measured soil water content responses (R. E. Ramig, USDA, ARS, Pendleton, Oregon, personal communication) during the overwinter period from August 1980 to April 1981 indicated a storage of 191 mm out of 300 mm of precipitation. This precipitation was 98% of the 17-year average shown in Appendix Table 2. The 191 mm of storage was partitioned as 67 mm stored in the top 30-cm increment of soil, 37 mm stored in the next lower 30-cm increment, 125 mm drained through the top 30 cm, and 88 mm drained through the 60-cm depth.

The partition and movement of soil water and the concentrations observed in Table 6 were used to compute the silicic acid (kg/ha) in each 15-cm layer below 15 cm (Appendix Table 10). Plots with a pH of 5.8 or greater (SM and PV) released and retained smaller amounts of silicic acid than did plots with a pH lower than 5.8 (+N, -N, FB). Even though the SM and PV plots retained a smaller amount than the other plots, only the SM plot retained a smaller percentage of that released from the 0 to 15-cm layer. Retention in the 15 to 60-cm layers as a percentage of that released from the 0 to 15-cm layer were 57, 51, 43, 52, 34, and 51% for the +N, -N, +N+L, FB, SM, and PV treatments, respectively.

Wetting and drying (Table 7, -N2 and SM2 treatments) decreased the release of silicic acid in the 0 to 15-cm layer compared to the -N and SM treatments (Table 7). However, these effects were minor compared to the retention in the lower layers. The severe exposure of the 0 to 15-cm layer to anhydrous ammonia and the minor influence on silica movement in the laboratory columns (Table 7) provides little evidence for direct field effects on release and movement of silicic acid in a Walla Walla silt loam.

The 15 to 30-cm soil layer in the +N plot retained 11 kg  $\text{H}_4\text{SiO}_4$ /ha of soil (Appendix Table 10). This amount was used to estimate how much of the surface area of a Walla Walla silt loam might be coated by  $\text{H}_4\text{SiO}_4$ . Ihler (1955) indicated that a  $\text{H}_4\text{SiO}_4$  molecule had a diameter of approximately 0.5  $\mu$ , and Mortland (1954) showed that the total surface area of a soil was highly related to cation exchange capacity. Calculations based on this information indicated that 0.001% of the 15 to 30-cm layer of a Walla Walla silt loam would be



covered by 11 kg  $H_4SiO_4$ /ha. However, this calculation supposes that the total surface area of the soil is available for  $H_4SiO_4$  coverage. If the area of a molecule of  $H_4SiO_4$  is  $0.25 \mu m^2$  (0.5  $\mu m$  diameter) then it could not enter internal areas of most clays, therefore, probably only the external surface would be available.

Soil from the 15 to 30-cm depth of the +N plot was washed through a 0.053-mm sieve to estimate the actual percentage of particles acting as sand-size material. Results indicated that 33% of the soil would not pass a 0.053 mm sieve. This is approximately 200% greater than sand-size material found during particle size analysis (Table 1).

Approximately 22% of the mechanical composition of this soil is made up of clay plus silt aggregated to a sand-size component. In a close-pack arrangement the ratio of silt to clay would be approximately 3 to 1. The nondispersed composition would then be approximately 33, 55, and 12% sand, silt, and clay, respectively. Assuming a sand, silt, and clay size of 1, 0.025, and 0.002 mm, respectively, 11 kg  $H_4SiO_4$ /ha would cover 0.3% of the external surface area of a soil with 33, 55, and 12% respectively of sand, silt, and clay. This percentage would probably be conservative because some of the surface area would be covered by cations and oxides. Three tenths of a percent seems like a small percentage of coverage, however, Torrent et al. (1980) found a duripan, in a soil in southern California, that only had 3.5%  $SiO_2$  as a cementing material. Based on these crude assumptions and calculations it would seem likely that  $H_4SiO_4$  could be instrumental in cementation of the high strength layer found in Walla Walla soils. An accurate estimate would require experimental measurements that determined the nature and extent of the surface coatings of silica.

## CHAPTER V

### CONCLUSION

This laboratory leaching experiment demonstrated silica leaching and deposition. This process was influenced by long term residue and fertilizer management of a Walla Walla silt loam soil. The laboratory columns did simulate the natural hydrologic situation and do indicate that depositions of approximately 11 kg silicic acid/ha per year may occur in these soils. This amount predicts that surface coverage of soil particles would be at 0.3% per year based on crude assumptions not verified experimentally.

Silicic acid movement and collection in the 15- to 30-cm layer (Table 7), which includes the pressure pan (Figure 1), are conservatively estimated for the field situation in which pH and organic matter returns are allowed to decrease. The laboratory flow system simulated flow under natural conditions in the 0- to 15-cm layer. However, in the three lower layers the flow arrangement overestimates flow under field conditions. After harvest, field soils are dry to a depth of 80 cm, but during late fall and early winter, soil water flow assumes a form dominated by the low hydraulic conductivity of the pressure pan. The plow layer of a Walla Walla silt loam is nearly saturated during late winter, because the pressure pan, nominally at 18- to 30-cm (Figure 1), may have saturated hydraulic conductivities as low as 2 cm/day (Allmaras et al., 1982). Flow below the pressure pan is always unsaturated. McKeague and Cline (1963c) indicate that unsaturation would likely not increase the concentration of silicic acid in the plow layer caused by low pH or reduced organic

matter return would therefore adjust quickly to the new environment of lower soluble silica and increased silica sorption in the pressure pan and below. Any decrease in water flow from a layer would be conducive to silicic acid retention in that layer.

The multiple linear relationship in Table 18 indicated that silicic acid concentrations and transfers are sensitive to short and long term pH and long term carbon addition changes. However, the soluble organic carbon or cations were not correlated to silicic acid release, retention, or concentration. Concentrations of silicic acid decreased as long-term carbon additions increased and as soil pH increased. Transfers of silicic acid decreased as long-term carbon additions and pH increased.

Desorption, movement, and sorption of silicic acid may effect such soil physical properties as decreased hydraulic conductivity, increased cementation and soil strength, or both when dry. Measured changes of these two physical properties associated with soluble silicic acid are lacking (McKeague and Cline, 1963c). This report also found no supporting data on changes in hydraulic conductivity and soil strength because of silicic acid movement. Because silicic acid concentration in soil solutions, and the associated movement, is susceptible to changes in soil management, silica solubility effects on soil physical properties deserve more attention.

## BIBLIOGRAPHY

- Acquaye, D. K. and J. Tinsley. 1965. Soluble silica in soils. p. 126. In E. G. Hallsworth and D. V. Crawford (eds.) *Experimental Pedology*. Butterworths, London.
- Alexander, G. B., W. M. Heston, and R. K. Iler. 1954. The solubility of amorphous silica in water. *J. Phys. Chem.* 58:453-455.
- Allmaras, R. R., Kathy Ward, C. L. Douglas, Jr., and L. G. Ekin. 1982. Long-term cultivation effects on hydraulic properties of a Walla Walla silt loam. *Soil and Tillage Res.* 2:265-279.
- Allmaras, R. R., Kathy Ward, P. E. Rasmussen, and C. R. Rohde. 1978. Soil acidification from long-term use of ammonium type nitrogen fertilizers. p. 55. In 1978 Progress Report - Columbia Basin Agric. Research. Oregon Agric. Expt. Station Special Report SM 78-4.
- Allmaras, R. R., R. W. Rickman, L. G. Ekin, and B. A. Kimball. 1977. Chiseling influences on soil hydraulic properties. *Soil Sci. Soc. Am. J.* 41:796-803.
- Andrews, W. B. 1956. Anhydrous ammonia as a nitrogenous fertilizer. *Adv. Agron.* 8:61-125.
- Beckwith, R. S. and R. Reeve. 1963. Studies on soluble silica in soils. I. The sorption of silicic acid by soils and minerals. *Aust. J. Soil Res.* 1:157-168.
- Beckwith, R. S. and R. Reeve. 1964. Studies on soluble silica in soils. II. The release of monosilicic acid from soils. *Aust. J. Soil Res.* 2:33-45.
- Bergman, I. and M. S. Paterson. 1961. Silica powders of respirable size. I. Preliminary studies of dissolution rates in dilute sodium hydroxide. *J. Appl. Chem.* 11:369-376.
- Buol, S. W., F. D. Hole, and R. J. McCracken. 1973. *Soil genesis and classification*. Iowa St. Univ. Press. Ames. 360 pp.
- Chapman, H. D., and P. F. Pratt. 1961. *Methods of analysis for soils, plants, and waters*. University of California. p. 31.
- Dempster, P. B. and P. D. Ritchie. 1953. Physicochemical studies on dust. V. Examination of finely ground quartz by differential thermal analysis and other physical methods. *J. Appl. Chem.* 3:182-192.
- D'Hoore, J. and J. K. Coulter. 1972. Soil silicon and plant nutrition. In soils of the humid tropics. *Natl. Acad. Sci., Wash. D.C.* p. 163.

- Flach, K. W., W. D. Nettleton, and R. E. Nelson. 1974. The micro-morphology of silica-cemented soil horizons in western North America. p. 715. In G. K. Rutherford (ed.) *Soil Microscopy*. Limestone Press, Kingston, Ont., Can.
- Gibb, J. G., P. D. Ritchie, and J. W. Sharpe. 1953. Physicochemical studies on dusts. VI. Electron-optical examination of finely ground silica. *J. Appl. Chem.* 3:213-218.
- Gifford, R. O. and Diana J. Frugoli. 1964. Silica source in soil solutions. *Science* 145:386-388.
- Greenberg, S. A. 1959. The chemistry of silicic acid. *J. Chem. Ed.* 36:218-219.
- Hingston, F. J. and M. Raupach. 1967. The reaction between monosilicic acid and aluminum hydroxide. I. Kinetics of adsorption of silicic acid by aluminum hydroxide. *Aust. J. Soil Res.* 5:295-309.
- Holt, P. F. and D. T. King. 1955. The chemistry of silica surfaces. *J. Chem. Soc. Part 1*:775-779.
- Humbert, R. P. and A. S. Ayres. 1957. The use of aqua ammonia in the Hawaiian sugar industry: II. Injection studies. *Soil Sci. Soc. Am. Proc.* 21:312-316.
- Ihler, R. K. 1955. *The colloid chemistry of silica and silicates*. Cornell Univ. Press, Ithaca, N.Y. 324 pp.
- Ihler, R. K. 1973. Effect of adsorbed alumina on the solubility of amorphous silica in water. *J. Coll. and Interface Sci.* 43:399-408.
- Jones, L. H. P. and K. A. Handreck. 1963. Effects of iron and aluminum oxides on silica in solution in soils. *Nature* 198: 852-853.
- Jones, L. H. P. and K. A. Handreck. 1965. Studies of silica in the oat plant. III. Uptake of silica from soils by the plant. *Plant and Soil* 23:79-96.
- Krauskopf, K. B. 1956. Dissolution and precipitation of silica at low temperatures. *Geoch. Cosmoch. Acta* 10:1-26.
- Leggett, G. E., L. C. Boawn, and C. L. Crawford. 1959. Unpublished report of investigations of chemical reactions of zinc in soils. USDA-ARS, Prosser, Wash. 11 pp.
- Leggett, G. E., L. C. Boawn, and C. L. Crawford. 1960. Unpublished report of investigations of chemical reactions of zinc in soils. USDA-ARS, Prosser, Wash. 9 pp.

- Mangum, Doris L. 1965. Influence of anhydrous ammonia on the solubility of soil organic matter. M.S. Thesis. Corvallis, Ore. St. Univ. 56 p.
- Marion, G. M., D. M. Hendricks, G. R. Dutt, and W. H. Fuller. 1976. Aluminum and silica solubility in soils. *Soil Sci.* 121:76-85.
- McDowell, L. L., and G. E. Smith. 1958. The retention and reactions of anhydrous ammonia on different soil types. *Soil Sci. Soc. Am. Proc.* 22:38-42.
- McKeague, J. A., and M. G. Cline. 1963a. Silica in soil solutions: I. The form and concentration of dissolved silica in aqueous extracts of some soils. *Can. J. Soil Sci.* 43:70-81.
- McKeague, J. A., and M. G. Cline. 1963b. Silica in soil solutions: II. The adsorption of monosilicic acid by soil and by other substances. *Can. J. Soil Sci.* 43:83-96.
- McKeague, J. A., and M. G. Cline. 1963c. Silica in soils. *Adv. Agron.* 15:339-396.
- McKeague, J. A., and R. J. St. Arnaud. 1969. Pedotranslocation: eluviation - illuviation in soils during the Quaternary. *Soil Sci.* 107:428-434.
- Miller, R. W. 1967. Soluble silica in soil. *Soil Sci. Soc. Am. Proc.* 31:46-50.
- Mortland, M. M. 1954. Specific surface and its relationships to some physical and chemical properties of soil. *Soil Sci.* 78:343-347.
- Okamoto, Go, T. Obura, and K. Goto. 1957. Properties of silica in water. *Geoch. Cosmoch. Acta* 12:123-132.
- Papendick, R. I., V. L. Cochran, and W. M. Woody. 1971. Soil water potential and water content profiles with wheat under low spring and summer rainfall. *Agron. J.* 63:731-734.
- Rand, M. C., A. E. Greenberg, and M. J. Taras, eds. 1975. Heteropoly blue method No. 426 C. pp. 490-492. In *Standard Methods for the Examination of Water and Wastewater*. 14th ed. Amer. Public Health Assoc., Wash. D.C.
- Rasmussen, P. E., R. R. Allmaras, C. R. Rohde, and N. C. Roager, Jr. 1980. Crop residue influences on soil carbon and nitrogen in a wheat-fallow system. *Soil Sci. Soc. Am. J.* 44:596-600.
- Raupach, M., and C. S. Piper. 1959. Interactions of silicate and phosphate in a lateritic soil. *Aust. J. Agric. Res.* 10:818-831.

- Russell, E. J. 1961. Soil conditions and plant growth. John Wiley and Sons, LTD. N.Y. 688 pp.
- Schnitzer, M., and J. G. Desjardino. 1969. Chemical characteristics of a natural soil leachate from a humic podzol. *Can. J. Soil Sci.* 49:151-158.
- Stanley, F. A., and G. E. Smith. 1956. Effect of soil moisture and depth of application on retention of anhydrous ammonia. *Soil Sci. Soc. Am. P.* 20:557-561.
- Sternes, G. L. 1966. Climatological data for Oregon's Columbia Basin counties. Corvallis. Ore. St. Univ. Coop. Ext. Ser. Spec. Rpt. 225.
- Torrent, J., W. D. Nettleton, and G. Borst. 1980. Genesis of a Typic Durixerlf of southern California. *Soil Sci. Soc. Am. J.* 44:575-582.
- Wada, K., and A. Inoue. 1974. Adsorption of monomeric silica by volcanic ash soils. *Soil Sci. Plant Nutr.* 20:5-15.
- White, D. E., W. W. Brannock, and K. J. Murata. 1956. Silica in hot spring waters. *Geoch. Cosmoch. Acta.* 10:27-59.

## APPENDIX



Appendix Table 1. Saturated hydraulic conductivities for three layers in each of five selected crop residue plots.<sup>1/</sup>

Treatment code <sup>2/</sup>	Surface (Ap) <sup>3/</sup>	Pressure pan	Subsoil (30 cm)
----- cm/day -----			
+N	35.8	2.0	16.2
-N	16.9	3.0	15.0
FB	27.1	2.5	15.1
SM	31.2	7.3	15.5
PV	42.2	5.2	15.4

<sup>1/</sup> Unpublished data, J. L. Pikel Jr., ARS-USDA, Pendleton, OR. Plots have received the indicated treatments since 1931 as indicated in Table 2.

<sup>2/</sup> Definition of treatment code symbols given in Table 2.

<sup>3/</sup> Surface conductivities were taken with an air-entry permeameter in stubble, which measures hydraulic conductivity at air-entry water content and approximates saturated hydraulic conductivity. Pressure pan and subsoil conductivities were taken with a double-ring infiltrometer in fallow, which directly measures saturated hydraulic conductivity.

Appendix Table 2. Monthly sums of precipitation (mm) over a 17-year period at the Columbia Basin Agricultural Research Center.<sup>1/</sup>

Crop yr. <sup>1/</sup>	Sept	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Total
52-year average	18.0	34.8	47.2	54.4	49.3	36.6	40.4	37.6	33.8	32.3	8.1	11.4	404.4
1964-65	15.5	31.5	46.0	112.5	97.5	11.9	5.3	29.5	26.2	34.8	19.0	33.8	463.6
1965-66	5.1	13.0	57.9	11.4	59.7	18.0	43.7	13.0	10.9	25.2	29.0	4.3	291.1
1966-67	11.7	27.9	58.4	72.6	71.1	8.1	38.4	40.6	24.1	14.0	1.0	0	368.0
1967-68	14.2	29.7	33.0	19.3	18.8	60.7	26.4	5.3	16.5	28.2	8.6	19.6	280.4
1968-69	21.1	34.5	68.8	67.3	66.5	19.8	10.9	58.7	32.0	19.0	1.5	0	400.3
1969-70	16.5	35.8	11.2	60.7	132.8	38.1	47.5	26.7	15.7	21.6	2.8	1.3	410.7
1970-71	25.9	35.6	56.4	25.9	36.6	19.6	32.5	41.9	42.2	79.8	16.0	8.4	420.6
1971-72	36.1	43.7	79.8	99.8	29.2	43.2	53.6	34.3	38.1	23.1	19.3	8.9	509.0
1972-73	12.4	16.8	29.0	62.7	22.6	22.6	32.2	14.7	26.2	3.0	0	2.3	244.6
1973-74	45.0	31.5	148.8	111.8	32.8	50.8	38.1	92.5	9.6	8.4	33.0	0	602.2
1974-75	0.5	8.9	39.6	44.7	94.7	42.7	24.6	43.7	17.3	17.5	1.3	35.0	370.6
1975-76	0	54.9	37.3	86.4	54.1	27.7	42.9	41.9	30.7	14.7	1.0	65.5	457.2
1976-77	11.2	13.5	11.9	15.0	22.9	14.5	43.7	11.7	43.2	7.9	3.0	56.1	254.5
1977-78	39.1	17.5	45.5	81.0	57.6	43.4	35.6	88.9	20.6	32.2	15.0	34.8	511.3
1978-79	40.9	0	42.7	57.9	33.3	39.1	44.2	46.2	29.2	4.6	3.0	52.8	394.0
1979-80	4.3	65.0	58.7	26.7	72.4	39.4	53.8	30.5	62.2	36.1	5.8	4.6	459.5
1980-81	31.5	75.2	46.0	50.5	32.0	58.7	58.4	32.8	58.4	53.8	10.2	0.5	508.0
1981-82 <sup>3/</sup>	38.4	41.2	61.2	83.0	65.0	47.2	50.5						
17-year average	19.6	31.5	51.3	59.2	54.9	32.8	37.1	38.6	29.5	24.9	9.9	19.3	408.6

<sup>1/</sup> From Wilkins, D. E., R. W. Rickman, and D. J. Rydrych (eds.), Columbia Basin Agricultural Research, Special Report 661, June 1982, p. 47.

<sup>2/</sup> Crop year basis is from 1 Sept. through 31 Aug. of the following calendar year.

<sup>3/</sup> Not included in 17-year average figures.

Appendix Table 3. Typical observations of silicic acid flow in and out of each soil layer in a leaching column.

----- Layer 1 -----							----- Layer 2 -----							
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Time after introduction of water	Collected liquid output	Total liquid output	Collected output % of total	Solute in collected output	Total solute output <sup>1/</sup>		Cumulative liquid input	Cumulative solute input	Collected liquid output	Total liquid output	Collected output % of total	Solute in collected output	Total solute output <sup>1/</sup>	
hrs.	-----mL-----		%	-----mmol-----	I	Σ	mL	mmol	mL	mL	%	-----mmol-----	I	Σ
3	728	1233	59.04	0.824	1.395	1.395	505	0.571	100	198	50.51	0.104	0.206	0.206
7	650	2334	59.04	0.766	1.298	2.693	616	1.103	195	583	50.60	0.227	0.448	0.654
23	1652	4921	61.57	1.975	3.207	6.650	1891	2.335	440	1518	48.42	0.533	1.101	1.755
31	550	5819	61.52	0.622	1.012	6.912	2239	2.725	160	1866	47.96	0.191	0.399	2.154
47	715	7037	61.03	0.832	1.363	8.274	2742	3.256	227	2369	47.36	0.316	0.667	2.821
55	406	7637	61.56	0.447	0.726	9.000	2936	3.535	91	2563	47.33	0.109	0.230	3.051
72	600	8614	61.54	0.679	1.103	10.103	3313	3.959	168	2940	46.97	0.201	0.428	3.478
102	705	9780	61.41	0.744	1.212	11.315	3774	4.427	183	3401	45.99	0.219	0.476	3.954

<sup>1/</sup> I = Incremental, Σ = Cumulative

Appendix Table 3 (continued)

-----Layer 3-----								-----Layer 4-----					
16	17	18	19	20	21	22	23	24	25	26	27	28	29
Cumulative liquid input	Cumulative solute input	Collected liquid output	Total liquid output	Collected output % of total	Solute in collected output	Total solute output <sup>1/</sup>		Cumulative liquid input	Cumulative solute input	Total liquid output	Total liquid output cumulative	Total solute output <sup>1/</sup>	
						I	Σ					I	Σ
mL	mmol	-----mL-----	-----	%	-----	-----mmol-----	-----	mL	mmol	-----mL-----	-----	-----mmol-----	-----
98	0.102												
288	0.323	107	193	55.44	0.100	.180	0.180	86	0.080	58	58	0.049	0.049
783	0.891	270	688	54.80	0.277	.506	0.686	311	0.309	225	283	0.244	0.294
971	1.099	97	876	54.11	0.105	.195	0.880	402	0.398	91	374	0.103	0.397
1247	1.450	130	1152	52.43	0.153	.292	1.172	548	0.537	146	520	0.170	0.566
1350	1.571	48	1255	51.95	0.051	.109	1.281	603	0.589	55	575	0.069	0.635
1559	1.798	69	1464	49.25	0.086	.175	1.456	743	0.678	140	715	0.179	0.814
1837	2.055	40	1742	43.69	0.049	.111	1.567	981	0.740	238	953	0.301	1.114

<sup>1/</sup> I = Incremental, Σ = Cumulative

Appendix Table 4. Sample calculation of the various leaching characteristics in a column (observations in Appendix Table 3).

<u>Column number</u>	<u>Column heading</u>	<u>Calculation description</u>
1	Time from introduction of water	-- cumulative hours after introduction of distilled water to layer 1.
2	Collected liquid output	-- actual mL collected from indicated layer at time indicated in column 1.
3	Total liquid output	-- cumulative mL leaving indicated layer at indicated time. Example in Appendix Table 3: column 3 gives amount leaving layer 1 at indicated time.
4	Collected output % of total	-- divide mL found in Appendix Table 3, column 2 by mL in column 3 of same table. i.e. $728 \div 1233 = 59.04\%$ of the total flow at 3 hrs was collected. Therefore, 40.96% entered the layer below.
5	Solute in collected output	-- from analyses of collected mL.
6	Total solute output	-- solute in collected output (Appendix Table 3, column 5) divided by decimal equivalent of % of total collected output (column 4). Example -- Appendix Table 3, layer 1, time 3 hrs., $0.824 \text{ mmol H}_4\text{SiO}_4$ (Appendix Table 3, column 5) $\div 59.04\%$ (Appendix Table 3, column 4) $\div 100$ gives $1.395 \text{ mmol H}_4\text{SiO}_4$ (Appendix Table 3, column 6).
7	Total solute output cumulative	-- cumulation of values from Appendix Table 3, column 6.
8	Liquid input cumulative	-- total liquid output (Appendix Table 3, column 3) minus collected liquid output (column 2). Example -- $1233 \text{ mL (column 3) minus } 728 \text{ mL (column 2) equals } 505 \text{ mL (column 8)}$ .
9	Solute input cumulative	-- total solute output (Layer 1, time x) minus solute in collected output (Layer 1, time x) plus solute input (Layer 2, time x-1). Example -- Appendix Table 3, layer 1, time 7 hrs. -- $[1.298 \text{ (column 6) minus } 0.766 \text{ (column 5)}]$ plus $0.571 \text{ (column 9, time 3 hrs.)} = 1.103 \text{ (column 9)}$ .
10-25		-- calculated same as 2 through 7 above.
26-29		-- all leachate, or 100% of total output, is collected from layer 4.

Appendix Table 5. Instrument settings for atomic absorption analyses of cations.

Ion	wavelength setting ( $\mu\text{m}$ )	Slit setting	Flame type and (action)	Sensitivity for 1% absorption
Ca <sup>1/</sup>	211-visible	4	air-acetylene (reducing)	0.08 ug/ml
Mg	285-UV	4	air-acetylene (oxidizing)	0.007 ug/ml
K	383-visible <sup>2/</sup>	4	air-acetylene (oxidizing)	0.04 ug/ml
Na	295-visible	4	air-acetylene (oxidizing)	0.015 ug/ml
Fe	249-UV	3	air-acetylene (oxidizing)	0.12 ug/ml
Al	309-UV	4	nitrous oxide-acetylene (reducing)	1.0 ug/ml

<sup>1/</sup> Solutions diluted with  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$  to reduce ionization.

<sup>2/</sup> A red filter was used to absorb all wavelengths less than 650  $\mu\text{m}$ .

Appendix Table 6. Parameters in the least squares fit of cumulative flow as an exponential function of time.<sup>1/</sup>

Depth (cm)	Parameter <sup>2/</sup>	Parameters for indicated treatment code <sup>3/</sup>									
		+N	+N+L	FB	FB-AN	SM	SM-AN	SM2	PV	-N	-N2
0-15	r <sup>2</sup> (%)	85	60	81	99	90	99	87	55	96	93
	a	291.8	1355.9	249.5	238.8	480.5	564.9	624.4	613.2	402.1	449.2
	10 <sup>3</sup> xb	708.7	315.3	595.7	823.2	812.0	700.0	383.7	546.6	793.6	301.4
15-30	r <sup>2</sup> (%)	76	86	74	99	67	99	84	65	88	98
	a	83.6	278.9	74.9	44.7	153.4	186.4	242.7	112.0	122.3	51.4
	10 <sup>3</sup> xb	686.5	489.7	771.2	1015.0	891.2	853.4	380.2	710.0	867.6	641.2
30-45	r <sup>2</sup> (%)	71	80	82	88	70	77	87	52	80	89
	a	36.8	93.6	44.9	79.2	76.2	109.2	164.0	41.9	62.7	160.6
	10 <sup>3</sup> xb	646.8	581.8	614.6	733.7	835.4	627.1	408.4	772.3	817.7	235.0
45-60	r <sup>2</sup> (%)	73	33	83	94	79	99	flow stopped	70	92	flow stopped
	a	10.0	25.3	16.0	95.6	16.5	15.0		19.8	26.6	
	10 <sup>3</sup> xb	636.8	530.6	616.2	553.6	744.8	831.4		775.7	687.0	
Ave b for 60 cm depth (10 <sup>3</sup> xb)		669.7	479.4	649.4	781.4	820.9	753.0	390.8	701.2	791.5	392.8

<sup>1/</sup> Equation:  $F=at^b$ , where F is cumulative flow in liters, t is hours drained, and a and b are parameters.

<sup>2/</sup> These were calculated by fitting both replications to the same curve.

<sup>3/</sup> Treatment codes given in Tables 2 and 3.

Appendix Table 7. Mean concentration of silicic acid and organic carbon in leachates from successive 15-cm soil layers of a Walla Walla silt loam as affected by long term nitrogen and residue treatments.

Plot	0-15 cm			15-30 cm			30-45 cm			45-60 cm		
	First one-half flow	Second one-half flow	Total flow	First one-half flow	Second one-half flow	Total flow	First one-half flow	Second one-half flow	Total flow	First one-half flow	Second one-half flow	Total flow
----- -Silicic acid (mol/m <sup>3</sup> ) -----												
+N <sup>1/</sup>	1.45	1.40	1.42	1.46	1.40	1.43	0.70	1.47	1.09	1.11	1.10	1.10
-N	1.16	0.93	1.05	1.29	1.22	1.26	1.28	1.09	1.18	1.01	1.31	1.16
-N2	0.74	0.80	0.77	1.23	0.97	1.10	0.83	3.01	1.92	-	-	0.86
+N+L	1.01	0.93	0.97	1.26	1.16	1.21	1.13	1.11	1.12	0.86	1.14	1.00
FB	1.44	1.22	1.36	1.32	1.23	1.28	1.03	1.10	1.07	1.00	1.34	1.17
FB-AN	1.08	1.14	1.11	1.58	2.37	1.97	1.61	1.66	1.64	1.12	1.29	1.20
SM	0.89	0.83	0.85	0.94	0.98	0.96	0.92	0.93	0.92	0.67	1.36	1.01
SM-AN	1.23	1.17	1.20	1.09	0.81	0.95	1.10	1.28	1.19	0.95	1.03	0.99
SM2	0.76	0.75	0.76	0.75	0.80	0.77	0.75	0.74	0.74	-	-	0.69
PV	1.03	0.92	0.97	0.94	0.98	0.96	0.80	0.72	0.76	0.81	0.89	0.85
----- Soluble organic carbon (mol/m <sup>3</sup> ) -----												
+N	6.29	2.42	4.35	9.98	3.91	4.94	11.45	4.29	7.87	15.72	5.82	10.77
-N	2.33	0.81	1.57	2.75	1.21	1.98	4.22	1.62	2.92	5.11	2.16	3.63
-N2	1.45	0.69	1.07	7.56	2.02	4.79	3.11	1.62	2.36	-	-	6.97
+N+L	2.68	1.55	2.12	4.39	2.45	3.42	5.04	2.76	3.90	11.13	4.86	8.00
FB	3.23	1.39	2.31	5.31	2.37	3.84	7.07	1.99	4.53	11.05	2.96	7.00
FB-AN	36.95	4.62	20.79	16.59	11.57	14.08	32.44	8.46	20.45	26.56	6.94	16.75
SM	3.44	1.11	2.27	5.43	2.11	3.77	5.65	1.72	3.69	9.19	3.49	6.34
SM-AN	57.22	5.66	31.44	39.24	45.30	42.27	46.71	76.09	61.40	61.05	24.08	42.57
SM2	2.84	1.19	2.01	4.39	2.21	3.30	2.71	2.13	2.45	-	-	7.83
PV	4.30	1.56	2.93	5.19	2.15	3.67	5.71	2.49	4.10	6.58	2.64	4.61

<sup>1/</sup>Definition of treatment code symbols given in Tables 2 and 3.



Appendix Table 8. Mean concentration of calcium and magnesium in leachates from successive 15-cm soil layers of a Walla Walla silt loam as affected by long term nitrogen and residue treatments.

Plot	0-15 cm			15-30 cm			30-45 cm			45-60 cm		
	First one-half flow	Second one-half flow	Total flow	First one-half flow	Second one-half flow	Total flow	First one-half flow	Second one-half flow	Total flow	First one-half flow	Second one-half flow	Total flow
----- mol/m <sup>3</sup> Calcium -----												
+N <sup>1/</sup>	0.26	0.07	0.16	0.60	0.16	0.38	0.92	0.27	0.60	1.36	0.40	0.88
-N	0.21	0.08	0.14	0.27	0.12	0.20	0.44	0.13	0.28	0.76	0.22	0.49
-N2	0.34	0.27	0.30	1.02	0.48	0.64	0.39	0.22	0.31	-	-	1.08
+N+L	1.36	0.18	0.77	1.32	0.18	0.76	1.86	0.30	1.08	4.27	0.21	2.24
FB	0.36	0.12	0.24	0.46	0.20	0.32	0.57	0.20	0.38	1.10	0.33	0.72
FB-AN	0.85	0.14	0.50	0.98	1.18	1.08	1.23	0.58	1.15	1.57	0.47	1.02
SM	0.30	0.09	0.20	0.47	0.16	0.32	0.58	0.23	0.41	2.02	0.43	1.22
SM-AN	1.18	0.16	0.67	1.96	0.52	1.24	2.76	1.34	2.06	3.34	1.41	2.37
SM2	0.31	0.20	0.26	0.56	0.27	0.42	0.42	0.39	0.40	-	-	1.06
PV	0.42	0.23	0.32	0.58	0.31	0.45	0.61	0.30	0.46	0.88	0.30	0.60
----- mol/m <sup>3</sup> Magnesium -----												
+N	0.16	0.03	0.09	0.36	0.08	0.22	0.53	0.18	0.36	0.92	0.28	0.60
-N	0.12	0.04	0.08	0.20	0.06	0.13	0.26	0.08	0.16	0.52	0.14	0.33
-N2	0.28	0.21	0.24	0.80	0.22	0.51	0.38	0.18	0.28	-	-	0.82
+N+L	0.58	0.08	0.34	0.74	0.18	0.46	1.09	0.16	0.62	2.70	0.26	1.48
FB	0.23	0.06	0.14	0.33	0.09	0.21	0.40	0.12	0.26	0.88	0.20	0.54
FB-AN	0.28	0.02	0.12	0.42	0.60	0.52	0.85	0.41	0.63	0.82	0.20	0.51
SM	0.14	0.03	0.08	0.22	0.09	0.16	0.29	0.15	0.22	1.48	0.28	0.88
SM-AN	0.08	0.10	0.09	0.92	0.24	0.58	1.60	0.65	1.12	1.80	0.65	1.22
SM2	0.22	0.13	0.18	0.38	0.17	0.28	0.26	0.24	0.24	-	-	0.70
PV	0.26	0.18	0.22	0.32	0.22	0.27	0.30	0.22	0.26	0.77	0.27	0.52

<sup>1/</sup> Definition of treatment code symbols given in Tables 2 and 3.

Appendix Table 9. Mean concentration of potassium and sodium in leachates from successive 15-cm soil layers of a Walla Walla silt loam as affected by long term nitrogen and residue treatments.

Plot	0-15 cm			15-30 cm			30-45 cm			45-60 cm		
	First one-half flow	Second one-half flow	Total flow	First one-half flow	Second one-half flow	Total flow	First one-half flow	Second one-half flow	Total flow	First one-half flow	Second one-half flow	Total flow
----- mol/m <sup>3</sup> Potassium -----												
+N <sup>1/</sup>	0.48	0.28	0.38	0.63	0.34	0.49	0.37	0.24	0.30	0.35	0.21	0.28
-N	1.19	0.58	0.88	0.61	0.40	0.51	0.50	0.38	0.44	0.51	0.42	0.46
-N2	0.69	0.68	0.68	1.12	0.71	0.92	0.68	0.58	0.63	-	-	0.88
+N+L	0.71	0.28	0.49	0.78	0.32	0.55	0.54	0.23	0.39	0.65	0.28	0.46
FB	0.36	0.28	0.31	0.49	0.36	0.42	0.41	0.27	0.34	0.45	0.28	0.37
FB-AN	0.72	0.22	0.47	0.62	1.08	0.85	0.78	0.49	0.64	0.48	0.37	0.43
SM	1.08	0.64	0.86	1.23	0.89	1.06	0.81	0.63	0.72	0.59	0.42	0.50
SM-AN	2.06	0.50	1.28	2.78	1.60	2.19	1.55	0.83	1.19	0.55	0.35	0.45
SM2	0.44	0.26	0.35	0.76	0.34	0.55	0.51	0.48	0.49	-	-	1.40
PV	0.73	0.56	0.64	0.60	0.56	0.58	0.47	0.37	0.42	0.36	0.25	0.30
----- mol/m <sup>3</sup> Sodium -----												
+N	0.27	0.06	0.17	0.23	0.12	0.18	0.29	0.22	0.25	0.41	0.27	0.34
-N	0.11	0.01	0.06	0.12	0.07	0.10	0.17	0.08	0.13	0.26	0.17	0.21
-N2	0.08	0.06	0.07	0.33	0.21	0.27	0.23	0.18	0.20	-	-	0.54
+N+L	0.22	0.08	0.15	0.35	0.10	0.22	0.48	0.18	0.33	0.80	0.30	0.55
FB	0.14	0.10	0.12	0.22	0.15	0.18	0.28	0.16	0.22	0.42	0.22	0.32
FB-AN	0.34	0.04	0.19	0.24	0.18	0.21	0.50	0.32	0.41	0.41	0.27	0.34
SM	0.10	0.04	0.07	0.22	0.08	0.15	0.31	0.11	0.21	0.70	0.38	0.54
SM-AN	0.14	0.04	0.08	0.71	0.06	0.39	2.84	0.71	1.78	6.13	1.97	4.05
SM2	0.06	0.05	0.06	0.18	0.12	0.15	0.21	0.20	0.21	-	-	0.60
PV	0.11	0.08	0.09	0.16	0.14	0.15	0.22	0.15	0.18	0.26	0.13	0.20

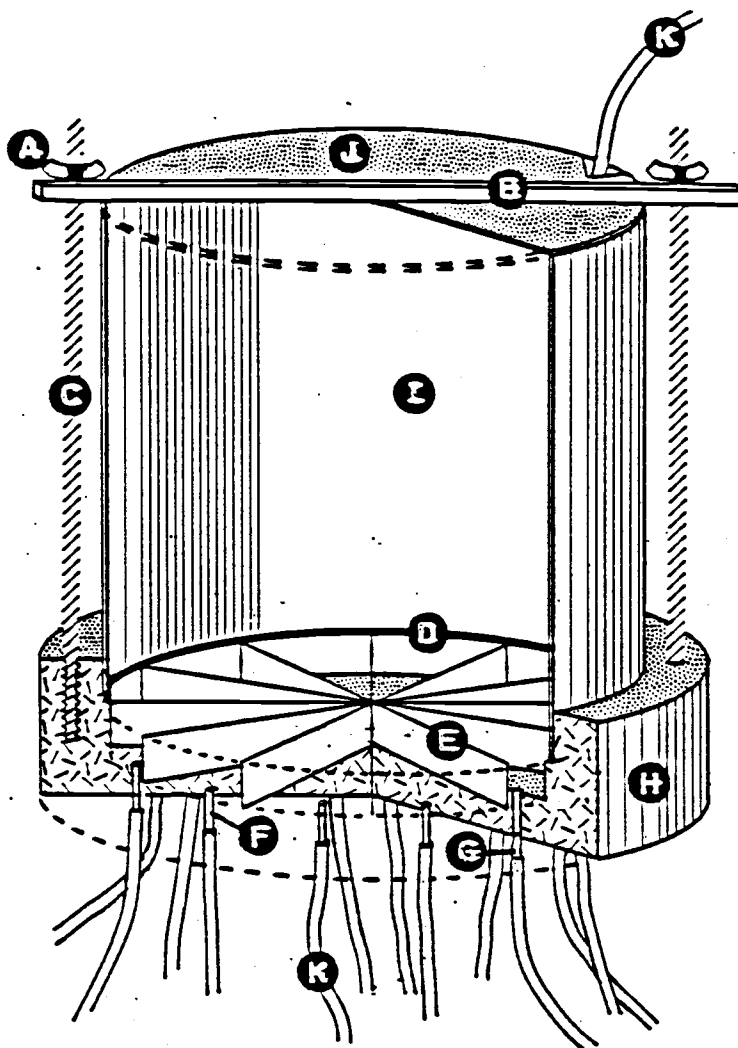
<sup>1/</sup>Definition of treatment code symbols given in Tables 2 and 3.

Appendix Table 10. Silicic acid leached from the top 15-cm layer and retained in the 15 to 60 cm layers during the winter recharge<sup>2/</sup> of a typical Walla Walla silt loam.

Treatment <sup>1/</sup> code	Release or retention (kg/ha) of silicic acid for indicated layers <sup>2/</sup>				
	0-15 cm	15-30 cm	30-45 cm	45-60 cm	15-60 cm
	released	- - - - - retained - - - - -			
+N	54	11	15	5	31
-N	50	13	8	6	26
+N+L	37	1	8	8	16
FB	52	13	11	3	27
SM	32	3	5	2	11
PV	37	8	9	2	19

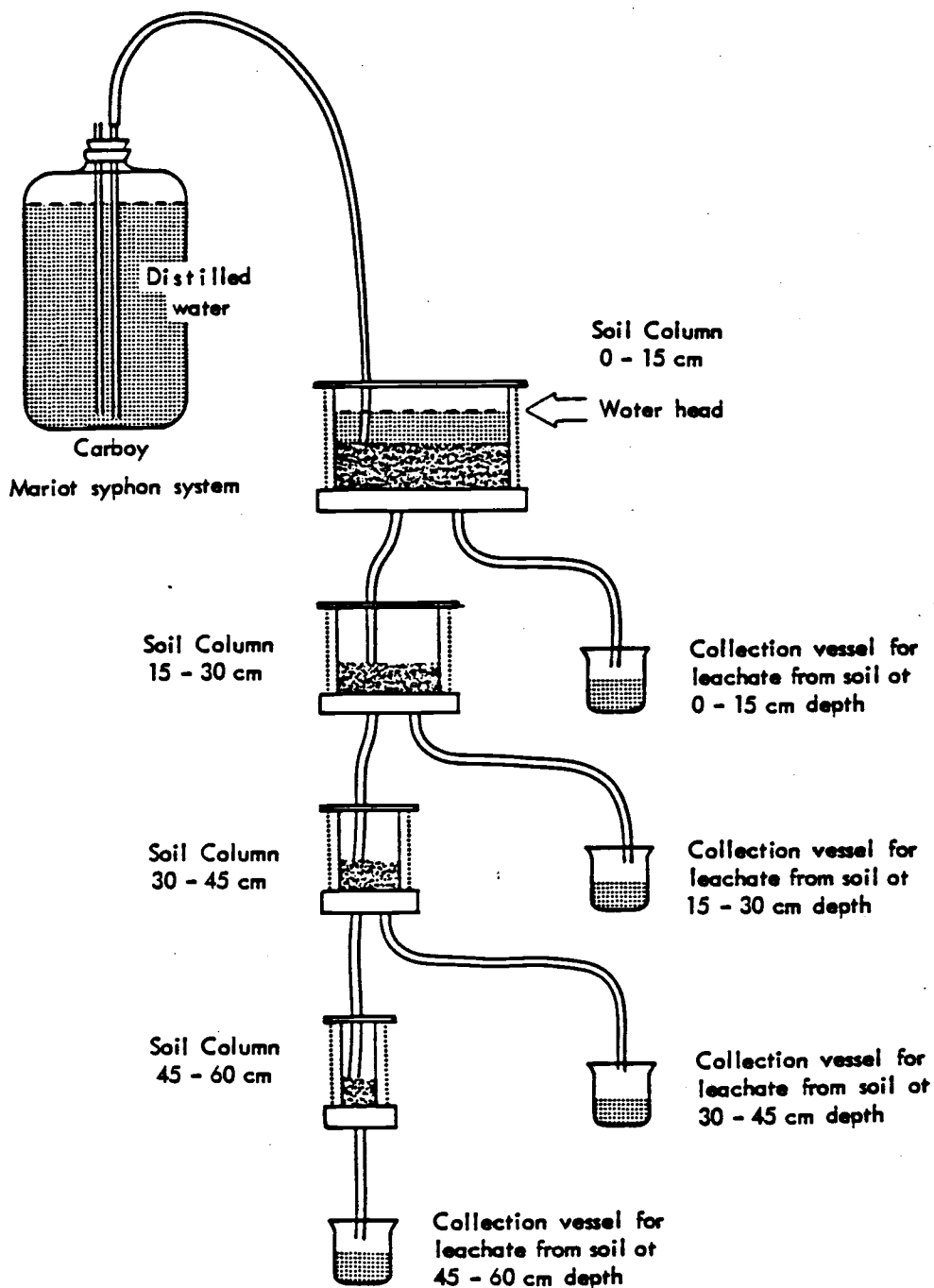
<sup>1/</sup> Definition of treatment code symbols given in Table 2.

<sup>2/</sup> Winter recharge period from 1 Aug. 1980 to 1 Apr. 1981.

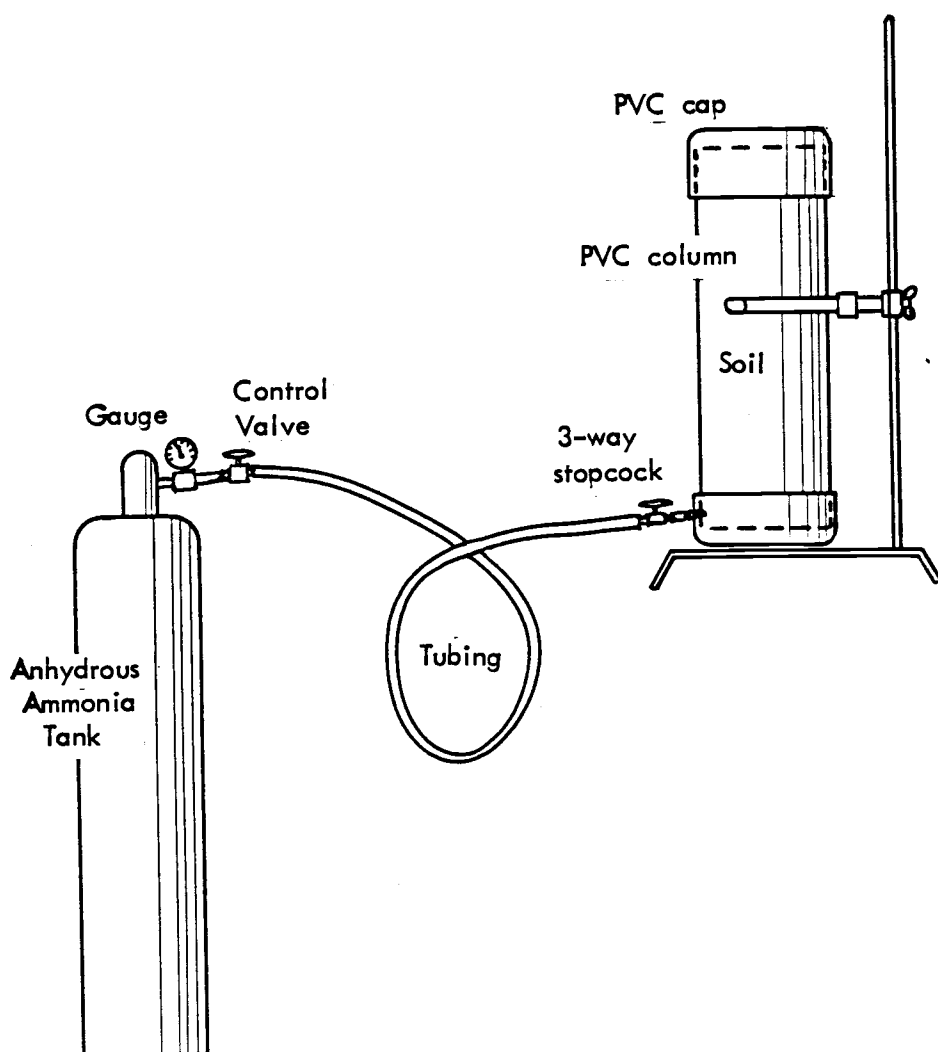


- A Wing nut
- B Plexiglass bar
- C Threaded rod
- D O-ring
- E Removable sample splitter (plexiglass)
- F Threaded (at lower end) drainage port
- G Plexiglass sprayer nozzle
  - For larger columns: TN 32 1/4 Npt X 3/8 hose NY
  - For smaller columns: TN 22 1/4 Npt X 1/4 hose NY
- H Machined plexiglass base
- I Clear cast acrylic top section: 1/4" or 1/8" wall
- J Plexiglass lid
- K Tubing

Appendix Figure 1. Cross-section view of leaching columns used to study constituent movement.



Appendix Figure 2. Schematic of leaching columns used to study constituent movement with soil depth.



Appendix Figure 3. Schematic of equipment for saturating soil with anhydrous ammonia.