

RESEARCH TECHNICAL COMPLETION REPORT
PROJECT A-021-IDA



**Temporal, Horizontal and
Vertical Variability
of Water Chemistry in
Unsaturated Zone of
Fine-Grained Soils**

Project Investigator

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Water Resources Research Institute
University of Idaho
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June 1969

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TEMPORAL, HORIZONTAL AND VERTICAL VARIABILITY
OF WATER CHEMISTRY IN UNSATURATED ZONE
OF FINE-GRAINED SOILS

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ABSTRACT

A method was developed for extracting water samples from unsaturated soils under low moisture content and concomitant high tension. A sample collection cell was constructed by enclosing a hydrophylic, cross-linked, dextran xerogel in seamless, dialyzer tubing with opening diameters of 48 angstroms. When the cell is placed in contact with a soil, water and its dissolved ions move through the membrane and into the hydrophylic substance. Because the ion exchange capacity of the xerogel is negligible, the water and ions can be replaced by distilled, deionized water and the effluent analyzed. However, chemical analysis of the effluent has revealed that results are not reproducible and that unreasonably high concentrations of some ions often result.

Combination tracer and infiltration tests have demonstrated that water moves through the loess soils of northern Idaho via discontinuities as well as through intergranular pore spaces. Whether the discontinuities are operative in the infiltration process depends on the surface condition and on the application rate. These must permit a saturated layer to form above the discontinuities before they can begin to conduct water preferentially.

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INTRODUCTION

Background Discussion

Investigators of the quality of waters within the zone of saturation frequently are confronted with the task of determining the origin of a particular combination of ions in solution. Often it is possible to attribute observed constituents to a particular rock type through which the water has moved subsequent to its entry into the zone of saturation. In other cases water quality within the ground-water body can be correlated with the position of the sampling point within the ground water flow system. The quality of the water at one point within a system may differ from the quality of the water at another point in that system because one of the points is connected to the recharge area by a longer flow line or because the flow line between the recharge area and one of the sampling points passes through a zone of lower permeability. A flow path through a low permeability zone slows the rate of movement of an individual water particle along that route and increases the length of time available for the addition of dissolved ions to the water particle following that route. Examples of cases such as those described above have been documented by Seaber (1965), Maderak (1965), Toth (1966), West, et. al. (1965), and Back (1960).

Quite often, however, variations in water quality within a ground water body are affected significantly by processes to which the water molecules are subjected while in transit through the zone of aeration. This effect is likely to be most pronounced in a recharge area within which the zone of aeration is greater than about 50 feet thick, where reasonably high permeability allows oxygen rich water to move deep into the unsaturated zone and where the rocks or soils are easily weathered due to a high content of ferromagnesian minerals. Attempts at unraveling the relation between soil and rock mineralogy and quality of ground and surface waters have been made by Harriss and Adams (1966), Wolff (1967), Miller (1961), and Feth, et. al. (1964).

Harriss and Adams (1966) conducted their studies with sampling points limited to surface water and ground-water bodies. Only soil samples (i.e., no water samples) from the unsaturated zone were analyzed. Nevertheless, on the basis of equilibrium diagrams, the investigators were able

to designate those soils in Oklahoma and Georgia which are in equilibrium with ground and surface water; consequently they were able to define those soils still experiencing active chemical weathering.

Miller (1961) also examined the relation between mineralogy and water quality by analyzing stream waters and rock chemistry. Miller conducted his studies in several basins at the southern end of the Sangre de Cristo Range in New Mexico. He chose for investigation basins which are lithologically "homogeneous" with respect to either quartzite, granite, or sandstone. Conclusions were based on the relation between chemical analysis of rock samples collected from the unsaturated zone in the basin and stream samples taken from that basin. Stream flow was derived from snow melt for a period of three months prior to the period of sampling. No samples were collected from the unsaturated zone; therefore, the effect of geochemical processes occurring in both the saturated and unsaturated zones were operative in producing the observed results. Nevertheless, this technique enabled the investigator to draw several conclusions regarding rock type and water quality. Included among the most significant conclusions are:

1. The solute content of waters draining sandstone is derived from carbonate cement and thin limestone which hold the sand grains together. Collectively these materials constitute less than 1 percent of the rock.
2. Waters draining a specific rock type are remarkably uniform in composition, even for different basins.
3. If relative mobility = $\frac{\text{percent of element in water}}{\text{percent of element in rock}}$, then the order of relative mobility among elements is Ca Na K Si Al.
4. Estimated values of chemical denudation rates based on the data collected indicate that solution weathering plays a more significant role in landscape sculpturing than previously has been believed.

Feth, et. al. (1964), examined the dependence of water quality on mineralogy observed within granitic basins in the Sierra Nevadas. Ground-water samples were obtained from perennial springs and streams. Samples representing water above the zone of saturation were limited to ephemeral springs. Water from these springs was assumed to be in contact with soil and saprolite (weathering residue) for periods of a few hours to a few weeks. Analysis of lithologic samples indicated that the plutonic rocks ranged from quartz diorite to quartz microcline gneiss. Among the more important

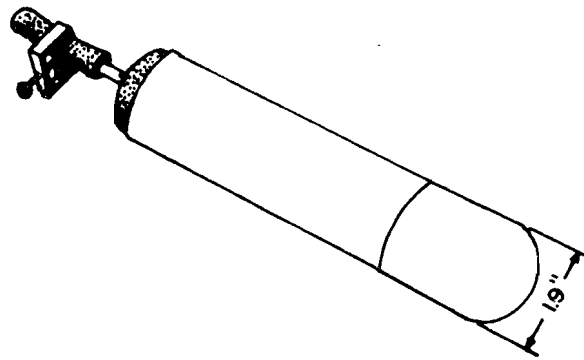
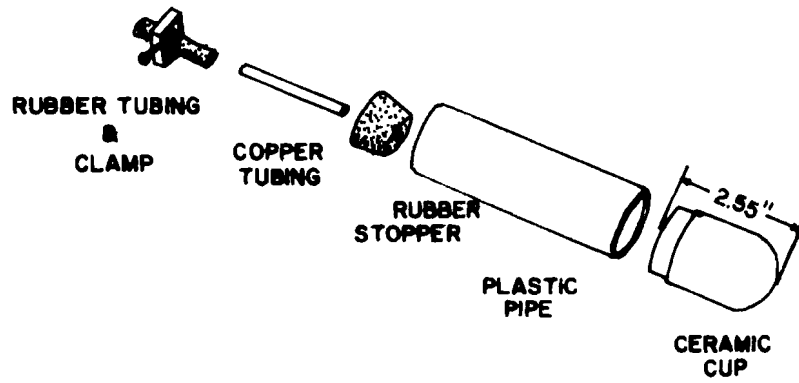


Fig. 1A Porous cup complete with attachments for creating a vacuum and collecting soil water
(Modified after Wagner, 1962)

conclusions reached by the investigators are:

1. Mineral content increases on the average 7.5 times as melt water comes in contact with soil and saprolite, then doubles again during deeper penetration of the water as it moves toward perennial springs.
2. The diversity in chemical type displayed by samples of snow disappears almost instantaneously when the melt water comes in contact with the lithosphere.
3. The common cations observed in solution are derived principally by hydrolysis of feldspar, hornblende, and biotite.
4. No statistically significant differences in chemical quality of the water were observed among samples from the several lithologic subcategories except for a greater concentration of chloride in water from granodiorite.

Of primary interest here is conclusion number 2. Because of the lack of a good sampling device, samples considered to be representative of chemical processes common to the zone above the water table were obtained from discharge points for bodies of water under positive pressure.

One of the most direct means of obtaining samples of water from the unsaturated zone has been described and utilized by Wagner (1962). This method employs a porous ceramic cup assembly such as the one portrayed in Figure 1A. The collection mechanism utilizes the fact that when the ceramic cup is in contact with very moist soil, capillary forces pull water from the soil through the walls of the cup and into the interior void. The pore diameters are so designed that "the pore size is such that water is held in these pores with a force sufficient to cause the cup to become sealed against air pressure of at least 15 PSI. (In other words air invasion will not occur at pressures \approx 15 PSI.)

A vacuum, therefore, may be created within the ceramic cup. In the event moisture in the soil is held at a tension of less than one atmosphere (true of very moist soils), water can be drawn through the pores of the ceramic wall and into the cup, due to suction developed by the vacuum within." This design facilitates the establishment of a gradient down which water will move, provided the soil moisture content is sufficient to sustain a negative pressure of less than one atmosphere. At more negative pressures the vacuum pump becomes ineffective and no gradient toward the cup can be

maintained. The design of the device is such that it need not be oriented in space in any particular fashion.

Wagner installed this device at depths of 6, 12, 24 and 36 inches in plots on 4 different soil types. A neutron probe was used to measure soil moisture. Water was collected whenever moisture content was thought to be sufficient to establish a negative pressure of ≤ 1 atmosphere in the soil water. Consequently, periods of sampling were subsequent to fairly heavy rainfalls. Several observations and conclusions resulted from the experiments, among the more significant of which are the following:

1. Water could be collected from the upper twelve inches of soil when the percent water by volume was greater than 29 percent. (All soils were silt loams.)
2. The volume of water collected by the ceramic cup was not always related to the moisture content in the layer in which the cup was installed. The moisture content of adjacent layers influenced the uptake.
3. When the moisture content (by volume) in a claypan at a depth of 24 inches was less than about 42 percent no water could be drawn from that layer. In addition, because 42 percent moisture content is only slightly less than the saturation moisture content and because 42 percent moisture content is coincident with about 1 atmosphere of negative pressure, it is normally impossible to collect samples from clays with this device.
4. The volume of water obtainable limits the number of chemical analyses that can be performed on a collected sample.

Wagner did not report any chemical analyses of the samples collected. His study establishes the limiting conditions under which the porous cup collecting device may be used successfully.

Using a sampling technique very similar to that of Wagner (1962), Wolff (1967) examined the quality of the water percolating through a mound of woodstock granite near Baltimore, Maryland. The granite is more specifically a quartz monzonite. During weathering the plagioclase feldspars decompose to form halloysite. The ratio of $4\text{H}_2\text{O}$ halloysite to $2\text{H}_2\text{O}$ halloysite increases with depth into the quartz monzonite. This change in halloysite significantly affects the quality of water as it moves downward through the weathered rock.

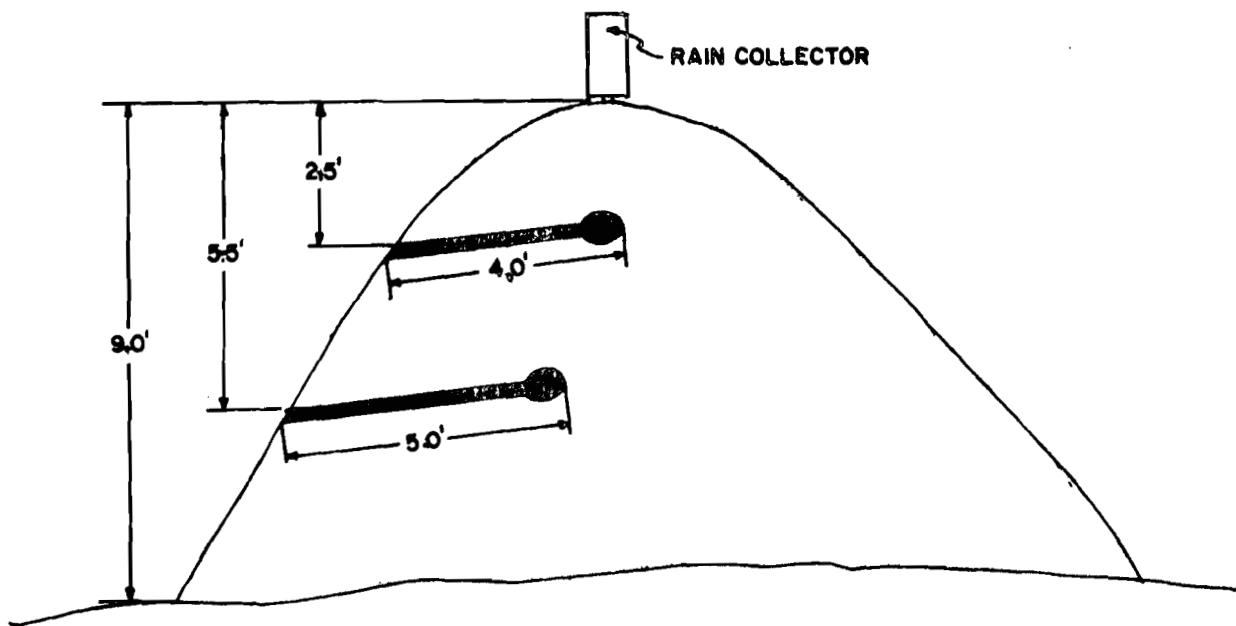


Fig.2A Diagrammatic representation of water sampling technique used to obtain samples from the woodstock granite (after Wolff, 1969)

Wolff obtained samples of water from the granite via the apparatus shown in Figure 2A. Suction was applied to the exposed end of each tube in an effort to create the maximum possible gradient. Under fairly high moisture conditions water could be collected from the tubes. Although difficulty was encountered because the ceramic cup contributed ions to the water, analysis of the water from the tubes revealed a higher concentration of dissolved solids at 2.5 feet below the surface than at 5.5 feet below the surface. Wolff attributes the decrease in total dissolved solids with depth to the increasing cation exchange capacity of the halloysite with depth. This decrease of total dissolved solids with depth differs from most documented cases where quality decreases with the length of time spent by the water in the system.

The need for an understanding of the fate of dissolved ions introduced by man into the zone of aeration is among the most prominent motivations for studies of the quality of water in the unsaturated zone. Examples of human activities which may contribute ions to this zone are agricultural fertilization, reuse of irrigation waters in which sodium and other ions accumulate, waste effluent reuse and infiltration and percolation of effluent from landfills or other waste disposal sites. In this regard the fate of radioactive constituents in percolating waters has received considerable attention. A specific case wherein such a device would be useful is the disposal of radioactive process cooling water and other wastes (normally low or intermediate level). Such wastes, which are discharged to trenches, swamps, and cribs, infiltrate through the soils toward the water table. Ion exchange properties of the soil are depended upon to retain fission products in the soil column. As would be expected, ground-water mounds form beneath disposal sites which receive appreciable volumes of water. The monitoring process normally consists of the withdrawal and analysis of ground water samples from wells located on and around a groundwater mound. (For more detailed discussion the reader should see Linderoth and Pearce (1959).)

Such a procedure is satisfactory for monitoring pollution of ground water; however, if undesirable ions are observed in dangerous concentrations in ground water, very little can be done in the way of corrective measures. If samples of water can be obtained and analyzed as the water moves down through the unsaturated zone, this problem can be minimized.

Last, but not least important to water quality studies, is the relation between the mode by which water moves through a porous medium and the

variations in quality which can be expected in the medium. Lewis and Burgy (1964), for example, showed that tritiated water can move through joints equal to or less than 0.01 feet wide in metamorphosed sedimentary and igneous rocks. The tritiated water subsequently was evapotranspired by oak trees whose roots penetrate the joints to depths of 70 feet. Movement of water through pore spaces in the matrix was considered negligible.

Objectives of Current Study

The foregoing background discussion clearly illustrates several points pertinent to studies of water in the unsaturated zone. The most important are:

1. The motivations for examination of the relation between water quality and the geochemistry of the materials in the unsaturated zone range from the desire for basic scientific information which is necessary for an understanding of natural processes, to the need for a technique for obtaining samples via which pollution can be monitored.
2. A need exists for a sampling device which is capable of obtaining insitu samples of soil moisture held under high negative pressure. Such a device would facilitate the separation of the dependence of stream and ground-water quality on processes operating in the saturated zone from the dependence on processes operating in the unsaturated zone. It would also provide a means of monitoring the migration of ions in solution through the unsaturated zone. Ideally the device should not destroy the sampling point, thereby permitting monitoring of temporal as well as spatial variations in water quality.
3. Investigations of water quality in either the saturated or the unsaturated zone should be contemporaneous with investigations of the mechanisms by which water moves through the porous media which is being monitored. It is unrealistic, for example, to consider the quality of water collected from the intergranular pore spaces in glacial till to be representative of the quality of water reaching the water table if the water moving through the till travels preferentially along discontinuities. Authentication for the occurrence of such conditions is provided by Williams and Farvolden (1967), Gaiser (1952), as well as Lewis and Burgy (1964).

It is toward points 2 and 3 that this study has been primarily directed. The efforts directed at point 2 are described in the subsequent section of this report. The efforts directed at point 3 are discussed in the summary at the end of this report.

INVESTIGATIONAL PROCEDURES PERTINENT TO OBTAINING AND ANALYZING SOIL MOISTURE SAMPLES

Materials Examined

The Palouse Formation is the stratigraphic unit within which the examination of the quality of water was attempted and within which the factors affecting the movement of water into and within the unsaturated zone were investigated. The Palouse Formation consists of loess deposits. The loess was derived from the glacial outwash that moved down the Columbia River drainage system during and after the Pleistocene Epoch (Reiger, 1952). Characteristics of the loess are discussed in greater detail by Reiger (1952) and in the published paper by Williams and Allman, which is referred to later in this report.

Design of Pits and Selection of Pit Sites

In order to gain access to the subsurface materials, 3 trenches 4 feet in width were excavated to a depth of 12 feet in the loess. The side walls and one end of each trench were cut vertically. The remaining end was sloped to provide access to the bottom of the trench. A considerable portion of the excavating was done by hand in order that the structural properties of the loess could carefully be examined as excavation proceeded. The vertical walls permitted the examination of a fresh section of the upper 12 feet; the walls also facilitated the installation of sampling devices at different depths within the loess.

The locations of the trenches were selected on the basis of a preliminary interpretation of the ground water flow system beneath each site. Two trenches are situated above a ground water recharge area where the water table is at least 30 feet below the bottom of the trench. The third is situated above a zone of lateral flow where the bottom of the trench is approximately 1 foot above the water table during the dry portion of the summer; during the wet portion of the year the water tables rises to a depth of about 3 feet in this trench. The reasoning behind these site selections was based on the assumption that discontinuities

and structural properties of the loess would be affected by contact with the water table and the capillary fringe. It was believed also that because of the removal of water by evapotranspiration, the quality of the water in the unsaturated zone would be influenced by the nearness of the sampling points to the water table, particularly where the distance from the ground surface to the water table is equal to or less than about 12 feet.

Sample Collection and Analysis

The sample collecting device designed for use in this study consists of 2 essential elements: 1) a hydrophilic substance which is capable of removing water from materials which are holding the water under tension, and 2) a permeable membrane which contains the hygroscopic substance. The membrane must allow water and dissolved ions to pass from the soil into the hygroscopic substance; at the same time it must prevent the loss of the enclosed substance and prevent the entry of soil particles. Experimentation proved that dialyzer tubing (also known as dialysis membrane) satisfactorily meets both requirements. (The word dialyzer or dialysis refers to a screening process whereby small molecules such as water and ordinary dissolved ions pass through a membrane whereas large molecules cannot). This material commonly is used in biochemistry to separate large particles, such as protein molecules or microorganisms, from smaller molecules contained in the same solvent. The membrane consists of cellulose regenerated by the viscose process. The membrane is pure cellulose except that it contains approximately 0.1 percent sulfur. Its adsorption capacity is negligible. The membrane is available with average pore diameters of 24 and 48 angstroms. The latter variety was used in this study in order to allow passage of soil water and all its dissolved constituents. The validity of this assertion is verified by the radii of several ions. The radii of Na, K, Mg, Ca, are .98, 1.33, .78 and 1.06 angstroms respectively. The corresponding hydrated radii are 5.6, 3.8, 10.8, and 9.6 angstroms, respectively (Grim, 1953, p. 148). The thickness of the membrane is 0.0008 inch, therefore, the length of a continuous column of water through it is at a minimum. Such a column must persist in order for water to be drawn from the soil into the hygroscopic substance within the membrane. The membrane was purchased in the form of seamless, 5/8 inch diameter tubing which was adaptable to the cell construction. In order to ascertain that it would function properly for purposes of the anticipated experiments, prior to the

use of the membrane distilled, deionized water was passed through the membrane and subsequently analyzed for sodium, potassium, calcium and magnesium. None of these ions was found in the water that had passed through the membrane. Solutions containing a known concentration of these ions were also passed through the membrane and analyzed with the atomic absorption spectrophotometer. No significant change occurred in the concentrations during passage through the membrane. It was concluded that it would suffice.

The primary requirements of the hydrophylic substance to be used in this study are a negligible ion exchange capacity, chemical inertness, and the ability to allow contained solutions to be washed out with deionized distilled water.

The initial substance selected for use within the membrane is known commercially as aquicide. This material consists of a sodium salt of carboxymethyl cellulose in a specially purified form. It is commonly used by biochemists to draw water and its smaller dissolved ions through dialysis membrane, thereby leaving behind large protein molecules. Experimentation revealed, however, that when deionized, distilled water is passed through aquicide saturated with deionized distilled water, the water passing through picks up variable amounts of sodium. A subsequent search for an explanation revealed that the sodium carboxymethyl cellulose salt holds some of the sodium ions only loosely. The sodium is, in fact, available to other dissolved materials as an exchange ion. Such a condition obviously would affect the sodium concentration in any solution introduced into the aquicide. The concentration of any ions exchanged for the sodium also would be altered. Consequently, the use of this substance was discontinued.

The zeolite mineral group was considered next as a substance for possible use in the collecting device. The zeolite group consists of hydrous aluminosilicates which take up and release water as water of hydration. Because of their very high affinity for water, they commonly are used for drying gases and organic liquids. Zeolites, however, have a high ion exchange capacity. In addition, they tend to retain small rather than large ions and molecules when solutions are passed through them. These properties could not be tolerated for purposes of this study.

The xerogel known commercially as sephadex finally was settled upon as the material which most satisfactorily meets the requirements specified.

Sephadex is a cross linked dextran, which is a polysaccharide synthesized microbiologically by the action of *Leuconostoc mesenteroides* strain NRRL B-512 on sucrose. The basic elements of the structure are sucrose molecules which are bonded into three-dimensional chains. These chains are cross linked with epichlorohydrin to form polymers which have the properties of a gel upon wetting. The abundance of hydroxyl groups on the polysaccharides accounts for the high affinity for water. The water uptake property of the gel is a function of the number of cross linkages and of the concentration of dextran relative to epichlorohydrin. Thus the product is available with several water uptake capacities. The common varieties have water regains of 2.5, 5.0, 7.5, 10.0 and 20.0 grams per gram. The greater the water regain value, the greater the time required for equilibrium to be established. The variety having a water uptake of 10 grams per gram was used in this study. The product is referred to by the manufacturer (Pharmacia Fine Chemicals) as sephadex, G-100.

Prior to use the product was tested by adding distilled, deionized water to the point of equilibrium. Additional water was passed through the sephadex and subsequently analyzed for Na, K, Ca, and Mg. The discharged water did not contain these ions except for trace amounts of sodium commonly observed in distilled, deionized water. Solutions containing known concentrations of these ions were also passed through the sephadex and subsequently analyzed. No change greater than 5 percent was observed in the effluent.

A 0.5-inch length of dialyzer tubing was filled with sephadex and the ends were sealed. The filled tubes were weighed, then placed inside a small, air-tight polyethylene bottle until used, thereby preventing water vapor uptake from the air by the sephadex. Initially soil moisture samples were obtained via 1.5-inch diameter horizontal holes drilled to a distance of 2 feet into the wall of the previously described pits. Plastic pipe was used to line the holes to within two inches of the end. Holes were installed along a vertical line at depths of 2, 4, 8, and 10 feet. They were sloped slightly toward the trench wall in order to preclude entry by precipitation. A thread was attached to the dialyzer tubing containing the sephadex. A cell was pressed against the end of each hole and allowed to remain for 4 days. The cell was then removed and after removal of all extraneous particles with air the cell was weighed immediately to determine water uptake.

During cold weather it was observed that the membrane sometimes freezes and adheres to the soil. Removal is impossible without breaking

the membrane, thereby destroying the sample. The sampling device is also ineffective in wet, clayey soil. Under such conditions the wet, clayey mud adheres to the sample and makes weighing impossible. Points in the soil column which become "muddy" apparently are related to the water conducting discontinuities which are described in greater detail in the published portion of this report.

After removal and weighing of the cell the analyses were performed in the following manner. The sephadex, soil water and dissolved ions were removed from the membrane by washing (with distilled deionized water) them into a nalgene funnel with a dacron filter. Both nalgene and dacron are inert. All wash water escaping from the medium was collected in a small nalgene bottle beneath the funnel. About 5 ml of water normally was required for removal of the sephadex was satisfied. Additional water was injected into the top of the column to replace the water contained therein. The water was added in 5 ml aliquots until 25 mls were collected in the nalgene bottle. The water was analyzed with a specific ion meter and/or an atomic absorption spectrophotometer.

The concentrations (in parts per million) for calcium and magnesium in the 25 ml elutions of the first set of samples collected were:

<u>Calcium</u>	<u>Magnesium</u>	<u>Water uptake (gms)</u>
3.4	4.1	.6351
6.1	7.2	.5382
7.1	6.3	.4321
7.3	5.6	.5472
18.0	30.8	.1148

These concentrations can be converted to values for the water collected from the soil by the following equation:

$$\text{elution conc. } \left(\frac{\text{mg}}{\text{liter}} \right) \times \frac{25 \text{ (liters)}}{1000} \times \frac{1}{\text{soil water uptake} \times 10^{-3} \text{ (liters)}}$$

Therefore, the actual values for concentration of calcium and magnesium are:

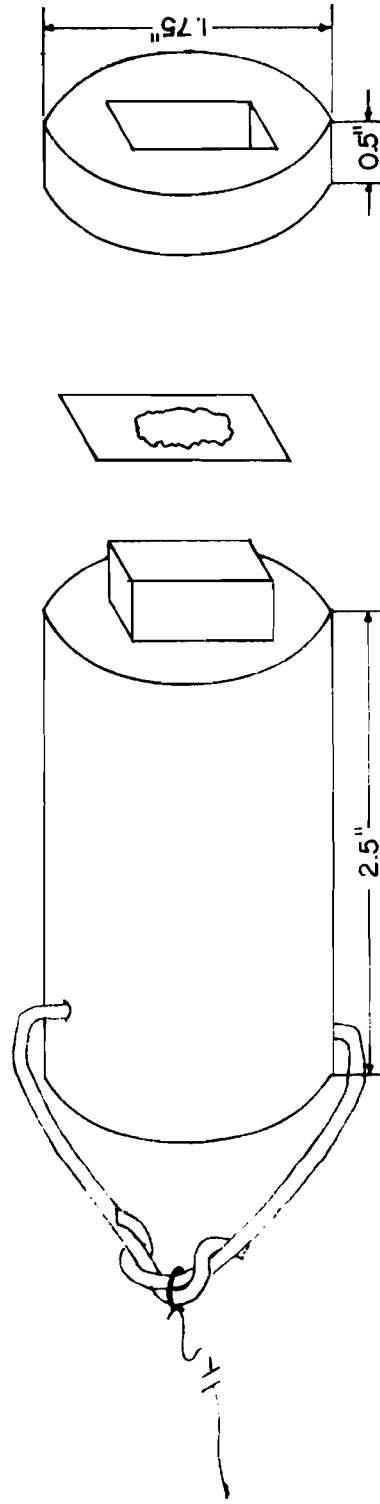
<u>Ca(PPM)</u>	<u>Mg(PPM)</u>
133.8	161.5
287.7	339.6
412.8	366.3
338.0	259.3
4090.9	7000.0

Because these values are unreasonably high, a comparison was made between these concentrations and those observed for calcium and magnesium in the shallow aquifer which underlies the loess in the Moscow basin (obtained from Jones and Ross, unpublished manuscript, 1968). That this aquifer receives recharge by movement of water through the loess is verified subsequently in this report. For this reason it is reasonable to expect similar concentrations of calcium and magnesium in the water from the two sources. Concentrations of calcium in 22 samples from the aquifer ranged from 9.0 to 113.2 ppm with an average value of 33.7 ppm. Magnesium in the same samples ranged from 1.8 to 28.4 ppm with an average concentration of 8.2 ppm. These data constitute more factual evidence that the concentrations observed in the samples from the unsaturated zone are unreasonably high.

Sodium and potassium were observed in the samples of soil moisture but only in trace amounts (.1ppm). Subsequent to the conclusion regarding the invalid calcium and magnesium values, several steps were taken to pinpoint and eliminate the source of error. A new sample collecting device was designed in order to minimize the possibility of water escaping from the cell via the vapor phase while the collecting device is in the auger hole. The material used is styrofoam and the design is portrayed in Figure 3A. In addition to minimizing vapor entry, this cell facilitates the use of less sephadex and makes easier the job of cleaning the membrane after its removed from the soil. The cell also requires use of a 2-inch diameter drillhole. With respect to vapor exchange, this action was considered primarily as a precautionary measure, because contemporaneous experiments revealed that the sephadex cell actually gains water while exposed to the water vapor. This conclusion was reached by weighing a cell before and after its suspension 1 centimeter above the bottom of a 3-foot deep auger hole. Water uptake from the vapor phase is in the order of 0.16 gms for each gram of soil water collected by a similar cell in contact with the soil at the bottom of the hole. Therefore, a minor diluting effect by vapor uptake would be expected.

An alternative method of moisture extraction was also attempted. Soil samples from which moisture was to be extracted were brought into the laboratory. Samples were placed in a Buchner funnel and closed off by a rubber diaphragm. A vacuum was applied to the apparatus in an effort to "squeeze" water out of the soil. The technique was tested at several moisture contents; as might be expected, it was observed that water was released only when sufficient water was added to bring the moisture content to near

Wire Holder
(expands when cell is rammed
into hole, holds cell in place)



Cord
(for extraction)

Cell Body
(styrofoam)

Sampling Medium

Cell Collar

Fig 3 A DESIGN OF SOIL MOISTURE COLLECTION DEVICE

saturation level. Therefore, in addition to destroying the sampling point, the device would be applicable only to unusual moisture conditions; consequently, use of it was discontinued.

Using the newly designed cell, additional sets of samples were collected (at different times) and analyzed; one set of samples was analyzed for calcium and the other for magnesium. The data for magnesium and calcium are presented in Tables 1 and 3, respectively.

In an effort to obtain information on the relation between moisture content, water uptake and magnesium content of the sample obtained, a sample of soil was removed from the back of each horizontal auger hole immediately after a collection device was withdrawn. The moisture content of these samples was obtained in the manner described by Schwab, et.al. (1966, p. 135). The results are presented in Table 2.

Comparison of Table 1 with Table 2 reveals no consistent relation between moisture content and magnesium concentration. However, comparison of columns 5 and 7 of Table 1 reveals that extremely high concentrations of magnesium are associated with low moisture uptakes by the sephadex. Inspection of the data from the samples collected prior to the implementation of the use of the styrofoam cells reveals a similar relation between both magnesium and calcium concentration and water uptake for those samples.

Subsequent to these observations, samples of the loess were brought into the laboratory. Analysis of samples obtained from them revealed similar high concentrations of calcium and magnesium. In addition, analysis of samples obtained from the same soil block yielded variations of up to 50 percent in the concentrations of calcium and magnesium. Consequently, the results are considered nonreproducible.

INTERPRETATION OF RESULTS OF CHEMICAL ANALYSIS

Considerable time has been spent reviewing the literature in an effort to explain the high concentrations of calcium and magnesium observed in the samples, as well as the nonreproducible nature of the results. The high concentrations must be attributed to a loss of water from the cell after its removal from the soil or to a selective uptake of calcium and magnesium during the extraction of water from the soil by the sephadex. A plausible explanation is inherent in the literature on clay water systems.

TABLE 1. DATA FOR WATER AND MAGNESIUM UPTAKE BY SEPHADEX CELL

Sample No.	Source of Sample	Initial Wt. of Cell(gms)	Final Wt. of Cell (gms)	Water Gain(gms)	Conc. Mg in Elution(ppm)	Conc. Mg in Soil Water(ppm)
1	Trench B 4 feet	0.1799	0.6199	0.4400	04.71	267.4
2	Trench B 8 feet	0.1726	0.4816	0.3090	02.24	181.2
3	Trench D 4 feet	0.1933	0.5366	0.3433	03.11	226.2
4	Trench D 8 feet	0.1685	0.6011	0.5326	03.80	180.5
5	Trench B 4 feet	0.2046	0.5209	0.3164	03.28	259.2
6	Trench B 8 feet	0.1640	0.2918	0.1278	03.23	632.5
7	Trench D 4 feet	0.2274	0.8580	0.6306	03.44	136.9
8	Trench D 8 feet	0.2005	0.2265	0.0260	05.34	5,130.0
9	Trench B 4 feet	0.1631	0.1716	0.0085	05.35	15,735.0
10	Trench B 8 feet	0.1634	0.3830	0.2196	02.99	340.2
11	Trench D 4 feet	0.1712	0.5787	0.4075	02.53	321.0
12	Trench D 8 feet	0.1607	0.5356	0.3749	02.87	191.2

TABLE 2. SOIL MOISTURE CONTENT DATA FOR SOILS FROM WHICH WATER QUALITY SAMPLES IN TABLE 1 WERE EXTRACTED*

Sample No.	Source of Sample	Wet Wt. of Sample(gms)	Dry Wt. of Sample(gms)	Wt. of Water Lost (gms)	Moisture Content (gms Water Lost/Dry Wt. of Sample)
1	Trench B 4 feet	15.5525	12.6208	2.9317	23.23
2	Trench B 8 feet	13.2251	11.4178	1.8073	15.83
3	Trench D 4 feet	14.8245	11.8884	2.9361	24.70
4	Trench D 8 feet	12.0735	10.4216	1.6519	15.85
5	Trench B 4 feet	10.3070	8.2520	2.0550	24.90
6	Trench B 8 feet	12.9351	11.2976	1.6375	14.49
7	Trench D 4 feet	12.0809	9.9438	2.1371	21.49
8	Trench D 8 feet	-----	-----	-----	-----
9	Trench B 4 feet	13.4120	10.7532	2.6588	24.73
10	Trench B 8 feet	-----	-----	-----	-----
11	Trench D 4 feet	-----	-----	-----	-----
12	Trench D 8 feet	-----	-----	-----	-----

*Blanks represent samples in which moisture content was sufficiently low to be considered unrepresentative of the true moisture content of the soil.

TABLE 3. DATA FOR WATER AND CALCIUM UPTAKE BY SEPHADEX CELL

Sample No.	Source of Sample	Initial Wt. of Cell(gms)	Final Wt. of Cell (gms)	Water Gain(gms)	Conc. Ca in Elution(ppm)	Conc. Ca in Soil Water(ppm)
1A	Trench B 4 feet	0.1821	0.6022	0.4201	3.2	190.3
2A	Trench B 8 feet	0.1932	0.5074	0.3142	4.0	320.3
3A	Trench D 4 feet	0.2410	0.4544	0.2134	1.5	602.4
4A	Trench D 8 feet	0.2120	0.6387	0.4267	3.0	173.7
5A	Trench B 4 feet	0.2014	0.6030	0.4016	2.6	160.6
6A	Trench B 8 feet	0.1940	0.5154	0.3214	4.1	319.8
7A	Trench D 4 feet	0.2313	0.4329	0.2016	2.5	307.4
8A	Trench D 8 feet	0.1742	0.4113	0.2371	5.3	506.3
9A	Trench B 4 feet	0.1631	0.5337	0.3706	4.0	270.1
10A	Trench B 8 feet	0.1892	0.5995	0.4103	2.3	142.7
11A	Trench D 4 feet	0.1924	0.5738	0.3814	4.4	290.3
12A	Trench D 8 feet	0.2132	0.4884	0.2752	3.5	316.5

The water molecule has a dipole moment of about 1.83×10^{-18} electrostatic units. Lennard, Jones and Pople (1951) regard the charges within the water molecule as being effectively located at the corners of a tetrahedron. In the liquid state each water molecule can form a hydrogen bond with another water molecule at each of the four corners of the tetrahedron. That this geometry actually prevails has been proven by x-ray analysis of ice crystals (Pauling, 1945). Additional evidence more directly associated with water, particularly at low temperatures, has been provided by Morgan and Warren (1938). Because of this polarizing property of water molecules, the structure of water in thin films or in the vicinity of other electrostatic forces often is complex. This complexity has led to considerable investigation of structured water, especially in the vicinity of cations associated with clay minerals. These charged ions attract water molecules electrostatically and subsequently become hydrated. A cation will hydrate if the potential energy of the water molecule is lower after being attracted to the cation than is the potential energy of the water molecule within the quasi-crystalline structure of pure water. Given sufficient water, water of hydration molecules can be exchanged for water molecules in the quasi-crystalline structure surrounding a cation at a rate which depends on the intensity of the ion-dipole bond. Adjacent to such a cation the electronic circuit of the water molecules are directed inward; that is, the oxygen side of the water molecule is directed toward the cation. If the cation were absent, its space would be occupied by a water molecule; two of the surrounding water molecules would have their protonic circuit directed toward the space and two would have their electronic circuit directed toward the space. Consequently, the quasi-crystalline structure of the water is disrupted in the vicinity of a cation. The degree of disruption depends on the size of the ion and its charge. In order to relate the possible importance of this disruption to uptake by sephadex of water and divalent cations from soils containing clay minerals (as does the Palouse loess), it is necessary to examine the hydration mechanisms of clay minerals which contain various cations.

Such an investigation was conducted by Hendricks, et al. (1940) for the clay mineral montmorillonite. The investigators used differential thermal analysis to distinguish variations in the energy of binding of water to montmorillonite. The method is considered reliable even though the energy variations are very small. Temperature of maximum rate of energy

absorption is considered the best measurement of order of binding energy. Curve maxima produced by loss of water adsorbed at low humidities occur at higher temperatures. This relation is in keeping with the concept that water held under low humidities (low moisture content) is subject to higher bonding energy than is water held at higher humidities. DTA curves were constructed by Hendrick, et. al. for montmorillonite with a variety of volumes of adsorbed water for the cations sodium, potassium, lithium, hydrogen, cesium, calcium, magnesium, strontium, and barium. X-ray diffraction diagrams were constructed for each ion and for each water content in order to relate hydration characteristics to lattice spacing of the clay. By analyzing the DTA peaks and comparing the peaks to water content and lattice spacing, the investigators concluded that montmorillonite containing divalent cations produces three types of hydration: water which is loosely attached to the slightly negatively charged clay mineral surface, structured water which is oriented around the hydrated cation but which is more loosely bound than the inner layer. Sodium and potassium, it is concluded, are not hydrated when they occupy the exchange positions on montmorillonite.

On this basis one can view the clay water system as consisting of "normally structured" water which grades through disrupted, tetrahedral water molecules, into water which is loosely held on the clay surface (probably both by capillary and electrostatic forces). A hydrated, exchangeable, divalent cation is associated with these two types of water through its structured water of hydration. Evidence that calcium or magnesium rather than sodium or potassium would be expected to occupy the exchange position is discussed by Robinson (1949). Robinson presents the following ease of replacement series: $H^+ > Ba^{++} > Sr^{++} > Ca^{++} > Mg^{++} > Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$. In other words, calcium or magnesium will replace sodium in an exchange position. Consequently, calcium and magnesium, when present in a soil, can be thought of as accumulating near the surfaces of the clay minerals in a soil, whereas sodium and potassium are replaced and are removed with normal free water movement. (Exceptions do occur. For example, if sodium or potassium is present in high concentrations, say in a soil irrigated with sodium rich water, sodium would become structurally associated with the clay mineral; such is not the case with the Palouse loess.) For a summary of the literature on this subject the reader may wish to refer to Low (1961) or Grim (1953).

These conditions may account for the high uptake of calcium and magnesium. The water which is brought into the collection cell may incorporate and transport into the sephadex some of the hydrated calcium and magnesium ions associated with the clay minerals in the loess. If such is the case, the concentrations observed would not be representative of the concentrations in the normally structured (i.e., tetrahedrally structured) water in the soil. The validity of this hypothesis hinges on whether the potential energy with which water is held in the sephadex at low moisture content is sufficient to cause hydrated, exchangeable cations to move into the cell. Because no information on this subject has been found in print the question cannot be resolved at present. Extensive differential thermal analysis probably would answer this question.

STATEMENT CONCERNING WATER MOVEMENT PORTION OF STUDY

As mentioned previously, excavation of the trenches and withdrawal of the soil moisture samples indicated that the Palouse loess contains certain structural features which are not common to most unconsolidated sediments. The muddy condition of some of the sample cells upon removal suggests that these structures may be related to water movement within the loess. Several techniques were utilized to interpret these structural features and to determine their relation to other hydrogeologic characteristics of the loess. The results of the experiments may be useful to conservation of the loess soils and to conservation of ground-water resources within the basin. These results are summarized in the following section.

SUMMARY

The research efforts incorporated in this project were directed at an understanding of the quality and the behavior of the water in the unsaturated zone of fine-grained soils. Under low moisture content, the water in fine-grained soils is under high negative pressure. Consequently, the collection of a sample of volume sufficient for analysis is difficult because a pressure more negative than that occurring in the soil must be created in order for a gradient to be established. The establishment of a gradient is in turn a prerequisite to the movement of water toward the sampling device. After considerable experimentation, a collection apparatus was designed which is capable of establishing such a gradient. The sample is collected within a hydrophylic, inert, cross-linked dextran gel enclosed within permeable dialysis membrane. The hydrophylic substance and the dialysis membrane are both enclosed within a styrofoam cartridge which, when in use, fits against the wall of a horizontal or vertical borehole. After the withdrawal of the cell from the soil the collected water is removed and analyzed. The collection device functions satisfactorily; however, analysis of samples collected has revealed that the results are not reproducible. In addition, many of the concentrations measured are believed to be unreasonably high.

Variations in the quality of the water in the unsaturated zone are related to the mechanism by which water moves through this zone. Specifically, because of surface area considerations, water moving exclusively through intergranular pore spaces would be expected to procure more dissolved ions enroute than water moving through discontinuities. Consequently the mechanisms by which water is transmitted through loess were investigated by tracer studies, by infiltration tests by the installation of piezometers and by x-ray diffraction diagrams. These experiments revealed that several variables have an inscutable effect on infiltration, percolation and ground water recharge in loess. The most significant variable appears to be the condition of the surface. Infiltration tests that have been conducted on a silty clay loam surface planted in winter wheat indicate that such surficial layers act as a limit to the infiltration capacity of the loess. Under these conditions infiltration capacity is less than 0.1 inches per hour. Concomitantly, erosion is most severe on these surfaces. Infiltration capacity through the intergranular pore spaces of the parent loess is between 1 and 1.5 inches per hour. Therefore, water must be accepted and transmitted by the

surficial layers at a rate of 1 to 1.5 inches per hour before the parent loess becomes the impeding layer. Additional infiltration tests suggest that this capacity is exceeded on grassy surfaces where steady state rates of 4 or more inches per hour can be expected. Under the climatic conditions in the Moscow basin erosion is minimal on such surfaces.

Measured infiltration rates in loess are often influenced by the presence of 5/16 inch diameter tubular openings which have been observed in the loess extending to depths of at least 30 feet. Frequency of the tubular openings decreases from about 10 per square feet near the surface to about 5 per square foot at depths of 20 to 25 feet. Near the surface most of the openings are filled with a material having an x-ray pattern that suggests a mixture of topsoil and loess. On the basis of infiltration tests using dyed water those openings that are not filled conduct water ahead of the saturation front. As water moves through the openings, it moves into smaller rootlet holes and intergranular pore spaces in the walls of the openings. Whether the openings are effective in the natural infiltration process depends on the condition of the surface and on intensity of precipitation. Sufficient water must be available from precipitation to saturate the soil above the openings and, in addition, the condition of the surface must be such that the available water can be transmitted through the soil between the surface and the tubular openings. The latter condition is met on grass covered surfaces on the loess. Precipitation sufficient to meet the first condition occurred at least twice during the spring of 1968. After the .58 and .55 inch rainfalls on March 25 and May 22, respectively, seeps were observed above the B-horizon beneath grassy surface in several cuts in the loess. A zone of positive pressure above the B-horizon is thereby indicated. Water levels in shallow piezometers responded to both events. The amount of precipitation required to produce a zone of positive pressure above the openings depends on the porosity and permeability of the soil layer and on the moisture content of that layer at the time of the precipitation event. If .5 inches of precipitation can be considered as somewhat representative of the minimum required for the formation of a zone of positive pressure during a given precipitation event, then, according to the data presented by Klages (1942), 7.77 percent of the precipitation events at Moscow, Idaho, are capable of producing a zone of positive pressure. However, at present these figures can be considered only as approximations; more data are needed for conclusive statements.

Two additional problems related to the quality of ground water were examined during the course of this project. These problems are the factors that control

the movement, both rate and route, of water through loess soils, and the role played by groundwater flow systems in the origin of the group of mineral deposits known as evaporites. The results of both these studies have been accepted for publication and are listed in the subsequent section entitled, "Publications Resulting from Project". A brief summary of these two publications follows.

Available brief hydrographs of shallow piezometers installed within the loess indicate the presence of local, gravity ground-water flow systems similar to those described by Toth (1966). Comparison of hydrographs of a stream and piezometers within one of these systems with records of precipitation reveals that the water table in the local flow systems fluctuates directly with precipitation during the wetter portions of the year, which occurs during the winter and early spring when evapotranspiration is at a minimum. Long term hydrographs of wells in artesian zones portray a similar fluctuation of potential in the upper, confined aquifers. Both lines of evidence suggest that ground water is recharged during the wet season by infiltration in and percolation through the loess. According to the hydrographs little recharge occurs during the growing season or early fall.

It is possible that by surface conditioning appropriate to maximization of infiltration, the tubular openings which are void can be utilized to induce ground-water recharge. Erosion concomitantly would be reduced. Examples of techniques that might be employed include rough tillage, contour strip-cropping, contour plowing and rotation of sod and hay crops with winter wheat.

The second paper prepared and published as an outgrowth of this research, deals with the general subject of ground-water flow systems as related to water quality. The source of the data for this article is a number of heretofore unrelated studies presented in the literature. The publication clarifies the relation to be anticipated between certain types of flow systems and the occurrence of certain types of water. It consists of an examination of basin and interbasin flow systems and the graphical illustration of how they are related to evaporate mineral dissolution, transportation, and accumulation by ground water.

Fluid potential measurements coupled with water quality studies which have demonstrated that water quality decreases with flow-path length; isotope studies which have shown that some brines are composed of meteoric water; and data on salt discharge rates all serve as evidence that regional and intermediate flow systems may supply appreciable dissolved materials to

evaporite basins.

A plausible explanation for the absence of poor quality water in some flow systems is inherent in the models. The absence of appropriate hydrogeologic boundary conditions limits the development of regional and intermediate systems and accentuates the smaller systems with shorter flow lines and concomitant better quality water. The accumulation of dissolved solids is thereby precluded in the ground waters of basins where such hydrogeologic conditions prevail.

An explanation of the occurrence in evaporite deposits of compounds not common to sea water is provided by the differences in the dissolved constituents of brines and those of sea water. Furthermore, cyclical variations within the evaporite deposits of a given basin may be explained by the cyclical addition of dissolved and suspended solids from marine or fresh surface-water sources to the more consistent quality of discharge from ground-water flow systems.

Mathematical models of ground-water flow systems offer a tool for the quantitative examination of the addition of dissolved solids to evaporite basins by ground water. Mass balance techniques can be utilized to assess the relative importance of ground-water and surface-water sources if evaporite basins are viewed as a part of the hydrogeological environment in which these flow systems are operative or have been operative. Freeze (1967) describes a procedure that may be applicable in some cases.

PUBLICATIONS RESULTING FROM PROJECT

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2. Williams, R. E., Ground-water Flow Systems and the Accumulation of Evaporite Minerals: Bull. Amer. Assoc. Petrol. Geologists (in press).
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