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SORPTION AND MINERAL EQUILIBRIA CONTROLS ON MOISTURE CHEMISTRY IN A C-HORIZON SOIL

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ABSTRACT

Sears, S.O. and Langmuir, D., 1982. Sorption and mineral equilibria controls on moisture chemistry in a C-horizon soil. J. Hydrol., 56: 287—308.

A study was made of the chemistry of soil moisture collected over a period of 12 months from sandy loam soils in central Pennsylvania. Samples were taken at depths of from 1 to 9 m by means of suction lysimeters. The prevalent chemical character of soil moisture was generally $Ca^{2+} > Na^+ > Mg^{2+} \approx K^+$, with $HCO_3^- > Cl^- > SO_4^{2-} \approx NO_3^-$ on both a mole and weight basis. Soil-moisture pH ranged from 5.20 to 6.74. Dissolved silica averaged 54 mg/l (as SiO_2) and was as high as 117 mg/l. The specific conductance ranged from 20 to 400 $\mu S/cm$. Total dissolved solids (TDS) in the water increased with decreasing atmospheric precipitation and increasing temperature. This was due to evapotranspiration, which increased TDS directly, and also indirectly by reducing soil relative permeabilities and increasing the contact time between soil minerals and water. A secondary cause was greater precipitation acidity during the warmer months and during periods of lower precipitation.

Soil colloids are predominantly Fe- and Mn-oxyhydroxides, with usually smaller amounts of illite and kaolinite. Total cation exchange capacity is 2—3 meq./100 g. Regression analysis of dissolved-ion activities showed that the aquo-cations are strongly buffered by Donnan equilibrium and selective adsorption with selectivities in the order $K^+ > H^+ > Mg^{2+} > Ca^{2+}$. Calculation of the degree of saturation of the soil moisture with respect to soil minerals showed that the soil moisture is undersaturated with respect to calcite, dolomite, amorphous silica and illite, and super-saturated with respect to quartz and probably also kaolinite. Sorption equilibria controlled major-cation concentrations at all depths in the soil, whereas solution—mineral equilibria did not limit concentrations of these cations.

INTRODUCTION

The region between the land surface and the groundwater table (the

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vadose zone) determines the composition of groundwater recharge and is the locus of most active weathering of the bedrock. Knowledge of chemical processes active in the vadose zone is required for understanding the chemical budgets of weathering and groundwater recharge. Among major controls on water composition are concentration by evapotranspiration, and the various interactions between water and soil materials.

These interactions include ion exchange, selective adsorption or fixation, and solution and precipitation of minerals. Ion exchange and selective adsorption reach equilibrium in seconds to days (Grim, 1968; Malcolm and Kennedy, 1970), while the attainment of solubility equilibrium may take much longer. For example, the time required for reconstitution of clays ranges from months to 10^4 yr. or longer (Kittrick, 1969; Hem and Lind, 1974; Henderson et al., 1976). Marshall et al. (1973) posed the following questions of fundamental importance in soil—water relationships:

(1) Is the chemistry of the vadose water dominated by colloid—chemical factors such as Donnan relationships or by solubility equilibrium with various mineral phases?

(2) How can these be distinguished if both are present?

The operation of Donnan equilibrium relationships and selective adsorption in soils has been well documented and is summarized by Kardos (1964) and Wiklander (1964). More recently, application of mineral stability data to soils has been published by Kittrick (1969, 1971a, b, c), Routson and Kittrick (1971), Weaver et al. (1971), and Henderson et al. (1976), among others. Attempts to combine these two approaches have been made by Marshall et al. (1973) and Upchurch et al. (1973). These investigations have mostly been concerned with the A- and B-horizon soils, where both soil samples and associated moisture are readily available. Studies have also been made in which the chemistry of surface and groundwaters was related to its previous modification by clay—mineral equilibria within the vadose zone (Feth et al., 1964; Garrels and Mackenzie, 1967; Paces, 1972; Norton, 1974; Miller and Drever, 1977).

The C horizon has been largely neglected by soil scientists and groundwater geochemists, lying as it does in between their principal zones of interest. The difficulty of obtaining representative soil and water samples from subsoils has also limited their detailed examination.

This report attempts to answer Marshall's questions for a deeper subsoil or C horizon to depths of 9 m. The soil studied was a sandy loam over dolomite bedrock in central Pennsylvania. Soil-moisture samples for chemical analysis were collected in situ by means of suction lysimeters (Parizek and Lane, 1970). Soil samples for determination of mineralogy and moisture content were obtained during lysimeter installation. A semi-empirical approach, based on regression analysis of soil-moisture chemical composition measured monthly for one year (October 1973—September 1974), was used to appraise the effects of ion exchange and selective adsorption. Solution—mineral equilibria were examined by computer calculation.

SAMPLING SITE

The sampling site is located ~4 km northwest of the city of State College, in Nittany Valley, Centre County, Pennsylvania. The site is beneath a grassy area immediately adjacent to a cornfield on one side and to deciduous woods on the other. The geology and groundwater hydrology of the general area have been described by Landon (1963) and Parizek et al. (1971), respectively, and the groundwater geochemistry by Langmuir (1971) and Jacobson (1973).

Soil at the site is the Morrison sandy loam (Cunningham et al., 1972), a residual soil developed by weathering of the underlying Upper Sandy Member of the Gatesburg Formation of Cambrian age. The Gatesburg is chiefly a sandy dolomite which contains large dolomite float boulders. Local bedrock depth is very irregular and ranges from 6—14 m, based on drilling with a truck-mounted auger. Depth to the water table under the site is 60—90 m.

METHODS OF SAMPLING AND ANALYSIS

Lysimeter installation

Water samples were collected from the C horizon with suction lysimeters* (Fig. 1). Lysimeter assembly and installation were carried out using the procedures described by Parizek and Lane (1970), except that we substituted nylon tubing for copper tubing. Suction lysimeters were installed at different depths in holes of 10—15 cm diameter drilled to 9 m total depth with a truck mounted auger. During the drilling, soil samples were collected from the auger for later laboratory analyses. The locations of the lysimeters at the sampling site and soil—bedrock and —groundwater relations are shown in Fig. 2.

Prior to lysimeter installation, distilled water (specific conductance ~4 μS/cm) was run through the lysimeter tips until the specific conductance of the water passing through the tips was less than 10 μS/cm. This was to minimize contamination of samples by the lysimeters themselves. The lysimeters were then buried in the soil, and a vacuum of ~0.3 atm. applied by means of a hand-pump. The vacuum caused soil water held with a matrix potential (capillary and osmotic attraction) less than 0.3 atm. to move from the soil into the lysimeter. This sampling method made it possible to obtain soil moisture from the same location over an extended period of time without removing the soil.

The water collected by the suction lysimeters is that which is held onto the soil particles with the least matrix potential. Isotopic fluctuations present in rainfall were observed at 9-m depths (Sears et al., 1976). This indicates

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* Manufactured by Soil Moisture Equipment Co. of Santa Barbara, California, U.S.A.
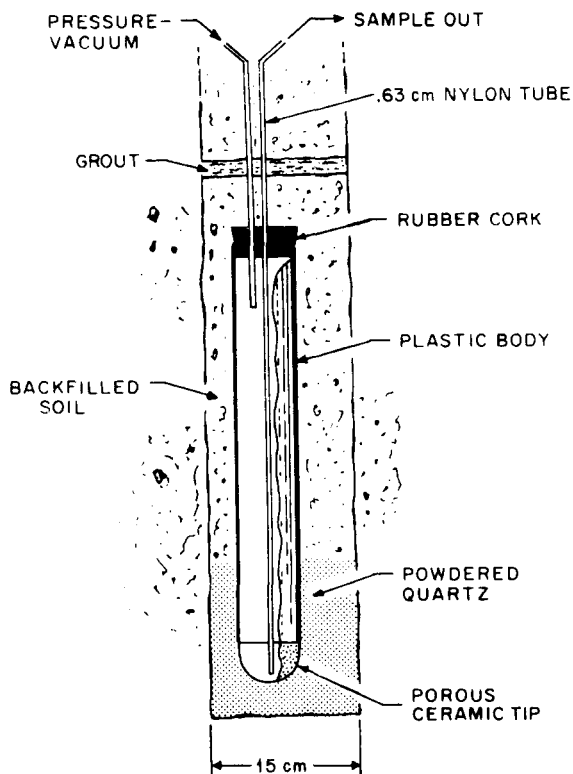
Fig. 1. Cross-section of a suction lysimeter from Parizek and Lane (1970). Vertical dimensions are not to scale. Distance from grout to lysimeter tip is ~2 m. The lysimeter is ~90 cm in length and 5 cm in diameter.

that the water collected by the lysimeters is infiltrating rapidly through the larger pores, and has not reached isotopic equilibrium with the bulk of the soil water. The waters collected in this study will also exhibit chemical differences with the soil water held in small pores. The lysimeter samples are considered representative of "gravitational" water, which moves downward to the water table and constitutes the bulk of groundwater recharge.

Although the use of lysimeters allows collection of relatively undisturbed samples, removing the water from the soil particles and storing it in a tube until collection induces some changes in the water chemistry. The most important of these for purposes of this paper is the exsolution of CO_2 from the water into the gas phase of the lysimeter. Sears (1976) calculated the extent of CO_2 exsolution. The maximum resultant error in pH for the volume of water samples (~750 ml) and the maximum time interval that the water was present in the lysimeters (1 month) should be a rise of ~$+0.11$ pH units. The data have not been corrected for this effect.

Besides CO_2 exsolution and contamination by the lysimeters, silica contributions by amorphous silica or other minerals contained in the quartz sand
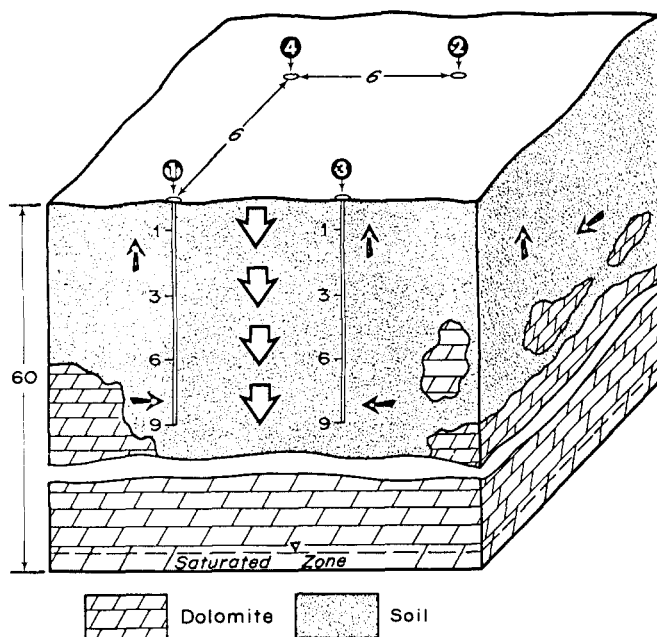
Fig. 2. Schematic block diagram of the research site, showing locations of lysimeters and holes with inferred relationships to bedrock and groundwater. *Open arrows* indicate the principal movement direction of soil water. *Smaller solid arrows* show the occasional direction of soil-water movement. Lysimeter depths are identical in all four holes. Dimensions are in meters.

(Fig. 1) in which the lysimeter tip is imbedded and by the lysimeters is a possibility. However, lysimeters were installed without sand in this and in other sampling sites. Such installations did not show lower silica levels. There is no indication that the sand contributed silica in excess of quartz saturation. Silica contributed by the lysimeters to pure water is less than expected from saturation with quartz (Wolff, 1967).

Once samples had collected in the suction lysimeters, the water was forced to the surface, using argon gas from a pressure tank. A 50-ml water sample was placed in a polyethylene bottle and acidified immediately for laboratory analysis of cations by atomic absorption spectroscopy. The pH was measured in the field after calibrating the electrode and meter with two nominal 4.0, 5.0 and/or 6.86 buffers adjusted to within $\pm 2^{\circ}C$ of the sample temperature. Measurements were made using a Coleman Medallion[®] pH-millivolt meter and a combination pH-reference electrode and are considered accurate to ± 0.05 pH units. Temperature was always measured in the field (precision $\pm 0.1^{\circ}C$) with a glass thermometer.

Laboratory analyses

Samples for cation and SiO_2 analyses were diluted with deionized water.

Ca^{2+}, Mg^{2+}, Na^+, K^+ and SiO_2 were determined on a Perkin Elmer[®] model *403* atomic absorption spectrophotometer, using procedures outlined by Brown et al. (1970), and are considered accurate to ±5%. Specific conductances (SpC's) were measured in the laboratory within 6 hr. of collection on a Beckman[®] model RC-*16* conductometer and corrected to 25°C. Sulfate, nitrate, bicarbonate and chloride were measured as described by Langmuir (1971). These analyses were required to compute the ionic strength of the water and adjust free-ion activities for the effects of ion pairs. The ionic strength of all water samples was less than $2 \cdot 10^{-2}$ m. Charge balances were not as good as when these same analytical techniques were used on local groundwaters. Anion equivalents commonly exceeded cation equivalents, due to the fact the Fe and Mn were not analyzed but may constitute an appreciable fraction of the cation charge in the lower-conductance samples (based on Fe and Mn data from Wright (1978)).

Soil analysis

Once collected in the field, soil samples were immediately sealed in plastic bags. The soils were analyzed for water content directly upon their return to the laboratory by drying at 110°C for 24 hr. The percent of the soil less than $4 \mu m$ in size was determined by pipette analysis, using a $Na_2C_2O_4$—Na_2CO_3 dispersing solution as described by Griffiths (1967). An X-ray slide for identification of the clay minerals and estimation of their relative amounts was also prepared from the <4-μm fraction of the samples. Relative percentages of the different clay minerals were calculated from X-ray peak heights of patterns from slides heated for 1 hr. at 180°C and from slides saturated with ethylene glycol (Griffin, 1971). Amounts of iron and manganese were determined by atomic absorption analysis of the leachate from boiling 0.5 g of soil in 120 ml of 10% HNO_3 for 1 hr. Slides of soil minerals were examined with a petrographic microscope in an attempt to detect trace amounts of carbonate minerals.

RESULTS

Results of the soil and water analyses are summarized in Tables I and II. More complete data, including the isotopic composition of oxygen, deuterium and dissolved inorganic carbon, are given in Sears (1976).

Soil

Results of the soil analyses show that the soil consists predominantly of quartz, with minor amounts of iron and manganese oxyhydroxides, illite, kaolinite and organic carbon. The organic carbon value given in Table I is an estimate from Cunningham et al. (1972) in this soil several kilometers

TABLE I

Composition of the C horizon (1—9 m deep) of Morrison loamy sand at the research site based on this study (see also text)

Component or fraction	Weight percent dry soil	Weight percent wet soil
Clay fraction ($<4\,\mu m$)	0.1—4% of total soil (mean 1.7%)	
Illite	30% of clay fraction	
Kaolinite	70% of clay fraction	
Fe as Fe_2O_3	2.4—3.2% (mean 2.7%)	
Mn as MnO_2	0.07—0.10% (mean 0.08%)	
Organic carbon[*]	0.04%	
Quartz	remainder (assumed)	
Water content (June 1973)		16—29% (mean 23%)

[*] Organic carbon content is an estimate from Cunningham et al. (1972).

away. Carbonate minerals were not detected in X-ray diffraction patterns of the soil samples nor in petrographic examination of soil material. However, large dolomite float boulders are known to be present based on outcrops and other nearby core holes. These boulders are believed to be the only source of carbonate minerals present at this location. Amorphous alumino-silicates (Paces, 1972) may be present but could not be identified by our analysis.

Water content at the time of sampling ranged from 16—29%. There was no appreciable increase or decrease in water content below 2 m. However, all holes showed a decrease in water content above 2 m, indicating that evapotranspiration was drying out the shallower soils.

Measurement of exchangeable cations on the Morrison sandy loam by Apgar and Langmuir (1971) and Cunningham et al. (1972) shows that total exchange capacity ranges from 1.7 to 5.0 meq./100 g of soil. Percent base saturation varies from 20 to 65%, and the order of preference of adsorbed cations is generally $H^+ \gg Ca^{2+} \approx Mg^{2+} > Na^+ \approx K^+$. Exchangeable aluminum was not determined by either study, and the exchangeable H^+ may include portions released by hydrolysis of adsorbed Al^{3+} (Clark, 1964). Since iron and manganese oxyhydroxides are present in appreciable amounts and have surface charge properties that vary with pH, the total cation exchange capacity of the soils will vary with the pH of the soil moisture.

Water

A total of 146 samples were analyzed for Ca^{2+}, Mg^{2+}, Na^+, K^+, HCO_3^-, Cl^-, SO_4^{2-} and NO_3^-. Sixty-eight of these samples were analyzed for SiO_2, and these are presented in Table II. Specific conductance, temperature and pH data are also given for these samples. Rainwater was collected systematically for isotopic analysis on the roof of the Deike Building on the Penn State

TABLE II

Chemical data for soil moisture samples and rainfall (hole locations are shown on Fig. 2; depth is in m; dissolved solids are in mg/l; temperature is in °C; specific conductance is in $\mu S/cm$, corrected to 25°C; saturation indices, free energies and $\log P_{CO_2}$-values are discussed in text)

Hole	Date	Depth	Ca^{2+}	Mg^{2+}	Na^+	K^+	HCO_3^-	NO_3^-	Cl^-	SO_4^{2-}	SiO_2	T	pH	SpC	SI_c	SI_d	$\log P_{CO_2}$	ΔG (ill–kaol) (kcal./mol)
3	Oct. 10, 73	3	108	7.3	21	5.0	144	53	55	17	95	12.7	6.47	106	-0.92	-1.44	-1.39	-4.00
1	Nov. 9, 73	6	1.8	0.7	3.1	1.3	15.1	7.4	3.7	1.7	55	11.1	5.87	38	-4.20	-4.34	-1.75	-5.97
2	Nov. 9, 73	6	2.6	0.5	3.1	1.4	18.3	4.4	4.1	1.5	59	10.0	5.99	44	-3.86	-4.16	-1.79	-5.75
2	Nov. 9, 73	9	1.0	0.4	1.6	1.0	9.8	3.0	2.4	1.7	15	10.0	6.01	26	-4.51	-4.65	-2.08	-6.79
3	Nov. 9, 73	6	72	2.8	14.3	4.7	118	14	59	6.0	95	10.0	6.64	285	-1.03	-1.68	-1.65	-3.89
3	Nov. 9, 73	9	7.9	0.9	5.1	1.8	23	7.0	17	5.5	70	10.5	6.28	88	-3.02	-3.44	-1.99	-5.06
4	Nov. 9, 73	6	7.5	0.6	11.4	1.9	35	8.3	5.2	5.5	51	10.5	5.96	110	-3.20	-3.69	-1.48	-5.80
4	Nov. 9, 73	9	46	1.9	11	3.7	35	27	30	50	95	9.5	6.74	235	-1.31	-1.95	-1.95	-3.87
3	Dec. 7, 73	3	8.2	0.8	5.5	2.1	21	11	8.6	1.8	22	10.2	6.21	92	-3.08	-3.53	-1.95	-5.92
3	Dec. 7, 73	1	10.2	1.3	14.1	3.0	66	40	8.7	4.7	109	7.4	6.39	196	-2.38	-2.80	-1.65	-4.39
1	Jan. 8, 74	1	3.4	1.0	7.9	4.6	2.9	28	5.7	0.1	41	3.2	5.88	81	-4.76	-5.01	-2.51	-5.60
1	Jan. 8, 74	6	2.1	0.6	2.2	1.3	6.1	4.7	1.8	0.7	76	8.5	5.76	31	-4.67	-4.89	-2.04	-5.90
2	Jan. 8, 74	6	2.6	0.6	2.9	1.6	10.2	4.2	2.6	0.2	74	8.6	5.62	39	-4.49	-4.76	-1.68	-6.05
3	Jan. 8, 74	1	7.1	1.1	11.2	2.9	21	26	5.8	0.1	101	2.7	6.18	100	-3.29	-3.68	-1.96	-4.73
3	Jan. 8, 74	6	8.5	0.8	11.3	1.8	32	5.8	2.4	15	55	8.3	5.86	106	-3.27	-3.75	-1.43	-5.84
4	Jan. 8, 74	9	29	1.2	8.5	2.9	31	15.6	14	7.0	112	7.9	6.54	156	-2.09	-2.74	-2.13	-4.18
3	Feb. 1, 74	3	44	3.8	12.4	3.1	14.6	8.1	2.1	55	67	7.1	5.87	254	-2.96	-3.45	-1.79	-5.30
1	Mar. 4, 74	6	1.7	0.6	2.9	1.4	4.1	8.7	2.3	2.6	53	9.4	5.54	32	-5.17	-5.34	-1.99	-6.53
1	Mar. 4, 74	9	1.6	0.6	2.6	1.4	4.9	10	2.5	1.9	41	10.1	5.52	34	-5.09	-5.25	-1.89	-6.65
2	Mar. 4, 74	6	2.7	0.8	1.8	1.6	9.8	4.3	3.1	7.7	63	9.4	5.57	43	-4.54	-4.75	-1.64	-6.20
2	Mar. 4, 74	9	1.4	0.3	1.0	0.8	4.1	5.0	2.4	1.9	15	9.7	5.46	24	-5.28	-5.57	-1.90	-7.70
3	Mar. 4, 74	3	12.3	1.0	4.0	2.4	35	9.8	11	2.5	91	6.2	6.17	85	-2.79	-3.30	-1.71	-4.91
3	Mar. 4, 74	6	19.6	1.6	6.7	1.3	48	10	5.3	10	91	9.6	6.65	137	-1.94	-2.43	-2.04	-4.08
3	Mar. 4, 74	9	4.4	0.5	1.4	1.6	9.0	6.0	2.4	3.9	67	9.7	5.94	40	-3.98	-4.40	-2.05	-5.77
4	Mar. 4, 74	1	14.8	1.4	4.6	1.6	3.7	31	2.7	18	40	4.7	5.92	92	-3.97	-4.46	-2.44	-5.89
4	Mar. 4, 74	9	21	1.2	3.5	2.7	32	15	3.5	8.5	72	9.6	6.10	117	-2.62	-3.19	-1.66	-5.12
1	Apr. 3, 74	1	1.6	0.7	10.9	1.1	0.0	23	3.7	4.2	38	5.5	5.51	69				-6.72
2	Apr. 3, 74	6	1.7	0.7	2.5	1.2	4.6	7.8	1.9	5.6	63	9.3	5.48	34	-5.16	-5.34	-1.88	-6.45
2	Apr. 3, 74	1	2.6	0.6	4.0	1.0	2.4	14	4.9	4.2	77	5.2	5.58	44	-5.22	-5.51	-2.28	-6.21
3	Apr. 3, 74	3	6.0	0.7	3.2	1.6	22	10	27	3.3	83	6.6	5.94	54	-3.51	-3.95	-1.67	-5.49
4	Apr. 3, 74	6	18.8	1.6	5.3	2.9	47	14	9.7	11	117	9.4	6.48	121	-2.14	-2.62	-1.88	+1.39
4	Apr. 3, 74	9	4.0	0.5	1.5	1.4	6.8	5.9	2.0	4.8	90	10.3	5.84	34	-4.25	-4.64	-2.06	-5.69
4	Apr. 3, 74	1	16.3	1.4	5.7	1.7	0.0	33	2.7	18	38	5.7	5.82	117				-6.76
4	Apr. 3, 74	3	23	1.4	5.7	1.9	19.5	7.8	2.4	30	34	7.4	5.84	159	-3.11	-3.68	-1.63	-6.09
4	Apr. 3, 74	6	4.6	0.6	28	1.6	47	12	2.8	26	41	9.2	6.02	152	-3.24	-3.63	-1.42	-5.86
4	Apr. 3, 74	9	14.5	1.1	3.7	2.1	28	15	3.6	15	50	9.8	5.98	104	-3.19	-3.58	-1.60	-5.66
2	May 1, 74	3	8.3	2.1	2.9	1.2	5.1	5.7	3.1	26	44	8.9	5.50	96	-4.44	-4.70	-1.86	-6.51
2	May 1, 74	6	17.3	3.4	2.4	2.1	5.6	5.8	3.2	35	59	9.8	5.40	160	-4.18	-4.48	-1.72	-6.21
3	May 1, 74	9	1.3	0.6	2.6	1.3	0.7	4.9	2.6	5.5	32	11.0	5.44	30	-6.10	-6.20	-2.65	-6.98
2	May 1, 74	6	22	1.9	6.5	3.2	48	10	8.2	14	77	9.5	6.37	137	-2.20	-2.69	-1.77	-4.57
4	May 1, 74	6	3.4	0.5	23	1.2	21	7.0	3.0	17	59	9.7	6.14	123	-3.57	-3.92	-1.89	-5.61

	Date																		
4	May 1, 74	9	10.5	1.0	6.5	1.9	19.5	11	2.7	16	42	10.6	6.19	97	3.05	3.49	1.96	5.52
1	Jun. 12, 74	6	2.3	0.8	1.9	1.1	1.2	8.5	1.6	10.0	29	10.8	5.42	114	−5.65	5.82	2.40	2.61
2	Jun. 12, 74	3	10.8	2.5	2.0	1.2	4.9	9.0	3.9	28	41	10.3	5.33	126	4.50	4.76	1.70	6.21
2	Jun. 12, 74	6	18.3	3.3	2.3	1.9	0.1	16	2.0	65	42	10.4	5.32	220	6.01	−6.32	−3.39	6.03
3	Jun. 12, 74	3	2.2	0.5	2.5	1.3	1.6	9.9	2.4	5.0	56	12.8	5.56	38	5.37	5.62	−2.40	−5.05
3	Jun. 12, 74	9	3.3	0.4	1.1	1.1	6.7	11	1.3	4.9	54	11.2	5.71	36	−1.43	−4.84	−1.94	4.98
3	Jun. 12, 74	1	16.2	1.4	7.3	1.7	4.9	41	2.5	20	32	16.3	5.67	137	3.90	4.34	2.01	−5.08
4	Jun. 12, 74	9	9.2	1.1	6.5	1.9	19.5	12	2.1	18	41	11.5	6.02	97	3.26	3.65	1.79	3.88
1	Jul. 15, 74	3	2.0	1.1	2.1	1.1	1.9	6.8	1.8	9.0	39	12.3	5.44	36	5.47	5.53	2.21	5.71
2	Jul. 15, 74	6	10.5	1.9	2.1	1.4	4.9	7.2	2.6	28	38	12.4	5.32	99	4.50	4.79	1.68	6.08
2	Jul. 15, 74	3	26	3.2	2.5	2.1	4.9	5.8	2.6	38	31	10.9	5.28	189	−4.16	−4.56	−1.66	−6.66
3	Jul. 15, 74	9	1.3	0.6	2.3	2.2	3.0	3.7	2.0	6.0	24	15.0	5.25	28	5.68	−5.77	1.83	−7.45
3	Jul. 15, 74	3	2.3	0.5	3.0	1.6	3.0	7.9	2.6	4.5	31	12.2	5.64	56	4.97	5.21	2.20	5.07
4	Jul. 15, 74	6	3.4	0.4	1.1	1.1	6.3	4.2	1.6	6.7	42	11.7	5.72	30	−4.43	−5.83	−1.96	6.51
1	Aug. 15, 74	6	17.2	1.3	6.3	1.6	6.7	12	2.4	29	31	11.3	5.64	120	−3.83	−4.33	1.87	−6.50
2	Aug. 15, 74	6	3.4	0.5	25	1.3	47	11	2.7	22	39	13.3	5.96	133	−3.39	3.74	1.35	6.14
2	Aug. 15, 74	9	1.6	0.8	1.9	1.0	1.2	5.6	1.4	5.8	36	11.8	5.35	30	−5.83	−5.91	−2.31	−7.10
3	Aug. 15, 74	6	15.5	2.3	2.4	1.8	4.1	5.9	2.1	61	42	11.0	5.27	130	−4.49	−4.84	1.72	6.76
3	Aug. 15, 74	3	1.3	0.6	2.3	1.0	1.2	3.5	2.1	7.7	26	11.5	5.20	26	−6.11	−6.22	−2.17	7.54
4	Aug. 15, 74	6	4.9	1.0	3.4	1.0	4.9	5.6	1.2	14	52	11.1	5.45	60	4.68	−4.96	−1.81	6.57
1	Sep. 12, 74	6	3.0	0.4	1.0	1.3	4.9	6.1	1.3	6.2	52	12.9	5.69	29	4.64	5.02	2.05	−6.34
2	Sep. 12, 74	9	15.5	1.2	5.9	1.6	12.2	12	23	20	31	15.0	5.49	109	3.74	−4.22	−1.45	−7.93
2	Sep. 12, 74	9	1.4	1.0	1.5	1.0	0.7	5.2	1.3	3.5	44	12.0	5.48	28	5.96	5.96	2.67	6.77
3	Sep. 12, 74	3	9.4	2.7	2.0	1.7	2.2	5.5	2.8	37	48	11.7	5.32	124	−4.91	5.11	2.03	6.60
4	Sep. 12, 74		1.0	0.3	0.9	0.6	1.7	3.7	1.5	2.0	27	12.3	5.58	26	5.67	−5.87	−2.40	7.25
	Sep. 12, 74		2.8	0.4	0.8	0.8	5.1	4.9	1.5	2.2	52	14.2	5.80	29	4.51	4.87	−2.14	6.36
	Sep. 12, 74		12.2	1.5	4.8	1.1	10.7	13	2.4	17	52		5.61	108	−3.76	−4.14	−1.63	−6.38
MAP3S precipitation (weighted average, Sep. 76—Jul. 78)			0.1	0.01	0.04	0.04	0.0	1.9	0.16	2.9								3.5–4.8

Campus. However, the concentrations of dissolved solids of this rain water are not considered representative of precipitation chemistry at the sample site, due to the urban location of the Deike Building. Beginning in September of 1976, precipitation was collected systematically in a rural setting ~ 5 km from the lysimeter site (Bowersox, 1980). This rain water was analyzed by Battelle Laboratories in Richland, Washington, as part of the MAP3S precipitation chemistry network analysis program (MAP3S Precipitation Chemistry Network, 1977, 1978). Average concentrations, weighted by the amount of precipitation, are shown in Table II for the period September 1976—June 1978. These values should be representative of the average recharge chemistry.

The saturation indices of calcite and dolomite [SI_c and SI_d, Langmuir (1971)] and the partial pressure of carbon dioxide were calculated on an IBM$^{\circledR}$ *370/168* computer using the program WATEQF (Plummer et al., 1976). Iron, manganese and aluminum were not analyzed, so similar calculations could not be made for the soil components involving these species. However, the free-energy change (ΔG_r^0) for the illite $\rightleftharpoons$ kaolinite reaction:

$$K_{0.6} Mg_{0.25} Al_{2.3} Si_{3.5} O_{10}(OH)_2 + 3.15H_2O + 1.1H^+ \rightleftharpoons 1.15Al_2Si_2O_5(OH)_4$$
$$+ 0.6K^+ + 0.25Mg^{2+} + 1.2H_4SiO_4 \tag{1}$$
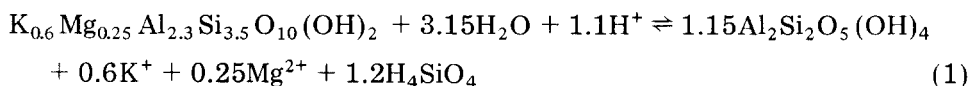
could be calculated assuming aluminum is conserved. Thermodynamic data on which the calculations were based are given in Truesdell and Jones (1974) except we used the free energy of formation for kaolinite given by Bassett et al. (1979) in our calculation of ΔG_r^0 for reaction (1). ΔG_r^0 was evaluated using ion and silica activities computed by WATEQF. While these ΔG_r^0-values cannot prove whether the solution is supersaturated or undersaturated with respect to kaolinite or illite, they do indicate whether reaction (1) will tend to move to the right or left. The computed free energies for reaction (1) are listed in Table II. These values all involve pH, uncorrected for CO_2 exsolution between sampling. Correction of the pH by a maximum error of $+0.11$ pH units does not change the carbonate saturation state of any sample, nor the direction in which reaction (1) would proceed.

CONTROLS ON WATER CHEMISTRY

Recharge—chemical relationships

The specific conductance of samples from individual lysimeters is plotted vs. time in Fig. 3. The conductance plots have been grouped by depth. The average temperature of all samples from the 1- and 9-m lysimeters and the average daily rainfall for the sampling period is also shown.

Comparison of the rainfall composition with the most dilute soil water samples (those with SPC $\approx 25 \mu$S/cm) shows an increase in Ca^{2+}, Mg^{2+}, Na^+,

K^+ and Cl^- by a factor of 10—30. The pH rises from 3.5 to 4.8 in the precipitation to a 5.2—6.0 range in the dilute soil water. Sulfate and nitrate concentrations are only slightly increased in the dilute soil water over their average values in precipitation.

These dilute samples have a fairly constant composition and represent a marked change in the precipitation after it enters the soil. Rain and snow in this area are a mixture of dilute sulfuric and nitric acids (Bowersox, 1980). As the precipitation moves downward through the soil, these acids attack organic matter (A and B horizons) and soil minerals, raising the pH and adding Ca^{2+}, Mg^{2+}, Na^+, K^+ and Cl^-. The most dilute samples in Table II represent a minimum change in the water chemistry. Still higher amounts of dissolved solids occur in most samples due to evapotranspiration and additional soil—water reactions.

Sample temperatures show a range of $\sim 15°C$ at 1 m, and $<5°C$ at 9 m. Increased temperatures at shallower depths were accompanied by increased drying of the soil by evapotranspiration, as evidenced by the decreased water content of soil samples above 2 m. During the hottest part of the year, the matrix potential in the soil exceeds the vacuum inside the lysimeters, and water was unable to move from the soil to the lysimeters. Therefore, the sample record is not as complete for the shallower lysimeters.

Seasonal fluctuations are evident in the chemistry of water from the 1-, 3- and 6-m lysimeters. The higher conductance waters were collected simultaneously from lysimeters at all three depths. The 9-m lysimeters show only a smooth decline in conductance over the year sampled, with a minor increase in one lysimeter at the end of the year.

Comparison of the conductance plots with the temperature and rainfall data shows that all but three of the samples with higher conductance were affected by higher temperatures, reduced precipitation, or both. The most pronounced peak in conductance, which was observed in seven of the sixteen lysimeters, was in June of 1974. These samples were collected immediately following a period of reduced rainfall from mid-May to mid-June, when the temperature of the 1-m lysimeters had risen to $15°C$ from a low of $3.5°C$ recorded in January.

Three lysimeters show an increase in conductance for February samples. Precipitation amounts were near average and temperatures minimal at this time. Analyses of these waters show that they contain relatively high amounts of calcium and bicarbonate, and the highest sulfate of all 146 samples. These samples are believed to have been affected by oxidation of pyrite contained in the Gatesburg Dolomite, which resulted in production of sulfuric acid and dissolution of carbonate rock. The presence of these samples in February may have been caused by flow through the soil from a different direction than in previous months.

There is an overall decline in conductance for many of the lysimeters over the year sampled. Whether this represents a long-term change in the soil chemistry or is related only to the period sampled cannot be determined
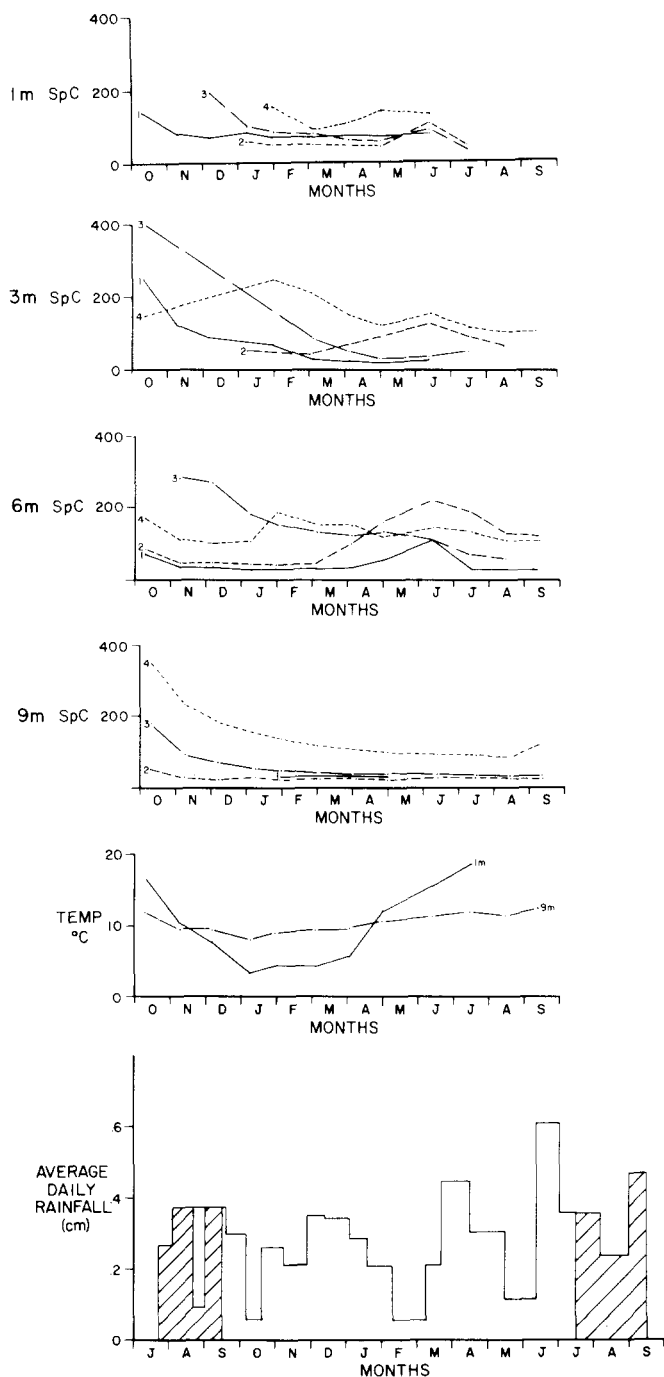
Fig. 3. Variation in specific conductance (in μS/cm) and temperature of soil moisture over year sampled. Average daily rainfall of sampling year and three months immediately preceding sampling year are also shown. *Numbers* at left indicate holes in Fig. 2.

from these data. The plot of average daily rainfall shows an increase in precipitation over the period sampled, which suggests that wetter soil conditions may have prevailed during the summer of 1974 than in the previous summer. For example, the total rainfall between July 15 and September 15 was 20% higher in 1974 than in 1973.

The general relationship between conductance and both temperature and reduced precipitation is due to: (1) concentration by evapotranspiration; and (2) reduction of relative permeability to water at lower water saturations (Hillel, 1971), resulting in decreased infiltration rates and a greater time for contact between soil minerals and water. A secondary effect is greater precipitation acidity during the warmer months and during periods of lower precipitation (Bowersox, 1980). Variation in these parameters is reflected in the specific conductance of the soil water at depths from 1 to 6 m. At 9-m depths, the fluctuations have been dampened out so that only variations on the scale of a year are observed.

Mineral solubility

The carbonate saturation indices, P_{CO_2}-values, silica concentrations and ΔG_r^0 for the illite $\rightleftharpoons$ kaolinite reaction in Table I reflect soil-water reactions with soil minerals and gases. However, mineral equilibria do not appear to limit species concentrations in the soil moisture. Infiltration rates are rapid enough so that water infiltrates to 9-m depths and is collected by the lysimeters before equilibrating. Results of the equilibria calculations show:

(1) All samples are undersaturated with respect to both calcite and dolomite, with the degree of undersaturation slightly greater for dolomite. That carbonate rock is being dissolved can definitely be established by measurement of the isotopic composition of dissolved inorganic carbon. Soil CO_2 in the sampling site had an isotopic composition of $-24\%_{00}$ (vs. PDB) while soil moisture had ^{13}C-values as positive as $-6.8\%_{00}$ (Sears, 1976). The only possible source for the additional ^{13}C in the soil water is from carbonate minerals. The dissolved carbon is isotopically too heavy to be explained by fractionation between dissolved carbonate species and a CO_2 gas phase (Deines et al., 1974). Apparently CO_2 generated by root respiration and the decay of organic matter at the site does not form a soil CO_2 gas phase sufficiently large to provide an "open" system for dolomite dissolution as described by Deines et al. (1974).

The carbonate minerals in the soil are present as large boulders of dolomite rock. Calcium values in soil moisture are as high as 108 mg/l, while magnesium remains at levels of less than 7 mg/l. Magnesium released by dolomite dissolution is therefore removed from solution. Magnesium removal is attributed to selective adsorption of Mg^{2+} by soil colloids as discussed in the next section. No calcite is believed present in these soils, and incongruent dissolution of the Gatesburg Dolomite by groundwater was refuted by Jacobson (1973).

(2) Carbon dioxide in the soil water has increased to levels 1 to 2 orders of magnitude above the amount in equilibrium with atmospheric CO_2. This increase is attributed to organic decay and plant-root respiration.

(3) Reaction (1) should proceed to the right, i.e. kaolinite should be forming at the expense of illite in all but one sample.

(4) Silica concentrations are generally supersaturated with respect to quartz and undersaturated with respect to amorphous silica (see Morey et al., 1964). The release of silica into solution by reaction (1) and its subsequent increase by evaporation during the drier months, is believed to contribute to the silica levels above those in equilibrium with quartz. The slight silica supersaturations with respect to amorphous silica in several samples may reflect sluggish kinetics, or the fact that atomic absorption measures the total SiO_2 present, including both silica polymers and monomeric silica acid ($H_4SiO_4^0$). The highest values may include some of these polymers. In general, however, amorphous SiO_2 saturation appears to be the ultimate control on silica levels in these waters. Another possibility is that silica and aluminum activities are in equilibrium with an amorphous aluminosilicate (Paces, 1978). Aluminum data were not available to test this hypothesis.

Ion exchange and selective adsorption

In a soil where the number of moles of bulk soil water relative to the number within the double layer of soil particles is low, the concentrations of ions (especially cations) will be strongly affected by exchange processes with the electrical double layer of the soil colloids. Ratios of adsorbed vs. dissolved cations in the soil at the sampling site were computed from the exchangeable cation data of Cunningham et al. (1972), assuming: (1) 50% soil porosity; (2) a dry-soil density of $2.6\,g/cm^3$; (3) a moisture content of 23 wt.%; and (4) average dissolved-cation concentrations and pH's from this study. The results show that except for sodium, over 95% of the total (exchangeable and dissolved) amount of each cation is present in the soil as an exchangeable ion. These counterions constitute a readily available buffer to minimize changes in dissolved-cation ratios.

There are two possible models for ion exchange. The first is that ions are only attracted to the exchanger by electrostatic forces, for which the Donnan equilibrium is the appropriate model. For example, considering the exchange of H^+ and K^+, if the Donnan model is appropriate:

$$K^+ + HX \rightleftharpoons H^+ + KX \tag{2}$$

where X indicates the exchanger phase. In this type of exchange, any cation exchanges for any other with equal facility, the only requirements being to maintain a charge balance on the clay surface and in the solution, and to maintain a constant electrochemical potential for each species throughout the system.

If the Donnan-type exchange dominates the soil-water—colloid chemistry, and the reservoir of exchangeable cations is large compared to the amount in solution, then the ratios $[Ca^{2+}]^{1/2}/[H^+]$, $[Mg^{2+}]^{1/2}/[H^+]$, $[K^+]/[Na^+]$, etc., should be maintained at fairly constant levels in spite of changes in ion concentrations introduced by other processes. This assumes that there is no long-term change in recharge water chemistry resulting in large volumes of water with significantly different ion ratios moving through the soil. Computation of these ratios for all samples, however, shows that variation in these ratios is only slightly less than the variation in individual cation concentrations. Table II shows that values of $[H^+]$, $[Ca^{2+}]$ and $[Na^+]$ show wide variations, while $[Mg^{2+}]$ and $[K^+]$ are maintained at fairly constant and low levels. Although reaction (1) is proceeding to the right, releasing Mg^{2+} and K^+ to the soil water, and Mg^{2+} is being added as a result of dolomite dissolution, some of this magnesium and potassium is apparently being re-adsorbed by the remaining illite.

Magnesium and potassium are evidently being removed by selective adsorption or fixation. Ideally, such reactions are reversible (Kardos, 1964) and may be superimposed on Donnan equilibrium processes in an unsaturated soil system (Marshall and McDowell, 1965). For potassium:

$$K^+ + X^- \rightleftharpoons KX \rightleftharpoons K_{(s)}X \tag{3}$$

where KX denotes Donnan adsorbed K^+ and $K_{(s)}X$ denotes selectively adsorbed K. The exchange capacity of the exchanger is not constant but is reduced when reaction (3) proceeds to the right, since the selectively adsorbed potassium is not as readily exchanged for other cations. However, a reduction in dissolved potassium will cause reaction (3) to move to the left and reduce the amount of "fixed" potassium and increase the amount of exchangeable potassium (Kardos, 1964). Stated differently, the writing of X^- in the reaction (3) infers the existence of a variable concentration of exchange sites.

The presence of both Donnan-type exchange and selective adsorption means that simple cation ratios will not be constant, since the amounts of dissolved and exchangeable Mg^{2+} and K^+ will be affected by reactions (3) as well as (2). However, the combined effects of ion exchange and selective adsorption can be examined by regressions of cation activities. Consider first the exchange of Ca^{2+} for Mg^{2+} under Donnan equilibrium:

$$Mg^{2+} + CaX_2 \rightleftharpoons Ca^{2+} + MgX_2 \tag{4}$$

If magnesium is simultaneously being selectively adsorbed so that 0.37 Mg^{2+} is adsorbed in addition to every 1.0 Mg^{2+} exchanged for Ca^{2+}:

$$0.37Mg^{2+} + 0.74X^- \rightleftharpoons 0.37Mg_{(s)}X_2 \tag{5}$$

Adding reactions (4) and (5) gives:

$$1.37Mg^{2+} + CaX_2 + 0.74X^- \rightleftharpoons MgX_2 + 0.37Mg_{(s)}X_2 + Ca^{2+} \tag{6}$$
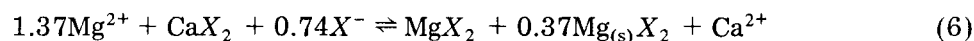
TABLE III

Regression equations based on 146 analyses of soil moisture from the Gatesburg site—also given are correlation coefficients for each equation and adsorption reactions that correspond to the empirical regression equations (the subscript s denotes specific adsorption of the species; slopes of all the regression equations are significantly different from unity at a 99.5% confidence level; the correlations are also significant at a 99.5% level)

Species	Regression equation	Correlation coefficient
H^+ vs. K^+	$pH = 1.32 \log[K^+] + 11.64$	0.66
Ca^{2+} vs. Mg^{2+}	$\log[Ca^{2+}] = 1.37 \log[Mg^{2+}] + 2.27$	0.78
Ca^{2+} vs. H^+ and K^+	$\log[Ca^{2+}]/[H^+] = 5 \log[K^+] + 23.9$	0.79
Mg^{2+} vs. H^+ and K^+	$\log[Mg^{2+}]/[H^+] = 4.3 \log[K^+] + 20.6$	0.81

The equilibrium constant for reaction (6) will be:

$$[Ca^{2+}][MgX_2][Mg_{(s)}X_2]^{0.37}/[Mg^{2+}]^{1.37}[CaX_2][X^-]^{0.74} = K_{eq} \qquad (7)$$

Taking logs and manipulating this expression gives:

$$\log[Ca^{2+}] = 1.37 \log[Mg^{2+}] + \log(K_{eq}[CaX_2][X^-]^{0.74}/[MgX_2][Mg_{(s)}X_2]^{0.37}) \qquad (8)$$

If the changes in the activities of MgX_2, $Mg_{(s)}X_2$, CaX_2 and X^- are small over the year, then a regression of $\log[Ca^{2+}]$ vs. $\log[Mg^{2+}]$ for all samples should give a straight line with a significant correlation coefficient, and a slope of 1.37.

Calculated regressions of monovalent—monovalent, divalent—divalent and divalent—two monovalent cation pairs are given in Table III. The regression analysis was performed on 146 samples, the total number for which the relevant cation analyses were made. The assumption that these are 146 independent samples with a normal frequency distribution, and not twelve replicates of sixteen samples (the number of months and lysimeters) appears to be justified. The conductance plots in Fig. 1 show that there is significant variation in water chemistry with time, depth, and between holes in which the lysimeters are located. All chemical species involved in the regression had approximately log-normal frequency distributions as indicated by moments analysis and χ^2-criteria (Griffiths, 1967).

Equations in Table III involving Ca^{2+}, Mg^{2+}, K^+ and H^+ all showed high correlation coefficients. Equilibrium processes involving ion exchange and selective adsorption with the oxides and clay minerals are believed to have caused these correlations. Regression analysis involving sodium and the above ions did not yield straight lines or significant correlation coefficients. Sodium is not a significant component of the double layer at low concentrations (Seatz and Peterson, 1964) and the ratio of exchangeable to dissolved sodium is the lowest for all species for which this was determined. Evidently, sufficient sodium is not present in the exchangeable form to

Reaction	Order of adsorption
$H^+ + 1.32K^+ + 2.32X^- \rightleftharpoons H_{(s)}X + 1.32K_{(s)}X$	$K^+ > H^+$
$1.37Mg^{2+} + CaX + 0.74X^- \rightleftharpoons Ca^{2+} + MgX + 0.37Mg_{(s)}X_2$	$Mg^{2+} > Ca^{2+}$
$H^+ + 5K^+ + CaX_2 + 4X \rightleftharpoons Ca^{2+} + HKX_2 + 4K_{(s)}X$	$K^+ > Ca^{2+}$ or H^+
$H^+ + 4.3K^+ + MgX_2 + 3.3X^- \rightleftharpoons Mg^{2+} + HKX + 3.3K_{(s)}X$	$K^+ > Mg^{2+}$ or H^+

create an effective buffer. All the reactions postulated in Table III include unoccupied surface sites, balanced by cations as reactants in solution but not in the double layer. That such sites exist in the soil is supported by the clay-related calculations of James and Parks (1982).

Two other processes which could result in high correlations between cations are addition of cations in constant proportions, by evaporation or dissolution of minerals with fixed composition, and thermodynamic equilibrium with soil minerals. Biological consumption would not be expected to produce a single relationship over an entire year in a soil zone, or even to be significant at the soil depths considered (1—9 m). That water is not in equilibrium with carbonates, quartz, or clays is evident from the WATEQF calculations. Addition of cations in constant proportions by dissolution or evapotranspiration would yield a slope of unity in the regression equations. For example, reaction (1) would produce a $[K^+]/[Mg^{2+}]$ ratio of 0.4, and taking logs of this relationship would give $\log[K^+] = \log[Mg^{2+}] + \log 0.4$. Slopes of all regression lines in Table I are significantly different from unity at a 99.5% confidence level.

The constancy of exchanger phase activities over the year cannot be demonstrated, since the soil could not be sampled following installation of the lysimeter. However, the fact that most of a given cation is contained on the exchanger phase makes buffering of the solution cations by that phase a reasonable assumption.

The reactions postulated for the observed regressions are shown in Table III. The operation of both Donnan equilibrium exchange and specific adsorption are required to explain the results. The relationship between H^+ and K^+ indicates that both species are selectively adsorbed, with 1.32 K^+ taken up for every H^+. Apgar and Langmuir (1971) found that H^+ occupies from 20 to 60% of the exchange sites in this soil, in spite of the fact that it is about three orders of magnitude lower in concentration in the solution than any other cation. Even considering the possible presence of Al^{3+} as part of the soil acidity, this is a strong indication of preferential adsorption of H^+

by the soil. Potassium represents a small fraction of the total exchange capacity. This is probably because the K^+ is fixed so strongly by the illite that it is unavailable as an exchangeable cation.

The behavior of Ca^{2+} and Mg^{2+} is best represented by exchange under Donnan equilibrium conditions accompanied by selective adsorption of Mg^{2+} in preference to Ca^{2+}. An additional 0.37 Mg^{2+} is adsorbed for every Mg^{2+} exchanged for Ca^{2+}. From Apgar and Langmuir (1971) and Cunningham et al. (1972), it can be seen that Mg^{2+} occupies a major fraction of the exchange sites, in spite of its low concentration in solution.

Both Ca^{2+} and Mg^{2+} exchange for H^+ and K^+ with the divalent ions exchanging for the pair of univalent ions under Donnan equilibrium conditions, while additional potassium is selectively adsorbed. An extra 4 K^+ are adsorbed if Ca^{2+} is the divalent ion, and 3.3 K^+ if Mg^{2+} is considered. This agrees with the conclusion that Mg^{2+} is adsorbed in preference for Ca^{2+}. By considering all the reactions in Table III, the order of preferential adsorption is $K^+ > H^+ > Mg^{2+} > Ca^{2+}$. Sodium is apparently the least preferred ion. This order does not coincide with that evident on a concentration basis from exchangeable cation analyses described earlier (i.e. $H^+ \gg Ca^{2+} \approx Mg^{2+} > Na^+ \approx K^+$). These analyses (Apgar and Langmuir, 1971; Cunningham et al., 1972) are based on short-term laboratory experiments, whereas the lysimeter samplings reflect longer-term equilibria of both readily exchangeable and specific adsorption reactions. Reactions with potassium and magnesium fixed on basal illite surfaces will be relatively slow to reach equilibrium (Grim, 1968).

The laboratory soil analyses would tend to measure rapidly exchangeable and not fixed ions. If amounts of fixed ions were determined in these laboratory measurements, the relative preferences given above might be identical.

Relative rates of equilibration and infiltration

Based on oxygen and deuterium isotope analysis of soil moisture and precipitation, some of the infiltrating precipitation collected by the lysimeters reaches a depth of 9 m within 1—3 months (Sears et al., 1976). Rates of Ba—K exchange (Malcolm and Kennedy, 1970), and Pb sorption (Soldatini et al., 1976; Zimdahl and Skogerboe, 1977) suggest that sorption equilibrium in soils may be attained in tens of seconds to 48 hr. Rates of solution equilibrium with clay minerals and carbonates vary widely, but are considerably slower. Laboratory clay synthesis and solubility results suggest that under optimum conditions such rates for clay minerals are on the order of months to a few years (Kittrick, 1966; Linares and Huertas, 1971; Routson and Kittrick, 1971; Harder, 1974; Hem and Lind, 1974).

Dissolution rates of carbonate minerals are on the order of ten times faster than such rates for clay minerals but slower than ion exchange. The presence of the dolomite in large boulders rather than disseminated evenly throughout the soil may mean that approach to saturation with carbonate minerals reflects the pathways the water follows during infiltration as well as the time available for dissolution.

As stated earlier, the water collected by the lysimeters is rapidly infiltrating, "gravitational" water which bypasses water held in smaller pores by higher capillary and osmotic attraction. Water held in the smaller pores will infiltrate at slower rates due to the higher matrix potential, and may have a different chemical composition and be more nearly saturated with respect to the soil minerals than the water collected by the lysimeters. This indicates that diffusion gradients should exist between the smaller pores and the larger pore waters sampled by the lysimeters.

SUMMARY AND CONCLUSIONS

Precipitation falling at the sampling site undergoes chemical changes by several mechanisms. The precipitation is a dilute mixture of sulfuric and nitric acids. As these acids contact organic and mineral material in the soil, Ca^{2+}, Mg^{2+}, Na^+, K^+ and Cl^- are added while H^+ decreases.

The combined effects of evaporation and transpiration are believed responsible for the major changes in water chemistry observed on the specific conductance vs. time graphs. These effects include both direct concentration of dissolved species, and indirect concentration by reduction of soil relative permeability, allowing greater reaction time for solution of soil minerals.

Analysis of the chemical composition of 146 soil moisture samples collected over one year shows that solubility equilibria involving calcite, dolomite, quartz, amorphous silica, and the reaction between illite and kaolinite, are not controlling the water chemistry. The possibility of equilibrium with other mineral phases cannot be ruled out, however. Regression analysis shows that ion exchange under Donnan equilibrium conditions accompanied by selective adsorption controls relationships between Ca^{2+}, Mg^{2+}, K^+ and H^+.

The samples studied represent "gravitational" water which is moving downward through the larger pores and recharging the local groundwater table. Continued buildup of dissolved species and attainment of solubility equilibrium is prevented by the short residence time of these waters in the C horizon.

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