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A Mechanism of Cation Transport in a Forest Soil

Many studies have considered quantities and rates of movement of various cation species of the soil solution. Relatively little attention has been given, however, to the mechanisms involved during short periods of rapid flux, such as those associated with a wetting front. One probable factor controlling cation leaching in a mineral forest soil is the anion level of the soil solution. The bicarbonate ion, which comprises a large portion of the total anions present in the soil solution, is formed from carbon dioxide dissolved in percolating water. Such carbon dioxide is derived primarily from microbial action in the forest floor. It is proposed that hydrogen ions associated with the bicarbonate ions replace exchangeable cations from the soil complex. During periods of moisture flow, these cations are transported along with the mobile bicarbonate ions. Experimental results indicate that this mechanism may play a significant role in the transport and leaching of cations in the soil.

Introduction

Various aspects of mineral nutrient cycling have been studied in both agriculture and forestry. Bormann and Likens (1967a) and Cole and Gessel (1968) outlined the aims and methods used in such studies. This article reports on one aspect of the cycling process, the transport process of elemental movement in the soil.

Much research in this field has emphasized cation leaching, particularly as it is related to nutrient additions in the form of fertilizers. In contrast, the mechanism of cation transport has received relatively little attention, although some hypotheses have been made. Cole and Gessel (1965) proposed that the anion component of the soil solution may play a controlling role in regulating cation leaching in a forest soil of the temperate climatic region. Since the soil has a large component of immobile negative charges in the form of the exchange complex, cation mobility is dependent on the production of a mobile anion. If the cation-anion balance of the soil solution is altered temporarily by the addition or subtraction of one ionic species, the equilibrium is restored by an equivalent change in the concentration of oppositely charged ions.

There are many sources of mobile anions. Typically, they originate as a consequence of some specific process such as respiration or nitrification. Limited amounts also enter the system with incoming precipitation and as a consequence of the solubility product of the soil parent material. Land management practices can also significantly influence

the anion sources. Cole and Gessel (1965) have recognized this potential reaction in forest fertilization studies. Other forest treatments such as clear-cutting have also been found to trigger increases in cation leaching by increasing the rate of nitrification (Bormann and Likens, 1967b).

The pH range of most acid, forest soil solutions is about 4 to 6. Most ions, other than the bicarbonate ion, occur only in minor quantities in these solutions because of the unfavorable pH conditions (Hem, 1959; Nye and Greenland, 1960) or because of the nature of their origins, as outlined below.

The bicarbonate ion is of particular interest, therefore, being a mobile anion of probable importance as a mechanism of cation transport in acid forest soils of the temperate region. Nitrate ion concentration in acid forest soils is characteristically lower than that of agricultural soils (Weetman, 1961). At low pH levels, nitrification proceeds slowly even in the presence of an adequate supply of substrate, and the bacterial species responsible for nitrification may even be totally absent (Alexander, 1961). A particular pH limit below which nitrification will not occur cannot be set, because of the variety of influencing factors in the soil. The rate markedly falls off below pH 6.0, however, and becomes negligible at pH 5.0.

Chloride ion levels are normally high in coastal areas only (Carroll, 1965; Wiklander, 1958). Sulfate levels are generally low in acid soils (Hem, 1959). Small amounts of HPO_4^{2-} ions may be present within the pH range of some acid forest soils, but high levels have not been found in the soil studied here (Cole and Gessel, 1965). Borate, fluoride, and other anions rarely occur in measurable quantities in the soil solution (Hem, 1959); thus, they comprise a negligible fraction of the total mobile anions.

Organic colloidal materials may contribute to the transport of cations in the soil (Wiklander, 1958). The pH values of the humic compounds in their "standard state" range from about 2.3 to 3.7 so that they usually carry a net negative charge in the soil solution (Toth, 1964). The amphoteric nature of soil humic colloids prevents definite prediction of their chemical behavior. In addition, degradation of such complexes may occur at pH levels above and below their isoelectric points, which may even lead to changes in the isoelectric points themselves, as well as to changes in the cation exchange capacity. Cations may, therefore, move with organic colloids to some extent, at least, in the near-surface soil where these are most concentrated.

An analysis of the studies by Remezov (1958, 1961), Remezov *et al.* (1964), and Shilova (1959) also suggests that the cation transport in many acid, forest soils of the temperate region may be related to the level of dissolved carbon dioxide in the soil solution. Carbon dioxide in the soil originates primarily from root respiration, from decomposition of organic matter, and from the atmosphere. Carbon dioxide can also exist in solution in the form of the carbonate ion, the bicarbonate ion, or carbonic acid. The form present is a function of pH at a given partial pressure of carbon dioxide and a given temperature. In many forest ecosystems, the pH of the soil solution is in the range (4.5 to 8.3) where dissolved carbon dioxide occurs predominantly as the bicarbonate ion. Where the bicarbonate ion comprises the major portion of the total anions in the soil solution, the associated hydrogen ions could replace readily available cations (e.g., sodium, potassium, magnesium, and calcium) from the soil exchange complex. These cations could then be transported along with the mobile bicarbonate ions.

Exploratory laboratory experiments have been made to (1) determine whether bi-

carbonate ions comprise the major portion of the anions of a forest soil solution, and to (2) examine the effect on the leaching of cations from the soil exchange complex by varying the level of the bicarbonate ion in the solution.

Methods

Soil was sampled from the B horizon of an Everett soil supporting a 36-year-old Douglas-fir (*Pseudotsuga menziesii* (Mirb.) Franco) plantation on the Cedar River Watershed, Washington. Cole and Gessel (1965) and Gessel and Cole (1965) gave a general description of the soil and site of sampling. A column of this soil 30 cm high was set up in a cast acrylic tube, 11 inches (27.94 cm) outside diameter and 1/8 inch (0.32 cm) thick, placed on a porous plate constructed from very fine glass beads. The soil was wetted, brought to moisture equilibrium at a tension of 120 cm of water, and maintained at this tension for the duration of the experiment. Water loss by evaporation from the top of the column was prevented by a cover.

Samples of soil solution from the column were analyzed for total ion concentration, using a recording conductivity bridge. Electrical conductance was converted to ionic concentration (Jackson, 1958). Sodium and potassium concentrations were determined with a spectrophotometer with flame attachments. Calcium and magnesium were determined with an atomic absorption spectrophotometer. Bicarbonate ion concentration was determined by titration with dilute sulfuric acid, using a pH meter to detect the end point at pH 4.5.

Ionic levels are expressed as activities rather than concentrations, because quantitative studies of ionic equilibria and ionic movement necessitate the knowledge of ionic activities. The method developed by Ponnampetuma *et al.* (1966) was followed for estimating ionic strength from specific conductance. Figure 1 of Hem (1961) was used to obtain activity coefficients for each ionic species from ionic strength. Activities for each ionic species were then calculated by multiplying the activity coefficients by the analytically measured concentrations. This method, tested and found reliable for the soil solutions of this study, enables the activity of a particular ionic species to be calculated simply from its measured concentration and the specific conductance of the solution.

The level of bicarbonate ions in the soil solution was varied by two methods. In the first, the temperature of the soil column was changed, and in the second, a concentrated atmosphere of carbon dioxide was imposed above the column.

Experiment 1. The soil column was cooled and allowed to reach temperature equilibrium at 3°C. One liter of distilled water at 3°C, previously boiled to eliminate dissolved carbon dioxide, was then added to the top of the soil column. Successive 100-ml aliquots of the soil solution were collected from the outlet at the base of the soil column and analyzed for their ionic components.

The soil column was then brought to equilibrium at 20°C. One liter of unboiled, distilled water at 20°C was then added. The soil solutions were collected and analyzed as before.

Experiment 2. A constant flow rate of solution was maintained in the above column by regulating the input of distilled water. Column temperature was set at 20°C. Room atmosphere above the column was maintained for the first hour of the experiment, carbon dioxide for the second hour, room atmosphere for the third hour, and

carbon dioxide for the fourth hour. Room atmosphere then replaced the carbon dioxide for the remaining period of the experiment. Successive 100-ml aliquots of the soil solution were collected and analyzed throughout these two cycles of carbon dioxide introduction.

Results

Experiment 1. The bicarbonate ion comprised the major portion of total anions in the soil solution (Figure 1). In addition, there were concomitant fluctuations in the level of total cations and the level of bicarbonate ions. The soil solution from the column at 3°C was less concentrated than that from the column at 20°C, even though the nutrient capital of the soil was slightly depleted during the first run at 3°C, and in spite of a lower average flow rate of 5.22 ml/min at 3°C than the 5.45 ml/min that was found at 20°C. The lower flow rate allowed more time for the soil solution to reach equilibrium with the cation exchange complex of the soil.

Experiment 2. A constant flow rate of 20 ml/min was maintained throughout the experiment (Figure 2). The two consecutive introductions of carbon dioxide above the soil column resulted in concomitant increases in bicarbonate ion and cation concentrations of the soil solution. There was a lag effect, however, of about 50 minutes. Correlation coefficients and simple regression equations were calculated (Table 1), using bicarbonate ion activity as the independent variable and cation activity as the dependent variable.

TABLE 1. Relationships between activities (meq/liter) of bicarbonate ions (independent variable) and cations (dependent variable) of soil solutions in experiment 2. Mean bicarbonate activity is 1.77 meq/liter.

Dependent variable	Mean Meq/liter	Correlation coefficient ¹	Constants in simple regression equation		Standard error of estimate
			Intercept	Slope	
Sodium	0.78	0.90	-0.34	0.63	±0.29
Potassium	0.07	0.70	0.04	0.02	±0.02
Magnesium	0.29	0.91	-0.06	0.20	±0.08
Calcium	0.19	0.83	0.00	0.11	±0.07
Total cations (by addition)	1.32	0.97	-0.37	0.96	±0.22
Total cations (calculated from conductivity)	2.03	0.98	0.12	1.08	±0.21

¹ All are significant at the 0.001 level.

Discussion

Results of both experiments (Figures 1 and 2) have established a close relationship between the level of dissolved carbon dioxide and the level of cations in the soil solution. Hydrogen ions associated with the mobile bicarbonate ions in solution presumably replace cations that move into solution from the soil exchange complex.

Studies by Russell and Appleyard (1915), Boynton and Reuther (1939), Boynton and Compton (1944), and more recently by Markarov (1966) have clearly demonstrated relationships between the amount of carbon dioxide in the soil and such factor

as temperature and soil moisture content. These cited studies have also shown that carbon dioxide in the soil varies with seasonal climatic changes. The level of cations in the soil solution should also be subject to fluctuations of such environmental factors if the mechanism proposed for cation movement is operative. Temperature and carbon dioxide concentration did result in changes in ionic activities of the soil solution. In

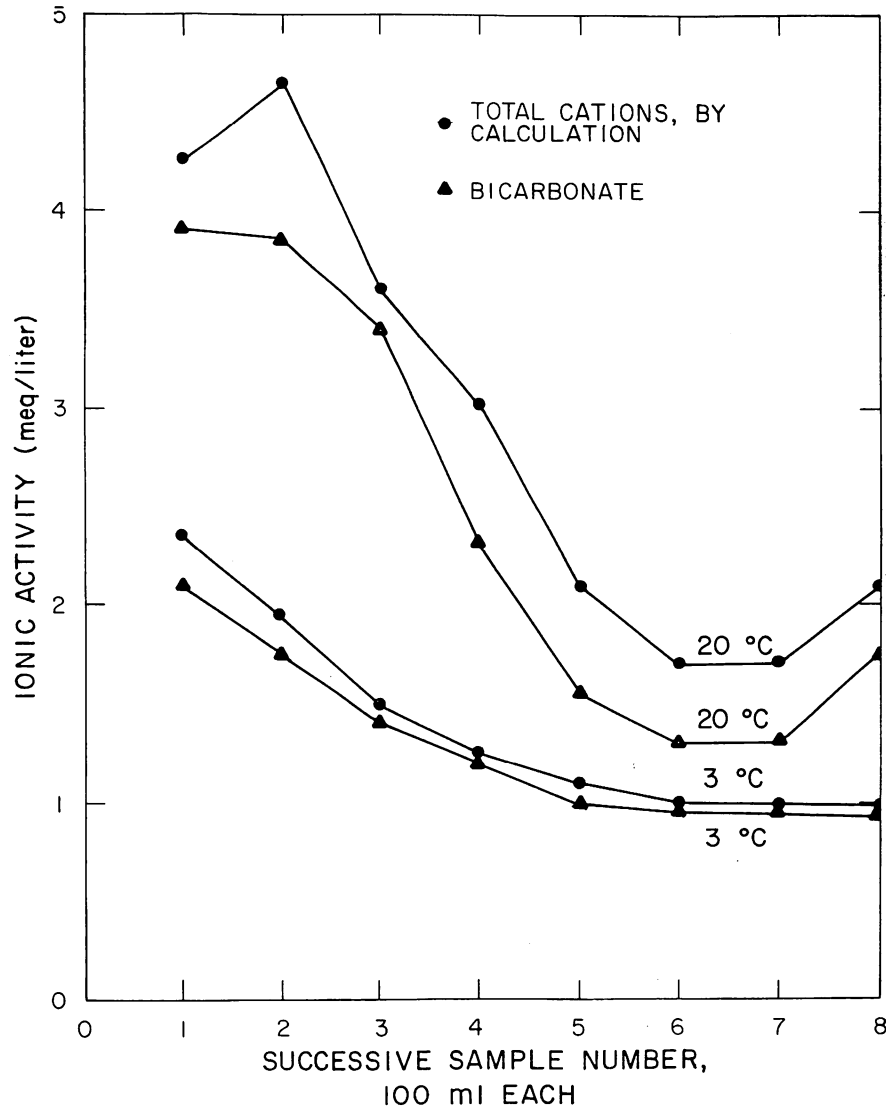


Figure 1. Effect of temperature of soil column on total ionic activity (anions or cations) and bicarbonate ion activity of soil solution.

fact, the level of cation leaching may even be predicted from the level of bicarbonate in the soil solution (Table 1).

This approach is subject to several restraints. As mentioned earlier, some mineral elements may move with colloidal material, particularly in the near-surface soil. In mineral soil with relatively little organic matter, however, this mechanism of elemental movement is probably less important than that proposed in this report, and becomes still less important with depth in the soil and with an increasing level of dissolved carbon dioxide in the soil solution. The approach presented here should further elucidate one important mechanism of cation transport in mineral soil.

The authors are currently using this exploratory design in the development of a more detailed approach to the study of ion movement in a forest soil. These studies will include an extensive field examination of factors influencing anion production. Additional laboratory experiments under controlled environmental conditions are planned to test a theoretical model of ion movement that is based on the hydrogen-cation exchange mechanism, including the factors controlling the level of bicarbonate ions in the soil solution.

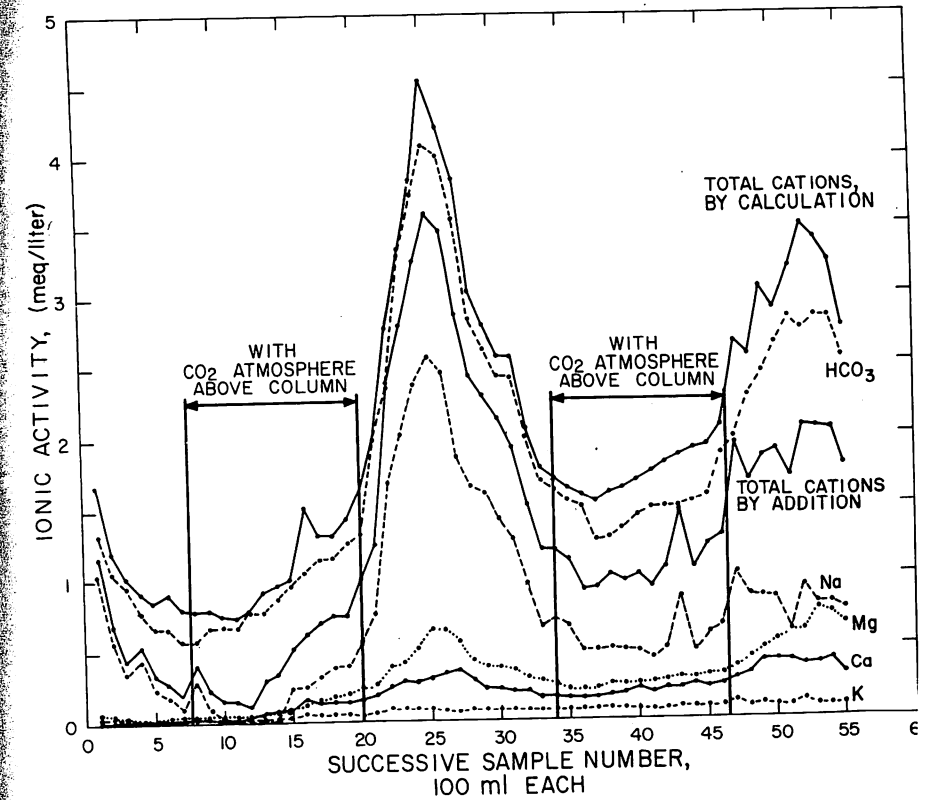


Figure 2. Effect of CO₂ atmosphere above soil column on ionic activities of soil solution, under conditions of constant soil-moisture flow and constant temperature of 20 °C.

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Ecology of the Pumice Desert, Crater Lake National Park

The Pumice Desert is a conspicuous natural feature within Crater Lake National Park. This rather barren, flat area of about 5½ square miles contrasts sharply with the surrounding forests of lodgepole pine (*Pinus contorta*). Explanations for this opening along the park's North Entrance Road have not been available. Why has plant succession proceeded so slowly in this area? Why have lodgepole pines only recently begun to invade? Which environmental factors are responsible?

The study reported herein was carried out in 1962 to (1) describe the existing vegetation and (2) measure selected environmental factors—air temperature, evaporation stress, and precipitation and soil temperature, nutrient level, and moisture. The data and the insight they have provided into factors contributing to the existence and maintenance of the Pumice Desert are the subject of this paper.

Description of Study Area

Geology and Physiography. The Pumice Desert is a flat, rather homogeneous-appearing area (Figure 1), with a slight depression running east-west through the center. Scattered washes also cause minor topographic variations. The two bench marks in the area probably represent the highest and lowest elevations: 5962 and 6010 feet.

The pumice covering the Pumice Desert was ejected by ancient Mount Mazar (Williams, 1942). Later eruptions contained a great deal of gaseous material which flowed down the slopes as glowing avalanches. These avalanches eventually became the glassy dacite pumice and basic scoria deposits which filled the valleys and depressions around Mount Mazama. The depth of these deposits in the Pumice Desert may be as much as 200 feet (Williams, personal communication).

Climate. Climatic data for Crater Lake National Park are provided by a U.S. Weather Bureau station located at Park Headquarters, about 14 miles south of the Pumice Desert at 6475 feet elevation (Sternes, 1963). Winters are fairly mild with mean monthly temperatures in the high twenties. Summers are cool with mean monthly temperatures in the mid-fifties.

Records kept at Park Headquarters from 1931-1964 show the average annual precipitation to be 68.61 inches. However, summer rainfall is slight, and most of the annual precipitation comes as winter snow.

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