

WATERSHED GEOCHEMISTRY: THE CONTROL OF AQUEOUS SOLUTIONS BY SOIL MATERIALS IN A SMALL WATERSHED

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SUMMARY

Laboratory and field data indicate that the aqueous geochemistry of a small watershed in siliceous materials is largely determined by reactions between soil and water. For dissolved SiO_2 , Ca^{+2} , K^+ , Na^+ , a reversible steady state is achieved in the soil within hours. The solute concentrations are in equilibrium with kaolinite, the end-product in the local weathering sequence. The processes occur in a drainage basin in which solution activities are the predominant form of erosion.

KEY WORDS Geochemistry Solutes Soils Drainage basin Kaolinite

INTRODUCTION

Stream water geochemistry reflects contributions from atmospheric, biologic, soil and bedrock sources. A question of some geomorphic significance concerns the relative importance of each of these sources in making a final contribution to stream solute concentrations. In this paper, we report the results of a pilot study designed to obtain information relating to the contribution of soil materials in a humid, mid-latitude drainage basin carved in siliceous rocks. The questions asked were whether an 'equilibrium' is achieved between soil materials and rain water; and if so, how quickly are the relevant solute levels approached; and finally, how do these levels compare with the solute levels in stream waters?

The strategy adopted was to approach field conditions of soil teaching in the laboratory. Various field measurements were taken for comparative purposes.

The data obtained indicate that soil-solution activities relating to silica and several cations rapidly approach steady state levels that may be approached in a reversible manner. Furthermore, the soil makes the major contribution to these solutes in stream water. The complex problem of determining the controls of the steady state, and whether the steady state is a true thermodynamic equilibrium, are not resolved, although it was found that the soil (and river waters) are in chemical equilibrium with respect to kaolinite, which is apparently the end-product of the weathering sequence under present conditions.

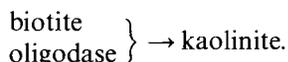
The experiments hopefully suggest a rich field of more closely controlled experiments that would elicit improved models of solution activity localization in drainage basins.

AREA OF STUDY

The project was carried out in a small watershed draining 0.4 km² of siliceous rocks lying 25 km north of Baltimore, Maryland. The basin receives approximately 1000 mm of precipitation per annum, of which some 20 per cent runs off as stream flow. The area is wholly underlain by the lower Pelitic Schist of the Wissahickon formation. Petrographic analysis indicates that quartz, muscovite, oligoclase, biotite and staurolite are quantitatively the most important minerals. From a modal analysis, the fresh

rock was found to comprise 64 per cent SiO_2 , 0.4 per cent CaO , 3.6 per cent K_2O and 0.9 per cent Na_2O .

The typical soil on the valley side slopes is a grey-brown podsollic silt-loam. The major soil minerals, determined by X-ray analysis, are quartz, muscovite, kaolinite and illite. Examination of thin sections indicates the weathering sequence



SOME PAST WORK ON SILICA GEOCHEMISTRY

Our study concentrates largely on silica in solution, since this is a fairly unambiguous indicator of the decomposition of siliceous minerals. The cations Ca^{+2} , K^{+} and Na^{+} were also studied, and occasional determinations of various other solutes (HCO_3^{-} , Al^{+3}) as well as pH were made for computational purposes. However, the significance of these solutes in terms of weathering is not clear, since, for example, rainwater makes a significant contribution to some of the cations.

The literature concerning silica in solution is large, but not generally directed to questions of immediate geomorphic significance. Polzer (1967) provides a brief review of the solution chemistry of silica, while Kennedy (1971) gives a detailed review of silica in stream water and notes, as do Edwards and Liss (1973), the relative constancy of dissolved silica in relation to other solutes in natural waters (in fact 90 per cent of ground water supplies in the U.S.A. have silicon concentrations in the range 7–43 mg SiO_2 per litre, Davis (1964)). Concerning controls of dissolved in soil waters, Elgawhary and Lindsay (1972) describe an equilibrium approached from both under- and over-saturation in soil suspensions, with a level near that predicted from equilibrium between kaolinite and montmorillonite, while Weaver, Jackson and Syers (1971) found solute activity functions for field fresh soil matrix solutions, to fall into areas of montmorillonite or kaolinite stability. However, Siever and Woodford (1973) and Edwards and Liss (1973) note the importance of possible sorption reactions, and the latter authors ascribe the silica constancy of natural waters to desorption of silicic acid from soil particles. Finally, Feth, Roberson and Polzer (1964), using a range of field data obtained in the Sierra Nevada, note the fact that natural waters are in equilibrium with kaolinite or montmorillonite, as well as the fact that the reactions involving silica in solution are apparently quite rapid.

THE EXPERIMENTAL RESULTS

The following experiments, designed to provide more specific information relating to the questions posed above, were performed on soils from our study area.

A typical valley-side slope was chosen for sampling. Two 75×18 cm plexiglass cylinders were sunk around undisturbed columns of soil, samples of which were taken for X-ray analysis. We removed the columns to a laboratory where water was fed steadily in a dropwise fashion from sealed feed-tanks onto the soil surface inside the cylinders which were also sealed. Water percolated through the columns which rested on a 2μ nylon mesh, and into a sealed 15 cm deep collecting vessel.

Although we used only inert materials in the construction of the apparatus, we took no special precautions to modify the laboratory conditions of temperature (20°C) or light (shaded).

We treated the two columns (A and B) concurrently, but differently. Column A was subjected to a continuous flow-through of distilled water from the feed vessel. Water took 2–4 hours to percolate the length of the column of soil. The flux was recorded in the collection vessel and samples were taken for chemical analyses (standard methods).

We subjected column A to two experiments. In the first, the soil was continuously leached for a nine week period by 75 litres of distilled water (the equivalent of 6 years of leaching under field conditions). Figure 1(a) shows the results of analyses for dissolved SiO_2 , Ca^{+2} , K^{+} and Na^{+} . pH maintained a constant value of 5.4. It is interesting to note that these solute concentrations show an initial change

in value and then assume fairly steady values. At the end of the first experiment, the water feed was discontinued and cool, dry air was forced through the column for one week. The flux of distilled water was then continued for a period of 14 weeks, during which time analyses were made for SiO_2 (Figure 1(b)). Again the concentration initially rose to a steady value of 7 p.p.m. (slightly lower than the first experiment value of 9 p.p.m.).

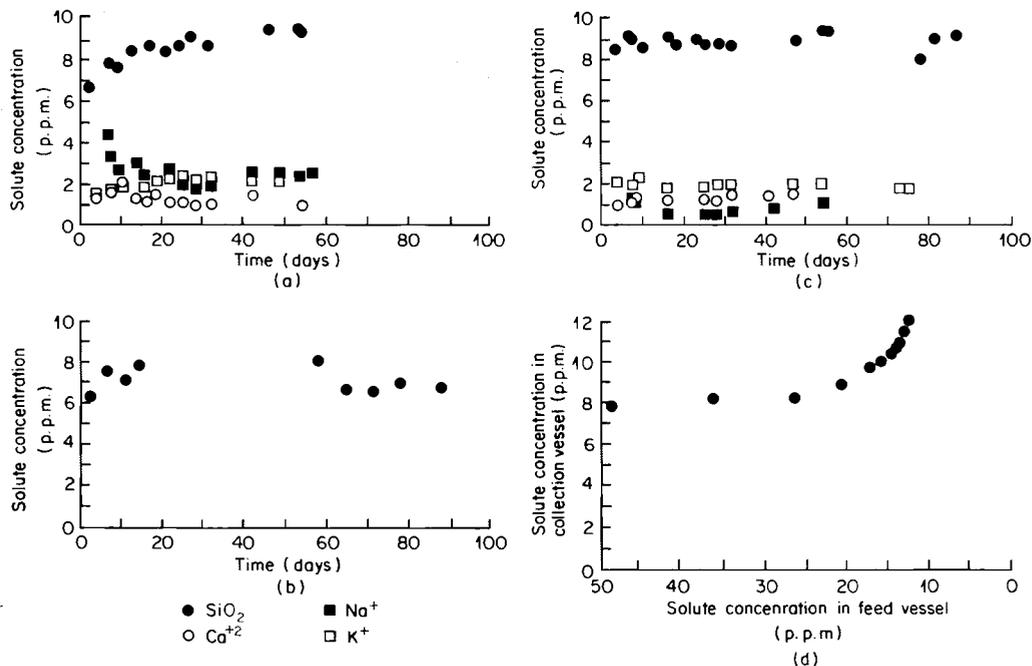


Figure 1. Concentration of solutes in the laboratory leaching experiments. (a) first period of continuous leaching with distilled water in column A, (b) second period of continuous leaching with distilled water in column A, (c) first period of continuous recycling with distilled water in column B (an SiO_2 concentration of 9.2 ppm was observed on the 30th day), (d) second period of continuous recycling with an initial 48.5 ppm SiO_2 solution in column B. See comments on diagram of Figure 1 itself

Column B was also subjected to two experiments. In the first case, 30 litres of (initially distilled) water were continuously recycled from the collection vessel to the feed vessel. A total flux of 120 litres of solution passed through the column during a 19 week run. Figure 1(c) shows the results of analyses for SiO_2 , Ca^{+2} , K^{+} and Na^{+2} ; pH was steady at 5.4. Again, we observed an approach to steady values, with SiO_2 reaching 9.0 p.p.m. The second experiment was carried out by replacing the solution in the feed vessel with a 48.5 p.p.m. solution of SiO_2 , obtained by dissolving $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ in distilled water and then removing the Na^{+} in a resin cation exchange in the hydrogen form. The recycling was commenced with this solution. Figure 1(d) illustrates the results of analyses for SiO_2 , which show a decline from 48.5 p.p.m. to less than 12 p.p.m. that occurred very rapidly.

DISCUSSION OF THE RESULTS AND FIELD DATA

We draw the following conclusions from the four experiments. The first experiment on column B indicates that steady state SiO_2 and cation concentrations are achieved which, in the case of SiO_2 at least, may be approached reversibly (experiment two on column B). Furthermore, the fact that water took less than two hours to percolate through the columns (by timing a tracer) indicates, from the results of experiment one on column A, that the steady values are rapidly achieved for SiO_2 and cations. We interpret the initial changes in solute concentrations as adjustments to laboratory conditions.

In order to obtain information that would indicate the relation between the experimental data and field conditions, field data on natural solute concentrations for the four major components of the hydrolo-

Table I. Solute concentrations of natural waters

Source of solutes		Solute concentration (ppm)			
		SiO ₂	Ca ⁺²	K ⁺	Na ⁺
Rain water 7 samples	Average	0.0	0.8	0.5	0.3
	range	—	—	—	—
Soil water 5 samples	Average	6.7	1.6	2.0	1.3
	range	5.3–9.0	1.3–1.8	1.8–2.1	1.0–1.0
Stream water 18 samples	Average	9.2	1.6	0.9	1.3
	range	7.4–12.2	1.0–2.0	0.8–1.4	1.0–1.0
Ground water 1 sample	Average	12.0	3.5	0.3	2.7
	range	—	—	—	—

gic cycle were gathered. Table I summarizes data on SiO₂, Ca⁺², K⁺ and Na⁺ concentrations in samples of water obtained from the atmosphere, soil, bedrock and stream within the watershed. The rain water, soil water and stream water samples were collected within metres of the soil sampling pits, but the only ground water analysis available was from a sample taken approximately three kilometres from the pits. More detailed information concerning stream water solutes may be found in Cleaves, Godfrey and Bricker (1970).

Soil water samples were collected by sinking a 150 × 8 cm cylindrical polyvinylchloride tube fitted with a Millipore filter 60 cm deep into the soil, and then drawing water under a vacuum. (Originally a whole set of commercial tubes fitted with mullite filters were emplaced, but we discovered that the mullite increased the soil pH to such a degree that silica solubility was markedly increased).

Firstly, we note from Table I that although no significant amount of SiO₂ is contributed by rainfall, 20–50 per cent of the cations found in the soil water may come from such sources. However, the laboratory experiments indicate that the field concentrations of the cations are obtainable from an input of distilled water, suggesting that atmospheric inputs of cations are not 'essential' to the aqueous geochemistry of our system.

Secondly, on comparing Figure 1 and Table I, we note that the average dissolved silica values from the field soil waters (approximately 7 p.p.m.) correspond fairly well with the laboratory equilibrium values of 7.0–9.0 p.p.m. A similar statement holds for the cations. The slightly higher laboratory values of solutes may be a temperature-dependent effect. These results are not at variance with the laboratory experiments, and hence indicate that with respect to SiO₂, Ca⁺², K⁺ and Na⁺ concentrations, the natural soil waters may be interpreted as being close a steady state that is rapidly achieved (i.e. within hours).

Third, the fact that stream SiO₂ concentrations (about 9.2 p.p.m.) are somewhat higher than the field soil water SiO₂ concentrations suggests a ground water SiO₂ contribution, since the one ground water analysis indicates 12.0 p.p.m. of silica. (On the other hand, stream and soil water cation concentrations are quite similar.)

CONCLUSIONS

We may tentatively conclude that the stream solute concentrations are probably determined to a large extent by soil/rain water reactions that occur fairly quickly (within hours).

The control of the reversible, steady state concentrations observed in the laboratory experiments is not directly determinable from the present work. On the one hand, we may plot the waters on phase diagrams showing the relation between aqueous solutions and simple mineral assemblages with respect to which the waters are in equilibrium. Phase diagrams for the systems (Na⁺/H⁺, H₄SiO₄) and (K⁺/H⁺, H₄SiO₄) were constructed using the assumption of chemical equilibrium, stoichiometrically pure solids, the inertness of quartz and a pH of 5.4 (see Garrells (1960)). All samples of water (field and laboratory) plot well within the kaolinite stability field. This corresponds to the known existence

of kaolinite in the soil. This possibly suggests the hypothesis of a kaolinite control of the solute concentration. On the other hand, as we noted in the brief literature review, there is some evidence that surface reactions, rather than simple mineral-water equilibria, are the controlling reactions in many soil water systems. Furthermore other reactive minerals are present and may contribute to the solution process, while kaolinite itself is highly surface active.

The unresolved and apparently complex question of the controls of the rapidly achieved soil water steady state, however, does not reduce the geomorphic significance of the fact that the soil appears to be the major source of stream solutes. This fact takes on greater significance when it is realized that over 90 per cent of the erosion in the basin appears to result from solution activity (Cleaves, Godfrey and Bricker (1970)).

It is suggested that further experiments along the lines suggested may yield more detailed and precise information concerning the solution processes.

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