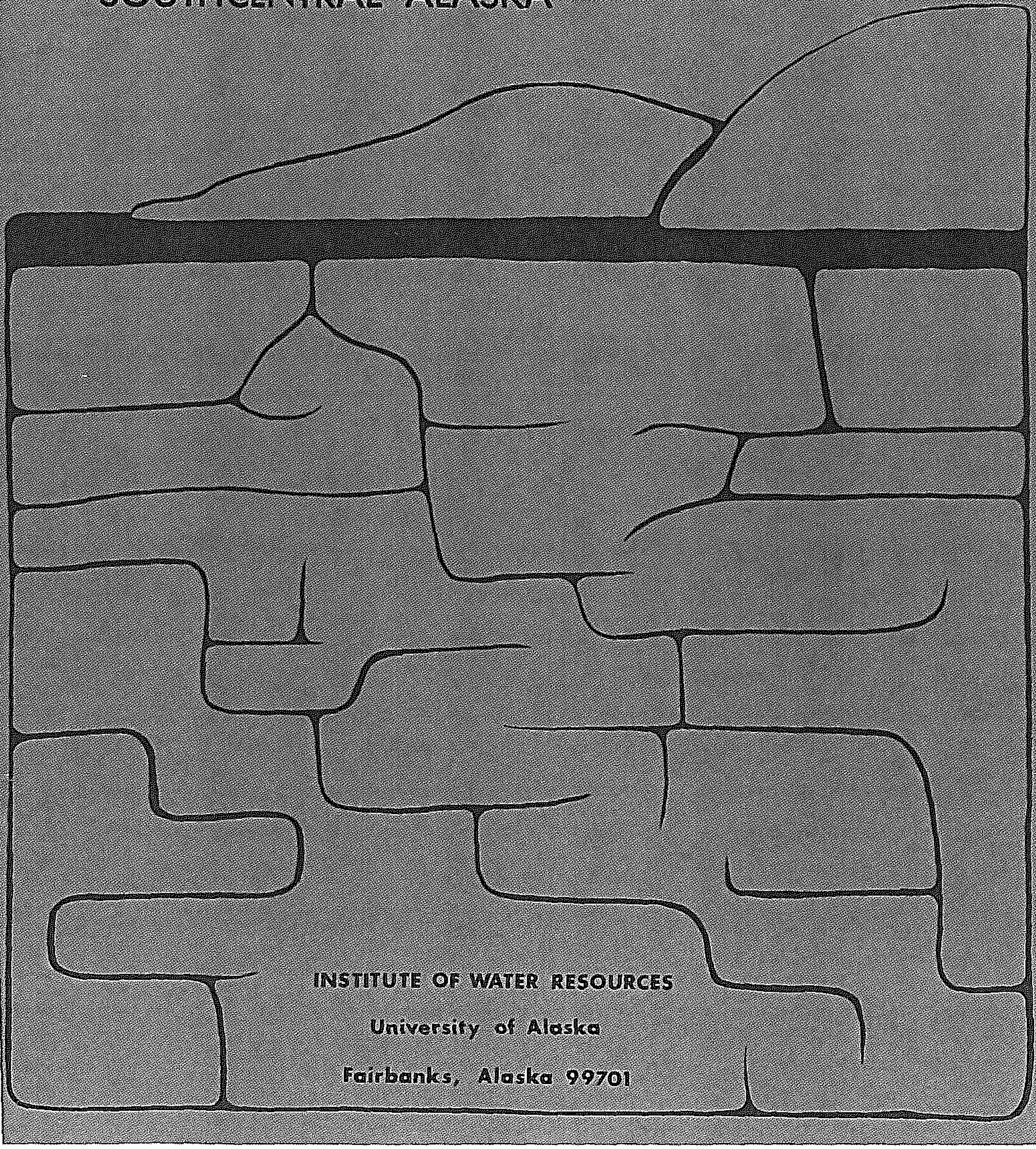
GEOLOGY AND GEOCHEMISTRY OF THE SHIP CREEK AND MONASHKA CREEK RESERVOIRS, SOUTHCENTRAL ALASKA



INSTITUTE OF WATER RESOURCES

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GEOLOGY AND GEOCHEMISTRY OF THE SHIP CREEK AND MONASHKA CREEK RESERVOIRS, SOUTHCENTRAL ALASKA

Geology and geochemistry of the Ship Creek adn Monashka Creek reservoirs, Southcentral Alaska
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ABSTRACT

Graywacke from the Ship Creek watershed, dissolves incongruently in distilled water. The dissolution appears to follow a first-order rate law which in integrated form is:

$$k = \frac{-2.303}{t} \quad \log \quad \frac{N_o - Q}{N_o}$$

where N_o is the concentration in ppm of Ca, Mg, Na or K in the graywacke, Q is the total quantity of these ions leached in time $t_{(days)}$, k is the rate constant in $days^{-1}$. Experimentally derived rate constants for the dissolution of graywacke in distilled water at 5°C are $\log k^{+2}_{CA}$, $-4.128\ day^{-1}$; $\log k^{+2}_{Mg}$, $-6.174\ day^{-1}$; $\log k^{+}_{Na}$, $-5.800\ day^{-1}$; and $\log k^{+}_{K}$, $-5.249\ day^{-1}$. The above constants are for 40 to +100 mesh graywacke. A surface area correction term must be inserted in the above equation if it is applied to a different size fraction.

Using the above equation and rate constants, the chemical composition of a water in contact with graywacke was calculated. With the exception of magnesium, the agreement between the calculated composition and that of Ship Creek water was good. Assuming that the groundwater in the Ship Creek watershed contacts about $1.5 \times 10^4 cm^2$ graywacke per liter, 120 to 360 days are required at 5°C to produce the concentration of ions observed in Ship Creek.

Release of exchangeable H^+ from the soil mat to the reservoir water will not significantly lower the pH of the water.

Leaching of heavy metals from sulfides contained in the bedrock of the two watersheds does not pose a water quality hazard.

Lineaments in the bedrock at Monashka Creek may provide channels through which water may seep from the reservoir. These are not expected to pose a problem in retaining water in the reservoir, but they may result in small, new springs down grade from the reservoir.

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INTRODUCTION

Both Anchorage and Kodiak, Alaska, have suffered from water shortages in the recent past. In Anchorage, the problem has been due to insufficient capacity of the system, not the unavailability of sources. However, as the population continues to grow, present supplies may be insufficient. In Kodiak, insufficiency of the present source has caused economic hardship by forcing the curtailment of production in fish canneries. As growth continues in the southcentral portion of Alaska, these and other communities are looking for new or increased supplies of water.

Groundwater in surficial deposits in these mountainous areas is frequently insufficient to meet the demand. Aquifers here are commonly too thin and areally restricted to provide the required quantities of water. If the surficial deposits consist of compact glacial tills or lacustrine deposits, permeabilities may be insufficient to provide an adequate water supply. Even where fluvial gravels are present and offer a groundwater source, excessive pumping in coastal areas presents the possibility of depleting aquifers and causing an encroachment of saline water.

Surface water supplies, already extensively utilized, are subject to undesirable seasonal variations. In glacially fed streams this results in drastic curtailment of flow in fall and winter. In streams not supplied by glacial melt, such as those currently being used for water supplies, undesirably low-flow conditions may exist throughout much of the late summer and winter. In order to reduce the impact of these low-flow periods, several coastal communities have constructed or are planning to construct reservoirs.

There are numerous geological and climatological similarities among Anchorage, Kodiak, and other Alaska Gulf coast communities. These communities are located in mountainous areas in which bedrock is composed of moderately metamorphosed marine sediments with associated marine volcanic rocks. Sulfide mineralization is not uncommon, although it is usually not areally extensive. Extensive valley glaciers have left glacial-fluvial deposits in low-lying areas. Post-glacial soils are thin and poorly developed in the narrow valleys where reservoir construction is possible.

PURPOSE AND SCOPE OF STUDY

The purpose of this study was to evaluate geologic and geochemical factors that might affect the quality of waters stored in the proposed Ship Creek and Monashka Creek reservoirs. The Ship Creek watershed was the primary object of study.

Laboratory aspects of the study were limited to leaching experiments on rocks and soils of the Ship Creek area. The results of these studies were interpreted as to the probably effects of these materials on the water quality of the reservoirs. A simplified mass-balance model that appears readily adaptable to computer manipulation was also considered.

LOCATION

Ship Creek heads about 10 miles southeast of Anchorage, Alaska, in the Chugach Mountains and flows 25 miles northwest to Cook Inlet near downtown Anchorage (Figure 1). It has a total drainage area of 117 square miles and, above the present diversion dam, a drainage area of 90 square miles (Barnwell *et al.*, 1972).

Monashka Creek heads in the mountains north of Kodiak, Alaska (Figure 1), and flows three miles east to Monashka Bay on the east side of Kodiak Island. It has a total drainage basin area of 5.5 square miles.

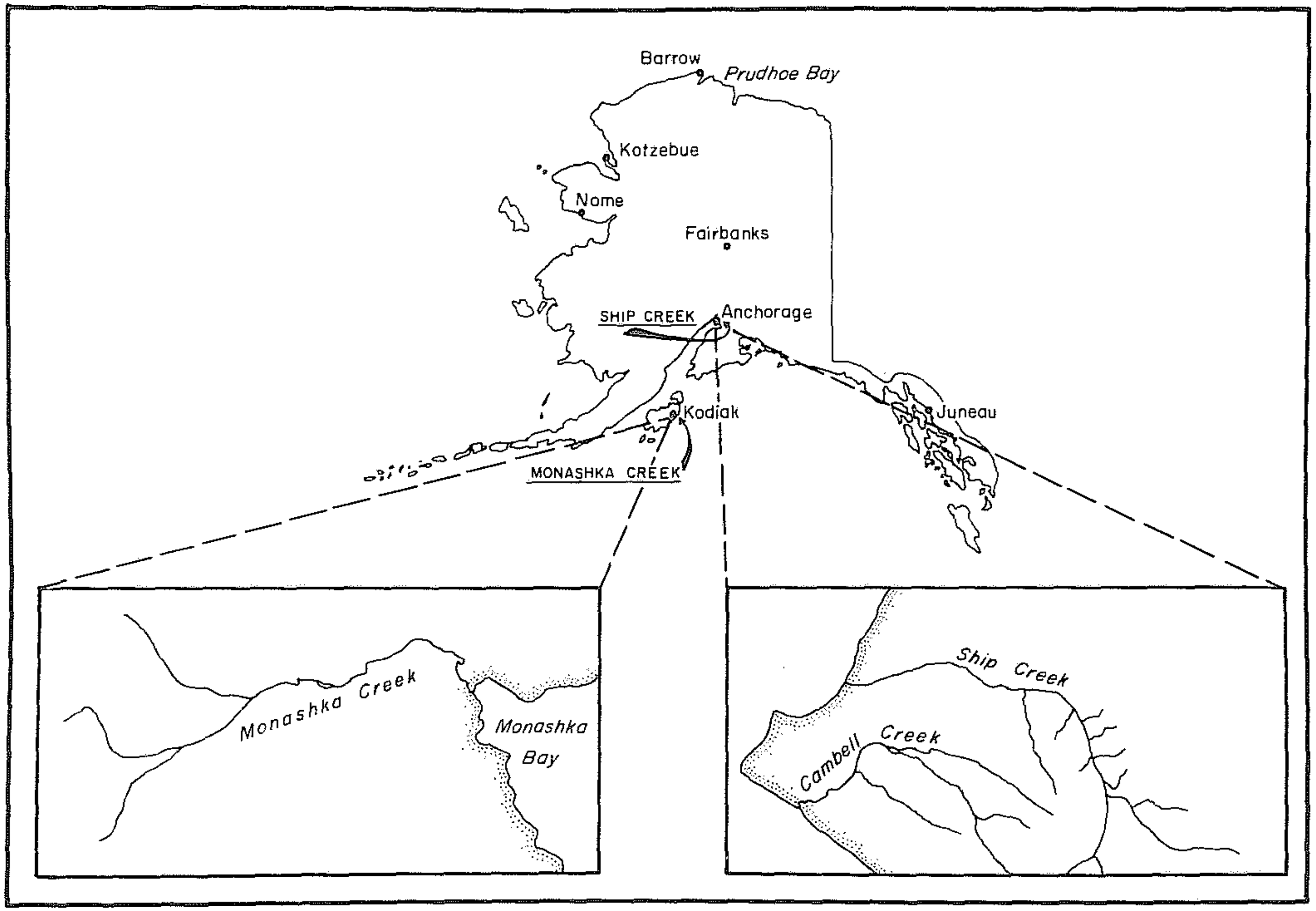

FIGURE 1: Location map of Ship Creek near Anchorage and Monashka Creek near Kodiak, Alaska.

RESERVOIRS

There is presently a water diversion dam on Ship Creek near the Chugach Mountain front on the Ft. Richardson Military Reservation. The small reservoir behind the dam is narrow and shallow and serves no storage function. It has filled with sediment rather rapidly and has required expensive dredging to maintain an open intake for the water treatment plant. It was not possible to gain access to most of the reservoir to take samples. The sediments, where observed in the upper part of the reservoir, appeared to be sands and gravels rather than silt. Much of the sediment may be moving into the reservoir by saltation or ice rafting rather than by suspension (Barnwell *et al.*, 1972).

Two reservoir sites are proposed for Ship Creek, a lower 300-foot high dam and an upper 200-foot high dam (Figure 2). The lower site would inundate the high-gradient channel below the nick point while the upper site would be above the nick point (See Figure 3). Either site will probably be subject to reduced sediment input compared to the present diversion dam. The lower site, situated in the high gradient portion of the channel, would be deeper and areally smaller than the upstream site. Both reservoirs would be capable of storing about 30,000 acre-feet of water (Barnwell *et al.*, 1972).

The Monashka Creek dam has been completed, although an option remains to increase its height. At present the earth-fill dam is about 20 feet high and diverts water to the old water system at the Pillar Creek Reservoir. Both reservoirs appear to have water of excellent chemical quality (see Appendix I), although the Pillar Creek Reservoir has a noticeable color. Neither pillar Creek nor Monashka Creek Reservoirs were cleared of vegetation or soil prior to inundation.

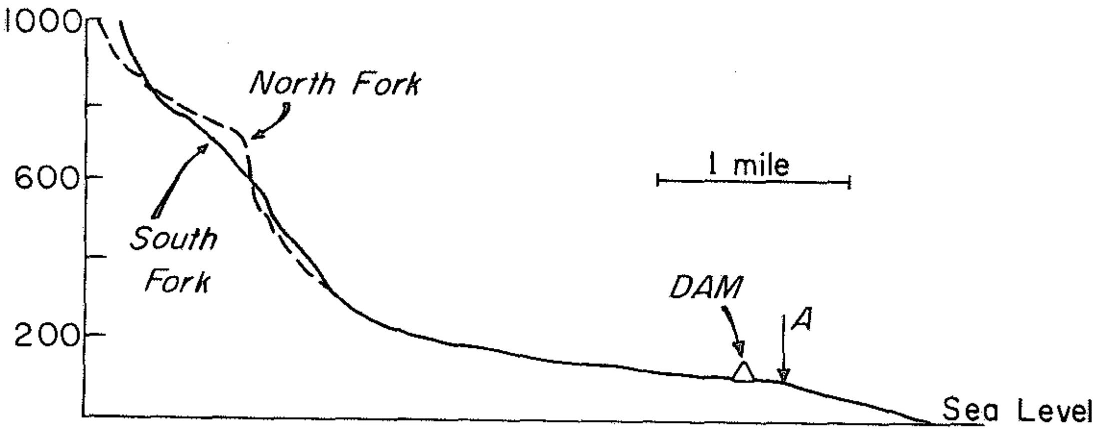

FIGURE 2: *Longitudinal profile of Monashka Creek. Nick point (A) is very close to new dam.*

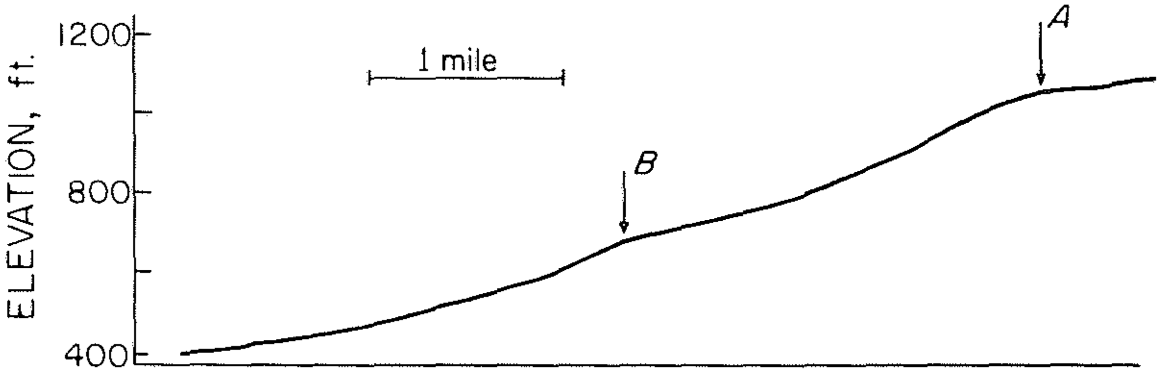

FIGURE 3: *Longitudinal profile of Ship Creek. Nick point (A) separates the low-gradient channel (65 ft/mile) upstream from the high-gradient channel (150 ft/mile) downstream. The inflection point (B) is due to the more resistant bedrock in Ship Creek Gorge.*

METEOROLOGY

There are no reliable precipitation data for Ship Creek. Continuous records maintained at Anchorage have little bearing on precipitation falling in the upper basin. The prevailing wind direction in the Cook Inlet region is from the Gulf of Alaska across the Chugach Mountains toward Cook Inlet. As a result, Anchorage is then located in the rain shadow of the mountains from which Ship Creek flows (Figure 4). The variability of precipitation is evident from data gathered on Eagle Glacier during the period of April 18 to July 15, 1968.* During this time, 6.8 inches of water fell on Eagle Glacier, while only 2.96 inches fell at the Anchorage Weather Bureau Station. Barnwell and others (1972) found the annual precipitation at Eagle Glacier to be 10 times that at Anchorage.

During 1972, Anchorage received 14.6 inches of precipitation, very close to the annual mean of 14.7 inches. During this period, however, runoff was 177,600 acre-feet for the 90.5 square mile basin which corresponds to an average precipitation of 24.4 inches. Inasmuch as there must be a loss of several inches to evapotranspiration, the average precipitation for the entire basin must be near 30 inches.

Precipitation data for Kodiak also do not apply to the Monashka Creek basin. During water year 1973, the National Weather Service recorded 51.9 inches of precipitation at Kodiak, nearly 5 inches below the mean annual precipitation of 56.7 inches. However, during the same period, runoff from

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*L. M. Mayo, 1974: personal communication.

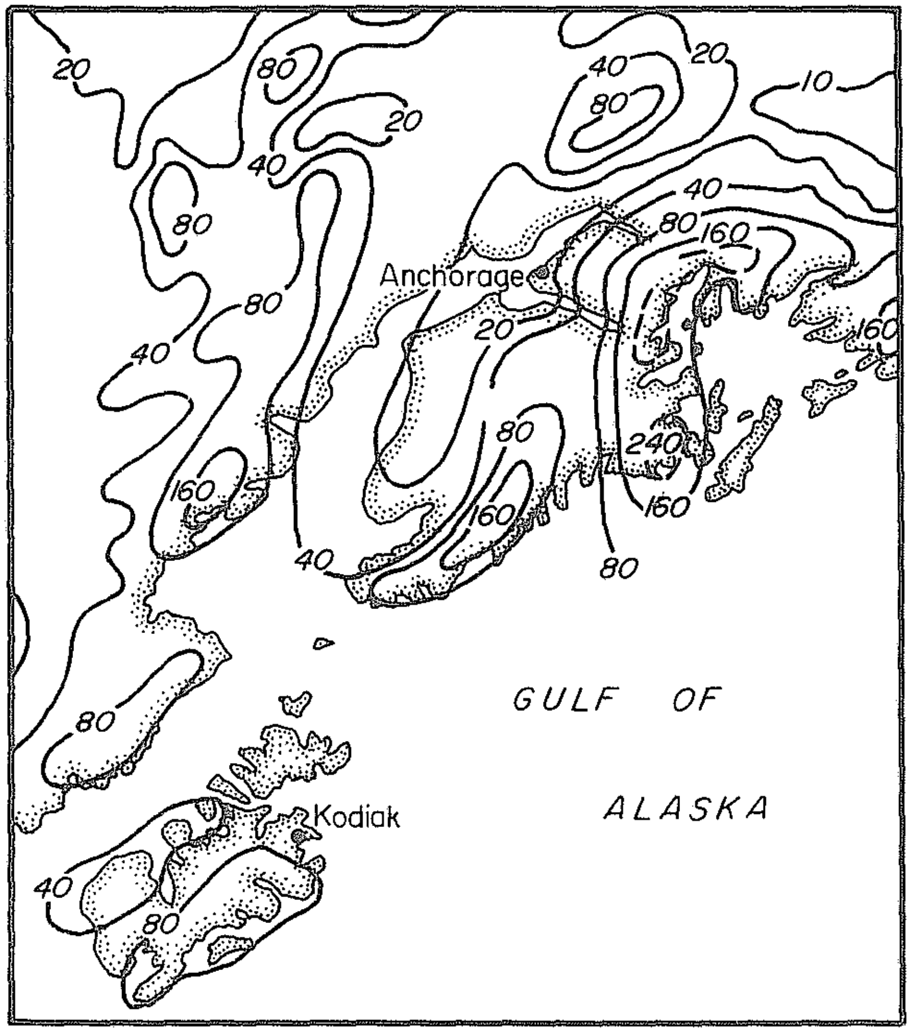

FIGURE 4: Precipitation in the Kodiak-Cook Inlet area from U. S. National Weather Service map. Isopleths are in inches of water.

the basin corresponded to a rainfall of 93 inches. Again, assuming some loss to evapotranspiration, the average precipitation for the basin must be nearly twice that recorded at Kodiak.

Thus, in both Ship Creek and Monashka Creek basins, the average precipitation in the basins must be about twice that recorded at the nearest weather service observations.

For the summer months since 1969 (Table 1) the Anchorage Water Utility has maintained an evaporation pan on Oilwell Road east of Anchorage. During the months of June, July, and August, the average monthly evaporation is 4.00 inches with a maximum of 11.9 inches in June, 1970. This maximum appears to be anomalous. If evaporation-pan data are to be used to estimate evaporation from a lake or reservoir, the values must be reduced by a factor of 0.6-0.8 (Chow, 1964) partially because the proposed reservoir is at a higher elevation than the evaporation site and because the water is very cold.

There are no data available on evaporation from the Kodiak area.

Table 1

Evaporation data for the summer months 1970-1973 near Ship Creek. Values are the total inches of water evaporated during the period.

Month	1970	1971	1972	1973	Average
June	11.9	3.74	3.14	3.38	3.42*
July	3.08	2.96	5.13	4.52	3.92
August	2.05	2.24	3.24	2.73	2.57

*excludes June 1970 value

GEOLOGY

BEDROCK GEOLOGY

Ship Creek

Rocks of the McHugh Complex (Clark, 1973) underlie most of the Ship Creek Basin. This complex consists of two distinct sequences, a metaclastic and a metavolcanic sequence. In the lower reaches of Ship Creek, a proposed reservoir site, metaclastics predominate. These rocks consist of weakly metamorphosed graywacke and slate with subordinate amounts of chert, siltstone, and sandstone. Metamorphic grade is in the prehnite-pumpellyite facies.

Two major faults cut the area (Clark, 1973). The Knik Fault forms the boundary between the Cook Inlet Basin and the Chugach Mountains to the east. The Eagle River Thrust Fault (Figure 5) separates rocks of the McHugh Complex from those of the Valdez Group which outcrop in the northcentral and eastern parts of the basin. Minor hematite mineralization is evident in the gouge zone of the Eagle River Fault. Sulfide mineralization, which occurs in small deposits in adjacent basins, is not evident in the vicinity of the proposed reservoir. Where the Eagle River Thrust Fault extends onto the basin floor about ½ mile upstream of the lower proposed reservoir, the fault is covered thickly by unconsolidated glacial-fluvial sediments. No post-Tertiary movement on the fault is evident.

Valdez Group sediment outcroppings northeast of the proposed reservoir consist of sandstones, siltstones, and conglomerates. Except in the headwaters of the North Fork, these sediments comprise a relatively minor portion of the bedrock of the Ship Creek Basin.

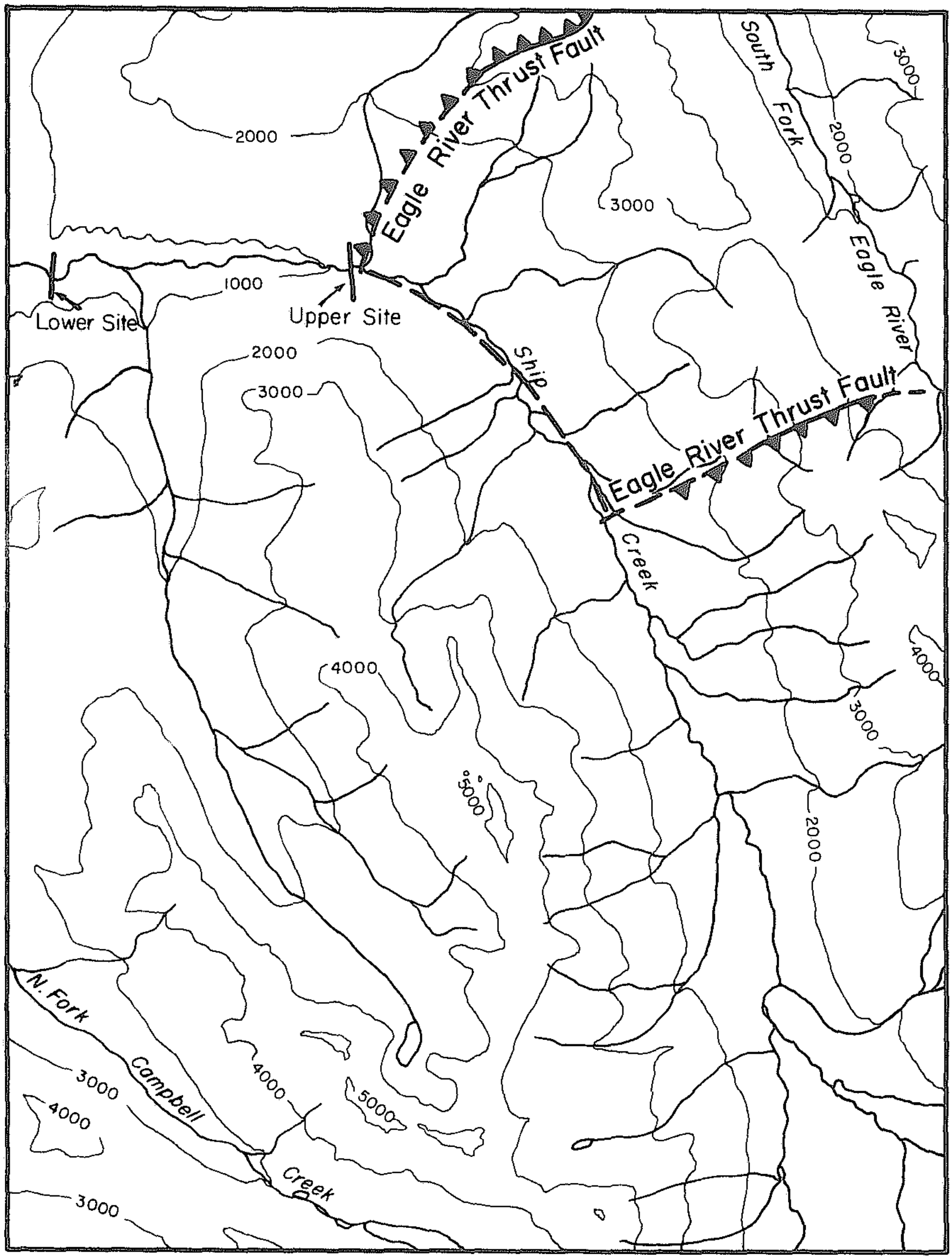

FIGURE 5: Map of Eagle River Thrust Fault and its proximity to two proposed dam sites.

A small number of wells have been completed in bedrock on the west flank of the Chugach Mountains above Anchorage (Zenone *et al.*, 1974). Fracturing and weathering appear to have been insufficient to permit significant permeability of the bedrock. Seeps along the base of the cliffs in the Ship Creek gorge between the present dam and the proposed dam indicate low permeability in weathered shale and no evident permeability in the more competent massive graywacke.

Monashka Creek

Bedrock underlying Monashka Creek basin also consists of graywacke and shale and probably represents rocks equivalent to the McHugh Complex and/or the Valdez Group. Bedrock in Monashka Creek basin is extensively fractured. Two sets of conjugate fracture sets are easily visible on aerial photographs and on the ground (Figure 6). One set trends N52W and N8E. The other trends N6W and N36E. These would appear to have been formed by two episodes of compression with principle stress axes oriented N21E and N22W. These fractures represent zones of weakness along which preferential weathering, glacial scouring, and fluvial erosion created topographic lows. The fractures may represent important groundwater conduits. A spring on the north side of Monashka Valley near the head of Monashka Creek Reservoir appears to flow from one of these fractures at a rate of about one cubic foot per second. The thin, discontinuous mantle of surficial deposits does not provide an effective aquifer. Outflow from the basin must be either as surface runoff or as groundwater in the bedrock.

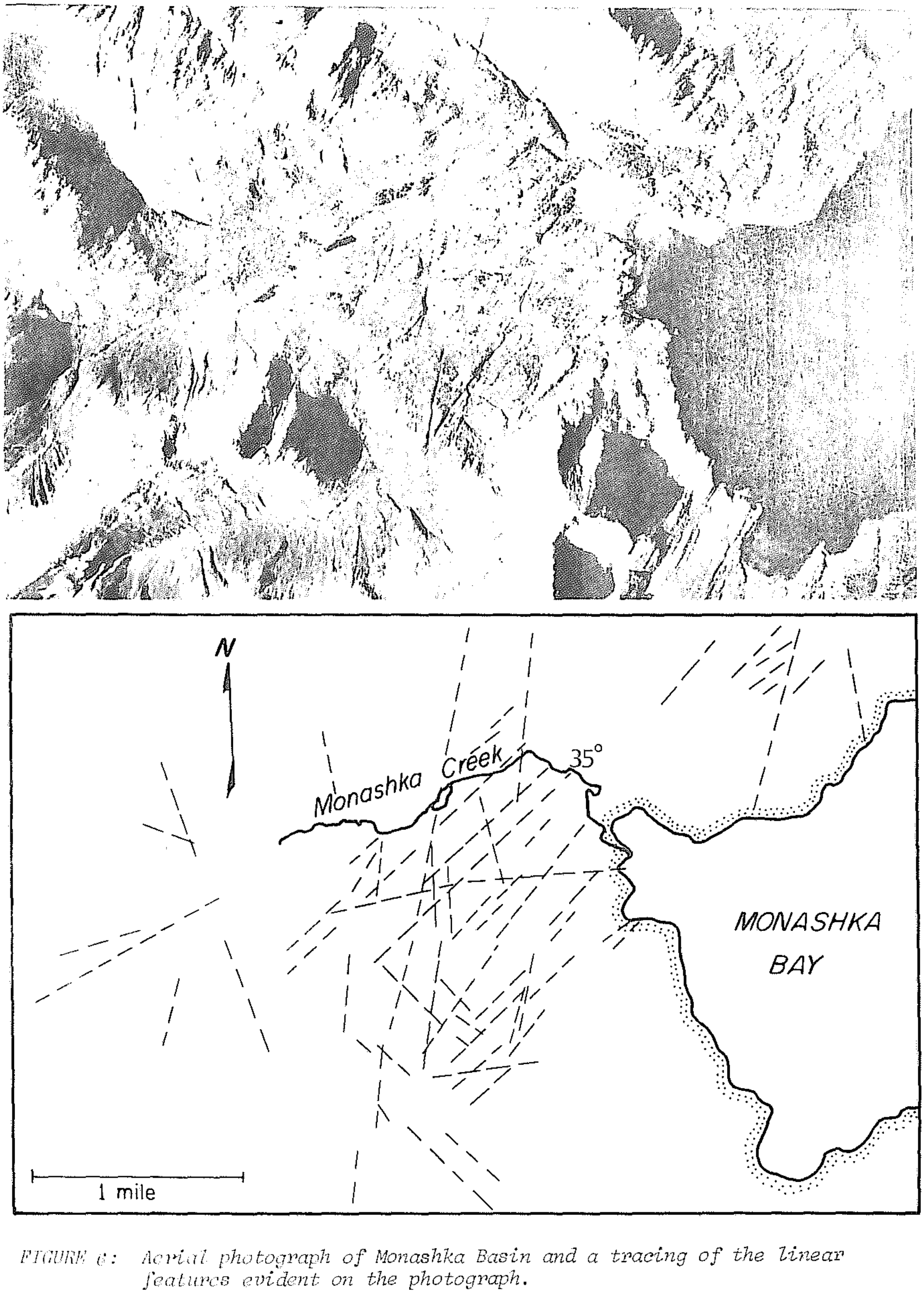

FIGURE 6: Aerial photograph of Monashka Basin and a tracing of the linear features evident on the photograph.

SURFICIAL GEOLOGY

Ship Creek

Both Ship Creek and Monashka Creek were extensively glaciated (Karlstrom, 1964). Glaciers in the Cook Inlet region at their greatest extent completely covered the basin floor and spilled into the Gulf of Alaska through the Shelikof Straits and the straits between Kodiak and Kenai Peninsula. Ship Creek has since been subjected to valley glaciation of lesser extent, while Monashka Creek has probably been ice-free. This has resulted in the development of more mature soils in Monashka Creek than in Ship Creek.

In Ship Creek Valley, glacial ice filled the valley above the level of several cols between Ship Creek and Eagle River basins, and ice flowed across the boundaries of present drainages. This interbasin flow transported glacial debris, including huge granite erratics which are clearly foreign to the Ship Creek basin. These thick, heterogeneous, deposits of glacial sediment bear little relationship to the local bedrock.

The tremendous thickness of glacial sediments is evident near the lower proposed dam where the creek has incised glacial sediments some 500 feet before encountering bedrock (Figure 7).

Monashka Creek

Glacial ice has also transported debris into Monashka Creek Basin. The low pass between Monashka Valley and Marmot Bay on the north side of Kodiak Island appears to have been a significant avenue of glacial flow. However, the glacial deposits appear to be areally much less extensive than

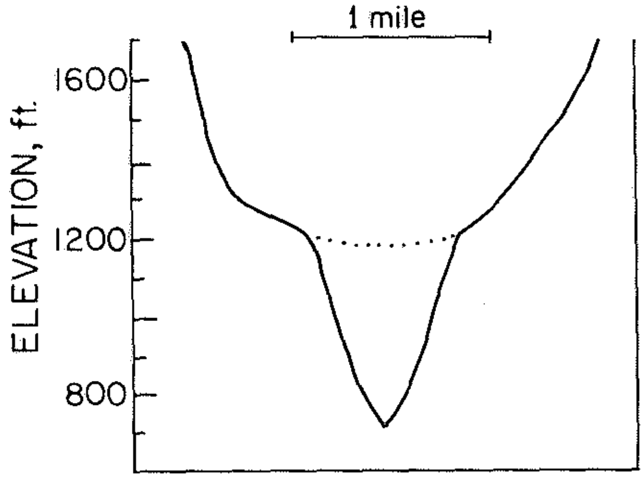

FIGURE 7: Cross section of Ship Creek near lower proposed dam site. The cross section shows a typical U-shaped glacial valley (profile dotted where inferred) with postglacial incision by Ship Creek. Glacial sediments have been incised nearly 500 feet without exposing bedrock.

in Ship Creek and are restricted to the extreme valley bottom, bedrock depressions and scours. Exposures of weathered bedrock are ubiquitous, even near the valley bottom.

Hydraulic Gradient

A longitudinal profile of Ship Creek (Figure 3) shows a marked inflection or "nick point" about 2 miles upstream from the proposed lower dam site. The gradient is about 65 feet per mile above the nick point and about 150 feet per mile below. This change in gradient is not related to the bedrock exposed in the Ship Creek gorge, but is due to a geologically recent change in base level near the mountain front. This event may have been the retreat of Eagle River Glacier past the mouth of Ship Creek, or the draining of a large glacial lake occupying what is now Cook Inlet, or less probable, movement along the Knik or some similarly oriented fault. The rapid headward erosion of this nick point may be a prime cause of rapid sedimentation in the present reservoir.

There is also a nick point in the extreme lower reaches of Monashka Creek (Figure 2). It may relate to recent changes in sea level. Since it is below the Monashka Creek dam and reservoir, it is of little concern from a sedimentation point of view. However, its close proximity to the new dam indicates that further studies of the rate of headward migration are warranted.

Soils - Sheep Creek

Soils in the Ship Creek basin are thin, generally poorly decomposed organic mats overlying very "fresh" or unweathered glacial sediments. Three environments encompass most of the basin; soil samples were collected from each of these. The first, containing sphagnum soil, is found on steep, north-facing slopes. These soils are very poorly decomposed and probably represent a cooler thermal regime where decomposition is retarded. The second environment consists of alder groves which cover most of the steeper slopes beyond the sphagnum environment. In general, the organic component of the soil is poor to moderately decomposed except in some gullies where the soil is continually wetted by surface runoff. Here, the soil has decomposed to a very dark organic muck. The third environment consists of hardwood groves which cover much of the valley bottom and the more gently sloping uplands. Here the soil consists of a poorly decomposed organic mat about 10 inches thick.

Soils - Monashka Creek

The soils of Monashka Creek basin differ markedly from those of Ship Creek and may reflect both the longer period since the area has been ice-free as well as a higher annual precipitation. In addition, soils here commonly rest on or near relatively impermeable bedrock so poorer drainage may contribute to rapid decomposition. Soil thickness is highly variable, reflecting bedrock relief. In bedrock depressions, deposits of organic silts may reach several feet in thickness while only a few feet away a thin organic layer may rest directly on weathered bedrock. In either case, the organic material is well decomposed compared with Ship Creek soils.

Landslides

Landslides or avalanches which might cause turbidity in reservoirs do not appear to be a threat either in Monashka or Ship Creek. From aerial photo interpretations, no avalanche or debris-slide paths were evident in the vicinity of proposed or existing reservoirs. A large debris-flow structure about 2 miles upstream from the upper proposed reservoir on Ship Creek appears to be an inactive rock glacier. A few small debris flows associated with this feature were probably caused by ice melt from the ice core of the rock glacier.

GEOCHEMISTRY

WATER QUALITY

Ship Creek is dominantly a calcium bicarbonate water of excellent quality. Only filtration, fluoridation, and chlorination are necessary to prepare this water for domestic use. Dissolved solids and hardness are less than 100 mg/l. (Appendix I).

Water temperature at the diversion dam ranges from 0°C in winter months to 15°C in late summer. During the summer of 1973, water temperature ½ mile above the diversion site did not exceed 10°C.

Concentrations of all components are within acceptable standards as specified by the U.S. Public Health Service (1962). Hayes (1974) noted anomalously high values for dissolved cadmium in one sample collected from the diversion facility. This may have been contamination from a galvanized intake screen and probably does not represent a significant hazard.

According to Barnwell *et al.* (1972), no significant daily changes or long-term variations in overall chemical quality have been observed over the past 20 years.

Initial plans for this study included detailed chemical analyses of water samples. However, it quickly became apparent that additional analyses would do little to define better the existing relationships among the dissolved species in Ship Creek water. As it became evident, after analyzing for several ionic species, that no new significant information was being obtained, further chemical analyses were discontinued. However, as shown in Figure 8, there is a good correlation between specific conductance and

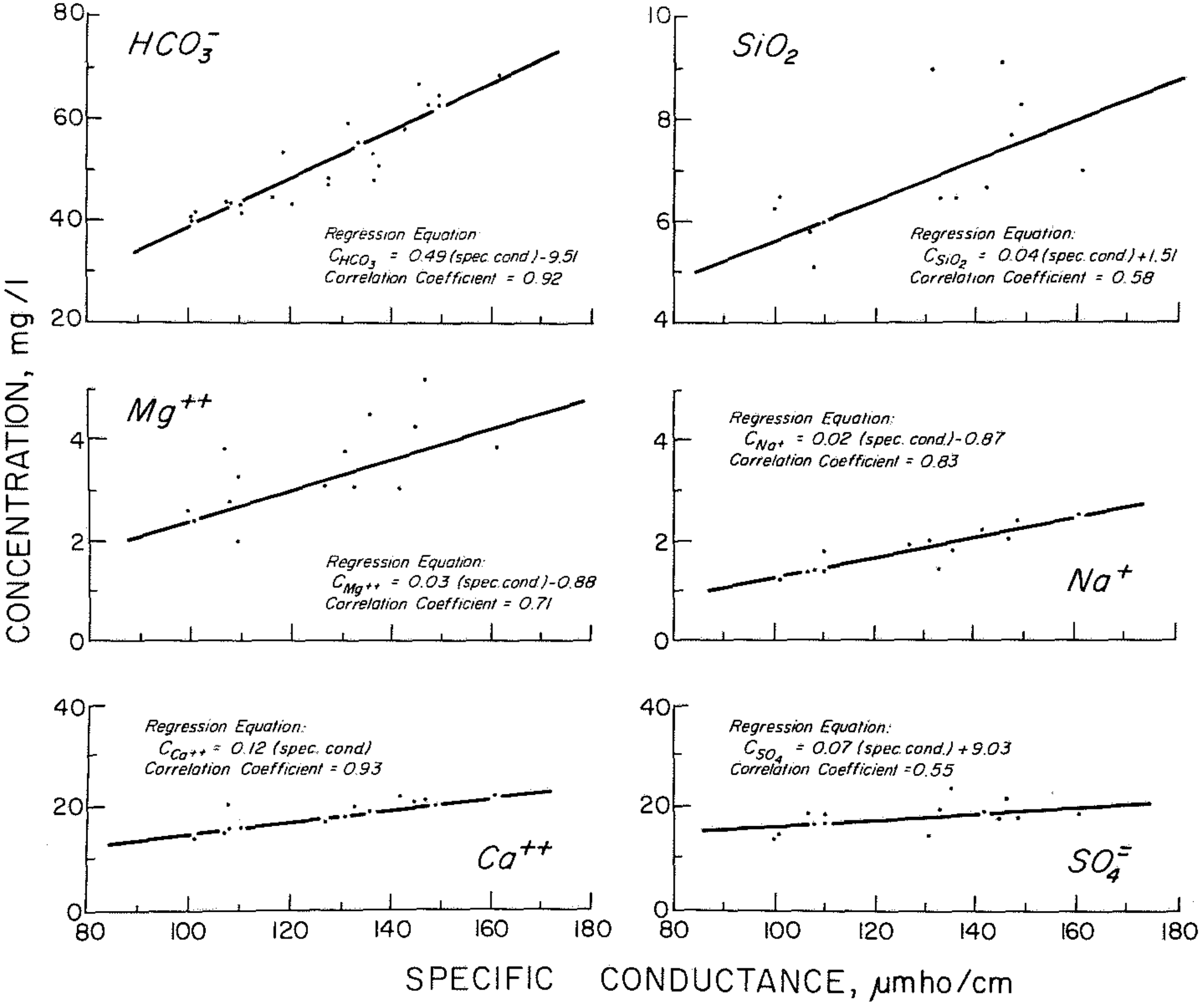

FIGURE 8: Concentration vs. specific conductance for various ions at Ship Creek.

the concentration of the major ions. This suggests that specific conductance measurements can be used to monitor short-term chemical changes in the reservoir waters.

SOILS

Mineralogy

All soil samples were treated with 50% hydrogen peroxide in order to oxidize the organic constituent. The inorganic residue was analyzed by X-ray diffraction. Where an identifiable mineral phase was present, it consisted of kaolinite, for Ship Creek samples, and kaolinite or chlorite for Monashka Creek samples.

Chemistry

The pH of all soil samples (Appendix II) was measured by dipping electrodes in a soil-water slurry which had been allowed to stand sufficiently long to have attained equilibrium (usually 1 hour). Although this is a normally accepted procedure, it may give anomalously low values due to abnormal junction potentials in a colloidal system (Bates, 1973). This "suspension effect" may result from two factors. The colloidal particles inhibit the mobility of ions in the test solution causing an anomalous potential between the liquid and the glass junctions or a similarly anomalous potential could be developed by a Donnan effect in which colloidal particles immobilized by gravity act as a semipermeable membrane producing a potential through the test solution. Whatever the cause, it appears that this procedure produces pH values lower than the true pH of the interstitial solution.

Although pH values should be viewed with some skepticism, they may provide a frame of reference for studying the effects of soils on reservoir waters. In this light they should be viewed as minimum values of pH or maximum values of acidity.

Of possible concern is the quantity of exchangeable hydrogen ion (H^+) available from a given volume of soil. To determine the quantity of exchangeable H^+ (Appendix II), soil slurries were titrated to neutrality with 0.1 N NaOH. As shown in Appendix II, there is a average of ∿0.05 milliequivalent (meq.) of exchangeable H^+ per cubic centimeter of valley-bottom soil. Because the soil is a nearly uniform mat about 35 cm thick, this value represents about 1.5 meq. exchangeable H^+ per square centimeter of reservoir bottom. If this quantity of H^+ were released quickly to the reservoir, the pH of the reservoir water would be drastically reduced, i.e., the water would become markedly acidic. However, the H^+ can only be released by exchange with cations present in the reservoir waters. A hypothetical reaction is shown as follows:

$$H^+_{(soil)} + Na^+_{(aq)} \rightleftharpoons Na^+_{(soil)} + H^+_{(aq)}$$

where $H^+_{(soil)}$ refers to exchangeable H^+ on the soil, and $Na^+_{(aq)}$ to the quantity of Na^+ (K^+, Ca^{+2}, etc.) in solution. In part, because of the low concentration of cations in solution, the reaction does not proceed far to the right (see Appendix V). This, coupled with the buffer capacity of the surface water, precludes any significant lowering of the pH of the reservoir waters by release of H^+ from the soil.

To verify that there would be no significant adverse effect on Ship Creek water, the soil sample with the greatest quantity of exchangeable H^+ was equilibrated with a sample of raw Ship Creek water in the ratio 35 cm^3 Soil/2,000 ml H_2O. Equilibration was carried out under aphotic conditions at a temperature of 0.5°C. These conditions most closely approximate water conditions during the winter when a significant demand might be made on the oxygen content. At this time, the ice cover would both inhibit oxygenation and reduce sunlight to photosynthetic organisms. Experiments conducted under these conditions demonstrated that pH was depressed an insignificant amount, 0.2 pH units from 7.2 to 7.0. Even this small depression is probably higher than that which would be expected in nature because all of the soil would probably release its H^+ over a period of time during which the reservoir would be continuously flushed.

The soils and surficial geology of Monashka Creek basin near Kodiak, Alaska, differ in several respects from those of Ship Creek. In these soil samples, the pH was nearly neutral. As mentioned previously, glaciation of the area has resulted in significant erosion, but has not resulted in thick deposits of glaciofluvial deposits as is the case in Ship Creek. Rather thin soils commonly rest on weathered bedrock rather than glacial deposits and more intense weathering of the underlying deposits is evident at Monashka Creek than at Ship Creek. The hazards of adversely affecting the quality of water at Monashka Creek by interaction with the soil mat appear to be less than at Ship Creek.

An existing reservoir on Pillar Creek, the adjacent drainage south of Monashka Creek, has good quality water. A bottom sample of this water had a pH of 7.0 and alkalinity of only 13.1. A bottom-water sample collected in Monashka Creek Reservoir in August, 1973, showed no detectable iron in solution. Thus, some of the concern regarding degradation of water quality by uncleared soils (Smith and Justice, 1975) may not be justified.

EXPERIMENTAL STUDIES

A principle objective of this study was to develop a laboratory technique to investigate water-rock interactions and to predict, by means of this technique, the composition of waters in contact with various bedrock types in the natural system. If the comparison proves satisfactory, then the effect on water quality of building a reservoir in a particular bedrock setting can be predicted from laboratory data. Because of the multiplicity of possible chemical reactions that can occur upon dissolution of a rock, such a system was considered too complex to treat on a mineral-by-mineral, reaction-by-reaction basis. Instead, an empirical approach was used here, in which the kinetics of the dissolution of a particular rock type (e.g. graywacke) were determined. From such kinetic data, the expected chemical composition of water in contact with a graywacke under natural environmental conditions can be calculated. The test of such calculations is obviously the comparison of the expected composition of the water with that of existing waters draining a graywacke area.

Column Studies

To evaluate short-term contributions of ions to the water from graywacke, leaching studies employing heated columns were carried out. In these studies, graywacke from the Ship Creek watershed was ground and sieved with the 40 to 100 mesh sizes selected for study. This fraction was quickly rinsed in cold distilled water, then in acetone and air dried. It was then placed in jacketed Pyrex glass columns and compacted with a small vibrator. The columns were 25 cm long, 1 cm inside diameter, and contained 32.0 gms of crushed graywacke. The columns and the distilled water which served as the leaching agent were maintained at 57°C throughout the experiments by means of a constant-temperature water bath. A flow rate of about 3 cm^3/min (about ½ pore volume/min) was maintained by an elevated reservoir. After passing through a coil in the constant temperature bath, the distilled water leachant entered the bottom of the column and exited from the top. Samples of effluent, 20 ml in volume, were collected periodically and analyzed for several major cations by means of atomic absorption spectrometry. The results of analysis of these samples are given in Appendix III and are summarized graphically in Figure 9.

Batch Studies

"Batch" or static leaching studies were employed to determine the compositional changes to be expected in a solution upon prolonged contact with graywacke or alluvium. These studies in particular served as the source of data from which kinetic equations were derived. In these experiments, 5.0 gm of 40 to 100 mesh graywacke or alluvium were placed in polyethylene bottles, containing 100 ml distilled water. The bottles were closed with screw-cap stoppers and the stoppers wrapped with plastic tape to prevent loss of fluid. The bottles were placed in a drying oven at either 37°C or 57°C for varying periods of time, or in the refrigerator at 5°C for the same time periods. The bottles were shaken by hand several times a week. At selected intervals of 5, 15, and 30 days, bottles were removed from the oven or refrigerator,

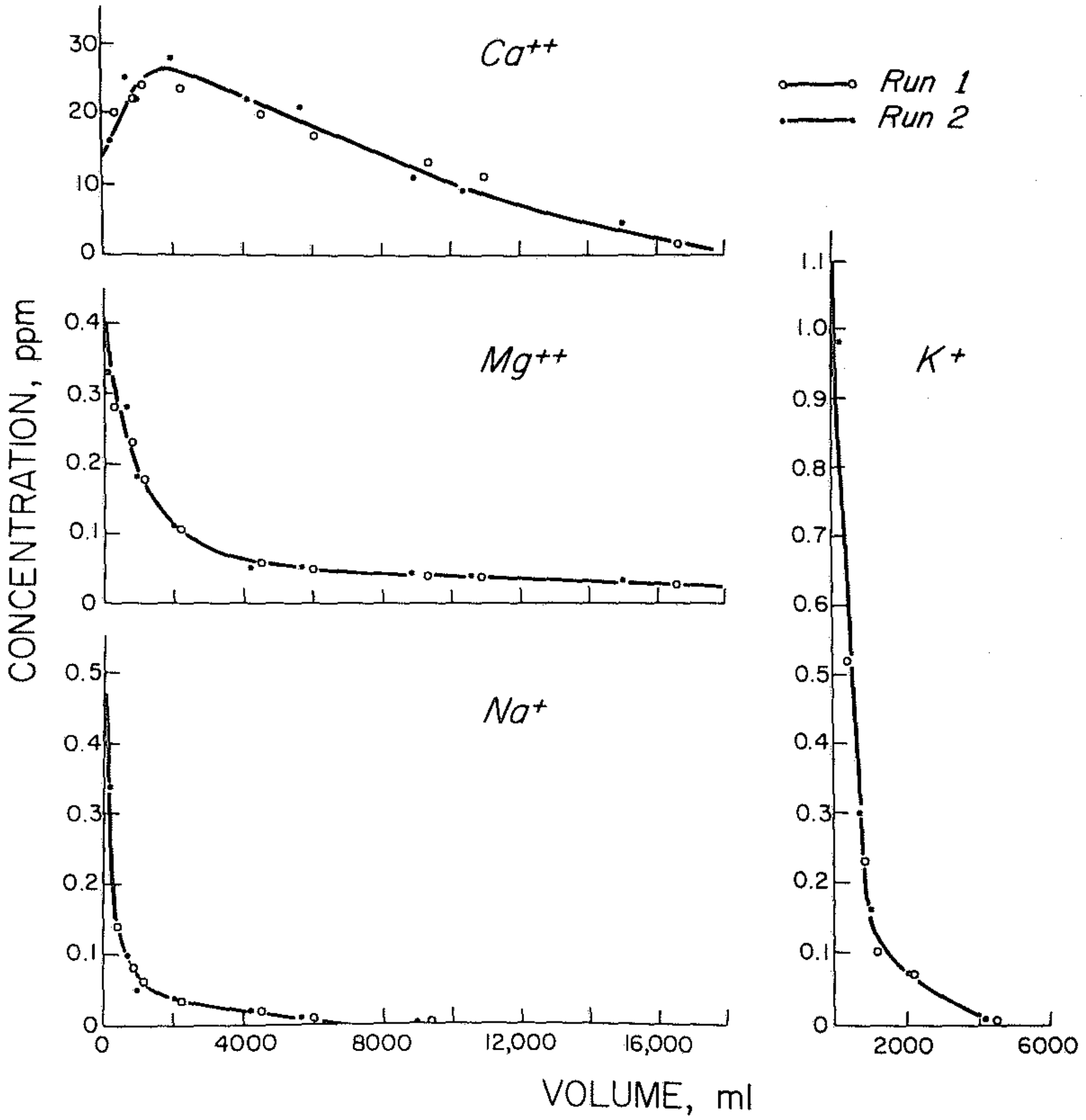

FIGURE 9: Graphs showing the instantaneous concentrations of calcium (Ca^{++}), magnesium (Mg^{++}), sodium (Na^{+}), and potassium (K^{+}) in the effluent solution versus the cumulative volume of effluent for the leaching, by distilled water, of crushed graywacke at 57°. Data are from Appendix III.

the contents quickly filtered, and the filtrate set aside for analysis. The experiments were replicated three times. The results of these experiments are shown in Appendix IV and graphically in Figure 10.

DISCUSSION OF KINETIC EQUATIONS

The application of kinetic equations to the problem of interaction of rock and water has been discussed in detail by Paćes (1973) and, most recently by Busenberg and Clemency (1976). Also the dissolution of calcite grains in the ocean as a function of depth has been discussed by Berner (1971). In these discussions, a diffusion-controlled process is envisaged and diffusion coefficients are calculated from a first-order equation of the same general form as the kinetic equation used here.

Like Paćes (1973), Busenberg and Clemency (1976) assume that a process describable by a parabolic rate law is involved in the dissolution of feldspar. In fact, Busenberg and Clemency suggest that four different processes are involved in the leaching of feldspar. The initial process involves exchange of hydrogen ions for the surface cations. This stage is very short and lasts about one minute at 25°C; the second stage lasts perhaps 50 hours and involves the release of large amounts of silica and other cations exclusive of aluminum. Stage three lasts about 19 days and is one in which the release of all species into the bulk solution follows a parabolic rate law. The final stage is one in which a steady state release of cations follows a linear kinetic law.

The model used in the present work is similar to, but much less detailed than, those of Paćes who, like Helgeson (1971), utilizes a parabolic rate law, and who envisages the dissolution process as being controlled by the develop-

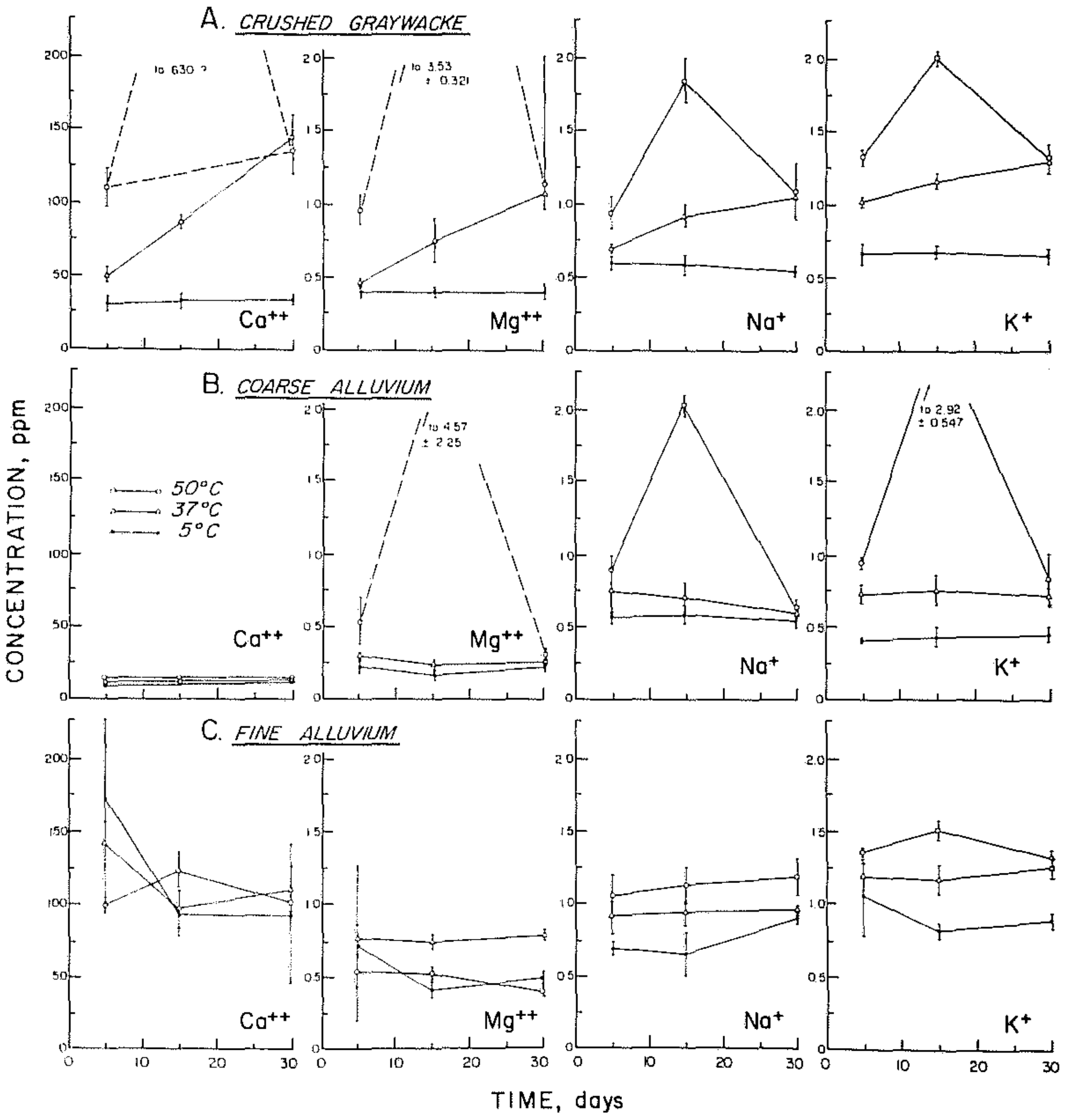

FIGURE 10: Graphs showing the concentration of calcium (Ca^{++}), magnesium (Mg^{++}), sodium (Na^{++}), and potassium (K^{+}) in solution upon leaching graywacke (A), coarse alluvium (B) and fine alluvium (C) at three different temperatures and three different time periods. Data are from Appendix IV.

ment of a cation-deficient aluminum-silicate layer on the grains through which the cations (e.g. Na^{+}, Ca^{+2}) from the unweathered surface must diffuse.

The model used here is concerned with the number of ions on the surface of the grain at any given time. It is assumed that this number is a function of the total number of the same ions in the bulk of the grain and that the energy required to remove these surface ions follows a Boltzman distribution. Because of electroneutrality requirements, the process of dissolution must involve either a simultaneous removal of anions (e.g. $H_3SiO_4^-$) or more likely, cation exchange in which the cation on the surface of the mineral grain is replaced with hydrogen ions from solution. The equation used here corresponds to the linear rate equation of Busenberg and Clemency and the data in Table 5 suggest that a parabolic rate law might be more appropriate; however, because of the scarcity of data points, a linear rate law was assumed. Busenberg and Clemency suggest that a linear rate law describing the dissolution kinetics of feldspar may be appropriate when the rate of formation of the secondary product layer is equal to the rate at which this layer is equal to the rate at which this layer is destroyed at the liquid-product interface.

Derivation of Rate Equation

Assumption: The more ions on the surface of a given grain, the greater will be the solution concentration of these ions with respect to time.

Let N be the number of a particular kind of ion on the surface of the graywacke grain.

$N = N_o 4\pi r^2 \Delta r$, where N_o is the concentration of these ions in the grain, which concentration is assumed to be uniform throughout the grain; r is the radius of the grain; and $4\pi r^2 \Delta r$ is the volume element at the surface of the grain from which the ions are leached. If r and Δr are constant, i.e the size of the surface volume-element is fixed, then the rate of change of the ions on the surface of the grain during dissolution is proportionate to N, or

$$\frac{dN}{dt} = -kN \qquad (1)$$

since the number of ions N decreases with time. rearranging:

$$\frac{dN}{N} = -kdt$$

or on integration

$$\ln N = -kt + c$$

or

$$N = e^{-kt+c}$$

at

$$t = t_o, \quad N = N_o$$

or

$$N_o = e^c$$

thus

$$N = N_o e^{-kt} \qquad (2a)$$

or in general

$$N = N_o 4\pi r^2 e^{-kt} = WN_o e^{-kt}$$

where

$$W = 4\pi r^2 = surface\ area$$

Actually the concentration in solution is measured. So let Q_t be the quantity of an ion in the leachate at any time t, since V, the volume of the leachate, is constant in batch runs, $Q_t = c_t \cdot V$, where Q_t and c_t are the instantaneous total quantities and concentrations of the ion in question in solution.

Since Q_t is obtained by the leaching of the grain, then from mass balance

$$Q_t = W\ (N_o - N_t)$$

$$Q_t = WN_o\ (1-e^{-kt}) \tag{3}$$

Solving for k

$$Q_t = WN_o - WN_o e^{-kt}$$

$$e^{-kt} = \frac{WN_o - Q_t}{WN_o}$$

$$-kt = \frac{ln\ (WN_o - Q_t)}{WN_o}$$

$$-k = \frac{2.303\ log\left(\frac{WN_o - Q_t}{WN_o}\right)}{t} \tag{4}$$

Equation 4 permits the determination of the rate constant, if N_o and Q are known. In the discussion that follows, the rate constants are derived for graywacke of an average surface area W of $4\pi r^2 \simeq 5.4 \times 10^{-4}\ cm^2$/grain for the range of particle sizes studied. *This surface area value does not appear in the calculations that follow. It must be considered when comparing results from the batch study to systems with a different grain size distribution.*

Estimation of N_o: The ions of interest are Na^+, K^+, Mg^{+2} and Ca^{+2}, inasmuch as these were analyzed for in the batch experiments. No analyses of the graywacke studied are available, so the concentration of these ions in an average graywacke are used to estimate N_o for each of the different ions. Using the data in Pettijohn's table (1963), Column A, the values of N_o are shown in Table 2.

Table 2

N_o values based on data from Pettijohn (1963)

Col. A	Wt. %	Wt. % Element in 5.0 g. Sample of Graywacke	(Mg N_o Element in 5.0 g Graywacke)
MgO	2.15	= 0.1075 x .603*= 0.0648 gms	= 64,800
CaO	2.54	= 0.1270 x .741*= 0.0941 gms	= 94,100
Na_2O	2.93	= 0.1465 x .742*= 0.1087 gms	= 108,710
K_2O	1.99	= 0.0995 x .830*= 0.0826 gms	= 82,600

*Gravimetric factors for elements in oxides.

Calculation of k for Different Ions at Different Temperatures: The data used are given in Appendix IV and shown graphically in Figure 9. From this figure, it is evident that, at all three temperatures, ions have been contributed to the solution by the graywacke. Furthermore, the higher the temperature and the longer the time of leaching, the greater the concentration of a given ion in the leachate. It also appears that, at 5°C, an appreciable quantity of ions is initially contributed, but that this contribution does not increase further with time at this temperature. Thus, there appears to be a rapid increase in concentration early in the leaching process, followed by very little subsequent change in concentration at 5°C over the time period studied.

As a consequence, the following process is assumed to be operative. Readily soluble compounds, e.g. halite or sulfate grains, fluids from fractured fluid inclusions, and ions loosely sorbed at surface of grains, are presumed to be removed easily and early in the leaching process. Subsequent increases in solution concentration are then due to slow dissolution of the minerals (primarily silicates) composing the graywacke. The first process leads to a threshold concentration. Thus, subsequent changes in solution concentration with time and temperature are not due to dissolution of easily soluble substances but, rather, to the slow dissolution of the silicates. Therefore, to determine rate constants for the dissolution of the graywacke, threshold concentrations (c_{th} = those concentrations of different ions present in the lowest temperature leachate at the shortest duration of leaching) were subtracted from the other concentrations at the different temperatures and leaching times. These corrected concentrations, Table 3, were then used to calculate the quantities Q_t leached at any time. These Q_t's were used to calculate the rate constants.

From the data in Table 4, three estimates of the rate constant can be obtained at 37°C, but only two rate-constant estimates were obtained for 57°C. At 57°C, the concentration passes through a maximum. It is assumed that this behavior is due to the formation of and re-equilibration with a new phase, leading to a decrease in concentration. This is tantamount to saying that the mineral phases present after 30 days leaching at 57°C are different from those originally present. Thus, only the data between 5 and 15 days leaching at 57°C were used to estimate the rate constant for this temperature.

Using the data of Tables 2 and 4 and Equation 4, the rate constants for the dissolution of graywacke were calculated as summarized in Table 5.

TABLE 3

Corrected Concentrations C_t* of ions (ppm) in leachate at different temperatures for different leaching times. (Modified from Appendix IV)

T°C	Ions	Time (days) 5	15	30
37	Mg^{++}	0.077 ppm	0.353 ppm	0.690 ppm
	Ca^{++}	15.6	53.6	112
	K^+	0.350	0.500	0.630
	Na^+	0.123	0.350	0.480
57	Mg^{++}	0.573	3.140	0.780
	Ca^{++}	77.6	597.	103.
	K^+	0.660	1.34	0.650
	Na^+	0.362	1.27	0.520

*Threshold Concentrations: Mg^{++} = 0.39 ppm K^+ = 0.67 ppm
Ca^{++} = 33.1 ppm Na^+ = 0.57 ppm

TABLE 4

Corrected Q_t, in μgm quantities of various ions, leached from 5.0 g of graywacke into 100 ml distilled water at 2 different temperatures for 3 different leaching times. ($Q_t = C_t \times 100$ ml)

T°C	Ions	Time (days) 5	15	30
37	Mg^{+2}	7.70	35.0	69.0
	Ca^{+2}	1560.0	5360.0	11200.0
	K^+	35.0	50.0	63.0
	Na^+	12.3	35.0	48.0
57	Mg^{+2}	57.3	314.0	78.0
	Ca^{+2}	7760.0	59700.0	10300.0
	K^+	66.0	134.0	65.0
	Na^+	36.2	127.0	52.0

TABLE 5

CALCULATION OF RATE CONSTANTS

Ion	T°C	t(days)	N_o(μgm)	Q_t(μgm)	-k(day^{-1})	log k	1/T °K
Mg^{+2}	37	5	64,800	7.70	$-2.377x10^{-5}$	-4.62	$3.226x10^{-3}$
		15	64,800	35.3	$-3.633x10^{-5}$	-4.44	"
		30	64,800	69	$-3.552x10^{-5}$	-4.45	"
						-4.503 average	
	57	5	64,800	57	$-1.760x10^{-4}$	-3.75	$3.030x10^{-3}$
		15	64,800	314	$-3.239x10^{-4}$	-3.49	"
						-3.62 average	
Ca^{+2}	37	5	94,100	1560	$-3.344x10^{-3}$	-2.48	$3.226x10^{-3}$
		15	94,100	5360	$-3.911x10^{-3}$	-2.41	"
		30	94,100	11200	$-4.224x10^{-3}$	-2.37	"
						-2.42 average	
	57	5	94,100	7760	$-1.722x10^{-2}$	-1.76	$3.030x10^{-3}$
		15	94,100	59700	$-6.71x10^{-2}$	-1.17	"
						-1.47 average	
K^+	37	5	82,600	35	$-8.478x10^{-5}$	-4.072	$3.226x10^{-3}$
		15	82,600	50	$-4.037x10^{-5}$	-4.394	"
		30	82,600	63	$-2.544x10^{-5}$	-4.595	"
						-4.354 average	

TABLE 5 Continued

Ion	T°C	t(days)	N_o(μgm)	Q_t(μgm)	-k(day^{-1})	log k	1/T °K
	57	5	82,600	66	$-1.599\text{x}10^{-4}$	-3.796	$3.030\text{x}10^{-3}$
		15	82,600	134	$-1.083\text{x}10^{-4}$	-3.966	"
						-3.881 average	
Na^+	37	5	108,710	12.3	$-2.263\text{x}10^{-5}$	-4.645	$3.226\text{x}10^{-3}$
		15	108,710	35.0	$-2.147\text{x}10^{-5}$	-4.668	"
		30	108,710	48.0	$-1.472\text{x}10^{-5}$	-4.715	"
						-4.715 average	
	57	5	108,710	36.2	$-6.662\text{x}10^{-5}$	-4.176	$3.030\text{x}10^{-3}$
		15	108,710	127.0	$-7.794\text{x}10^{-5}$	-4.108	"
						-4.142 average	

Estimation of Rate Constants for Dissolution of Graywacke at 5°C: From the data in Appendix IV and Figure 9, it is apparent that very little change in concentration of the ions of interest occurs at 5°C over the time period 5 to 30 days. Because there is no apparent measurable change in concentration with time, the procedure used at higher temperatures to estimate rate constants cannot be used here. Instead, the rate constants at 5°C are estimated from those at higher temperatures by means of the Arrhenius equation:

$$k = A_e^{(-Ea/RT)}$$

If $\ln k$ is plotted versus the reciprocal of the absolute temperature, a straight line should result. Because only 2 temperatures were available, the data were not plotted inasmuch as the relation must be linear. From the linear equations for the 4 different ions, the rate constants at 5°C were estimated from the values of $\log k$ in Table 5. These constants are given in Table 6. See Appendix VIII, for a sample calculation.

Estimation of Activation Energy: The activation energy, ΔH, i.e. that energy that must be supplied the ions before they are freed from the surface and able to dissolve, can be calculated from an integrated form of the Arrhenius equation:

$$\log \left(\frac{K_2}{K_1}\right) = \frac{\Delta H}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Using the average rate constants for the various ions at 37°C and 57°C, the activation energies for the dissolution of these ions from the graywacke are shown in Table 7.

TABLE 6

Calculated Rate Constants*
for Dissolution of Graywacke
at 5°C

Ion	log k (day^{-1})
Ca^{+2}	-4.218
Mg^{+2}	-6.174
Na^{+}	-5.800
K^{+}	-5.249

*See Appendix VIII
for sample calculations.

TABLE 7

Calculated Activation Energies

Ion	ΔH (kcal/mole)
Mg^{+2}	20.6
Ca^{+2}	22.2
K^{+}	11.0
Na^{+}	13.4

It should be noted that the activation energies for the divalent cations are about twice those of the monovalent cations. This is expected inasmuch as the coulombic attraction of the ions in a solid is of the form $\frac{Z_1Z_2e^2}{r}$ where Z_1 and Z_2 are the charges on the cations and anions respectively, e the charge on the electron and r the distance between the cations and anions. To a first approximation, if the charge of the anions on the surface of the dissolving mineral grain is constant with respect to the different ions, and if the ions are of approximately the same size (which they are not) so that the distance r separating the cations and anions is about the same for the different ions, then the coulombic attraction of the divalent cations should be about twice that of the monovalent cations. It is tempting to carry this argument further. For example, the ionic radii of the cations for octahedral coordination (Shannon and Prewitt, 1969) are:

Na^+	1.16A
K^+	1.52A
Mg^{+2}	.86A
Ca^{+2}	1.26A

These ions arranged according to coulombic attraction are $Mg^{+2} > Ca^{+2} > Na^+ > K^+$. The ions arranged according to measured activation energy of dissolution are $Ca^{+2} > Mg^{+2} > Na^+ > K^+$. Although probably coincidental, the similarity of the two series is intriguing.

Comparison of Results from Batch Studies with those from Column Studies: The total quantity Q_t of ions leached from the graywacke in the column experiments was obtained by numerical integration of the curves shown in Figure 8, which gave the instantaneous composition of the effluent as a function of the total volume of leachate put through the column at that particular time. Values of Q_t^{col} for the different ions are shown in Column 3 of Table 8. These values were compared with predicted values from the batch studies by first calculating the threshold quantities $Q_{th}/5.0\ g$ leached in the batch runs from 5.0 gms graywacke (See Table 3). These quantities were then multiplied by 6.40 to give the estimated threshold quantities $Q_{th}^B/32.0\ g$

to be expected (Column 2, Table 8) if 32.0 gm, the quantity of graywacke in the columns were leached. The quantity of ions to be expected by dissolution of the graywacke in the columns is given by the difference between $Q_T^{col} - Q_{th}^B/32.0\ g$ to give Q_L^{col} (Column 4, Table 8). Next the quantity Q_L^B of ions leached in the batch runs was calculated using the rate constants at 57°C, for the different times (= t_c^o) required at the average flow rate of 3.61 ml/min to reduce the ionic concentration in the effluent to the detection limit of the analytical method, effectively 0 ppm for the elution curve shown in Figure 8. These times t_c, shown in Column 5 of Table 8 are: 3.46 days for Ca^{+2} and Mg^{+2}, 1.44 days for Na^+, and 0.87 days for K^+. The different values of Q_L^B were obtained from Equation 5

$$Q_L^B = N_o - N_o\ (e^{-kt_c}) \qquad (5)$$

The N_o's for the different ions are given in Table 2. The quantity Q_L^B (Equation 5) must be multiplied by 6.40 to give the quantity leached from 32.0 gm graywacke in a batch experiment at 57°C. The quantities actually leached and those predicted from the batch experiments are shown in the last column of Table 8. Clearly, greater quantities of Ca^{+2}, Mg^{+2} and K^+ were

TABLE 8

Comparison of Quantity (Mgms = Micrograms) of Ions Leached
In Column Runs With That Predicted from Batch Studies

Ion	$Q_{th}^B/5.0\ g$	$Q_{th}^B/32.0\ g$	Q_T^{col}	Q_L^{col}	$t_c(days)$	Q_L^B	ΔQ
Mg^{+2}	39.	250	1,100	850	3.46	344	+506
Ca^{+2}	3310.	21,180	227,600	206,400	3.46	66,620	+139,800
K^+	67.	429	798	369	0.87	61	+308
Na^+	57	365	323	-32	1.44	72	-104

leached from the columns than would be predicted by results of the batch experiments. This should not be surprising inasmuch as, in the column experiments, the graywacke was continuously leached by distilled water, thus the concentration gradient at the solid-solution interface was greater in the column experiments than in the batch experiments which should result in a greater leaching rate in the column experiments. Although the agreement between predicted and actual quantities leached is not as good as hoped for, nonetheless the results agree within an order of magnitude. It is clear, however, that rate constants derived from column experiments must be used when it is necessary to know the concentration of ions resulting from the leaching of graywacke at high flow rates (See Appendix VII for such constants). As shown in Appendix VII, the leaching rate for the column is 2 to 6 times faster than that in the batch studies. However, if the flow rate of leachate through the graywacke is so slow that static leaching conditions are approached, then rate constants derived from batch experiments can be used. Under these conditions, the effect of a constant flow rate can be taken into account, using Equation 6, which permits the calculation of the instantaneous ionic concentration C_i^x at a constant flow rate for a given volume of leachate.

$$C_i^x = \frac{N_o k e^{-kt}}{a} \qquad (6)$$

where t is the time in days corresponding to the leachate volume V_t at a constant flow rate a; N_o is the original concentration of the element x in the graywacke; and k is the batch rate-constant for that ion at the temperature of interest. This equation is derived in Appendix VI. Note that implicit to this equation is the assumption that the flow of leachate over the graywacke grains does not increase the rate of leaching. This is only true at very low flow rates.

COMPARISON OF THE COMPOSITION OF WATER CALCULATED FROM THE RATE EQUATION WITH THAT OF SHIP CREEK

A bar graph of the average concentration of Na^+, K^+, Ca^{+2}, and Mg^{+2} for Ship Creek, calculated from the data in Appendix IV, is shown in Figure 11. Shown in Figure 11A is a bar graph of the concentration of these ions in an average graywacke (data from Table 2). Rearranging Equation 3 and solving for t using the rate constants at 5°C (Table 6) for the Ca^{+2} concentration of 18 mg/l (average stream concentration), it was found that about 300 days would be required for this concentration of Ca^{+2} to be reached in the batch experiments at 5°C. Using Equation 5, the concentration of the various ions in the batch solution of 100 ml volume for a leaching time of 360 days were calculated. These results are plotted as a bar graph in Figure 11B where a close similarity between the composition of the Ship Creek waters and that calculated for the experiment is clearly evident. The agreement between predicted and actual concentration of Na^+, K^+, and Ca^{+2} is satisfactory. The agreement between predicted and actual Mg^{+2} concentration is poor. The time required to reach the actual Mg^{+2} concentrations in Ship Creek using the analysis of Ship Creek and the calculated rate constants would be about 4,000 years. Alternatively, the rate constant for the dissolution of Mg^{+2} must be about 1×10^{-5} day^{-1} if the magnesium levels in Ship Creek are to be reached in 360 days. Yet another alternative: if the rate constant (Table 6) and 360 days are used, a magnesium concentration in the graywacke of about 20% would be required, which is clearly an impossibility. In essence, there is a discrepancy of a factor of 10 in these results. At present this discrepancy has not been resolved.

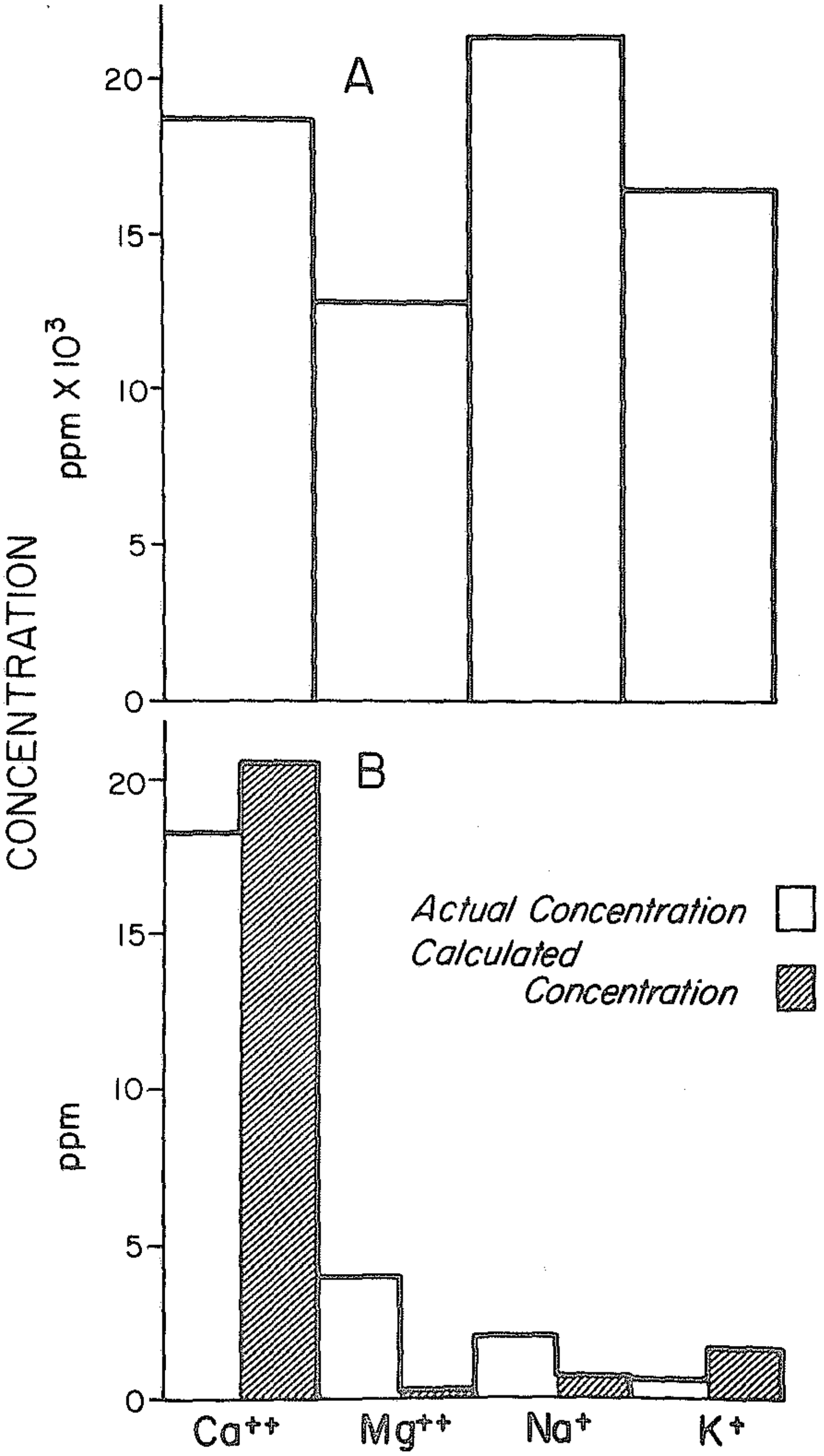

FIGURE 11: The concentration of calcium (Ca^{++}), magnesium (Mg^{++}), sodium (Na^{+}), and potassium (K^{+}) in (A) an average graywacke (Pettijohn, 1964) and in (B) Ship Creek (unshaded) and the concentration expected (shaded) in Ship Creek at 5°, based on rate equation calculation.

With regard to the dissolution of graywacke, it is very evident that graywacke dissolves incongruently insofar as bulk composition is concerned. Because of electroneutrality requirements, the leaching of Na, K, Ca, and Mg must either be accompanied by a simultaneous leaching of silicate anions, which is improbable, or more likely by the exchange of protons from the water for the cations of the minerals. Although the calcium content of the average graywacke (Table 2) is less than that of sodium and only slightly more than that for potassium, the calcium concentration in solution is at least 10 times that of sodium and potassium. This fact is reflected in the rate constant for calcium which is an order of magnitude greater than those for Na^+, K^+ or Mg^{+2}. The reason for the rapid dissolution of calcium is not known. Because of its size and charge, the calcium ion in solution is more hydrated than either the sodium or potassium ion. Thus, even though it takes more energy to remove the Ca^{+2} ion from the surface of the grain, the ion, once hydrated, may not easily shed the hydrated sheath and return to a surface site but may remain in solution. A similar argument could be made for Mg^{+2}, yet the experimental data do not support it. If our experimental results for Mg^{+2} are correct, and we have no reason other than the lack of agreement with the Ship Creek water to suspect one, then it is possible that Mg^{+2} in our experiments is reacting with the alumina-silicate "rind" or with dissolved silica, perhaps forming sepiolite or a similar phase as Garrels and Mackenzie (1967) suggest might occur in more concentrated solutions. If so, this implies that our data for the dissolution of Mg^{+2} pertain to a possible secondary phase formed at the 37°C and 57°C temperatures of the experiment, and do not pertain to the original Mg^{+2} bearing phases or their dissolution at 5°C. This obviously implies that such a phase is not present in the natural system, otherwise the

Mg^{+2} concentration would be lower. That such a phase could form rapidly within several days at 37°C and not form at 5°C over extended time periods in the natural system does not seem reasonable. Nonetheless, the possibility of secondary phases in these experiments cannot be discounted. The concentration maxima exhibited in Figure 9 are surely suggestive of the development of new phase(s).

To relate the experimental results and rate equations to a watershed requires that an estimate be made of the surface area of the fractured rock with which waters of the watershed are in contact. Paćes (1973, Appendix I) concludes that, for a fractured granitic terrain, one liter of groundwater contacts from 10^4 to 10^7 cm^2 of granite surface. It is assumed here that the same range of values holds for fractured graywacke terrain as well.

The surface-to-volume ratio of the graywacke in the batch experiments, assuming spherical grains 40 to 100 mesh diameter, was calculated to be about $5x10^3 cm^2$/liter. Therefore, the equivalent surface area of the graywacke in the experiments is less than that with which natural waters might come in contact. As a result, for the same temperature, more time would be required in the experimental system than in the natural system to produce a concentration equivalent to that in the natural waters.

The laboratory experiments would be more applicable to the natural system had crushed graywacke of 200 mesh been used (equivalent to $1.4x10^4 cm^2$/liter). Such a 3-fold increase in surface area has the effect of increasing the N_o's used in the rate equations by 3 fold. As a result, the time required to achieve concentrations equivalent to those in Ship Creek should be reduced from the calculated values of 360 days to about 120 days. No experiments were performed using graywacke crushed to 200 mesh so this assumption has not been checked. Such contact time is in reasonable agreement with that calculated by Pacés for waters from the Sierra Nevada batholith.

SPECULATIONS ON THE NATURE OF THE RESIDUAL PHASE FROM THE LEACHING OF GRAYWACKE

Without data on the quantity of silica and alumina leached from the graywacke during these experiments, it is impossible to describe chemically the residual phase(s) that results. However, relative to the graywacke, such phases must be deficient, particularly in calcium and less so in sodium, potassium, and magnesium. From the data of Busenberg and Clemency (1976) for the dissolution of feldspars, these residual phases must also be silica deficient and alumina rich. Clay minerals such as chlorite or kaolinite would satisfy such chemical requirements. Because such minerals are residual, i.e. they are less soluble phases than the minerals of the unleashed graywacke and may even be in equilibrium with the leachate, they will not dissolve readily. The failure of the fine fraction of the alluvium to display a dissolution behavior like that of the graywacke (Figure 10) is probably due to the enrichment in clay minerals of this size fraction.

MODELING THE RESERVOIR SYSTEM

A computer model of the reservoir system is beyond the scope of the present study. However, it appears that a simple model of the system can be made to quantify the effects of impoundment on the quality of water in the reservoir.

The model which seems appropriate is analogous to a continuous, stirred-tank reactor. Basic assumptions necessary to this model are:

1. The reservoir is continuously and perfectly mixed.
2. Climatologic and hydrologic data from the historic record are typical for conditions in the future. It is suggested that data for 1972 be used for input data for the Ship Creek model inasmuch as precipitation at Anchorage that year was very close to the value of mean annual precipitation.
3. The rate equations derived in this paper for static leaching are applicable to bank storage conditions in the stream and reservoir.

A flow chart for the simple reservoir model is shown in Figure 12.

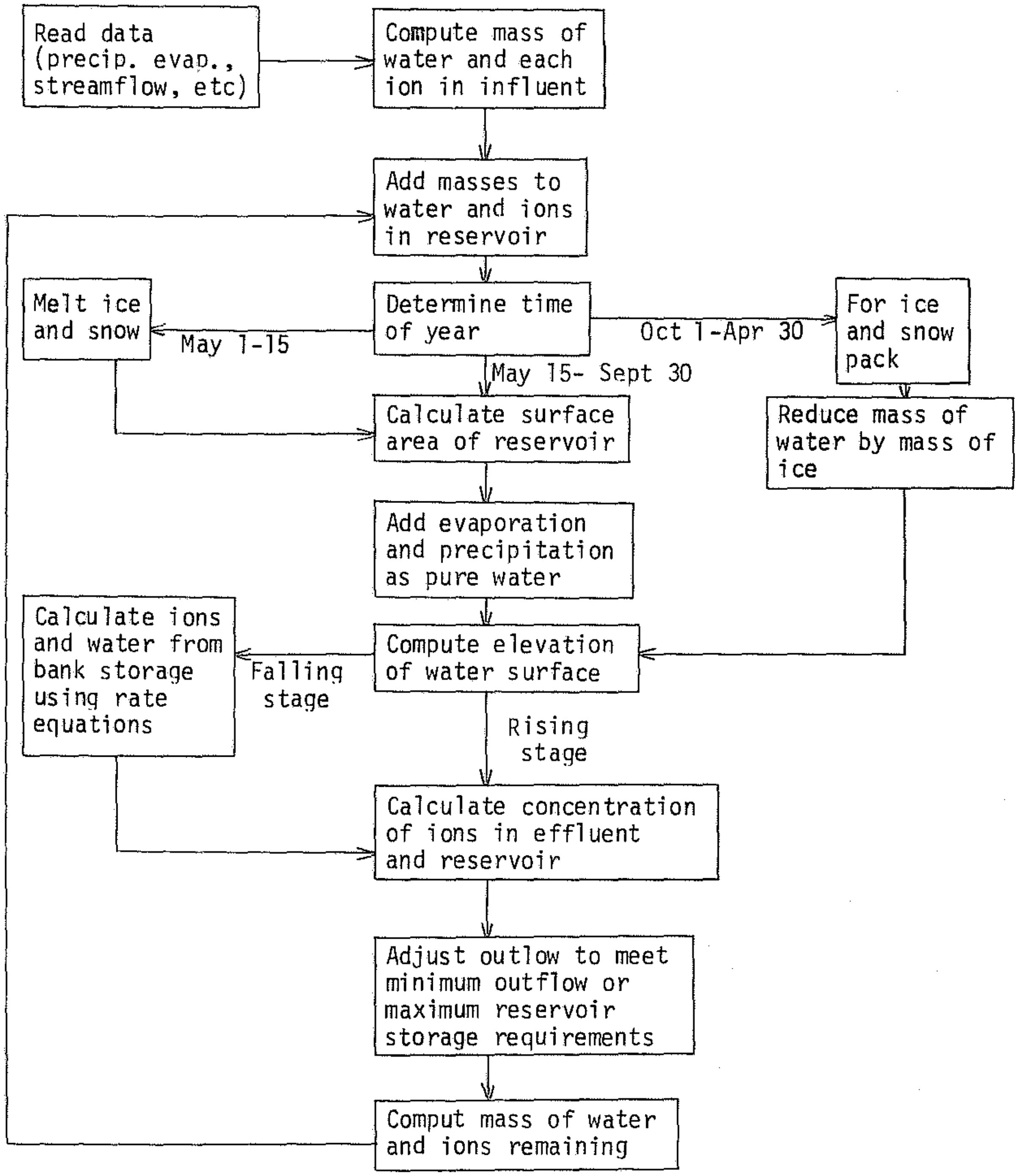

FIGURE 12: Flow chart for a simple reservoir model.

CONCLUSIONS

GEOLOGIC

Leaching of sulfide minerals from bedrock does not pose a hazard to water quality at either the Ship Creek or Monashka Creek Reservoirs.

High-gradient reaches existing below a prominent nick point on Ship Creek may result in rapid headwater erosion and a consequently high sediment input to the present diversion reservoir. The proposed reservoir will flood these reaches and thus may receive a lower sediment input.

Headwater migration of a nick point on Monashka Creek may pose a minor threat in the future to the present dam.

The sets of lineaments at the Monashka Creek reservoir site may provide channels for water to seep from the reservoir. If so, then new springs and increased flow of old springs situated down gradient and on these lineaments can be expected. Loss of water along these lineaments is not expected to pose a serious problem.

GEOCHEMICAL

Flooding of acidic soils will not significantly affect the pH of the reservoir waters by liberation of exchangable hydrogen ions from these soils. Bacterial degradation of organic matter may detrimentally affect the pH and quality of the reservoir water but the extent of this effect cannot be predicted at this time.

Laboratory experiments in which rock is leached with distilled water at different temperatures and for various time periods are a very useful way to study water-rock interactions. Such kinetic data can be used to derive rate equations describing the dissolution of the rock. Thus, it seems that the dissolution of graywacke follows a first-order rate equation. The rate equation derived here is based upon the concentration of the various ions in the rock, which conentration is adjusted by a surface-area term. As a result, if the rate constants derived here are typical of all graywackes, then by knowing the chemical composition of any other graywacke, the chemical composition of water in contact with that graywacke can be predicted, taking into account of course any particle size differences that may exist between the graywacke studied here and that for which predictions are to be made.

Utilizing this approach, it appears that, with the exception of Mg^{+2}, the concentration of the major cations in Ship Creek can be attained in nature by leaching of the metagraywacke of the McHugh Complex by rain water at an average temperature of 5°C, for a time period of 4 months to a year. The uncertainty in estimating the time required to produce this composition is due mainly to uncertainty in the value of the surface area of the graywacke which the rain and ultimately the groundwater contact. The above contact times are probably maxima and the composition could be attained in a matter of a few days to tens of days if the surface area is significantly larger than that used in the above estimates.

Similar predictions based upon the rate equations for the concentration of magnesium to be expected in Ship Creek cannot produce the observed concentration in any reasonable time. The reason for this discrepancy is not known.

The experimental method used here appears to be satisfactory for studying the dissolution of bedrock and coarse alluvium. The dissolution of the fine-grained fraction of alluvium and, presumably, soils yields ambiguous results which are not amenable to the same kinetic interpretation. The reason for this difference in behavior of the materials studied is not known.

From the results of the laboratory study, it is clear that graywacke dissolves incongruently, with calcium being removed about ten times faster than either sodium or potassium. The activation energy for the dissolution of divalent cations from the graywacke is about 20 kcal/mole while that for the monovalent cations is about 10 kcal/mole. This difference in activation energies is due to the stronger coulombic attraction of the divalent cations.

Finally, it appears that a simple computer model can be constructed that would utilize hydrologic data and the rate equations derived here to predict changes in water quality in the Ship Creek reservoir during the course of a year. Such a model was beyond the scope of this study but an approach to modeling the system is provided by the flow chart included in this work.

SUGGESTIONS FOR FUTURE WORK

The chemical composition of the graywacke from the Ship Creek area must be determined. These data should then be used with Equation 4 to derive corrected rate constants for the dissolution of this graywacke. Using these corrected constants, another comparison of predicted versus actual composition of Ship Creek should be made.

The static leaching experiments should be repeated using different size fractions of carefully sized and chemically analyzed graywacke. The surface area of these size fractions should be measured. From this experiment, the effect of surface area can be measured and compared with values predicted from the rate equations. Special effort should be made to obtain precise values for dissolved silica and aluminum species, as well as the other major cations. This may involve using analytical techniques other than atomic absorption spectrometry. At least 4 temperatures should be investigated: perhaps 25°C, 35°C, 45°C, and 55°C, with perhaps 60-day runs at the lowest temperatures. In this way, better estimates of the rate constants can be obtained. In particular, however, by having more than two temperature points, it can be determined if the dissolution follows a first-order rate law or if a higher order rate law is needed.

The reason for the anomalous behavior of magnesium must be determined. The refined rate constants obtained in the above experiment will serve as a check on the rate constant derived in the present work. If predictions based on the laboratory study still do not agree with the magnesium concentration in Ship Creek, then another source for magnesium in Ship Creek or the presence of a new mineral phase in the experiments should be sought.

Studies should be carried out in which carefully sized and analyzed graywacke are leached in columns at different temperatures and carefully controlled flow rates. From such studies, an empirical relation between leaching rate and residence time can be obtained which would permit a more precise estimate of the effect on the chemical composition of water and the flow rate of this water through the rocks.

Static leaching experiments should be repeated using graywacke from Monashka Creek. Such studies should also be done on a variety of rock types to determine rate constants for the dissolution of these rocks.

A computer model should be completed to predict chemical changes in the Ship Creek and Monashka Creek Reservoirs.

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APPENDICES

APPENDIX I

Chemical analyses of Ship Creek water from U.S.G.S. Water Supply Papers 1740, 1640, and 1570 and from Barnwell *et al.* (1972). Chemical analyses for iron, manganese, and silica showed levels to be generally below detection limits.

DATE	10/10/58	12/18/58	2/20/59	4/27/59	5/7/59	6/2/59	6/6/59	6/10/59	6/15/59	6/18/59	6/22/59	6/30/59
FLOW	156	58	45	53	88	556	619	622	584	640	608	332
SiO_2 (ppm)	6.5	7.7	8.3	9.1	9.0		6.5	5.1	6.0	5.8		
Fe "	.04			.04	.07		.02			.02		
Ca "	19	21	20	21	18		14	16	16	15		
Mg "	4.5	5.2	5.2	4.3	3.8		2.4	2.8	3.3	3.8		
Na "	1.8	2.0	2.4	2.8	2.0		1.2	1.4	1.4	1.4		
K "	.5	.3		.5	.6		.4	.4	.4	.4		
HCO_3^- "	49	64	66	68	60	40	42	44	42	44	45	44
$SO_4^=$ "	24	22	18	18	15	14	15	17	19	19		
Cl^- "	2.5	2.5	2.5	1.0	1.0		1.0	1.0	1.0	1.0		
F^- "	0	0	0	0	.2		0	0	0	0		
NO_3^- "	.3	.5	.8	2.1	1.3		.1	.1	.1	.0		
Dis. Sol. (ppm)	83	93	89	92	81		62	66	68	68		
Hardness "	66	74	72	70	60	42	45	52	54	53	55	62
Sp. Cond. (μmhos)	136	147	149	145	131	100	101	108	110	107	116	120
pH	7.4	6.9	6.8	6.8	7.0	7.4	7.5	7.2	7.5	7.2	7.3	7.3
Previous day flow (cfs)	138	60	43	52	82	514	605	619	594	607	630	352

DATE	7/21/59	7/31/59	G.H. 1/24/58	G.H. 3/11/58	G.H. 4/28/58	G.H. 5/13/58	G.H. 3/29/58	8/13/59	8/24/49
FLOW	248	307	62	42	76	130	224	181	811
SiO_2 (ppm)			8.0	7.7	8.4	6.8	5.7		6.3
Fe "			.02	.17	.02	.02	.05		
Ca "	17		21	21	19	17	18		14
Mg "	3.1		4.1	3.6	5.3	3.4	3.7		2.6
Na "	1.9		2.3	2.0	2.2	2.0	2.0		2.3
K "	.1		.5	.4	.3	.2	.2		2.3
HCO_3^- "	49	48	65	63	70	54	49	52	41
$SO_4^=$ "			19	18	16	16	21		15
Cl^- "	2.5		2.0	1.0	1.5	1.0	2.5		.2
F^- "			.1	.1	.0	.1	.0		
NO_3^- "			.3	1.	.5	1.1	.2		1.4
Dis. Sol. (ppm)			89	86	87	74	77		62
Hardness "		72	70	.68	70	56	60	74	46
Sp. Cond. (μmhos)	127	127	152	145	144	124	130	137	100
pH	7.1	7.5						7.5	6.5
Previous day flow (cfs)	241	310	64	43	69	126	234	181	

Appendix II. Description of Soils and Soil Chemistry Data for Ship Creek and Monashka Creek Soils

Area	Sample	Environment	Dry wt g(100cm^3)	pH	Enchangeable H^+ meg/100g	Meg/100cm^3
Ship Creek	A-17	dry, alder grove soil	86.48	5.6	3.59	3.1
	A-20	hardwood grove soil	84.53	5.4	3.19	12.7
	A-22	wet alder soil	91.30	7.1	none	none
	A-29	sphagnum soil	37.56	4.9	8.52	3.2
	A-30	hardwood grove soil	87.80	5.2	6.26	5.5
Monashka Creek	K-14	organic mat on graywacke	119.17	7.0	none	none
	K-15	organic silt	85.69	6.40	0.12	0.1
	K-16	organic silt	93.03	6.49	0.11	0.1

APPENDIX III: Results of Column Experiments at 57°C

Sample No.	Time (hrs)	Flow Rate (ml/min)	Na	Ca	Mg	K	Vol. Total (ml)
2-1	1.00	6.83	0.14	20	.28	.52	409
2-2	3.39	3.41	.080	22	.23	.23	898
2-3	5.00	3.31	.061	24	.10	.10	1215
2-4	10.22	3.35	.034	23	.105	.07	2265
2-5	21.42	3.45	.020	20	.057	n.d.*	4550
2-6	28.72	3.45	.009	17	.047	"	6054
2-7	45.18	3.34	n.d.	13	.036	"	9382
2-8	53.17	3.34	"	11	.034	"	10985
2-9	76.37	5.00	"	n.d.	.025	"	16604
3-1	1.00	3.88	.340	16	.33	.98	233
3-2	3.39	3.20	.098	25	.28	.30	720
3-3	5.00	3.00	.050	22	.18	.16	1008
3-4	10.22	3.20	.020	28	.11	.07	2036
3-5	21.42	3.31	.020	22	.06	n.d.	4264
3-6	28.72	3.28	.009	21	.052	"	5707
3-7	45.18	3.34	n.d.	11	.039	"	8988
3-8	53.17	3.37	"	9	.036	"	10599
3-9	76.33	2.93	"	3.9	.028	"	15025
4-1	1.17	4.84		0.9	.034	.54	
4-2	4.27	2.77		n.d.	.023	.30	
4-3	10.58	4.14		"	.015	.18	
4-4	21.45	3.15		"	.010	.07	
5-1	1.17	4.33		0.9	.033	.62	
5-2	4.27	2.20		n.d.	.020	.35	
5-3	10.58	3.06		"	.015	.18	
5-4	21.45	2.37		"	.017	.06	

APPENDIX III Continued

Sample No.	Time (hrs)	Flow Rate (ml/min)	Na	Ca	Mg	K	Vol. Total (ml)
6-1	0.08	10.6		51	.72	30.	
6-2	1.03	10.6		74	.33	.77	
6-3	5.18	1.53		75	.32	1.43	
6-4	21.74	2.53		52	.57	.12	
6-5	26.22	2.40		40	.17	.06	
6-6	51.75	2.50		49	.11	.06	
7-1	0.08	7.64		18	.33	1.91	
7-2	1.03	7.64		.6	.30	.48	
7-3	5.18	4.47		n.d.	.21	.28	
7-4	21.74	1.32		"	.17	.19	
7-5	26.22	1.00		"	.09	.05	
7-6	51.75	1.45		"	.06	n.d.	

*Signifies that the concentration of this ion was below the analytical detection limit.

APPENDIX IV: Chemical Analyses for the Dissolution of Graywacke and Alluvium (Mg^{++})

		GRAYWACKE			COARSE ALLUVIUM (greater than 100 mesh)			FINE ALLUVIUM (less than 100 mesh)		
		5 days	15 days	30 days	5 days	15 days	30 days	5 days	15 days	30 days
5°	A	.35	.42	.45	.26	.18	.25	.50	.44	.44
	B	.44	.36	.35	.21	.16	.24	.61	.35	.46
	C	.37	.38	.34	.20	.15	.21	1.03	.41	.54
	Ave	.387	.387	.380	.223	.163	.233	.713	.400	.480
	S.D.	.047	.031	.061	.032	.015	.021	.500	.046	.043
37°	A	.49	.92	1.18	.29	.26	.25	.85	.72	.76
	B	.46	.70	1.09	.27	.20	.25	.65	.70	.72
	C	.45	.61	.97	.29	.23	.26	.75	.78	.83
	Ave	.467	.743	1.08	.283	.230	.253	.750	.733	.770
	S.D.	.021	.159	.105	.012	.030	.006	.100	.042	.056
57°	A	.85	3.4	.51	.66	6.5	.31	.47	.53	.35
	B	1.06	3.9	2.2	.59	2.1	.24	.64	.53	.41
	C	.98	3.3	.79	.31	5.1	.39	.48	.48	.43
	Ave	.963	3.53	1.19	.520	4.57	.313	.530	.513	.397
	S.D.	.106	±.321	±0.91	.185	±2.25	±0.075	.095	±0.029	±0.042

APPENDIX IV: Chemical Analyses for the Dissolution of Graywacke and Alluvium (Ca^{++})

		GRAYWACKE			COARSE ALLUVIUM (greater than 100 mesh)			FINE ALLUVIUM (less than 100 mesh)		
		5 days	15 days	30 days	5 days	15 days	30 days	5 days	15 days	30 days
5°	A	36	38	45	10	12	9	251	75	71
	B	25	29	32	9	9	12	162	112	52
	C	29	31	33	7	7	14	104	88	150
	Ave	30.1	32.7	36.7	8.7	9.3	11.7	172	91.7	91.0
	S.D.	5.54	4.73	7.23	1.53	2.52	2.52	74.	18.8	51.9
37°	A	44	82	133	15	10	10	134	109	99
	B	48	87	135	12	9	10	130	81	130
	C	54	91	167	12	10	11	157	98	97
	Ave	48.7	86.7	145	13.0	9.67	10.3	140	96	109
	S.D.	5.03	4.51	19.1	1.73	0.58	0.58	14.6	14.1	185
57°	A	125	700	153	12	165	13	100	125	115
	B	100	760	138	15	330	13	100	110	107
	C	107	430	118	13	320	17	92	131	110
	Ave	111	630	136	13.3	272	14.3	97.3	122	111
	S.D.	12.9	176	17.6	1.53	92.5	2.31	4.62	10.8	4.04

APPENDIX IV: Chemical Analyses for the Dissolution of Graywacke and Alluvium (Na^{++})

		GRAYWACKE			COARSE ALLUVIUM (greater than 100 mesh)			FINE ALLUVIUM (less than 100 mesh)		
		5 days	15 days	30 days	5 days	15 days	30 days	5 days	15 days	30 days
5°	A	.61	.66	.61	.41	.35	.48	1.37	.78	.86
	B	.65	.68	.70	.43	.42	.40	.84	.86	.88
	C.	.76	.67	.66	.38	.48	.45	.97	.83	.93
	Ave	.673	.670	.657	.407	.417	.443	1.060	.823	.890
	S.D.	.078	±.010	±.045	.025	±.065	.040	±.276	±.040	±.036
37°	A	1.00	1.26	1.30	.80	.72	.70	1.09	1.26	1.30
	B	1.06	1.11	1.30	.70	.68	.68	1.30	1.12	1.29
	C	1.00	1.13	1.31	.70	.86	.77	1.16	1.09	1.16
	Ave	1.02	1.17	1.30	.733	.753	.717	1.18	1.16	1.25
	S.D.	±.035	±.085	±.006	±.058	±.095	±.047	±.107	±.091	±.078
57°	A	1.29	2.00	1.43	.93	2.29	.77	1.33	1.42	1.35
	B	1.30	2.06	1.26	.97	3.16	.68	1.37	1.51	1.37
	C	1.39	1.97	1.26	.90	3.30	1.03	1.32	1.57	1.26
	Ave	1.33	2.01	1.32	.933	2.92	.827	1.34	1.50	1.33
	S.D.	±.055	±.046	±.098	±.035	±.547	±.182	±.026	±.075	±.059

APPENDIX IV: Chemical Analyses for the Dissolution of Graywacke and Alluvium (K^+)

		GRAYWACKE			COARSE ALLUVIUM (greater than 100 mesh)			FINE ALLUVIUM (less than 100 mesh)		
		5 days	15 days	30 days	5 days	15 days	30 days	5 days	15 days	30 days
5°	A	.61	.65	.56	.58	.59	.53	.73	.80	.93
	B	.62	.54	.54	.60	.63	.50	.70	.51	.92
	C	.55	.56	.52	.54	.52	.55	.65	.63	.87
	Ave	.593	.583	.540	.573	.580	.527	.693	.647	.907
	S.D.	±.038	±.059	±.020	±.031	.056	±.025	.040	±.146	±.032
37°	A	.72	.82	1.20	.91	.64	.57	.82	.85	.97
	B	.69	.96	.99	.71	.64	.60	.91	.93	.95
	C	.67	.98	.96	.62	.82	.60	1.03	1.01	.93
	Ave	.693	.920	1.050	.737	.700	.590	.920	.930	.950
	S.D.	±.025	±.087	±.131	±.148	±.104	±.017	±.105	±.080	±.020
57°	A	1.05	1.95	1.00	.88	2.10	.69	1.22	1.20	1.05
	B	.92	1.66	1.30	.78	1.95	.59	.96	1.21	1.18
	C	.82	1.91	.97	1.01	2.01	.61	.98	.99	1.30
	Ave	.932	1.84	1.09	.890	2.02	.630	1.05	1.13	1.18
	S.D.	±.115	±.157	±.182	±.115	.075	±.058	±.145	±.125	±.125

APPENDIX IV: Chemical Analyses for the Dissolution of Graywacke and Alluvium (Fe^{++})*

		GRAYWACKE			COARSE ALLUVIUM (greater than 100 mesh)			FINE ALLUVIUM (less than 100 mesh)		
		5 days	15 days	30 days	5 days	15 days	30 days	5 days	15 days	30 days
57°	A	ǂ		11.71		.36	.21			
	B			2.44		4.4	.21			
	C			2.63		6.3	.44			

*Iron analyses for static leaching experiments. All numbers are in mg/l.

ǂOnly the nine samples indicated had iron concentrations above the detection line.

Appendix V: Calculation of Approximate Equilibrium Constant for the Ion Exchange Reaction of the Reservoir Waters and Organic Soil Mat.

This calculation is based upon the quantities of exchangeable H^+ in the soil mat, as given in Appendix III, Column 7, the results of the equilibration experiment described on page , and the chemical composition of Ship Creek water given in Appendix I.

As shown in Appendix I, the water of Ship Creek is essentially a calcium-bicarbonate water. At pH 7.2 (the initial conditions of the experiment, p.), the bicarbonate content of the water is about 60 mg/l or 1×10^{-3} moles/l. The pH of this water is governed by the first ionization of carbonic acid.

$$H_2CO_3 \qquad H^+ + HCO_3^-$$

for which the ionization constant K, is $10^{-6.4}$. At pH 7.2 and 1×10^{-3} m/L HCO_3^-, the H_2CO_3 concentration calculated from the expression for the ionization constant is:

$$H_2CO_3 = \frac{(H+)(HCO_3^-)}{K_i} = \frac{(10^{-7.2})(10^{-3.0})}{10^{-6.4}} = 10^{-3.8}$$

In the equilibration experiment, at equilibrium, the final pH was 7.0, whereas the initial pH was 7.2. The problem to be solved is to determine how much H^+ was liberated from the soil with the result that the pH of the $H_2CO_3 - HCO_3^-$ system was reduced from 7.2 to 7.0.

Recasting the expression for the first ionization constant:

$$(H^+) = \frac{K_i(H_2CO_3)}{(HCO_3^-)}$$

Note that as (H^+) is increased, (HCO_3^-) decreases and (H_2CO_3) increases by the same quantity. If X is the fractional decrease in (HCO_3^-), then:

$$(10^{-7}) = \frac{3.98x10^{-7}\ (1.585x10^{-4}\ (1+X))}{(1x10^{-3}\ (1=X))}$$

Solving for X, it is found that $X = 0.23$, or HCO_3^- must decrease by 23%. Because (HCO_3^-) initially was $1x10^{-3}$, and (HCO_3^-) finally was $0.77x10^{-3}$, then 0.23x10-3 moles/L of H^+ was released via the ion-exchange reaction.

The cations concentration of Ship Creek is about $1.4x10^{-3}$ equivalent liter (See Appendix I), which, for convenience, will be designated (Na^+). The ion exchange reaction is:

$$H^+\ Org + Na^+ \qquad Na^+\ Org + H^+$$

and

$$K_{eq} \cong \frac{(H^+)\ (Na^+Org)}{(Na^+)\ (H^+Org)} \cong \frac{(H^+)}{(Na^+)}$$

Because the release of $2.3x10^{-4}$ moles H^+ requires the exchange of $2.3x10^{-4}$ equivalents of other cations, then at equilibrium:

$$K \cong \frac{(2.3x10^{-4})}{(1.4x10^{-3} - 2.3x10^{-4})} \cong$$

or the ion exchange reaction does not proceed far to the right. To liberate all the exchangeable H^+ on the organic mat would require a five-fold increase in the cationic concentration of the reservoir water. Such an increase would also increase the buffer capacity of the water and hence the organic mat should have little or no effect on the pH of the reservoir water even as a result of such a drastic compositional change as this.

Appendix VI: Derivation of Equation 6

Derivation of Equation 6 gives the instantaneous concentration of an ion in the effluent of a column as a function of time, the rate of flow of solution through the column, and the leaching rate determined from batch studies. In this derivation it is assumed:

1. The flow rate is constant
2. The flow is slow enough for batch-type rate constants to be applicable.
3. The solution is at constant temperature.
4. The same grain-size fraction is used in both batch and column studies.

For the column, the instantaneous concentration of an ion at any time is $C_i^x = dQ/dV$, where Q is the total quantity of ions leached from the rock and V is the total volume of solution put through the column up to time t. From batch studies, $Q = N_o - N_o e^{-kt}$ where N_o is a constant equal to the concentration in parts per million of the ion in question in the rock, k is the rate constant at the temperature of interest, and t is the time in days. The rate of change of Q with respect to time at constant volume is:

$$\frac{\partial Q}{\partial t_V} = N_o k e^{-kt}$$

The flow rate through the column is $\frac{dV}{dt} = a$, where a is assumed to be constant.

Because a is constant, $\frac{dt}{dV} = \frac{1}{a}$.

Relating the instantaneous concentration in the effluent to the leaching rate from batch studies and the flow rate through the column:

$$C_i^x = \frac{dQ}{dV} = \frac{dQ}{dt} x \frac{dt}{dV}$$

$$C_i^x = \frac{N_o k e^{-kt}}{a}$$

Appendix VII: Leaching-Rate Constants Estimated from Column Data.

Using the elution curves shown in Figures through , the total quantity Q_t of a particular ion eluted in time t at a constant flow rate is calculated by obtaining the area under the curve from t_o to t, where t is obtained by dividing the cumulative volume by the average flow rate of 3.61 ml/min. From this quantity Q_t, the threshold quantity, Q_{th} corresponding to the easily eluted ions shown in Table , is subtracted. The difference Q_L is the quantity of ions leached from the silicate surface. The value of N for the different ions in the graywacke is obtained by mulitiplying the value of N in the batch studies by 6.4 in order to correct for the difference in mass of the 32.0 gm graywacke in the column versus the 5.0 gm graywacke in the batch runs. Note that, because the same grain size fraction was used in both column and batch studies, it is not necessary to correct for a difference in grain size. Having obtained Q_i and N, for the t of interest, Equation 4 is used as before for the dynamic leaching of Mg^{+2}, Ca^{+2}, Na^{+} and K^{+} at 57°C are as follows:

Ion	k column (day^{-1})	k batch (day^{-1})	k col/ k batch
Mg^{+2}	5.93×10^{-4}	2.39×10^{-4}	2.48
Ca^{+2}	1.21×10^{-1}	3.39×10^{-2}	3.57
Na^{+2}*	3.65×10^{-4}	7.24×10^{-5}	5.04
K^{+}	8.03×10^{-4}	1.32×10^{-4}	6.09

*The threshold value for Na^{+} was not subtracted in this calculation.

In general, the leaching rate in the columns is from 2 to 6 times faster than that in the batch runs.

APPENDIX VIII: Calculation of Rate Constant at 5°C.

Example: Calculate rate constant for Mg^{+2} dissolution at 5°C from Arrhenius equation.

Data: Rate constants at 37°C and 57°C

Method: A plot of *log k* versus 1/T (°K) should be a straight line, if dissolution of graywacke follows a first-order rate law. Because only 2 points are available here, such a plot must be a straight line. Hence a 2-point formula is applicable.

$(Y_2 - Y_1) = m\,(X_2 - X_1)$

Let: $Y_2 = \log k_{57°} = -3.62 \text{ day}^{-1}$

$Y_1 = \log k_{37°} = -4.503 \text{ day}^{-1}$

$X_2 = 1/T_{°K} = \frac{1}{330°K} = 3.030x10^{-3}°K^{-1}$

$X_1 = 1/310 = 3.226x10^{-3}°K^{-1}$

Solving for m, we find $m = -4.505°k \text{ day}^{-1}$

Recasting the 2-point formula and solving for Y_2 at $T = 5°C$.

or $1/278°k = 3.597x10^{-3}$, where $Y_1 = -4.503$

$Y_2 = -4.505k \text{ day}^{-1} (3.597-3.225) + (-4.503) = -6.174$ or $\log k_{5°C} = -6.174 \text{ day}^{-1}$