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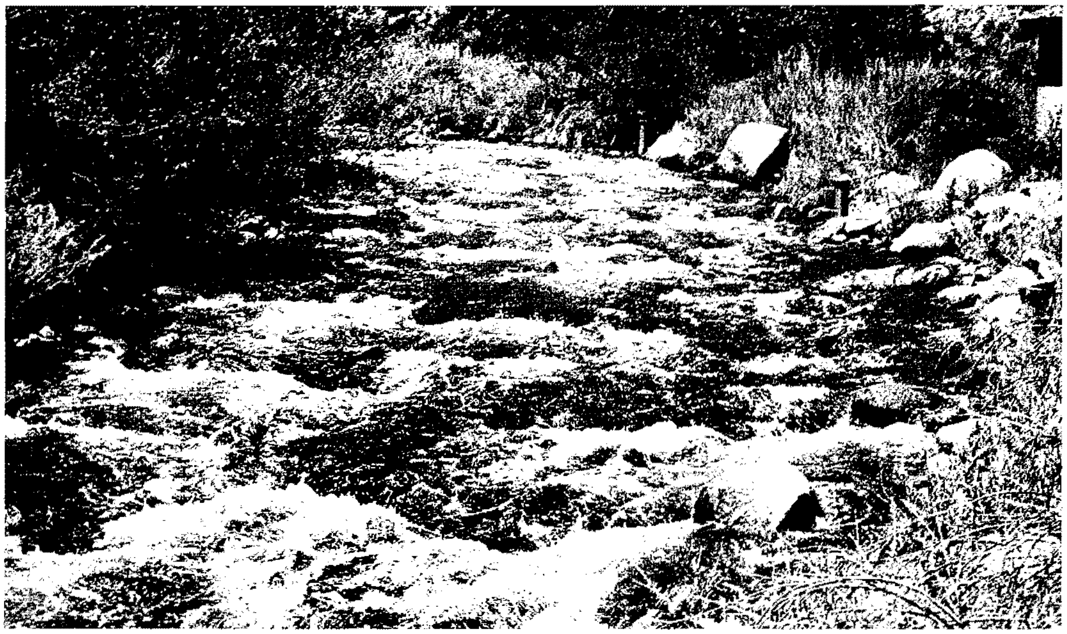

Utah Water Research Laboratory
College of Engineering
Utah State University
Logan, Utah 84322

April 1981

WATER QUALITY SERIES
UWRL/Q-81/02

CALCIUM CARBONATE PRECIPITATION AS INFLUENCED BY STREAM PRIMARY PRODUCTION

by

Gretchen L. Rupp
V. Dean Adams

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ABSTRACT

The potential influence of periphyton photosynthesis on calcium carbonate precipitation was studied for the Logan River, Bear River Mountains, northern Utah. The water chemistry, hydrology, and benthic primary production of the river were monitored for one year. Periphyton photosynthesis and calcium carbonate precipitation were measured concurrently in laboratory experiments utilizing radioisotopic tracers. These experiments investigated the effects of water temperature, velocity, and macronutrient concentration on photosynthetically induced calcium carbonate precipitation.

In these experiments, the biological induction of calcium carbonate precipitation was not correlated with water nutrient level. It did, however, reflect water temperature, and was greatest at approximately 10°C. Furthermore, benthic calcium carbonate precipitation decreased nearly uniformly as water velocity increased.

Application of the experimental results to the Logan River system suggests that biological activity would have the greatest influence in the high-altitude, first and second-order tributaries to the river, and would decline in importance in the downstream direction. Biological activity may account for up to 25 percent of the precipitation of calcium carbonate in the Logan River during certain times of the year.

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INTRODUCTION

Nature of the Problem

The ions of the bicarbonate-hardness system (Ca^{2+}, Mg^{2+}, HCO_3^-, CO_3^{2-}) constitute a major portion of the dissolved solids in many fresh waters. This system affects water quality in a number of vital ways. To begin, salinity is a growing problem in many parts of the Great Basin and in the Colorado River drainage system. Since calcium carbonate is the major salt precipitated from solution in the streams of limestone watersheds, the bicarbonate-hardness system may exert a significant effect on the total dissolved solids (TDS) content of streamwaters, as well as on the sodium adsorption ratio (SAR) of the waters. Furthermore, in-stream metal toxicity has been diagnosed in many parts of the United States (cf. Boney 1975; Leland et al. 1977). Anions of the bicarbonate-hardness system readily complex dissolved metals (Stumm and Morgan 1970), and there is evidence that these complexes are substantially less toxic than hydroxy metal complexes or uncomplexed metal cations (Tarbata 1969; Pagenkopf et al. 1974). In addition, phosphorus, the nutrient most frequently implicated in nuisance algal blooms, may be removed from solution with precipitating calcium carbonate (Boischot et al. 1950; Cole et al. 1953). The bicarbonate-hardness system may thereby have a governing influence on aquatic production. Finally, crystalline calcium carbonate readily sorbs dissolved organic compounds, which are thought to comprise the chief energy source in some lotic food webs (Wetzel 1975).

Explosive population growth in the Western states has strained water-delivery systems for irrigation, municipal use and recreation. Extensive stream diversion projects have been carried out, and more are planned. Alteration of streamflow regimes has been shown to substantially impact the functioning of stream ecosystems, particularly at the level of the periphyton, the primary producers. Since stream primary production may exert a major influence on calcium carbonate dynamics, streamflow alteration might be expected to effect substantial changes in the bicarbonate-hardness system.

This system has recently taken on added importance to western streams. Acid precipitation has been documented in isolated, high-altitude watersheds in the Colorado Rockies (Lewis and Grant 1980). Since the bicarbonate-hardness system is the major buffering system in fresh waters, factors controlling calcium carbonate chemistry will have a substantial influence on the degree of change brought about by acid precipitation falling on stream channels.

A thorough understanding of the potential responses of the bicarbonate hardness system is essential for environmental impact assessment of changing the flow regime of western streams. This study addressed the responses associated with the influence of lotic photosynthesis on the calcium carbonate system. The study involved both long-term field studies and short-term laboratory experiments. A similar study involving lentic systems is reported by Messer et al. (1981).

Objectives

The general project objective was to assess the potential impact of periphyton photosynthesis on calcium carbonate dynamics. The field setting for this study was a hard-water mountain river, the Logan River, in the Northern Wasatch Range, Utah. The specific objectives were to:

1) Develop a laboratory radiotracer technique for measuring both the periphyton photosynthetic rate and the calcium carbonate and orthophosphorus precipitation rates.

2) Perform laboratory experiments to quantify the relationship between calcium carbonate precipitation and orthophosphorus sorption in the periphyton matrix.

3) Perform experiments to determine the relationship between periphyton photosynthesis and calcium carbonate precipitation under various water velocity, temperature and nutrient conditions.

4) Monitor physical and chemical variables, as well as periphyton community parameters, in the Logan River through an annual cycle.

5) Relate the laboratory results to these field conditions to predict the magnitude of the photosynthetic influence on calcium carbonate dynamics in a natural stream.

LITERATURE REVIEW

Origin and Chemistry of Calcium Carbonate in Streams

Organic decay and the respiration of plant roots and soil microbes produce carbon dioxide, which dissolves in water infiltrating through the soil mantle. The resulting groundwater may have a carbon dioxide content many times greater than that of rainwater at equilibrium with the atmosphere (Ruttner 1963). Carbonic acid is formed in the groundwater by the hydration of carbon dioxide:

$$CO_2\ (aq) + H_2O \rightleftharpoons H_2CO_3\ (aq) \quad . \quad . \quad . \quad (1)$$

In turn, the dissociation of carbonic acid produces hydrogen ion which attacks limestone:

$$H^+ + CaCO_3(s) \rightleftharpoons Ca^{2+}\ (aq) + HCO_3^-\ (aq) \quad . \ . \ . \ . \ . \ . \ . \quad (2)$$

This subterranean weathering of carbonate sedimentary rock is the chief source of dissolved calcium in streamwater (Hem 1970).

As acidic groundwater emerges from springs, dissolved carbon dioxide is lost to the air. Calcium carbonate solubility decreases, and massive precipitation may occur immediately downstream from the springs (Golubić 1973). Such travertine deposition has been studied at springs in the German Alps (Irion and Müller 1968), and in a karst region of Arizona (Cole and Batchelder 1969). In general, carbon dioxide and alkalinity concentrations decrease, and pH and temperature increase, downstream from carbonate springs (Golubić 1973). Thus, any biologically-induced changes in the $CaCO_3$ dynamics of hard-water streams occur against a backdrop of chemically-induced changes.

Calcite is the most stable $CaCO_3$ mineral, and the one predominantly formed in fresh waters of low ionic strength and low temperature (Krauskopf 1979). Its equilibrium solubility is defined by the equation

$$(Ca^{2+})\ (CO_3^{2-}) = K_{sp} \cong 4 \times 10^{-9}\ @\ 20^{\circ}C \quad . \ . \ . \ . \ . \ . \ . \quad (3)$$

where (Ca^{2+}) and (CO_3^{2-}) are the activities of calcium and carbonate ion, respectively, and K_{sp} is the solubility product constant for calcite. In most hard waters, calcium is present in great abundance, and it is carbonate ion activity which determines the potential for calcite precipitation. The abundance of carbonate ion is regulated through the formation and dissociation of carbonic acid:

$$CO_2\ (g) \rightleftharpoons CO_2\ (aq) \quad . \ . \ . \ . \ . \ . \ . \quad (4)$$

$$CO_2\ (aq) + H_2O \rightleftharpoons H_2CO_3 \quad . \ . \ . \ . \ . \ . \quad (5)$$

Since $CO_2(aq)$ and H_2CO_3 are analytically indistinguishable, $H_2CO_3^*$ is understood to represent a composite species in the dissociation equations:

$$H_2CO_3^* \rightleftharpoons H^+ + HCO_3^- \quad . \ . \ . \ . \ . \ . \ . \quad (6)$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \quad . \ . \ . \ . \ . \ . \ . \ . \quad (7)$$

The potential for calcium carbonate precipitation is therefore strongly dependent on pH. It is also a function of water temperature and of ionic strength. The temperature-dependency of calcite precipitation has been formulated as

$$\log K_{sp} = 13.87 - 0.040T - 3059/T \quad . \ . \quad (8)$$

where temperature (T) is in degrees Kelvin (Plummer 1975). Ionic strength influences calcite solubility through the "indifferent salt effect," in which long-range electrostatic interactions with other ions diminish the activities of calcium and carbonate. In addition, the true activities of calcium and carbonate ions may deviate from those calculated on the basis of these long-range interactions due to the formation of soluble metal-ligand complexes. Such ion-pairing is often considered to be negligible in fresh water (Garrels and Christ 1965); however, in solutions of divalent electrolytes, it may be widespread (Butler 1964). Ion-pairing has been shown to significantly influence the carbonate equilibria of a hard-water lake in New York (Brunskill 1969). The effect of ion-pairing is to increase mineral solubility, sometimes by several orders of magnitude, over that predicted simply on the basis of the indifferent salt effect (Stumm and Morgan 1970).

Kinetic considerations have also been shown to be of paramount importance in calcite precipitation. Solutions of calcium carbonate in pure water precipitate spontaneously when supersaturated by a factor of two (Krauskopf 1979). Yet natural waters are frequently found to be very strongly supersaturated with respect to calcite; indeed, Kelts and Hsü (1978) concluded that lake waters seldom reach equilibrium with respect to calcite. Several factors apparently influence calcite precipitation kinetics. Calcium carbonate nucleation has been shown to occur much more rapidly in Mg-free seawater than in normal seawater (Pytkowicz 1965). This is a statistical phenomenon, with Ca^{2+}-Mg^{2+} interactions occurring much more readily than Ca^{2+}-$CO_3{}^{2-}$ interactions because of the very high Mg^{2+} concentration in seawater. De Boer (1977) demonstrated experimentally that the abundance of seed crystals strongly influences the kinetics of $CaCO_3$ precipitation. However, this is not likely to be a limiting factor in natural aquatic systems, where numerous potential crystallization sites exist.

The presence of organic compounds has been shown to alter the kinetics of calcite precipitation under a wide variety of conditions. It has been demonstrated in the laboratory that various organic acids, by complexing calcium ion, adsorb to calcite crystals and inhibit crystal growth (Kitano and Hood 1965). The occurrence of such adsorption on a large scale has been shown for Lawrence Lake, Michigan (Otsuki and Wetzel 1974; Wetzel and Otsuki 1974). In this hard-water lake, yellow organic acids are seasonally removed from solution by adsorption to precipitating calcium carbonate. In carefully controlled kinetic experiments, Reynolds (1978) investigated the effects of natural plant polyphenols on the growth of calcite crystals in artificial Lake Powell water. The presence of these compounds completely altered the mode of crystallization. Reynolds postulated that polyphenol adsorption changes the crystal growth pattern from a spiral dislocation mechanism to a much slower polynuclear spreading mechanism.

$CaCO_3$ - Phosphorus Interactions

The sediment component of aquatic ecosystems is recognized as a major sink for inorganic phosphorus (cf. Bartleson 1971; Hwang et al. 1976). Dissolved phosphorus has been shown to interact specifically with calcite in a number of natural waters. Eyster (1958) asserted that orthophosphate acted to prevent calcite precipitation in Bass Lake, a Michigan marl lake. Otsuki and Wetzel (1972) observed the removal of dissolved phosphate during calcite precipitation in the water of Lawrence Lake, Michigan. They suggested that the biogenic precipitation of calcite, and the consequent phosphorus depletion, represented a density-determined self-limiting mechanism for phytoplankton. Suspended calcite has been shown to sorb orthophosphate in the Maumee River system in northern Ohio (Green et al. 1978).

Kinetic experiments have suggested two distinct mechanisms for the sorption of phosphate by calcite crystals. Cole et al. (1953) observed that, at orthophosphate phosphorus concentrations of less than 3×10^{-4} M (9 mg P/l), phosphorus was removed from solution at a rate directly proportional to the rate of calcite precipitation. They interpreted this as evidence for the mono-layer adsorption of phosphate onto calcite crystals. However, at similar phosphate levels (2.4×10^{-4} M P, or 7.2 mg P/l) Clark and Turner (1955) observed the co-precipitation of hydroxyapatite with calcite. Both Clark and Turner (1955) and Cole et al. (1953) found rapid removal of phosphorus at high orthophosphate concentrations. This was interpreted as the precipitation of dicalcium phosphate.

Griffin and Jurinak (1974) also observed that phosphorus sorption onto calcite involved two distinct mechanisms. They concluded that phosphate removal was a surface-mediated phenomenon, which proceeds very rapidly at first, then at a very slow rate. The rapid reaction, second-order with respect to phosphate, was explained as surface sorption of phosphate ions onto calcite crystals. The slower, first-order reaction was interpreted as the formation of calcium phosphate heteronuclei on the crystal surfaces.

Photosynthesis and $CaCO_3$ Precipitation

A correlation between aquatic photosynthesis and calcite precipitation in the marl lakes of Europe and North America was noted early in this century. Minder (1922) first pointed out that plankton photosynthesis can cause a flocculent precipitate in the water column which is the same material as the calcareous coating seen on aquatic macrophytes, and that the precipitation processes are identical. He expressed the photosynthetic effect on the calcite equilibrium by the equation

$$Ca^{2+} + 2HCO_3^- \rightleftharpoons CO_2\ (aq) + H_2O + CaCO_3\ (s) \quad . \ . \ . \ . \ . \ . \ . \ (9)$$

in which uptake of each mole of CO_2 results in the precipitation of one mole of $CaCO_3$ from solution. Ruttner (1963) noted that algae which take up bicarbonate ion exert a greater effect on pH, and hence could potentially induce more $CaCO_3$ precipitation, than those which take up CO_2. This is because the enzyme-catalyzed uptake of bicarbonate involves the release of strong base to the medium:

$$HCO_3^- \rightleftharpoons CO_2 + OH^- \quad . \ . \ . \ . \ . \ . \ . \ . \ (10)$$

Although the phrase "algal CO_2 uptake" is generally used, algae growing in alkaline, hard water utilize bicarbonate preferentially (Wetzel 1975), and it is likely that this is the more important process in these waters.

Biogenic calcium carbonate precipitation has historically been of great interest to geologists. It has long been recognized that an understanding of the biology of calcareous freshwater algal communities is the key to the interpretation of fossil stromatolites. Following the lead of Tilden (1897), early twentieth-century geologists developed elaborate systems for the classification of recent carbonate deposits on the bases of algal association and gross morphology. Eventually, it was pointed out that the degree of calcification of a freshwater alga is a function of water chemistry, and should not be used as a taxonomic characteristic (Butcher 1945). Nonetheless, morphological, taxonomic and textural studies of recent calcareous algal mats are vital to the characterization of ancient sedimentary environments (cf. Monty and Hardy 1976; Halley 1976; Kelts and Hsü 1978). Golubić (1976) commented on the preponderance of blue-green algae in such associations. He hypothesized that Cyanophytes are so prevalent in these associations, revalent in these associations, relative to other aquatic plants, because they thrive in waters of relatively high pH, in which $CaCO_3$ precipitation is favored. Eggleston and Dean (1976) and Pentecost (1978) stated that the matted growth form and gelatinous sheaths of Cyanophytes enable them to trap suspended mineral matter. Crystals of $CaCO_3$ precipitated in situ have been distinguished from trapped crystals by optical microscopy and electron microscopy (cf. Irion and Müller 1968). However, these examinations give little clue as to the relative significance of the two sources of solid precipitate, and do not distinguish between chemically and biologically-induced $CaCO_3$ precipitation. In addition, diagenesis of trapped crystals is readily observed (Golubić and Fischer 1975). Hence the real importance of photosynthesis in the accretion of benthic carbonate material has never been elucidated on a microscopic scale (Golubić 1973).

Several qualitative and semi-quantitative field studies have investigated the relationship between algal photosynthesis and $CaCO_3$ precipitation. Strong and Eadie (1978) publicized a series of striking LANDSAT photographs of "whitings" in Lakes Erie, Ontario, and Michigan during the summer of 1973. Using scanning electron microscopy, they determined that the white color of the lakes was caused by high concentrations of autochthonously precipitated calcite several meters below the water surface. They also examined concurrent temperature and productivity data for Lake Michigan, but were unable to ascertain how much of the precipitation was attributable to phytoplankton activity and how much to heightened summertime water temperatures.

Brunskill (1969) reported a study in which he was able to estimate the relative importances of chemical and biological factors in calcite precipitation. In this study, the water chemistry of Fayetteville Green Lake, New York, was closely monitored, and precipitation rates were determined from sediment trap data. Phytoplankton production was assayed by light-and-dark bottle ^{14}C tests. The observed range of photosynthetic rates was very great; however, even at the highest rates measured, Brunskill concluded that photosynthetic activity could not have contributed substantially to the observed precipitation.

The dynamics of inorganic carbon have been extensively studied in Lawrence Lake, Michigan (Otsuki and Wetzel 1974; Wetzel and Otsuki 1974). Alkalinity and calcium-ion budgets constructed over a one-year period suggested that substantial calcium carbonate precipitation occurs during the summer months in Lawrence Lake. The investigators concluded that this precipitation was not initiated by increasing water temperatures, because its onset lagged a month behind a 10-degree spring warming. They pointed out the strong temporal correlation between calcium carbonate precipitation and heightened phytoplankton production and argued for the photosynthetic induction of massive epilimnetic precipitation.

Kelts and Hsü (1978) made a detailed study of the sedimentology and water chemistry of Lake Zurich, a deep, hard-water lake in Switzerland. They found that varve calcite layer thickness was not strongly correlated with summer phytoplankton production, as measured by sediment organic matter. Their microscopic examinations revealed that calcite crystals which grew on the surfaces of macrophytes were much smaller than those formed in suspension in the epilimnion. Kelts and Hsü attributed this to the short time periods during which photosynthetically-induced calcite supersaturation persists. During 1975, the authors closely monitored the physical, chemical and biological characteristics of the Lake Zurich epilimnion. They found that dissolved CO_2 was completely removed by a spring diatom bloom; the onset of calcite precipitation followed shortly thereafter. Precipitation continued until November. Because of heightened water temperature, the summer precipitation event could not be definitely ascribed to photosynthetic CO_2 uptake.

Megard (1969) performed somewhat similar limnological investigations of six Minnesota lakes, with the goal of quantifying the relationship between photosynthesis and calcite precipitation. Calcite precipitation rates were calculated from the Ca^{2+} and alkalinity depletion in the epilimnion. Dilution effects were taken into account by monitoring the concentration of Mg^{2+}, which was assumed to be conservative. Phytoplankton production was assayed by the light-and-dark O_2 method. The ratio of epilimnetic Ca^{2+} depletion to photosynthetic CO_2 uptake was found to be approximately one to four for all six lakes. Megard explained the negative deviation from the predicted one to one ratio as a kinetic effect, resulting from the complexation of calcite nucleation centers by dissolved organic compounds. He concluded that calcite precipitation was induced by abiotic factors at only one time of year, when spring ice breakup allowed large quantities of dissolved CO_2 to escape from the lakes into the atmosphere. Calcite precipitation at all other times was attributed to photosynthetic activity.

Green and Smeck (1979) studied particulate calcite in the Maumee River system of northern Ohio. They distinguished calcite crystals formed within the stream (secondary crystals) from erosional calcite (primary crystals) by optical microscopy. Although the Maumee River was supersaturated for the entire duration of the study, the in-stream calcite crystallization rate fluctuated considerably over periods of days. The induction of crystallization was apparently unrelated to water temperature or calcium ion concentration. However, Green and Smeck found that the abundance of secondary suspended calcite crystals was correlated with high densities of phytoplankton cells. They concluded that algal CO_2 uptake was the principal factor inducing calcite precipitation in the Maumee River and its tributaries.

One quantitative study examining stream periphyton and $CaCO_3$ precipitation has been published (Pentecost 1978). In this investigation, long-term growth rates of lotic carbonate deposits in 27 British streams were estimated by measuring marked deposits or by noting the rate at which a surface layer of carborundum was buried by the accumulation of carbonate. The photosynthetic activities of the associated blue-green algae were measured by light-and-dark bottle $^{14}CO_2$-uptake experiments. When these results were projected into the long term, it was found that only 1 to 2 percent of the observed carbonate accumulation could be ascribed to algal CO_2 uptake. However, no attempt was made to estimate what proportion of the accumulated carbonate represented suspended minerals which has been trapped and incorporated into the deposits. In fact, the author noted that crystals seemed to have an affinity for the gelatinous sheaths of the Cyanophytes.

Stream Primary Production

In most lotic ecosystems, periphyton production far outweighs Tracheophyte or phytoplankton production (Cummins 1974). Consequently, biogenic calcite precipitation in whitewater rivers should be controlled by the factors which regulate periphyton community structure and metabolism. These will be discussed very briefly here; for more detailed reviews, refer to articles by Whitton (1975) and Patrick (1977).

Light intensity exerts a major influence on all plant communities. In lotic systems, both community composition and productivity have been shown to depend on illumination. Pfeiffer and McDiffett (1975) found that the net productivity of a Pennsylvania stream periphyton assemblage varied directly with light intensity. Lengthening natural illumination has been shown to increase diatom community diversity and biomass; a lengthening of artificial illumination period has a similar but lesser effect (Patrick 1971). McConnell and Sigler (1959) described a patchy distribution of periphyton in the Logan River and attributed this in part to differential shading along the course of the river.

Clearly, water temperature influences both periphyton community composition and metabolism. Considerable effort has been devoted to delineating the temperature tolerance ranges of periphytic diatoms (reviewed by Patrick 1977). The range of the gelatinous Chrysophyte Hydrurus, indigenous to mountain rivers, is generally ascribed to a "preference" for cold water (Whitton 1975). Phinney and McIntire (1965) and McIntire (1966a) examined periphyton metabolism under various temperature regimes in laboratory streams. They derived a respiratory Q_{10} of approximately two for the communities. Photosynthetic production was found to be more complex, co-varying with temperature and light intensity. This is in keeping with independent physiological experiments indicating that the light reaction of photosynthesis is essentially temperature-independent, while the enzyme-catalyzed dark reaction is temperature-dependent (Raven 1974).

Stream velocity is the most obvious physical distinction between lotic and lentic environments, and its significance to the lotic periphyton has been investigated in detail. Ruttner (1963) emphasized the importance of vigorous water movement in renewing nutrients and removing metabolic waste products from the boundary layer adjacent to the benthic community. In investigations of the so-called "current demand" of periphyton communities in through-flowing laboratory streams, McIntire (1966b, 1968) found that different communities developed under different current regimes, with blue-green algae dominating at high velocities. Whitford and Schumacher (1964) measured respiration and ^{32}P uptake of filamentous green algae at various current velocities in the laboratory. They concluded that both respiration and production were accelerated at higher water velocities, and that the acceleration was greater for lotic species than for lentic species. Lock and John (1979) found that even very low water velocities increased periphyton ^{32}P uptake rates over those measured in quiescent water.

Stream chemistry, particularly nutrient content, also controls benthic community composition and metabolic rates. Schultz (1979) found that the photosynthesis of periphyton communities in oligotrophic laboratory streams was sharply increased by spikes of inorganic nitrogen and phosphorus. The influence of various chemical species on the development of freshwater diatom communities has been reviewed by Patrick (1977).

The nearly infinite combinations of physical and chemical factors impinging on the stream periphyton result in complex and changing patterns of productivity. Many investigators have found major variations in lotic primary production over short distances, as between stream "runs" and "riffles" (cf. McConnell and Sigler 1959; Duffer and Dorris 1966; Marker 1976). In the headwaters of calcareous mountain streams, water velocities are very high. These waters are nutrient-poor, but rich in organic matter. Travertine is actively deposited in this environment. Higher-order streams have much lower water velocities, and elevated nutrient and turbidity loads. Very different periphyton assemblages might be expected in the two environments. In general, diatoms, blue-green algae and some Chrysophytes predominate in lower-order streams; filamentous green algae and macrophytes predominate in higher-order streams (Cummins 1974). Plant biomass is generally greater in the downstream reaches of a river, presumably because of heightened nutrient concentration (Hynes 1970).

Few studies have traced periphyton production over long stream reaches during all times of the year. However, Pennak and Lavelle (1979) performed such a study in the headwaters of the Arkansas River in Colorado. They measured production using photosynthesis/respiration chambers at stations ranging from 1400 to 2800 meters in altitude. The results showed little apparent relation to station elevation or time of year. No general productivity change along the course of the river was evident at any time of year. In addition, five of the six stations showed net productivity at some times and net respiration at others; the trends were unique to each station. The lowest station, at Pueblo, Colorado, was autotrophic throughout the year.

MATERIALS AND METHODS

Field Monitoring Site

Monitoring of physical and chemical parameters was carried out in the Logan River at the Utah Water Research Laboratory (UWRL). The instrumentation was located at the mouth of Logan Canyon, in the Bear River Range of the Wasatch Mountains (Figure 1). Above this point, the Logan River watershed has an area of 570 km^2, ranging in elevation from 1460 m to 3040 m above sea level. The watershed receives an average of 64-76 centimeters of precipitation a year, of which 60-90 percent falls as snow. The flow of the river is to a small degree regulated at a small hydroelectric plant 8 kilometers upstream from the study site.

The geologic strata underlying the Logan River watershed are Paleozoic, of Cambrian to Pennsylvanian age (Ricks 1956). They are chiefly limestones, with some dolomites, shales and limey sandstones. These formations store and discharge considerable volumes of groundwater. Except for a snowmelt runoff event in April through June, the flow in the Logan River consists almost entirely of groundwater base flow.

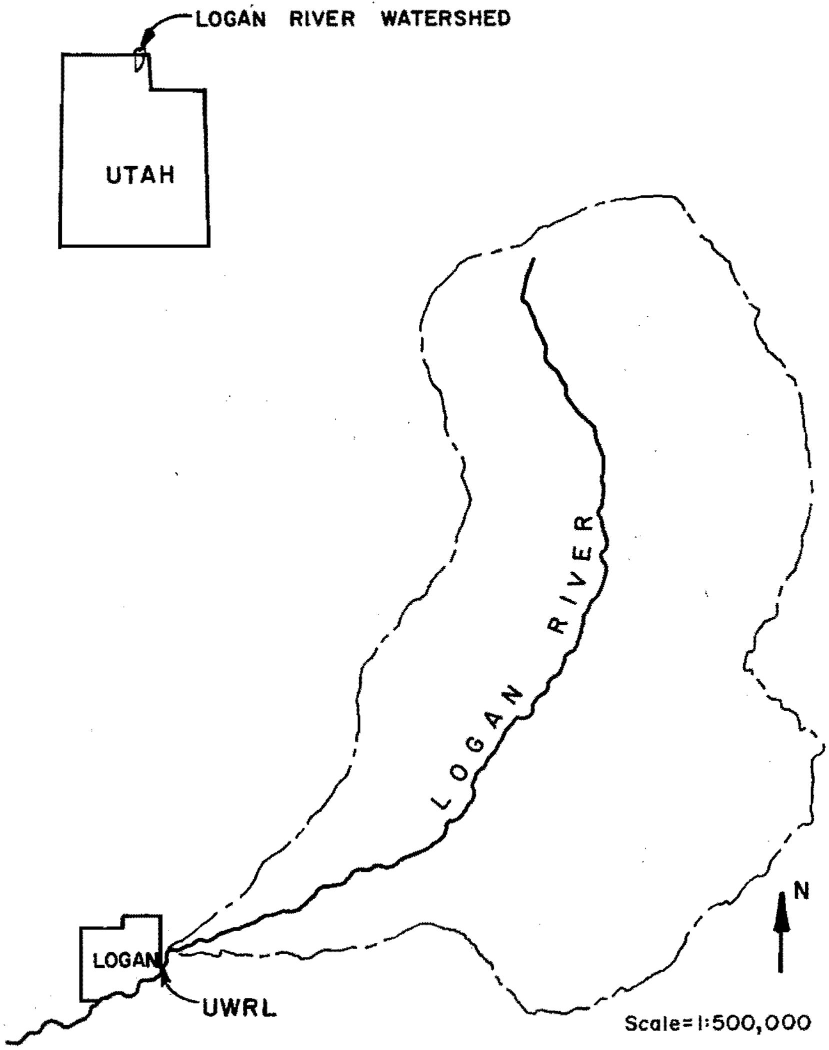

Figure 1. Watershed of the Upper Logan River, Bear River Range, Utah.

Hydrology and Water Chemistry

A continuous record of the Logan River discharge was kept from May 1979 to June 1980. Staff gage height was monitored automatically by a Stevens Level Recorder, which was housed in a stilling well 200 meters upstream from the UWRL.

River water temperature was measured and water samples were collected from the river immediately below the bridge at the UWRL. All samples were taken in the early morning. The samples were analyzed for pH, alkalinity, calcium, hardness, dissolved organic carbon, particulate organic carbon, specific conductance, dissolved oxygen, nitrate, nitrite, ammonia, orthophosphorus, total phosphorus, suspended solids, and volatile suspended solids. Analytical procedures which were used during this study are given in Table 1. Subsamples to be analyzed for organic carbon (dissolved and particulate) and oxidized nitrogen (NO_3-N and NO_2-N) were preserved using phosphoric acid and chloroform, respectively; all remaining tests were performed immediately.

Water samples were collected and analyzed from May 1979 through June 1980. Calcium, alkalinity, pH and temperature were determined bimonthly. All other parameters were analyzed on a monthly basis.

Benthic Community Measurements

Characteristics of the Logan River periphyton community were monitored using an underwater platform containing artificial substrates. The platform was tethered to the bridge at the UWRL, and was kept submerged at a constant depth of 25 cm through the use of floats (Figure 2). The substrates consisted of twenty 10 x 10 cm smooth stone blocks, approximately 3 cm thick, which were cut from limestone cobbles taken from the river.

Each month from April 1979 to May 1980, ten substrates containing 8-week-old periphyton communities were removed from the platform. Five substrates were assayed for chlorophyll, the other five for biomass and solid calcium. Preparatory to chlorophyll analysis, the growth on a substrate was scraped into a 50-ml centrifuge tube containing 25 ml of 90 percent acetone. The extract was sonicated for 30 seconds, then stored for two days at 4°C in darkness. Particulate matter was settled out by centrifugation, and the chlorophyll concentration of the clarified suspension was determined fluorimetrically (Turner 1973). Community biomass was measured as ash-free dry weight (Vollenweider 1969). The ash from biomass analyses was dissolved in dilute hydrochloric acid, and community calcium content was determined by EDTA titration of these extracts (APHA 1975).

Before it was dried, a small aliquot ($\sim$ 0.1 ml) was removed from each biomass suspension and made into a semi-permanent slide for periphyton community composition analysis. Slides were prepared and counted by the method outlined by McNabb (1960). The 20 most frequently encountered microalgae species were enumerated for each slide. Cell counts were converted to volumes by measuring 30 random individuals of each species, and deriving average cell volumes (Castenholz 1960). Slide preparations were not made from substrates containing macroalgae. Instead, algal volume was determined by measuring the algae's displacement of water in a graduated cylinder.

Benthic community photosynthesis and respiration were determined five times during an annual cycle, using in situ light-and-dark chambers (Pfeiffer and McDiffett 1975). Cement-and-pebble patio blocks 15 inches in diameter were placed in the river at the field monitoring station. Periphyton communities similar to those of the surrounding river bottom developed on these blocks. For an in situ productivity measurement, a patio block holding a "steady-state" (> 8 weeks old) periphyton community was placed in a 14-liter lucite chamber, which was filled with river water and submersed in the river. The chamber's contents were circulated by a submersible pump, and the dissolved oxygen

Table 1. Procedures for chemical analyses performed at the Utah Water Research Laboratory.

Parameter	Method	Reference
pH	Glass Electrode	APHA (1975) p. 460
Alkalinity	Potentiometric	APHA (1975) p. 228
Calcium	EDTA Titrimetric Method	APHA (1975) p. 189
Hardness	EDTA Titrimetric Method	APHA (1975) p. 202
Organic Carbon	Ampoule Method	Menzel and Vaccaro (1964)
Specific Conductance	Conductivity Cell	APHA (1975) p. 71
Dissolved Oxygen	Winkler Method, Azide Modification	APHA (1975) p. 443
Nitrate	Cadmium Reduction	APHA (1975) (automated) p. 620
Nitrite	Diazotization	APHA (1975) (automated) p. 620
Ammonia	Indophenol	Solorzano (1969), APHA (1975) p. 416
Orthophosphorus	Ascorbic Acid	Strickland and Parsons (1968), APHA (1975) p. 481
Total Phosphorus	Persulfate Digestion	APHA (1975) p. 476
Suspended Solids	Gravimetric	APHA (1975) p. 94

content of the water was continuously monitored by an oxygen electrode (APHA 1975) (Figure 3). After approximately 2 hours, the clear top was replaced by a black top, the chamber was refilled and replaced in the river, and oxygen concentration was monitored for another 2 hours. In order to verify the oxygen electrode readings, duplicate water samples were taken from the chamber at the beginning and end of both light and dark experiments. These samples were fixed immediately and later titrated for dissolved oxygen by the Winkler method with azide modification (APHA 1975).

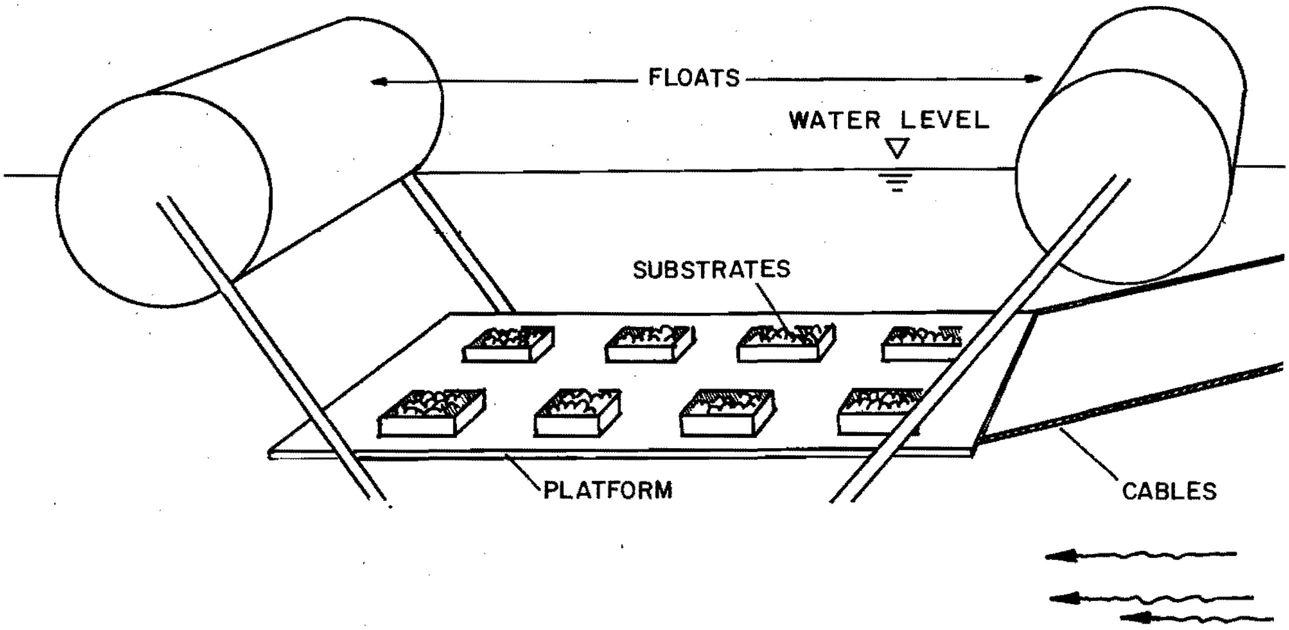

Figure 2. Periphyton sampler with limestone substrates.

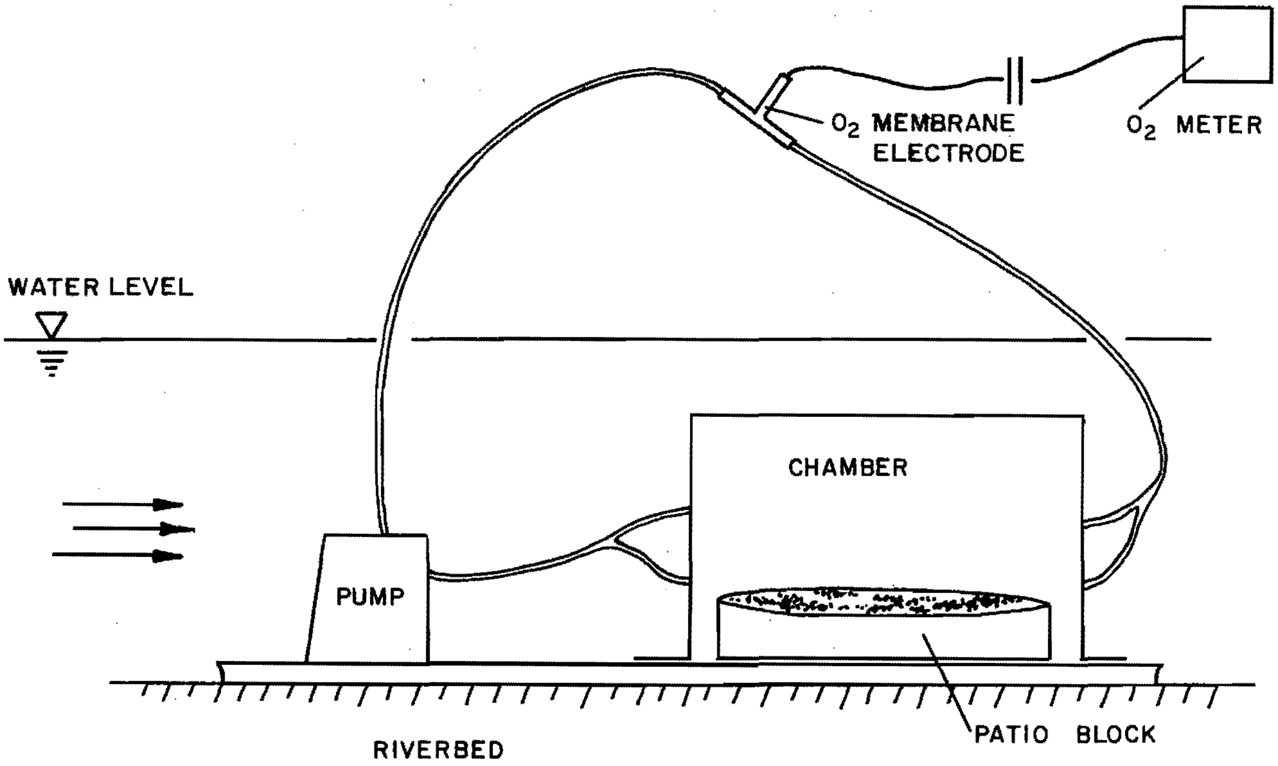

Figure 3. The submersible photosynthesis-respiration apparatus.

Synoptic Study

In October 1979, a synoptic productivity-respiration survey of the Logan River was conducted. Patio blocks were set out in four reaches of the river system: Spawn Creek, a small tributary of the Temple Fork of the Logan River; Twin Bridges, approximately 24 km upstream from the UWRL; at the UWRL; and in central Cache Valley, at the Logan 6th West Bridge (Figure 4). Eight weeks after they were set out, the patio blocks were used in productivity-respiration experiments, as described above. Following an experiment, the patio-block periphyton communities were extracted with 90 percent acetone for chlorophyll analysis (Schultz 1979). Then 2-liter water samples were collected, packed in ice and immediately brought back to the laboratory for analysis of pH, alkalinity, calcium, hardness, and specific conductance. In addition, stream discharge at each site was estimated using cross-sectional analysis (USBR 1967). For this analysis, water velocity was measured to the nearest 0.06 m/sec using a Marsh-McBirney Model 201 portable current meter.

Mineralogic Analyses

Several samples of Logan River suspended sediment and benthic precipitate were collected in the vicinity of the UWRL. Suspended sediment was collected by filtering several liters of river water through acid-washed glass fiber filters, drying the filters, and carefully scraping the collected solids from the filters. The dried samples were ground by mortar and pestle. X-ray diffraction analysis was performed on a Siemens Krystalloflex-4 equipped with a copper tube and a nickel filter. Two replicates of each sample were analyzed.

Benchtop Radiotracer Experiments

Artificial streams, with through-flowing Logan River water, were set up in the laboratory. Cement-and-pebble substrates, approximately 10 x 20 cm square, were placed in the streams, which were illuminated 12 hours per day by "Optima-50" fluorescent lights (Duro-Test Inc.), at approximately 17 lux. Within four weeks, the substrates developed periphyton communities similar to those on the river bottom.

The relation between algal photosynthesis and the precipitation of calcium carbonate was examined in a series of benchtop radioisotope labeling experiments which utilized these colonized substrates. Carbon-14, added as aqueous $NaH{*}CO_3$, was used in all experiments to trace both photosynthetic activity and calcium carbonate precipitation. Experiments concerning phosphorus co-precipitation also included phosphorus-32, which was added as aqueous $KH_2{*}PO_4$. Calcium carbonate precipitation was also measured in some experiments utilizing calcium-45, added as aqueous ${*}CaCl_2$. All radioisotopes were procured from ICN Radiopharmaceuticals.

Experiments were performed in an opaque plexiglass photosynthesis-respiration chamber (Figure 5). The water temperature was maintained within a 1°C range by the circulation of heated or cooled water through coils within the experimental chamber. The water in the chamber was stirred gently throughout each experiment by a magnetic stirrer. Illumination of 15 lux was provided from above by "Optima-50" fluorescent lights (Duro Test Corporation).

Experiments were performed as follows. Eight liters of river water were poured into the chamber and stirred gently until the

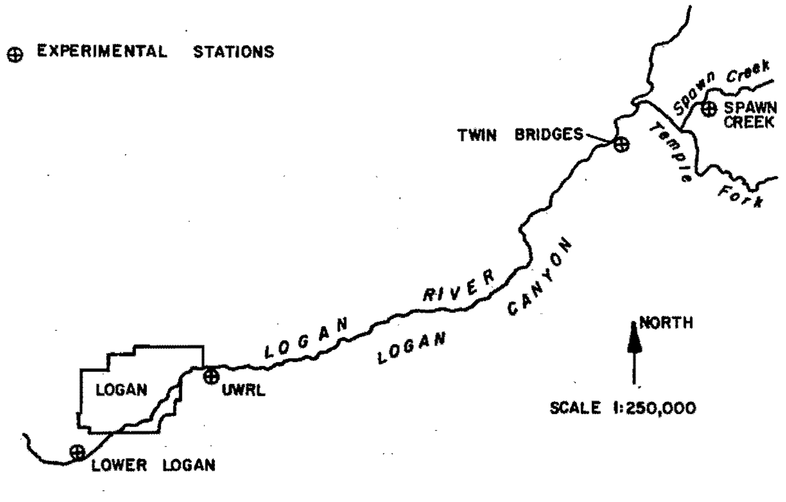

Figure 4. Synoptic study experimental stations.

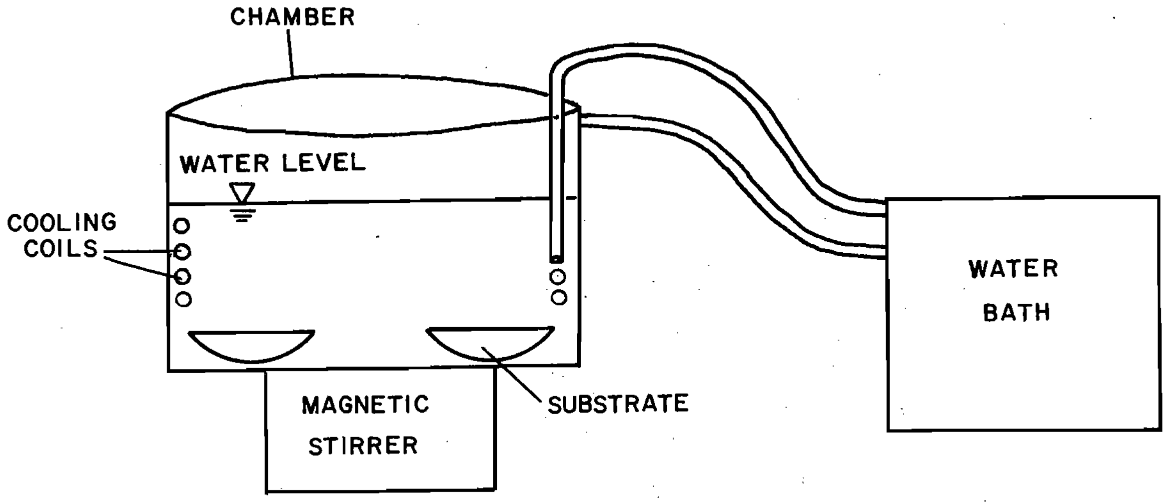

Figure 5. Apparatus used in the benchtop radiotracer experiments.

desired temperature was reached. Radioisotope was then added and allowed to mix completely into the water. Two algae-covered substrates were placed in the chamber, which was loosely covered by either a clear top or a black top. The system was stirred for 2 hours, then the substrates were removed.

The temperature-dependence of biogenic $CaCO_3$ precipitation was tested by performing experiments at 5, 10, 15, and 20°C. The effects of macronutrient concentration were examined by spiking the river water with various nitrate and orthophosphate additives (in the forms of aqueous $NaNO_3$ and KH_2PO_4, respectively). The macronutrient concentrations tested were the following:

1) (control): 10 µg/l PO_4-P, 110 µg/l NO_3-N.
2) 100 µg/l PO_4-P, 1000 µg/l NO_3-N.
3) 500 µg/l PO_4-P, 5000 µg/l NO_3-N.
4) 1000 µg/l PO_4-P, 10,000 µg/l NO_3-N.

In addition, for these experiments micronutrient levels were elevated by the addition of concentrated micronutrient solution to the river water (Table A-1, Appendix A). The final concentrations were those of the Nutrient Algal Assay Medium (NAAM) (Miller et al. 1978). The algae were acclimated to the elevated nutrient conditions for 6 hours prior to the beginning of each experiment.

Radioisotope which precipitated within the algal matrix during the course of an experiment was redissolved for assay in the following manner. First each substrate was placed in a 15-liter chamber and fixed with 10 ml of 10 percent formaldehyde. Distilled water was added to cover the substrate, the chamber was covered, and CO_2 was gently bubbled up through it from an airstone beneath the substrate. After 30 minutes, the substrate was removed, and 5 ml of solution was added to 15 ml of scintillation cocktail (PCS, Amersham) in a liquid scintillation vial. Duplicate samples were prepared and counted.

Several experiments were performed to ascertain whether radioactive CO_2 was purged from the chambers by the bubbling procedure. In these experiments, the gas leaving the chamber was funneled through a small Teflon tube, the end of which rested in a scintillation vial containing 2 ml of ethanolamine. This vial was replaced every 10 minutes for 30 minutes, and 15 ml of scintillation cocktail was added to each of the CO_2-saturated ethanolamine samples. Carbon-14 activity of these samples was assayed, and the percentage of total activity lost from the chamber as ^{14}C was calculated. In this way, it was determined that an insignificant fraction of the ^{14}C was purged from the bubbling chambers as CO_2 (Table A-2, Appendix A).

Dual-labeling experiments utilizing both ^{14}C and ^{45}Ca were used to check the assumption that all ^{14}C found in the precipitated fraction was actually $Ca^{14}CO_3$. In this case, the mole ratio of Ca to C in this fraction should be one to one. Ratios calculated from the dual-labeling experiments were quite variable, and cannot be said to confirm or deny the validity of the assumption (Table A-3, Appendix A).

After the CO_2 treatment, the substrates were further treated to assay for radioisotope taken up by the algae. First, the algal cells were lysed and removed from the substrates by immersion in 90 percent aqueous acetone and gentle scrubbing with a soft brush. The acetone was distilled from each extract using a Kaderna-Danish concentrating apparatus. Periodic analyses showed that no ^{14}C distilled off with the acetone. A 0.5-ml sample of the final aqueous suspension was transferred to a scintillation vial containing 4.5 ml of water and 15 ml of scintillation cocktail. Triplicate samples from each substrate were prepared and counted.

Samples of the experimental water, redissolved precipitate and algal suspension were analyzed on a "Tri-Carb" liquid scintillation counter (Packard). Quench correction was by the external standards ratio method (Wang et al. 1975). Carbon-14 and calcium-45 were counted together in a low-energy channel, while phosphorus-32 was counted in a separate high-energy channel. In carbon-calcium double-labeling experiments, aqueous samples were passed through a small cation-exchange column prior to counting. Both these samples and untreated samples were counted, and the calcium-45 activity was calculated as the difference between the two counts.

Water Velocity Experiments

The effect of stream current velocity on calcium carbonate precipitation was tested using a laboratory stream (Figure 6). Seventy-five liters of river water were continuously circulated through the stream by a low-head vertical sump pump. Water temperature was maintained at 12° ± 1°C by a refrigeration unit. Water velocity was adjusted by altering the pump drive belt setting and the channel inclination. The surface velocity of the water in the channel was calibrated to ± 4 cm/s using an electronic timer with electrodes at the upper and lower ends of the channel, and a small float to trigger the electrodes. Illumination of 15 lux was provided by Duro-Test "Optima-50" fluorescent light tubes.

At the beginning of each experiment, four of the cement-and-pebble substrates holding 8-week-old algal communities were placed in the channel. The channel was loosely covered with either a clear or a black-painted lucite top. Five hundred microcuries of carbon-14 were added to the water, which was circulated for 12 hours. At the conclusion of the experiment, the radioactive algae, calcium carbonate and water samples were prepared and counted as described above for the benchtop experiments.

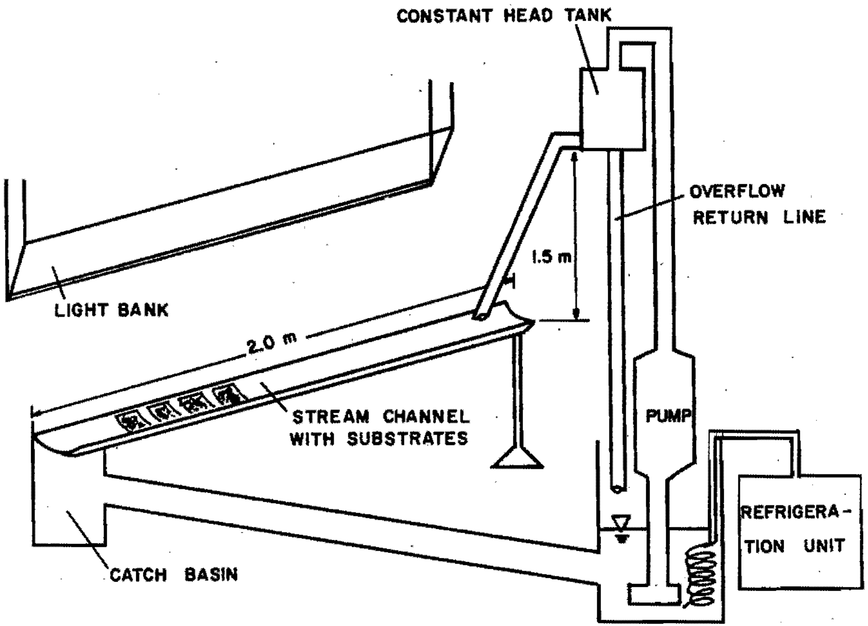

Figure 6. Recirculating laboratory stream.

RESULTS

Hydrology and Water Chemistry

The results of the Logan River discharge monitoring program are compiled in Table B-1, (Appendix B) and graphed in Figure 7. The hydrologic regime of the Logan River is dominated by a snowmelt runoff event, which in 1980 began abruptly in mid-April, reached a maximum in early May, and declined gradually until early July. Other years follow this general pattern but with some variation in timing. Runoff during the remainder of the year is groundwater-derived base flow. Summer thunderstorms and upstream irrigation diversions cause minor perturbations in this flow regime. This type of hydrograph, comprised of groundwater base flow and spring runoff events, is characteristic of mountain rivers throughout the Intermountain West.

Table B-2 (Appendix B) contains the chemical data derived from the Logan River water sampling program. Only those parameters of immediate importance to the calcium-bicarbonate system will be discussed. Figure 8 illustrates the total hardness of the river water over one year. The greatest hardness observed was 217 mg/l as $CaCO_3$; the least was 126 mg/l. Except for a marked dilution effect associated with snowmelt, total hardness showed little change over time. This is as expected, given the groundwater origin of the streamflow. Dissolved calcium followed a similar pattern, ranging between 37 and 85 mg/l (Figure 9). Dissolved magnesium was calculated as the difference between total hardness and calcium concentrations. The magnesium component of hardness ranged from zero, following drainage of the First Dam Reservoir in February 1979, to 32 percent, in October 1979. On the average, dissolved magnesium comprised 15 percent of total hardness.

River temperature, a major influence on chemical solubility, is plotted in Figure 10.

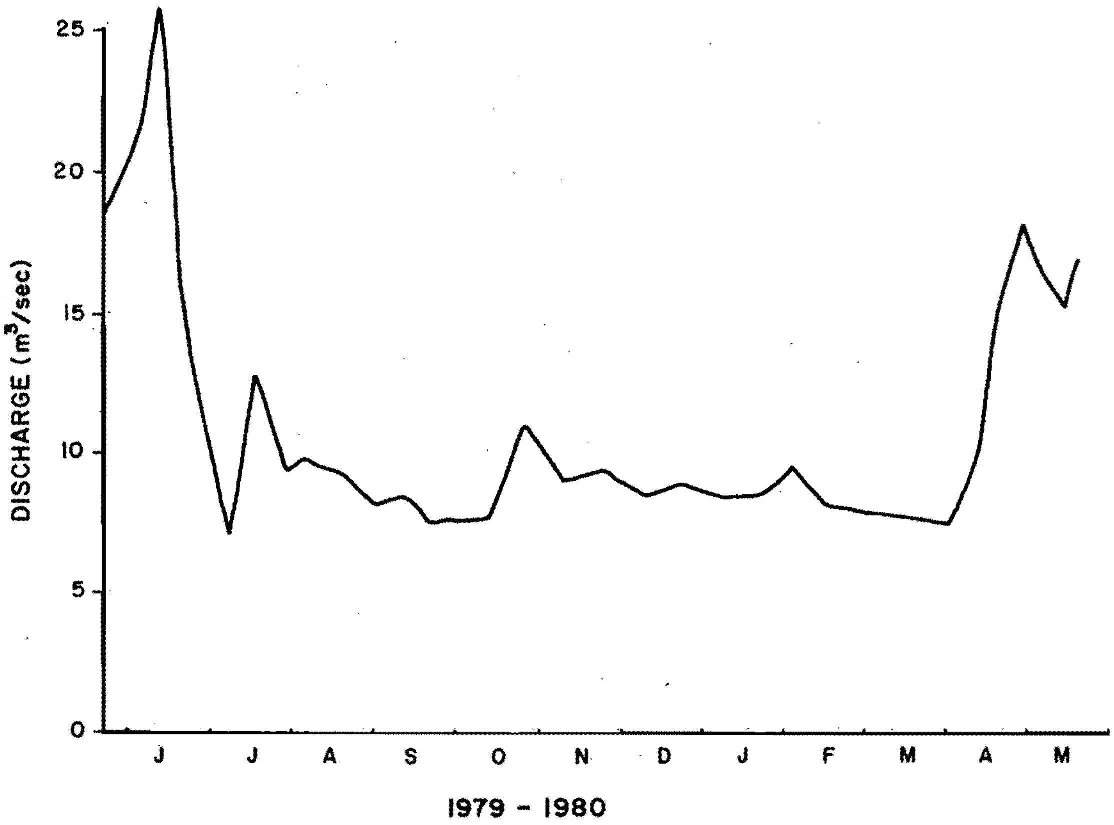

Figure 7. Discharge of the Logan River at the Utah Water Research Laboratory.

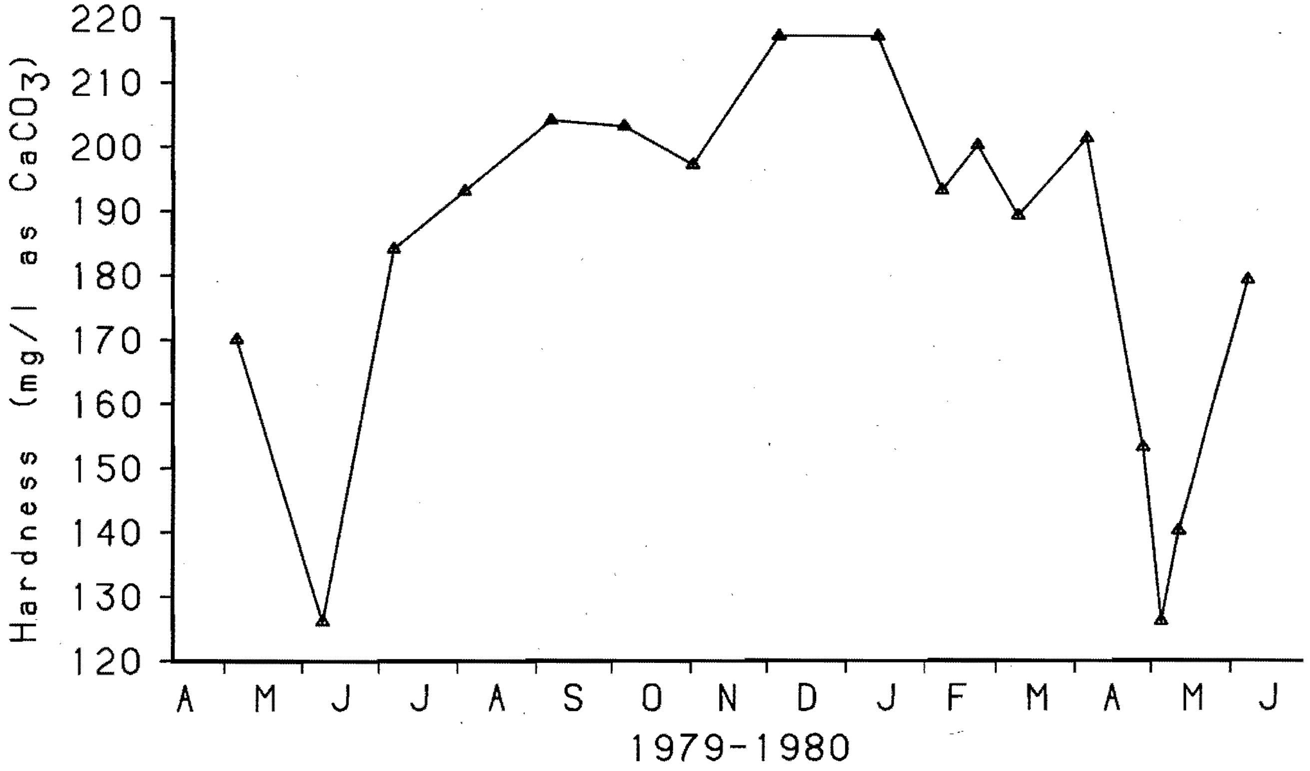

Figure 8. Total hardness of the Logan River at the Utah Water Research Laboratory.

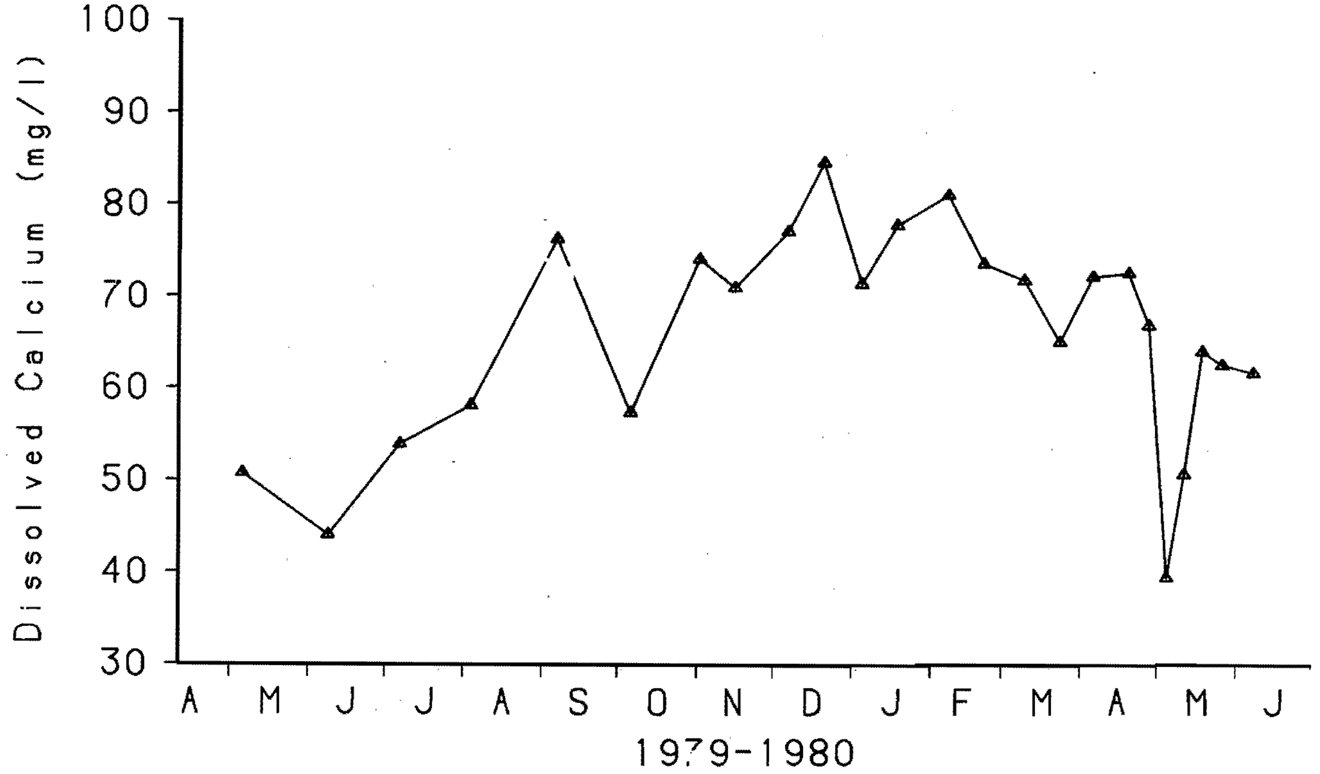

Figure 9. Dissolved calcium of the Logan River at the Utah Water Research Laboratory.

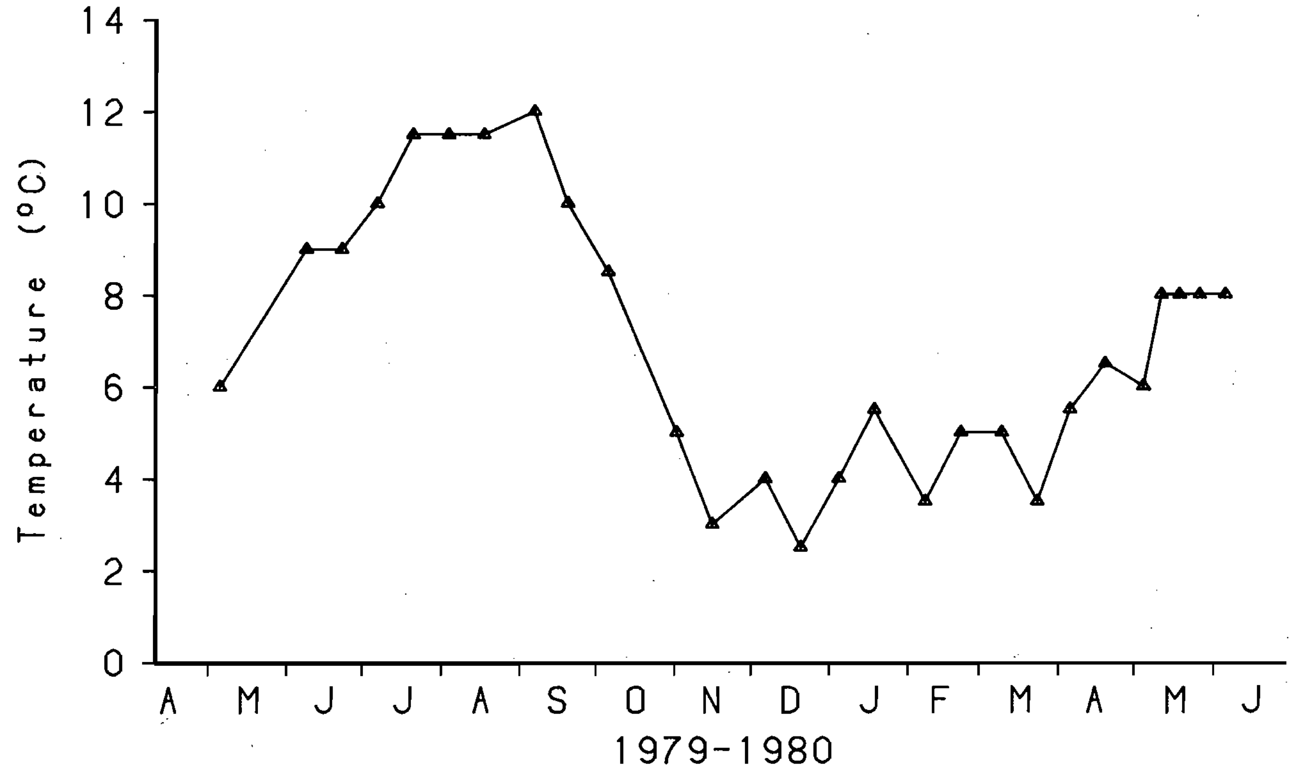

Figure 10. Water temperature of the Logan River at the Utah Water Research Laboratory.

For the period of measurement, minimum water temperature was 2.5°C, measured in December 1979. The maximum temperature measured was 12°C, which was reached in September 1979.

Figure 11 shows the variation of alkalinity in the Logan River over the sampling period. Dilution by snowmelt in the spring of 1979 and 1980 was clearly the major influence on measured alkalinity. Alkalinity and total hardness were closely correlated throughout the study period, confirming that the carbonate species are the predominant source of alkalinity in the Logan River.

River water pH is plotted in Figure 12. The highest pH observed was 8.4; the lowest was 7.9. These two measurements were made within one month of each other (summer 1979). There was no seasonal pattern to the variation of river water pH. Although samples were taken at the same time of day each month, the variability of measured pH may reflect the productivity of upstream algae.

Figure 13 shows the specific conductance of the Logan River. As might be predicted, conductance was lowest when streamflow included large volumes of spring snowmelt, during July 1979 and April-May 1980. In general, specific conductance was high during months of base flow (July through March) and low during snowmelt runoff (April through June).

The data collected allow calculation of the ion activity product (IAP) for calcite in the Logan River. The ratio of the IAP to a temperature-specific solubility product constant is the calcite saturation index. Index values between zero and one indicate undersaturation of the water with respect to $CaCO_3$, a value of one indicates saturation, and values greater than one denote supersaturation. Ion activity products and calcite saturation indices were calculated using an iterative algorithm which accounted for both ion pairing and the indifferent salt effect (FORTRAN program by Stan Peterson, Department of Soils and Biometeorology, Utah State University, as modified by Messer et al. (1981). Calcite saturation indices for the Logan River are compiled in Table 2. The Logan River was saturated or supersaturated with respect to calcite for 7 of the 14 months during which river chemistry was monitored. Saturation indices ranged from 0.50 (July 1979) to 1.7 (November 1979).

Benthic Community Measurements

Figure 14 shows the biomass of the periphyton communities which became established on the in-stream periphyton sampler. Biomass peaked sharply in July 1979 and in January 1980. These peaks coincided with the

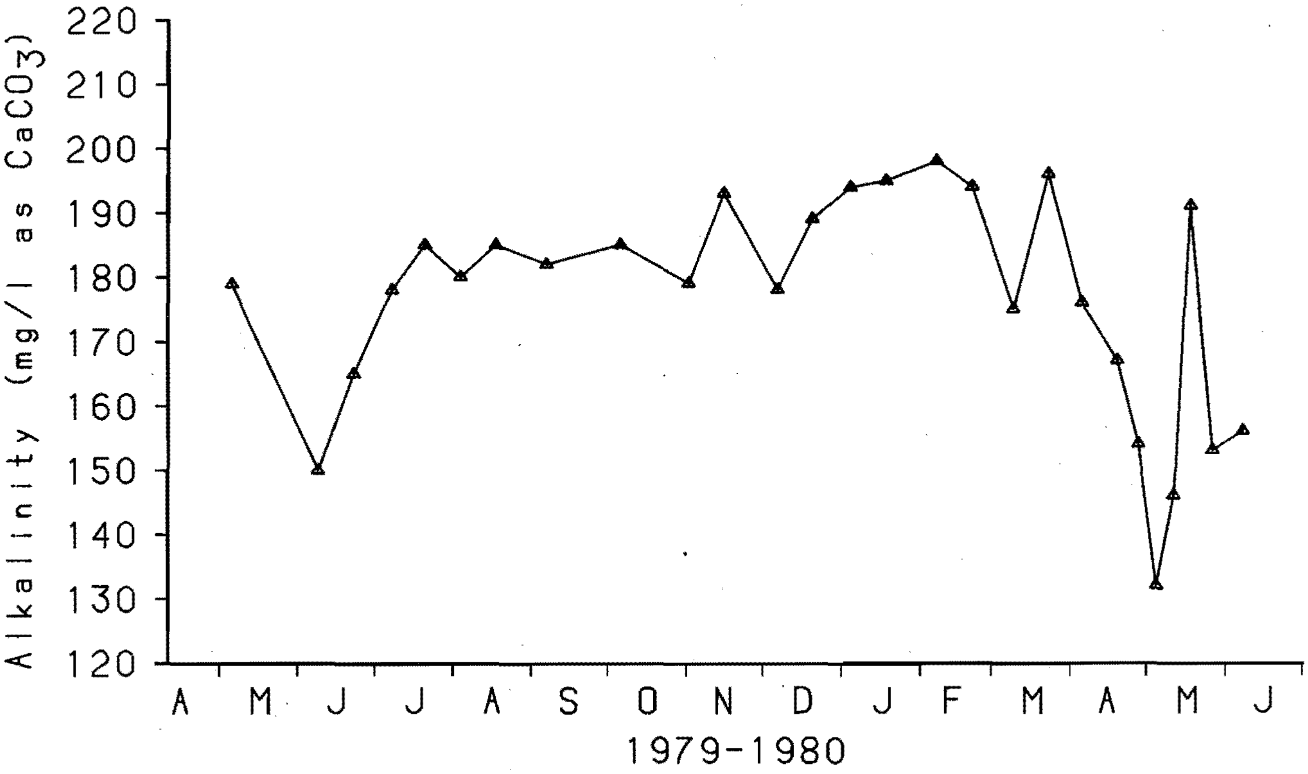

Figure 11. Alkalinity of the Logan River at the Utah Water Research Laboratory.

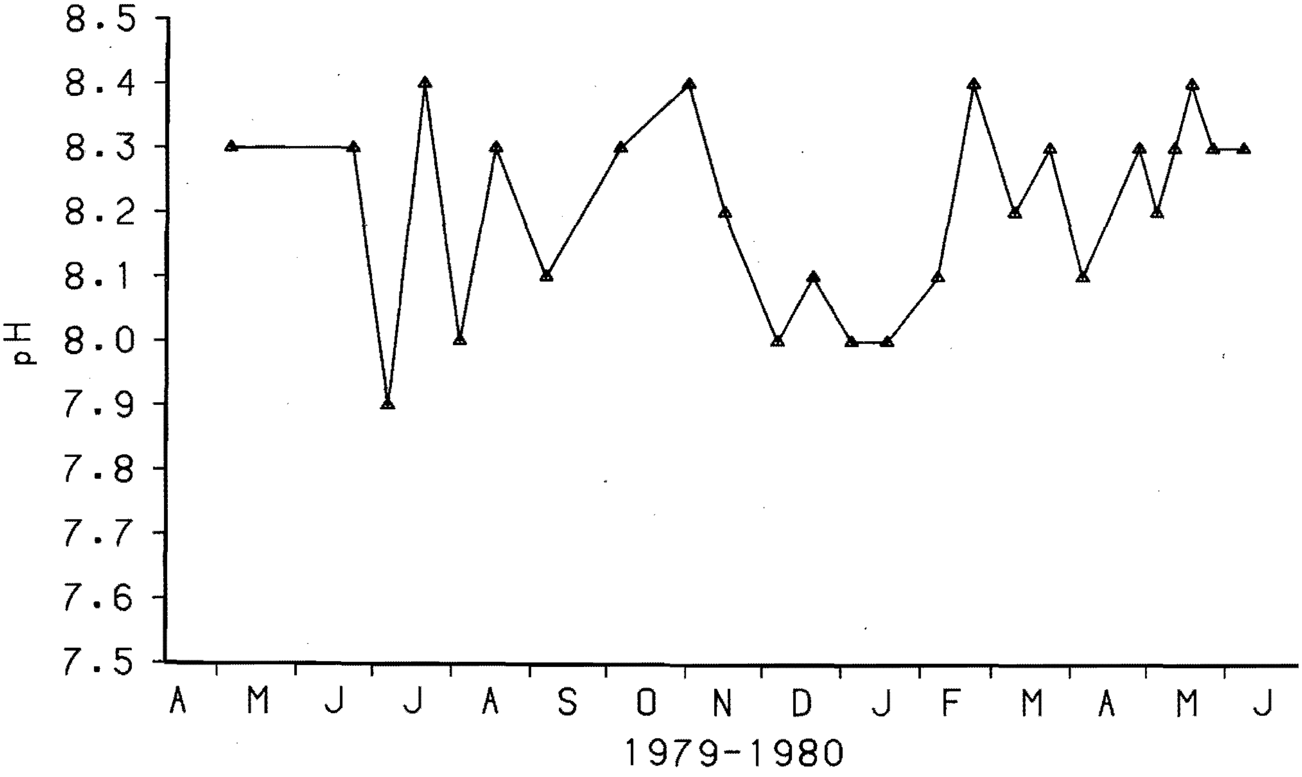

Figure 12. pH of the Logan River at the Utah Water Research Laboratory.

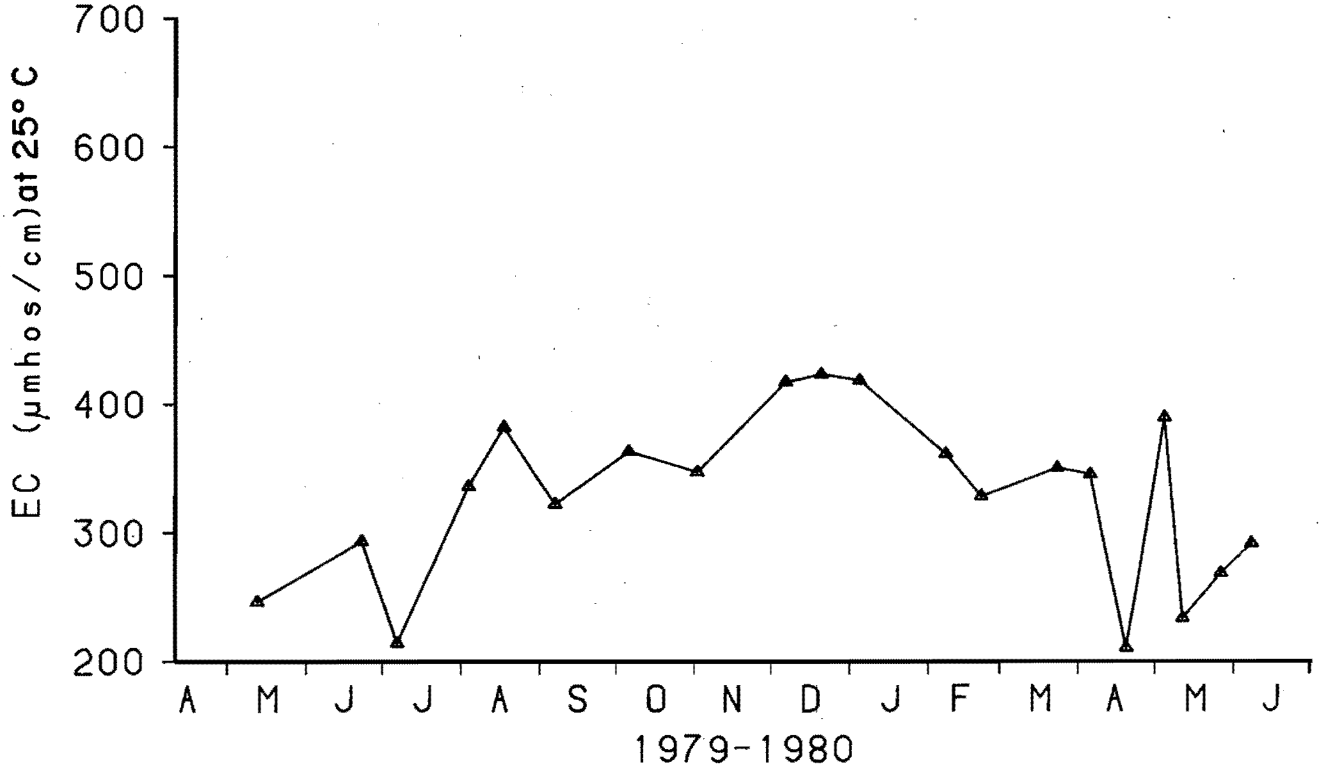

Figure 13. Specific conductance of the Logan River at the Utah Water Research Laboratory.

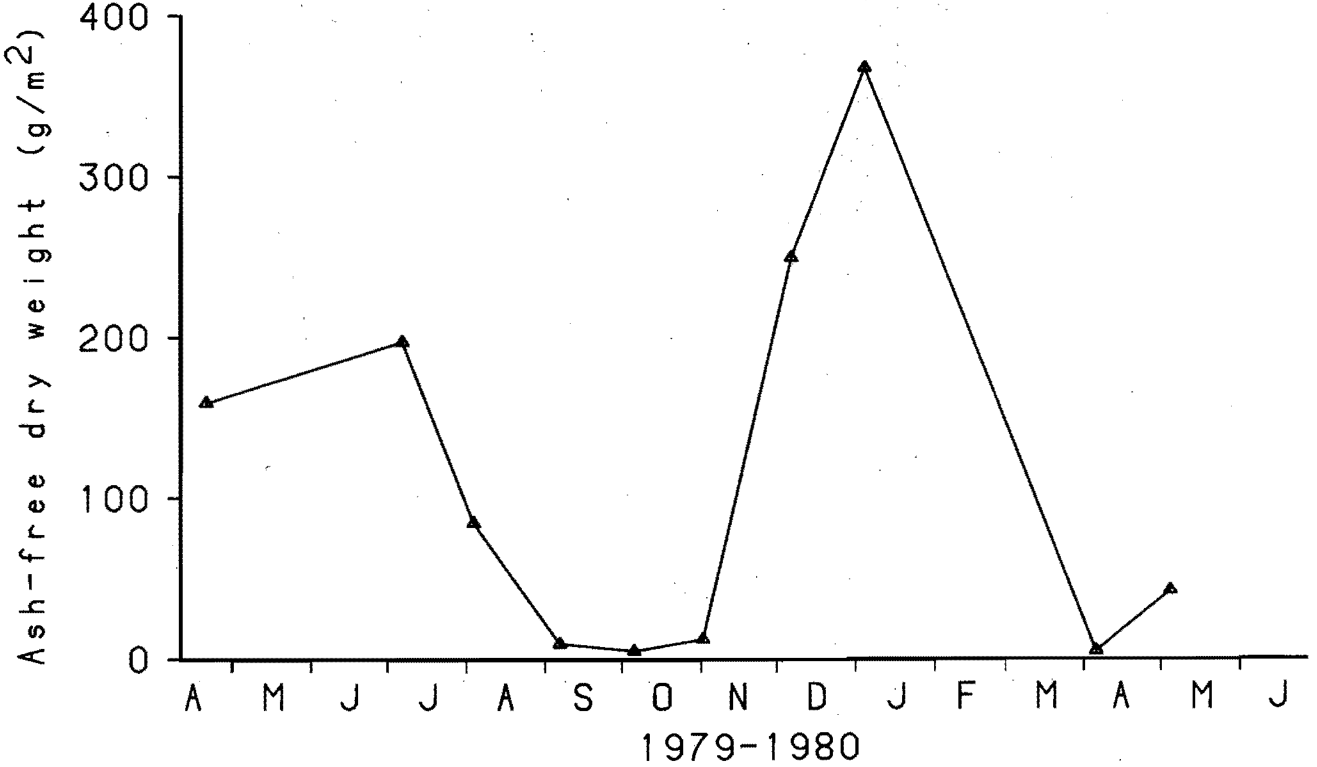

Figure 14. Biomass (as ash-free dry weight) of algal communities colonizing limestone substrates in the Logan River.

Table 2. Calcite saturation of the Logan River at the Utah Water Research Laboratory.

Date	Calcite Saturation Index
1979	
May 3	1.0
June 7	1.3
July 5	0.50
August 2	0.71
September 6	1.1
October 4	1.2
November 1	1.7
December 6	0.68
1980	
January 3	0.62
February 7	0.92
March 6	1.0
April 3	0.78
May 1	0.56
June 3	1.2

presence of the Chrysophyte Hydrurus, as shown in Figure 15. The other components of the algal community were various species of attached diatoms and the colonial blue-green alga Microcystis. When it was present, Hydrurus so dominated the community that the microalgae made little contribution to the total community biomass.

Chlorophyll a measurements (Figure 16) are not completely in agreement with biomass measurements. A marked chlorophyll peak did occur in winter 1979-1980; however, the summer 1979 bloom of Hydrurus was not reflected in chlorophyll measurements. The acetone extracts of these periphyton samples were very dark, and it is possible that other compounds interfered with the fluorescence spectrometry of chlorophyll a. It is also possible that the Hydrurus was senescent at the time of the July sampling; very little Hydrurus was present one month later (Figure 14).

In order to ascertain whether the amount of solid calcium associated with periphyton

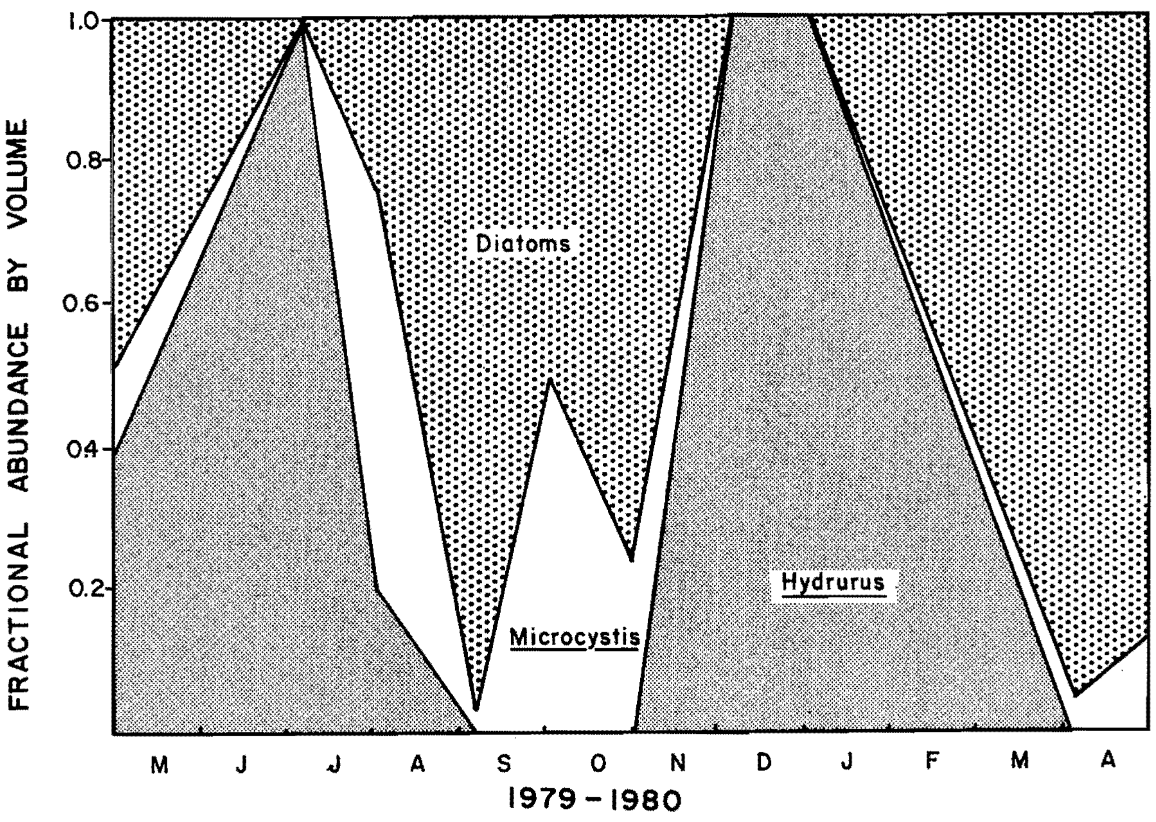

Figure 15. Composition of algal communities colonizing limestone substrates in the Logan River.

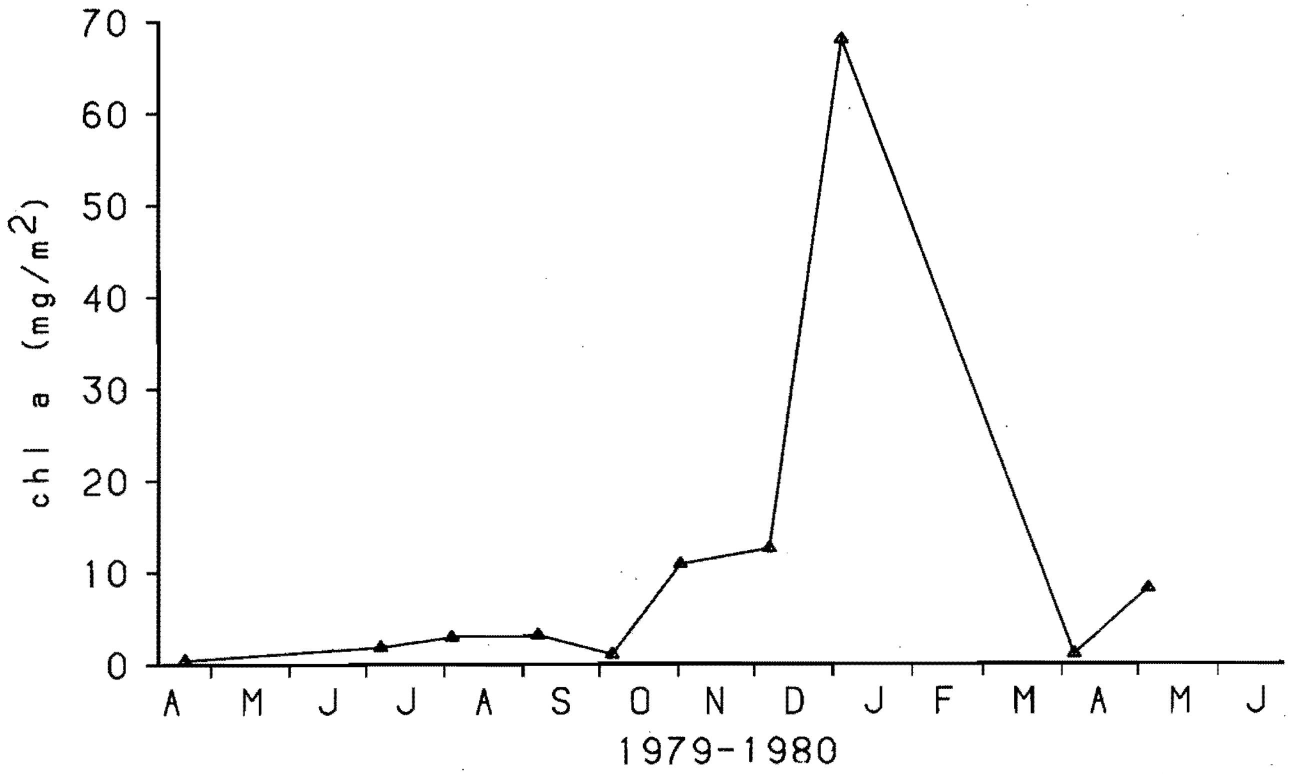

Figure 16. Chlorophyll a of algal communities colonizing limestone substrates in the Logan River.

communities was related to the algal mass, substrate solid calcium was monitored through time. Average monthly values are shown in Figure 17. Monthly averages of biomass and solid calcium can be seen to exhibit similar trends (see Figures 15 and 17). Since the masses of both calcium and periphyton ranged over more than two orders of magnitude, the data from individual substrates have been log-transformed for comparison. These transformed data (Figure 18) show a strong linear relationship (r significant at the 1 percent level). Whether algal biomass influences the accretion of solid calcium through photosynthetically-induced precipitation or simply by trapping suspended $CaCO_3$ cannot be inferred from these data.

The temporal correlation between the accretion of benthic calcium and the calcite saturation index of the Logan River is also noteworthy. According to Figure 17, the precipitation of $CaCO_3$ was rapid in mid-summer (July-August 1979) and mid-winter (December 1979). This conclusion is borne out by Table 2, which shows that the calcite saturation indices during these months were markedly lower than at any other times during the sampling period.

The results of the light-and-dark chamber productivity experiments are shown in Figure 19. Each point represents a mean value from two experiments conducted within one week of each other. In every experiment, photosynthetic production was greater than respiration. Gross productivity was highest in August 1979 (175 mg O_2/m^2-hr), when the patio-block periphyton community was comprised chiefly of diatoms, with some mosses. Productivity was nearly as high in January 1980 (173 mg O_2/m^2-hr), when the substrate was thickly colonized by Hydrurus. Lower rates of production were observed in autumn and spring (95 and 75 mg O_2/m^2-hr, respectively), when the filamentous green alga Vaucheria dominated the periphyton. Benthic respiration rates were very similar in autumn, winter, spring and early summer, ranging from 30 to 43 mg O_2/m^2-hr. A respiration rate of 149 mg O_2/m^2-hr was observed in August 1979. This is attributable to a heavy growth of Simulid larvae on the river bottom at that time. Overall, these data suggest that the photosynthetic influence on $CaCO_3$ precipitation should be of greatest importance in the winter, when the production/respiration ratio is highest and flow is low.

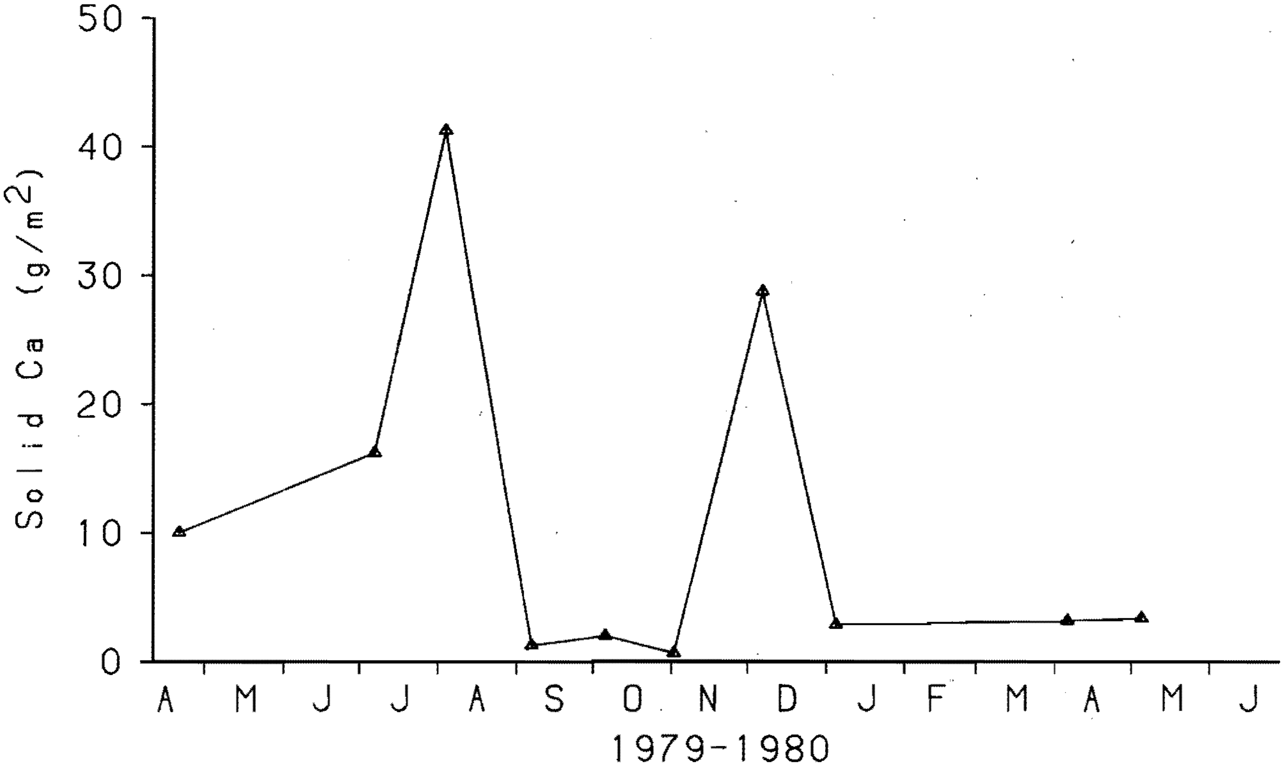

Figure 17. Solid calcium associated with algal communities colonizing limestone substrates in the Logan River.

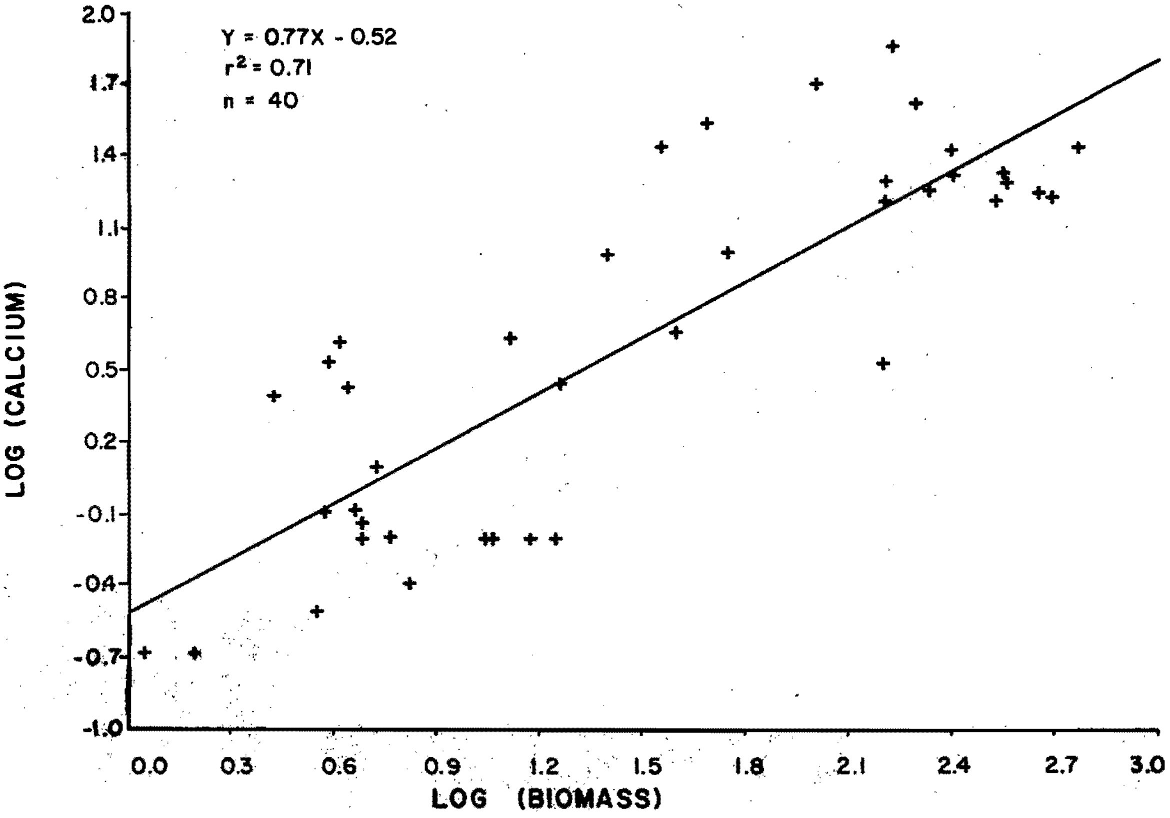

Figure 18. The relationship between algal biomass and solid calcium on limestone substrates in the Logan River. Both masses are expressed as mg/m^2.

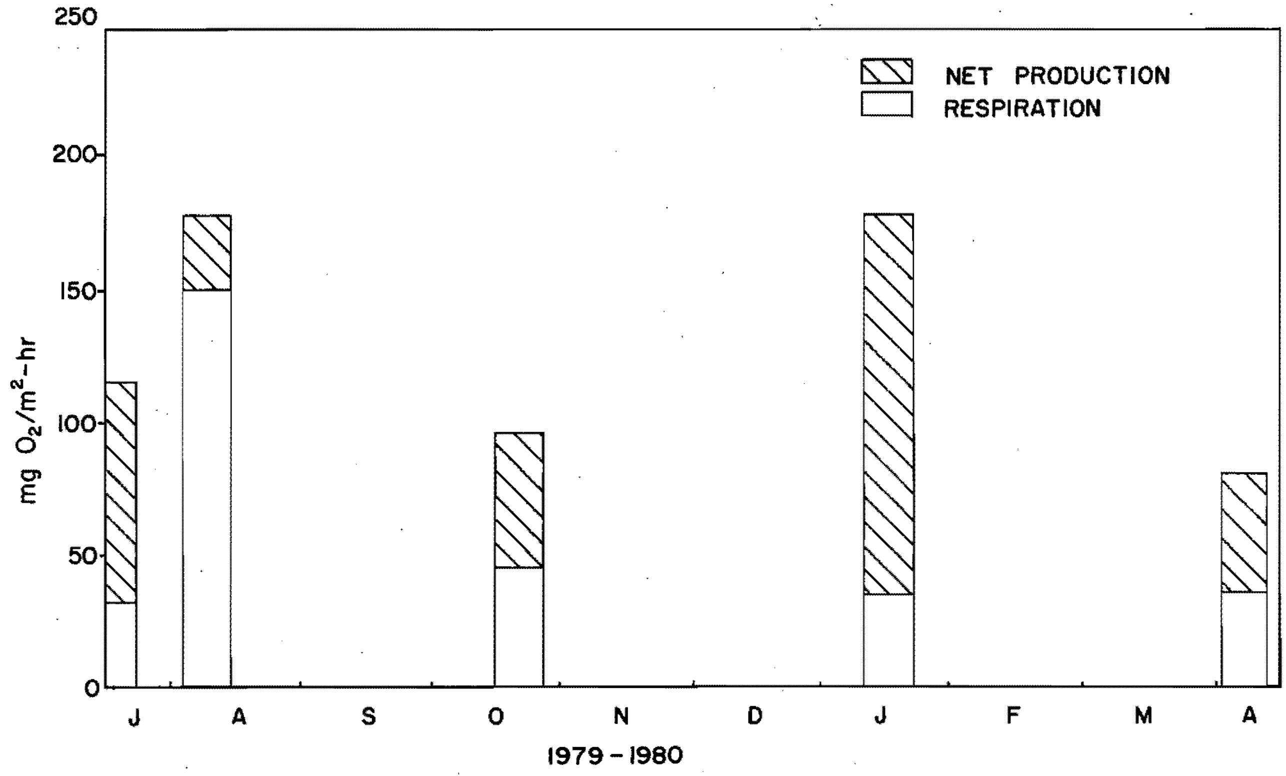

Figure 19. Productivity and respiration of the Logan River benthos at the Utah Water Research Laboratory.

Synoptic Study

Table 3 shows the values of biological parameters measured in four reaches of the Logan River. The benthic community of the small headwater stream Spawn Creek had the greatest net productivity, 109 mg O_2/m^2-hr. However, the lowest chlorophyll a level, 0.06 mg/m^2, was also measured at this station. This community was composed of sessile diatoms and numerous small colonies of the blue-green nitrogen-fixer Nostoc. The Twin Bridges and UWRL stations in the central reach of the Logan River showed considerably lower biological activity, having net productivities of 48 and 53 mg O_2/m^2-hr, respectively. The benthic communities at these sites were dominated by diatoms and included some Nostoc colonies. These communities had chlorophyll a values of 0.32 and 0.38 mg/m^2, respectively. Neither uptake nor evolution of oxygen was measured in the experiment performed at the Lower Logan River station. The river carried a heavy load of suspended matter at this station, and had a generally soft bottom with some rocks. The substrates placed at this station were thinly colonized by Microcystis. Despite its apparent inactivity, this benthic community had the highest chlorophyll a content measured, 0.52 mg/m^2.

Carbonate chemistry data for the river water at the four experimental stations are compiled in Table 4. The pH of the river water decreased steadily downstream from the Spawn Creek station, where it was 8.5. Measured alkalinity was greatest at the Spawn Creek and Lower Logan stations (195 and 215 mg/l as $CaCO_3$, respectively). The dissolved calcium concentration measured 66 mg/l at the Spawn Creek station. It decreased slightly at the middle stations, and increased again as the river flowed through the valley, to 86 mg/l at the Lower Logan station. Specific conductance was low at all stations; it was greatest at the Lower Logan station (505 µmhos/cm @ 25°C). The $CaCO_3$ saturation index ranged from three to five at the four stations. Reflecting the water chemistry, it declined downstream from Spawn Creek, then increased again at the Lower Logan station.

The dissolved and particulate-matter loading of the river increases sharply as the river enters the valley, primarily due to an influx of irrigation return flow. This loading accounts for the increases in alkalinity and specific conductance observed at the Lower Logan station. Two distinct processes could account for the decreases in pH, alkalinity, calcium concentration and specific conductance downstream from Spawn Creek through Logan Canyon. A major influx of surface runoff following a rainstorm would manifest itself through dilution of the river water. Since no precipitation occurred

Table 3. Benthic productivity at four stations in the Logan River system, October 1979.

Station	Elevation (m)	Discharge (m^3/sec)	Gross Productivity (mg O_2/m^2-hr)	Respiration (mg O_2/m^2-hr)	Net Productivity (mg O_2/m^2-hr)	Chlorophyll a (mg/m^2)
Spawn Creek	2200	0.11	173	64	109	0.06
Twin Bridges	1707	2.5	76	28	48	0.32
UWRL	1420	9.9	95	42	53	0.38
Lower Logan	1358	12.9	0	0	0	0.52

Table 4. Carbonate chemistry at four stations in the Logan River system, October 1979.

Station	Temperature (°C)	pH	Alkalinity (mg/l as $CaCO_3$)	Ca (mg/l)	Mg Hardness (mg/l as $CaCO_3$)	EC (µmhos/cm @ 25°C)	$CaCO_3$ Saturation Index
Spawn Creek	9	8.5	195	66	35	375	5.6
Twin Bridges	7	8.5	175	57	42	180[a]	4.2
UWRL	7	8.2	170	57	62	305	3.2
Lower Logan	11	8.2	215	86	44	505	3.8

[a] This value is considerably lower than would be predicted on the basis of the other values.

during the week preceding these measurements, and since magnesium concentration did not decrease, the data suggest that $CaCO_3$ precipitation occurred in the canyon section of the river. This observation is substantiated by the fact that the decreases in calcium and alkalinity were chemically equivalent (0.4 meq/l), as would be expected from $CaCO_3$ precipitation.

The degree to which this precipitation may have been photosynthetically-induced cannot be ascertained from the field data. However, the results of the productivity experiments suggest that potential biological impact on carbonate chemistry is greatest in the headwater creeks of the Logan River watershed. These are also the stream reaches where equilibrium considerations mandate the greatest $CaCO_3$ precipitation. Conversely, although chemical measurements indicate that the Lower Logan should also be characterized by substantial $CaCO_3$ precipitation, biological activity may not contribute to this precipitation. An intermediate situation exists in the canyon section of the river, where benthic photosynthesis probably has a moderate influence on river water carbonate chemistry. These conclusions are summarized in Table 5.

Table 5. Predicted influences of water chemistry and benthic photosynthesis on $CaCO_3$ precipitation in the Logan River.

Stream Reach	$CaCO_3$ Precipitation Predicted from the Saturation Index	$CaCO_3$ Precipitation Predicted from Algal Productivity
Headwaters Creeks	High	High
Canyon Section	Moderate	Moderate
Valley Section	High	Low

Mineralogic Analyses

Table 6 shows the results of X-ray diffraction analyses of various benthic and suspended minerals from the Logan River. The mineral portion of the suspended sediment was chiefly composed of quartz, and also contained calcite and dolomite. Matter adhering to the river rocks and having no visible organic component contained calcite, and in some cases traces of dolomite and quartz. Calcite was the only mineral detected in those benthic precipitate samples which were enmeshed in algal mats. No phosphorus-containing minerals were detected in either suspended or benthic sediments. If apatite co-precipitates with calcite in the Logan River, it does so in trace amounts.

Radiotracer Experiments

A set of ^{14}C-labeling experiments were carried out at various temperatures, using the laboratory benchtop apparatus. As a check of experimental technique, the algal carbon assimilations under light and dark conditions were first compared (Table 7). Measured dark uptake (a combination of real carbon uptake and ^{14}C contamination) ranged

Table 6. Mineralogy of benthic precipitates and suspended sediments in the Logan River, as determined by X-ray diffraction.

Sampling Site	Sample Type	Minerals Detected
Above First Dam reservoir	Suspended Sediments	Quartz[a] Calcite Dolomite
River at UWRL	Suspended Sediments	Quartz[a] Calcite Dolomite
River at UWRL	Benthic Precipitate, no Algae	Calcite[a] Dolomite Quartz
River at UWRL	Benthic Precipitate, no Algae	Calcite
Spawn Creek	Benthic Precipitate, no Algae	Calcite
River at UWRL	Benthic Precipitate with Filamentous Algae	Calcite

[a] Most abundant.

Table 7. Periphyton carbon uptake under light and dark conditions, calculated from C-14 uptake.

	Light		Dark	
Temperature (°C)	n	Rate of Uptake (mg C/m^2-hr)	n	Rate of Uptake (mg C/m^2-hr)
5	6	3.70 ± 1.5	4	0.32 ± 0.12
10	8	3.90 ± 1.9	6	0.50 ± 0.60
15	4	3.60 ± 1.4	4	0.50 ± 0.28
20	4	2.00 ± 0.62	4	0.27 ± 0.11

from 9 to 14 percent of corresponding light uptake, averaging 12 percent of light uptake. The relative contributions of ^{14}C contamination and actual algal uptake to dark carbon assimilation cannot be distinguished. Therefore, total measured carbon uptake under dark conditions was used as a control value for the results of each treatment. This was done by calculating net photosynthetic carbon assimilation as measured light assimilation minus mean dark assimilation for each treatment.

A comparison of carbon precipitation with photosynthetic activity under several temperature regimes is shown in Table 8. Net precipitation of carbon as a function of photosynthetic activity decreased as water temperature increased. In 5°C water, the net carbon precipitated was equivalent to 82 percent of the photosynthetically-assimilated carbon. At an experimental temperature of 20°C, this ratio was reduced to zero. The experimental variances within treatments were considerable; coefficients of variation ranged from 0 to 72 percent. However, a least-squares linear regression indicates that the results obtained at different experimental temperatures are significantly different at the 1 percent level (Table 9).

It is evident from Table 8 that the precipitation of solid carbon declined relative to photosynthetic activity for two reasons. First, algal carbon assimilation declined sharply from 15° to 20°. In addition, carbon precipitation under light conditions was no greater than that under dark conditions at this temperature. By making the assumption that photosynthetic activity in darkness was negligible, the proportions of carbon precipitation attributable to photosynthesis and to chemical solubility can be calculated. Table 10 shows the result of such a calculation. The second column represents both chemically and photosynthetically-induced $CaCO_3$ precipitation. The third column shows carbon precipitation in the absence of photosynthesis. The next column shows the difference between these two, or photosynthetically-induced precipitation. This is depicted as the percent of total precipitation in the last column. Under these experimental conditions, photosynthetic activity accounted for more than 80 percent of all $CaCO_3$ precipitation at 10°C or below. This fraction declined to 60 percent at 15°C, and at 20°C photosynthetic activity had a negligible effect on carbon precipitation.

Table 11 shows the rates of carbon assimilation and precipitation which were measured during the nutrient-enrichment experiments. No apparent acceleration of photosynthetic carbon uptake resulted from increasing the inorganic macronutrient concentrations. Nor was there an evident effect on net carbon precipitation rates, or on precipitation to assimilation ratios. Analysis of variance was performed on both the assimilation and precipitation data. The results, summarized in Table 12, show that, not only were no trends discernible, but there were no meaningful differences between the results observed at any two nutrient levels. In these experiments, neither biological activity nor the precipitation of inorganic carbon varied consistently as a function of macronutrient concentration.

Table 13 summarizes the results of the tracer experiments in which water velocity was varied. Although the within-treatment variance is substantial, there is an apparent trend towards lower ratios of carbon precipitation to algal carbon uptake as water velocity increases. An analysis of variance of these data indicates that the trend is significant at the 5 percent level (Table

Table 8. Periphyton carbon uptake and solid carbon precipitation under varied temperature conditions.

Temperature (^{o}C)	Net C Uptake (mg/m^2-hr)[a]	Net C Precipitation (mg/m^2-hr)[b]	$\frac{\text{C Precipitated}}{\text{C Taken Up}}$	
5	4.40	2.35	0.535	
	5.47	3.35	0.610	$\bar{X}$ = 0.82
	3.65	3.70	1.00	s^2 = 0.043
	4.07	4.45	1.10	CV = 25%
	1.14	0.80	0.730	
	1.55	1.40	0.935	
10	0.55	0.01	0.020	
	0.78	0.165	0.210	
	2.05	2.25	1.10	
	3.00	2.70	0.895	$\bar{X}$ = 0.71
	6.35	2.45	0.390	s^2 = 0.26
	4.65	8.10	1.75	CV = 72%
	5.45	2.60	0.670	
	4.00	2.60	0.645	
15	5.25	2.30	0.435	
	3.75	2.25	0.600	$\bar{X}$ = 0.38
	2.00	0.535	0.265	s^2 = 0.025
	1.55	0.305	0.195	CV = 41%
20	2.30	0	0	$\bar{X} \equiv 0$
	0.625	0	0	s^2 = 0
	1.90	0	0	CV = 0
	2.00	0	0	

[a] Calculated as gross C uptake - average dark C uptake.

[b] Calculated as gross C precipitation - average dark C precipitation

Table 9. Linear regression of carbon precipitated to carbon assimilated ratios at four experimental temperatures.

Regression equation: $Y = -0.055X + 1.17$ . . . (11)

where Y = C precip/C assimilated

X = temperature, degrees C

$r^2 = 0.42$

$n = 22$

r is significant at the 1 percent level.

Table 10. Precipitation of carbon under light and dark conditions, at four experimental temperatures.

Temperature (Degrees C)	Mean Total Light Precipitation (mg C/m^2-hr)	Mean Dark Precipitation (mg C/m^2-hr)	Mean Light-Dark Precipitation (mg C/m^2-hr)	Photosynthetically-Induced Precipitation (% of Total)
5	3.25	0.590	2.70	82
10	3.60	0.675	2.90	81
15	2.20	0.885	1.30	60
20	2.25	2.40	0	0

Table 11. Periphyton carbon assimilation and carbon precipitation at four nutrient concentrations, @ 15°C. n = 6 for each treatment.

Treatment	PO_4-P (μg/l)	NO_3-N (μg/l)	C Assimilation (mg/m^2-hr)	C Precipitation (mg/m^2-hr)	C Precipitated / C Taken Up
1 (control)	10	110	4.60 ± 0.85	7.00 ± 5.30	1.53
2	100	1,000	4.10 ± 0.75	7.00 ± 3.70	1.70
3	500	5,000	4.00 ± 1.50	5.85 ± 3.30	1.45
4	1,000	10,000	4.50 ± 1.10	6.55 ± 3.90	1.45

14). The regression equation for these data is

$$Y = -0.56X + 0.92 \quad \ldots \ldots \ldots \quad (12)$$

where X = water velocity (m/sec) and Y is the ratio of carbon precipitated to carbon taken up. For this equation, $r^2 = 0.36$, n = 22, and r is significant at the 5 percent level.

The co-precipitation or sorption of orthophosphorus by $CaCO_3$ was examined in ^{14}C - ^{32}P dual-labeling experiments. Phosphorus and carbon precipitation at several water temperatures are plotted in Figure 20. Trends determined from mean values are quite similar for the two elements. In both cases, precipitation rates were low at experimental temperatures below 10°C, higher at intermediate temperatures, and low again at high temperatures (> 20°C). The mole ratio of precipitated phosphorus to precipitated carbon ranged from 0.007 to 0.03. Mean phosphorus precipitation was 1.5 percent of mean carbon precipitation (Table B-3, Appendix B). However, these data are quite variable, and are contradictory to the temperature-variation results discussed above. Consequently, no specific conclusion can be drawn regarding a stoichiometric relation between $CaCO_3$ precipitation and phosphorus sorption/precipitation.

Table 12. Analysis of variance of algal carbon assimilation and inorganic carbon precipitation at four nutrient enrichments.

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	F
Algal Carbon Assimilation				
Among Treatments	3	1.9	0.38	0.28
Within Treatments	20	27.2	1.36	
Inorganic Carbon Precipitation				
Among Treatments	3	6.0	2.0	0.097
Within Treatments	20	411	20.6	

Neither F is significant.

Table 13. Algal carbon assimilation and inorganic carbon precipitation at three water velocities. T = 12°C.

Water Velocity (m/sec)	Algal Uptake[a] (mg C/m^2-hr)	Precipitation[a] (mg C/m^2-hr)	C Precipitated / C Taken Up	
0.50	2.35	2.80	1.20	
	2.40	1.30	0.545	
	2.30	1.20	0.515	
	2.90	1.95	0.660	$\bar{X} = 0.635$
	4.70	2.35	0.500	
	5.70	2.50	0.440	
	7.35	3.10	0.420	
	6.20	5.15	0.830	
0.81	3.45	1.90	0.545	
	5.20	2.20	0.420	
	4.70	2.95	0.625	
	4.05	2.50	0.620	$\bar{X} = 0.425$
	3.60	2.00	0.560	
	3.30	1.00	0.295	
	3.85	1.40	0.360	
	4.00	0	0	
1.13	1.85	0.40	0.220	
	2.05	0.90	0.425	
	2.80	0.55	0.200	
	1.90	0	0.0	$\bar{X} = 0.315$
	9.70	3.30	0.34	
	10.7	6.25	0.585	
	5.55	2.25	0.410	
	7.00	2.40	0.345	

[a] Calculated by subtracting mean control (dark) value from measured value.

Table 14. Analysis of variance of carbon precipitated to carbon assimilated ratios at three water velocities. Ratios have been treated as percents for the analysis.

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	F
Among Treatments	2	4249	2125	4.51
Within Treatments	21	9885	471	

F is significant at the 5 percent level.

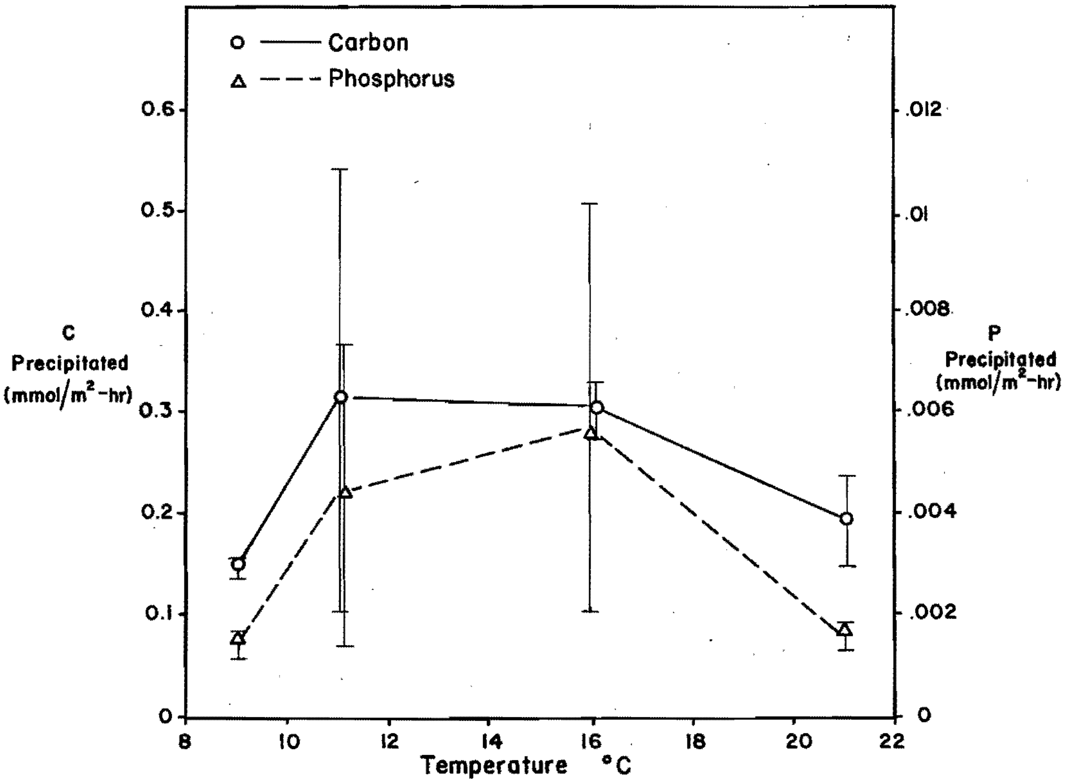

Figure 20. Precipitation of phosphorus and carbon as functions of water temperature.

DISCUSSION

Experimental Methods

As previously discussed, the potential entrapment of suspended $CaCO_3$ in the periphyton matrix prohibits the use of in-stream measurements to assess the rate of $CaCO_3$ precipitation as a function of periphyton photosynthesis. Schultz (1979) performed a series of laboratory-stream experiments in which both periphyton photosynthesis and $CaCO_3$ precipitation were measured. In these experiments, photosynthetic carbon uptake was calculated from the increase in stream-water pH over the course of an experiment. The precipitation of $CaCO_3$ was determined from the decrease of Ca^{2+} in the streamwater. Although the results suggested a correlation between photosynthesis and $CaCO_3$ precipitation, the observed chemical changes were quite small. Schultz concluded that classical wet chemistry techniques were not sufficiently precise for the measurement of precipitation and photosynthetic rates during short-term experiments. Consequently, the first major task of the current study was the development of precise techniques for measuring these two rates.

Because of the relatively high precision attainable using radioisotopes, it was decided to utilize ^{14}C to trace both photosynthetic carbon uptake and $CaCO_3$ precipitation. The marked difference in carbon uptake between light and dark experiments showed that the methods developed provided a satisfactory measurement of photosynthesis. The measurement of solid $CaCO_3$ could not be as readily verified. Experimental data were handled under the assumption that the ^{14}C detected in the precipitated phase was entirely in the form of $Ca^{14}CO_3$. While solubility considerations suggest that the precipitation of carbonates other than $CaCO_3$ from Logan River water could not have been important, it is possible that ^{14}C was taken up by algae and subsequently exuded as organic carbon. Such compounds, adsorbed to $CaCO_3$ crystals, would have been treated as $Ca^{14}CO_3$ in the calculation of precipitated carbon. However, this process is unlikely to have occurred on a large scale during the short-term experiments performed in this study.

$CaCO_3$ - Phosphorus Interactions

The calculated values of precipitated carbon and precipitated phosphorus derived from the ^{14}C-^{32}P dual-labeling experiments show great within-treatment variance (Table B-3, Appendix B). This is attributable to several factors, some common to all the labeling experiments, some peculiar to the phosphorus experiments. Overall, the greatest source of experimental error was the range of periphyton community types which became established on the lab-stream substrates. An effort was made to select substrates which appeared alike for each experiment. Consequently, replicate samples within experiments were quite similar. In addition, the ^{14}C-^{32}P experiments had two extra sources of variance. "Spillover" of ^{32}P counts into the scintillation-counter ^{14}C channel was strongly suspected in several experiments where algae apparently took up considerable amounts of ^{14}C in the dark. This would have resulted in erroneously high calculated rates of carbon precipitation, and low rates of phosphorus precipitation. Furthermore, the apparent "precipitation" of phosphorus may have included substantial P adsorption onto the surface polysaccarides of the periphyton community. In experiments investigating ^{32}P uptake by periphyton, Lock and John (1979) found that adsorption of orthophosphorus onto cell surfaces represented 25-50 percent of the total community P uptake. Hence, the surface of an actively metabolizing periphyton community is probably not an appropriate place to measure the inorganic precipitation of phosphorus. In the past, investigations of phosphorus-calcite interactions have entailed quantifying the losses of P and Ca from supersaturated $CaCO_3$ solutions. It is felt that such experiments, perhaps incorporating radioisotopes, can provide better models of inorganic P dynamics than can experiments attempting to take biological activity into account.

Photosynthesis and $CaCO_3$ Precipitation

It might be predicted that $CaCO_3$ precipitation in darkness would be a logarithmic function of absolute temperature, reflecting solubility considerations alone. Precipitation in the light, on the other hand, should show a more complex temperature-dependence, because of the involvement of algal enzymatic processes. When radiotracer experiments were performed in the laboratory to investigate the effects of varied water temperature on $CaCO_3$ precipitation, both of these expectations were borne out. Figure 21 compares the observed photosynthetically and chemically-induced $CaCO_3$ precipitation with $CaCO_3$ solubility. The temperature-dependence of dark precipitation was indistinguishable from the temperature-dependence of calcite

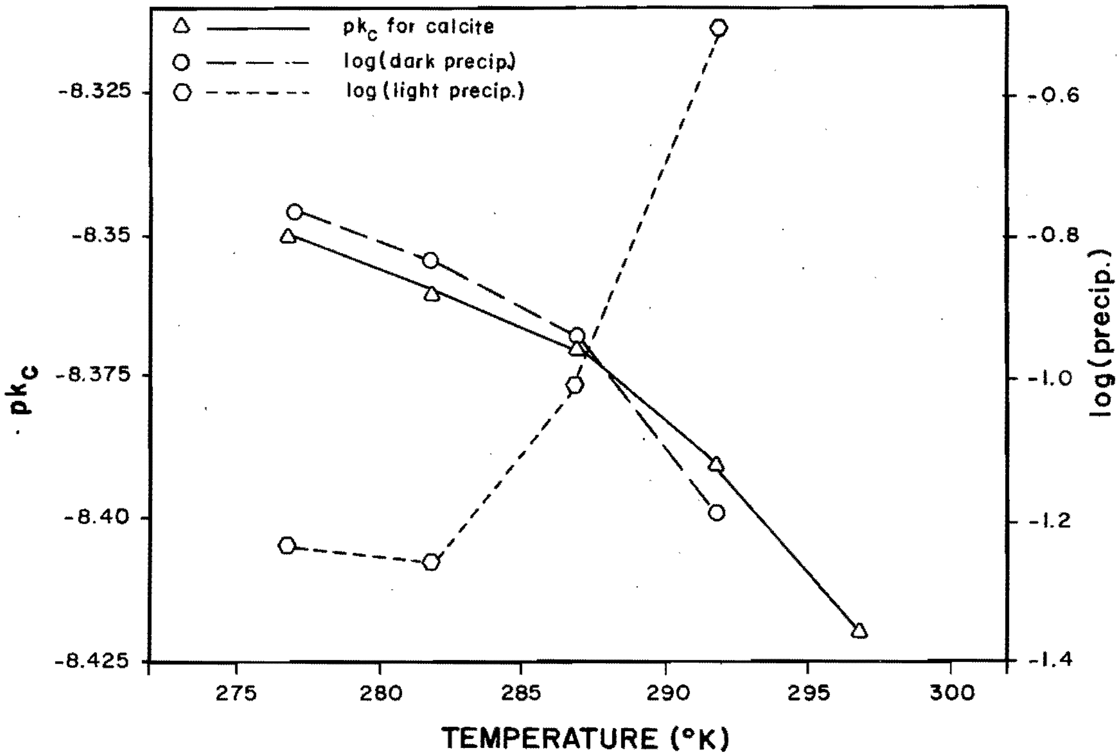

Figure 21. Calcite solubility and measured $CaCO_3$ precipitation as functions of temperature. Calcite pK_c values from Kelts and Hsü (1978).

solubility. Dark precipitation increased approximately logarithmically with increasing temperature. Conversely, the precipitation attributable to photosynthesis was greatest at 10°C, and dropped off sharply at higher temperatures. The observed decline in photosynthetic activity at high temperatures may have been partially responsible for the decrease in precipitation. In addition, algal respiration may have accelerated at higher temperatures. The results of the light-and-dark chamber experiments in the Logan River suggested that, for the same periphyton community, the ratio of respiration to photosynthetic production was much higher at summer water temperatures (12-13°C) than at winter temperatures (1-2°C). An increased respiratory production of CO_2 would offset the effects of photosynthetic CO_2 uptake and result in relatively less biogenic $CaCO_3$ precipitation at high temperatures.

In these experiments, the amount of $CaCO_3$ precipitated in the absence of photosynthesis followed the trend of calcite solubility. This indicates that the process was not kinetically constrained. The results of the nutrient-enrichment experiments point to the same conclusion. An initial set of experiments, three per treatment, each lasting 2 hours, was performed. Then experiments lasting 6 hours (again three per treatment) were carried out. If kinetic factors were involved, the longer experiments would have yielded higher carbon precipitation rates. As the raw data of Table B-4 (Appendix B) show, no such differences were evident. Therefore, the results of the 2 and 6-hour experiments were combined for analysis. In laboratory-stream experiments employing Logan River periphyton communities, Schultz (1979) measured marked increases in photosynthesis resulting from nutrient enrichment of streamwater. The observed acceleration of photosynthesis was a maximum 6 hours after the addition of nutrients to the streamwater. Similar acceleration of periphyton photosynthesis was not observed in the nutrient-enrichment experiments of this study. Since these experiments lasted 6 hours or less, the algae were first acclimated to the elevated nutrient levels for 6 hours prior to the beginning of each experiment. This may have been an insufficient acclimation time. Alternatively, the algae may have experienced temperature stress at the experimental temperature (16°C), causing them to be unresponsive to the nutrient spikes. In either case, these data do not permit the prediction of the biogenic $CaCO_3$ precipitation rate based on nutrient levels. Such a relation would certainly differ between algal communities, and, within one community, between times of year. Therefore, a correlation between nutrient level and $CaCO_3$ precipitation was not investigated further. Instead, the effect of streamwater nutrient concentrations on biogenic $CaCO_3$ precipitation might be estimated through the use of a periphyton productivity model (cf. Schultz 1979).

Water velocity in a stream might be expected to influence the photosynthetic production of $CaCO_3$ precipitation in two distinct ways. As previously discussed, water velocity influences the type of periphyton community which develops on a lotic substrate. Periphyton communities which differ with respect to photosynthetic rate, physical structure, and the species of carbon utilized in photosynthesis would affect $CaCO_3$ precipitation differently. In addition, water velocity might be expected to influence the way each community affects precipitation. In moving water, the pH increase caused by photosynthetic carbon assimilation is confined to a narrow zone adjacent to the substrate (Figure 22). Drag forces against the benthic surface are responsible for the creation of this boundary layer, which is characterized by relatively low water velocity and a low rate of advective mixing with the main stream. At higher water velocities, the top of the boundary layer is continually sheared off by the fast-moving water. Thus, the chemical products of algal photosynthesis are mixed into the main stream, and a localized pH increase favorable to $CaCO_3$ precipitation is prevented. It might be predicted, therefore, that increased water velocity diminishes the importance of photosynthesis to $CaCO_3$ precipitation. In the present study, photosynthetically-induced precipitation was observed to decrease with increasing water velocity (Table 13). The range of velocities tested was somewhat narrow. The highest water velocity tested in this experiment, 1.13 m/sec, is slightly less than the highest water velocity measured in the Logan River at the UWRL during the study (1.2 m/sec). However, the laboratory stream system used in this study did not allow the testing of water velocities less than 0.75 m/sec. Since the water chemistry and light levels were the same in the benchtop and lab stream experiments, it is instructive to compare the results of the two. In the benchtop experiments, water movement was very slight. For a temperature of 12°C and a water velocity of 0-0.1 m/sec, the benchtop results predict a ratio of 0.65-0.7 mole C precipitated per mole C assimilated by the periphyton (Figure 23). This is somewhat less than a prediction based on the lab stream experiments, and suggests a diminution in the effects of water velocity at low velocities.

Because of the boundary-layer narrowing effect, it is possible that microcrystals of $CaCO_3$, formed in the algal matrix, were increasingly swept into suspension in the streamwater as water velocity was increased. Future experiments of this type should check for this possibility. The check might be performed by monitoring suspended $CaCO_3$ using a dialysis membrane or some other very fine filter.

Particular care must be taken in extrapolating the velocity-precipitation relationship to natural streams. In these laboratory-stream experiments, the water flowing over the substrates was quite shallow, having an average depth of 2 cm. The "average" velocities used in these calculations are not, therefore, comparable to the average water velocities of natural streams, as calculated by cross-sectional analysis or other standard techniques. In order to apply the velocity-precipitation equation to a natural stream,

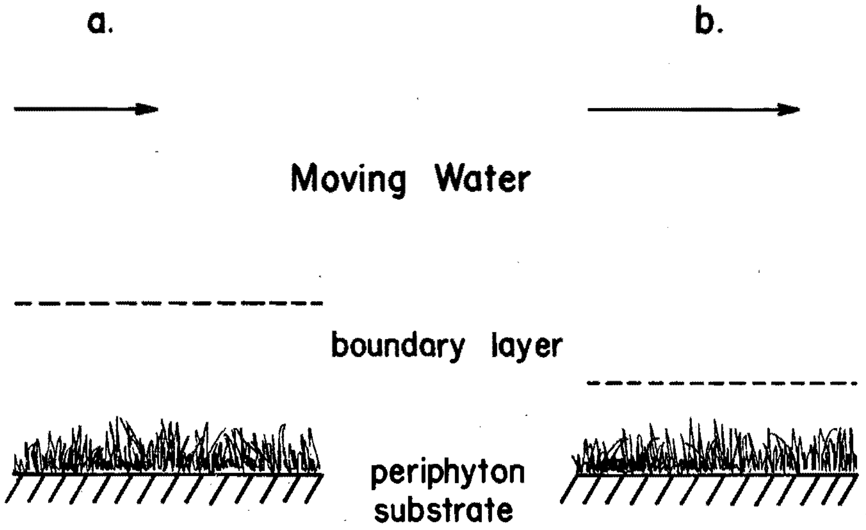

Figure 22. Boundary layer width as a function of average water velocity.

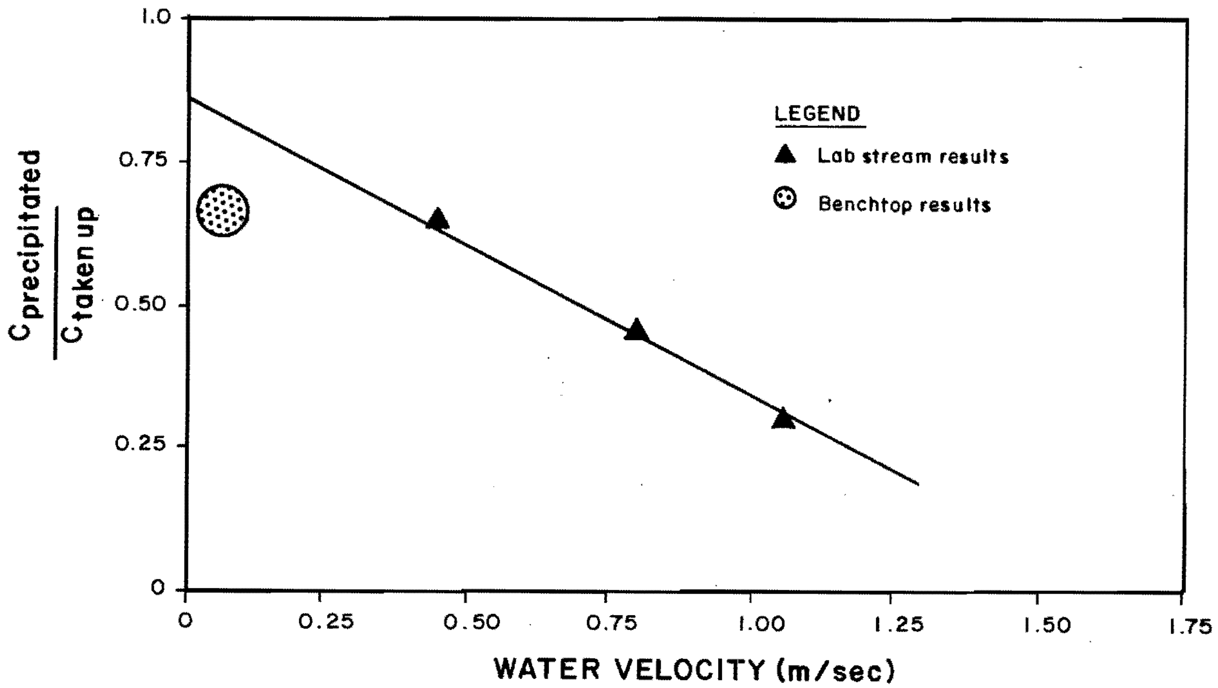

Figure 23. Biogenic carbon precipitation as a function of water velocity. Data from both benchtop and laboratory stream experiments.

an average water velocity along the streambed must be measured.

The dependence of biological $CaCO_3$ precipitation on water velocity indicates that the accretion of benthic $CaCO_3$ may vary over short distances in natural streams. Particular reaches of mountain rivers are frequently classified as either "riffles"--broad, shallow stretches having turbulent flow--or "runs"--deep stretches with near-laminar flow and quiet pools. The results of the laboratory-stream experiments suggest that the buildup of carbonates should proceed much more readily in stream runs than in riffles. In addition, the stream borders, which have much lower water velocities than the main channel, should be relatively favorable places for the accretion of $CaCO_3$.

Field Results

The Logan River hydrograph for the period May 1979 to May 1980 shows a sharp division of streamflow into snowmelt and base flow (Figure 7). While this basic pattern of discharge is observed every year in mountain rivers, the cumulative annual discharge, which depends on precipitation, may vary considerably between years. The volume of overland runoff (derived from snowmelt) determines the $CaCO_3$ saturation index of the river water during the spring. In addition, the relative contributions of photosynthesis and supersaturation to $CaCO_3$ precipitation in the stream depend on stream discharge. Table 15 shows annual runoff data compiled for the canyon section of the Logan River over 53 years. During this period, the maximum and minimum cumulative annual flows differed by a factor of four. A significant difference in runoff between consecutive years might be anticipated from the coefficient of variation (31 percent). Thus, it is probable that, during a heavy spring runoff, the canyon section of the Logan River is undersaturated with respect to $CaCO_3$ for several months. In this circumstance, the only environment conducive to $CaCO_3$ precipitation is that of the hydrodynamic boundary layer above the periphyton mat. A predominance of base flow should have the opposite effect. Since base flow is derived from carbonate-rich groundwater, photosynthesis makes relatively little contribution to $CaCO_3$ precipitation, on a mass basis, during months when base flow and the degree of $CaCO_3$ saturation are high.

Table 15. Annual discharge characteristics of the Logan River, 1897-1950. Data from USGS (1954).

Mean Annual Discharge	2.54×10^8 m^3
Maximum Annual Discharge	4.61×10^8 m^3
Minimum Annual Discharge	1.12×10^8 m^3
Standard Deviation	7.90×10^7 m^3
Coefficient of Variation	31%

Water chemistry data obtained in this study indicated that Logan River water did not deviate substantially from saturation with respect to calcite (Table 2). Saturation indices were low during spring runoff (April-May 1980) and during periods of heavy periphyton growth (July-August 1979 and December-January 1979-1980). However, even during a period of base flow with low algal production (autumn 1979), the calcite saturation index did not reach two. At no time during this study did the river water approach the calcite supersaturation observed in lentic systems. The CO_2-rich springs which feed the river along its entire course may be largely responsible for the equilibrium conditions observed in the Logan River.

Field observations also suggested that $CaCO_3$ precipitation is not favored year-round in the Logan River. While heavy carbonate deposits were evident during the summer, little mineral matter adhered to benthic rocks during the spring. This may reflect the dissolution of solid carbonates or the influence of physical scouring during spring runoff. In either case, there is apparently no net accumulation of benthic $CaCO_3$ in the middle reaches of the Logan River over the course of a year.

The monitoring of water chemistry in the Logan River was accompanied by several types of biological monitoring: measurements of benthic biomass, chlorophyll, productivity, and respiration. The objective of the biological monitoring was to assess the long-term variations in the biological factors which might influence $CaCO_3$ precipitation. In addition, the data provide a means to compare the Logan River periphyton with that of other streams.

One aspect of the biological monitoring program was the measurement of periphyton biomass and the mass of the associated solid calcium, for communities colonizing smooth limestone substrates. As Figure 18 shows, $CaCO_3$ accretion is best depicted as an exponential function of biomass. This is a somewhat different relationship than that derived from laboratory experiments, in which $CaCO_3$ precipitation was related to algal carbon uptake in a linear fashion (Table 9). This discrepancy arises from differences between the two experimental methods. The accumulation of plant biomass over time, which was the productivity measure used in the field study, is a direct function of net primary productivity. However, an assay of the algal assimilation of ^{14}C measures something between gross and net primary productivity (Vollenweider 1969). In addition, the field data were taken at all times of the year, when water temperatures ranged from 2 to 13°C. As the laboratory experiments showed, the relation between $CaCO_3$ precipitation and periphyton carbon assimilation varies with temperature. Finally the periphyton communities of the river certainly trapped some suspended $CaCO_3$ crystals, which contributed to the total mass of benthic calcium. On the whole, the laboratory and field measures of $CaCO_3$ accretion vs periphyton photosynthesis cannot be judged to disagree.

The chlorophyll _a_ content of a benthic community is often used as a measure of periphyton standing crop. In the current study, the chlorophyll _a_ levels of 2-month-old periphyton communities on smooth limestone substrates were measured (Figure 16). Except during a bloom of _Hydrurus_, these averaged less than 10 mg/m^2. McConnell and Sigler (1959) measured the chlorophyll _a_ from communities colonizing river-bottom cobbles at several stations in the canyon section of the Logan River. They derived an average chlorophyll _a_ content of 300 mg/m^2 for this section. In another long-term productivity study, chlorophyll _a_ from periphyton communities colonizing cobbled patio stones in Spawn Creek, in the Logan River watershed, was extracted. These communities seldom contained less than 20 mg/m^2 of chlorophyll _a_ (Runke 1978, personal communication). A study reported by Schultz (1979) entailed chlorophyll _a_ measurement of periphyton communities of the Upper Strawberry River of the Uinta Mountains, Utah. Summertime chlorophyll contents of these communities ranged from 20 to 125 mg/m^2; winter levels were much higher. Clearly, the rock substrates used in the current study were colonized by unusually sparse periphyton communities. This is attributable to both the nature and placement of these substrates. The platform on which they rested was positioned horizontally in the main channel of the river. In addition, the rock substrate surfaces were buffed smooth, so that the periphyton and associated $CaCO_3$ could be readily and quantitatively sampled. The periphyton communities on these substrates were therefore subjected to a very high rate of scouring by suspended matter. Schultz (1979) has asserted that such scouring exerts a major control on periphyton communities in mountain rivers. Therefore, although they reveal the seasonal trends characteristic of the benthic community, neither the chlorophyll nor the biomass data gathered in this study can be considered to represent actual periphyton community parameters in the river. Future sampling programs of the type described herein would be best carried out in the peripheral portions of the stream. This would require the use of a substrate-carrying device which could be submersed in very shallow (10-15 cm deep) water.

The synoptic field study of productivity was designed to elucidate different biological trends: those manifest in the upstream-downstream direction of the river. Net periphyton production was of particular interest, since it determines the potential for biologically-induced $CaCO_3$ precipitation. As measured by the light-and-dark chamber oxygen method, net periphyton production declined downstream from the headwater creeks of the Logan River (Table 3). Chlorophyll concentrations showed the opposite trend, increasing consistently from Spawn Creek to the lower Logan River. Such an inverse relationship between standing crop and algal productivity is frequently observed (cf. Whitford and Schumacher 1964; Pfeiffer and McDiffett 1975). This relationship has been attributed to physical self-shading by benthic communities, and to competition for scarce nutrients. Regardless of its cause, this inverse relationship obviates the use of benthic chlorophyll a as a measure of potential biogenic $CaCO_3$ precipitation in rivers. The current study indicates that benthic biomass, measured as ash-free dry weight, provides a better estimate of potential biogenic precipitation. Better yet is an active, short-term measure of algal production, such as oxygen evolution or pH change. These data can be readily converted into algal carbon assimilation rates, from which potential biogenic $CaCO_3$ precipitation can be estimated.

The temperature and velocity experiment results discussed herein permit the formulation of an equation by which to make such estimates. Combination of Equations 11 and 12 yields the equation for biogenically precipitated $CaCO_3$,

$$C_{\text{precip(biol.)}} = C_{\text{assimilated}}(1.02-0.0275T-0.25V) \qquad \text{. . . . . . . (13)}$$

where $C_{\text{precip.}}$ and $C_{\text{assim.}}$ are in mg/m^2-hr, T = temperature, degrees C, and V = water velocity along the stream bottom in meters/sec. Table 16 shows the input data, and the results of applying this formula to the four experimental stations of the synoptic field study (a carbon assimilation factor of 1.2 has been assumed (Fogg 1969)). According to this prediction, more than 400 mg/m^2-hr of $CaCO_3$ may be biogenically precipitated in Spawn Creek during the month of October. Somewhat lower precipitation rates, 238 and 269 mg $CaCO_3$/m^2-hr, are predicted for the Twin Bridges and UWRL stations, respectively. No biogenic $CaCO_3$ precipitation is predicted for the lower Logan River.

These predictions must, of course, be interpreted cautiously. The river must be supersaturated with respect to $CaCO_3$ for precipitation to occur at all; this is not always the case. Water temperature and periphyton productivity vary temporally, both seasonally and diurnally. Many measurements are required to assign representative values to these variables. Furthermore, water velocity may differ substantially between adjacent pools and riffles in a mountain stream. For all of these reasons, estimates of the rates of biogenic $CaCO_3$ precipitation are applicable only to the seasons and the particular sites where the requisite hydrologic, chemical, and biological measurements are made.

With these cautions in mind, one can further evaluate the importance of biological activity to the $CaCO_3$ equilibrium of the Logan River. From the synoptic study data, calcium mass loading rates can be calculated for the river at the four field stations. From these and the calculated precipitation rates, the proportion of dissolved calcium which is removed by biogenic precipitation at each station can be estimated (Table C-1, Appendix C). When stream width is taken into account, this measure is converted to calcium lost per kilometer of stream course. According to such calculations, the biogenic precipitation of 1 percent of the dissolved calcium requires the following stream lengths: Spawn Creek - 1.5 km; Twin Bridges - 7.1 km; UWRL - 18.9 km. No biologically caused precipitation of calcium from the lower Logan River is predicted.

Further calculation can provide a gross estimate of the relative magnitudes of physico-chemical and biogenic $CaCO_3$ precipitation in the Logan River. Between the Spawn Creek and Twin Bridges stations, there was a 13 percent decrease in dissolved calcium at the October sampling. The length of this stream reach is approximately 7.5 km; the upper half is creek, the lower half part of the Logan River. Assuming the biogenic $CaCO_3$ precipitation rates at the two stations are each effective over half the total reach, 3.75 (1/1.5) + 3.75 (1/7.1) = 3.0 percent of all dissolved calcium might have been lost due to biological activity over this reach. Thus, 23 percent (3/13) of the precipitation of $CaCO_3$ in this stream reach can be attributed to biological activity. This conclusion is contrary to Pentecost's (1978) finding that less than 1 percent of $CaCO_3$ precipitation in a fast-moving stream could be attributed to biological activity. This

Table 16. Prediction of biogenic $CaCO_3$ precipitation at four stations in the Logan River. Field data from October 1979.

Station	Temperature (°C)	Weighted Mean Bottom Water Velocity (m/sec)	Net Carbon Assimilation (mg C/m^2-hr)	Biogenic $CaCO_3$ Precipitation (mg $CaCO_3$/m^2-hr)
Spawn Creek	9	0.82	90.8	425
Logan River at Twin Bridges	7	0.45	40.0	238
Logan River at UWRL	7	0.39	44.2	269
Lower Logan River	11	0.33	0	0

discrepancy may reflect the differences between the communities studied, or the effects of the trapping of suspended $CaCO_3$, which were not taken into account in that study.

The contribution of biological activity to $CaCO_3$ precipitation in October is probably intermediate between the summer and winter values. Summer algal productivity is heightened considerably over autumn productivity. However, the high flows and elevated water temperatures of summer should induce substantial physico-chemical precipitation, lessening the relative importance of biological production in the river. On the other hand, the low $CaCO_3$ saturation indices and low flows of winter should effect only moderate physico-chemical precipitation. Since periphyton production in winter is high, it may account for more than 23 percent of all precipitation in the headwaters creeks during that season. In general, the estimates derived herein suggest that, for some lotic systems, photosynthetic activity may be an important regulator of carbonate dynamics.

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

Laboratory and field studies investigating the environment of calcium carbonate precipitation in hard-water streams were carried out. The objective was to assess the importance of periphyton photosynthesis to the induction of $CaCO_3$ precipitation. Biogenic $CaCO_3$ precipitation was found to vary as a function of water temperature and velocity. It was determined that, in the Logan River system, biological activity may in some places be nearly as important as chemical solubility in mediating $CaCO_3$ precipitation. The following specific conclusions were reached:

1. According to X-ray diffraction analysis, calcite was the only $CaCO_3$ mineral in the suspended sediment and benthic precipitate of the Logan River.

2. Because the accretion of benthic $CaCO_3$ in large part reflects the trapping of suspended crystals, field measurements alone did not provide a satisfactory estimate of biogenic $CaCO_3$ precipitation.

3. The precipitation of $CaCO_3$ from Logan River water in the absence of photosynthesis was found to mirror the temperature dependence of calcite solubility.

4. Photosynthetically-induced $CaCO_3$ precipitation was found to be greatest at a water temperature of 5°-10°C, and to decline to zero at 20°C.

5. Biogenic $CaCO_3$ precipitation was not correlated with streamwater macronutrient concentrations.

6. The accumulation of biogenically-precipitated $CaCO_3$ declined with increasing water velocity. At a temperature of 12°C, biogenic $CaCO_3$ precipitation declined from 64 percent to 32 percent of assimilated carbon, at velocities of 0.50 and 1.13 m/sec, respectively.

7. The calcite saturation index of the Logan River decreased measurably in response to spring snowmelt and periphyton blooms.

8. The calcite supersaturation seen in hard-water lakes was not observed in the Logan River, which was close to equilibrium calcite saturation throughout the 14-month field study.

9. Lotic periphyton communities colonizing smooth substrates in high-energy locations are not representative of benthic communities.

10. Short-term, in-stream productivity experiments are superior to standing-crop estimates as predictors of biogenic $CaCO_3$ precipitation.

11. In the Logan River system, photosynthetically-induced $CaCO_3$ precipitation may account for more than 25 percent of the removal of calcium from solution.

12. In a mountain river system, photosynthetically-induced $CaCO_3$ precipitation is greatest in high-altitude, headwater creeks, decreasing steadily downstream.

13. Biogenic $CaCO_3$, expressed as the ratio of precipitated to assimilated carbon, might be expected to accrete most rapidly in the "runs" and along the periphery of mountain streams.

The results of this study suggest that diversion or other alteration of the flow regimes of western streams may, through the periphyton, have a number of impacts on streamwater chemistry. Any alteration which decreases the periphyton production of a $CaCO_3$-saturated stream would diminish $CaCO_3$ precipitation, thereby raising streamwater dissolved mineral content, but lowering the sodium adsorption ratio. Dissolved and particulate phosphorus and organic compounds would be more labile than before. These effects would be particularly marked in small streams, and less important, possibly unmeasurable in large ones.

Recommendations

Based on the results of this study, the following recommendations for future research are made:

1. The effects of water velocity on $CaCO_3$ precipitation need further study, particularly at low velocities.

2. The seasonal pattern of benthic $CaCO_3$ accumulation or removal has not been delineated. A program of precise and frequent field measurements would be necessary to determine whether a net accumulation of precipitate occurs.

3. Many hard-water systems, both lakes and streams, are reported to be supersaturated with respect to calcite. The Logan River is near equilibrium with respect to calcite. The physical and biological reasons for this discrepancy have yet to be elucidated.

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APPENDIX A

DETAILS OF LABORATORY METHODS

Table A-1. Micronutrient concentrations in the benchtop nutrient-enrichment experiments.

Element	Concentration (μg/l)
Boron	32.5
Cobalt	0.354
Copper	0.004
Iron	33.1
Manganese	115.
Molybdenum	2.88
Zinc	1.57

Table A-2. Loss of ^{14}C during CO_2 treatment of radioactive substrates. ^{14}C detected in ethanolamine is expressed as a percent of the total ^{14}C counts in the aqueous extract.

Trial	CO_2 Collection Time During Treatment (Minutes)	^{14}C Collected (% of Total ^{14}C)
1	0-10	1.0
	10-20	0.7
	20-30	0.3
2	0-10	0.8
	10-20	1.0
	20-30	0.3
3	0-10	0.6
	10-20	0.0
	20-30	1.0
4	0-10	0.6
	10-20	1.5
	20-30	0.2
5	0-10	0.5
	10-20	1.5
	20-30	0.0

Table A-3. Measured precipitation of calcium and carbon, calculated from ^{14}C - ^{45}Ca dual-labeling experiments.

Trial	C Precipitated (mmole/hr)	Ca Precipitated (mmole/hr)	Mole Ratio Ca/C
1	6.3×10^{-3}	7.6×10^{-2}	12.
2	6.5×10^{-3}	3.7×10^{-2}	5.7
3	1.8×10^{-2}	1.6×10^{-2}	0.89
4	4.7×10^{-3}	6.5×10^{-2}	14.
5	1.6×10^{-2}	6.3×10^{-2}	3.9
6	6.7×10^{-2}	4.5×10^{-2}	0.67
7	3.1×10^{-2}	2.9×10^{-2}	0.94
8	5.6×10^{-3}	8.1×10^{-2}	15.
9	9.3×10^{-3}	1.5×10^{-1}	16.

APPENDIX B

HYDROLOGY, WATER CHEMISTRY, AND SELECTED LABORATORY RESULTS

Table B-1. Mean daily discharge of the Logan River at the Utah Water Research Laboratory, 1979-1980.

Date	Mean Flow (m^3/sec)	Date	Mean Flow (m^3/sec)
1979		7/15	8.5
5/25	18.0	7/16	9.0
5/26	18.5	7/17	10.0
5/27	18.0	7/18	11.0
5/28	19.0	7/19	12.0
5/29	19.5	7/20	13.0
5/30	20.0	7/21	13.0
5/31	20.0	7/22	12.5
6/1	20.5	7/23	12.5
6/2	20.5	7/24	12.0
6/3	21.0	7/25	11.5
6/4	21.0	7/26	11.0
6/5	21.5	7/27	11.0
6/6	22.0	7/28	10.5
6/7	23.0	7/29	10.0
6/8	23.5	7/30	10.0
6/9	24.0	7/31	9.5
6/10	24.5	8/1	9.5
6/11	25.0	8/2	9.5
6/12	25.5	8/3	9.5
6/13	25.5	8/4	10.0
6/14	25.0	8/5	10.0
6/15	24.0	8/6	10.0
6/16	23.0	8/7	10.5
6/17	22.0	8/8	10.0
6/18	21.0	8/9	9.5
6/19	20.0	8/10	9.5
6/20	19.0	8/11	9.5
6/21	18.0	8/12	9.5
6/22	17.0	8/13	9.0
6/23	16.0	8/14	9.0
6/24	15.0	8/15	9.5
6/25	14.5	8/16	9.0
6/26	14.0	8/17	9.0
6/27	13.0	8/18	9.5
6/28	12.5	8/19	9.0
6/29	12.0	8/20	9.0
6/30	11.0	8/21	9.5
7/1	11.0	8/22	9.0
7/2	10.5	8/23	9.0
7/3	10.0	8/24	9.0
7/4	10.5	8/25	8.5
7/5	10.0	8/26	8.5
7/6	9.5	8/27	8.5
7/7	9.0	8/28	8.5
7/8	8.5	8/29	8.0
7/9	8.0	8/30	8.0
7/10	7.5	8/31	8.0
7/11	7.0	9/1	8.0
7/12	7.0	9/2	8.0
7/13	7.5	9/3	8.0
7/14	8.0	9/4	8.5

Table B-1. Continued.

Date	Mean Flow (m^3/sec)	Date	Mean Flow (m^3/sec)
9/5	8.0	10/27	11.0
9/6	8.0	10/28	10.0
9/7	8.5	10/29	10.5
9/8	8.5	10/30	10.5
9/9	8.5	10/31	10.5
9/10	8.5	11/1	10.0
9/11	8.0	11/2	10.0
9/12	8.0	11/3	10.0
9/13	8.0	11/4	9.5
9/14	8.0	11/5	9.5
9/15	7.5	11/6	10.0
9/16	7.5	11/7	9.5
9/17	7.5	11/8	9.0
9/18	7.5	11/9	9.0
9/19	7.5	11/10	8.5
9/20	7.5	11/11	8.5
9/21	7.0	11/12	8.5
9/22	7.0	11/13	8.5
9/23	7.5	11/14	8.5
9/24	7.5	11/15	8.5
9/25	7.5	11/16	9.0
9/26	7.5	11/17	9.0
9/27	7.5	11/18	9.0
9/28	7.5	11/19	9.0
9/29	7.5	11/20	9.5
9/30	7.6	11/21	9.0
10/1	7.5	11/22	9.0
10/2	7.5	11/23	9.5
10/3	7.0	11/24	9.5
10/4	7.5	11/25	9.0
10/5	7.0	11/26	9.5
10/6	7.5	11/27	9.5
10/7	7.5	11/28	9.0
10/8	8.0	11/29	9.0
10/9	8.0	11/30	9.0
10/10	7.5	12/1	9.0
10/11	7.5	12/2	9.5
10/12	7.5	12/3	9.0
10/13	8.0	12/4	9.0
10/14	8.0	12/5	8.5
10/15	8.0	12/6	9.0
10/16	8.0	12/7	9.5
10/17	8.5	12/8	8.0
10/18	9.0	12/9	8.5
10/19	8.5	12/10	8.5
10/20	9.0	12/11	8.5
10/21	9.5	12/12	8.5
10/22	10.0	12/13	8.5
10/23	10.5	12/14	9.0
10/24	10.5	12/15	8.5
10/25	11.0	12/16	8.5
10/26	11.0	12/17	8.5

Table B-1. Continued.

Date	Mean Flow (m^3/sec)	Date	Mean Flow (m^3/sec)
12/18	8.5	1/26	8.5
12/19	9.0	1/27	8.5
12/20	9.0	1/28	9.0
12/21	9.0	1/29	8.5
12/22	9.0	1/30	9.0
12/23	8.5	1/31	9.0
12/24	8.5	2/1	9.0
12/25	9.0	2/2	9.0
12/26	9.0	2/3	9.0
12/27	9.0	2/4	9.5
12/28	8.5	2/5	9.5
12/29	8.5	2/6	9.0
12/30	8.5	2/7	9.0
12/31	8.5	2/8	9.0
		2/9	8.5
1980		2/10	8.0
1/1	9.0	2/11	8.5
1/2	8.5	2/12	8.5
1/3	8.5	2/13	8.5
1/4	8.5	2/14	8.0
1/5	8.5	2/15	8.0
1/6	8.5	2/16	8.0
1/7	9.0	2/17	8.5
1/8	9.0	2/18	8.0
1/9	8.5	2/19	8.5
1/10	8.5	2/20	8.0
1/11	8.0	2/21	8.5
1/12	8.5	2/22	8.5
1/13	8.5	2/23	8.0
1/14	8.0	2/24	8.5
1/15	8.5	2/25	8.5
1/16	8.5	2/26	8.5
1/17	8.5	2/27	8.0
1/18	8.5	2/28	8.0
1/19	9.0	2/29	8.0
1/20	8.5	3/1	8.0
1/21	8.5	3/2	8.0
1/22	8.5	3/3	7.5
1/23	8.5	3/4	8.0
1/24	8.0	3/5	8.0
1/25	8.0	3/6	8.0

Table B-1. Continued.

Date	Mean Flow (m^3/sec)	Date	Mean Flow (m^3/sec)
3/7	8.0	4/16	14.0
3/8	7.5	4/17	14.5
3/9	7.5	4/18	15.0
3/10	7.0	4/19	15.5
3/11	8.0	4/20	16.0
3/12	7.5	4/21	16.0
3/13	7.5	4/22	16.5
3/14	7.5	4/23	17.0
3/15	7.5	4/24	17.5
3/16	7.5	4/25	18.0
3/17	8.0	4/26	17.5
3/18	8.0	4/27	18.0
3/19	8.0	4/28	18.0
3/20	7.5	4/29	17.5
3/21	8.0	4/30	17.0
3/22	8.0	5/1	16.5
3/23	7.5	5/2	16.5
3/24	7.5	5/3	16.5
3/25	7.0	5/4	16.0
3/26	7.5	5/5	16.0
3/27	7.5	5/6	15.5
3/28	7.5	5/7	15.5
3/29	7.0	5/8	15.0
3/30	7.0	5/9	15.0
3/31	7.0	5/10	15.0
4/1	7.0	5/11	15.0
4/2	7.5	5/12	15.5
4/3	7.5	5/13	15.5
4/4	8.0	5/14	15.0
4/5	8.0	5/15	16.0
4/6	8.5	5/16	16.5
4/7	9.0	5/17	16.5
4/8	8.5	5/18	17.0
4/9	9.0	5/19	17.0
4/10	9.5	5/20	16.5
4/11	10.0	5/21	16.5
4/12	11.0	5/22	17.0
4/13	11.0	5/23	17.0
4/14	12.0	5/24	17.5
4/15	13.0	5/25	17.0

Table B-2. Water chemistry of the Logan River at the Utah Water Research Laboratory, 1979-1980.

Parameter	Value	Parameter	Value
Date: 5/3/79		Date: 6/7/79	
pH	8.3	pH	8.0
Alkalinity	170 mg/l as $CaCO_3$	Alkalinity	150 mg/l as $CaCO_3$
Calcium	51 mg/l	Calcium	43 mg/l
Total Hardness	170 mg/l as $CaCO_3$	Total Hardness	125 mg/l as $CaCO_3$
Dissolved Organic Carbon	- mg/l	Dissolved Organic Carbon	2.5 mg/l
Particulate Organic Carbon	- mg/l	Particulate Organic Carbon	0.4 mg/l
Specific Conductance	246 µmhos/cm @ 25°C	Specific Conductance	290 µmhos/cm @ 25°C
Dissolved Oxygen	10.6 mg/l	Dissolved Oxygen	10.5 mg/l
Nitrate+nitrite-N	240 µg/l	Nitrate+nitrite-N	100 µg/l
Ammonia-N	<5 µg/l	Ammonia-N	<5 µg/l
Orthophosphorus	10 µg/l	Orthophosphorus	26 µg/l
Total Phosphorus	31 µg/l	Total Phosphorus	31 µg/l
Total Suspended Solids	7.2 mg/l	Total Suspended Solids	6.0 mg/l
Volatile Suspended Solids	3.0 mg/l	Volatile Suspended Solids	3.5 mg/l

Table B-2. Continued.

Parameter	Value	Parameter	Value
Date: 7/5/79		Date: 8/2/79	
pH	7.9	pH	8.0
Alkalinity	178 mg/l as $CaCO_3$	Alkalinity	180 mg/l as $CaCO_3$
Calcium	54 mg/l	Calcium	58 mg/l
Total Hardness	183 mg/l as $CaCO_3$	Total Hardness	190 mg/l as $CaCO_3$
Dissolved Organic Carbon	0.8 mg/l	Dissolved Organic Carbon	- mg/l
Particulate Organic Carbon	0.3 mg/l	Particulate Organic Carbon	- mg/l
Specific Conductance	214 μmhos/cm @ 25°C	Specific Conductance	336 μmhos/cm @ 25°C
Dissolved Oxygen	9.6 mg/l	Dissolved Oxygen	8.7 mg/l
Nitrate+nitrite-N	110 μg/l	Nitrate+nitrite-N	85 μg/l
Ammonia-N	10 μg/l	Ammonia-N	<5 μg/l
Orthophosphorus	8 μg/l	Orthophosphorus	2.9 μg/l
Total Phosphorus	115 μg/l	Total Phosphorus	15.0 μg/l
Total Suspended Solids	3.0 mg/l	Total Suspended Solids	1.2 mg/l
Volatile Suspended Solids	1.0 mg/l	Volatile Suspended Solids	0.9 mg/l
Date: 9/6/79		Date: 10/4/79	
pH	8.1	pH	8.3
Alkalinity	182 mg/l as $CaCO_3$	Alkalinity	185 mg/l as $CaCO_3$
Calcium	76 mg/l	Calcium	57 mg/l
Total Hardness	204 mg/l as $CaCO_3$	Total Hardness	203 mg/l as $CaCO_3$
Dissolved Organic Carbon	0.7 mg/l	Dissolved Organic Carbon	1.7 mg/l
Particulate Organic Carbon	1.8 mg/l	Particulate Organic Carbon	0.2 mg/l
Specific Conductance	322 μmhos/cm @ 25°C	Specific Conductance	363 μmhos/cm @ 25°C
Dissolved Oxygen	8.9 mg/l	Dissolved Oxygen	9.7 mg/l
Nitrate+nitrite-N	120 μg/l	Nitrate+nitrite-N	110 μg/l
Ammonia-N	<5 μg/l	Ammonia-N	<5 μg/l
Orthophosphorus	3.9 μg/l	Orthophosphorus	1.0 μg/l
Total Phosphorus	8.9 μg/l	Total Phosphorus	29 μg/l
Total Suspended Solids	2.0 mg/l	Total Suspended Solids	1.0 mg/l
Volatile Suspended Solids	1.1 mg/l	Volatile Suspended Solids	0 mg/l
Date: 11/1/79		Date: 12/6/79	
pH	8.4	pH	8.1
Alkalinity	185 mg/l as $CaCO_3$	Alkalinity	178 mg/l as $CaCO_3$
Calcium	74 mg/l	Calcium	77 mg/l
Total Hardness	198 mg/l as $CaCO_3$	Total Hardness	216 mg/l as $CaCO_3$
Dissolved Organic Carbon	- mg/l	Dissolved Organic Carbon	1.2 mg/l
Particulate Organic Carbon	- mg/l	Particulate Organic Carbon	0.3 mg/l
Specific Conductance	350 μmhos/cm @ 25°C	Specific Conductance	417 μmhos/cm @ 25°C
Dissolved Oxygen	10.6 mg/l	Dissolved Oxygen	9.5 mg/l
Nitrate+nitrite-N	100 μg/l	Nitrate+nitrite-N	145 μg/l
Ammonia-N	<5 μg/l	Ammonia-N	5 μg/l
Orthophosphorus	3.0 μg/l	Orthophosphorus	8.0 μg/l
Total Phosphorus	10 μg/l	Total Phosphorus	29 μg/l
Total Suspended Solids	<1 mg/l	Total Suspended Solids	1.4 mg/l
Volatile Suspended Solids	<1 mg/l	Volatile Suspended Solids	<1 mg/l

Table B-2. Continued.

Parameter	Value	Parameter	Value
Date: 1/3/80		Date: 2/7/80	
pH	8.0	pH	8.1
Alkalinity	194 mg/l as $CaCO_3$	Alkalinity	198 mg/l as $CaCO_3$
Calcium	71 mg/l	Calcium	81 mg/l
Total Hardness	216 mg/l as $CaCO_3$	Total Hardness	190 mg/l as $CaCO_3$
Dissolved Organic Carbon	1.0 mg/l	Dissolved Organic Carbon	1.3 mg/l
Particulate Organic Carbon	0.4 mg/l	Particulate Organic Carbon	0.7 mg/l
Specific Conductance	420 µmhos/cm @ 25°C	Specific Conductance	360 µmhos/cm @ 25°C
Dissolved Oxygen	10.6 mg/l	Dissolved Oxygen	11.0 mg/l
Nitrate+nitrite-N	170 µg/l	Nitrate+nitrite-N	210 µg/l
Ammonia-N	<5 µg/l	Ammonia-N	<5 µg/l
Orthophosphorus	23 µg/l	Orthophosphorus	5.0 µg/l
Total Phosphorus	95 µg/l	Total Phosphorus	14 µg/l
Total Suspended Solids	1.3 mg/l	Total Suspended Solids	23 mg/l
Volatile Suspended Solids	<1 mg/l	Volatile Suspended Solids	4 mg/l
Date: 3/6/80		Date: 4/3/80	
pH	8.2	pH	8.1
Alkalinity	175 mg/l as $CaCO_3$	Alkalinity	176 mg/l as $CaCO_3$
Calcium	71 mg/l	Calcium	72 mg/l
Total Hardness	192 mg/l as $CaCO_3$	Total Hardness	200 mg/l as $CaCO_3$
Dissolved Organic Carbon	1.3 mg/l	Dissolved Organic Carbon	1.3 mg/l
Particulate Organic Carbon	0.2 mg/l	Particulate Organic Carbon	2.0 mg/l
Specific Conductance	350 µmhos/cm @ 25°C	Specific Conductance	345 µmhos/cm @ 25°C
Dissolved Oxygen	10.7 mg/l	Dissolved Oxygen	10.5 mg/l
Nitrate+nitrite-N	210 µg/l	Nitrate+nitrite-N	110 µg/l
Ammonia-N	<5 µg/l	Ammonia-N	<5 µg/l
Orthophosphorus	<1 µg/l	Orthophosphorus	1.3 µg/l
Total Phosphorus	13 µg/l	Total Phosphorus	10 µg/l
Total Suspended Solids	4 mg/l	Total Suspended Solids	4 mg/l
Volatile Suspended Solids	3 mg/l	Volatile Suspended Solids	1 mg/l
Date: 5/1/80		Date: 6/5/80	
pH	8.2	pH	8.3
Alkalinity	131 mg/l as $CaCO_3$	Alkalinity	156 mg/l as $CaCO_3$
Calcium	39 mg/l	Calcium	61 mg/l
Total Hardness	122 mg/l as $CaCO_3$	Total Hardness	185 mg/l as $CaCO_3$
Dissolved Organic Carbon	4.5 mg/l	Dissolved Organic Carbon	2.4 mg/l
Particulate Organic Carbon	0 mg/l	Particulate Organic Carbon	0.3 mg/l
Specific Conductance	380 µmhos/cm @ 25°C	Specific Conductance	290 µmhos/cm @ 25°C
Dissolved Oxygen	10.5 mg/l	Dissolved Oxygen	10.1 mg/l
Nitrate+nitrite-N	260 µg/l	Nitrate+nitrite-N	150 µg/l
Ammonia-N	102 µg/l	Ammonia-N	<5 µg/l
Orthophosphorus	29 µg/l	Orthophosphorus	9.0 µg/l
Total Phosphorus	136 µg/l	Total Phosphorus	34 µg/l
Total Suspended Solids	58 mg/l	Total Suspended Solids	14 mg/l
Volatile Suspended Solids	4 mg/l	Volatile Suspended Solids	3 mg/l

Table B-3. Precipitation rates of carbon and phosphorus at various temperatures.

Temperature (°C)	C Precipitated (mg/m^2-hr)	P Precipitated (mg/m^2-hr)	Mole Ratio $\frac{\text{P Precipitated}}{\text{C Precipitated}}$
9	1.85	0.039	0.0081
	1.75	0.046	0.010
11	6.40	0.225	0.014
	5.75	0.225	0.015
	1.37	0.0465	0.013
	1.51	0.050	0.013
16	3.85	0.315	0.032
	3.80	0.255	0.025
	3.60	0.735	0.0080
	3.30	0.067	0.0080
21	2.75	0.0515	0.0070
	1.85	0.0390	0.0080

Table B-4. Algal carbon assimilation and carbon precipitation for two time periods and four nutrient levels.

Treatment	PO_4-P (µg/l)	NO_3-N (µg/l)	Duration (Hours)	C Assimilation Rate (mg/m^2-hr)	C Precipitation Rate (mg/m^2-hr)
1 (control)	10	110	2	3.75	2.85
				5.55	7.20
				4.25	8.50
			6	3.70	17.80
				4.35	2.75
				5.80	2.95
2	100	1000	2	2.95	4.75
				4.35	2.50
				3.95	12.60
			6	3.50	10.80
				5.10	7.50
				4.90	3.90
3	500	5000	2	2.90	5.10
				3.55	7.65
				6.05	6.05
			6	5.95	11.90
				2.40	2.65
				2.85	1.80
4	1000	10,000	2	4.25	10.70
				3.05	13.0
				4.50	4.15
			6	3.70	2.90
				5.30	5.70
				6.30	2.85

APPENDIX C

CALCULATIONS OF $CaCO_3$ DYNAMICS IN THE LOGAN RIVER

Table C-1. Biogenic precipitation of $CaCO_3$ as a removal mechanism for dissolved calcium in the Logan River.

A. Spawn Creek

1. $66 \text{ mg/1} \times \frac{\text{mole}}{40 \times 10^3 \text{ mg}} \times \frac{10^3 \text{ 1}}{\text{m}^3} = 1.65 \text{ mole Ca}^{2+}/\text{m}^3$

   $1.65 \text{ mole/m}^3 \times 0.11 \text{ m}^3/\text{sec} = 0.182 \text{ mole/sec} = 653 \text{ mole Ca}^{2+}/\text{hr} = \text{Ca}^{2+}$ mass loading.

2. $\frac{40 \text{ mg Ca}}{100 \text{ mg CaCO}_3} \times 425 \text{ mg CaCO}_3/\text{m}^2 - \text{hr}/\frac{40 \times 10^3 \text{ mg}}{\text{mole}} = 4.25 \times 10^{-3} \text{ mole Ca}^{2+}/\text{m}^2$

   $- \text{hr} = \text{Ca}^{2+}$ precipitation rate.

3. $\frac{4.25 \text{ NO}^{-3} \text{ mole/m}^2 - \text{hr}}{635 \text{ mole/hr}} = 6.51 \times 10^{-6} = 6.51 \times 10^{-4}$ percent of Ca^{2+} lost/m^2.

   Average stream width = 1 m.

   1536 m or 1.54 km is required to remove 1 percent of dissolved Ca^{2+}.

B. Twin Bridges

1. $57 \text{ g/m}^3 \times \frac{\text{mole}}{40 \text{ g}} \times 2.5 \text{ m}^3/\text{sec} \times \frac{3600 \text{ sec}}{\text{hour}} = 12830 \text{ mole Ca}^{2+}/\text{hr}$.

2. $238 \left(\frac{100}{40}\right) \times \frac{\text{mole}}{40 \times 10^3 \text{ mg}} = 2.38 \times 10^{-3} \text{ mole/m}^2 - \text{hr} = \text{Ca}^{2+}$ precipitation rate.

3. $\frac{2.38 \text{ NO}^{-3}}{12830} = 1.86 \times 10^{-5}$ percent/m^2 Ca^{2+} lost.

   Average width = 7.6 m.
   Loss per meter of river course = 1.4×10^{-4} percent of total Ca^{2+}.
   7.1 km is required for precipitation of 1 percent of Ca^{2+}.

C. Utah Water Research Laboratory

1. $57 \text{ g/m}^3 \times 9.9 \text{ m}^3/\text{sec} \times 3600 \text{ sec/hr} \times \frac{\text{mole}}{40 \text{ mg}} = 50790 \text{ mole Ca}^{2+}/\text{hr}$.

2. $269 \left(\frac{40}{100}\right) \times \frac{\text{mole}}{40 \times 10^3 \text{ mg}} = 2.69 \times 10^{-3} \text{ mole Ca}^{2+}/\text{m}^2 - \text{hr} = \text{Ca}^{2+}$ precipitation rate.

3. $2.69 \times 10^{-3}/50790 = 5.30 \times 10^{-6}$ percent/m^2 Ca^{2+} lost.

   Average width = 10 m.
   loss = 5.30×10^{-6} percent/$\text{m}^2 \times 10 \text{ m} = 5.3 \times 10^{-5}$ percent/m
   18.9 km is required for precipitation of 1 percent of Ca^{2+}.
