EFFECTS OF SURFACE AND GROUNDWATER INTERACTIONS ON THE SOLUTION CHEMISTRY OF A SUBTROPICAL KARST STREAM

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ABSTRACT

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Freshwater ecosystems in the Edwards Plateau region of Texas face threats from a variety of anthropogenic disturbances, including groundwater pumping, impoundment, siltation, agricultural practices, and the introduction of exotic species (Bowles and Arsuffi 1993). Local streams are characterized by extreme hydrologic variability, a karst geology that fosters high connectivity between ground and surface water flow paths, and populations of endemic species. These potentially fragile ecosystems offer significant economic, scientific, and aesthetic value to the region, and a better understanding of their physical, chemical, and biological processes is critical for future protection and remediation efforts. The Blanco River is a little-studied karst stream that traverses the Texas Hill Country and Balcones Fault Zone regions associated with the eastern Edwards Plateau. It is intimately connected with the Trinity Aquifer, the Balcones Fault Zone Edwards Aquifer, and the San Marcos River, all being extremely valuable regional resources. This study characterizes water quality in the Blanco River from the headwaters to mouth, with particular attention given to the effects of spring and tributary inputs on concentrations of dominant ions calcium, magnesium, and bicarbonate. Surface waters were almost always saturated with respect to calcite and dolomite, with the highest degrees of saturation found in the headwaters. Spring water was consistently undersaturated and exhibited very low variability in temperature. Historical correlations between discharge and concentrations of specific ions are considered as evidence of active diagenesis, specifically dedolomitization, in rock units of the Blanco River. A greater concentration of dolomitic weathering products in the headwaters region also supports this conclusion. Two 24-hour monitoring events examining trends in major dissolved ions and organic matter revealed high daytime levels of calcite and dolomite saturation and two potential mechanisms for retention of energy in the Blanco River ecosystem.

CHAPTER I

EFFECTS OF SURFACE AND GROUNDWATER INTERACTIONS ON WATER QUALITY IN A SUBTROPICAL KARST STREAM

INTRODUCTION

Karst rock units including silicates, evaporates, and carbonates are generally defined as having a higher degree of rock solubility in natural waters (Gunn 1986). Carbonates such as calcite and dolomite are the most commonly occurring of these. The dominant erosive process involved in karst geomorphology is chemical weathering. Carbonic acid, generated by carbon dioxide being added to the water or soil solution, dissolves the limestone crystal lattice, releasing the component ions. Over time, infiltration of water into bedrock allows for the growth of cracks and channels that can transport larger amounts of flow over longer distances underground. The ion chemistry of rivers and streams in karst areas is normally dominated by constituents of the local limestone in high concentrations.

The dissolution of karst rock often creates ideal conditions for the formation of aquifers. Aquifer systems are a source of water for humans and also give rise to springs and seeps that often support a diverse biota, including populations of endemic organisms. Larger human populations and increased pumping of groundwater threatens the high degree of natural biodiversity associated with these features. Understanding how physical and chemical forces interact in karst streams is critical for protection and remediation efforts seeking to preserve these valuable ecosystems.

The Blanco River is a little-studied karst stream in the eastern part of the Edwards Plateau region of central Texas. Approximately 140 km in length, it descends 250 meters in elevation and passes through the three towns of Blanco, Wimberley, and San Marcos, Texas (Guadalupe-Blanco River Authority 1961). The river's 1,070 km^2 drainage basin crosses two different regions of the Edwards Plateau: the Texas Hill Country and the Balcones Fault Zone (Barker and Ardis 1996). Seepage from streams draining the Hill Country off of the Edwards Plateau to the south and east provides recharge to the Balcones Fault Zone Edwards Aquifer; median annual recharge from the Blanco River between 1934 and 2004 was estimated to be 4.40×10^7 $m^3 \cdot yr^{-1}$ (35,700 acre-feet$\cdot yr^{-1}$), or about 6% of the total recharge to the aquifer (Edwards Aquifer Authority 2005).

The Balcones Fault Zone Edwards Aquifer supplies water to large human populations; in 1975 it was designated the first sole-source aquifer in Texas for the city of San Antonio. Subterranean flow in the aquifer moves mostly east-northeast and discharges naturally at the Comal, Hueco, and San Marcos springs. The San Marcos Springs, the terminal release point for the aquifer, is the second largest spring in Texas, with a mean historic flow of 4.5 m^3/sec (161 cfs) (Ogden et al. 1986). The six major orifices and numerous smaller openings of the springs form the headwaters of the San Marcos River, and support many endemic or range-restricted organisms, including *Zizania texana* (Texas wild rice), *Eurycea nana* (San Marcos salamander), and *Etheostoma fonticola* (fountain darter) (Groeger et al. 1997). The Blanco River supplies water to the San Marcos River through both ground and surface water pathways. Potentiometric surface analysis and water loss studies indicate that significant spring recharge comes directly from the lower Blanco River (Ogden et al. 1986). The Blanco River flows into the San Marcos River 7.2 km downstream from the springs (Groeger et al. 1997). There the larger size of the Blanco River watershed and the associated terrestrial inputs can have a significant effect, increasing variability in physical and chemical characteristics downstream of their confluence.

Like many of the rivers and streams of central Texas, the Blanco River is prone to fast moving, large volume flows created by the short duration, heavy precipitation events typical to the region. Rivers in central Texas are among the flashiest and most variable perennial rivers in the world (Slade 1986, Poff and Ward 1989, Groeger and Bass 2005). Conversely, flows may cease for extended periods in some sections of the river, and what surface flow remains in other areas may be entirely dependent on groundwater emerging from numerous seeps and springs along the river's course as well as tributary surface flows. The Blanco River channel is intersected by several normal faults, and resulting fractures, bed displacements, and other structural changes have led to a short-circuiting of surface flows. The greatest loss in stream flow in the Blanco River occurs between 84 and 73 river km from the mouth, where water infiltrates the bedrock in an area of highly fractured limestone created by an anticlinal flexure. According to a previous investigation, water moves in "open fractures or joints through the channel-entrenched carbonate" to appear as base-flow gain downstream (Buckner and Thompson 1964). Other sections of discontinuous surface flow are interspersed along the Blanco River drainage.

The two major tributaries of the Blanco River are the Little Blanco River and Cypress Creek. The Little Blanco River intersects the Blanco River 77 km from the mouth, and it too depends on underground flow paths. Several persistent pools that ostensibly originate from spring inputs were observed downstream of the monitoring site when upstream flows were nonexistent. Cypress Creek is a 43 kilometer stream (only the lower 22 km are perennial) which flows through the Wimberley to meet the Blanco River approximately 48 km upstream from the mouth (Bonner et al. 2002). Cypress Creek is fed by a large limestone spring known as Jacob's Well (DeCook 1963). The Jacob's Well springs stopped flowing temporarily for the first time in recorded history in the summer of 2000, a phenomenon attributed to drought and increased development in the Wimberley area.

The hydrologic variability of the Blanco River affects its chemistry as well as the different ecological communities that exist within its waters. Plant, invertebrate, and fish communities must be well adapted to the dynamic nature of the system in order to persist. It is highly likely that the Blanco River supports populations of organisms found nowhere else in the world; one plant species and 90 animal species have been tentatively identified as endemic to permanent aquatic habitats in the Edwards Plateau region (Bowles and Arsuffi 1993).

The combination of above and below-ground flow paths in the mainstem and tributary Blanco River drainages should produce unusual relationships between discharge and the dissolved solute load. In river systems, concentrations of dissolved ions have a strong tendency to decrease in response to increasing discharge (Walling and Webb 1986, Meybeck 1996). During higher flows, runoff is moved quickly to and through the channel and has little time to pick up solutes. Some rare cases exhibit a concentration rather than a dilution effect in response to increasing discharge. There was a positive correlation between discharge and specific conductance in four of the streams contributing recharge to the Balcones Fault Zone Edwards Aquifer (Groeger and Gustafson 1994). Two different causes for this phenomenon in other systems have been suggested. Rains following an extended dry period may act as a flushing mechanism for solutes accumulated in the channel during dry periods in summer. Alternatively, base flows in contact with a lower rock unit may have a more dilute chemical signature than when the water table rises and comes into contact with more soluble formations. There have been no studies to investigate this phenomenon in subtropical karst systems, where climate, geology, and hydrology may interact in a regionally unique way.

I had two major goals in initiating this study. First, I wanted to characterize water quality in a subtropical karst stream from headwaters to mouth, to determine current baseline conditions, and in conjunction with other scientists establish the response and distribution of the riverine biological community to the physical and chemical components of the ecosystem. This is especially important in light of growing local human populations and the regional stress they place upon surface and groundwater resources. Secondly, I was particularly interested in exploring the dynamics of chemical dissolution and precipitation of the limestone bedrock within this subtropical karst river, where ground and surface waters are alternately the major pathway for downstream water movement. Interactions between dominant ions calcium, magnesium, and bicarbonate, as well as other factors that influence their solubility processes, were studied.

METHODS

Eight sites on the Blanco River were selected for this study with consideration given to position, accessibility, proximity to urban areas, and representation of different microhabitats such as riffles, runs, or pools (Figure 1). Site names correspond to distance upstream from the river mouth in river km (Guadalupe-Blanco River Authority 1961). Elevations of study sites and significant landmarks taken from the survey were compared with readings taken with a handheld GPS unit and found to be similar.

Site 127 was adjacent to private property, upstream of Blanco, Texas and downstream of several perennial seeps that meet the river on the property. Site 117 was located at Wayne Smith Lake, one in a series of small overflow impoundments upstream of the Highway 281 bridge in Blanco. Sites 101 and 71 were adjacent to private property between Blanco and Wimberley, Texas. Site 42 was located in Wimberley approximately 6.4 km downstream from the confluence with Cypress Creek. Sites 14 and 6 were located at road crossings in the city of San Marcos.

Additional sites on the Little Blanco River and Cypress Creek were also selected for this study. The Little Blanco River study site was located approximately 1 kilometer upstream from the confluence with the Blanco River (30.040878N, -98.252515W). The Cypress Creek site was located approximately 0.87 km upstream from the confluence with the Blanco River (29.996667N, -98.097681W).

Water quality variables were measured on 18 dates in 2003, 2004, and 2005. Readings and discrete samples were made from the bank in areas with stream flow. Temperature, pH, dissolved oxygen, and specific conductance were measured using a

Hydrolab™ Minisonde calibrated one day prior to each sampling event. Alkalinity was measured by potentiometric titration to pH 4.8 using 0.02 N H_2SO_4 (Wetzel and Likens 2000). Turbidity was measured using a Fisher Scientific Turbidometer. Ca^{2+} and Mg^{2+} were measured by atomic absorption (American Public Health Association 1998). Soluble reactive phosphorus (SRP) was determined using the ascorbic acid method (Murphy and Riley 1962). NO_3-N was measured by second-derivative UV spectroscopy (Crumpton et al. 1992).

Historical physical and chemistry data, including discharge, temperature, pH, specific conductance, and calcium, magnesium, bicarbonate, and nitrate-nitrogen were taken from United States Geological Survey records (2005). I used discharge data from 1924 to 2003 and chemistry data from 1963 to 1997. It should be noted that historical concentrations of bicarbonate were measured by titration to an endpoint of pH 4.5.

Saturation with respect to calcite (SI_{CaCO_3}) and dolomite ($SI_{CaMg(CO_3)_2}$) was determined by dividing the component ion activity products by the respective equilibrium constant: (Kelts and Hsu 1978)

$$SI_{CaCO_3} = \frac{(Ca^{2+}) \times (CO_3^{\ 2-})}{K_{CaCO_3}}$$

$$SI_{CaMg(CO_3)_2} = \frac{(Ca^{2+}) \times (Mg^{2+}) \times (CO_3^{\ 2-})^2}{K_{CaMg(CO_3)_2}}$$

where parentheses indicate ion activities. The equilibrium constant for calcite (K_{CaCO3}) was calculated using the temperature-dependent expression (Kelts and Hsu 1978):

$$\log K_{CaCO_3} = 13.87 - (0.04035 \times T) - (3059 / T)$$

where T stands for temperature. Temperature-dependent equilibrium constant values for dolomite ($SI_{CaMg(CO_3)_2}$) were taken from Langmuir (1964) as cited in Thrailkill (1972). Ion activity products for calcium, carbonate and magnesium were determined by multiplying their concentration by their calculated ion activity coefficient (Kelts and Hsu 1978):

$$(CO_3^{2-}) = [CO_3^{2-}] \times \gamma CO_3^{2-}$$

$$(Ca^{2+}) = [Ca^{2+}] \times \gamma Ca^{2+}$$

$$(Mg^{2+}) = [Mg^{2+}] \times \gamma Mg^{2+}$$

where parentheses indicate ion activities and brackets indicate concentration. Ion activity coefficients for calcium and carbonate were calculated using the Debye-Hückel relation (Stumm and Morgan 1996):

$$\log \gamma = \frac{-A \times Z^2 \times \sqrt{I}}{1 + a_t \times B \times \sqrt{I}}$$

where A and B are constants for a given solvent at a specified temperature, Z is the valence of the ion, a_t is the ion size parameter, and I is the ionic strength of the solution.

Temperature was recorded every six minutes at Sites 127, 101, and 6 from 5/20/04 to 9/20/04 using StowAway® XTI Temperature Loggers (Onset Computer Corporation). The devices were placed in the best developed channel to ensure constant immersion, and shaded locations were selected to prevent heating from direct contact with sunlight.

The section of river between Sites 101 and 71 had no visible surface flow from 01/09/04 to 03/14/04. Surface flow was observed to have ceased in the same area in the second week of June 2005 and remained dry for the remainder of the study. A large spring located downstream from Site 71 (30.035946N, -98.223084W), Valley View Spring, appeared to be the initial source for surface flows downstream from this area; however, springs with openings smaller than 1 cm were observed nearby emerging from the bedrock of the river channel. The orifice of Valley View Spring was much larger, approximately one meter in width. When accessible, water from the spring was sampled and analyzed in 2004 and 2005. Temperature logger devices identical to those described above recorded temperatures at Valley View Spring and Site 101 every 6 minutes from 06/23/05 to 09/11/05.

RESULTS

In 2004, a relatively wet year, Blanco River discharges were greater than 3rd quartile historical levels from March through December. In 2005, flows approached median historical levels after March and continued to decrease for the remainder of the period of study. Several high discharge events were sampled, including Site 6 on June 30, 2004, when mean daily discharge was 105 m^3/s (3,708 cfs). Surface flows in the Little Blanco River were typically dry in the summer, and so the chemistry summary reflects a winter sampling bias.

Mean water temperatures from the thermistors placed at Sites 127, 101, and 6 showed a clear warming trend from upstream to downstream during the summer of 2004, corresponding to an increase of about 1.1°C over 121 km (Table 1). Median daily temperature ranges and variability both decreased moving downstream. Dissolved oxygen in the Blanco River tended to be near saturation with the atmosphere, with 82%

of dissolved oxygen readings between 80 and 120% saturation (Figure 3, Table 2). These dissolved oxygen concentrations appeared to reflect a healthy stream ecosystem, and diel variations also supported this conclusion (see Chapter 2).

Stream turbidity was consistently low, except at Site 117 (Wayne Smith Lake) where it was usually three to four times higher than that of other Blanco River sites (Figure 4). The mean turbidity at Site 6 reflects extremely high values recorded during storm flows on June 6 and 30, 2004. Specific conductance did not have a discernable trend from headwaters to mouth (Figure 5). Of the three dominant ions measured in this study, specific conductance was most strongly correlated with alkalinity ($r^2 = 0.43$). Alkalinity was highest at Site 127 and decreased moving downstream (Figure 6). Median Ca:Mg ratio for the Blanco River was 1.44, but upstream of Site 71 the ratio was usually closer to 1:1 (Figure 7). The combined charge of the two cations was typically equivalent to measured alkalinity. Site 127 and Site 42 were most highly saturated with calcite and dolomite (Figures 8 and 9). Site 127 exhibited the highest degrees of saturation with dolomite at warmer temperatures (greater than 20°C), up to a maximum of 22 times saturation. Site 117 and Site 6 had the lowest median saturation values for calcite and dolomite. The highest median concentration of SRP were found at Site 71 (Figure 10). The greatest concentrations of NO_3-N were found at Sites 117, 101, and 71 (Figure 11).

Compared to the Blanco River, water emerging from Valley View Spring was low in pH and dissolved oxygen, but high in specific conductance, alkalinity and concentrations of calcium, soluble reactive phosphorus, and nitrate-nitrogen (Table 2). The spring water was consistently undersaturated with respect to calcite and dolomite. This thermistor record reflects a time when surface flows were non-existent between the two locations and the spring system appeared to be the origin of flows downstream. Median water temperature of the spring water was more than 6°C cooler than Site 101 and varied very little over this period (Table 1).

Data collected by the USGS indicated that specific conductance and Ca^{2+} and HCO_3^- were lowest in summer months, but Mg^{2+} showed little to no variation from month to month (Figure 12). Ca^{2+} and HCO_3^- increased with increasing discharge (r^2 = 0.29 and 0.31, respectively), while Mg^{2+} concentrations decreased ($r^2 = 0.54$) (Figure 13). Specific conductance was not significantly related to discharge.

DISCUSSION

During this study, the Blanco River appeared to have stable communities of primary producers, including phytoplankton, periphyton, and submerged and emergent macrophytes. There was no evidence of any problematic imbalance between diel photosynthesis and respiration at any of the sites. Greater and more variable concentrations of SRP and NO_3-N found at Sites 101 and 71 may have anthropological origins; however, patterns in historical land use were not investigated for this study. Alternatively, spring inputs like those from Valley View Spring could supply this area with additional nutrients. Edwards Aquifer water gained significant amounts of NO_3-N by the time it emerged at the San Marcos Springs, relative to the rivers that feed it (Groeger and Gustafson 1994).

One of the most distinctive qualities of the Blanco River was the high degree of saturation with calcite and dolomite observed in nearly every sample. The water was often quite pale in color, presumably the result of in-stream calcite precipitation reactions. The river bed itself was often covered with a fine layer of precipitated material, most noticeably at Site 127. Lower levels of calcite saturation at Site 117 could indicate that calcite precipitation contributed to elevated turbidities found there. Past studies have recorded decreases in water clarity corresponding to the onset of calcite precipitation in fresh water lakes (Brunskill 1969, Koschel et al. 1983, Weidemann et al. 1985). Additional turbidity may be caused by increased planktonic production or the accumulation of other organic particles in the water column.

The weathering of dolomite or magnesium-rich limestone seems to be especially influential on solute concentrations in the Blanco River. Springs draining dolomites or dolomite-related rocks have a Ca:Mg ratio near unity, while that of springs draining limestone rocks are 3 to 7 times that (Shuster and White 1971). Generally, limestone containing dolomite is much less soluble than those having a higher concentration of calcium (Gunn 1986). Increased solubility of dolomite at higher temperatures, however, has allowed the development of striking karst landforms in tropical regions. Suspended and settled precipitates observed in the Blanco River are probably entirely calcitic, as magnesium fails to precipitate even under extremely high saturation conditions (Land 1998). The low median Ca:Mg ratio and high levels of dolomite saturation found at Site 127 indicates that the most recent aggressive dolomite solution in the drainage was taking place in the headwaters. The elevated concentrations of Mg^{2+} upstream appeared to be diluted downstream by waters draining rock units richer in calcite.

A portion of this water is supplied by two major tributaries, similar for the most part in origin and chemical characteristics to the Blanco River. While the effects of their confluence did not seem to be particularly drastic, water from the Little Blanco River and Cypress Creek has the potential to sustain mainstem surface flows and provide more water rich in dissolved limestone. That being said, the paucity of data collected from the Little Blanco River was due to the frequent lack of stream flow at the monitoring site. The intermittent tributary seemed to have little effect on Blanco River chemistry during the study, but the next Blanco River site downstream of the confluence (Site 71) was possibly too distant to detect any influence. Water from Cypress Creek had a more observable effect on the Blanco River. Elevated pH, specific conductance, calcium, as well as higher degrees of saturation with calcite and dolomite recorded at the site downstream of the confluence (Site 42) may have resulted from solute-rich inflows from spring-fed Cypress Creek. The increase in solute concentrations may have also been influenced by spring outflows in the Blanco River channel upstream of the confluence. A stream flow gain of 0.4 m^3/s (14 cfs) was traced to springs in an area between 18.3 and 19.3 km upstream from the mouth of Cypress Creek (Buckner and Thompson 1964).

Groundwater from springs like Valley View Spring could be a significant driver for temperature and dissolved ion dynamics in the Blanco River. Valley View Spring water was cooler than Blanco River surface water in the summer and warmer in the winter. Groundwater was found to be an important source and sink for thermal energy for a Pennsylvania karst stream, depending on season, and stream temperatures were strongly related to surface and groundwater interactions (O'Driscoll and DeWalle 2006). Chemically, the spring water was enriched in Ca^{2+} and alkalinity relative to Blanco River surface water, but undersaturated with calcite and dolomite. There may also have been associated gains in dissolved nutrients SRP and NO_3-N. The size of the preceding underground pathway(s) and the rate of CO_2 introduction may be inferred from saturation conditions observed in Valley View Spring outflows. Higher pH and undersaturated conditions in spring water suggest that CO_2 introduction is occurring more rapidly than the process of calcite or dolomite dissolution (Thrailkill 1972). Conduit springs, emerging from pipe-like pathways created by flow entrainment and chemical dissolution, are more likely to be undersaturated than those created by slower moving water seeping through smaller, more convoluted openings (Shuster and White 1971). Rapidly flowing groundwater moving through large passages was suggested to be the cause of undersaturation in groundwater and spring water associated with the Edwards Aquifer (Abbott 1977). As a result, cavern formation in the Edwards Aquifer is most extensive near the distal end of the flow system.

Texas surface waters show a strong trend of decreasing specific conductance from west to east corresponding to increased rainfall (Groeger and Ground 1994). However, in the Edwards Plateau region, those systems farthest to the east exhibited higher specific conductance (Groeger and Gustafson 1994). The drainages in this region clearly possess hydrological features that exhibit a unique chemical response to changing hydrological conditions. Storm flow data suggest a threshold for the positive relationships between discharge and concentrations of Ca^{2+} and HCO_3^-. Samples from Site 6 during high discharge events on 6/10/04 and 6/30/04 do not reflect a proportional increase in dissolved solute concentration, but rather they were more dilute with respect to median values from 2003-2005. The sample from 6/30/04, when the daily mean discharge was over 100 times greater than base flow levels, was the only time water was found to be undersaturated with respect to calcite at Site 6. However, samples associated with storm flows were obtained on the falling limb of the hydrograph, so I could not determine whether this was the late stage of a "flushing" effect.

Summer decreases in concentrations of Ca^{2+} and HCO_3^- probably result from a combination of lower discharge and higher daily temperatures. Solubility of calcium carbonate decreases with increasing temperature (Drever 1997). Historically, concentrations of Ca^{2+} and HCO_3^- in the Blanco River decreased with increasing temperature ($r^2 = 0.43$ and 0.42, respectively). There was no relationship between Mg^{2+} concentrations and temperature in the historical data.

The process of active diagenesis in Blanco River rock units could explain both the relationships between discharge and dominant ion concentrations as well as the greater abundance of dolomitic weathering products in the headwaters. In the late Miocene period, faulting along the Balcones fault zone raised the Edwards Plateau in the north and west relative to sea level and enabled the formation of a circulating freshwater aquifer (Ellis 1986). Since that time, rocks in the aquifer underwent several major near-surface diagenetic changes, including extensive dedolomitization. In this process, freshwater flushing replaces gypsum and magnesium in dolomitic rocks with calcite. The resulting dedolomite can be more soluble than the original dolomite (Evamy 1967). Isotopic ratios suggest dedolomitization continues in the present-day (Ellis 1986). High concentrations of sulfate, possibly resulting from dissolved gypsum, have been recorded in the upper Blanco River (Guadalupe-Blanco River Authority 2003). Sulfate concentrations, like magnesium, exhibited a negative relationship with flow. Increased discharge could allow water in subterranean flow paths to reach more soluble, magnesium-poor calcites, creating the concentration effect observed for Ca^{2+} and HCO_3^- in the historical record.

During storm flows, the amount of water flowing through the system overwhelms the concentration effect and dissolved solutes become diluted.

The streams recharging the Balcones Fault Zone Edwards aquifer are similar in chemistry (Groeger and Gustafson 1994). Like the Blanco River, spatial and temporal patterns in the ion content of each stream are presumed to be driven by the physical and chemical weathering processes occurring in their underlying geological forms. Past and present data suggest that these streams would not exhibit higher salinities in a drier climate, thanks in large part to the unique solution mechanics affecting the local karst and the tight connectivity between surface and groundwater flow paths. Endemic aquatic organisms, including species not yet identified, depend on water from springs and seeps to maintain base flows as well as the consistent thermal and chemical conditions to which they have adapted. The perpetuity of these valuable ecosystems and their associated biotic assemblages will depend on human diligence in preserving the supply of environmental groundwater flows.

CHAPTER II

DIEL VARIATION IN MAJOR DISSOLVED IONS AND ORGANIC MATTER IN THE HEADWATERS OF A SUBTROPICAL KARST STREAM

INTRODUCTION

Processes affecting the formation and transport of particulate organic matter (POM) in aquatic ecosystems have been recognized as critical pathways of energy supply to lotic communities (Ward et al. 1994). Few of these processes are understood well enough to make useful comparisons of their biological importance in different streams. As a source of organic matter, particle-particle interactions such as flocculation or adsorption could be as important as leaf litter inputs to lotic freshwater systems.

Past studies have demonstrated the importance of calcium carbonate precipitation as a pathway for the aggregation of organic particles in hard-water lentic systems. Large amounts of organic acids were removed from lake water with precipitating calcium carbonate by adsorption and incorporation during crystal nucleation (Otzuki and Wetzel 1973). Aggregation of organic particles with denser inorganic particles was found to increase particle sizes, enhance settling and reduce the residence times in the water column of lakes (Weilenmann et al. 1989). Coreactions tied to calcite precipitation events were shown to create a "self-purification" system in hard-water lakes, decreasing phytoplankton biomass as well as phosphorus concentrations in the water column, thereby reducing the potential for eutrophication (Koschel et al. 1983, Koschel 1990). Murphy et al. (1983) found that the disappearance of phosphate was correlated with an increase in pH and a reduction of Ca^{2+} and alkalinity associated with calcite precipitation events. There is less information available regarding this process in lotic systems. Separate treatments of Ca^{2+}, Mg^{2+}, and higher salinity seawater resulted in a rapid physiochemical flocculation process and a dramatic increase in the rate of POC formation in water from a small North Carolina swamp stream, normally low in ionic strength (Mulholland 1981).

A two-year study of water quality of the Blanco River (Blanco, TX) revealed consistently high levels of saturation with calcium carbonate and dolomite at the most upstream site, ostensibly maintained by seeps, springs, and spring-fed tributaries rich in the dissolved constituents of dolomitic limestone (see Chapter 1). Nodules and crusts, which appeared to be composed of calcite bound up with organic matter, were frequently observed on the flat, shallow bedrock channel at the site. It appeared that the precipitation of calcium carbonate was contributing to the aggregation of particulate organic matter in this subtropical karst stream. In order to better understand underlying processes governing pathways of energy in the Blanco River, I sought to characterize diel variation in water quality and to describe effects of calcium carbonate precipitation reactions on particulate organic matter and dominant ion concentrations.

METHODS

Two 24-hour sampling events were used to characterize diel variation of dissolved ion content and particulate organic matter in the headwaters of the Blanco River. The study site was located approximately 20 km upstream from Blanco, Texas, at Site 127 as described in Chapter 1 (Figure 1). Hydrolab™ readings and whole water samples were taken from the middle of the stream every two hours beginning at 06:00 CST August 30 and September 22, 2005. Temperature, pH, dissolved oxygen, and specific conductance were measured with a Hydrolab™ Minisonde calibrated on the first day of each monitoring event. Water samples were filtered in the field through three replicate 0.45 μm Whatman GF/F filters using a vacuum flask and a controlled-pressure vacuum pump. Alkalinity was measured before and after filtration in the field by potentiometric titration to pH 4.8 using 0.02 N H_2SO_4 (Wetzel and Likens 2000). Subsamples of whole and filtered water were preserved with nitric acid and later analyzed for Ca^{2+} and Mg^{2+} by atomic absorption (American Public Health Association 1998). Saturation with respect to calcite (SI_{CaCO3}) and dolomite ($SI_{CaMg(CO3)2}$) was determined calculated as described in Chapter 1.

For the September sampling event, total and volatile suspended solid content was determined by drying filters to 105°C and combusting at 550°C (American Public Health Association 2001). Total suspended solid content was calculated by subtracting initial weight from dried weight, and volatile content was determined by subtracting combusted weight from dried weight. Turbidity was also measured in the field in September using a Fisher Scientific Turbidometer.

RESULTS

Daily average stream flow as recorded by a United States Geological Survey Blanco River discharge gauge on August 30 and September 22, 2005 was 1.87 and 1.61 m^3/s (66 and 57 cfs), respectively (USGS 2005). This gauge is located more than 80 km downstream from the study site, and reflects significant amounts of additional discharge from spring and tributary inputs, most notably the Little Blanco River and Cypress Creek. In both cases, daily average discharge was reflective of low summer flows fairly typical for that month based on data from 1924 to 2005.

Stream temperatures on both dates ranged from 21-36 °C, with the highest temperatures at 14:00 (Figure 13). Stream pH was slightly higher in August, and on both dates there was a daytime increase of approximately 0.3 standard units. Concentrations of dissolved oxygen ranged from 6.4 to 9.1 mg/L and exceeded 120% saturation in both September and August from 10:00 to 16:00. Dissolved oxygen saturation never fell below 80% during either study period. There was no discernable trend over time in differences between ion content of filtered and unfiltered water.

Specific conductance and individual concentrations of major dissolved ions decreased during the daylight hours on both sampling events (Figure 14). The lowest concentrations of alkalinity and Ca^{2+} were recorded at 14:00 on both dates. Mg^{2+} made up a greater portion of the cationic charge at all times except at 22:00 September 22. Daytime decreases in Mg^{2+} were shorter and less dramatic than that of Ca^{2+} and alkalinity. Distinct maxima in Ca^{2+} occurred in the late night hours in both sampling periods (24:00 in August, 22:00 in September). Specific conductance was negatively related to temperature on both sampling dates (r^2 = 0.96 in August, 0.97 in September). Specific conductance was also closely related to alkalinity in a positive relationship (r^2 = 0.98). Concentrations of dissolved ions were generally higher in September. Saturation with calcite and dolomite increased during the day and peaked at 18:00 on both dates (Figure 15).

There was no clear trend over time in suspended solids, but the proportion of volatile substances appeared to peak in the early morning hours and at 18:00 (Figure 16). Turbidity values were between 4 and 6 NTU, with a distinct peak at 18:00 of 9 NTU.

After observing the aggregation of froth material on the stream surface at the study site in August, greater care was taken in September to document the phenomenon. Floating bubbles were first observed in the stream flow at 12:00, and appeared to originate upstream of the study site. Over the next several hours, bubbles became trapped in an eddy current just downstream of the sampling point and a thin layer of foam began to accrue. By 18:00, the foam had accumulated in large packs on one side of the stream, raised three to four centimeters off of the surface of the water in some areas. Fragments of suspended plant matter and microinvertebrates were visible in the bubble mass. Due to the preponderance of the froth in the sampling area at 18:00, it was difficult to exclude foam from my water sample. Two of the three filter replicates became clogged and would not fully filter the sample even after extended vacuum application. Particulate matter contained in the foam appeared to contribute to the high amount of VSS and turbidity observed at this data point. The foam began to disperse around 0:00 on September 23, and shortly after sunrise the eddy was free of bubbles.

DISCUSSION

Concentrations of Ca^{2+} and alkalinity are typically higher in times of greater discharge in the Blanco River (See Chapter 1). Site-specific primary production or water temperatures may explain the greater amounts of these ions observed at the study site in September when Blanco River discharge was recorded to be lower than in August.

The additive charges of Ca^{2+} and Mg^{2+} exceeded that of alkalinity, suggesting the influence of anion(s) other than HCO_3^-, CO_3^{2-}, and OH^-. Sulfates were previously found in high concentrations in the upper Blanco River (Guadalupe-Blanco River Authority 2003). The sulfate probably originates from dissolved gypsum deposits, which would account for the elevated concentrations of magnesium observed in the headwaters (described in Chapter 1). Active dedolomitization, by which magnesium in dolomitic limestone is dissolved and replaced by calcite in the presence of dissolved gypsum, is thought to be an ongoing diagenetic process in rock units associated with the Balcones Fault Zone Edwards Aquifer (Ellis 1986). The ratio of calcium to magnesium in August and September 2005 was the lowest observed in my study of the Blanco River.

Two mechanisms that could induce calcite supersaturation are (1) biogenic, as carbon dioxide is assimilated during photosynthesis, and (2) physical-chemical, as temperature or other factors interact to effect the solubility of carbon dioxide and calcite (Kelts and Hsu 1978). Summer heating created a threefold to fourfold increase in calcite supersaturation in the epilimnion of a New York lake (Brunskill 1969). In the Blanco River, calcite saturation responded more quickly to sunrise and sunset than to changes in temperature, suggesting primary production had a more immediate effect.

In the daytime, primary production brings about a decrease in dissolved carbon dioxide and increase in stream pH, and supersaturation of calcite increases to an even greater level. A decrease in dissolved constituents is observed as chemical precipitation reactions occur in the water column or on substrate. As production gives way in the evening to respiration, pH levels fall, and constituent concentrations rise to nighttime levels. The daytime decrease in magnesium is probably less pronounced because dolomite fails to precipitate even at extremely high levels of saturation (Land 1998).

The lack of a difference in concentrations of Ca^{2+}, Mg^{2+}, and alkalinity between filtered and non-filtered water samples might suggest that calcite precipitated directly on a substrate or settled out quickly from the stream flow. Calcium carbonate nodules found along the bottom of a river outlet in Montana were formed by the photosynthetic and metabolic processes of attached algae, and coincided with times of high seasonal productivity (Moore 1983). Attached algae has been observed at Site 127 and other sites on the Blanco River. It is possible that not all of the precipitated calcite resolubilizes simultaneously; reaction rates of inorganic carbonate equilibria are reduced by organo-carbonate associations that isolate the mineral from the surrounding water (Suess 1970). The short, distinct nighttime peaks in Ca^{2+} observed in the Blanco River on both dates (24:00 in August, 22:00 in September) may have resulted from precipitated minerals on the bedrock dissolving back into the stream.

The origin of the bubbles at the study site was not directly observed, but it seems likely that they were created by the overflow of a 3-meter dam located approximately 750 meters upstream. Petersen (1986) found an increase in particulate organic carbon below a waterfall in a Swedish stream. Dissolution of bubbles in sea water produced new aggregations of particulate matter, the size of which was relative to the initial size of the bubble (Johnson and Cooke 1980). Judging by the material observed to be caught up in the froth in the Blanco River, and the drastic increase in turbidity and volatile organic matter when foam was included in the sample, there is at least a temporary aggregation effect associated with the accumulation of the froth accumulations. The appearance and aggregation of the foam coincided with times of highest calcite saturation, suggesting that adsorption may also play a significant role in the aggregation of these particles.

Based upon water quality data and firsthand observations, it seems likely that bubble-induced formation of particles and calcium carbonate adsorption are important mechanisms for formation of particulate organic matter in the Blanco River. This has implications for Blanco River nutrient and carbon dynamics, especially in the headwater region where calcite precipitation reactions probably occur on a daily basis. The rate of particle formation was found to control the location where dissolved organic matter becomes available as food, thereby affecting the size and distribution of filter-feeding microinvertebrate communities (Lush and Hynes 1973). Filter-feeders play an important role in stream ecology by reducing downstream energy and nutrient losses, a valuable control mechanism for natural habitats in unidirectional flow systems (Wallace et al. 1977). Large populations of filter-feeders are particularly valuable as a vehicle for the retention of seston ranging in size from 10 - 150 μm (McCullough et al. 1979). Uptake of particulate organic matter by Simuliidae accounted for 11% of whole-stream deposition in a cold desert spring stream (Monaghan et al. 2001). Dense populations of larval *Simulium* and *Hydropsyche* were observed at the study site on both dates, as well as at other sites on the Blanco River. These communities appeared to be particularly concentrated in areas of shallow overflow below both natural and man-made waterfalls and impoundments.

The installation of numerous low water crossings and low-head dams is one of the most obvious and widespread anthropological alterations to the Blanco River ecosystem and hydrology. Some of these structures are two to three meters high and their overflows create substantial amounts of whitewater at the base. Even the smallest of these may enhance settling mechanisms of organic matter on the upstream side by means of coprecipitation with calcite, while creating areas of greater turbulence and extensive bubble formation on the downstream. Greater rates of in-stream particle formation may also enhance the success of populations of filter-feeders in the Blanco River, especially in upstream areas where the natural concentration and size of particulate organic matter might otherwise be lower. Nutrients and organic carbon that might otherwise be lost downstream are retained in the ecosystem. This alteration may have positive and negative effects on populations of endemic species adapted to chemical conditions created by unregulated natural discharge. More study is needed to quantify the effects that these small dams have on carbon and nutrient retention in hard-water subtropical streams like the Blanco River.

TABLES

Table 1. Median temperature and median daily temperature ranges (ºC) at Sites 127, 101, and 6 from 5/20/2004 to 9/2/2004, and at Site 101 and Valley View Spring from 6/23/2005 to 9/11/2005.

	5/20/04 – 9/2/04			*6/23/05 – 9/11/05*	
	Site 127	Site 101	Site 6	Site 101	Valley View Spring
Temperature	27.13 *s d.= 2 05*	27.24 *s d.= 1 77*	28.29 *s d.= 1 51*	29.24 *s d = 1.54*	22.98 *s d = 0 89*
Daily Range	3.30 *s d = 1 85*	2.99 *s d = 0 70*	1.65 *s d.= 0 56*	3.32 *s d.= 1 13*	0.17 *s d = 0.11*

Table 2. Median values for selected parameters measured in the Blanco River, Little Blanco River, Cypress Creek, and Valley View Spring from 2003-2005.

	Blanco River	Little Blanco River	Cypress Creek	Valley View Spring
Temperature (°C)	22.98	19.38	19.98	23.08
	n = 129, s d. = 6.36	*N = 5, s.d = 6 38*	*n = 17, s.d = 4.22*	*n = 7, s d.= 4 75*
pH	7.92	7.59	7.68	7.26
	n = 129, s d = 0 17	*N = 5, s d = 0 15*	*n = 17, s.d.= 0 14*	*n = 7, s d = 0.16*
Dissolved O_2 (mg/L)	8.66	8.00	8.83	6.25
	n = 124, s d = 1.51	*N = 5, s.d = 1 60*	*n = 16, s d = 1 12*	*n = 7, s d.= 1 91*
Sp. Cond. (μS/cm)	439	455	522	475
	n = 129, s d.= 49	*n = 5, s.d = 52*	*n = 17, s.d = 38*	*n = 7, s d = 47*
Turbidity (NTU)	3.1	2.3	2.1	2.1
	n = 128, s d = 6 7	*n = 6, s.d.= 0 5*	*n = 17, s d = 0 7*	*n = 6, s d = 0.4*
Alkalinity (meq/L)	3.93	4.30	4.92	4.26
	n = 128, s d.= 0.54	*n = 6, s.d.= 0 42*	*n = 17, s d = 0 53*	*n = 6, s.d = 0.29*
Calcium (meq/L)	2.32	2.56	2.95	2.72
	n = 111, s.d = 0 29	*n = 4, s d = 0 17*	*n = 15, s d = 0 36*	*n =5, s.d = 0 44*
Magnesium (meq/L)	1.60	1.60	1.60	1.55
	n = 111, s d.= 0.32	*n = 4, s.d.= 0.26*	*n = 15, s.d = 0 35*	*n = 5, s d = 0 57*
Ca : Mg	1.44	1.56	1.74	1.59
	n = 111, s d.= 0.39	*n = 4, s d = 0 45*	*n = 15, s d.= 0.57*	*n = 5, s.d.= 0 49*
SI $CaCO_3$	1.93	1.63	1.76	0.53
	n = 111, s d.= 0 83	*n = 3, s d = 0 30*	*n = 15, s.d.= 0 56*	*n = 5, s.d = 0 31*
SI $CaMg(CO_3)_2$	3.82	1.21	3.50	0.24
	n = 111, s.d.= 4.94	*n = 3, s d.= 0.47*	*n = 15, s d = 2 15*	*n = 5, s d = 0 69*
SRP (μg/L)	4.1	2.0	3.2	5.1
	n = 104, s.d = 6.37	*n = 4, s.d.= 7 2*	*n = 14, s.d.= 3 1*	*n = 4, s d.= 0.81*
NO_3-N (μg/L)	316	196	209	452
	n = 100, s d = 234	*n = 4, s d = 95*	*n = 13, s d = 115*	*n = 4, s d.= 79*

FIGURES

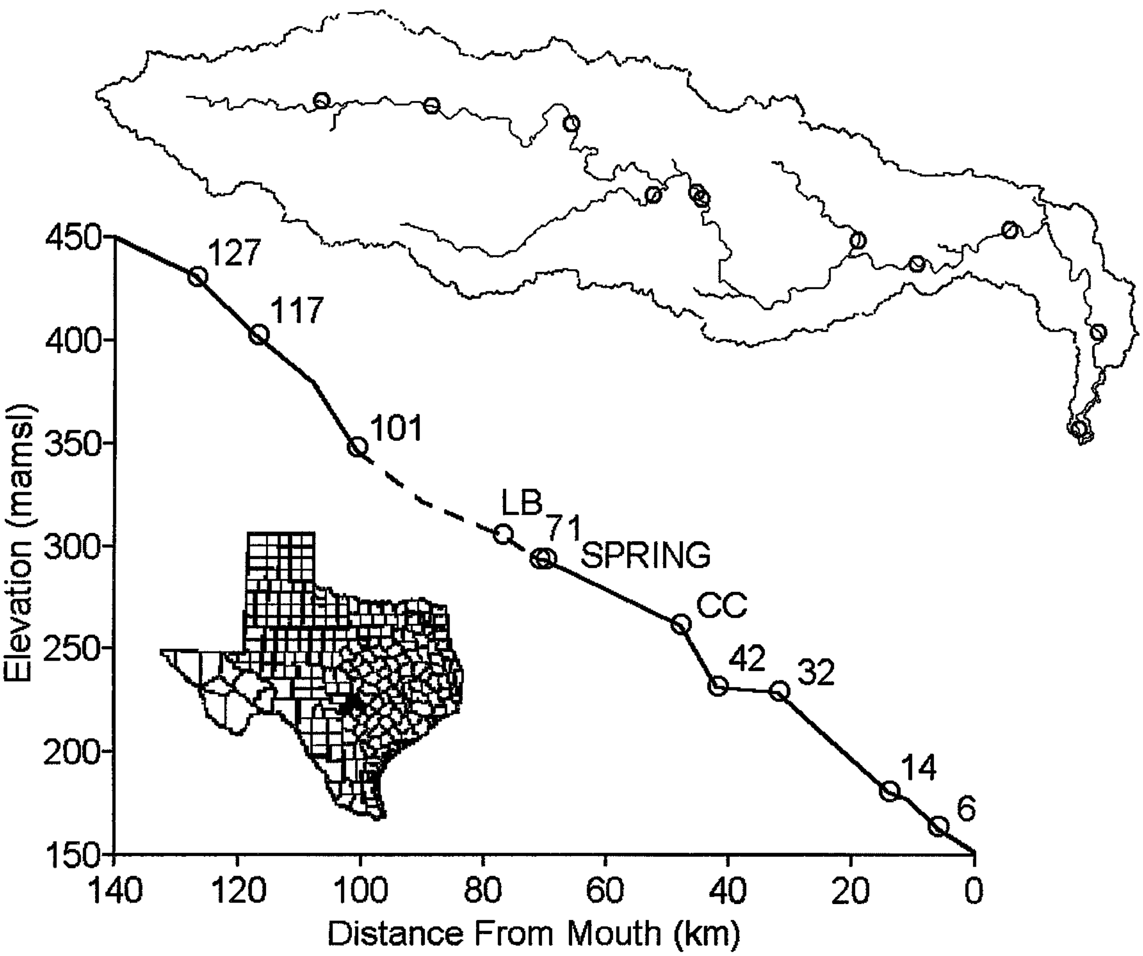

Figure 1. Location of study sites and map of the Blanco River drainage basin. Study sites are noted by km upstream from mouth. LB and CC note confluences with the Little Blanco River and Cypress Creek, respectively. Dashed line represents area of intermittent surface flow.

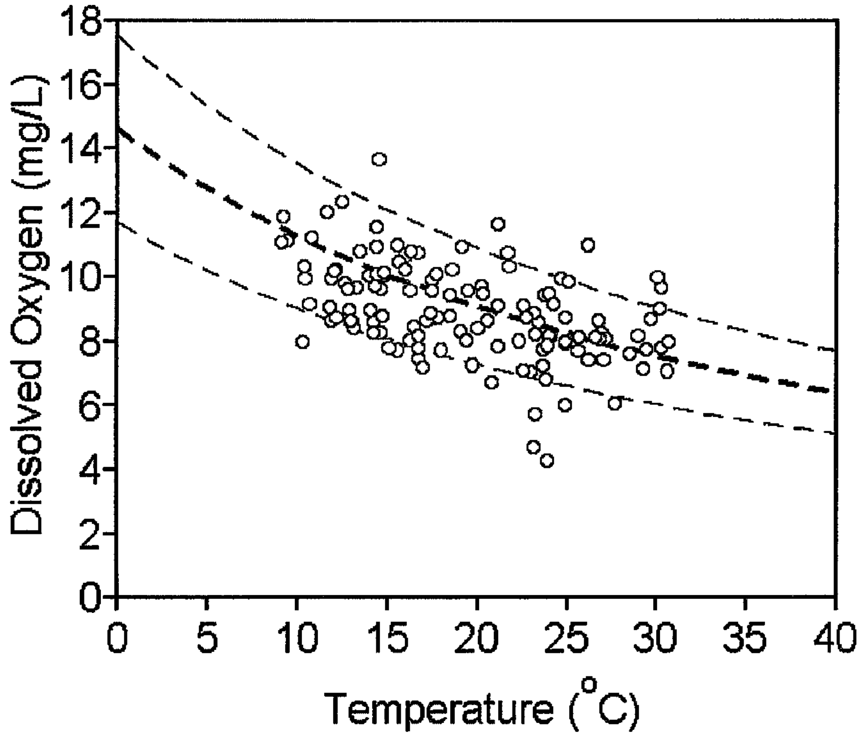

Figure 2. Dissolved oxygen (mg/L) in relation to temperature (ºC) from 2003 to 2005. Dashed lines indicate 80, 100, and 120% saturation.

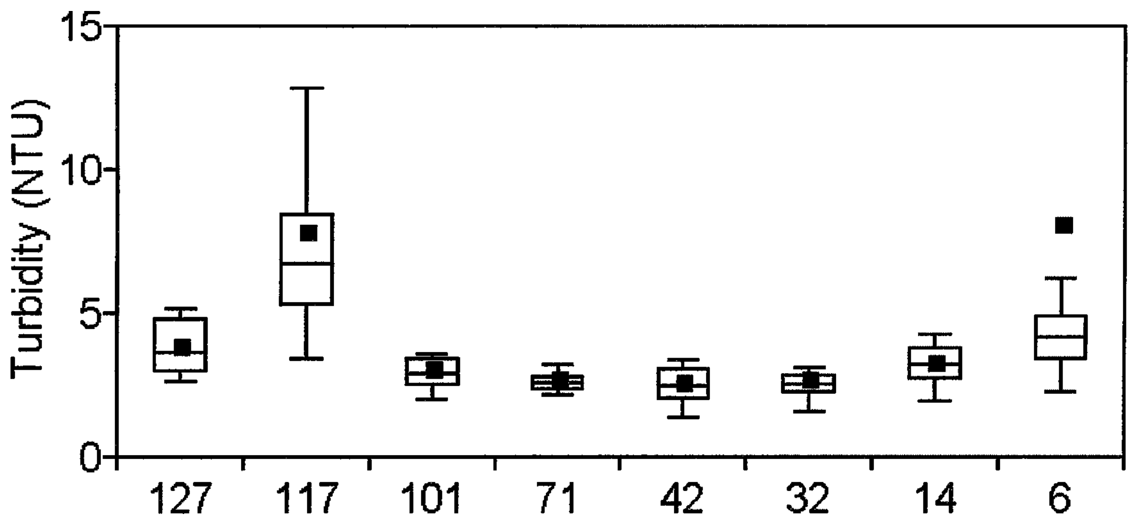

Figure 3. Turbidity (NTU) by study site from 2003 to 2005. The line and point in the boxes represent the median and mean, respectively. The upper and lower edges of the box are the 75th and 25th percentiles. Whiskers represent 90th and 10th percentile.

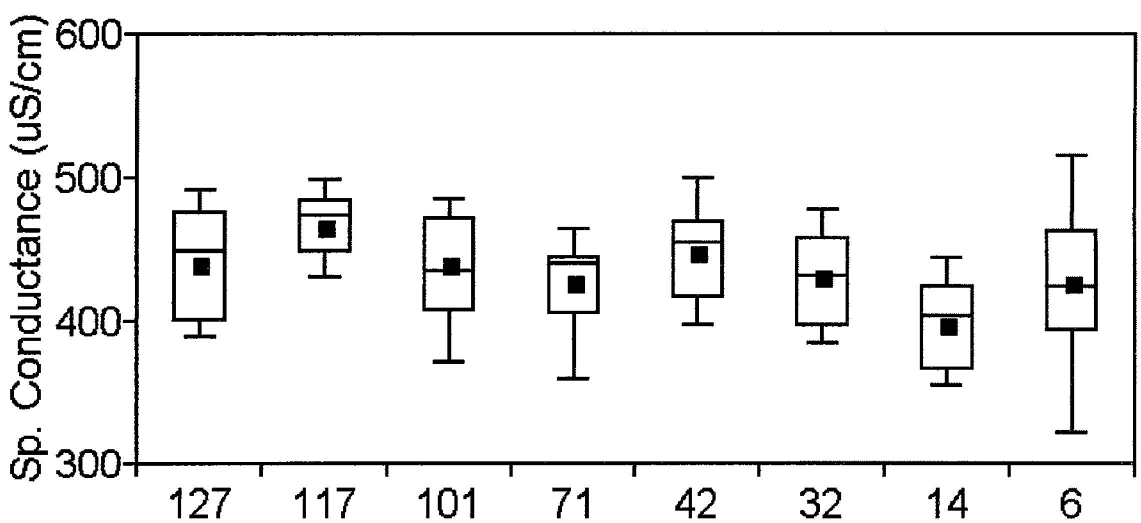

Figure 4. Specific conductance (μS/cm) by study site from 2003 to 2005. The line and point in the boxes represent the median and mean, respectively. The upper and lower edges of the box are the 75th and 25th percentiles. Whiskers represent 90th and 10th percentile.

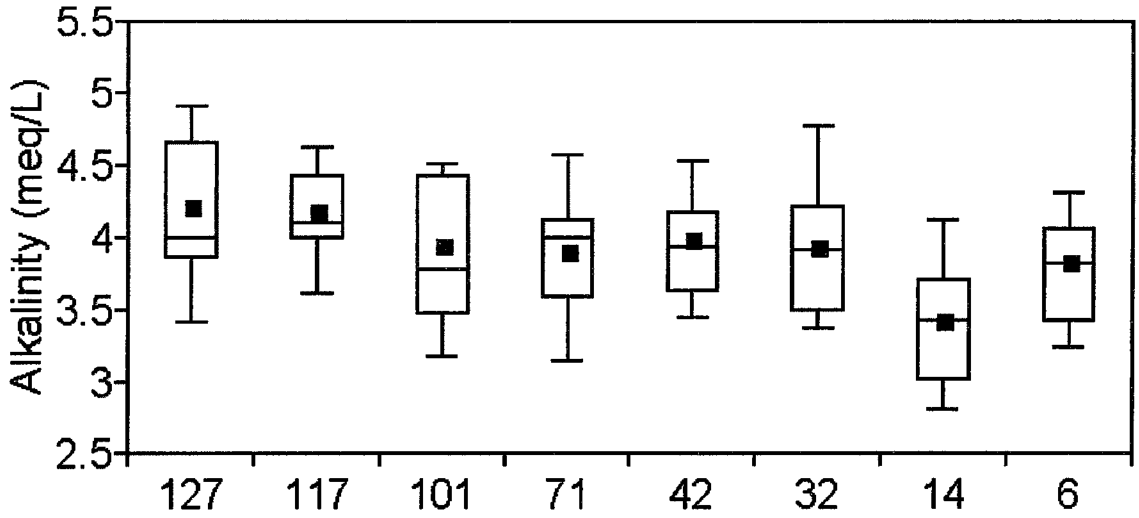

Figure 5. Alkalinity (meq/L) by study site from 2003 to 2005. The line and point in the boxes represent the median and mean, respectively. The upper and lower edges of the box are the 75th and 25th percentiles. Whiskers represent 90th and 10th percentile.

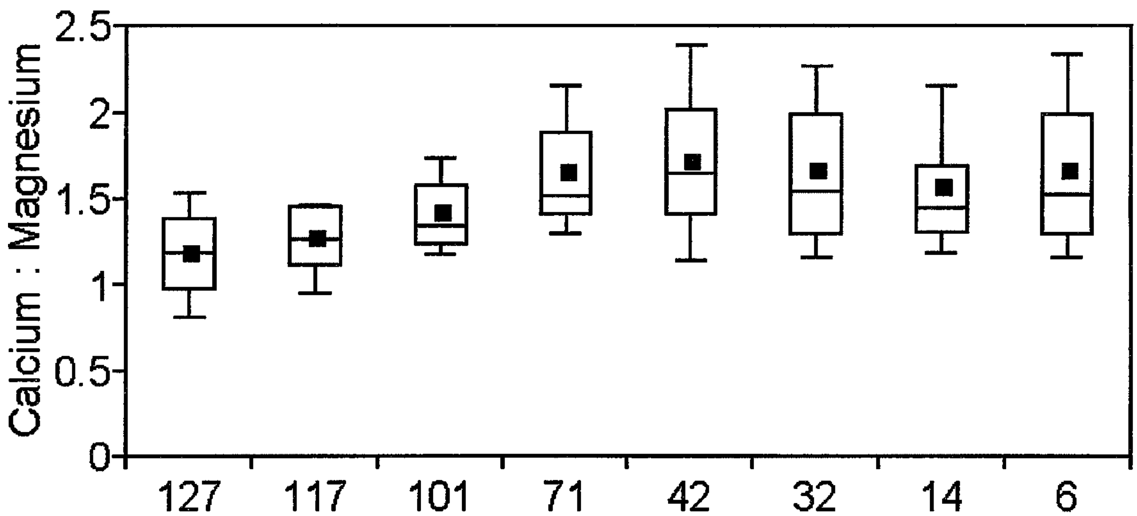

Figure 6. Ratio of calcium to magnesium by study site from 2003 to 2005. The line and point in the boxes represent the median and mean, respectively. The upper and lower edges of the box are the 75th and 25th percentiles. Whiskers represent 90th and 10th percentile.

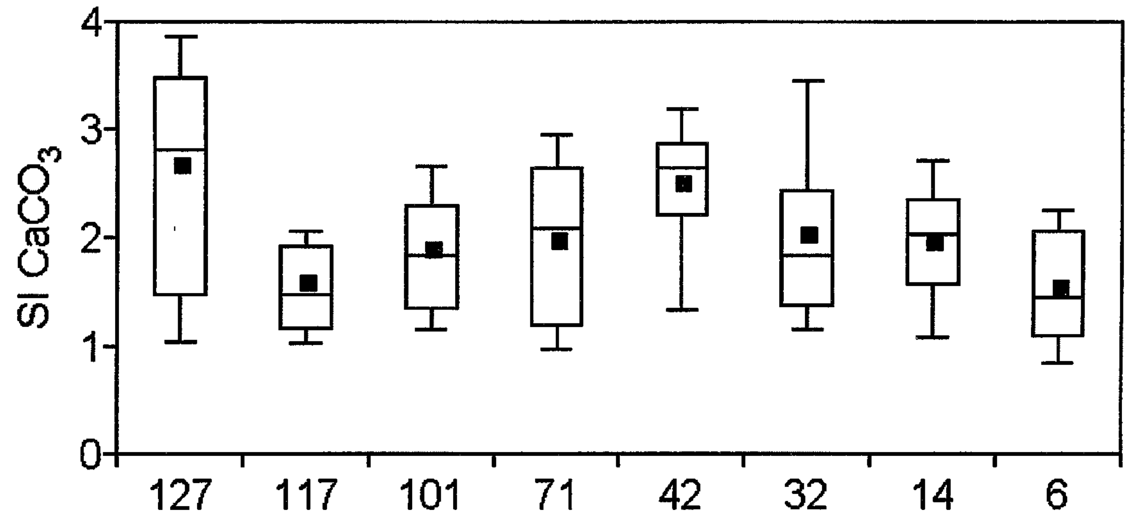

Figure 7. Saturation with $CaCO_3$ by study site from 2003 to 2005. The line and point in the boxes represent the median and mean, respectively. The upper and lower edges of the box are the 75th and 25th percentiles. Whiskers represent 90th and 10th percentile.

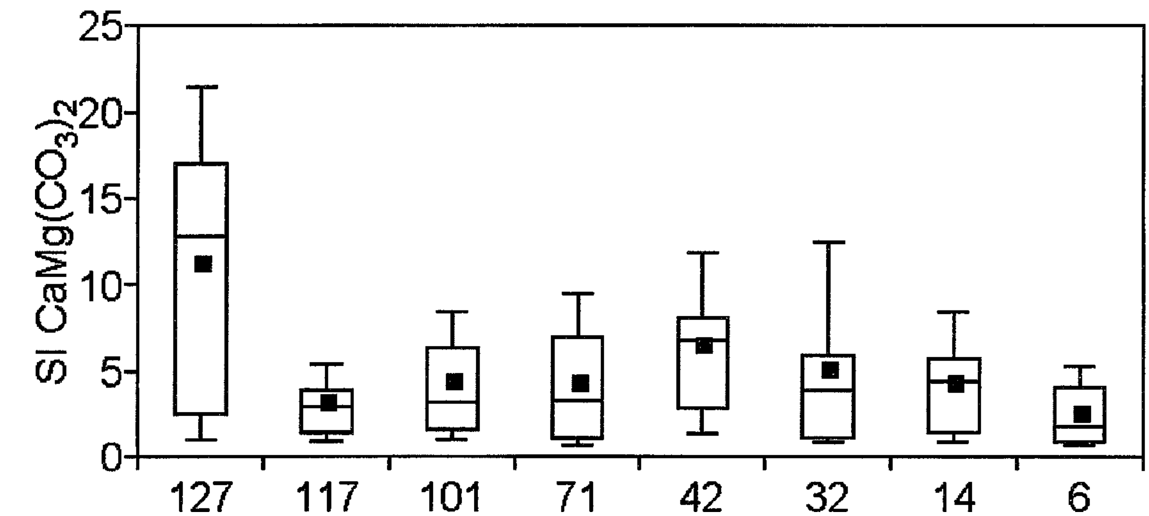

Figure 8. Saturation with $CaMg(CO_3)_2$ by study site from 2003 to 2005. The line and point in the boxes represent the median and mean, respectively. The upper and lower edges of the box are the 75th and 25th percentiles. Whiskers represent 90th and 10th percentile.

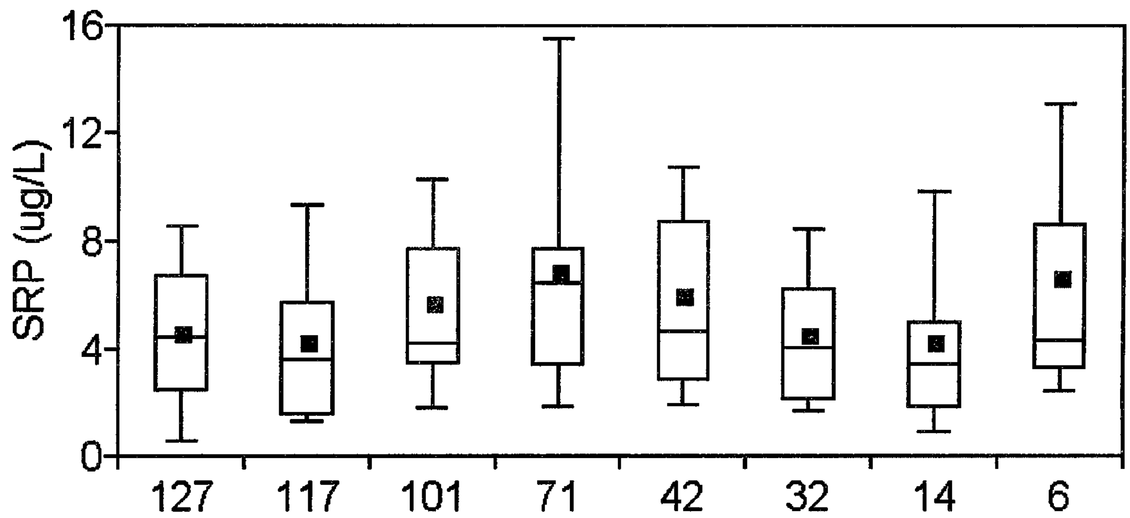

Figure 9. Soluble reactive phosphorus (SRP) (μg/L) by study site from 2003 to 2005. The line and point in the boxes represent the median and mean, respectively. The upper and lower edges of the box are the 75th and 25th percentiles. Whiskers represent 90th and 10th percentile.

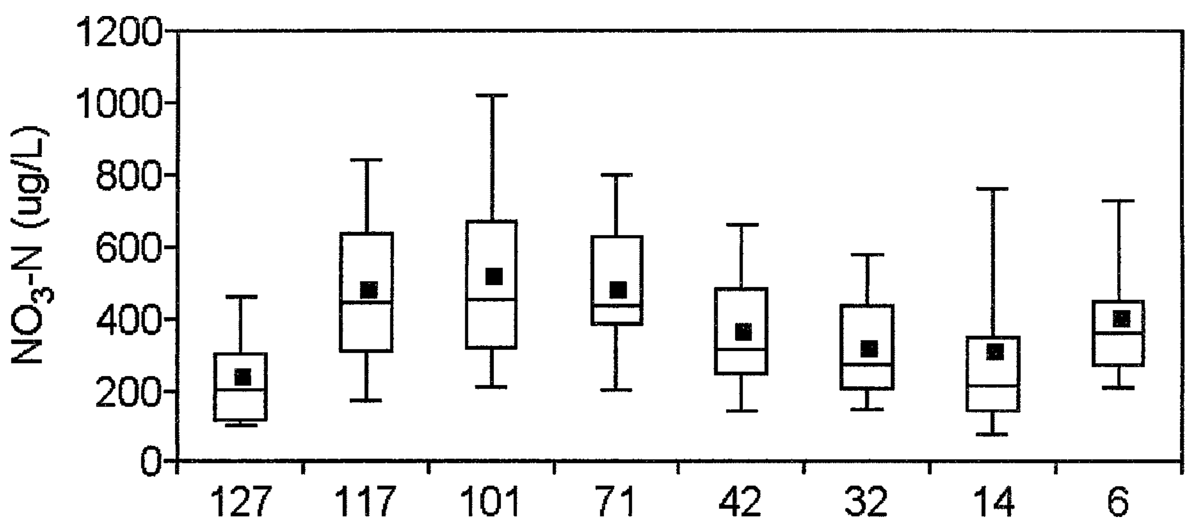

Figure 10. Nitrate-nitrogen (NO_3-N) (μg/L) by study site from 2003 to 2005. The line and point in the boxes represent the median and mean, respectively. The upper and lower edges of the box are the 75th and 25th percentiles. Whiskers represent 90th and 10th percentile.

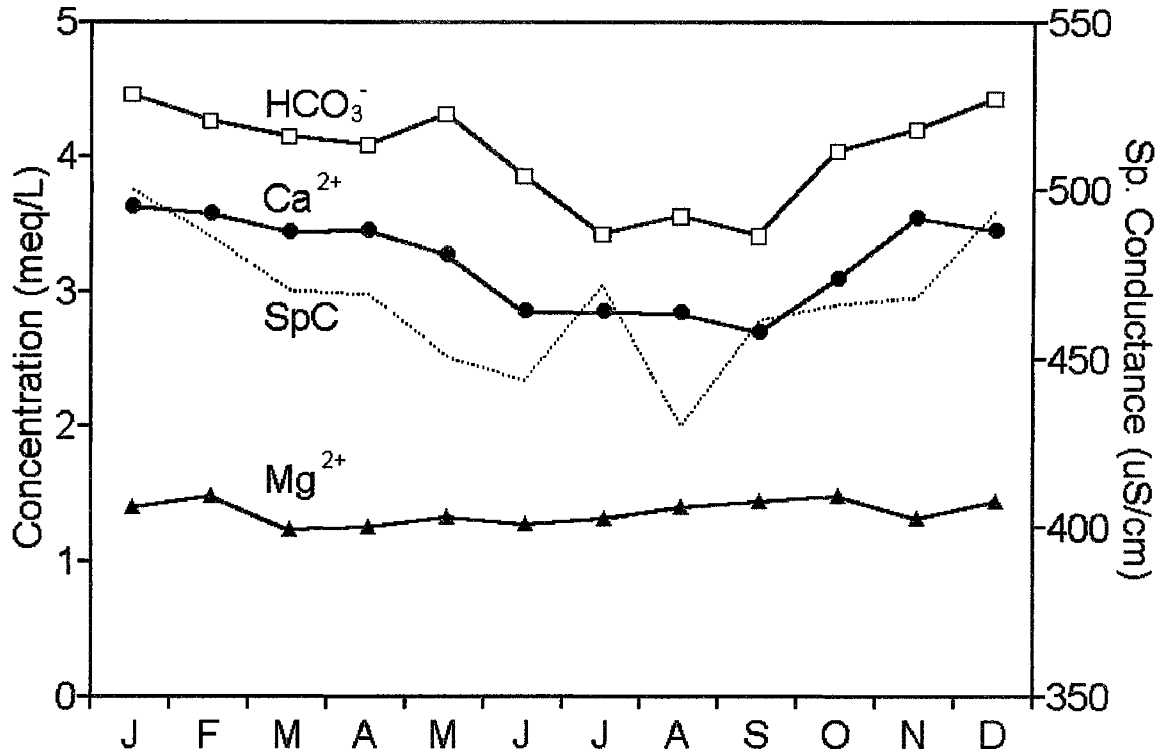

Figure 11. Median monthly concentrations of HCO_3^-, Ca^{2+}, and Mg^{2+} (meq/L), and specific conductance (μS/cm) from 1963 to 1997.

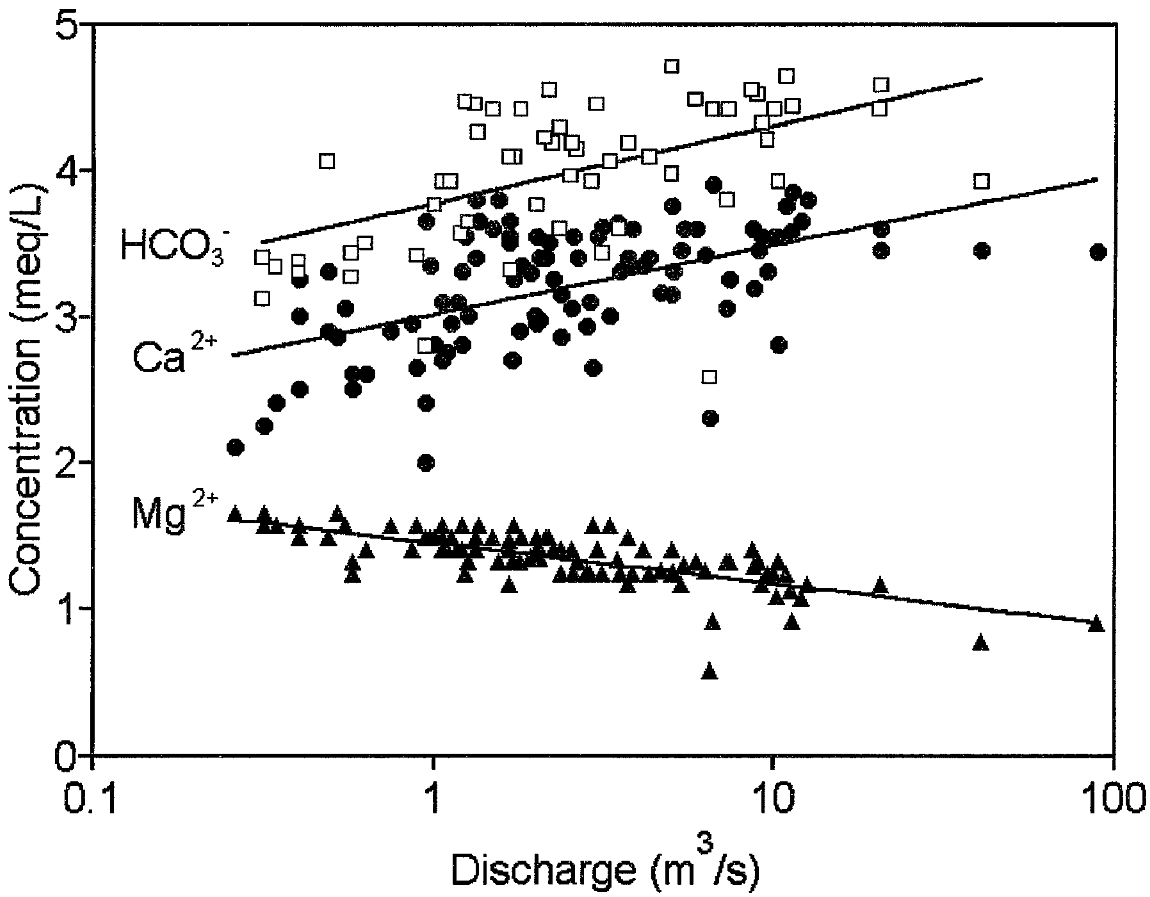

Figure 12. Concentrations of HCO_3^-, Ca^{2+}, and Mg^{2+} (meq/L) in relation to discharge (m^3/s) from 1963 to 1997.

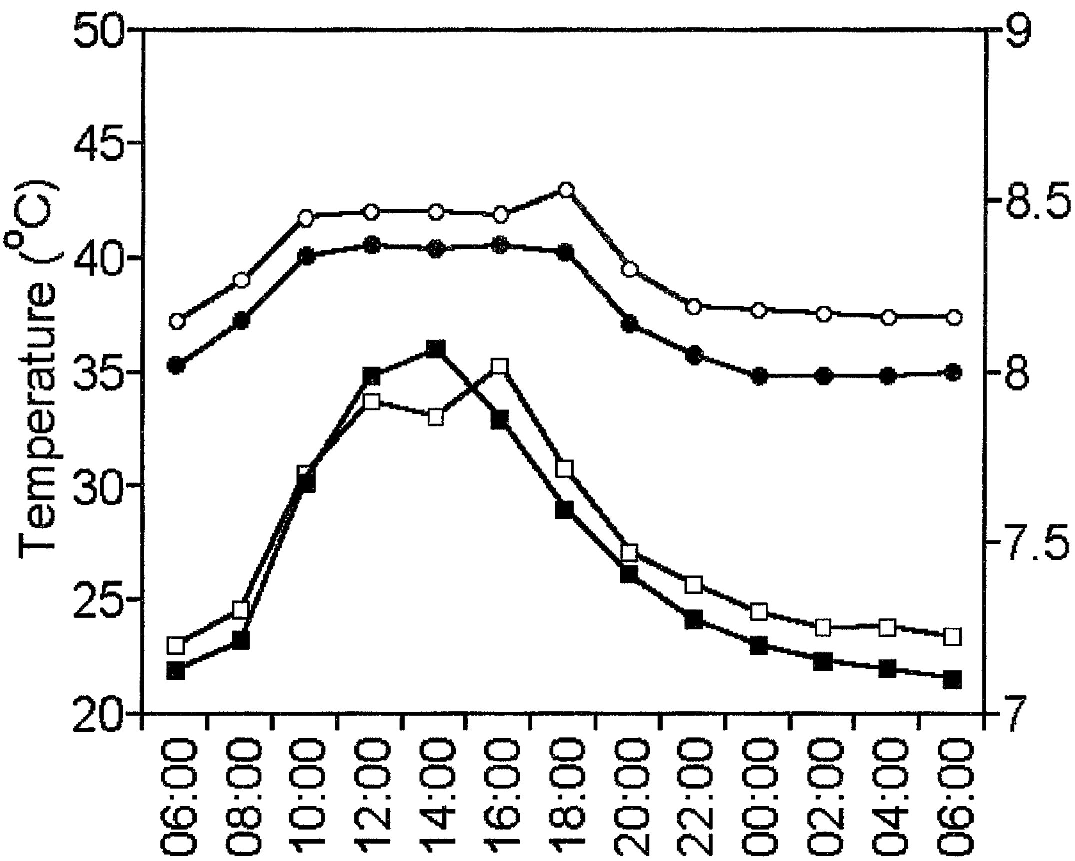

Figure 13. Temperature (°C) and pH over time from 8/30/05 to 8/31/05 (open symbols) and from 9/22/05 to 9/23/05 (filled symbols).

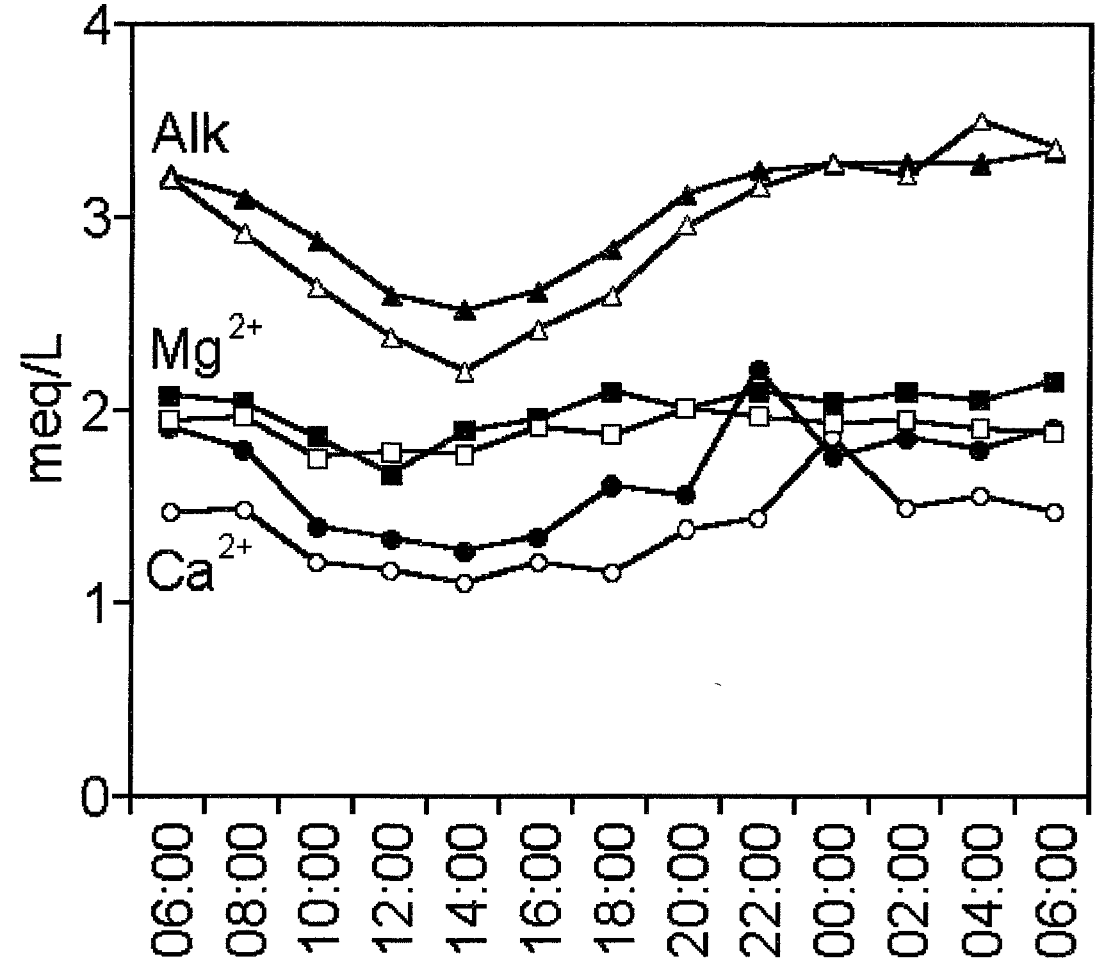

Figure 14. Concentrations of Ca^{2+}, Mg^{2+}, and alkalinity (meq/L) over time from 8/30/05 to 8/31/05 (open symbols) and from 9/22/05 to 9/23/05 (filled symbols).

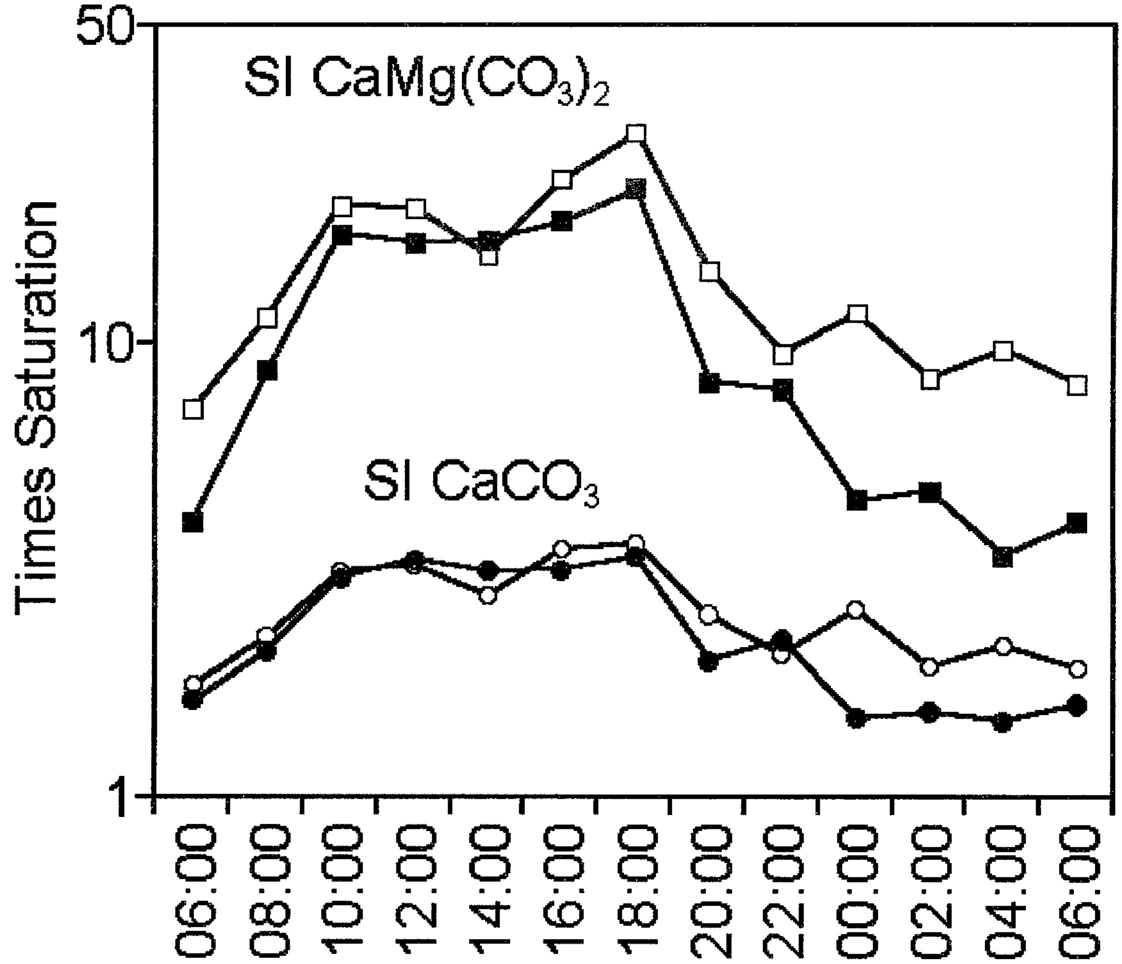

Figure 15. Saturation with respect to calcite and dolomite over time from 8/30/05 to 8/31/05 (open symbols) and from 9/22/05 to 9/23/05 (filled symbols).

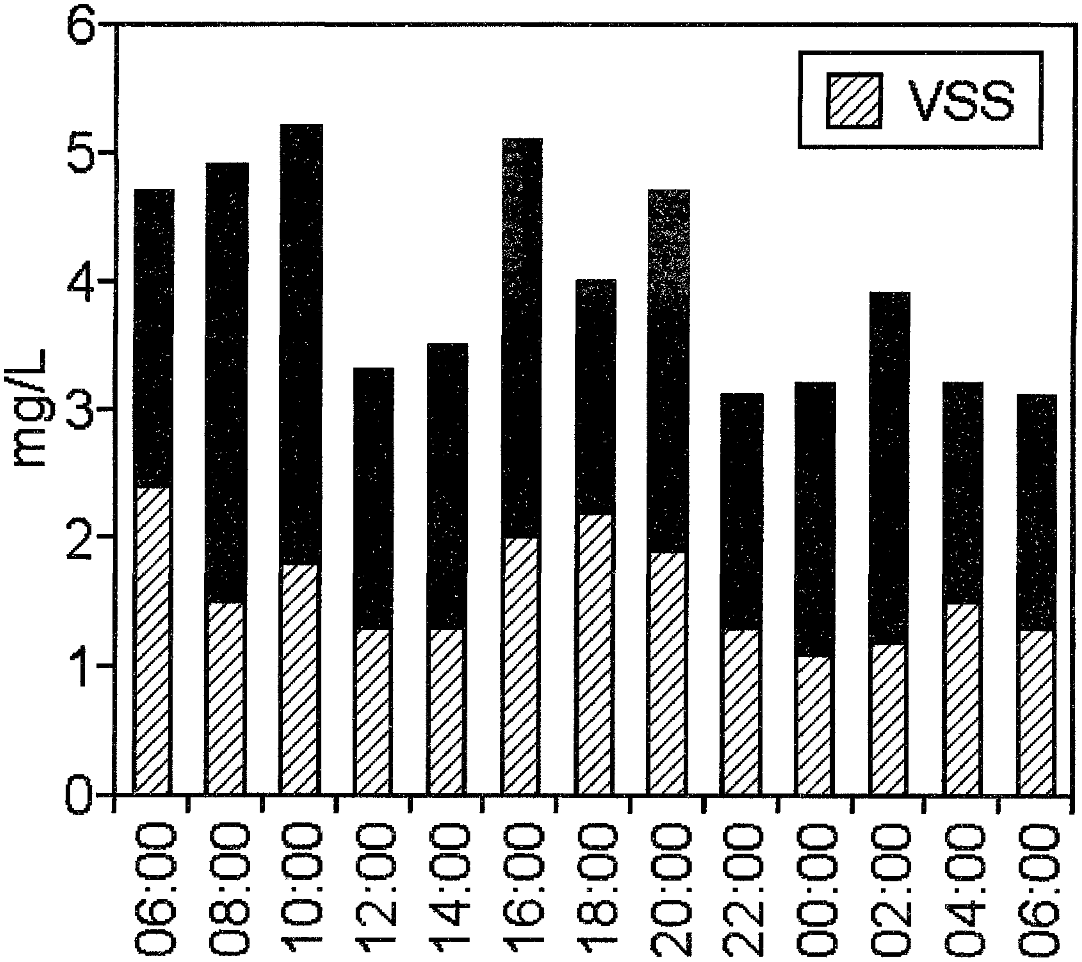

Figure 16. Total and volatile suspended solids (mg/L) over time from 9/22/05 to 9/23/05. Black portion represents fixed suspended solid content.

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