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Evolution of chemical composition along river drainage networks

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EVOLUTION OF CHEMICAL COMPOSITION ALONG RIVER DRAINAGE NETWORKS

BY

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ABSTRACT

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Surface water chemistry from a tropical and temperate rivers system was studied in order to understand the controls on longitudinal variation of stream chemistry. In the Rio Icacos-Blanco system in Puerto Rico, I examined changes in stream chemistry associated with a change in bedrock composition from intrusive quartz diorite (upstream) to volcaniclasitc material (downstream). Overall, after sea-salt correction, most solutes decreased consistently with distance downstream. The silica to alumina ratio, however, changed sharply with changes in the underlying bedrock. Other indices of weathering rates and processes showed strong similarities despite the change in bedrock. The dominance of silica, alkalinity, calcium and sodium (after sea-salt correction) in surface waters suggests that anorthite and albite are the dominant minerals within the entire basin, and they are weathering rapidly (silicon to Na + K $\geq$4) with the bisiallitization type of weathering (silica to alumina >2). Human influences on river chemistry in the Icacos-Blanco system appear to be minor, as nutrients (N and P) show little change along the drainage network.

Sampling of tributaries and source points at high and low elevation within the uniform intrusive bedrock of the Icacos was undertaken to identify spatial variability in weathering processes. Landslides are frequent in the basin, and expose fresh mineral surfaces to weathering. Concentrations of weathering products were inversely related to pCO_2, suggesting that the availability of primary reactive minerals, rather than carbonic acid concentrations, limits weathering.

In the temperate Bagmati drainage system in Kathmandu valley, Nepal, population density appears to be the most fundamental control on the chemistry of surface waters. Concentrations in the Bagmati were extraordinarily high for nitrogen and phosphorus, and both nutrients and major ions were found in proportions similar to those in raw domestic sewage. The contribution of chemical weathering processes to water quality of the Bagmati does not seem to be significant within the Kathmandu valley. Ammonium contributes almost all nitrogen in the total dissolved nitrogen and the concentration of nitrate is negligible, probably due to rapid denitrification and limited nitrification within the stream channel under relatively low oxygen conditions.

CHAPTER I

EVOLUTION OF CHEMICAL COMPOSITION ALONG RIVER DRAINAGE NETWORKS

Introduction

River or stream water chemistry is influenced by many factors such as geology of the basin, climate, flow regime, vegetation, biotic productivity and anthropogenic activity. Gibbs (1970) proposed that surface waters could be divided into three classes based on factors affecting their chemistry: those affected primarily by atmospheric precipitation, rock dominance and evaporation-crystallization processes. River or stream water chemistry is strongly influenced by atmospheric precipitation, which contributes dissolved salts to a watershed (Stallard and Edmond, 1981; McDowell et al., 1990; Gaillardet et al., 1999). The importance of the underlying geology on the control of stream water solutes is also widely known (Stallard and Edmond, 1983; Lewis et al., 1987; Drever, 1988; Billett et al., 1996; Chen et al., 2002; Millot et al., 2002). Weathering of different bedrocks produces stream chemistry of different composition. Finally, loss of water by evapotranspiration affects stream water chemistry by causing an overall increase in solute concentration, and this tendency is particularly evident in larger catchments (Billett et al., 1996).

The chemical composition of river or stream water is often variable along the drainage network and the nature of this variability changes from basin to basin. Many large catchments show increased concentration with distance downstream due to

evapotranspiration (Billett et al., 1996). In contrast, aluminum and DOC concentrations in streams of the Hubbard Brook Experimental Forest, New Hampshire show decreasing trends with distance downstream (Lawrence et al., 1986) while base cations and silica show increasing trends in the Falls Brook watershed of Hubbard Brook (Johnson et al., 1981). Alkalinity, base cations and silica decrease in stream water exponentially with elevation in Switzerland (Drever and Zobrist, 1991). Small catchments in northern Scotland show decreased concentrations of dissolved free carbon dioxide and DOC with distance downstream (Dawson, 1995). DIC concentration shows increasing trends with distance downstream in the Ottawa River basin in Canada (Telmer and Veizer, 1999). Different chemical species show different trends along drainage networks depending on the nature of the chemical species and factors in the surrounding watershed.

Groundwater inputs may be the fundamental control on stream water chemistry at low flow in many catchments (Tranter et al., 1993, Billett et al., 1996). Weathering rate is thought to accelerate when groundwater passes from the ridge top area to the stream (McDowell, 1998) and thus groundwater inputs from various sites in a watershed might drive differences in stream chemistry. Groundwater also affects the ecology of surface water by sustaining stream base flow and supplying nutrients and inorganic ions (Hayashi and Rosenberry, 2002). Frequently the source of solutes in groundwater is weathering in the soil. Higher plants and their associated microflora accelerate chemical weathering through exudation and turnover of carbonic and organic acids and buildup of high levels of CO_2 in close proximity to primary minerals (Berner, 1991; Drever and Zobrist, 1992; Bormann et al., 1998). Most of the CO_2 produced in soils diffuses upward to the

atmosphere but some is dissolved into soil water, and transported further into the subsurface by groundwater recharge (Kessler and Harvey, 2001) where it can accelerate weathering. Human activities also affect surface water chemistry by different types of land use such as agricultural effluent, domestic and industrial wastes and mining wastes (Billett and Cresser, 1992; McDowell et al., 1995; Gaillardet et al., 1999).

Numerous studies have suggested the importance of subsurface flow paths as a control on stream chemistry (Johnson et al., 1969; Peters and Driscoll, 1987; Lawrence and Driscoll, 1990; Billett and Cresser, 1992; Tranter et al., 1993; Raiswell, 1984). Delayed flow waters are solute rich and exhibit high partial pressure of carbon dioxide (pCO_2). The high pCO_2 is generated by the production of HCO_3^- during the dissolution of aluminosilicates and may be diminished or lost as a consequence of post-mixing chemical weathering reactions and degassing in open channels (Tranter et al., 1993; Raiswell, 1984). Hydrologic exchange of water between the stream and the hyporheic zone influences chemical weathering rates and hence chemistry of surface waters (Gooseff et al., 2002).

The chemical composition of both tropical and temperate drainage networks primarily changes due to changes in parent material, availability of pCO_2, human activities and atmospheric inputs. Various authors have examined the causes of change in chemical composition along temperate drainage networks (Johnson et al., 1981, Lawrence et al., 1986, Drever and Zobrist, 1991, Dawson, 1995, Billett et al., 1996, Telmer and Veizer, 1999) but few studies examine changes in chemical composition along tropical drainage networks, which highlights the need for further research.

Tropical ecosystems play major roles in global biogeochemical cycles (White et al., 1998; Aitkenhead and McDowell, 2000; Lal et al., 2000). Weathering rates are known to be high in tropical environments, but it is not clear weather temperature alone can account for this observation. The release rates of CO_2 from tropical ecosystems are typically higher than from other ecosystems (Aber and Melillo, 2001) and as a consequence the partial pressure of carbon dioxide (pCO_2) in soils, soil water, and surface water should also be high. This high pCO_2 probably drives the high rate of weathering found in wet tropical climates (White and Blum, 1995, Ludwig et al., 1998).

Human activities also control surface water chemistry in various ways such as deforestation, agricultural practices, industrial effluents, land use, and domestic waste. Human population density has strong effects on nitrate losses from humid tropical catchments (McDowell, 2001). The effects of different types of land use (Billett and Cresser, 1992; McDowell et al., 1995) and other factors such as agricultural effluent, domestic and industrial wastes and mining wastes on surface water chemistry are well known (Gaillardet et al., 1999).

Acidic deposition is another human alteration of biogeochemical cycles that affects stream chemistry and weathering rates. Acid deposition inputs are about equal to the internal sources of protons in driving weathering reactions at the Hubbard Brook ecosystem (Likens and Bormann, 1995). Acid deposition has resulted in acidification of surface and soil waters and increases in aluminum concentration. Such changes in chemical composition create ecological stress that affects forested landscapes and aquatic

ecosystems (Driscoll et al., 2001) and alters the ability of the ecosystem to retain nutrients (Bailey et al., 2002).

Johnson et al. (1981) examined the geochemical effects of acid rain at the Hubbard Brook Experimental Forest, New Hampshire based on the long term data at Falls Brook watershed. The authors suggested that a two step neutralization processes occurs within the watershed. Hydrogen ion is first neutralized by the dissolution of reactive alumina in soils. The total acidity including both aluminum and hydrogen ion is subsequently neutralized by the chemical weathering of primary silicate minerals, which depends on the residence time of water in the soils. The silica release rate from HBEF was similar to other temperate watersheds but less than the Rio Icacos watershed (Johnson et al., 1981; McDowell and Asbury, 1994). Spatial variation of aluminum chemistry in the streams of Hubbard Brook Experimental Forest, New Hampshire is due to the variation of vegetation type and mineral soil depth within the watershed (Lawrence et al., 1986).

Chemical weathering and surface water chemistry

Chemical weathering is a fundamental process controlling surface water chemistry. Rates of chemical weathering depend primarily on the amount of carbon dioxide present (Holland, 1984; White and Blum, 1995; Gaillardet et al., 1999; Andrews and Schlesinger, 2001; Millot et al., 2002) as well as other variables such as bedrock type (Stallard and Edmond, 1983; Drever, 1988) and temperature (Velbel, 1993; McDowell and Asbury, 1994; Dorn and Brady, 1995). The global budget of CO_2 is an important driver of weathering rates over geologic time (White and Blum, 1995; Walker et al., 1981; Brady and Carroll, 1994). Carbon dioxide is the most important greenhouse gas, which plays a vital role in global warming. It is known that only ~50 percent of the anthropogenic emission (7.3 Giga-tones/year) of CO_2 stays in the atmosphere and the rest of the CO_2 is taken up by oceans and land (IPCC, 1990; Graves and Reavey, 1996; Joos et al., 2001). The greenhouse effect is a global concern because of its far-reaching consequences for climate, and carbon dioxide is the chief component of global warming. The consumption of atmospheric and soil CO_2 by chemical weathering is equal to the bicarbonate fluxes in watersheds with aluminosilicate minerals, and is equal to half of bicarbonate fluxes in watersheds with carbonate minerals (Amiotte Suchet and Probst, 1995; Gaillardet et al., 1995; Ludwig et al., 1998).

Partial Pressure of Carbon Dioxide (pCO_2):

The carbon dioxide concentrations in some major rivers such as the Amazon, Yangtze and Rhine are about 10-15 times greater than expected for equilibrium with the atmosphere (Telmer and Veizer 1999). The partial pressure of carbon dioxide (pCO_2) in the Ottawa River and its tributaries is a function of soil respiration and the soils in the upland basins have higher pCO_2 than the lowland basins (Telmer and Veizer (1999). The partial pressure of carbon dioxide (pCO_2) in temperate soils ranges from 5 to >20 times that of the atmosphere (Holland, 1978). Dawson et al. (1995) reported the pCO_2 in the Dee River system in northern Scotland, is about 15 times higher than atmospheric values. The fluctuation of pCO_2 in tropical rivers is a significant area for research. The Amazon River system exhibits high levels of respiration relative to productivity (Richey et al., 1980) and high pCO_2 values are expected in such a respiration-dominated system (Stallard and Edmond, 1987). It is very important to know the partial pressure of carbon dioxide (pCO_2) in tropical rivers or streams to know its role in regulating solute release in the watershed. There have been few data reported for tropical rain forest soils and surface waters (Johnson et al., 1975). A range of 5-100 times atmospheric values for pCO_2 seems reasonable for tropical soils, and surface waters samples have pCO_2 values in the range of those in soils because of the high level of respiration (Stallard and Edmond, 1987).

Bedrock Type:

Chemistry of surface water is largely affected by the parent material of the basin in which it drains (Gibbs, 1970; Stallard and Edmond, 1983; Lewis et al., 1987; Drever,

1988; Dorn and Brady, 1995; Billett et al., 1996). Billett et al., (1996) showed the spatial variability of stream water chemistry along the length of the stream and this control of stream water solute chemistry reflected the changes in the underlying lithology. Chemistry of surface waters within the Amazon watershed is mainly controlled by the substrate lithology (Stallard and Edmond, 1983). The major element chemistry of the Changing is mainly controlled by rock weathering and carbonate dissolution is the dominant process in its basin (Chen et al., 2002).

Underlying lithology has been shown to control stream water solute chemistry in Scottish upland catchments. The pH and basic cations show significant spatial variability along the length of seven streams and suggest that small-scale spatial changes in stream water chemistry may provide a useful tool for identifying changes in the underlying geology in poorly exposed areas (Billett et al., 1996). Billett et al. (1996) sampled at approximately 250 m intervals along the length of the mainstreams of seven catchments in Scotland and observed spatial variability along the length of the mainstream due to changes in parent material which suggests the importance of underlying geology in controlling stream chemistry.

Substrate lithology and erosion regime exert the most fundamental control on the chemistry of surface waters within the Amazon catchments (Stallard and Edmond, 1983). Rivers that drain siliceous bedrock types are relatively high in silica and low in total cations. Those that drain carbonates are relatively high in alkalinity and possess intermediate levels of total cations, while those that drain evaporates are rich in sulfate and chloride and are highest in total cations. This indicates that susceptibility to

weathering has a significant role in determining overall input rates provided that the reactive lithologies are found in a weathering-limited region such as the Andes (Stallard and Edmond, 1983).

Climate:

Rates of weathering of silicate minerals depend on surface temperature or other climatic factors (Walker et al., 1981; Brady and Carroll, 1994; Lasaga et al., 1994; McDowell and Asbury, 1994; Dorn and Brady, 1995; White and Blum, 1995; Gaillardet et al., 1999; White et al., 1999; Millot et al., 2002). The warm climate in tropical regions enhances biotic activity, which increases the partial pressure of carbon dioxide in surface waters due to high rates of respiration and as a consequence increases dissolution of aluminosilicates. The coupling between silicate weathering and climate depends on the sensitivity of weathering rates to changes in global temperature and atmospheric carbon dioxide, enhancing stable climatic conditions that make a suitable environment for life on the earth (Brady, 1991; Berner et al., 1983; Berner and Berner, 1997). An increase in biotic productivity would increase weathering rate, supporting the feedback between weathering and temperature (Schwartzman and Volk, 1989; Volk, 1987). Chemical weathering rates of the Slave Province are four to five times lower than those of the Grenville Province of the Canadian Shield suggesting that climate (temperature and precipitation) is the most plausible factor for such a discrepancy (Millot et al., 2002). Gaillardet et al. (1999) reported a contrasting result with White and Blum (1995) and

Millot et al. (2002) that temperature and runoff are not overriding parameters controlling chemical weathering rates of silicates deduced from large river chemistry.

The spatial variability of carbon chemistry of waters along the Ottawa River basin is controlled by the rates and products of rock weathering and susceptibility of different minerals to weathering and by soil respiration rates (Telmer and Veizer, 1999). The generation of carbonic acid by respiration in the soil is much higher in the well developed soils of the lowlands than in the thin soils of the uplands. Carbon isotopes indicate that 61% of the DIC in the Ottawa River originates from organic respiration of organic materials and 39% from carbonate dissolution. This illustrates the resistant nature of silicate rocks and the dominant role of carbonates in controlling the chemistry of surface waters in which they are found (Telmer and Veizer, 1999). The concentration of carbon dioxide varies along the drainage networks due to degassing and about 30% of the riverine DIC flux is lost as degassing of CO_2 to the atmosphere from the Ottawa River and its tributaries (Telmer and Veizer, 1999).

Mechanical Denudation:

Mechanical denudation exerts fundamental control on the chemistry of surface waters (Stallard and Edmond, 1983; Drever, 1988; Edmond and Huh, 1997; Gaillardet et al., 1999; Millot et al., 2002). Rates of chemical weathering accelerate in tectonically active belts, consuming large amounts of carbon dioxide and hence influencing global climate (Edmond and Huh, 1997). Chemical weathering rates of silicates show a strong correlation with physical erosion rates because weathering is enhanced when mechanical

erosion continuously refreshes mineral surfaces and precludes the development of thick soils (Gaillardet et al., 1999). Watersheds in warm climates are characterized by a wide variability of chemical weathering rates and such variability is explained by the variability in physical denudation rate of low erosion regimes in Guyana (1.12 tons km^{-2} yr^{-1}) compared to active erosion regimes in Puerto Rico (16.67 tons km^{-2} yr; Millot et al., 2002).

Regional variability in chemical composition of surface water

Surface water chemistry is affected by various factors. At the global scale, White and Blum (1995) documented weathering rates of sixty-eight watersheds of the world underlain by granitoid rocks. Weathering of granitoid rocks under tropical conditions in the Rio Icacos watershed in the Luquillo Experimental Forest, as reported first by McDowell and Asbury (1994), was later shown to have the fastest documented weathering rate of any silicate terrain in the world (White et al., 1998). The silica flux of Rio Icacos watershed is approximately five times higher than the temperate rainforest watersheds of Jamieson Creek, British Columbia (4°C) and Indian River, Alaska (6°C). Such large differences in silica flux appear despite similarity in annual precipitation, dense vegetation (different species), very steep topography and high physical erosion rates in all these watersheds. Hence topography and physical erosion are less important than climate (primarily temperature and precipitation) in controlling chemical weathering rates in watersheds (White and Blum, 1995). Warmer temperature is thought to be responsible for the higher silica release from Rio Icacos than from similar temperate watersheds (McDowell and Asbury, 1994).

Gaillardet et al. (1999) compiled data on the 60 largest rivers of the world to calculate the contribution of major lithologies, rainfall and temperature to river dissolved load. They found that silicate weathering contributes the highest fraction to the total dissolved load from the tropical Orinoco River while in the Seine River, which drains a largely sedimentary basin of dense human population, contributes the least. On a global

scale, silicate weathering contributes 26% of the total dissolved solid flux transported into the ocean and CO_2 consumption by rock weathering is 0.252 GtC yr^{-1}, 40% of which is due to the weathering of silicates (Gaillerdet et al., 1999).

Slave Provience (Canada) appears to have the lowest chemical weathering rate and Rio Icacos has the highest chemical weathering rate of grainitoid watersheds of the world reflecting climatic control on the chemical weathering rate (Millot et al., 2002). Hot climate watersheds are also characterized by an important variability of chemical weathering rate that is explained by physical erosion fluxes (Millot et al., 2002).

The rocks of the Caura River drainage in Venezuela contain some easily weathered minerals, including feldspar and hornblendes in the granitic rocks that contribute major amounts of silica and sodium and calcium, magnesium and potassium (Lewis et al., 1987). The spatial variability in bedrock is reflected in spatial variability of river chemistry. The silicon released from this watershed is nearly three times less than Rio Icacos although both watersheds are lying in the same tropical region underlain by similar granitoid rocks.

There have been various studies on stream chemistry but systematic evolution of stream chemistry in a tropical watershed has not been carefully examined. There are various studies that explain spatial variability in chemical composition along drainage networks (Johnson et al., 1981; Stallard and Edmond, 1983; Dawson et al., 1995; Billett et al., 1996; Telmer and Veizer, 1998). This study will examine the mechanisms which might drive spatial variability in chemical composition along the drainage network in a

small tropical watershed. It will also examine the evolution of drainage chemistry in a heavily urbanized basin in Nepal.

Objectives of study

My overall research plan is to examine longitudinal changes in stream chemistry of a temperate and tropical river system and to infer the likely causes of any longitudinal variation in stream chemistry. The tropical study site is the Rio Icacos-Blanco system in Puerto Rico. The temperate study site is the Bagmati River in Nepal. The Rio Icacos-Blanco has few people in its headwaters and more people at downstream sites. Similar variations in population density have been observed for the Bagmati River, although population density is much higher than in the Rio Icacos-Blanco system. Hydrological and meteorological observations have been made in the Rio Icacos watershed of the Luquillo Experimental Forest by the United States Geological Survey (USGS) since 1945. This watershed has been examined for chemical studies since the 1980s. Chemical weathering processes in the tropical ecosystems are responsible for much of the solute and sediment discharge to tropical river systems (McDowell et al., 1995). Both the warm temperature and high precipitation at the site are thought to contribute to this high weathering rate. The extent to which pCO_2 in the basin contributes to the high weathering rates is unknown, although HCO_3^- flux is high for a non-carbonate terrain (McDowell and Asbury, 1994).

The principal source of solutes within the Rio Icacos-Blanco watershed will be investigated. The Rio Icacos watershed is underlain by quartz diorite while further downstream the Rio Blanco basin is underlain by volcaniclastic rock. This geologic break along the Rio Icacos-Blanco system plays a significant role in controlling the chemistry

of stream water. The Rio Icacos watershed is underlain by the Rio Blanco stock, a quartz diorite (Seiders, 1971). The Rio Blanco stock is dominated by quartz and plagioclase with minor amounts of biotite, hornblende, and K-feldspar, magnetite, and apatite (Seiders, 1971; White et al., 1998). Clays and sandy clay loams are the dominant soils in the Rio Icacos watershed, of the Picacho-Utuado series (Boccheciamp, 1977). The Rio Blanco area is likely dominated by basalt consisting of calcic plagioclase feldspar and pyroxenes and a minor amount of laumontite, a calcium rich zeolite with quite variable silica to alumina ratio or granite (high proportions of silica and potassium) and minor amounts of phillipsite, a zeolite mineral with variable silica and alumina ratio and rich in potassium and sodium. Shallow and moderately deep soils are found in the Humacao area of the Rio Blanco watershed.

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CHAPTER II

LONGITUDINAL VARIATION OF CHEMISTRY IN A TROPICAL WATERSHED OF THE LUQUILLO EXPERIMENTAL FOREST, PUERTO RICO

Abstract

Surface water chemistry from the Rio Icacos mainstream, its tributaries within the Luquillo Experimental Forest (LEF), and the Rio Blanco were studied in order to understand the controls on longitudinal variation of stream chemistry along a drainage network. Solute concentrations were higher in the upstream than the downstream reaches of the Rio Icacos basin, and stream chemistry changed quickly after crossing from quartz diorite to volcaniclastic parent material in the Blanco. Variability in stream solute concentrations was closely related to the variability in dissolved inorganic carbon in drainage waters and the variation in underlying lithology. Ratios of silicon to bedrock base cations can be used to indicate the nature and rate of chemical weathering in a basin. In the Icacos-Blanco system, the average ratio of silicon to the sum of sodium and potassium was ≥ 4 in all samples, indicating that chemical weathering of aluminosilicate bedrock is occurring at high rates within the entire Rio Icacos-Blanco basin. The dominance of silica, alkalinity, calcium and sodium in surface waters suggests that anorthite and albite are the dominant minerals weathering within the basin. The ratios of silica to alumina and silicon to alkalinity in stream water remained the same within each bedrock type, but changed as the stream crossed from the intrusive bedrock to the

volcaniclastic material. The constancy of these ratios within each bedrock type indicates that the principal weathering type remained the same, with the bisiallitization type of weathering occurring dominantly throughout the entire Rio Icacos-Blanco basin. Chemical weathering rates coupled with changes in parent material appear to be the primary cause for the longitudinal variability of chemical composition along the Rio Icacos-Rio Blanco system.

Introduction

Tropical ecosystems cover only 25% of the Earth's land surface but are responsible for 50% of the total global discharge, 38% of the delivery of dissolved ions, and 65% of the delivery of dissolved silica to the global ocean (Meybeck, 1987; White et al., 1998). The disproportionate importance of tropical regions in these global budgets, particularly silicon, is due to the rapid weathering of silicate rocks in tropical ecosystems (McDowell and Asbury, 1994; McDowell et al., 1995; Treguer et al., 1995; White et al., 1998; Braun et al., 2005). Silicate rocks consume higher amounts of carbon dioxide during weathering than other rock types (Brady, 1991; Velbel, 1993; Ludwig et al., 1998; Gaillardet et al., 1999; Millot et al., 2002) and rates of chemical weathering depend on temperature (Brady and Carroll, 1994; Dorn and Brady, 1995; White and Blum, 1995; White et al., 1999). The global budget of CO_2 is an important driver of weathering rates over geologic time (White and Blum, 1995; Walker et al., 1981; Brady and Carroll, 1994).

The consumption of atmospheric and soil carbon dioxide by chemical weathering is equal to the bicarbonate fluxes derived from weathering of aluminosilicate minerals and equal to half of the bicarbonate fluxes derived from weathering of carbonate minerals based on known dissolution reactions (Garrels and Mackenzie, 1971; Kempe, 1979; Meybeck, 1987; Amiotte Suchet and Probst, 1995; Gaillardet et al., 1995; Ludwig et al., 1998; Raymond and Cole, 2003). The production rates of CO_2 from tropical ecosystems by soil and root respiration and other biological processes are typically higher than from other ecosystems (Aber and Melillo, 2001) and as a consequence, the partial pressure of carbon dioxide (pCO_2) in tropical soils, soil water, and surface water should also be high. This high pCO_2 probably contributes significantly to the high rate of weathering found in

wet tropical climates, in addition to the effects of temperature (White and Blum, 1995, Ludwig et al., 1998). The importance of underlying geology on the control of stream water chemistry is also widely known (Stallard and Edmond, 1983; Lewis et al., 1987; Drever, 1988; Billett et al., 1996; Chen et al., 2002; Millot et al., 2002).

The chemical composition of river water along both tropical and temperate drainage networks primarily changes due to changes in parent material, the availability of pCO_2, human activities and atmospheric inputs. Various authors have examined the causes of change in chemical composition along temperate drainage networks (Johnson et al., 1981, Lawrence et al., 1986, Drever and Zobrist, 1992, Dawson, 1995, Billett et al., 1996, Telmer and Veizer, 1999) but few studies have examined changes in chemical composition along tropical drainage networks. Some studies have shown the role of bedrock in regulating solutes along tropical drainage networks (Stallard and Edmond, 1983; Lewis et al., 1987) and others have highlighted the role of climate in regulating solutes (White and Blum, 1995; White et al., 1999; Barun et al., 2005). Weathering of grainitoid rocks under tropical conditions in the Rio Icacos watershed of the Luquillo Experimental Rain Forest was reported first by McDowell and Asbury (1994) and was later shown to be the fastest documented weathering rate of any silicate terrain on earth (White et al., 1998; Millot et al., 2002; Braun et al., 2005). The extent to which pCO_2 in the tropical Rio Icacos basin contributes to its high weathering rates is unknown, although HCO_3^- flux is high for a non-carbonate terrain (McDowell and Asbury, 1994). The Rio Icacos-Blanco system was chosen for study because variations in parent material along the drainage network with little change in climatic conditions would allow investigation of the role of parent material in the regulating solute release. The fluctuation

of pCO_2 in tropical rivers and its role in chemical weathering is a significant area for research. Surface water samples from the Rio Icacos main stem, its major tributaries and along the entire Icacos-Blanco system were examined in order to investigate the factors controlling longitudinal variation of chemistry in a tropical watershed. This paper will attempt to describe the role of chemical weathering rates and underlying lithology in regulating changes in solute concentrations along the tropical Rio Icacos-Blanco system in northeastern Puerto Rico.

2. Study area

This research was conducted in the Rio Icacos watershed within the Luquillo Experimental Forest (LEF) in northeastern Puerto Rico, and the downstream Rio Blanco watershed in the town of Humacao (Figure 2.1). The LEF is also called the Caribbean National Forest and is administered by the United States Department of Agriculture (USDA) Forest Service. The LEF has been divided into four different forest classes based on elevation and the dominant tree species (Brown et al., 1983). The Icacos watershed is better characterized than the Blanco (McDowell and Asbury, 1994; White et al., 1998). The tabonuco (*Dacryodes excelsa*) forest type is found at elevations of 200-600 m. Colorado (*Cyrilla racemiflora*) forest type covers the elevation range of 600-750 m. Palm (*Prestoea montana*) forest type occurs usually at high elevation, typically between 600 to 900 m. Poorly drained areas and stream channels at any elevation are also suitable sites for this forest type. The fourth, elfin (*Tabebuia rigida*) forest is located above 900 m.

The Rio Icacos watershed is one of the study areas of the NSF Long Term Ecological Research program (LTER) in Puerto Rico. The Rio Icacos watershed is located in a lower montane wet Colorado forest and the entire Rio Icacos basin is covered with 75% Colorado, 24% palm, and 1% elfin forest types and has an average channel slope of 1.4% (McDowell and Asbury, 1994). The watershed area is 326 hectares with an elevation range of 15m-800 m. Average annual rainfall is 4200 mm with a strong orographic effect (White et al., 1998) and the mean annual temperature is 24.5°C in the Icacos-Blanco basin. The USGS gauges the mainstem Icacos, its tributary the Guaba, and downstream on the Rio Blanco (Figure 2.1). Because of the steep slopes and limited

access to most of the Rio Icacos, human disturbance has not been as extensive as it was at lower elevations (Brown et al., 1983). Stream water chemistry is controlled by marine aerosols due to the close proximity of the sampling sites to the ocean in both the Icacos-Blanco sites.

2.1. Geologic setting:

The Icacos-Blanco basin has two primary geological formations, the intrusive Rio Blanco stock and a volcaniclastic basalt formation. The Rio Icacos watershed is underlain by the Rio Blanco stock, a quartz diorite (Seiders, 1971). The Rio Blanco stock is dominated by quartz and plagioclase with minor amounts of biotite, hornblende, and K-feldspar, magnetite, and apatite (Seiders, 1971; White et al., 1998). Clays and sandy clay loams are the dominant soils in the Rio Icacos watershed, of the Picacho-Utuado series (Boccheciamp, 1977). The Rio Blanco basin is underlain by volcaniclastic rock dominated by basalt consisting of calcic plagioclase feldspar and pyroxenes and minor amounts of laumontite, a calcium rich zeolite with quite variable silica to alumina ratio based on the chemistry of waters draining through it (Drever, 1988). Soils in the Humacao area of the Rio Blanco watershed are shallow to moderately deep Inceptisols (Boccheciamp, 1977).

3. Materials and Methods

3.1. Sample collection:

Water samples for full chemical analysis were collected twice from the Rio Icacos main stem, major tributaries at the main stem, and Rio Blanco during the summers of 2001 and 2002. During summer 2002 a third set of samples from the Rio Icacos mainstream alone was also collected. 103 samples were taken from the Rio Icacos-Blanco drainage system including major tributaries. Samples were collected from the Icacos-Blanco main stem in order to determine the effects of changes in lithology on concentration of major solutes in the drainage system. Additional samples were taken from tributaries along the main stem of the Icacos-Blanco system in order to determine the variation in major solutes in the different geologic regions. Based on the concentrations of major solutes from different types of samples, the principal weathering type and extent of weathering within the entire basin were evaluated. Physical parameters including water temperature, pH, electrical conductivity (EC) and dissolved oxygen were measured at the time of sampling with YSI models 63 and 55 handheld meters.

Samples for dissolved inorganic carbon (DIC) analysis were not filtered and were placed directly collected in glass autosampler vials. For most analyses, each water sample was filtered with a pre-combusted glass microfiber filter (Whatmann GF/F with a pore size 0.7μm) in the field directly into 60 mL acid washed polyethylene bottles. Samples were frozen and shipped to the Water Quality Analysis Laboratory of the University of New Hampshire for analysis. Samples were also taken in 30 mL acid-washed polyethylene bottles and kept refrigerated for dissolved silica analysis.

3.2. Analytical Methods:

DIC was analyzed with a Shimadzu TOC-5000. Dissolved Organic Carbon and total dissolved nitrogen (TDN) were measured with high temperature Pt-catalyzed combustion using a Shimadzu TOC-V_{CSH} with a Shimadzu Total Nitrogen Measuring Unit (TNM-1) or Shimadzu TOC-5000 with an Antek Chemiluminescent NO detector (Merriam et al., 1996). Dissolved organic carbon (DOC) was measured as non-purgeable organic carbon. DON was calculated by subtracting inorganic nitrogen (NO_3^- - N + NH_4^+ - N) from total dissolved nitrogen (TDN).

Alkalinity was measured by titration on the day of sampling in the field lab at Sabana Field Station of the US Forest Service. Ten ml of sample was titrated with 0.005N HCl using a mixed indicator (methyl red and bromo-chresol green) relative to a standard solution of Na_2CO_3. Major anions (Cl^-, NO_3^- and SO_4^{2-}) were measured on a high performance liquid chromatography (HPLC) with a Dionex self-regenerating suppressor (4mm), Ionpac AS4A analytical column and a Waters 431 conductivity detector. Ammonium (NH_4^+) was analyzed using the automated phenate hypochlorite method with sodium nitroprusside enhancement, and PO_4^{3-} with the automated ascorbic acid reduction method. Ammonium (NH_4^+), orthophosphate (PO_4^{3-}) and dissolved silica (SiO_2) were analyzed by automated flow injection analysis colorimetry using a Lachat QuickChem AE. Dissolved silica was analyzed by automated molybdate reactive silica. Major cations (Na^+, K^+, Mg^{2+}, and Ca^{2+}) were analyzed on an isocratic HPLC using an Alltech Universal Cation column, with Nitric acid/EDTA mobile phase and a conductivity detector. Partial pressure of carbon dioxide (pCO_2) and bicarbonate (HCO_3^-

) were calculated in stream water based on pH, DIC and water temperature (Stumm and Morgan, 1996). Silica to alumina ratio was calculated based on the chemical composition of feldspars (Tardy, 1971). The charge balance error (CBE), defined as the ratio of difference between sum of cations and sum of anions to sum of cations and sum of anions, was expressed as a percentage. Mathematically,

$CBE = (Scat - San)/ (Scat + San)*100$

Where, Scat and San are sums of measured cations and anions in milliequivalents $liter^{-1}$. Sea-salt can be corrected by using the molar ratios of various elements relative to marine aerosols (Keene et al., 1986; McDowell et al., 1990; Millot et al., 2002). In this paper, I used chloride concentration as a reference species to correct the contribution of sea-salt in stream waters for SO_4^{2-}, Na^+, K^+, Mg^{2+} and Ca^{2+} and present the sea-salt corrected chemical species with an asterisk.

4. Results

4.1. Physical parameters:

Average water temperature was 22°C in the Rio Icacos and increased to 26°C at the downstream Rio Blanco (Table 2.1). pH was 7.0 in the Rio Icacos main stem and increased to 7.4 in the Rio Blanco main stem. The average electrical conductivity was 67 $\mu S\ cm^{-1}$ in the Rio Icacos main stem and increased to 105 $\mu S\ cm^{-1}$ in the main stem of the Rio Blanco. The average dissolved oxygen was 8.26 $mg\ l^{-1}$ in the Rio Icacos main stem and increased to 8.52 $mg\ l^{-1}$ in the main stem of the Rio Blanco. Within the Rio Icacos mainstream, pH ranged from 6.95 to 7.05 and showed systematic decreases from headwater areas to downstream (Table 2.2). Electrical conductivity showed a similar systematic downstream decrease (74.3$\mu S\ cm^{-1}$ to 62.4$\mu S\ cm^{-1}$) along the Rio Icacos main stem. Dissolved oxygen was slightly higher in headwaters than downstream and ranged from 8.06 $mg\ l^{-1}$ to 8.4 $mg\ l^{-1}$ along the Rio Icacos main stem.

4.2. Chemical parameters:

4.2.1 Spatial variability of major solutes along the Rio Icacos-Blanco system:

The average value of dissolved inorganic carbon (DIC) observed along the entire Icacos-Blanco system was 8 $mg\ l^{-1}$ and DIC ranged from 7 $mg\ l^{-1}$ to 10 $mg\ l^{-1}$ along the main stem of the Rio Icacos. Dissolved inorganic carbon was higher in upstream than downstream sites in the Icacos basin and a similar concentration trend was observed in major tributaries at the main stem and concentration increased in the downstream Blanco site (Table 2.2). The average alkalinity was 26 $mg\ l^{-1}$ and increased from 21.6 $mg\ l^{-1}$ to 29 $mg\ l^{-1}$ downstream along the Rio Icacos main stem. Silica averaged 24 $mg\ l^{-1}$ and

ranged from 21.7 mg l^{-1} to 25.6 mg l^{-1} along the Rio Icacos mainstem; concentrations increased as drainage water passed from the quartz diorite of the Icacos into the Rio Blanco. Silica concentrations decreased with distance downstream on the Rio Icacos main stem, and tributary inputs to the main stem also decreased with distance downstream. Base cation concentrations showed small but systematic declines along the Icacos main stem that mirrored the patterns in silica concentrations, and showed large increases at the lowermost Rio Blanco site. Dissolved inorganic carbon concentration was an excellent predictor of Si concentrations, explaining 97% of the variance in Si concentrations (Table 2.3). It was also a strong predictor of sum of base cations (Table 2.3)

Marine aerosols contributed much of the chemical load in stream water in both the Rio Icacos and Rio Blanco (Table 2.1). The contribution of marine aerosols to cation concentrations varied along the stream channel and appeared to increase downstream (Figure 2.2). Sodium was greatly affected by sea-salt aerosols, which contributed 68% (on average) to total Na concentrations; sulfate and calcium were least affected, with a sea-salt contribution of 0-5% (Table 2.1). The downstream Rio Blanco sampling sites were more affected by sea-salt (except for sulfate and magnesium) than were the upstream Rio Icacos sites. The contribution of sea-salt to the total concentration of each species was $Na^{+} >> Mg^{2+} > K^{+} >> Ca^{2+}$ for all sampling stations in the Icacos and Blanco.

After correction for sea salt concentrations, calcium was the dominant cation in stream water followed by sodium, magnesium and potassium (Table 2.1). The contributions of calcium, sodium, magnesium and potassium in milliequivalents were 51%, 25%, 20% and 4% respectively to the sum of cations with the following order:

Ca^{2+}>> Na^{+}> Mg^{2+}>> K^{+} in all types of samples. This result suggests that calcium and sodium bearing minerals are the dominant minerals within the basin. The contribution of bicarbonate, chloride, sulfate, nitrate and phosphate were 64%, 29%, 4%, 1% and <1% respectively to the total sum of anions with the following order: HCO_3^->> Cl^->> SO_4^{2-} >NO_3^- >PO_4^{3-} in all types of samples. This result suggests that bicarbonate was the dominant anion, released as a result of weathering within the basin since there are no lithologic sources of bicarbonate within the basin.

The ratio of bicarbonate to non sea-salt sodium also supports the role of lithology in the variation of these chemical species along the drainage system, and the ratio clearly separates with the geologic boundary (Figure 2.3). The relationship between sum of calcium and magnesium concentrations with the ratios of bicarbonate to silicon clearly separates the geologic boundary and shows the role of lithology in the variation of chemical composition along the drainage system (Figure 2.4). Furthermore, the relationship between the ratio of sodium to calcium and ratio of bicarbonate to silicon clearly explain the variation in mineralogy for the variation of chemistry along the Rio Icacos-Blanco drainage system (Figure 2.5).

4.2.2 Chemical weathering within the basin:

Dissolution of plagioclase minerals (mostly albite and anorthite) and formation of kaolinite appears to drive river chemistry in the Icacos basin. Pyroxene and calcic plagioclase dissolution appeared as the dominant mineral in the Blanco area based on the stream chemistry. The variation in composition between two sites may be from other minerals as well.

Silicon, bicarbonate and base cations are byproducts of chemical weathering and showed similar concentrations along the drainage network with the exception of the most downstream station on the Blanco (RBS2), where non sea-salt Na, Ca, Mg and K all increased dramatically, up to 10-fold over upstream sites (Table 2.2). With the exception of RBS2, all other sites suggest weathering of plagioclase feldspars dominates stream chemistry. No strong evidence of human impacts on the Icacos-Blanco system was observed. Despite increasing human population density in the basin with distance downstream, nutrients that typically respond to human impacts (nitrate, phosphate) showed only modest increases with distance downstream.

The ratio of silica to alumina showed was relatively constant along the Rio Icacos main stem but was dramatically higher in the Blanco sites. The constancy of silica to alumina and silicon to bicarbonate ratios in samples within the two geologically uniform regions suggests major weathering processes in each remained the same (Figure 2.6), and the differences in two regions suggest the different proportion of chemical composition and solubility nature of minerals. The discrepancy in ratio is probably due to abundant availability of magnesium in Blanco site.

The ratios of silicon to the sum of sodium and potassium Si/ (*Na+*K), a measure of weathering extent of plagioclase minerals, were 4.31, 4.79, and 4.30 for the Rio Icacos mainstream, major tributaries at the main stem, and Rio Blanco, respectively (Table 2.1). Bisiallitization weathering, in which two moles of Si are produced for each mole of alumina, occurred in both the Icacos and Blanco basins. Average ratios of silica to alumina were above 2 at all sample sites (Table 2.1, Fig. 2.6). Formation of kaolinite, higher ratios of silicon to the sum of sodium and potassium, higher ratios of silicon to

base cations and the bisiallitization type of weathering all collectively reflect the extensive chemical weathering within the entire Rio Icacos-Blanco basin.

5. Discussion

5.1 Spatial variability of major solutes along the Rio Icacos-Blanco system:

Quantifying the effects of changes in bedrock type reveals a smooth transition in most descriptions of stream chemistry from the uppermost reaches of the Icacos to the low elevation Blanco sites. The base cation concentrations at all sites after correction for sea salt are within the range appropriate for dissolution of granitic rocks (Meybeck, 1987), and the dominance of calcium and sodium in stream water suggests that plagioclase dissolution is the dominant weathering process as observed earlier for the Rio Icacos (McDowell and Asbury, 1994). Most descriptions of weathering intensity and source materials that I have generated for this chapter show steady changes with distance downstream, such as the sum or Ca+Mg versus bicarbonate/Si, which is a measure of dissolution of pyroxene. This smooth transition in stream chemistry across bedrock types is not unexpected, as stream chemistry reflects the proportional contributions from the entire watershed, not just the contributions from the downstream drainage area adjacent to a given sampling point.

The exception to these smooth transitions in stream chemistry across the changes in bedrock type is the ratio of SiO_2/Al_2O_3, which shows a sharp break below the tuff and slope break occurring at the Icacos-Blanco transition (Figure 2.6). The ratio of SiO_2/Al_2O_3 is an indicator of weathering type; above a ratio of 2.0, the bisiallitization type of weathering is occurring (Tardy, 1971). Throughout the Icacos-Blanco system, the bisiallitization type of weathering is occurring. Increases in the ratio of SiO_2/Al_2O_3 at the Blanco sites also suggest that this ratio also is a sensitive indicator of the overall influence of bedrock composition on water chemistry. Variation in the chemical species

released during weathering reflects the solubility of the minerals involved, availability of carbonic acid, and hydrologic conditions, and the released species in turn have a significant effect on stream chemisty.

Understanding the effects of geology on stream chemistry at this site is complicated by the lack of a detailed geologic map throughout the Icacos-Blanco system. Seiders (1971) provides a detailed map of the geology of the Icacos (that portion of the basin above I3, which is at 3000 m downstream of the headwaters). The map shows intrusions of tuff between stations IS4 and IS3, which correspond to a dramatic change in the slope of the basin. Between stations 3 and 4, the Icacos changes from a sand-filled, low gradient stream to a series of waterfalls and plunge pools with high average stream gradient. This shift in stream geomorphology is striking, and is a dominant feature of the Icacos-Blanco basin.

Variation in mechanical erosion within the basin may be significant in driving variation in chemical weathering rates. A factor of ten increase in physical denudation results in a 4.5-fold increase of chemical denudation and demonstrates the tight coupling between mechanical erosion and chemical fluxes (Millot et al., 2002). Mechanical denudation due to relief is the most significant factor controlling the geochemistry of the Amazon River (Gibbs 1967). Chemical weathering rates of silicates show a strong relationship with mechanical denudation rates because weathering is enhanced when mechanical erosion continuously refreshes mineral surfaces (Reynolds and Johnson, 1972; Stallard and Edmond, 1983; Edmond and Huh, 1997; Millot et al., 2002). The Icacos has a very high frequency of landslides, and its steep flanks drain into the relatively flat main stem of the Rio Icacos. Mechanical erosion of these headwaters is

probably important in producing the high weathering rates seen throughout the basin by this study and earlier ones (McDowell and Asbury 1994; White et al. 1998).

Release of weathering products in the Icacos is tightly coupled to HCO_3 concentrations in stream water, but is unrelated in the Blanco (Fig. 2.7). Production of HCO_3 from weathering is a dominant source of alkalinity in this watershed, as there are no carbonate minerals in the basin. The production of Si and HCO_3 approaches the theoretical molar ratio of 2 moles bicarbonate produced for each mole of silica released during the weathering of plagioclase. The decrease in HCO_3 per mole of Si released in the Blanco is likely the result of increased pyroxene content in the Blanco bedrock.

The pCO_2 values which we have obtained for the Icacos-Blanco system (2-4 times saturation; Table 2.1) are lower than those typically observed in the Amazon River (Richey et al. 1980). The Amazon, unlike the Icacos, has high levels of respiration fueled in part by primary productivity in the river (Richey et al., 1980) and high pCO_2 values are expected in such a respiration-dominated system (Stallard and Edmond, 1987).

Initial cation release from biotite is significantly faster than cation release from plagioclase at lower temperatures (White 1998, White et al. 1999). This observation may be responsible for my observation that (*K/*Na) ratios vary with sampling location and temperature in the Icacos-Blanco system. The average potassium to sodium ratio (0.14) and average ratio of silicon to sum of sodium and potassium (4.3) which I obtained are very similar to those observed by McDowell and Asbury (1994), reflecting the lack of temporal variability in weathering processes in the basin (Table 2.4). The decrease in stream (K*/*Na) ratios with temperature along the Icacos-Blanco drainage reflects

differences in the temperature sensitivity of biotite and plagioclase weathering (Figure 2.8).

Marine aerosols can contribute much of the chemical load to a watershed, and the contribution of marine aerosols varies with proximity to the ocean (Stallard and Edmond, 1981; McDowell et al., 1990; Gaillardet et al., 1999). My results clearly show this pattern for sodium, which was greatly affected by sea-salt aerosol in all samples along the drainage system but also showed clear increases in sea-salt contributions as a function of distance to the Caribbean Sea (Figure 2.2).

Marine aerosols and chemical weathering are the dominant controls on most dissolved solutes in the Rio Icacos-Blanco drainage system. At the lowermost site on the Rio Blanco, however, modest increases in dissolved organic carbon and inorganic nitrogen suggest that anthropogenic activities may also have an effect on stream chemistry in the Blanco.

5.2 Evidence of chemical weathering within the basin:

The weathering type occurring in the Icacos-Blanco system was evaluated by considering the chemical composition of feldspar to calculate the ratios of silica to alumina based on the chemical composition of stream waters (Tardy, 1971). Tardy described three types of weathering based on the silica to alumina ratio. If the ratio is greater than two, the weathering type is considered to be bisiallitization, in which base cations are completely removed and a portion of the silica remains in situ with two silica layers per alumina. The average ratios of silica to alumina were 2.31, 2.57, and 4.18 respectively for the Rio Icacos mainstream, major tributaries at mainstream, and Rio

Blanco respectively indicating that the bisiallitization type of weathering occurs throughout the entire Rio Icacos-Blanco basin.

The ratios of silicon to base cations and silicon to the sum of sodium and potassium can be use to evaluate the extent of chemical weathering (Huh et al., 1998). This can also be evaluated based on the formation of weathering products like kaolinite and gibbsite. Conversion of sodium plagioclase to kaolinite gives a ratio of silicon to sum of sodium and potassium (Si/*Na+*K) of 2; conversion to gibbsite gives a ratio of 3, and conversion of K-feldspar to illite also gives a ratio of 3. Ratios higher than 3 indicate complete removal of basic cations from the aluminosilicate minerals. The average ratios of silicon to sum of sodium and potassium were 4.31, 4.79, and 4.30 for the Rio Icacos mainstream, major tributaries at the mainstream, and Rio Blanco respectively. These ratios suggest that chemical weathering of aluminosilicate minerals is very extensive within the entire Rio Icacos-Blanco basin, with complete removal of basic cations from the aluminosilicate minerals. The ratio showed systematic declines within each geologic zone but along the entire drainage system its pattern was reversed.

5.3 Comparison of weathering extent with other granitoid watersheds:

On a global scale, silicate weathering contributes 26% of the total dissolved solid flux transported into the ocean and CO_2 consumption by rock weathering is 0.252 Gt C yr^{-1}, 40% of which is due to the weathering of silicates (Gaillerdet et al., 1999). Silicon flux in small Caribbean watersheds is exceptionally high in comparison to global averages (McDowell and Asbury, 1994; McDowell et al., 1995). Several compilations of granitoid weathering rates testify to the fact that the Icacos is the fastest weathering

aluminosilicate terrain in the world (e.g. White and Blum 1995; Millot et al. 2002). Among all the granitoid watersheds of the world, silica and sodium concentration was much higher in the Rio Icacos watershed than the other watersheds. Much higher silicon (Figure 2.9) was released from the tropical Rio Icacos rainforest relative to temperate rainforests with comparable precipitation in British Columbia and Alaska, and White and Blum (1995) have argued that temperature is most important in driving the high rates of chemical weathering in the Icacos. Such large differences in silica flux appear despite similarity in annual precipitation, dense species rich vegetation, very steep topography and high physical erosion rates in both of these watersheds. Hence White and Blum, (1995), argued that topography and physical erosion are less important than climate (primarily temperature and precipitation) in controlling chemical weathering rates in watersheds.

In contrast, Millot et al. (2002) argued that physical erosion is centrally important in driving variability in chemical weathering rates. The rocks of the Caura River drainage in Venezuela contain some easily weathered minerals, including feldspar and hornblendes in the granitic rocks that contribute major amounts of silica and sodium and calcium, magnesium and potassium (Lewis et al., 1987). The silicon released from this watershed is nearly three times less than Rio Icacos although both watersheds are lying in the same tropical region underlain by similar granitoid rocks. This suggests that the differences in silicon concentration between the Caura and Icacos area probably due to variations in mechanical denudation rate.

Comparison of the Icacaos and another tropical watershed, the Mengong, provides further support for the importance of mechanical denudation in controlling chemical

weathering fluxes. The fluxes of silica and non-sea salt sodium from the Rio Icacos watershed are 16 and 40 times higher than the Mengong Brook watershed at Nsimi, South Cameroon respectively, as reported by Braun et al. (2005). Such wide differences in silica and sodium fluxes appear despite similar lithology, vegetation, climatic condition and topography in the two basins, and are thought to be due to differences in mechanical denudation rates (Braun et al. 2005). Variation in physical erosion (mechanical denudation) thus appears to be the most important factor controlling variation in chemical weathering rates among tropical granitoid watersheds.

6. Conclusion

The concentration trends of major solutes like silicon, alkalinity and base cations are slightly higher in the upstream side than the downstream side of the Rio Icacos basin but the trend reverses as the parent material changes. Such a longitudinal variation of major solutes along the Rio Icacos-Blanco drainage network is due to the variability of dissolved inorganic carbon and the solubility of parent material. The higher ratio of silicon to sum of base cations testifies to the high rates of aluminosilicate weathering occurring along the Rio Icacos-Blanco drainage system. The primary minerals, albite and anorthite are sources for the major solutes and appear to vary systematically with the distance downstream, depending primarily on the availability of dissolved inorganic carbon and variation in relief along the geologically uniform basin. Hence it is clear that the dissolved inorganic carbon coupled with the availability of reactive mineral surface regulates the solute release rates in a geologically uniform landscape. The ratios of silica to alumina and silicon to alkalinity suggest that the bisiallitization type of weathering has been dominantly occurring within the entire Rio Icacos-Blanco basin and constancy of this ratio in the separate geologic regions explains why the principal weathering process remains the same across the Icacos-Blanc landscape. The ratio of silicon to sum of sodium and potassium (Si/*Na+*K) is greater than four throughout the basin and attests to the complete weathering of aluminosilicates that takes place within the entire Rio Icacos-Blanco basin. The chemical weathering rates coupled with the parent materials are responsible for the longitudinal variability of chemical composition along the Rio Icacos-Blanco system.

Table 2.1. Average physical parameters and chemical concentrations of major chemical species in the Rio Icacos mainstream, major tributaries at mainstream, tributary transects, Rio Blanco mainstream and tributaries at mainstream on Blanco during summer 2001-2002. Asterisks represents seasalt corrected values.

Measured parameter	Rio Icacos Mainstem			NSS*	Tributaries at mainstem on Icacos			NSS*	Rio Blanco Mainstem			NSS*	Tributaries at mainstem on Blanco			NSS*
		mg/L	meq/L	meq/L		mg/L	meq/L	meq/L		mg/L	meq/L	meq/L		mg/L	meq/L	meq/L
WT (C)	21.9				21.9				25.5				24.1			
pH	7.0				6.9				7.5				7.5			
EC (uS)	67.1				60.6				110.8				84.1			
DO		8.26				7.99				8.47				8.05		
NPOC		1.43				1.17				2.39				1.87		
TDN		0.271				0.182				0.366				0.114		
DON		0.062				0.053				0.263				0.078		
Alk		25.7	0.421			21.1	0.346			45.0	0.738			35.5	0.581	
HCO_3^-		37.5	0.614			15.8	0.259			61.1	1.001			45.3	0.743	
Cl		6.68	0.188			6.55	0.185			15.40	0.434			9.15	0.258	
SO_4-S		0.451	0.009	-0.011		0.387	0.008	-0.011		2.160	0.045	0.000		1.590	0.033	0.006
NO_3-N		0.195	0.003			0.117	0.002			0.150	0.002			0.030	0.000	
PO_4-P		0.014	0.000			0.010	0.000			0.009	0.000			0.008	0.000	
San			0.622				0.541				1.220				0.873	
Scat			0.579				0.520				1.250				0.717	
CBE (%)	-3.6				-2.0				1.2				-9.8			
NH_4-N		0.014	0.001			0.013	0.001			0.020	0.001			0.005	0.000	
Na		5.86	0.255	0.093		5.62	0.244	0.085		11.3	0.490	0.116		6.75	0.294	0.072
K		0.63	0.016	0.012		0.584	0.015	0.012		1.78	0.046	0.038		0.500	0.013	0.008
Mg		1.36	0.111	0.074		1.22	0.101	0.064		5.33	0.438	0.353		1.940	0.160	0.109
Ca		3.93	0.196	0.189		3.19	0.159	0.152		5.52	0.275	0.259		5.02	0.250	0.240
SiO_2		23.9				21.2				19.8				24.1		
Si/(*Na+*K)	4.31				4.79				3.39				5.22			
SiO_2/Al_2O_3	2.31				2.57				4.25				4.11			
DIC (mmol/L)	0.355				0.327				1.133				0.795			
mCO_2(mmol/L)	0.046				0.066				nd				nd			
cCO_2(mmol/L)	0.064				0.086				0.130				0.050			
pCO_2(µatm)	3542				2602				4162				1482			

WT= Water temperature, CBE = Charge balance error

San=Sum of anions, Scat= Sum of cations, mCO_2 = Directly measured by Gas Chromatograph and cCO_2 = Calculated

Table 2.2 Spatial changes in average physical and chemical parameters of stream waters along Rio Icacos-Blanco River system during summer 2001-2002.

Sample Name	WT °C	pH	EC µS	DO mg/L	DIC mg/L	NPOC mg/L	TDN mg/L	Alk meq/L	Cl meq/L	*SO_4 meq/L	NO_3 meq/L	PO_4 µeq/L	NH_4 µeq/L	*Na meq/L	*K meq/L	*Mg meq/L	*Ca meq/L	SiO_2 mg/L
RIS10	21.0	7.4	74	9.4	10.59	1.10	0.34	0.50	0.21	0.02	0.009	3.20	0.33	0.13	0.017	0.09	0.23	28
RIS9	21.2	7.1	73	8.9	9.83	1.21	0.32	0.50	0.19	0.02	0.007	2.69	0.41	0.11	0.014	0.08	0.19	28
RIS8	21.4	7.1	74	8.4	9.55	1.35	0.37	0.48	0.19	0.01	0.011	1.63	0.44	0.10	0.014	0.08	0.22	26
RIS7	21.7	7.1	70	8.4	8.86	1.50	0.29	0.45	0.18	0.01	0.009	1.15	0.44	0.10	0.012	0.08	0.20	25
RIS6	21.9	7.0	62	8.1	8.85	1.44	0.24	0.44	0.19	0.01	0.008	0.82	0.55	0.09	0.012	0.07	0.20	24
RIS5	22.5	7.0	66	8.1	8.08	1.40	0.24	0.39	0.19	0.01	0.007	0.57	0.53	0.09	0.012	0.07	0.17	23
RIS4	22.2	6.9	63	8.3	7.13	1.46	0.22	0.35	0.19	0.01	0.006	0.68	2.59	0.08	0.012	0.07	0.15	22
RBS7	25.7	7.6	78	8.9	9.32	1.73	0.43	0.52	0.23	0.03	0.005	0.74	0.35	0.09	0.012	0.08	0.21	22
RBS3	25.3	7.6	74	9.3	12.72	2.36	0.21	0.49	0.39	0.02	0.007	0.69	0.60	0.02	0.011	0.07	0.18	19
RBS2	25.7	7.1	162	7.4	18.81	3.08	0.45	1.20	0.68	0.22	0.021	1.11	3.22	0.24	0.089	0.91	0.39	19
RIST1	21.5	7.6	53	9.0	3.13	0.78	0.19	0.28	0.20	0.00	0.010	0.64	0.64	0.08	0.007	0.05	0.12	20
RIST2	21.5	6.8	55	8.6	3.84	1.65	0.16	0.35	0.18	0.00	0.007	0.81	0.42	0.08	0.006	0.07	0.16	21
RIST3	21.7	6.5	20	8.6	4.00	0.37	0.17	0.32	0.19	0.00	0.009	0.68	1.03	0.09	0.010	0.05	0.10	22
RIST4	22.1	6.5	44	8.7	3.87	0.46	0.15	0.28	0.19	0.01	0.009	0.43	1.67	0.07	0.008	0.05	0.13	18
RIST5	21.7	6.9	55	8.8	4.09	1.26	0.12	0.33	0.18	0.01	0.006	0.94	0.49	0.07	0.008	0.06	0.14	21
RIST6	21.5	6.8	50	8.6	3.42	0.62	0.19	0.27	0.19	-0.01	0.013	0.84	0.54	0.07	0.009	0.04	0.12	20
RIST7	22.5	6.2	55	7.5	4.49	0.59	0.08	0.30	0.13	-0.01	0.004	0.56	1.92	0.03	0.009	0.04	0.10	15
RIST8	21.6	6.5	54	8.6	4.97	0.48	0.14	0.38	0.16	0.00	0.010	1.13	1.01	0.10	0.012	0.06	0.11	24
RIST9	23.5	6.7	43	7.9	2.28	1.62	0.12	0.18	0.19	0.00	0.003	0.62	8.56	0.07	0.004	0.04	0.07	15
RIST10	22.4	6.8	69	8.4	5.41	0.82	0.11	0.38	0.20	-0.01	0.003	1.03	4.11	0.09	0.011	0.07	0.12	20
RIST11	21.6	6.9	51	8.7	4.79	0.36	0.16	0.45	0.16	-0.01	0.007	1.71	0.64	0.10	0.008	0.05	0.12	29
RIST12	21.5	6.8	56	8.7	4.33	0.50	0.11	0.38	0.14	-0.01	0.006	0.98	0.27	0.07	0.008	0.04	0.08	23
RIST13	21.2	6.9	58	8.8	5.10	0.57	0.12	0.47	0.15	-0.01	0.006	0.68	0.20	0.09	0.011	0.06	0.14	26
RIST14	21.3	7.3	62	9.2	4.60	0.70	0.15	0.43	0.17	0.00	0.006	1.72	0.23	0.13	0.011	0.08	0.18	26
RBS6	23.6	7.2	96	7.7	10.79	1.02	0.06	0.64	0.29	0.15	0.000	0.75	0.19	0.08	0.003	0.17	0.31	28
RBS5	24.1	7.5	62	8.6	8.17	1.79	0.13	0.44	0.22	0.02	0.004	0.76	0.48	0.08	0.012	0.06	0.17	22
RBS4	24.6	7.8	92	8.6	9.69	2.80	0.16	0.66	0.26	0.05	0.002	0.76	0.47	0.06	0.010	0.10	0.2	22

Table 2.3 Linear regression parameters describing relationship of dissolved inorganic carbon with released solutes along the Rio Icacos-Blanco drainage system during summer 2002. Asterisk represent seasalt corrected values.

Measured parameters	Intercept	Slope	R^2	P-value
Alk	8.1222	2.6665	0.75	<0.0001
*Scat	3.8614	0.4426	0.78	<0.0001
Si	9.6402	0.2514	0.36	<0.01

Table 2.4. Comparison of average chemical composition with a previous study of the Rio Icacos basin. Asterisk represents sea-salt corrected values.

Measured parameters	HCO_3^- (meq/L)	Si (meq/L)	*Na (meq/L)	*K (meq/L)	*Mg (meq/L)	*Ca (meq/L)	Si/*Na+*K	*K/*Na
Rio Icacos[1]	0.346	1.218	0.069	0.010	0.064	0.160	4.36	0.14
This study	0.421	1.588	0.092	0.012	0.075	0.189	4.31	0.14

[1]Data from McDowell and Asbury (1994). Used data are the mean concentration at the outlet.

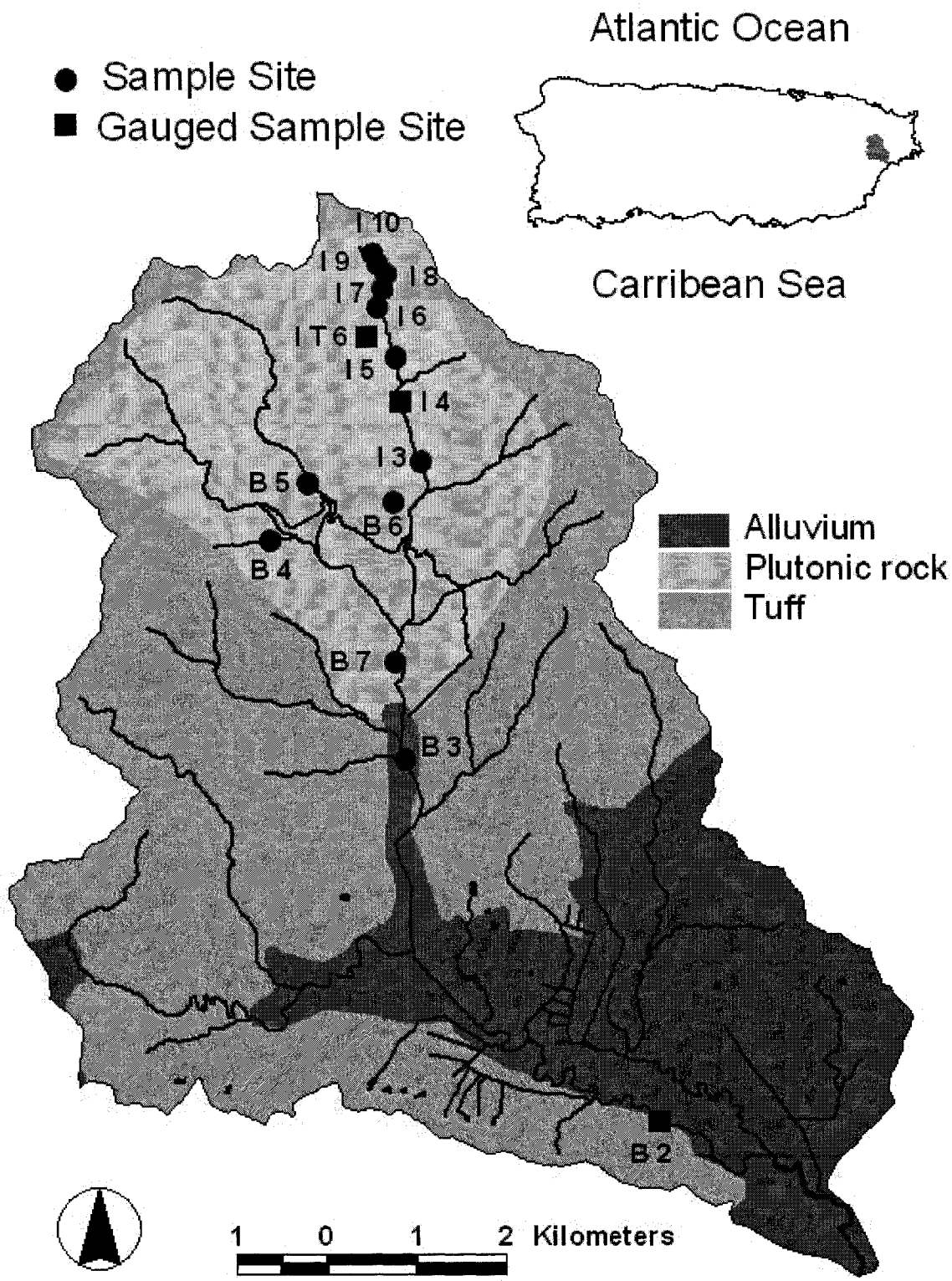

Figure 2-1. Blanco watershed and sampling locations

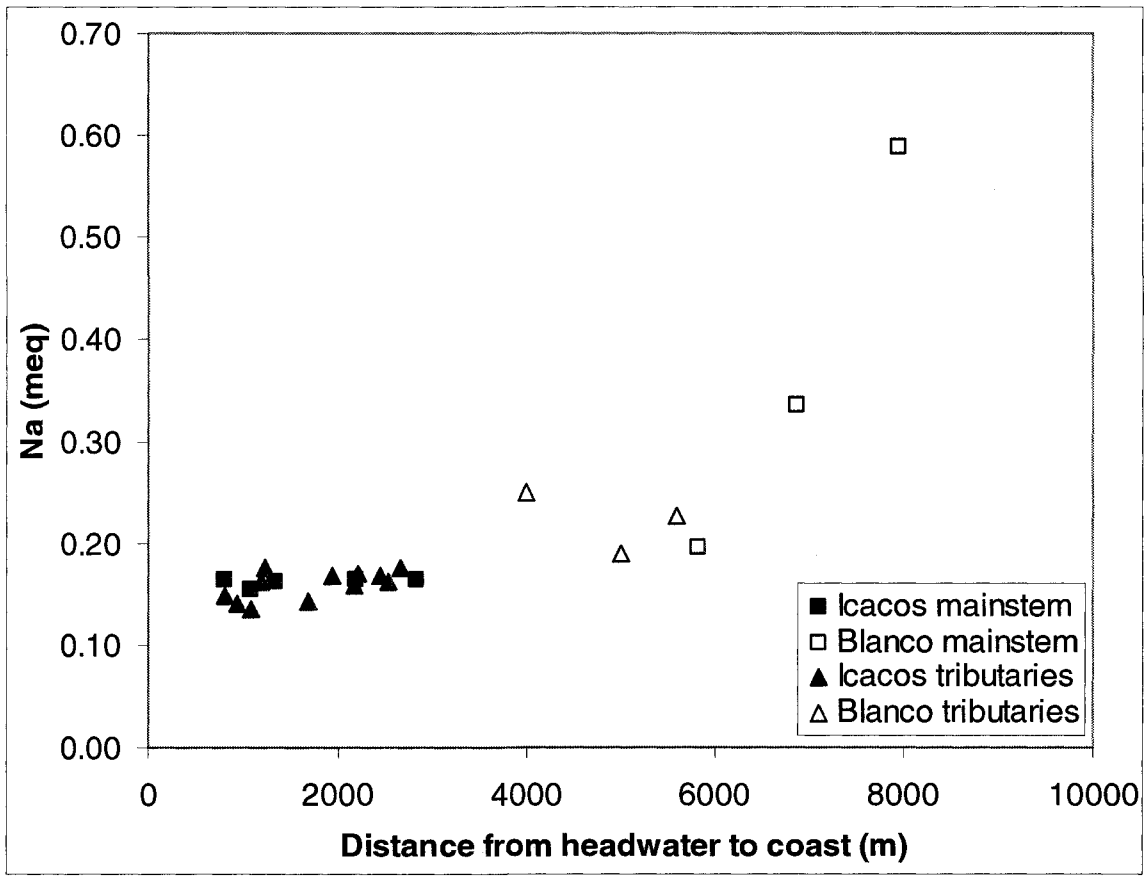

Figure 2.2 Variation of sea-salt derived sodium along the Rio Icacos-Blanco drainage system during summer 2001-2002. Four to five times sampled, n = 97. Distance is measured from headwaters to coastal sites.

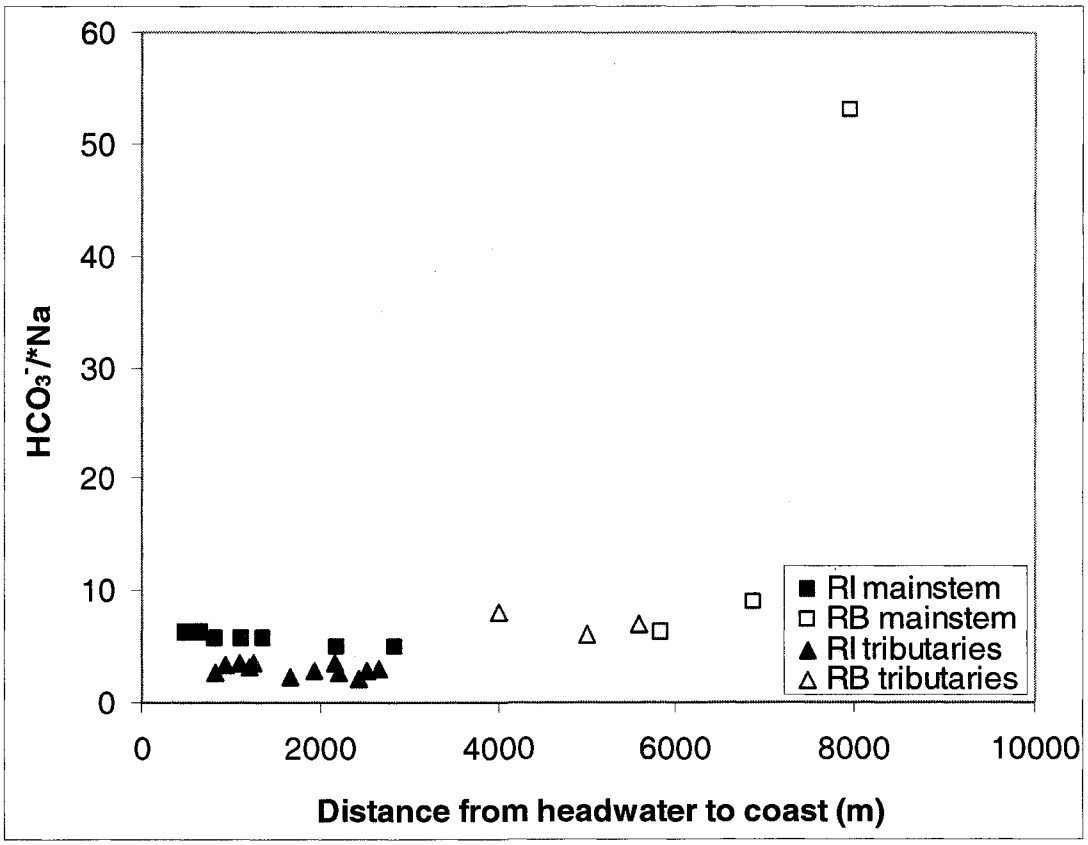

Figure 2.3 Variation of molar ratio of bicarbonate to sodium along the Rio Icacos-Blanco drainage system during summer 2002. Two to three times sampled, n = 57.

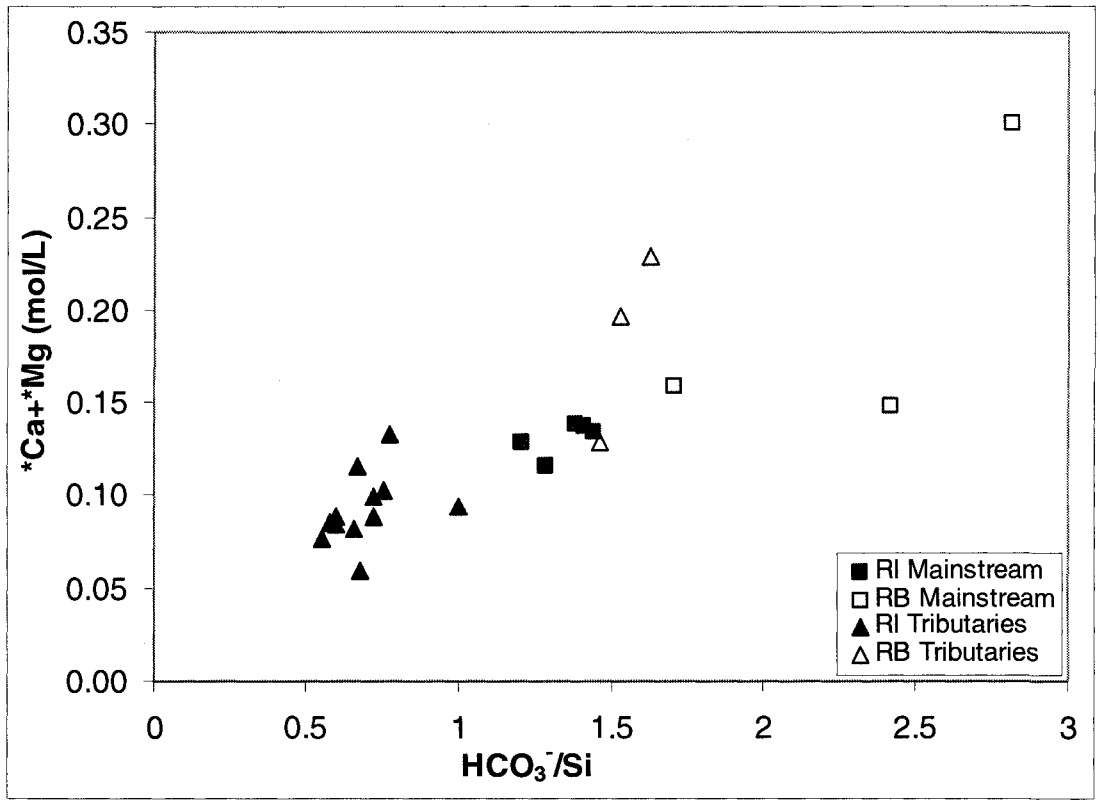

Figure 2.4 Relationship between sum of calcium and magnesium and the ratio of bicarbonate to silicon along the Rio Icacos-Blanco drainage system during summer 2002. Two to three times sampled, n = 51.

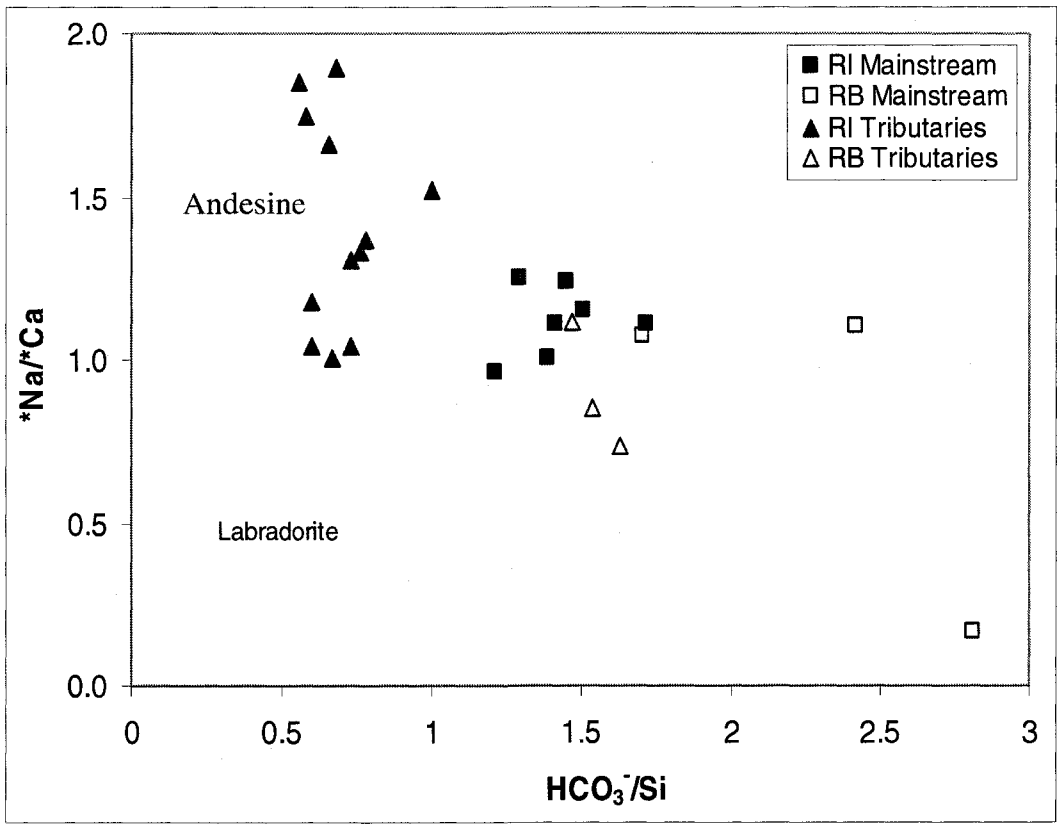

Figure 2.5 Relationship between average ratio of sodium to calcium and average ratio of bicarbonate to silicon during summer 2002. Two to three times sampled, n = 57.

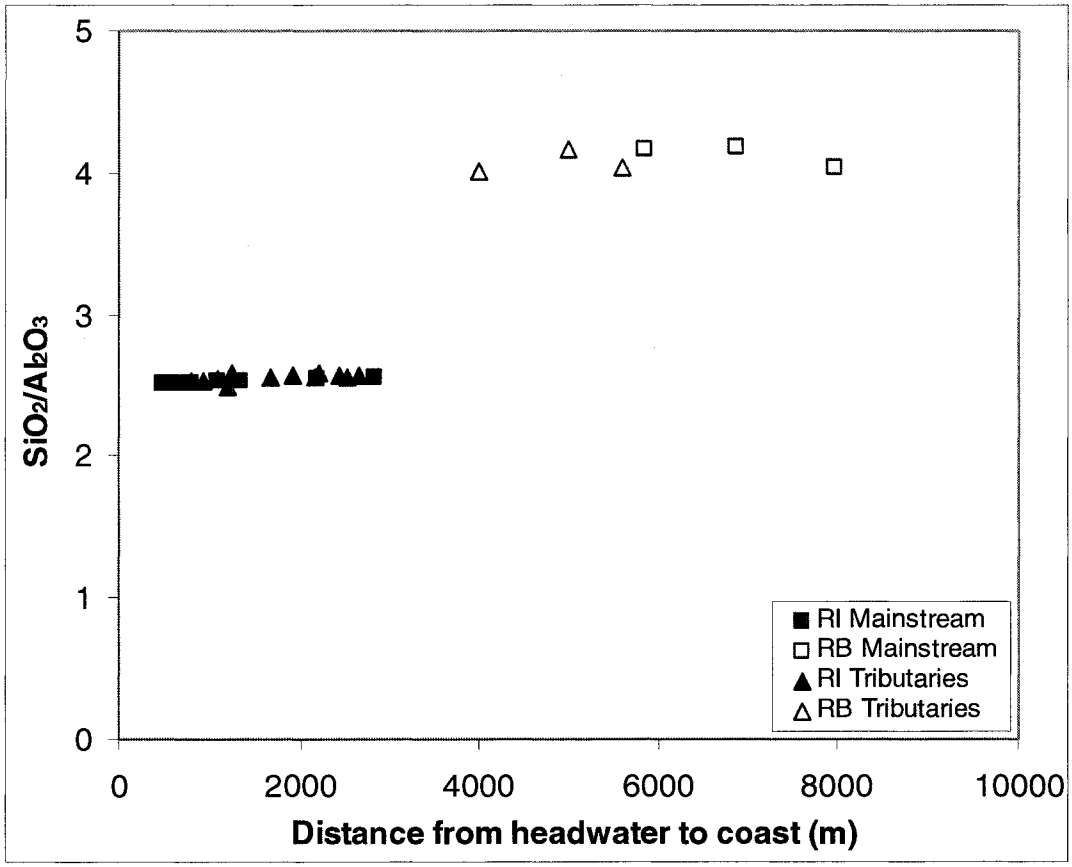

Figure 2.6 Variation of average ratio of silica to alumina along the Rio Icacos-Blanco drainage system during summer 2002. Two to three times sampled, n = 57.

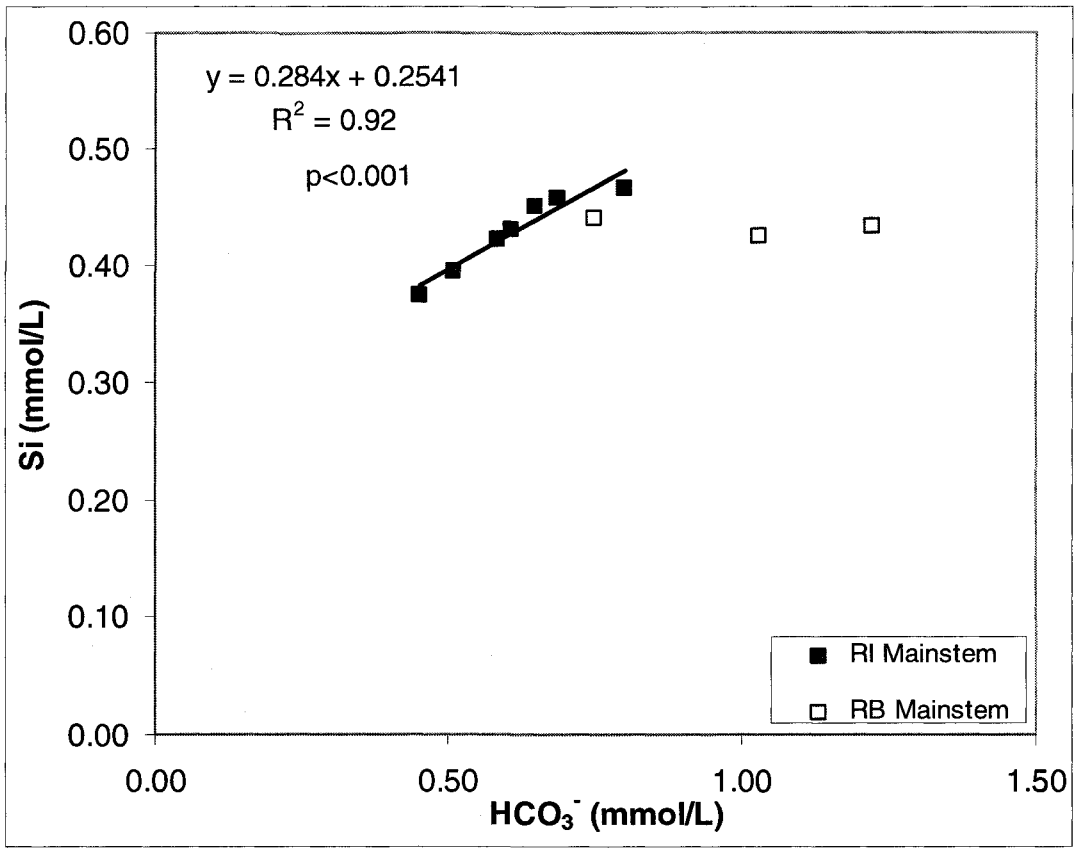

Figure 2.7 Relationship between average silicon and average bicarbonate along the Rio Icacos-Blanco drainage system during summer 2002. Two to three times sampled, n = 57.

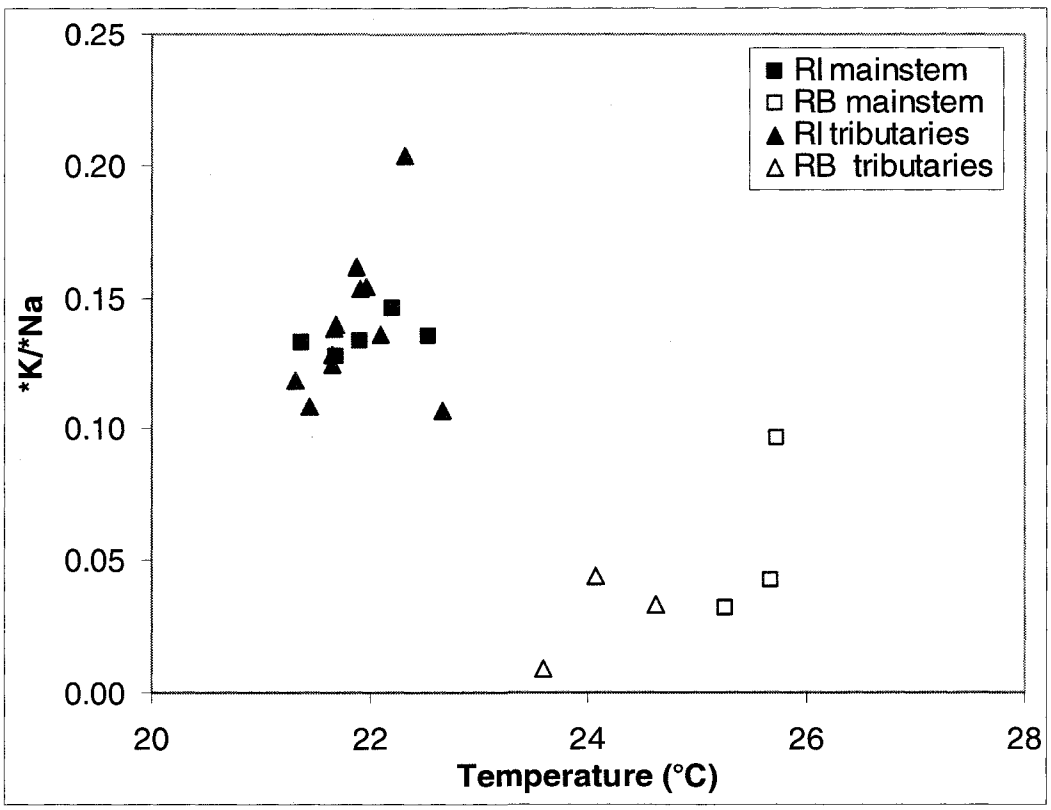

Figure 2.8 Relationship between average ratios of potassium to sodium and temperature along the Rio Icacos-Blanco drainage system during 2001-2002. Four to five times sampled, n = 97.

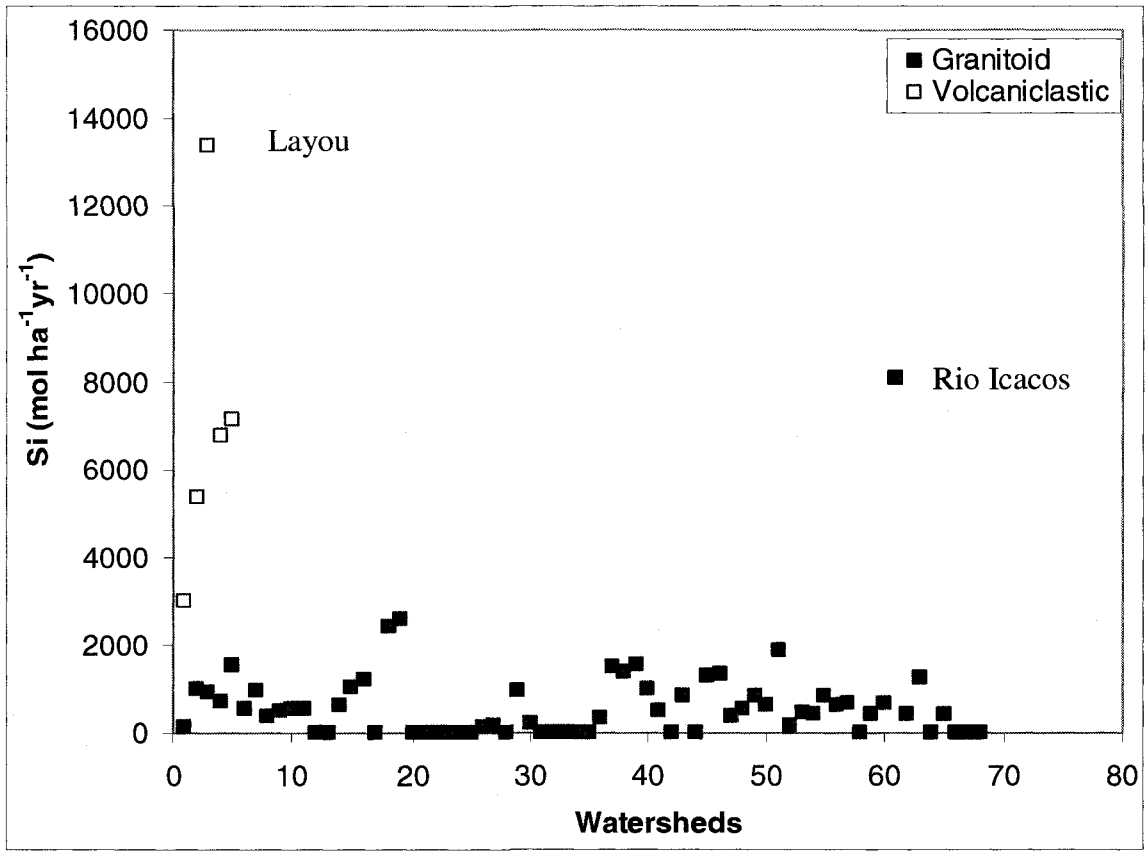

Figure 2.9 Comparison of silicon flux of Rio Icacos with other granitoid watersheds of the world and other tropical watersheds in the same area with different bedrock types (Data Source: McDowell and Asbury, 1994; McDowell et al., 1995; White and Blum, 1995). Granitoid watersheds, n = 68; Volcaniclastic watersheds, n = 5.

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CHAPTER III

SPATIAL VARIABILITY IN MAJOR SOLUTES WITHIN THE RIO ICACOS WATERSHED OF THE LUQUILLO EXPERIMENTAL FOREST, PUERTO RICO

Abstract

Surface water chemistry throughout the Rio Icacos basin within the Luquillo Experimental Forest, Puerto Rico was studied to investigate the factors regulating spatial variability in major solutes. Concentrations of silicon, alkalinity and the sum of base cations were much higher in the main stem than at other sites, and were progressively lower at tributaries to the main stem, source points originating at upper elevations, and source points originating at lower elevations. The dominance of calcium and sodium after sea-salt correction reflects the weathering of plagioclase feldspar, the dominant mineral in the basin. The partial pressure of pCO_2 is much higher in the low-elevation source points than at other positions in the landscape; when coupled with the relatively low concentrations of Si and base cations at these sites, this suggests that the availability of primary reactive minerals, rather than carbonic acid concentrations, limits weathering in these low-elevation sources that are relatively close to the main stem. Carbon dioxide is the dominant component of DIC in erosional environments and lower elevation source points, and bicarbonate is the dominant component of DIC in the main stem, tributaries at the main stem and upper source point sites. Mechanical denudation appears to enhance chemical weathering

rates not only by refreshing reactive mineral surfaces but also by contributing carbon dioxide from the decomposition of organic-rich material in landslides, which occur frequently. The bisiallitization type of weathering is dominant within the entire Rio Icacos basin, based on the ratios of Si to Al. The spatial variability of major solutes depends primarily on the availability of fresh primary reactive minerals, carbon dioxide concentrations and hydrolysis conditions.

Introduction

Biogeochemical processes play a major role in driving spatial variability of surface water chemistry in forested landscapes. Chemical weathering processes are one of the dominant sources of dissolved solutes in surface waters of most landscapes, but the drivers responsible for regulating solute release are likely to vary from biome to biome. Rates of chemical weathering depend primarily on mineralogy of the bedrock in a basin, temperature, and the availability of carbon dioxide in a system (Gibbs, 1970; Garrels and Mackenzie, 1971; Stallard and Edmond 1983; Holland, 1984; White and Blum, 1995, Millot et al., 2002). The effects of climate on the rates of chemical weathering of silicate minerals have received considerable attention in the literature (Walker et al., 1981; Brady and Carroll, 1994; Lasaga et al., 1994; Dorn and Brady, 1995; White and Blum, 1995; Gaillardet et al., 1999; White et al., 1999; Millot et al., 2002), because weathering of silicate rocks consumes higher amounts of carbon dioxide than most other rocks (Brady, 1991; Velbel, 1993; Ludwig et al., 1998; Gaillardet et al., 1999). The global budget of CO_2 is considered to be an important driver of weathering rates over geologic time (White and Blum, 1995; Walker et al., 1981; Brady and Carroll, 1994). The consumption of carbon dioxide by chemical weathering during the dissolution process is equal to the bicarbonate fluxes in the silicate minerals and equal to half of the bicarbonate fluxes in the carbonate minerals based on the dissolution reactions (Garrels and Mackenzie, 1971; Kempe, 1979; Meybeck, 1987; Amiotte Suchet and Probst, 1995; Gaillardet et al., 1995; Ludwig et al., 1998; Raymond and Cole, 2003).

Tropical ecosystems play a major role in global biogeochemical cycles and are likely to have substantial effects on the global carbon budget and delivery of solutes to the global ocean (Stallard and Edmond, 1983; Meybeck, 1987; Lal et al., 2000). Chemical weathering rates can be very high in humid tropical environments (e.g. McDowell and Asbury 1994), but it is not clear whether climate alone can account for this observation (White and Blum 1995; Millot et al. 1992). The weathering of grainitoid rocks under tropical conditions in the Rio Icacos watershed initially reported by McDowell and Asbury (1994) was later shown to be the fastest documented weathering rate of any silicate terrain in the world (White et al., 1998; Braun et al., 2005; Millot et al., 2002). The primary sites for this extremely fast weathering in the Icacos basin are not known, nor is it clear what specific biogeochemical factors contribute to this high weathering rate.

Surface water from the main stem, tributaries at the main stem, tributary transects, and upper and lower elevation source points was sampled in the Rio Icacos basin to investigate the factors responsible for spatial variability of major solutes. I hypothesized that variability in pCO_2 would drive spatial variability in solute concentrations, with high concentrations of weathering products associated with high pCO_2.

2. Study area

The research was conducted in the Rio Icacos watershed within the Luquillo Experimental Forest (LEF) in northeastern Puerto Rico (Figure 3.1). The LEF is also called the Caribbean National Forest and is administered by the United States Department of Agriculture (USDA) Forest Service. The LEF has been divided into

four different forest classes based on the dominant tree species (Brown et al., 1983). The tabonuco (*Dacryodes excelsa*) forest type is found at elevations of 200-600 m. Colorado (*Cyrilla racemiflora*) forest type covers the elevation range of 600-750 m. Palm (*Prestoea Montana*) forest type occurs usually at high elevation, typically between 600 to 900 m. Poorly drained areas and stream channels are suitable sites for this forest type. The fourth, elfin (*Tabebuia rigida*) forest is located above 900 m.

The Rio Icacos watershed is one of the study areas of NSF Long Term Ecological Research program (LTER) in Puerto Rico. The Rio Icacos watershed is located in a lower montane wet Colorado forest and the entire Rio Icacos basin covered with 75% Colorado, 24% palm, and 1% elfin forest types and has an average channel slope of 1.4% (McDowell and Asbury, 1994). The watershed area is 326 hectares with an elevation range of 600-800 m. Annual average rainfall is 4200 mm with a strong orographic effects and the mean annual temperature is 22°C (White et al., 1998). The USGS gauges the main stem Icacos and its tributary the Guaba (Figure 3.1). Past human land use in the Rio Icacos basin was relatively minor because of the steep slopes. Marine aerosols have a strong influence on stream water chemistry due to the proximity of the Rio Icacos to the sea (McDowell and Asbury 1994; Chapter 2).

The Rio Icacos watershed is underlain by the Rio Blanco stock, a quartz diorite (Seiders, 1971). The Rio Blanco stock is dominated by quartz and plagioclase with minor amounts of biotite, hornblende, and K-feldspar, magnetite, and apatite (Seiders, 1971; White et al., 1998). Clays and sandy clay loams are the dominant soils in the Rio Icacos watershed, of the Picacho-Utuado series (Boccheciamp, 1977).

Sample sites were established on the main stem of the Rio Icacos, at the mouths of tributaries entering the Icacos, in transects along several of the major tributaries, and at source points from high and low elevations. High elevation source points drained the flanks of the Rio Icacos basin, where slopes at times exceeded 50%. Low-elevation sources drained less steep terrain closer to the main stem. Source points were defined as the first appearance of flowing water in the headwaters of tributaries to the Icacos. High elevation source points appeared to originate from landslides or other mass wasting events with a variety of ages. Some of the upper elevation source points were on very recent landslides with bare bedrock of approximately 100-1000 m^2 exposed by the slide. Even at low elevations, source points were frequently associated with relatively fresh mass wasting, although none of the low-elevation source points drained freshly exposed bedrock surfaces.

3. Materials and Methods

3.1. Sample collection

Water samples were collected from the Rio Icacos main stem, tributaries at the main stem, transects along tributaries and twice from a set of upper and lower elevation source points during winter 2005. 108 samples were taken for this study including main stem, major tributaries and tributary transects collected during 2002 and 2005. DIC and carbon dioxide samples were not filtered and were collected directly into syringes or autosampler vials. For all remaining analyses, water samples were filtered with a pre-combusted glass microfiber filter (Whatman GF/F with a pore size 0.7μm) in the field. Samples were taken directly into 60 ml acid washed polyethylene bottles, refrigerated and frozen in the field lab at El Verde Field Station, and sent frozen to the Water Quality Analysis Laboratory of the University of New Hampshire for analysis. Samples were also taken in 30 ml acid-washed polyethylene bottles and refrigerated in the field lab at El Verde Field Station and sent to University of New Hampshire unfrozen for dissolved silica analysis. Physical parameters including water temperature, pH, and electrical conductivity and dissolved oxygen were measured at the time of sampling with YSI models 63 and 55 handheld meters, respectively.

3.2. Analytical Methods

Dissolved inorganic carbon (DIC) was analyzed in the acidified water samples on the day of sampling with a gas chromatograph. Dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) were measured with high temperature Pt- catalyzed combustion using a Shimadzu TOC-V_{CSH} with a Shimadzu Total Nitrogen Measuring

Unit (TNM-1) or Shimadzu TOC-5000 with an Antek chemiluminescent NO detector (Merriam et al., 1996). Dissolved organic carbon was measured as non-purgeable organic carbon. DON was calculated by subtracting inorganic nitrogen (NO_3^- - N + NH_4^+ - N) from total dissolved nitrogen (TDN).

Alkalinity was measured by titration on the day of sampling in the field lab at El Verde. Ten ml of a sample solution was titrated with 0.005N HCl using a mixed indicator (methyl red and bromo-chresol green) relative to a standard solution of Na_2CO_3. Major anions (Cl^-, NO_3^- and SO_4^{2-}) were measured using high performance liquid chromatography (HPLC) with a Dionex self-regenerating suppressor (4mm), Ionpac AS4A analytical column and a Waters 431 conductivity detector. Major cations (Na^+, K^+, Mg^{2+}, and Ca^{2+}) were analyzed on a similar HPLC using an Alltech Universal Cation column, with Nitric acid/EDTA mobile phase and conductivity detection. For nutrients and SiO_2, samples were analyzed with identical chemistries using either a Lachat QuickChem AE (before 2005) or a Westco Smart Chem robotic analyzer (2005). Ammonium (NH_4^+) was analyzed using the phenate hypochlorite method with sodium nitroprusside enhancement; PO_4^{3-} was measured with the ascorbic acid reduction method, and dissolved silica (SiO_2) was analyzed as molybdate-reactive silica. Partial pressure of carbon dioxide (pCO_2) in stream water was estimated based on pH, DIC and water temperature (Stumm and Morgan, 1996). Carbon dioxide content of water samples was also measured directly on the day of sampling using gas chromatography with thermal conductivity detection. Sea-salt inputs to a basin can be estimated using the molar ratios of various elements found in marine aerosols (Keene et al., 1986; McDowell et al., 1990; Millot et al., 2002). In

this paper, we used chloride concentration as a reference species to correct the contribution of sea-salt in stream waters for SO_4^{2-}, Na^+, K^+, Mg^{2+} and Ca^{2+} and present the sea-salt corrected chemical species with an asterisk.

4. Results

4.1. Physical parameters

The average water temperature was 19.3°C in the upper elevation source points and 19.4°C in the lower elevation source points of the Rio Icacos basin. The average pH was 6.5 in the upper source points and 5.5 in the lower source points (Table 3.2). The average electrical conductivity of the upper source points was 51.6μS cm^{-1} and 40.1μS cm^{-1} in the lower source points within the Rio Icacos basin. The average dissolved oxygen was 5.9 mg l^{-1} and 3.7 mg l^{-1} in the upper and lower source points, respectively. The main stem shows slightly higher values of physical parameters than the source point samples (Table 3.1). Physical parameters of the tributaries and tributary transects were nearly the same as main stem samples.

4.2. Chemical parameters

4.2.1 Spatial variability of major chemical species in source points within the basin

Silica, alkalinity, and sea-salt corrected base cations with the exception of K^+ followed similar trends, with highest concentrations in the main stem, intermediate concentrations in the high-elevation source points, and lowest concentrations in the low-elevation source points (Table 3.1). The average silica concentration was 13.6 mg l^{-1} in the upper source points and 6.8 mg l^{-1} in the lower source points, values which were much lower than those obtained in the Rio Icacos main stem (25 mg l^{-1}). Alkalinity (mainly as bicarbonate) was the dominant anion in all sites except the lower elevation source points, in which the contributions of alkalinity and chloride were equal. Concentrations of bicarbonate were higher (15.8 mg l^{-1}) in the upper elevation source points than the lower elevation (10.4 mg l^{-1}), and both were lower than the main

stem (25 mg l^{-1}; Table 3.5). Among all the sampling points within the Rio Icacos basin, silicon and bicarbonate were strongly related (Figure 3.2). Base cations after sea-salt correction showed systematic variations within the Rio Icacos basin, with higher concentrations in the main stem than source points (Table 3.1). After correction for sea salt concentrations, calcium was the dominant cation in stream water followed by sodium, magnesium and potassium. Concentrations of calcium, sodium, magnesium and potassium in milliequivalents were: $Ca^{2+} >> Na^{+} > Mg^{2+} >> K^{+}$ in all sites except the lower section of the basin where magnesium was slightly higher than sodium. The contribution of marine aerosols did not show any systematic variation pattern within the Rio Icacos basin and sodium was greatly affected by sea-salt aerosols (Figure 3.3).

The average observed value of DIC was 4.84 mg l^{-1} and 8.73 mg l^{-1} in the upper source points and lower source points, respectively. Bicarbonate showed the opposite pattern, with highest concentrations in the upper source points and lowest in the Icacos main stem. Among all dissolved inorganic carbon species bicarbonate was the dominant form of carbon in the main stem followed by upper elevation source points and lower elevation source points and the reverse trend was observed for the carbonic acid and the partial pressure of carbon dioxide (Table 3.3).

4.2.2 Variation in chemical weathering products within the Rio Icacos basin

Elements derived from rock weathering (Si and sea-salt corrected base cations) tended to be highest in the main stem and lowest in the low-elevation tributaries (Table 3.1). They were also strongly correlated with HCO_3 and alkalinity, but not pCO_2 (Figure 3.4). Silicon concentrations showed very tight relationships with

dissolved inorganic carbon (DIC) in both upper and lower-elevation source points except those passing through landslides (Table 3.4). Sea-salt corrected Na was tightly correlated with Si concentrations (Figure 3.5). The sum of base cations after the sea-salt correction was tightly correlated with DIC in both the upper-elevation and lower-elevation source points (Table 3.4). The relationship between average ratios of silica to alumina with sodium showed systematic variation within the Rio Icacos basin, suggesting variation in sodium plagioclase dissolution (Figure 3.6). Proton concentrations were tightly correlated with bicarbonate along the Rio Icacos main stem indicating the conversion of carbonic acid to bicarbonate during the dissolution of minerals and similar trends were found in tributaries, tributary transects and upper source points excluding landslide and lower source points within the basin (Fig. 3.7).

Hydrogen ion did not show any relationship with the DIC concentration in upper and lower source points within the Rio Icacos basin. Bicarbonate ion showed very strong relationship with the DIC within the basin except lower source points. Only lower source points showed very strong relationship of carbonic acid with DIC. This result is different from that of the Rio Icacos mainstream. The linear regression parameters describing the relationship of measured major solutes, hydrogen ion, and pH and dissolved carbonic species with DIC within the Rio Icacos basin are compiled in Table 3.4.

5. Discussion

Spatial variation of silica and other weathering products in the Icacos basin appears to be due largely to variation in weathering rates, with only a minor influence of variation in mineralogy on stream chemistry. Throughout the basin, dissolution of plagioclase feldspar appears to dominate weathering processes, as the ratio of silica to alumina ranges from 2.5-2.8 (Fig. 3.6). The differences in concentrations between upper-elevation and lower-elevation sources are striking; many solutes in lower-elevation source points are almost double those in the higher-elevation sites. Given the relatively uniform mineralogy in the basin (Seiders 1971; White et al. 1998), this variation in solute concentrations could be due to differences in contact time between water and the weathering rind, availability of the DIC needed to fuel carbonic acid production, or differences in the accessibility of fresh weathering surfaces.

The steepness of upper elevation slopes argues against the importance of hydrologic contact time in producing the observed patterns in solute concentrations. Contact time should be shorter in the shallower soils on the steep flanks of the upper elevation Rio Icacos compared to the deeper soils of the lower-elevation sources points, and thus can not explain the variation in solute concentrations. Nor does spatial variation in DIC or H^+ explain the spatial variation in weathering-related solutes. Concentrations of DIC in the lower elevation sites were nearly double those of the upper elevation ones, and both H^+ and carbonic acid concentrations were also consistently higher in the more dilute low-elevation source points (Tables 3.1, 3.3). The availability of fresh reactive mineral surfaces appears to be the most likely explanation for the spatial variability in major solutes that I have observed. Landslides

are frequent in the Rio Icacos basin (Larsen and Torres Sanchez 1996) and frequently expose fresh bedrock. Sediment losses are high in the basin, exceeding 3,000 kg ha^{-1} yr^{-1} (McDowell and Asbury 1994). Although landslides and other mass wasting events also occur at lower elevations, they do not result in extensive exposure of fresh bedrock surfaces. This high mechanical denudation rate in the Icacos basin accentuates spatial variability in the production of weathering products. Various authors have shown a strong relationship of chemical weathering rates of silicates with mechanical denudation rates because weathering is enhanced when mechanical erosion continuously refreshes mineral surfaces (Gibbs, 1967; Reynolds and Johnson, 1972; Stallard and Edmond, 1983; Edmond and Huh, 1997; Gaillardet et al., 1999; Millot et al., 2002).

Relationships between pCO_2, HCO_3^-, and weathering products in the Rio Icacos basin also point to the strong relationships between weathering rates and spatial variability in stream chemistry. During weathering, carbonic acid reacts with silicate minerals to produce one mole of HCO_3^- for each mole of CO_2 that is consumed during the release of SiO_2. Throughout the basin, Si concentrations were strongly related to HCO_3^- (Figure 3.2) and HCO_3^- concentrations were inversely related to pCO_2 (Table 3.3). The other weathering products (non-sea salt base cations) were also tightly related to Si concentrations (Fig. 3.5). The proportions of calcium, sodium, magnesium and potassium (in milliequivalents) were $Ca^{2+} >> Na^+ > Mg^{2+} >> K^+$ in all the surface waters throughout the basin, which is typical for mineral dissolution from granitic rocks (Meybeck, 1987). Each of these observations suggests that spatial

variability in stream chemistry of the Icacos basin clearly reflects spatial variability in chemical weathering rates.

Silica concentrations found among the surface waters of the Rio Icacos encompassed the full range of surface water Si concentrations observed in global compilations of Si flux in granitic terrain. In the Icacos, concentrations in surface waters range from nearly 0 to 0.5 mmol l^{-1}, similar to the range that is observed globally (White and Blum 1995). Although the relatively high temperature and runoff in the Icacos contribute to the extremely high Si concentrations that are observed at the watershed mouth (Table 2.1; McDowell and Asbury 1994), the basin provides an excellent observatory to document the imprint of weathering processes on stream chemistry over a broad range of site conditions.

The high pCO_2 values obtained in this study are consistent with global observations showing super-saturation of surface waters worldwide (Cole and Caraco 2001). Other tropical rivers also exhibit high pCO_2, although the data set is sparse for small tropical rivers. The main stem of the Amazon River is super-saturated with CO_2 due to its high levels of respiration relative to productivity (Richey et al., 1980; Richey et al. 2002). In most rivers, however, the super-saturation is likely due to inputs of organic or inorganic C from terrestrial sources (Cole and Caraco 2001). In the River Dee in northern Scotland, for example, pCO_2 is about 15 times higher than atmospheric values. This is equal to the highest values we have observed (Table 3.3), and is presumably due to carbon inputs from the peat-rich landscape (Dawson et al. 1995). I suspect that the high frequency of landslides in the Icacos basin (Larsen and Torres-Sanchez 1996) is a significant driver of the high pCO_2 levels in source points

(Table 3.3). Landslides in the Luquillo Mountains redistribute organic matter from standing biomass to soil organic carbon (Walker et al. 1996), and thus would tend to increase soil air CO_2 concentrations and pCO_2 of their drainage waters.

The concentrations of major solutes in the Rio Icacos basin observed in this study (2002-2005) were very similar to those observed by McDowell and Asbury (1994) for 1983-1986 (Table 3.5). This suggests that the major weathering process within the Rio Icacos watershed have remained relatively constant over two decades, despite the passage of two major hurricanes that caused considerable damage to vegetation in the Icacos basin and short-term changes in groundwater chemistry (McDowell et al. 1996).

The average ratios of silica to alumina within the Rio Icacos exceeded 2.0, and thus show that the bisiallitization type of weathering is dominant within the basin (Table 3.1). The weathering type was evaluated by considering the chemical compositions of feldspars suggested by Tardy (1971). The ratio of silica to alumina remained nearly the same in all types of samples within the Rio Icacos, suggesting that major weathering processes remained the same. The silica to alumina ratio was greater than 3 in soil samples of the Picacho series in the Luquillo Mountains of Puerto Rico and ratios varied depending into the different horizons (Jones et al., 1982). The ratio of silicon to sum of sodium and potassium was greater than 2 for the main stem, upper source points, and lower source points (Table 3.1), which indicates complete removal of base cations from plagioclase minerals (Huh et al., 1998). The extraordinarily high ratio (17) in the lower source points indicates less availability of primary minerals in that section of the basin.

6. Conclusion

Major solutes such as silicon, alkalinity and the sum of base cations showed similar variation trends within the Rio Icacos basin, suggesting that all these chemical species are released from the same source. The dominance of calcium and sodium suggests that plagioclase is the dominant mineral within the basin. Mechanical denudation appeared to enhance chemical weathering rates not only by refreshing reactive mineral surfaces but also by contributing carbonic acid due to the decomposition of organic matter (dead trees) incorporated into the landslide. Concentrations of base cations were low in the lower-elevation source points despite tremendous amounts of carbon dioxide, suggesting that the lack of primary reactive minerals at these sites limits weathering rates. The synchronized appearance of all major solutes and high ratios of silicon to sum of sodium and potassium show that extensive chemical weathering of aluminosilicates is occurring within the entire Rio Icacos basin. The average ratios of silica to alumina confirmed that the bisiallitization type of weathering is occurring within the entire Rio Icacos basin. The availability of fresh primary reactive minerals, hydrogen ions and conditions for hydrolysis appear to be primarily responsible for the spatial variability of major solutes within the Icacos basin.

Table 3.1 Average physical parameters and chemical concentrations of major chemical species in the Rio Icacos mainstream, upper source points and lower source points within the Rio Icacos basin during winter 2005. Asterisks represent sea salt corrected values.

Measured	Rio Icacos Mainstem			Upper source points			Lower source points		
parameter		mg/L	meq/L		mg/L	meq/L		mg/L	meq/L
WT (C)	19.4			19.3			19.4		
pH	7.1			6.5			5.5		
EC (µS)	58			52			40		
DO		8.12			5.97			3.65	
DIC		4.26			4.84			8.73	
DOC		0.39			1.23			0.76	
TDN		0.180			0.197			0.251	
DON		0.013			0.019			0.072	
Alk		25.18	0.413		15.78	0.259		10.36	0.170
Cl		5.16	0.146		7.45	0.210		6.12	0.173
*SO_4-S		1.201	0.025		0.419	0.009		0.286	0.006
NO_3-N		0.163	0.012		0.667	0.011		0.663	0.011
PO_4-P		0.011	0.0011		0.018	0.0006		0.004	0.0001
San			0.611			0.511			0.377
Scat			0.534			0.497			0.317
CBE (%)	-6.58			-0.77			-7.78		
NH_4-N		0.004	0.00020		0.0350	0.0020		0.0370	0.0021
*Na		2.710	0.118		1.551	0.067		0.527	0.023
*K		0.280	0.0073		0.304	0.008		0.334	0.0085
*Mg		0.810	0.066		0.588	0.048		0.372	0.031
*Ca		3.61	0.18		2.76	0.137		1.22	0.061
SiO_2		19.21			13.62			6.80	
Si/(*Na+*K)	3.1			4.0			17.3		
SiO_2/Al_2O_3	2.59			2.64			2.72		

WT= Water temperature, CBE = Charge balance error
San=Sum of anions, Scat= Sum of cations

Table 3.2 Spatial changes in average physical and chemical parameters of the Rio Icacos main stem, tributaries at the main stem and upper and lower source points within the Rio Icacos basin during winter 2005.

Sample Name	WT °C	pH	EC uS/cm	DO mg/L	DIC mg/L	CO_2 mmol/L	DOC mg/L	TDN mg/L	DON mg/L	Alk mg/L	Cl mg/L	SO_4^{2-} mg/L	NO_3^- mg/L	PO_4^{3-} µg/L	NH_4^+ µg/L	Na^+ mg/L	K^+ mg/L	Mg^{2+} mg/L	Ca^{2+} mg/L	SiO_2 mg/L	H^+ µg/L
RIS4	19.1	6.8	50	8.1	3.38	0.00005	0.45	0.14	0.03	19.7	5.5	0.33	0.11	0.78	4.1	5.21	0.34	1.03	3.13	16	0.15
RIS5	19.6	6.9	53	8.0	3.52	0.00008	0.41	0.14	0.02	21.5	5.4	0.31	0.11	3.33	5.9	5.25	0.35	1.03	3.22	17	0.14
RIS6	19.6	6.9	56	8.0	3.83	0.00007	0.40	0.16	0.03	24.2	5.5	0.32	0.12	3.37	6.4	5.45	0.39	1.07	3.17	18	0.12
RIS7	19.4	7.0	62	8.3	4.06	0.00004	0.55	0.18	0.02	24.9	5.3	0.36	0.16	13.35	-0.2	5.60	0.40	1.19	3.53	18	0.09
RIS8	19.4	7.1	61	8.3	4.89	0.00004	0.31	0.21	-0.09	28.0	3.4	2.40	0.29	17.10	3.9	5.75	0.42	1.18	3.81	21	0.09
RIS9	19.4	7.2	63	8.2	5.17	0.00003	0.29	0.21	0.04	28.9	5.5	0.38	0.17	17.20	1.3	5.80	0.41	1.23	4.40	22	0.07
RIS10	19.3	7.4	64	8.0	4.98	0.00006	0.29	0.23	0.04	29.1	5.6	0.39	0.19	21.05	3.1	6.09	0.43	1.34	4.75	22	0.04
RIST1	19.3	6.8	40	8.1	3.21	0.00007	0.51	0.13	0.02	17.0	5.9	0.37	0.11	2.90	9.3	5.23	0.26	0.94	2.86	16	0.18
RIST2	18.9	6.9	49	8.1	4.17	0.00006	0.48	0.12	0.01	18.7	5.7	0.27	0.10	0.86	6.3	5.12	0.26	1.13	3.00	17	0.13
RIST3	19.4	6.7	48	7.8	3.96	0.00010	0.34	0.13	0.00	17.7	6.0	0.30	0.11	4.02	12.3	5.41	0.45	0.98	2.84	16	0.19
RIST4	19.8	6.6	41	7.7	3.51	0.00008	0.40	0.23	0.03	12.1	6.1	0.46	0.18	0.45	31.0	4.74	0.39	0.75	2.16	12	0.28
RIST5	18.9	6.9	47	8.1	3.45	0.00003	0.78	0.20	0.10	18.0	5.9	0.39	0.09	4.49	2.8	5.17	0.55	1.09	2.86	16	0.12
RIST6	19.4	6.9	44	8.3	2.87	0.00003	0.48	0.15	0.01	14.5	6.0	0.31	0.12	9.05	11.3	5.04	0.40	0.90	2.65	16	0.12
RIST7	19.8	6.2	42	7.2	4.81	0.00019	0.90	0.13	0.02	13.3	6.9	0.38	0.06	0.00	42.3	4.39	0.43	0.98	2.64	11	0.59
RIST8	19.2	6.8	47	8.0	3.46	0.00011	0.33	0.13	0.02	18.9	5.3	0.33	0.10	7.50	6.8	5.03	0.42	0.97	3.08	17	0.17
RIST9	19.2	6.4	40	7.1	1.79	0.00010	0.82	0.19	0.02	9.5	6.6	0.39	0.12	0.00	47.8	4.61	0.32	0.94	1.74	10	0.43
RIST10	19.6	6.7	58	7.3	3.87	0.00012	0.70	0.10	0.01	21.1	6.6	0.39	0.05	1.68	36.1	5.92	0.53	1.26	3.05	16	0.19
RIST11	19.3	6.9	58	8.0	4.75	0.00008	0.33	0.12	0.01	24.6	7.0	0.30	0.10	6.81	11.0	6.43	0.60	1.25	4.01	20	0.12
RIST12	19.0	6.9	48	7.9	4.86	0.00005	0.35	0.10	0.01	21.3	5.3	0.33	0.09	4.34	11.2	5.17	0.42	1.14	3.33	17	0.12
RIST13	19.0	6.8	44	8.0	5.43	0.00006	0.40	0.12	0.00	24.3	6.2	0.27	0.11	3.61	8.1	5.54	0.43	1.37	3.99	19	0.16
RIST14	18.8	7.2	44	7.8	3.66	0.00000	0.40	0.16	0.03	23.2	5.5	0.34	0.13	7.64	4.5	5.56	0.45	1.17	3.52	19	0.06
RISSP1	20.0	7.1	64	7.3	4.77	0.04	0.25	0.09	0.02	26.1	6.1	1.56	0.27	14.44	7.9	5.38	0.53	1.39	4.38	17	0.09
RISSP2	20.6	5.3	45	1.1	22.52	1.44	0.84	0.13	0.01	18.4	8.0	0.90	0.18	6.43	103.8	6.43	0.24	0.93	2.30	16	4.71
RISSP3	18.8	4.3	39	5.0	0.37	0.02	3.03	0.24	-0.14	0.0	7.8	2.08	1.22	4.70	141.9	4.21	0.48	0.56	1.05	1	51.69
RISSP4	20.1	5.6	41	3.8	5.64	0.39	0.34	0.26	0.01	5.1	8.1	1.55	1.06	3.72	15.3	5.39	0.35	0.75	1.45	14	2.74
RISSP5	20.0	7.0	53	6.7	3.34	0.04	0.41	0.16	0.05	21.2	6.7	1.08	0.47	39.14	3.1	6.60	0.52	1.11	3.23	20	0.11
RISSP6	18.6	7.5	53	5.9	2.58	0.02	1.09	0.24	0.04	20.7	8.4	1.67	0.85	21.81	13.8	6.92	0.61	1.37	3.88	16	0.03
RISSP7	18.8	7.1	54	8.3	2.98	0.03	0.90	0.20	0.04	20.6	6.9	1.44	0.64	22.12	21.4	5.62	0.52	1.26	3.98	16	0.07
RISSP8	18.9	7.1	60	8.2	2.76	0.03	0.86	0.18	0.05	24.8	7.0	1.28	0.56	41.74	9.0	6.11	0.55	1.24	4.19	18	0.09
RISSP9	18.6	6.9	61	5.6	1.04	0.00	2.80	0.32	0.07	7.5	8.2	1.91	0.99	2.10	32.9	4.99	0.34	1.16	2.15	7	0.14
RISSP10	18.8	6.9	46	7.7	2.41	0.01	1.75	0.16	0.06	13.5	7.3	1.25	0.44	20.12	5.1	5.48	0.45	1.10	2.54	11	0.14
RISSPL1	20.1	5.3	50	2.4	12.24	0.72	0.74	0.21	0.05	17.5	6.4	1.21	0.54	-0.38	57.0	4.74	0.72	1.10	1.79	11	4.55
RISSPL2	20.0	5.4	33	5.8	6.35	0.73	0.85	0.21	0.04	5.3	5.5	0.69	0.73	3.68	7.5	2.88	0.55	0.46	0.72	7	4.45
RISSPL3	18.8	5.7	37	2.9	3.75	0.17	0.73	0.17	0.06	9.2	6.5	1.16	0.30	0.00	49.7	3.76	0.23	0.63	1.17	3	2.08
RISSPL4	19.3	5.4	36	3.4	13.17	0.77	0.48	0.22	0.04	7.4	5.9	1.40	0.75	8.41	15.0	3.90	0.31	0.95	1.77	7	3.88
RISSPL5	19.7	6.1	55	2.9	11.92	0.55	1.17	0.25	0.15	21.9	6.9	1.28	0.16	0.55	90.6	4.70	0.74	1.04	1.88	11	0.73
RISSPL6	18.4	4.9	29	4.5	4.98	0.43	0.59	0.44	0.10	0.8	5.5	1.17	1.50	8.76	4.5	3.72	0.22	0.53	0.75	1	11.6

Table 3.3 Average dissolved carbonic species along the Rio Icacos mainstream, upper source points and lower source points within the Rio Icacos basin during winter 2005. All units are in mmol/L except the partial pressure of carbon dioxide (pCO_2). pCO_2 values are the average calculated values based on water temperature, pH, and DIC.

Measured parameter	Rio Icacos main stem	Upper source points	Lower source points
DIC	0.355	0.400	0.730
H_2CO_3	0.064	0.240	0.620
HCO_3^-	0.291	0.160	0.110
CO_3^{2-}	0.000	0.000	0.000
CO_2 (calculated)	0.064	0.240	0.620
CO_2 (measured)	0.046	0.200	0.560
pCO_2 (uatm)	1568	6212	15241

Table 3.4 Linear regression parameters describing the relationship of dissolved inorganic carbon with weathering products, hydrogen ion, pH and inorganic carbon species in the Rio Icacos mainstem, upper and lower source points within the Rio Icacos basin during winter 2005. Asterisks represent sea salt corrected values. Bscat = sum of base cations.

Measured	Rio Icacos mainstem				Upper source points				Lower source points			
parameter	Intercept	Slope	R^2	P-value	Intercept	Slope	R^2	P-value	Intercept	Slope	R^2	P-value
Si	0.420	0.202	0.96	<0.001	5E-05	0.81	0.75	<0.01*	2E - 06	0.159	0.69	<0.05
Alkalinity	0.073	0.080	0.95	<0.001	2E-05	1.21	0.83	<0.01*	4E - 08	0.2334	0.39	0.1
*Bscat	0.031	0.080	0.90	<0.01	5E-05	0.63	0.78	<0.01*	-5.E-06	0.113	0.74	<0.05
H^+	0.000	-5.E-05	0.84	<0.01	1.E-04	-0.14	0.10	ns	7E - 06	-0.004	0.14	ns
pH	5.991	0.248	0.73	<0.05	5.487	5863	0.43	ns	5.213	366.66	0.10	ns
H_2CO_3	1.E-04	-1.E-05	0.43	ns	-0.0002	0.981	0.97	<0.001	4E - 05	0.792	0.87	<0.01
HCO_3^-	-1.E-04	1.E-04	0.98	<0.001	-2E-05	0.884	0.98	<0.001*	-4.E-05	0.208	0.32	ns
CO_3^{2-}	-5.E-07	2.E-07	0.65	<0.05	4.E-06	0.533	0.39	ns	-7E-06	0.0304	0.25	ns
CO_2 (aq)	1.E-04	1.E-05	0.43	ns	-2.E-04	0.981	0.97	<0.001	4E - 05	0.792	0.87	<0.01
pCO_2	2935	-321	0.43	ns	-3903	3.E+07	0.97	<0.001	733	2.E+07	0.87	<0.01

* Excluding landslide sampling sites

Table 3.5 Comparison of major solutes of the Rio Icacos main stem, upper and lower source points within the Rio Icacos basin during 2005 with previous study at the Rio Icacos. [1]Data from McDowell & Asbury, 1994

Measured Parameters	Upper source points	Lower source points	Rio Icacos mainstream	[1]Previous study
HCO_3^- (mg/L)	15.8	10.4	25.18	21.1
Na^+ (mg/L)	5.71	3.95	5.59	5.07
K^+ (mg/L)	0.46	0.46	0.39	0.51
Mg^{2+} (mg/L)	1.09	0.78	1.15	1.2
Ca^{2+} (mg/L)	2.9	1.3	3.72	3.33
SiO_2 (mg/L)	13.6	6.8	19.21	18.3

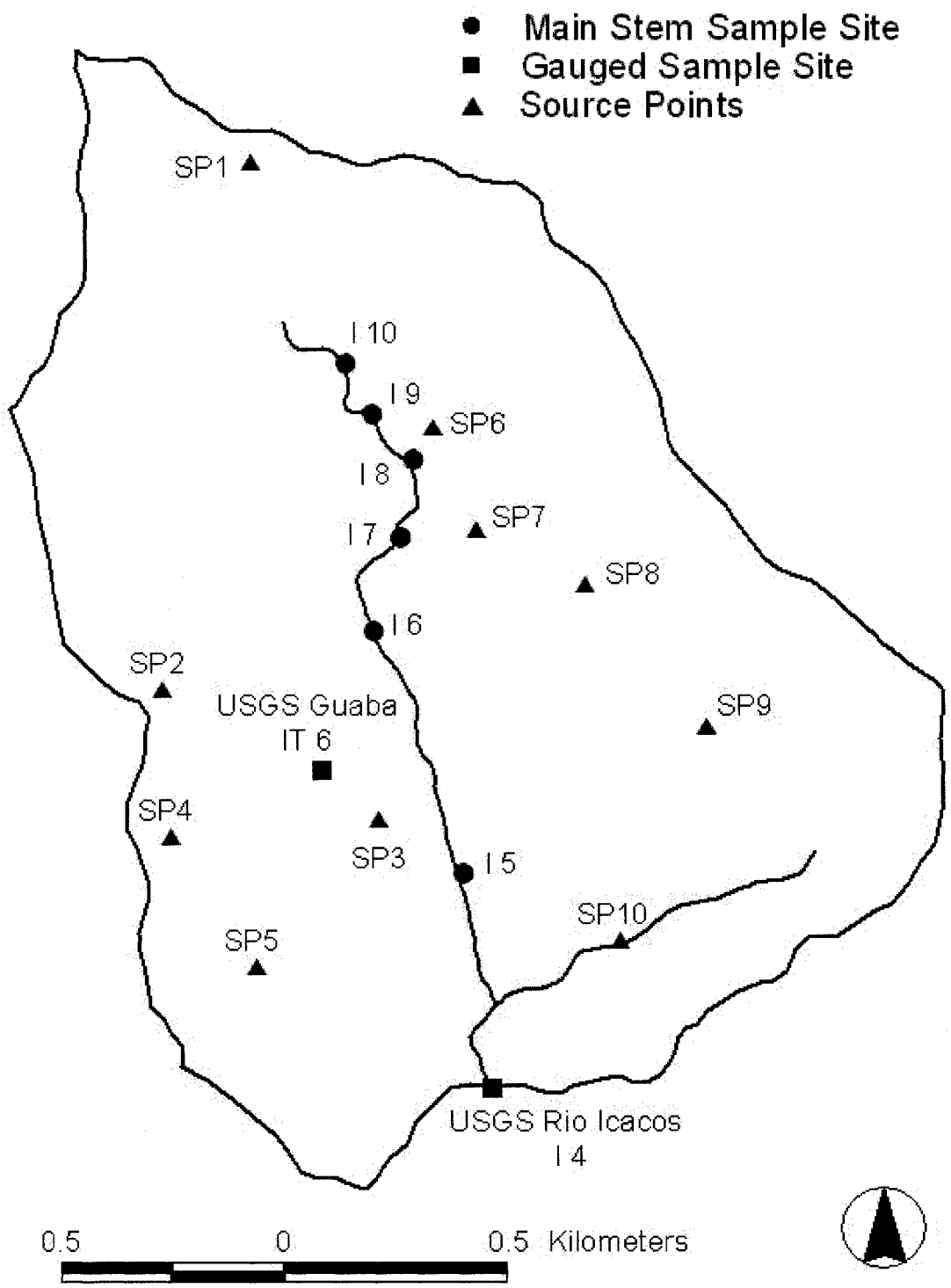

Figure 3.1. Rio Icacos main stem and source point sampling locations

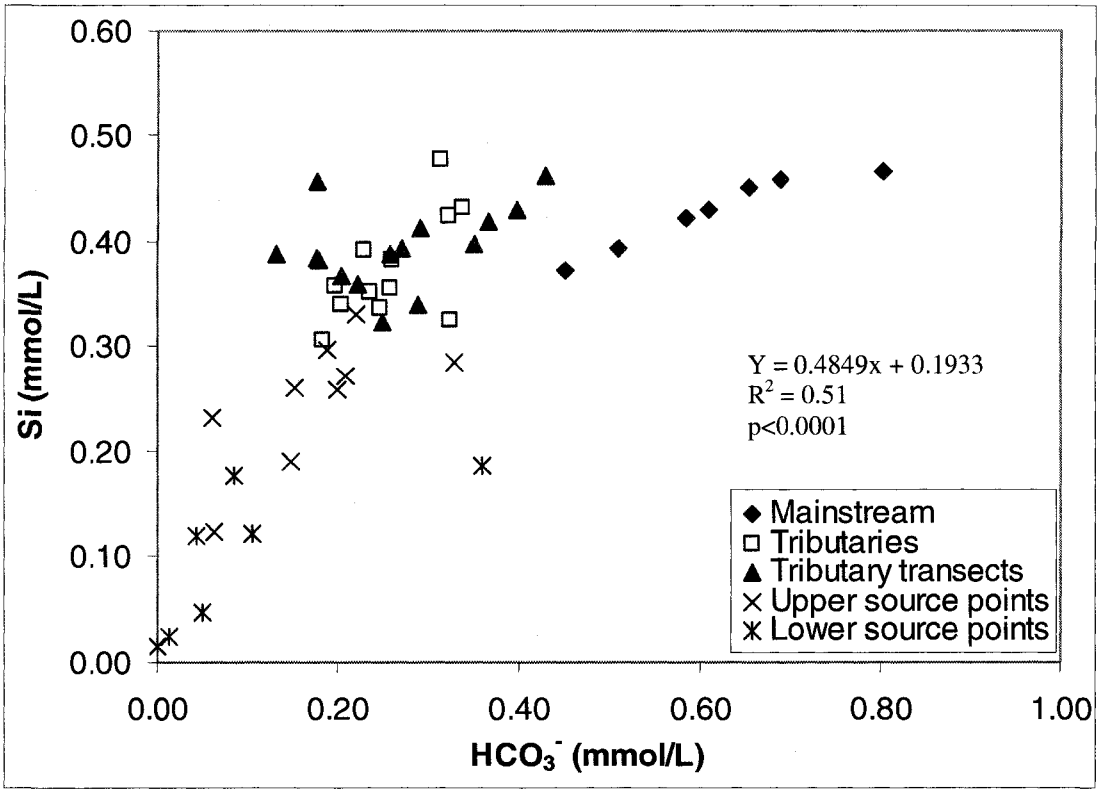

Figure 3.2 Relationship between average silicon and average bicarbonate along the Rio Icacos mainstream, major tributaries at the mainstream, tributary transects and source points with the Rio Icacos basin during summer 2002 and winter 2005. Sampled two to three times, n = 108.

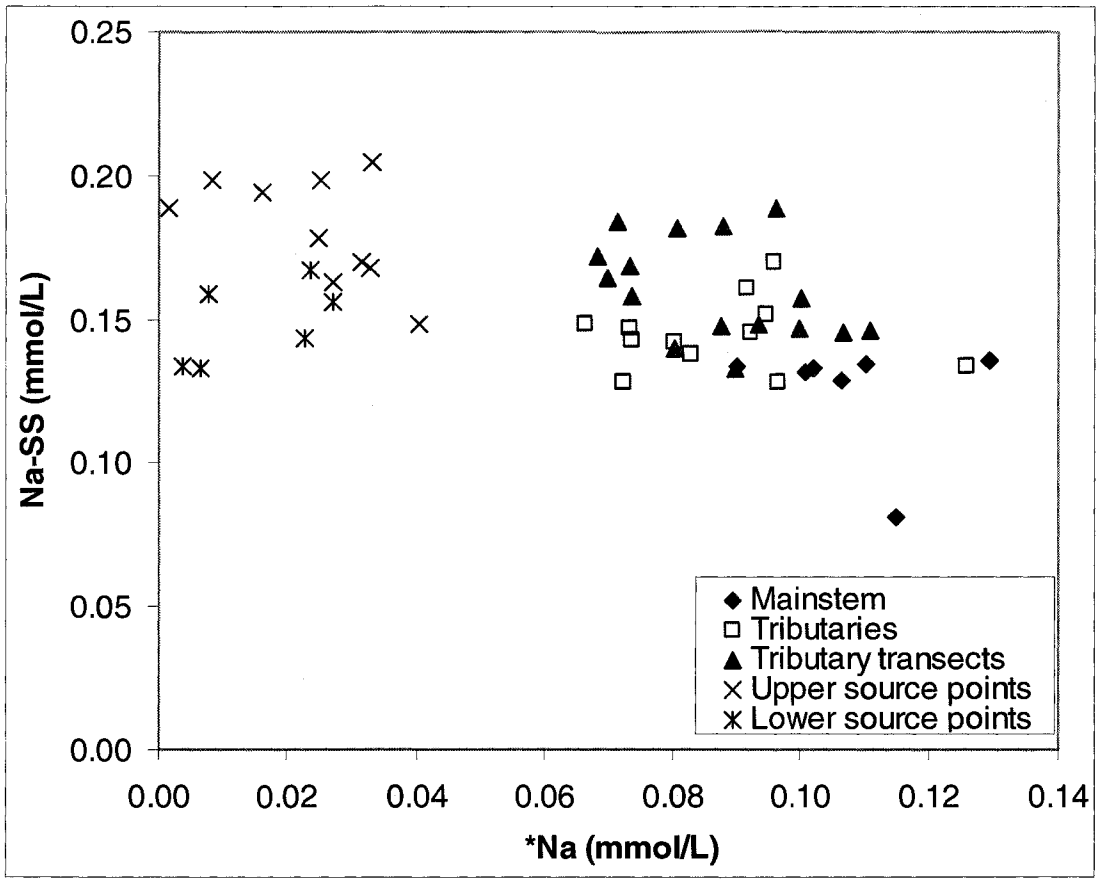

Figure 3.3 Relationship between sea-salt contributed sodium and non sea-salt contributed sodium along the Rio Icacos mainstem, tributaries at the mainstem, tributary transects, and upper and lower source points within the basin during summer 2002 and winter 2005. Sampled two to three times, n = 108.

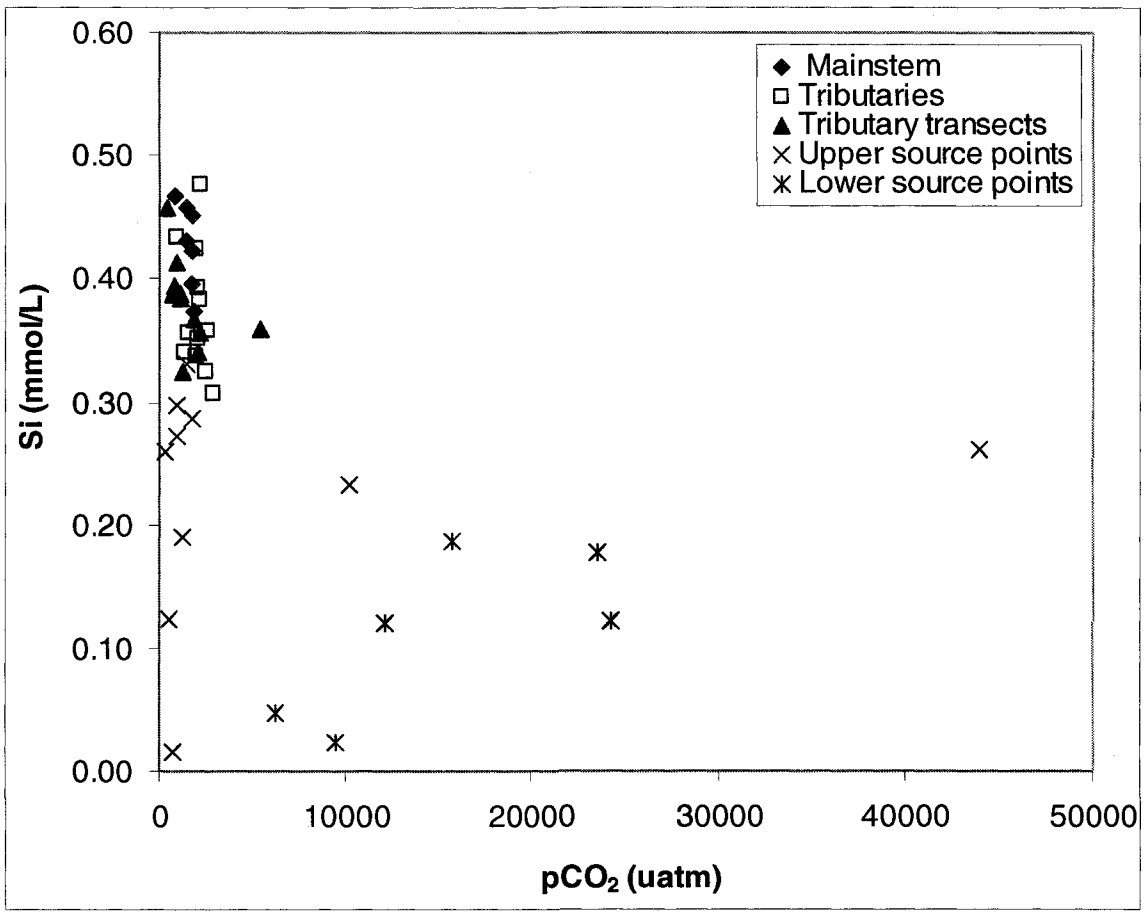

Figure 3.4 Relationship between silicon and partial pressure of carbon dioxide (pCO_2) concentration along the Rio Icacos main stem, major tributaries at the main stem, tributary transects, and upper and lower source points within the Rio Icacos basin during summer 2002 and winter 2005. Sampled two to three times, n = 108.

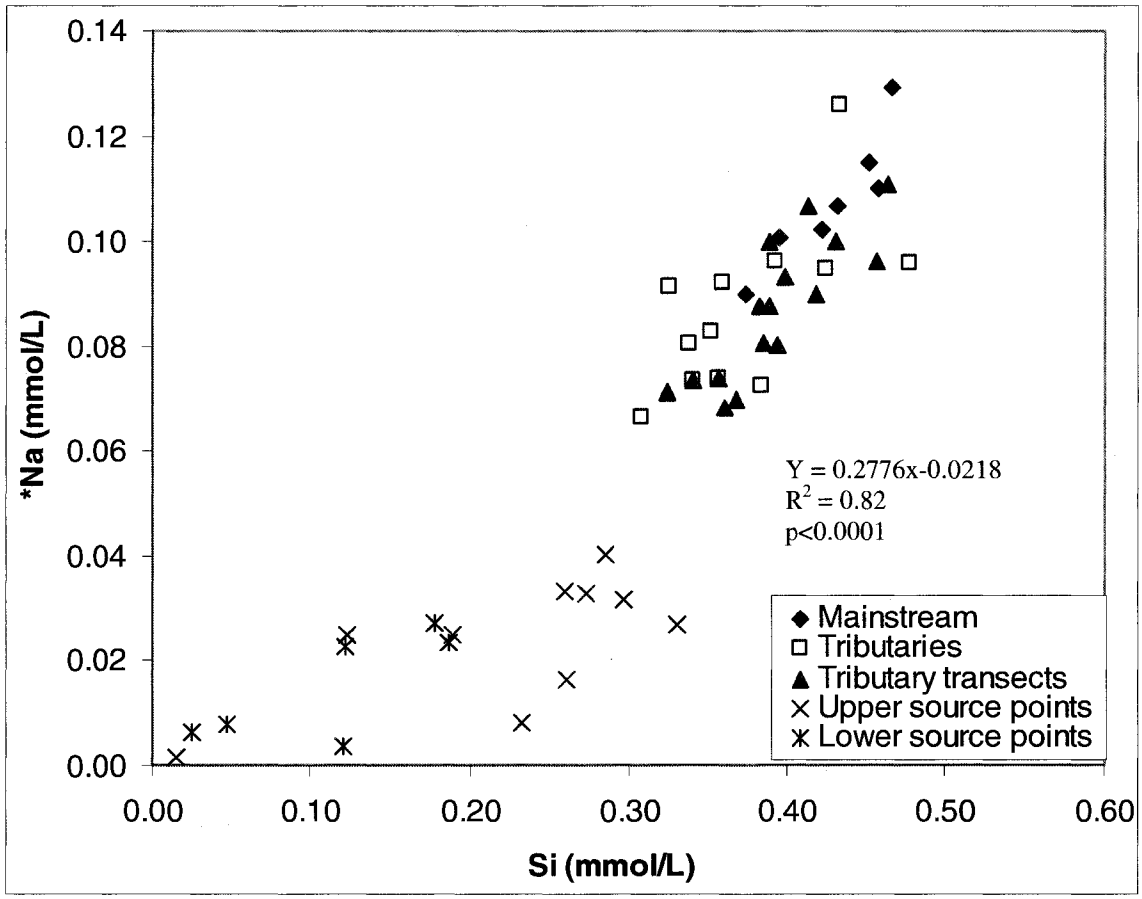

Figure 3.5 Relationship between sodium and silicon along the Rio Icacos mainstream, major tributaries at the mainstream, tributary transects, and source points within the Rio Icacos basin during summer 2002 and winter 2005. Sampled two to three times, n = 108.

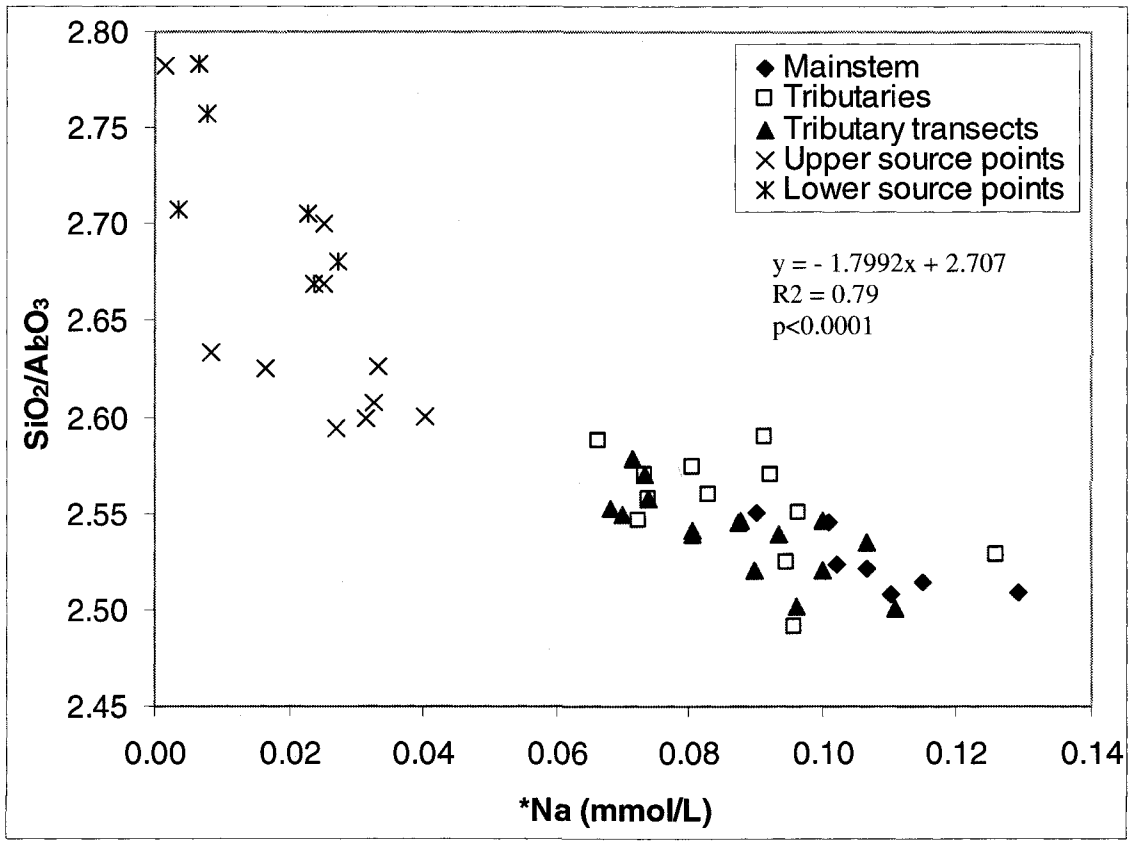

Figure 3.6 Relationship between ratios of silica to alumina and sodium along the Rio Icacos main stem, major tributaries at the mains stem, tributary transects and upper and lower source points within the Rio Icacos during summer 2002 and winter 2005. Sampled two to three times, n = 108.

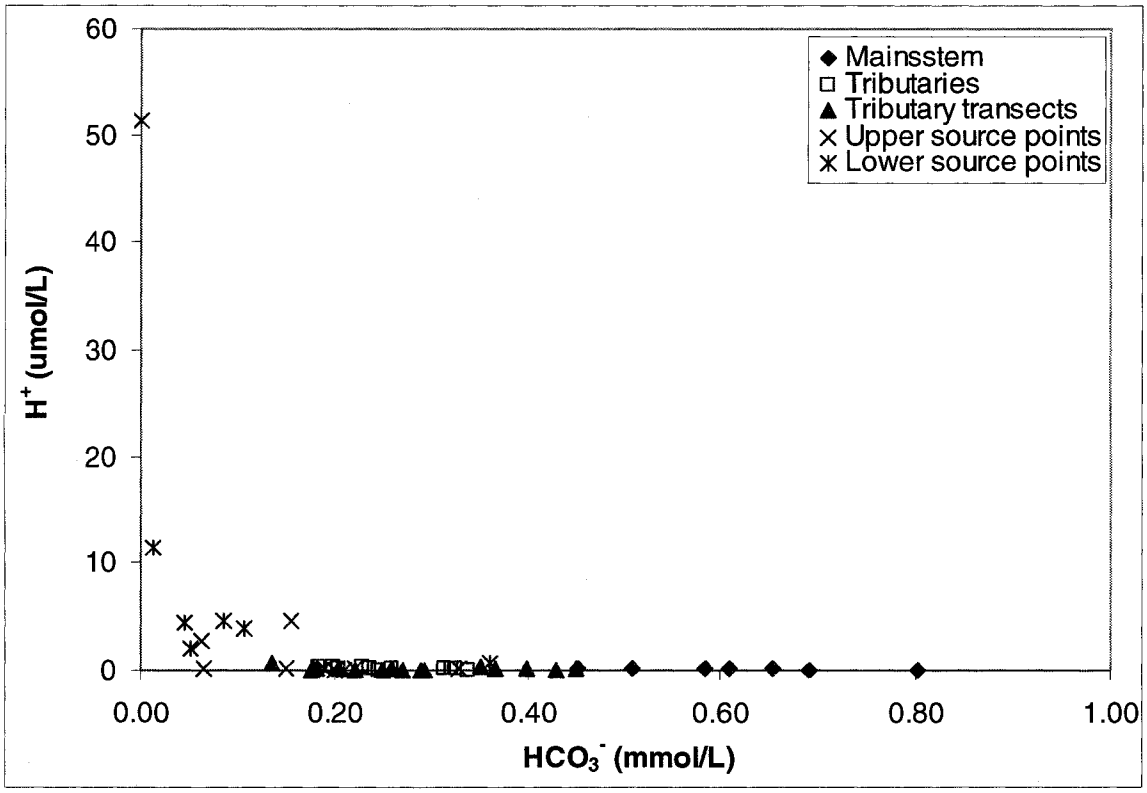

Figure 3.7 Relationship between hydrogen ion and bicarbonate ion along the Rio Icacos main stem, major tributaries at the main stem, tributary transects and upper and lower source points within the basin summer 2002 and winter 2005. Sampled two to three times, n = 108.

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CHAPTER IV

EVOLUTION OF CHEMISTRY ALONG THE BAGMATI DRAINAGE NETWORK IN KATHMANDU VALLEY

Abstract

A systematic study of the chemistry of the Bagmati River in Kathmandu valley was conducted to understand the influence of human and geochemical processes on chemical concentrations along the drainage system. Population density appears to be the most fundamental control on the chemistry of surface waters within the Bagmati drainage system. For all constituents studied, concentrations increase with distance downstream and many parameters show strong relationships with human population density adjacent to the river. The composition of river water suggests that sewage effluent entering the river has a major effect on water quality. Concentrations were highest during summer and lower during the winter monsoon season. The contribution of chemical weathering processes to water quality of the Bagmati appears to be minor within the Kathmandu valley. Dominant cations and anions when expressed in equivalents per liter were $Na^+ >> Ca^{2+} > K^+ >> Mg^{2+}$ and $Cl^- >> SO_4^{2-} > PO_4^{3-} >> NO_3^-$ respectively along the Bagmati drainage system. Ammonium contributes almost all nitrogen in the total dissolved nitrogen fraction and the concentration of nitrate is negligible, probably due to rapid denitrification and limited nitrification within the stream channel under relatively low oxygen conditions. Decreases in sulfate along the stream channel may also be due to the

reduction of sulfate to sulfide due to heavy organic matter loading. Water quality is unacceptable for any use and the whole ecosystem is severely affected due to human activities within the urban areas. Based on a comparison of downstream and upstream water quality, it appears that the human population along the Bagmati is primarily responsible for the changes in surface water chemistry observed along the drainage system within Kathmandu valley

1. Introduction

Human activities control surface water chemistry through the effects of deforestation, agricultural practices, industrial effluents, land use practices and disposal of domestic wastes (Gibbs, 1967; Reeder et al., 1972; Meybeck and Helmer, 1989; Billett and Cresser, 1992; Lenat and Crawford, 1994; McDowell et al., 1995; Collins and Jenkins, 1996; Gaillardet et al., 1999; Rose 2002). Surface water ecosystems are most impacted by human populations compared to groundwater (Peters, 1984; Flintrop et al., 1996; Roy et al, 1999; Vorosmarty et al, 2000; Malmquist and Rundle, 2002; UNEP, 2002).

Population density is known to be effective in predicting yields of sodium, potassium, chloride and sulfate in streams of the United States (Peters, 1984). Caraco et al. (2003) have shown that population density also drives variation in nitrogen flux globally. McDowell et al. (1995) reported the highest concentration of inorganic nitrogen from areas with the highest population density in Caribbean catchments. Anthropogenic impacts due to human activities appear to be the main cause of high dissolved and suspended chemical loads in the Seine River, France, and such pollution is either due to agriculture or industrial and commercial effluents (Roy et al., 1999). The Rhine River in Europe is chemically affected by human population and considered one of the most polluted rivers in the world (Flintrop et al., 1996). Many parts of the developing world will experience large increases in water demand and increased pollutant loads over the

next few decades due to increased population growth and urbanization (Vorosmarty et al., 2000) but the effects of this development are largely unknown in many parts of the world.

The Bagmati River is a major river in Nepal which originates in the central northern mountains and runs through urban areas of Kathmandu valley. The Department of Hydrology and Meteorology (DHM), Nepal has been examining the chemistry of the Bagmati River since 1992 with a primary emphasis on documenting changes in DO, COD, BOD and electrical conductivity (FPAN-DISVI, 1988; DHM, 1996, ENPHO, 1997). Previous results suggest that the Bagmati river water is highly polluted, primarily due to untreated raw sewage disposal and other inputs such as industrial wastes (ITECO, 2003). Since 1995, there has been growing public concern over the direct dumping of solid wastes and direct discharge of untreated sewage to the Bagmati River, and the government formed a committee in order to prevent further environmental degradation of surface and groundwater quality of Kathmandu valley (BASP, 2002). A sewage construction project has already completed its first phase of work in the upper Bagmati basin and is planning to construct sewer pipelines and wastewater treatment plants from headwater areas to the lower Bagmati basin, including our entire study area (BASP, 2002).

The Bagmati is one of the main sources of drinking water for Kathmandu valley and every day about 30 million liters of water are tapped from the Bagmati and its tributary Bishnumati, as well as other smaller streams (DNPWC, 2003). Given the increasing population growth in the Bagmati, its importance as a water supply, and the

relative lack of information on water chemistry, the primary objective of this study was to quantify changes in water quality along the length of the river as a function of human activities and population density in the drainage basin. By examining changes in the relative abundance of solutes, we hope to infer the dominant sources of water pollution. River water samples were collected several times from different locations along the Bagmati River in order to document the variation in chemical species and their regulating factors.

2. Study area

This research was conducted in the Bagmati River and the urban area of Kathmandu valley, Nepal (Figure 4.1). The Bagmati River originates in Shivpuri in the northern mountains of Kathmandu, which is about 30 km from Kathmandu valley. Kathmandu valley is situated at an altitude of 1350 m and surrounded by forested mountains and the Himalaya. Kathmandu valley is a circular basin occupying about 525 km^2 and the Bagmati is the only major river system in the valley. The Bagmati River drains 3500 km^2 before crossing the lower Terai plain and the International boundary into the Indian state of Bihar, and eventually draining into the Ganges River (JICA, 1990, BIWMP, 2003). The Bagmati River is a perennial river that originates in the midland or Mahabharata range of mountains and is fed by precipitation as well as groundwater regeneration including springs (WECS, 2002). Bagmati River water is clear and fresh before entering the Kathmandu valley as it drains pristine forested areas and the riverbank contains high-grade metamorphic rocks. Bishnumati, Manohara, Hanumante, Godawari, Tukucha, Balkhu, Kodku and Nakhu are all tributaries that originate at the different corners of the valley and contribute chemical loads to the Bagmati mainstream. It is said that Kathmandu valley was a lake in the ancient past and was made habitable by cutting the hills to the south of the valley to drain off the water (DOI, 2000).

The Shivapuri watershed (215 km^2) supplies most of the water demand of the Kathmandu valley and is situated at the boundary of three districts: the northern part of Kathmandu district, the southern part of Nuwakot district and the western part of Sindhupalchowk district (ENPHO, 1997). Water use of Bagmati River has been

estimated to be 66% for irrigation, 31% for water supply and 3% for industrial use (MHPP, 1994).

The city of Kathmandu is the largest metropolitan city in the country (~ 0.7 million people) and the total population of Kathmandu valley is about 1.7 million. The current growth rate of Nepal is 4.6 percent per decade (CBS, 2003). Nepal Water Supply Corporation in Kathmandu was established in 1973 (NWSC, 2001) and the population at that time was less than 0.6 million in Kathmandu valley and less than 0.3 million in Kathmandu Metropolitan City alone. The extremely high population growth within Kathmandu valley over the last 30 year has created water stress and quality problems due to high demands for freshwater along with increasing urban and agriculture activities. The population density shows systematic increases from headwater areas to the lower reaches of the Bagmati sub-basin. Data on population in Wards within the Kathmandu metropolitan city are available, but only some wards stretch from river reach to the core area of the city. The population density used in this study is density for some distance along the river reach, but not density for the entire sub-basin between two sampling points. The lower section of the Bagmati sub-basin is the main city area while the headwater area is only recently urbanizing and hence population density there is much lower than the lower reaches of Bagmati sub-basin. Sewer inputs are mixed with the river water only after treatment in headwater areas, while in the lower reaches of the Bagmati sub-basin raw sewage is mixed directly into the river without treatment.

The riverbed consists of bedrock, sand and gravel deposits up to boulder size in the headwaters and recent alluvial soils with clay, sand and fine gravel in the central and

lower reaches of Kathmandu valley (Shrestha et al., 1998). Average annual rainfall is 1621 mm and the mean annual temperature is 20°C with the range between 1.3°C in December and 32°C in June in the Kathmanu valley (DHM, 2003). The Department of Hydrology and Meteorology (DHM) gauges the river at Chovar, in the southern part of the valley. Soils of the Kathmandu valley are fertile and land use is mainly agricultural activities and urban development. The land use in Kathmandu valley is residential (53%), agricultural (18%), service (11%), mixed use (7%), Forest (6%), others (3%) and business (2%) (KMC, 2001). Previous research has shown that the Bagmati River water quality is heavily polluted in terms of DO, COD, BOD and ammonium due to direct disposal of solid waste and sewage (DHM, 1996).

There are a few industrial point sources draining into the Bagmati River such as dump sites and outfalls from garment and carpet factories. There are about 1500 different industrial activities in Kathmandu district and this number may exceed 2000 in the whole valley (MIC, 2004). They may also contribute chemical loads to the river system although there has not been any research on their effects on water quality. A brief summary description of the basin is given in Table 4.1.

2.1. Geologic setting

The Kathmandu valley is composed of two series of geological succession: one is quaternary, which overlies the lower portions of the valley and the other is in the age of Precambrian to Devonian that surrounds the Kathmandu valley (JICA, 1990). The Kathmandu valley is underlain by metamorphic rock comprising gneisses, granites,

quartzites and marbles or limestone, sandstones, shales and phyllites (Shrestha et al., 1998; Juttner et al., 2003). Argillaceous limestone contains a high proportion of clay mineral and includes slates, shales, clay stones, and mudstones. Mudstones are non-fissile rock containing approximately equal amounts of clay and silt largely quartz, shales are fissile rocks usually containing >50% clay minerals. Slates are low grades metamorphic rocks and shales are the most abundant (Fairbridge and Bourgeois, 1978).

3. Materials and Methods

3.1. Sample collection

Water samples were collected from each site on the Bagmati River on five different dates. One set was collected during winter 2002, and four sets were collected during winter to summer 2003. Each water sample was filtered with a pre-combusted glass micro fiber filter (Whatmann GF/F with a pore size 0.7μm) in the field. Samples were taken in 60 mL acid washed polyethylene bottles, refrigerated in Kathmandu, and brought frozen to the Water Quality Analysis Laboratory of the University of New Hampshire for analysis. Samples were also taken in 30 ml acid washed polyethylene bottles, refrigerated in Kathmandu and sent unfrozen to University of New Hampshire for dissolved silica analysis. Population density in each sub-watershed basin was estimated based on the ward area and ward population within the sub watershed.

3.2. Analytical Methods

Each water sample was analyzed for: Na^+, Ca^{2+}, K^+, Mg^{2+}, NH_4^+, Cl^-, SO_4^{2-}, PO_4^{3-}, NO_3^-, dissolved organic carbon (DOC), total dissolved nitrogen (TDN) and SiO_2. Dissolved organic carbon (DOC) was analyzed as non-purgeable organic carbon with combustion and analysis of end products using a Shimadzu TOC-$V_{CSH.}$ Samples are injected into a 720°C-furnace containing platinum catalyst (Pt on silica beads) where carbon compounds are converted to CO_2 and measured with a Non-Dispersive Infrared Detector (NDIR). Total dissolved nitrogen (TDN) was measured with combustion and analysis of end products using a Shimadzu TOC-5000 coupled to an Antek 720 nitrogen

detection where nitrogen compounds are converted to NO and measured using a Chemiluminescent N detector (Merriam et al., 1996). This technique performs at 680°C. DON was calculated by subtracting inorganic nitrogen (NO_3^- - N + NH_4^+ - N) from total dissolved nitrogen (TDN). Major anions (Cl^-, NO_3^- and SO_4^{2-}) were measured on a high performance liquid chromatograph (HPLC) with a Dionex self-regenerating suppressor (4mm), Ionpac AS4A analytical column and a Waters 431 conductivity detector. Ammonium (NH_4^+ - N) and Orthophosphate (PO_4^{3-} P) were analyzed by automated flow injection analysis colorimetry using a Lachat QuickChem AE. Ammonium (NH_4^+ - N) was analyzed using the automated phenate hypochlorite method with sodium nitroprusside enhancement, and PO_4^{3-} P with the automated ascorbic acid reduction method. Major cations (Na^+, K^+, Mg^{2+}, and Ca^{2+}) were analyzed on an isocratic HPLC using an Alltech Universal Cation column, with nitric acid/EDTA mobile phase and conductivity detection. Dissolved silica (SiO_2) was analyzed as molybdate-reactive silica using a Lachat QuickChem AE.

4. Results

4.1. Spatial variability in chemical composition

The Bagmati River in Kathmandu valley is a remarkable river in terms of its pollutant load for many nutrients and ions. The electrical conductivity was more than three times higher (up to 330 μmhos cm^{-1}) and the dissolved oxygen was nearly 50% lower in the downstream reaches than the upper reaches (Table 4.2). Water of the Bagmati River is within the buffering range of pH along the drainage system. All the chemical parameters measured except nitrate and dissolved organic nitrogen showed much higher concentrations in the lower reaches than the upper reaches of the Bagmati drainage system with some values more than 10-fold higher in downstream than upstream reaches (Table 4.2). Increases in phosphate and ammonium were particularly large; PO_4-P increased from 0.05 to 2.7 mg l^{-1}, and NH_4-N increased from 0.8 to 24 mg l^{-1} (Table 4.2). Many constituents were tightly correlated with each other, for example phosphate was correlated with ammonium as well as sodium (Table 4.4). The proportion of major chemical species in urban reaches of the Bagmati drainage matched those in municipal wastewater (Figure 4.2).

Dissolved oxygen showed a significant decline with distance and the lowest observed average value (2 mg l^{-1}) was found at the lowermost Bagmati basin (Table 4.2). The smell of sulfide was evident during sampling at the downstream stations where large inputs of organic matter are discharged to the river, and gas bubbles were also observed at these stations. Nitrate concentrations were low throughout the basin, and were particularly low at the urban sampling stations (Table 4.2).

Most constituents measured showed progressive increases with distance downstream, and distance was a statistically significant predictor of concentration for Mg, Ca, and TDN (Table 4.4). Electrical conductivity also showed statistically significant increases with distance along the Bagmati drainage basin. Phosphate concentration consistently increased downstream, as did base cations, ammonium and chloride. Phosphate was tightly correlated with both chloride and ammonium (Fig. 4.3 and 4.7), suggesting that all of these ions originated from the same anthropogenic sources. Neither sulfate nor dissolved organic nitrogen (DON) showed consistent trends in concentration along the Bagmati drainage network. All the chemical parameters measured showed much higher concentrations in summer compared to winter (Table 4.5).

The major cation and anions in milliequivalents per liter were found in the following order: $Na^+ >> Ca^{2+} > K^+ >> Mg^{2+}$ and $Cl^- >> SO_4^{2-} > PO_4^{3-} >> NO_3^-$. The molar ratio of sodium to chloride, a measure of the importance of aluminosilicate weathering, was low (Na:Cl = 1.2). Silica concentration was much lower than base cations and the ratio of silica to sum of base cations, another measure of the influence of aluminosilicate weathering on water chemistry, was <0.5 along the Bagmati River within Kathmandu valley.

4.2. Effect of population density on chemical composition of Bagmati river waters

Population density varies along the Bagmati drainage basin and consistently increased with distance downstream (Table 4.1). All the measured chemical parameters

except nitrate and dissolved organic nitrogen (DON) showed significant relationships with population density and hence anthropogenic inputs from various sources due to human population appear to be the prime drivers of chemical load into the Bagmati River system within Kathmandu valley (Tables 4.3 and 4.4). Dissolved oxygen and conductivity measured by DHM (1996) also showed significant relationships with population density. Ammonium contributed almost all the N measured as total dissolved N and showed a particularly strong relationship with population density (Figure 4.5).

5. Discussion

5.1. Spatial variability in chemical composition of surface waters

Almost all the measured chemical parameters showed systematic increases from headwater areas to the downstream reaches that appeared to be associated with inputs of untreated domestic sewage, and concentrations of many constituents were many times higher than the world average river (Table 4.6). Meybeck, (1998) found that phosphate and ammonium (3.63 mg l^{-1} and 24.7 mg l^{-1}, respectively) were very high in an urbanized stream in the Seine basin, and ranked among the top seven in concentration among a set of 200 world major rivers. Concentrations of phosphate and ammonium in the Bagmati basin (3 mg l^{-1} and 20 mg l^{-1}, respectively) are in the same range as in the Seine basin and thus place the Bagmati among the most heavily polluted rivers in the world. Agricultural activities within the sub-basin, urban development, landfills, and sewer inputs into the drainage waters also are likely to have affected the chemistry of surface waters within the drainage systems. Data are not available to assess their specific contribution to water quality. The small excess sodium over chloride and the low ratio of silica to base cations (Si/Bscat <0.5) both suggest that inputs of sodium and other base cations from dissolution of aluminosilicates contribute little to the solute load in the Bagmati. The large imprint of human activities on base cations and major anions in river water, as well as the widely known impacts on nutrients, have been observe in several earlier studies (Meybeck and Helmer, 1989; Roy et al. 1999; Rose, 2002; Galindo et al., 2004).

Chloride contributes the largest amount to the total sum of anions in the Bagmati drainage system and anthropogenic sources are likely responsible for such high

concentrations of chloride within the drainage basin. Anthropogenic sources were found to be dominant for chloride in several previous studies (Roy et al. 1999; Meybeck and Helmer, 1989). The relatively low sulfate concentrations in comparison to chloride which I have observed were probably due at least in part to sulfate reduction to sulfide occurring as a result of the high organic matter loading to the Bagmati. This has been observed in previous studies of urban rivers (Rose, 2002; Galindo et al., 2004).

Nitrate concentrations were low relative to total dissolved N throughout the basin, and were particularly low in the downstream urban stations (Table 4. 2), suggesting that oxygen limits nitrification and enhances denitrification in much of the Bagmati. Similar results have been observed in other polluted ecosystems (Wendland et al. 1993; Flintrop et al., 1996; Gunten and Zobrist, 1993). Although the values reported previously for dissolved oxygen show that no stations were effectively anoxic during their study (DHM 1996), our biogeochemical data (very low ratio of nitrate to total dissolved N; presence of sulfide at the sampling sites) provide strong evidence that oxygen concentrations were very low when sampled in 2002-2004. A progressive deterioration of water quality is likely to have occurred in the 10 years separating our two studies.

Base cations, ammonium, chloride, and phosphate ions all appear to be released from the same anthropogenic sources in the Bagmati, as their concentrations are tightly coupled throughout the drainage basin (Table 4.4). These sources appear to be dominated by untreated domestic sewage, given the high concentrations of organic matter in the river, the presence of high human population densities along the river with no treatment systems, the consistent elemental ratios with distance downstream, and the fact that

elemental ratios in the river mirror those found in domestic sewage (Table 4.6). The upstream sampling sites are sparsely populated and anthropogenic inputs into the stream or stream bank are less than those at the densely populated downstream sites. Furthermore, sewage inputs are not delivered directly into the headwater sampling sites as they are in the downstream reaches of the Bagmati.

In addition to domestic sewage inputs, agricultural and industrial effluents are also likely to be contributing some chemical loads to the Bagmati drainage within Kathmandu valley. Most of the farmers use chemical pesticides and fertilizers in their farm land and the excess of those chemical species including BOD, nutrients like orthophosphate, ammonium, nitrate and potassium are found in agricultural surface runoff (ITECO 2003). Fertilizer inputs from nearby terraced crop land also may have contributed to the Bagmati nutrient load (Collins and Jenkins, 1996). The other possible source of chemical species in the Bagmati are industries such as carpet or garment factories that discharge effluent directly into the river.

5.2. Effect of population density on chemical composition of surface waters

Population density and urbanization appear to have large effects on drainage waters in the Bagmati basin within Kathmandu valley. ENPHO (1997) showed that the water quality of Shivapuri watershed serves as a drinking water supply to the Kathmandu valley, is within WHO guidelines for most parameters. Their analysis also indicated, however, that some sites in this relatively pristine basin showed impaired water quality due to the influence of human settlements, agricultural activities, animal grazing and

environmental factors such as landslides and high water discharge. My analysis of the Bagmati shows pervasive effects on water quality that affect all parameters, not just those typically associated with sewage (nutrients and organic matter). Population density appears to be the driver of spatial variability in all base cations along the Bagmati (Fig. 4.8), and concentrations were as high as those observed by Meybeck (1998) in the highly polluted Seine river system in France.

Although the influence of weathering on the concentrations of base cations in the Bagmati appears to be minor, there does appear to be some influence of bedrock geology or other geochemical processes on SiO_2 concentrations. Silica showed a small but statistically significant increase with distance downstream and human population density (Table 4.3). Because there are no significant sources of SiO_2 in human sewage or most other human activities, this increase in SiO_2 may be due to due to spatial variation of mineralogy in the Kathmandu valley. The headwaters of the Bagmati contain mica gneiss and biotite schist with muscovite granite, whereas the bedrock in the lower reaches of the Bagmati basin consists of fine grained phyllite and quartz containing argillaceous limestone and includes slates, shales, claystones and mudstones. Alternately, some unknown source from the urban areas may be contributing modest amounts of SiO_2 to the Bagmati.

5.3. Ecological Stress due to urban runoff

All the measured chemical parameters except nitrate show extremely high concentrations and water quality appears unacceptable for drinking, other domestic use,

industrial use, or irrigation. Water quality is below levels recommended by WHO. This poor water quality associated with urban runoff in Kathmandu creates severe biological effects such as reduced biological diversity due to lack of dissolved oxygen, reduced primary productivity as a result of prolonged turbidity, and excessive fungal growth as a result of enhanced nutrients (Ellis, 1995). Although my sampling did not provide a quantitative assessment of the effects of urban activities on the benthic community of the Bagmati, no benthic organisms were observed during sampling at urban stations, whereas in the upper reaches of the Bagmati basin a variety of flora and fauna (algae, fishes, insects) was observed during sampling. These anecdotal observations were consistent with data reported by FPAN-DISVI (1988), who found that the greatest diversity of benthic organisms was found in the upper Bagmati basin, and that the number of taxa gradually decreased downstream. They found that only the most pollution-tolerant species among the Ephemeroptera were found in the lowermost reach of Bagmati, and other less tolerant groups such as Plecoptera were absent. This variation pattern of benthic communities mirrors the changes in dissolved oxygen and chemical loads which was observed along the drainage system (FPAN-DISVI, 1988).

The quality of surface and groundwaters of Kathmandu valley appear to have degraded considerably since the 1980s. Before 1980, the Bagmati was relatively clear and fresh like the pristine forested streams in its headwaters (ITECO, 2003; Bhatt, personal observation after 1980s). Water quality has degraded since then, and population has more than doubled in the intervening decades (CBS, 2003). Various policies and legislation related to water resource management have been enacted in Nepal during the

past forty years. They include the Soil and Watershed Conservation Act 1982, the Land Act 1964, National Parks and wildlife Conservation Act of 1973, the Nepal Water Supply Corporation Act of 1990, the Environmental Protection Act of 1996, the Forest Act of 1993, the Water Resources Act of 1992, the Local self-governance Act of 1992 and the Kathmandu Valley Strategy on Water Supply and Sanitation 2000 (WECS, 2002). Despite these attempts to control water pollution and protect water supplies, water quality has degraded due to weak enforcement (Guragain et al., 2002). Water pollution in the Bagmati River is causing severe economic losses as well as environmental damage and risks to human health for millions of people. Human activities are primarily responsible for creating these problems not only in the Bagmati River but also in other parts of the country, and effective management of watersheds and waste disposal must be undertaken to reverse this degradation of water quality.

6. Conclusion

A detailed study was carried out to evaluate chemistry of the Bagmati River, which drains a heavily urbanized basin in Kathmandu valley. All the measured solutes except nitrate showed higher concentration in the lower reaches of the Bagmati than the headwater areas. This longitudinal variation of major measured solutes is most likely due to the variability in population density and the large amounts of sewage entering the river. Drainage water chemistry changes with the seasons as winter samples are more dilute than summer due to higher runoff. All the chemical parameters show strong correlations with population density except nitrate and DON, reflecting population density as the most likely driver of chemical load in drainage waters of the Bagmati. The small excess of sodium over chloride suggests that the contribution of base cations from aluminosilicate is not significant within the basin, and this is also supported by the small ratio of silicon to sum of base cations (Si/Bscat <0.5). Ammonium contributes almost all nitrogen into the total dissolved nitrogen. The whole Bagmati ecosystem is disturbed due to severe pollution and its waters are not recommended for any use. Anthropogenic activities due to human population are mainly responsible for the variation of chemistry in drainage waters of Bagmati within the Kathmandu valley.

Table 4.1 Description of the Bagmati drainage basin within Kathmandu valley. Population density and ward area from CBS, 2003.

Sample Name	Site Name	Distance (km)	Channel substrate	People/ha
BR-1	Gokarna	0	Sand and boulders	40
BR-2	Jorpati	1	Sand and boulders	60
BR-3	Gaurighat	6	Sand and boulders	105
BR-4	Sinamangal	8	Clay, sand and fine gravel	207
BR-5	Minbhawan	10	Clay, sand and fine gravel	241
BR-6	Shankhamul	12	Clay, sand and fine gravel	205
BR-7	Thapathali	14	Clay, sand and fine gravel	273
BR-8	Teku	15	Clay, sand and fine gravel	237
BR-9	Balkhu	16	Clay, sand and fine gravel	232
BR-10	Chovar	17	Clay, sand and fine gravel	250

Table 4.2 Average physical parameters and chemical concentrations of major chemical species in the Bagmati River during 2002, 2003 and 2004.

Measured parameters	BR upstream	BR downstream
	mg/L	mg/L
*WT (°C)	22.7	21.4
*EC (µS)	101.7	330.3
*pH	6.9	7
*DO	6.8	3.6
*COD	42.7	89.8
*BOD	20.4	32.4
DOC	2.71	14.58
TDN	2.19	15.25
DON	1.48	1.09
Cl^-	4.74	31.05
SO_4^{2-}	2.18	4.84
NO_3^- N	0.22	0.23
PO_4^{3-} P	0.04	1.53
NH_4^+- N	0.50	13.93
Na^+	8.75	34.93
K^+	2.20	10.21
Mg^{2+}	1.67	4.52
Ca^{2+}	5.43	13.53
Bscat	18.04	63.20
SiO_2	11.95	17.62

Bscat = Sum of base cations, *Data source: DHM, 1996.

Table 4.3 Linear regression parameters describing relationship between measured chemical species with the population density along the Bagmati drainage network within the Kathmandu valley during 2002, 2003 and 2004.

Measured Parameters	Intercept	Slope	R^2	P-value
DOC (mg/L)	-0.586	0.051	0.88	<0.001*
TDN (mg/L)	-2.826	0.077	0.97	<0.0001
DON (mg/L)	1.537	-0.002	0.01	ns
Cl- (mg/L)	-4.454	0.149	0.92	<0.0001
SO_4^{2-} (mg/L)	1.175	0.014	0.55	<0.05*
NO_3^- N (mg/L)	0.230	0.000	0.01	ns
PO_4^{3-} P (mg/L)	-0.529	0.009	0.94	<0.0001
NH_4^+- N (mg/L)	-4.593	0.078	0.94	<0.0001
Na^+ (mg/L)	-0.796	0.151	0.96	<0.0001
K^+ (mg/L)	-0.865	0.047	0.98	<0.0001
Mg^{2+} (mg/L)	0.550	0.017	0.82	<0.001
Ca^{2+} (mg/L)	2.122	0.049	0.85	<0.001
Bscat (mg/L)	0.998	0.263	0.97	<0.0001
SiO_2 (mg/L)	10.234	0.031	0.60	<0.01

Bscat = Sum of base cations, * Only considered eight sites

Table 4.4 Pearson correlation matrix and matrix of probabilities among some major chemical parameters in the water samples from Bagmati drainage system within Kathmandu valley during 2002, 2003 and 2004. POpD is population density, Bscat is the sum of base cations.

Parameters	Dist	PopD	Cl	NO_3	SO_4	PO_4	DOC	TDN	DON	NH_4	Na	K	Mg	Ca	Bscat	SiO_2
Dist	1.00															
PopD	0.92*	1.00														
Cl	0.85	0.96**	1.00													
NO_3	0.14	-0.03	0.09	1.00												
SO_4	0.32	0.56	0.72	0.16	1.00											
PO_4	0.83	0.97**	0.96**	-0.07	0.60	1.00										
DOC	0.75	0.73	0.76	-0.04	0.42	0.72	1.00									
TDN	0.91*	0.98**	0.95**	-0.03	0.51	0.98**	0.73	1.00								
DON	0.25	-0.09	-0.20	0.35	-0.58	-0.24	-0.07	-0.03	1.00							
NH_4	0.82	0.97**	0.96**	-0.13	0.63	0.99**	0.72	0.97**	-0.27	1.00						
Na	0.86	0.98**	0.98**	-0.05	0.67	0.98**	0.79	0.97**	-0.20	0.98**	1.00					
K	0.90*	0.99**	0.98**	0.02	0.60	0.98**	0.75	0.99**	-0.12	0.98**	0.99**	1.00				
Mg	0.98**	0.90*	0.85	0.05	0.30	0.83	0.80	0.92*	0.25	0.82	0.87	0.89	1.00			
Ca	0.97**	0.92*	0.89	0.18	0.37	0.88	0.79	0.93*	0.14	0.86	0.88	0.93*	0.96**	1.00		
Bscat	0.92*	0.99**	0.98*	0.01	0.59	0.98**	0.80	0.98**	-0.09	0.97**	0.99**	0.99**	0.92*	0.94**	1.00	
SiO_2	0.82	0.78	0.74	0.15	0.21	0.78	0.65	0.86	0.27	0.76	0.75	0.80	0.84	0.85	0.80	1.00

Table 4.5 Seasonal variations of average chemical concentrations of chemical species along the Bagmati drainage system within Kathmandu valley during 2002, 2003 and 2004.

Measured parameters	Winter Season		Summer Season		Monsoon Season	
	BR upstream mg/L	BR downstream mg/L	BR upstream mg/L	BR downstream mg/L	BR upstream mg/L	BR downstream mg/L
DOC	1.93	22.35	2.91	11.74	3.05	5.22
TDN	4.00	22.23	4.39	44.72	0.82	4.61
DON	3.41	2.90	2.22	6.13	0.31	0.77
Cl^-	3.97	37.04	13.41	100.45	3.40	9.21
$SO4^{2-}$	2.69	7.38	4.74	7.26	1.28	2.32
NO_3^- -N	0.228	0.212	0.040	0.005	0.317	0.346
PO_4^{3-} -P	0.039	2.019	0.128	6.47	0.027	0.328
NH_4^+ -N	0.37	19.12	3.313	38.58	0.19	3.49
Na^+	5.95	35.21	20.73	127.19	8.16	18.30
K^+	1.53	9.97	4.23	28.01	2.09	5.27
Mg^{2+}	0.96	3.29	2.40	6.39	1.96	4.41
Ca^{2+}	3.92	14.14	6.52	10.50	5.63	8.95
Bscat	12.36	62.61	33.87	172.08	17.85	36.92
SiO_2	14.81	19.33	17.37	22.21	6.60	11.40

Bscat = Sum of base cations

Table 4.6 Comparison of some major chemical constituents of Bagmati River water during 2002-2004 with the typical concentration of municipal waste (Lamb, 1985) and urban sites of Seine River (Meybeck, 1998). All units are in mg l^{-1}.

Chemical parameters	Municipal wasterwater Typical concentration	Bagmati River (av) (2002-2004)	Seine River (Urban sites)
Phosphorus	7	3	3
Total Nitrogen	40	24	18
Calcium	40	11	110
Sodium	75	60	65
Chloride	90	49	78

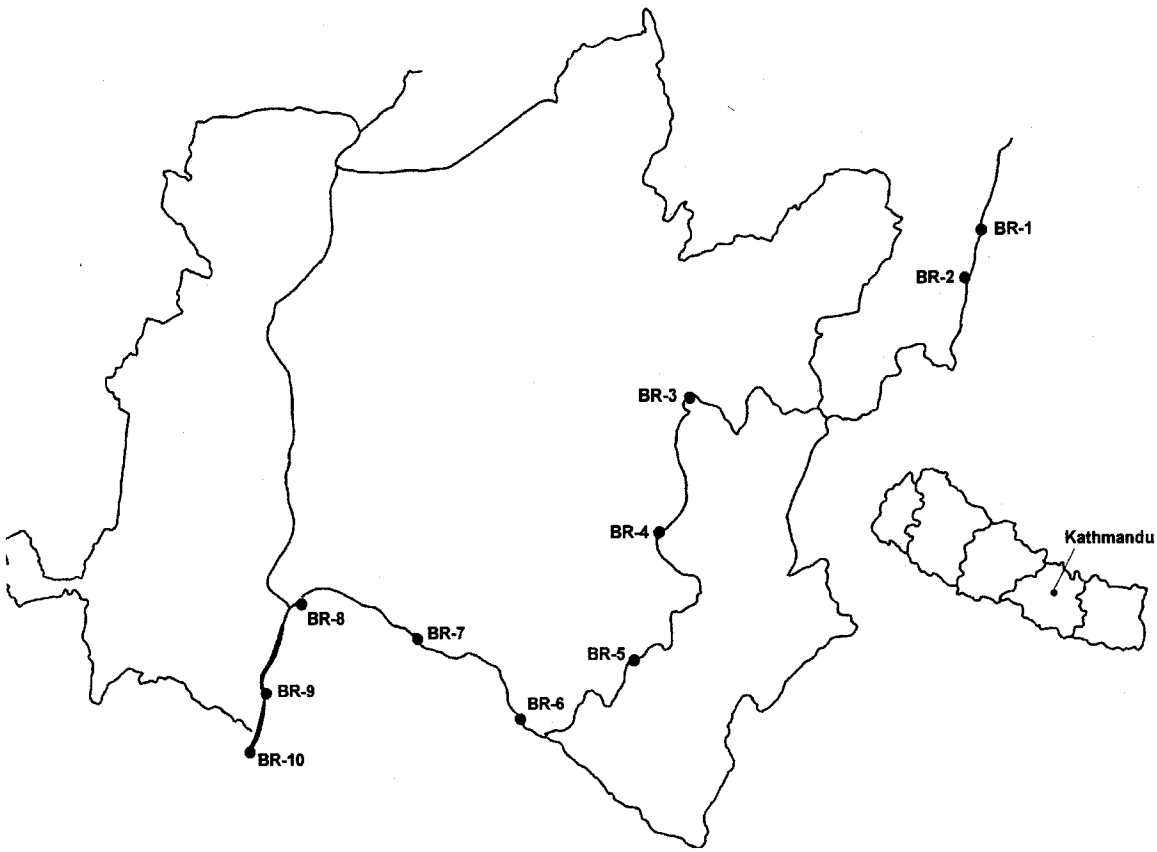

Figure 4.1 Sampling locations of Bagmati River within Kathmandu metropolitan city.

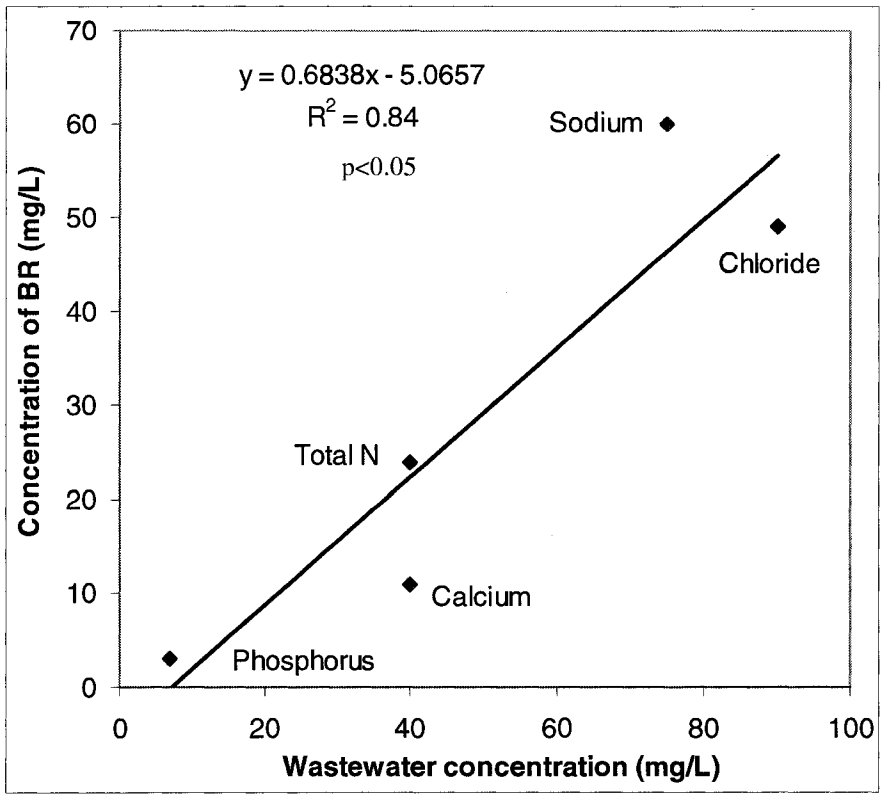

Figure 4.2 Relationship between major chemical parameters in Bagmati River water during 2002-2004 and typical concentrations of municipal wastewater taken from Lamb (1985). Sampled six times, n = 60.

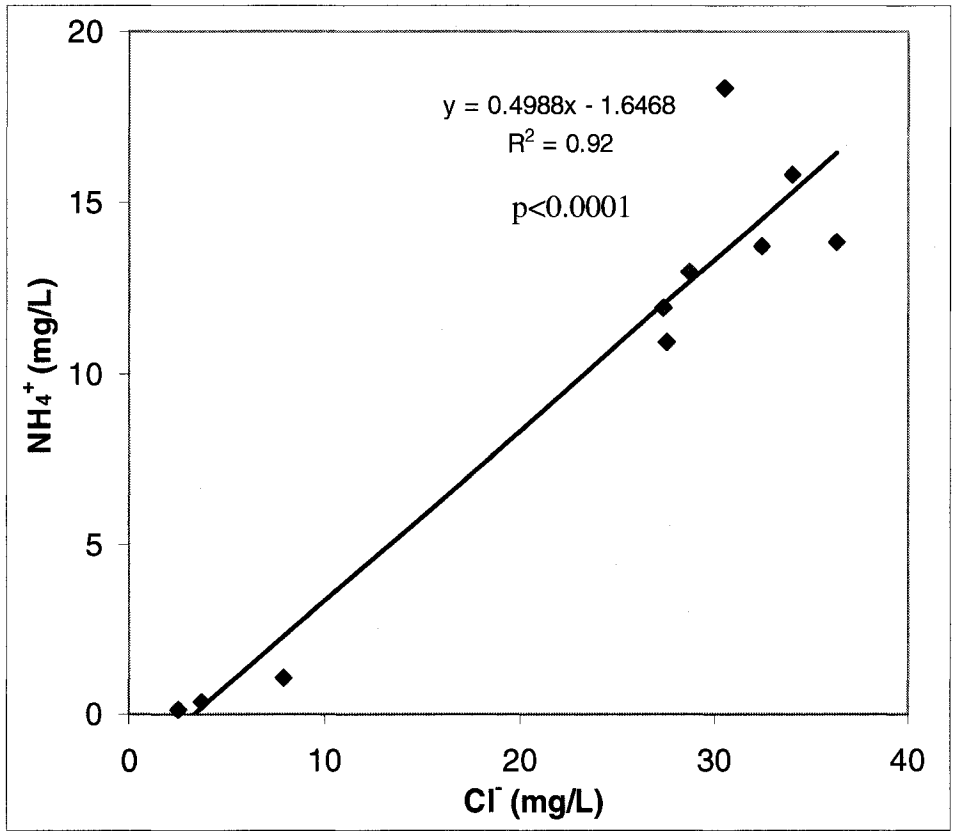

Figure 4.3 Relationship between ammonium and chloride along the Bagmati drainage within Kathmandu valley during 2002-2004. Sampled six times, n = 60.

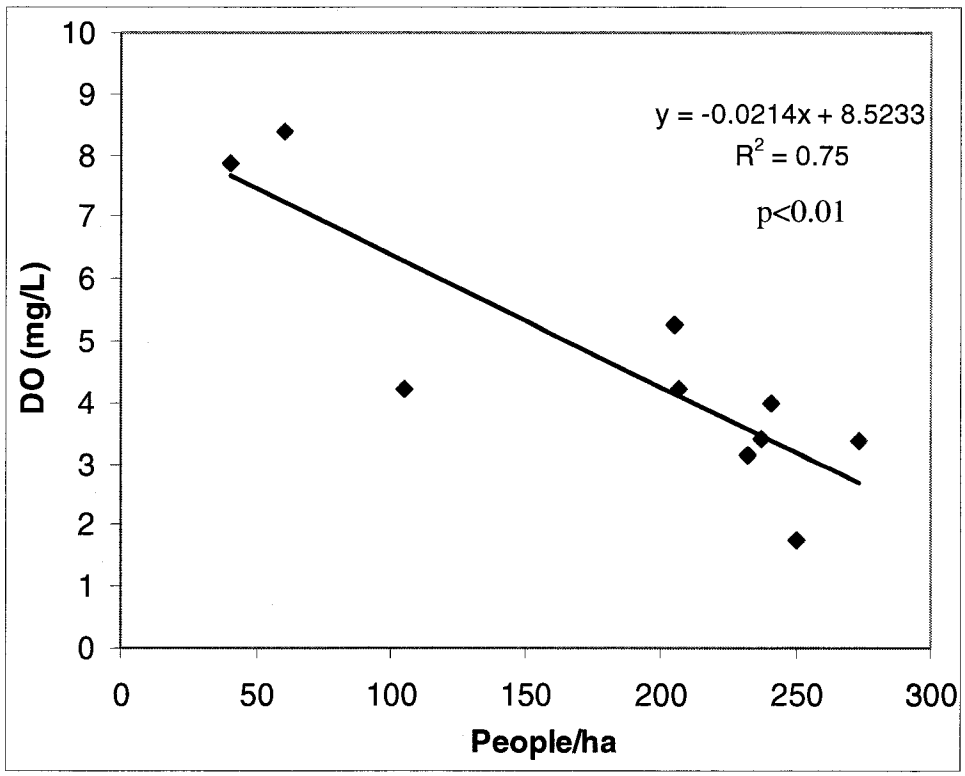

Figure 4.4 Relationship between DO and population density along the Bagmati drainage system within Kathmandu valley (DO data Source: DHM, 1996).

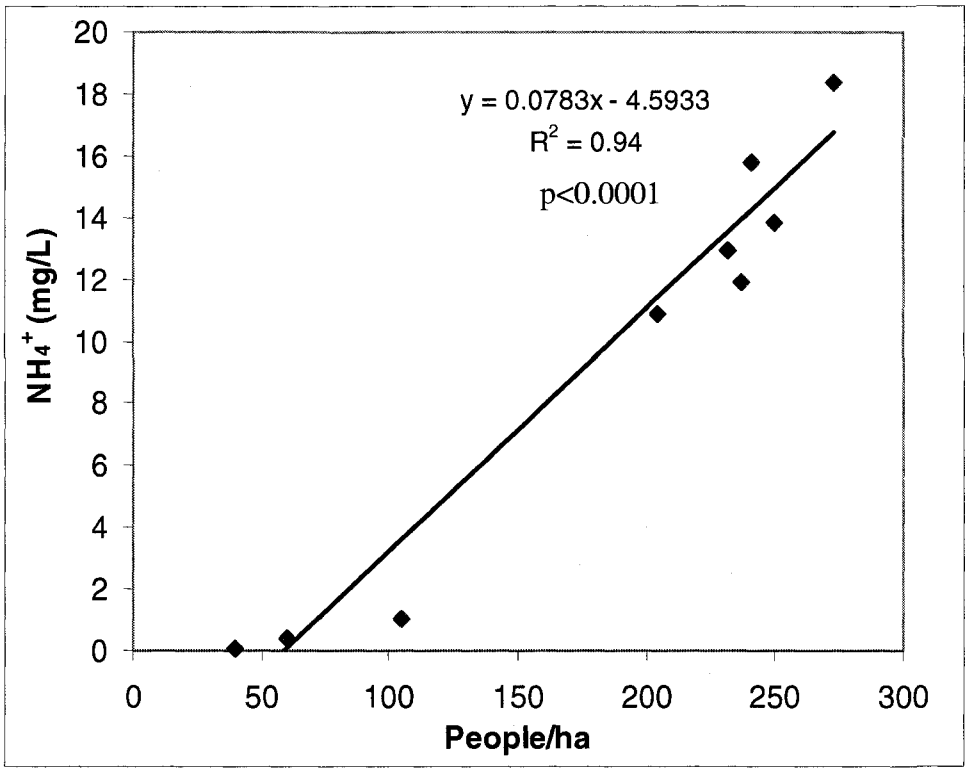

Figure 4.5 Relationship between ammonium and population density along the Bagmati drainage within Kathmandu valley during 2002-2004. Sampled six times, n = 60.

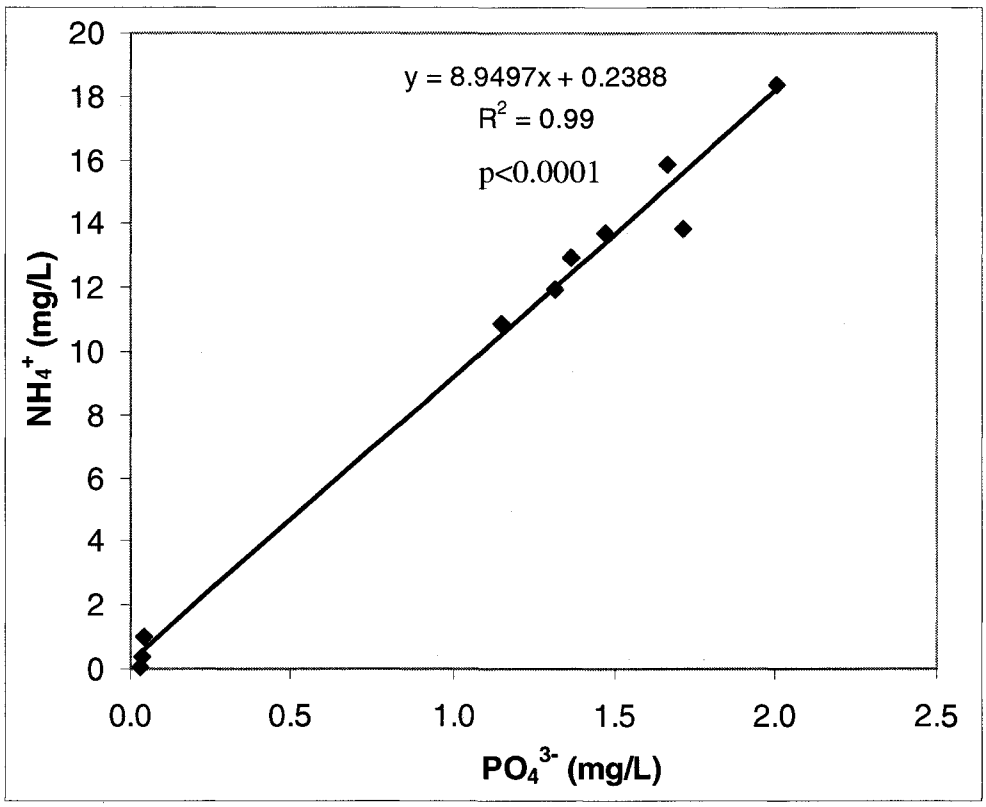

Figure 4.6 Relationship between phosphate and ammonium along the Bagmati drainage within Kathmandu valley during 2002-2004. Sampled six times, n = 60.

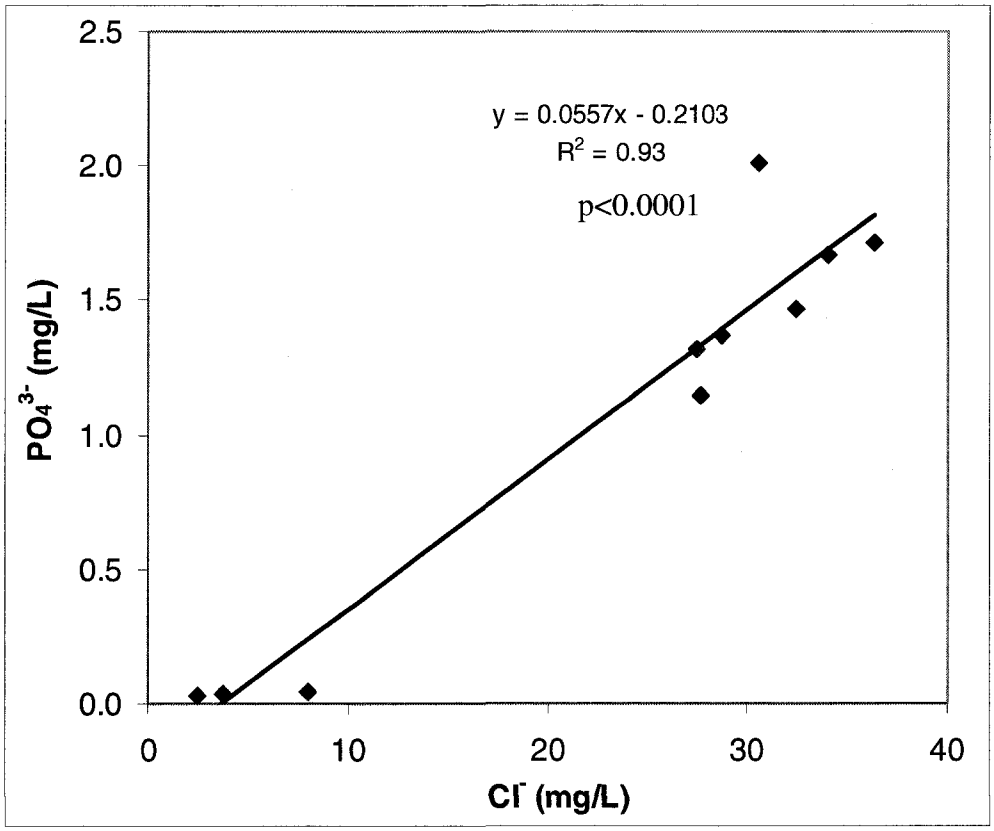

Figure 4.7 Relationship between phosphate and chloride along the Bagmati drainage within Kathmandu valley during 2002-2004. Sampled six times, n = 60.

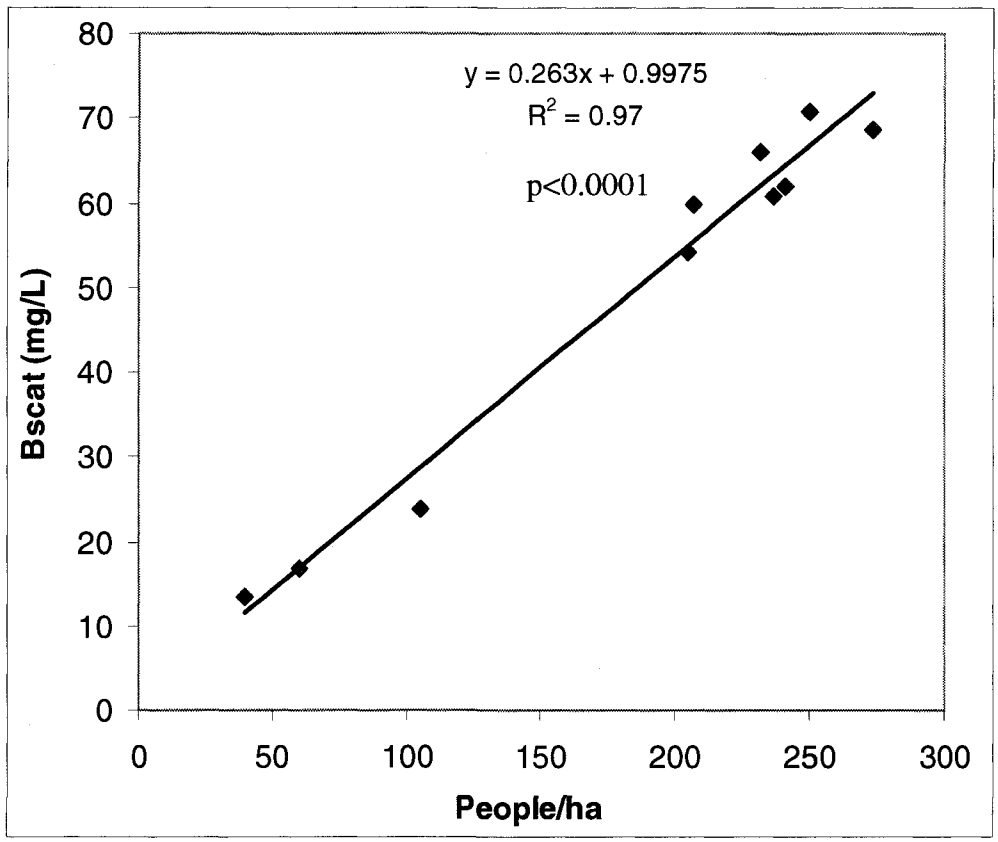

Figure 4.8 Relationship between sum of base cations with population density along the Bagmati drainage within Kathmandu valley during 2002-2004. Sampled six time, n = 60.

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APPENDICES

Appendix A.1. Physical parameters of the water samples within the Rio Icacos-Blanco drainage system during summer 2001.

Sample Name	Collection Date	Site	Sub-site	Elevation (m)	WT (°C)	pH	EC (µS/cm)	DO mg/L
RIS4	20-Jul-01	Rio Icacos	Mainstream		22.4	7.20	79.3	7.76
RIS5	20-Jul-01	Rio Icacos	Mainstream		23.2	7.24	83.8	7.43
RIS6	20-Jul-01	Rio Icacos	Mainstream		22.2	7.31	93.2	7.45
RIS7	23-Jul-01	Rio Icacos	Mainstream	638	21.7	7.19	91.6	7.61
RIS8	23-Jul-01	Rio Icacos	Mainstream	638	21.3	7.26	98.3	7.52
RIST1	20-Jul-01	Rio Icacos	Tributaries		22	7.22	101.3	7.73
RIST2	20-Jul-01	Rio Icacos	Tributaries		21.9	6.80	83.78	7.63
RIST3	20-Jul-01	Rio Icacos	Tributaries		22.3	7.04	78.6	7.33
RIST4	20-Jul-01	Rio Icacos	Tributaries		22.6	6.92	70.2	7.03
RIST5	20-Jul-01	Rio Icacos	Tributaries		22.6	7.12	76.6	7.58
RIST6	20-Jul-01	Rio Icacos	Tributaries		22.4	7.10	66.2	7.43
RIST7	20-Jul-01	Rio Icacos	Tributaries		24.1	7.01	68.4	7.69
RIST8	20-Jul-01	Rio Icacos	Tributaries		22.4	7.12	74.8	7.26
RIST9	23-Jul-01	Rio Icacos	Tributaries	631	23.9	6.55	56.5	5.82
RIST10	23-Jul-01	Rio Icacos	Tributaries	634	22.9	6.92	77.2	7.02
RIST11	23-Jul-01	Rio Icacos	Tributaries		21.5	7.06	103.3	7.35
RIST12	23-Jul-01	Rio Icacos	Tributaries	638	21.6	6.97	78.6	7.36
RIST13	23-Jul-01	Rio Icacos	Tributaries		21.3	7.10	88.8	7.47
RIST14	23-Jul-01	Rio Icacos	Tributaries	638	21.4	7.33	85.2	7.61
RBS2	13-Jul-01	Rio Blanco	Mainstream	15	24.6			
RBS3	13-Jul-01	Rio Blanco	Mainstream	45	24.9			8.5
RBS4	13-Jul-01	Rio Blanco	Tributaries	505	24.4			7.5
RBS5	15-Jul-01	Rio Blanco	Tributaries	500	23.6			7.75
RBS6	15-Jul-01	Rio Blanco	Tributaries	576	22.8			7.08
RBS7	15-Jul-01	Rio Blanco	Mainstream	579				
RIS4	6-Aug-01	Rio Icacos	Mainstream			6.48	52.2	
RIS5	9-Aug-01	Rio Icacos	Mainstream		22.5	6.88	53.8	7.12
RIS6	9-Aug-01	Rio Icacos	Mainstream		22.1	6.90	53.4	7.08
RIS7	9-Aug-01	Rio Icacos	Mainstream	638	22	6.92	53.7	7.66
RIS8	9-Aug-01	Rio Icacos	Mainstream	638	21.6	6.88	62.1	7.9
RIST1	6-Aug-01	Rio Icacos	Tributaries		21.7	6.66	48.3	7.62
RIST2	6-Aug-01	Rio Icacos	Tributaries		21.9	6.85	49.1	7.6
RIST3	9-Aug-01	Rio Icacos	Tributaries		22.2	6.80	51.2	7.11
RIST4	9-Aug-01	Rio Icacos	Tributaries		22.5	6.70	52.2	6.96
RIST5	9-Aug-01	Rio Icacos	Tributaries		22.4	6.96	46.1	7.5
RIST6	9-Aug-01	Rio Icacos	Tributaries		22.1	6.90	47.8	7.76
RIST7	9-Aug-01	Rio Icacos	Tributaries		22.8	6.69	47.6	6.76
RIST8	9-Aug-01	Rio Icacos	Tributaries		22.1	6.68	47.8	7.08
RIST9	9-Aug-01	Rio Icacos	Tributaries	631	23.1	6.63	36.4	7.08
RIST10	9-Aug-01	Rio Icacos	Tributaries	634	23	6.81	55.2	7
RIST11	9-Aug-01	Rio Icacos	Tributaries		21.9	6.78	51.5	7.11
RIST12	9-Aug-01	Rio Icacos	Tributaries	638	22	6.91	51.5	7.61
RIST13	9-Aug-01	Rio Icacos	Tributaries		21.6	6.79	55.6	7.35
RIST14	9-Aug-01	Rio Icacos	Tributaries	638	21.8	6.95	49.4	8.04

Appendix A.1. Continued.

Sample Name	Collection Date	Site	Sub-site	Elevation (m)	WT (°C)	pH	EC (µS/cm)	DO mg/L
RBS2	3-Aug-01	Rio Blanco	Mainstream	15	23.4	7.20	119.3	7.34
RBS3	3-Aug-01	Rio Blanco	Mainstream	45		7.26	68.1	
RBS4	3-Aug-01	Rio Blanco	Tributaries	505	23.9	7.46	81.6	8.31
RBS5	3-Aug-01	Rio Blanco	Tributaries	500	23.6	7.30	52.8	7.72
RBS6	3-Aug-01	Rio Blanco	Tributaries	576	23.1	7.10	108.8	6.46
RBS7	3-Aug-01	Rio Blanco	Mainstream	579	26.2	7.36	71.4	8.2

Appendix A.2. Physical parameters of the water samples within the Rio Icacos-Blanco drainage system during summer 2002.

Sample Name	Collection Date	Site	Subsite	WT (°C)	pH	EC (µS/cm)	DO (mg/L)
RIS10	8-Jul-02	Rio Icacos	Mainstream	20.9	7.41	75.5	9.45
RIS9	8-Jul-02	Rio Icacos	Mainstream	21.2	7.16	74.5	8.75
RIS8	6-Jul-02	Rio Icacos	Mainstream	21.2	7.08	65.7	9.32
RIS7	6-Jul-02	Rio Icacos	Mainstream	21.4	7.12	69	9.4
RIS6	6-Jul-02	Rio Icacos	Mainstream	21.6	7.01	23.2	9.08
RIS5	6-Jul-02	Rio Icacos	Mainstream	22.3	6.87	63.1	8.9
RIS4	6-Jul-02	Rio Icacos	Mainstream	21.8	6.89	58.4	8.8
RIST1	10-Jul-02	Rio Icacos	Tributaries	21.5	7.6	53.3	9.01
RIST2	10-Jul-02	Rio Icacos	Tributaries	21.5	6.82	54.6	8.56
RIST3	10-Jul-02	Rio Icacos	Tributaries	21.7	6.54	19.5	8.59
RIST4	10-Jul-02	Rio Icacos	Tributaries	22.1	6.49	44	8.66
RIST5	8-Jul-02	Rio Icacos	Tributaries	21.7	6.87	54.7	8.75
RIST5A	10-Jul-02	Rio Icacos	TribTransect	21.7	7.16	58	8.73
RIST5B	10-Jul-02	Rio Icacos	TribTransect	21.7	7.35	59.2	8.75
RIST5C	10-Jul-02	Rio Icacos	TribTransect	21.3	7.29	59.5	8.95
RIST6	8-Jul-02	Rio Icacos	Tributaries	21.5	6.78	50	8.64
RIST6A	15-Jul-02	Rio Icacos	TribTransect	21.5	6.77	51.7	7.8
RIST6B	15-Jul-02	Rio Icacos	TribTransect	21.4	7.08	50.01	8.82
RIST6C	15-Jul-02	Rio Icacos	TribTransect	21.3	6.18	38.5	6.6
RIST6D	15-Jul-02	Rio Icacos	TribTransect	21.4	7.16	22.8	8.96
RIST6E	15-Jul-02	Rio Icacos	TribTransect	21.3	7.53	0	9.24
RIST6F	15-Jul-02	Rio Icacos	TribTransect	21.7	6.94	47.5	7.82
RIST7	13-Jul-02	Rio Icacos	Tributaries	22.5	6.18	55.1	7.47
RIST8	8-Jul-02	Rio Icacos	Tributaries	21.6	6.46	53.5	8.56
RIST8	23-Jul-02	Rio Icacos	TribTransect	21.7	6.65	56.7	7.52
RIST8A	23-Jul-02	Rio Icacos	TribTransect	21.5	6.72	57.8	8.25
RIST8B	23-Jul-02	Rio Icacos	TribTransect	21.4	6.68	60.2	8.08
RIST8C	23-Jul-02	Rio Icacos	TribTransect	21.2	7.27	61.8	8.98
RIST9	13-Jul-02	Rio Icacos	Tributaries	23.5	6.65	42.8	7.88
RIST10	8-Jul-02	Rio Icacos	Tributaries	22.4	6.78	68.6	8.37
RIST11	13-Jul-02	Rio Icacos	Tributaries	21.6	6.94	51.1	8.68
RIST12	8-Jul-02	Rio Icacos	Tributaries	21.5	6.78	55.8	8.74
RIST13	8-Jul-02	Rio Icacos	Tributaries	21.2	6.87	58	8.82
RIST14	8-Jul-02	Rio Icacos	Tributaries	21.3	7.25	62.3	9.23
RIST14A	8-Jul-02	Rio Icacos	TribTransect	21	7.45	46.4	9.05
RBS2	12-Jul-02	Rio Blanco	Mainstream	26.8	7.06	191.8	7.48
RBS3	12-Jul-02	Rio Blanco	Mainstream	25.6	8	80.8	10.02
RBS4	12-Jul-02	Rio Blanco	Tributaries	24.9	8.06	103.2	9.36
RBS5	12-Jul-02	Rio Blanco	Tributaries	24.2	7.64	69.8	9.55
RBS6	12-Jul-02	Rio Blanco	Tributaries	23.2	7.31	52.8	8.67
RBS7	12-Jul-02	Rio Blanco	Mainstream	26.1	7.92	86.5	9.55

Appendix A.2. Continued.

Sample Name	Collection Date	Site	Subsite	WT (°C)	pH	EC (µS/cm)	DO (mg/L)
RIS10	23-Jul-02	Rio Icacos	Mainstream	21.1	7.35	69.8	9.43
RIS9	23-Jul-02	Rio Icacos	Mainstream	21.2	7.06	68	9.09
RIS8	23-Jul-02	Rio Icacos	Mainstream	21.4	6.95	67.6	8.86
RIS7	23-Jul-02	Rio Icacos	Mainstream	21.8	6.97	62.5	8.98
RIS6	23-Jul-02	Rio Icacos	Mainstream	21.8	6.94	62.9	8.86
RIS5	23-Jul-02	Rio Icacos	Mainstream	22	6.84	60.2	8.8
RIS4	23-Jul-02	Rio Icacos	Mainstream	21.8	6.87	58.6	8.89
RIST1	29-Jul-02	Rio Icacos	Tributaries	22	6.51	49.8	8.36
RIST2	29-Jul-02	Rio Icacos	Tributaries	21.9	6.63	52.7	8.72
RIST3	29-Jul-02	Rio Icacos	Tributaries	22.1	6.41	54.8	8.63
RIST4	29-Jul-02	Rio Icacos	Tributaries	22.4	6.36	53.3	9
RIST5	2-Aug-02	Rio Icacos	Tributaries	27.1RT	6.68	60.4	
RIST5A	2-Aug-02	Rio Icacos	TribTransect	27.2RT	6.78	58.8	
RIST5B	2-Aug-02	Rio Icacos	TribTransect	27.3RT	6.87	68.3	
RIST5C	2-Aug-02	Rio Icacos	TribTransect	27.2RT	7.15	67.7	
RIST6	31-Jul-02	Rio Icacos	Tributaries	21.7	6.8	51	8.98
RIST6A	31-Jul-02	Rio Icacos	TribTransect	21.5	6.84	51.2	9.17
RIST6B	31-Jul-02	Rio Icacos	TribTransect	21.5	6.98	51.8	9.83
RIST6C	31-Jul-02	Rio Icacos	TribTransect	21.5	6.21	46.4	8.23
RIST6D	31-Jul-02	Rio Icacos	TribTransect	21.7	6.94	52.3	8.91
RIST6E	31-Jul-02	Rio Icacos	TribTransect	21.5	7.44	57.6	9.42
RIST6F	31-Jul-02	Rio Icacos	TribTransect	22.3	6.96	51.2	8.84
RIST7	23-Jul-02	Rio Icacos	Tributaries	22.4	6.28	55.7	7.05
RIST8	29-Jul-02	Rio Icacos	Tributaries	22.1	6.51	55.4	8.57
RIST8A	29-Jul-02	Rio Icacos	TribTransect	21.9	6.55	56.7	8.57
RIST8B	29-Jul-02	Rio Icacos	TribTransect	21.5	6.52	58	8.37
RIST8C	29-Jul-02	Rio Icacos	TribTransect	21.4	7.1	59.5	7.85
RIST8D	29-Jul-02	Rio Icacos	TribTransect	21.1	6.69	62.6	10.45
RIST9	23-Jul-02	Rio Icacos	Tributaries	22.6	6.62	47.5	8.04
RIST10	23-Jul-02	Rio Icacos	Tributaries	22.8	6.84	73.4	7.38
RIST11	23-Jul-02	Rio Icacos	Tributaries	21.5	6.78	66.4	7.35
RIST12	23-Jul-02	Rio Icacos	Tributaries	21.7	6.84	57.4	8.63
RIST13	23-Jul-02	Rio Icacos	Tributaries	21.3	6.82	61	7.56
RIST14	23-Jul-02	Rio Icacos	Tributaries	21.6	7.19	59.3	9.23
RIST14A	23-Jul-02	Rio Icacos	TribTransect	21.2	7.42	61.9	8.4
RBS2	2-Aug-02	Rio Blanco	Mainstream	28.1	6.86	218.7	
RBS3	2-Aug-02	Rio Blanco	Mainstream	25.6	7.96	77.5	
RBS4	2-Aug-02	Rio Blanco	Tributaries	25.2	8.02	102.9	
RBS5	2-Aug-02	Rio Blanco	Tributaries	24.9	7.61	71.1	
RBS6	2-Aug-02	Rio Blanco	Tributaries	25.3	7.24	114.2	
RBS7	2-Aug-02	Rio Blanco	Mainstream	24.2	7.89	83.8	
RIS10	6-Aug-02	Rio Icacos	Mainstream	20.9	7.38	77.9	
RIS9	6-Aug-02	Rio Icacos	Mainstream	21.2	7.08	76.9	
RIS8	6-Aug-02	Rio Icacos	Mainstream	21.3	7.07	72.1	
RIS7	6-Aug-02	Rio Icacos	Mainstream	21.4	7.05	71	
RIS6	6-Aug-02	Rio Icacos	Mainstream	21.6	6.92	68.5	
RIS5	6-Aug-02	Rio Icacos	Mainstream	22.4	6.87	65.6	
RIS4	6-Aug-02	Rio Icacos	Mainstream	22.5	6.85	62	

Appendix A.3. Physical parameters of the water samples within the Rio Icacos-basin during winter 2005.

Sample name	Collection Date	Site	Sub-site	WT (°C)	pH	EC uS/cm	DO mg/L
RIS4	1-Feb-05	Rio Icacos	Mainstream	19.1	6.82	49.8	8.06
RIS5	1-Feb-05	Rio Icacos	Mainstream	19.6	6.86	52.6	7.97
RIS6	1-Feb-05	Rio Icacos	Mainstream	19.6	6.92	55.7	8.01
RIS7	1-Feb-05	Rio Icacos	Mainstream	19.4	7.04	61.9	8.32
RIS8	1-Feb-05	Rio Icacos	Mainstream	19.4	7.06	61.4	8.34
RIS9	1-Feb-05	Rio Icacos	Mainstream	19.4	7.19	62.8	8.22
RIS10	1-Feb-05	Rio Icacos	Mainstream	19.3	7.44	63.6	7.95
RIST1	2-Feb-05	Rio Icacos	Tributary	19.3	6.75	39.6	8.07
RIST2	2-Feb-05	Rio Icacos	Tributary	18.9	6.88	48.7	8.13
RIST3	2-Feb-05	Rio Icacos	Tributary	19.4	6.72	48.1	7.78
RIST4	2-Feb-05	Rio Icacos	Tributary	19.8	6.56	41.4	7.73
RIST5	2-Feb-05	Rio Icacos	Tributary	18.9	6.92	46.5	8.06
RIST6	2-Feb-05	Rio Icacos	Tributary	19.4	6.92	44.1	8.25
RIST7	2-Feb-05	Rio Icacos	Tributary	19.8	6.23	42	7.18
RIST8	3-Feb-05	Rio Icacos	Tributary	19.2	6.77	46.8	8.02
RIST9	3-Feb-05	Rio Icacos	Tributary	19.2	6.37	40.1	7.09
RIST10	3-Feb-05	Rio Icacos	Tributary	19.6	6.72	57.6	7.33
RIST11	3-Feb-05	Rio Icacos	Tributary	19.3	6.92	57.6	7.95
RIST12	3-Feb-05	Rio Icacos	Tributary	19	6.94	48.2	7.85
RIST13	3-Feb-05	Rio Icacos	Tributary	19	6.81	44.3	8.04
RIST14	3-Feb-05	Rio Icacos	Tributary	18.8	7.2	44.1	7.84
RISW1A	7-Feb-05	Rio Icacos	Groundwater	19.5	6	104.8	2.12
RISW1B	7-Feb-05	Rio Icacos	Groundwater	19.6	5.46	42.3	2.2
RISW2A	7-Feb-05	Rio Icacos	Groundwater	20.2	5.88	76.8	1.23
RISW2B	7-Feb-05	Rio Icacos	Groundwater	20.4	5.84	86.6	1.32
RISW3A	7-Feb-05	Rio Icacos	Groundwater	22	6.3	174.3	1.48
RISW3B	7-Feb-05	Rio Icacos	Groundwater	21.6	5.78	67.6	1.92
RISW4A	7-Feb-05	Rio Icacos	Groundwater	21	6.21	68.3	2.95
RISW5A	7-Feb-05	Rio Icacos	Groundwater	20.3	5.64	46.9	2.48
RISW5B	10-Feb-05	Rio Icacos	Groundwater				
RISW6A	7-Feb-05	Rio Icacos	Groundwater				
RISW6B	7-Feb-05	Rio Icacos	Groundwater				
RISW7A	7-Feb-05	Rio Icacos	Groundwater	20.8	6.01	81.8	2.67
RISW7B	7-Feb-05	Rio Icacos	Groundwater	20.8	5.56		3.37
RISW8A	7-Feb-05	Rio Icacos	Groundwater	23.3	6.03		

Appendix A.3. Continued

Sample name	Collection Date	Site	Sub-site	WT (°C)	pH	EC uS/cm	DO mg/L
RISSP1	8-Feb-05	Rio Icacos	Upper Source	20	7.1	67.2	5.95
RISSP2	8-Feb-05	Rio Icacos	UpperSoure	20.6	5.46	57.8	1.15
RISSP3	10-Feb-05	Rio Icacos	UpperSoure	18.5	4.68	40	3.63
RISSP4	10-Feb-05	Rio Icacos	UpperSoure	20	5.5	40.7	3.44
RISSP5	10-Feb-05	Rio Icacos	UpperSource	20	7.16	54.1	7.81
RISSP6	14-Feb-05	Rio Icacos	Upper Source	18.6	7.88	55.8	6.64
RISSP7	14-Feb-05	Rio Icacos	Upper Source	18.8	7.12	56	8.15
RISSP8	14-Feb-05	Rio Icacos	Upper Source	18.9	7.23	61	8.16
RISSP9	14-Feb-05	Rio Icacos	Upper Source	18.8	6.98	75.3	5.79
RISSP10	14-Feb-05	Rio Icacos	Upper Source	18.9	6.84	38.7	7.86
RISSPL1	16-Feb-05	Rio Icacos	Lower Source	20.3	5.77	53	1.6
RISSPL2	16-Feb-05	Rio Icacos	Lower Source	19.5	5.07	28.7	4.48
RISSPL3	17-Feb-05	Rio Icacos	Lower Source	18.9	5.57	32.6	3.18
RISSPL4	18-Feb-05	Rio Icacos	Lower Source	19.5	5.3	35.8	3.48
RISSPL5	18-Feb-05	Rio Icacos	Lower Source	20	6.39	47.3	3.68
RISSPL6	18-Feb-05	Rio Icacos	Lower Source	18.9	4.73	30	4.46
RISSP1	17-Feb-05	Rio Icacos	Upper Source	19.9	7.02	61	8.68
RISSP2	17-Feb-05	Rio Icacos	Upper Source	20.5	5.2	32	1.05
RISSP3	17-Feb-05	Rio Icacos	Upper Source	19	3.9	37.8	6.43
RISSP3A	17-Feb-05	Rio Icacos	Upper Source	20.2	4.93	33.1	6.82
RISSP4	16-Feb-05	Rio Icacos	Upper Source	20.1	5.63	41.6	4.18
RISSP4A	16-Feb-05	Rio Icacos	Upper Source	20.6	6.08	53.1	7.57
RISSP5	16-Feb-05	Rio Icacos	Upper Source	19.9	6.77	51.1	5.62
RISSP6	21-Feb-05	Rio Icacos	Upper Source	18.6	7.2	49.3	5.2
RISSP7	21-Feb-05	Rio Icacos	Upper Source	18.8	7.14	52.2	8.39
RISSP8	21-Feb-05	Rio Icacos	Upper Source	18.9	6.9	59.7	8.15
RISSP9	21-Feb-05	Rio Icacos	Upper Source	18.4	6.76	47.5	5.48
RISSP10	22-Feb-05	Rio Icacos	Upper Source	18.7	6.86	53.6	7.6
RISSPL1	22-Feb-05	Rio Icacos	Lower Source	19.9	4.92	47.3	3.22
RISSPL2	22-Feb-05	Rio Icacos	Lower Source	20.4	5.64	37.7	7.14
RISSPL3	22-Feb-05	Rio Icacos	Lower Source	18.6	5.8	40.5	2.69
RISSPL4	21-Feb-05	Rio Icacos	Lower Source	19	5.53	36.8	3.38
RISSPL5	21-Feb-05	Rio Icacos	Lower Source	19.4	5.89	63.4	2.03
RISSPL6	21-Feb-05	Rio Icacos	Lower Source	17.8	5.15	27.8	
RISW1A	18-Feb-05	Rio Icacos	Groundwater	20.2	6	101.1	1.51
RISW1B	18-Feb-05	Rio Icacos	Groundwater	20.1	5.46	42	2.68
RISW2A	18-Feb-05	Rio Icacos	Groundwater	20.9	5.94	57.7	1.6
RISW2B	18-Feb-05	Rio Icacos	Groundwater	20.4	5.87	43.4	1.34
RISW3A	18-Feb-05	Rio Icacos	Groundwater	20.5	6.3	140.5	1.8
RISW3B	18-Feb-05	Rio Icacos	Groundwater	20.7	5.76	57.8	2.24
RISW4A	18-Feb-05	Rio Icacos	Groundwater				
RISW5A	18-Feb-05	Rio Icacos	Groundwater	22.7	5.7		
RISW6B	18-Feb-05	Rio Icacos	Groundwater	22.9	5.03		
RISW7A	18-Feb-05	Rio Icacos	Groundwater	20.9	5.86	73.6	2.1
RISW7B	18-Feb-05	Rio Icacos	Groundwater	20.6	5.69	28.5	3.23
RISW8A	18-Feb-05	Rio Icacos	Groundwater	22.4	6.28		2.84

Appendix A. 3. Continued.

Sample name	Collection Date	Site	Sub-site	WT (°C)	pH	EC uS/cm	DO mg/L
RISSP1	22-Feb-05	Rio Icacos	Upper Source	19.7	6.32	61.7	8.86
RISSP2	22-Feb-05	Rio Icacos	Upper Source	20.4	5.64	69.3	0.84
RISSP3	22-Feb-05	Rio Icacos	Upper Source	18.5	4.69	40.7	5.98
RISSP4	22-Feb-05	Rio Icacos	Upper Source	19.3	5.47	41.9	3.92
RISSP5	22-Feb-05	Rio Icacos	Upper Source	19.8	6.08	54.2	8.7
RISSP6	23-Feb-05	Rio Icacos	Upper Source	18.6	7.02	53.3	4.36
RISSP7	23-Feb-05	Rio Icacos	Upper Source	18.8	6.89	52.5	7.92
RISSP8	23-Feb-05	Rio Icacos	Upper Source	19	6.83	59.9	8.3
RISSP9	23-Feb-05	Rio Icacos	Upper Source	18.4	6.97	48.6	6.42
RISSP10	24-Feb-05	Rio Icacos	Upper Source	18.8	6.96	53.8	7.72
RISSPL1	24-Feb-05	Rio Icacos	Lower Source	20.1	6.72	45.2	5.69
RISSPL2	24-Feb-05	Rio Icacos	Lower Source	20.5	6.42	30.1	7.54
RISSPL3	24-Feb-05	Rio Icacos	Lower Source	18.8	5.66	44.4	2.69
RISSPL4	23-Feb-05	Rio Icacos	Lower Source	19.1	5.27	17.2	3.44
RISSPL5	23-Feb-05	Rio Icacos	Lower Source	21.6	6.27	51.2	6.01
RISSPL6	23-Feb-05	Rio Icacos	Lower Source	18.4	5.12	28.1	3.37

Appendix A.4. Physical parameters of the water samples along the Bagmati River within Kathmandu valley. Data source: DHM, Nepal, 1996.

Sample Name	Collection Date	Site	Sub-site	Distance (Km)	WT(av) (°C)	pH (av)	EC(av) (µS/cm)	DO (av) (mg/L)
BR-1	DHM, 1996	Bagmati	Gokarna	0	21.8	6.98	55.5	7.87
BR-2	DHM, 1996	Bagmati	Jorpati	1	23.0	6.93	84.3	8.38
BR-3	DHM, 1996	Bagmati	Gaurighat	6	23.3	6.85	165.4	4.23
BR-4	DHM, 1996	Bagmati	Sinamangal	8	22.4	6.80	190.2	4.22
BR-5	DHM, 1996	Bagmati	Minbhawan	10	21.8	6.91	237.4	4.01
BR-6	DHM, 1996	Bagmati	Shankhamul	12	20.1	7.07	239.7	5.27
BR-7	DHM, 1996	Bagmati	Thapathali	14	21.5	7.09	383.3	3.38
BR-8	DHM, 1996	Bagmati	Teku	15	21.0	7.11	434.6	3.40
BR-9	DHM, 1996	Bagmati	Balkhu	16	21.7	7.18	402.9	3.14
BR-10	DHM, 1996	Bagmati	Chhovar	17	21.3	7.11	424.1	1.75

Appendix B.1. Chemical parameters of water samples from the Rio Icacos-Blanco drainage system during summer 2001.

Sample Name	Collection Date	Site	Sub-site	NPOC mg/L	TDN mg	Cl^- mg /L	SO_4^{2-} mg	NO_3^- mg	PO_4^{3-} mg	NH_4^+ mg/L	Na^+ mg /L	K^+ mg /L	Mg^{2+} mg /L	Ca^{2+} mg /L	SiO_2 mg /L
RIS4	20-Jul-01	Rio Icacos	Mainstream	0.620	0.240	7.40	0.398	0.146	0.009	0.007	6.19	0.611	1.42	2.37	25.3
RIS5	20-Jul-01	Rio Icacos	Mainstream	0.530	0.270	7.11	0.397	0.157	0.009	0.006	6.47	0.689	1.55	4.60	26.5
RIS6	20-Jul-01	Rio Icacos	Mainstream	0.440	0.270	7.46	0.423	0.184	0.009	0.006	6.76	0.696	1.62	5.13	28.3
RIS7	23-Jul-01	Rio Icacos	Mainstream	0.630	0.284	6.73	0.439	0.232	0.017	0.003	6.56	0.656	1.68	5.07	28.3
RIS8	23-Jul-01	Rio Icacos	Mainstream	0.430	0.389	7.25	0.435	0.341	0.025	0.002	7.14	0.775	1.76	6.31	29.4
RIST1	20-Jul-01	Rio Icacos	Tributary	0.560	0.250	7.91	0.459	0.160	0.009	0.008	6.25	0.552	1.32	3.29	21.6
RIST2	20-Jul-01	Rio Icacos	Tributary	0.550	0.190	7.16	0.379	0.110	0.009	0.003	6.11	0.591	1.59	3.94	24.1
RIST3	20-Jul-01	Rio Icacos	Tributary	0.420	0.240	7.66	0.349	0.139	0.006	0.014	5.91	0.6	1.23	3.37	21.5
RIST4	20-Jul-01	Rio Icacos	Tributary	0.650	0.190	7.77	0.462	0.087	0.008	0.025	5.70	0.623	1.16	3.05	21.3
RIST5	20-Jul-01	Rio Icacos	Tributary	0.730	0.180	7.25	0.503	0.089	0.010	0.005	5.87	0.575	1.51	3.72	23.6
RIST6	20-Jul-01	Rio Icacos	Tributary	0.470	0.250	7.41	0.368	0.170	0.008	0.003	5.63	0.564	1.12	2.96	20.4
RIST7	20-Jul-01	Rio Icacos	Tributary	0.840	0.150	7.80	0.423	0.076	0.006	0.012	5.32	0.554	1.31	3.03	15.7
RIST8	20-Jul-01	Rio Icacos	Tributary	0.370	0.270	6.32	0.375	0.147	0.009	0.006	5.73	0.616	1.37	4.04	24.1
RIST9	23-Jul-01	Rio Icacos	Tributary	2.040	0.149	6.17	0.393	0.019	0.005	0.060	5.07	0.437	0.95	1.55	10.4
RIST10	23-Jul-01	Rio Icacos	Tributary	0.710	0.146	7.52	0.378	0.061	0.013	0.027	6.30	0.517	1.26	3.18	19.8
RIST11	23-Jul-01	Rio Icacos	Tributary	0.430	0.182	7.39	0.310	0.143	0.016	0.007	6.93	0.669	1.53	4.39	25.6
RIST12	23-Jul-01	Rio Icacos	Tributary	0.550	0.163	6.16	0.384	0.113	0.009	0.002	5.84	0.603	1.38	4.07	22.1
RIST13	23-Jul-01	Rio Icacos	Tributary	0.560	0.191	6.24	0.322	0.140	0.015	0.002	6.16	0.604	1.79	5.29	25.6
RIST14	23-Jul-01	Rio Icacos	Tributary	0.660	0.194	6.33	0.412	0.160	0.018	0.002	6.70	0.635	1.61	4.70	26.6
RBS2	13-Jul-01	Rio Blanco	Mainstream	5.070	0.460	31.44	13.96	0.127	0.012	0.013	28.23	6.319	19.77	10.95	10.8
RBS3	13-Jul-01	Rio Blanco	Mainstream	4.810	0.340	23.07	1.428	0.060	0.011	0.006	8.52	0.693	1.73	3.53	9.3
RBS4	13-Jul-01	Rio Blanco	Tributary	5.880	0.260	12.41	1.171	0.015	0.007	0.006	5.72	0.575	1.43	4.14	10.0
RBS5	15-Jul-01	Rio Blanco	Tributary	1.590	0.140	10.03	0.687	0.035	0.010	0.007	6.56	0.646	1.41	3.85	22.5
RBS6	15-Jul-01	Rio Blanco	Tributary	1.180	0.120	12.97	3.094	0.000	0.011	0.003	7.77	0.428	3.11	8.42	26.3
RBS7	15-Jul-01	Rio Blanco	Mainstream	1.400	0.360	9.15	0.753	0.055	0.009	0.003	6.57	0.668	1.56	4.77	21.0
RIS4	6-Aug-01	Rio Icacos	Mainstream	2.150	0.250	6.03	0.477	0.139	0.008	0.010	4.54	0.531	1.04	2.81	16.7
RIS5	9-Aug-01	Rio Icacos	Mainstream	2.230	0.259	5.98	0.492	0.144	0.007	0.007	4.42	0.53	0.99	3.00	17.7
RIS6	9-Aug-01	Rio Icacos	Mainstream	2.750	0.296	5.84	0.497	0.158	0.011	0.009	4.46	0.562	1.05	3.12	18.4
RIS7	9-Aug-01	Rio Icacos	Mainstream	2.680	0.365	5.78	0.509	0.212	0.014	0.009	4.40	0.601	1.08	3.37	18.5
RIS8	9-Aug-01	Rio Icacos	Mainstream	2.700	0.456	6.20	0.577	0.300	0.017	0.010	4.69	0.617	1.18	4.11	18.8

Appendix B.1. Continued.

Sample Name	Collection Date	Site	Sub-site	NPOC mg/L	TDN mg	Cl^- mg /L	SO_4^{2-} mg	NO_3^- mg	PO_4^{3-} mg	NH_4^+ mg/L	Na^+ mg /L	K^+ mg /L	Mg^{2+} mg /L	Ca^{2+} mg /L	SiO_2 mg /L
RIST1	6-Aug-01	Rio Icacos	Tributary	1.360	0.240	6.61	0.481	0.159	0.007	0.009	4.57	0.501	0.89	2.16	18.1
RIST2	6-Aug-01	Rio Icacos	Tributary	2.080	0.175	6.05	0.411	0.076	0.007	0.003	4.23	0.441	1.02	2.37	18.3
RIST3	9-Aug-01	Rio Icacos	Tributary	1.560	0.245	6.21	0.393	0.134	0.006	0.015	4.55	0.484	0.94	2.72	19.8
RIST4	9-Aug-01	Rio Icacos	Tributary	1.280	0.190	6.39	0.522	0.079	0.005	0.025	4.46	0.538	0.97	2.50	19.7
RIST5	9-Aug-01	Rio Icacos	Tributary	3.230	0.209	5.83	0.575	0.071	0.006	0.004	4.06	0.432	0.97	2.61	16.0
RIST6	9-Aug-01	Rio Icacos	Tributary	1.210	0.243	6.31	0.421	0.182	0.007	0.006	4.40	0.473	0.88	2.41	17.5
RIST7	9-Aug-01	Rio Icacos	Tributary	1.450	0.184	6.53	0.523	0.074	0.005	0.019	3.91	0.453	1.04	3.24	11.0
RIST8	9-Aug-01	Rio Icacos	Tributary	1.430	0.228	5.44	0.424	0.127	0.009	0.007	4.20	0.54	1.00	2.91	19.5
RIST9	9-Aug-01	Rio Icacos	Tributary	2.240	0.160	5.60	0.702	0.043	0.003	0.051	28.74	1.977	4.09	2.16	9.2
RIST10	9-Aug-01	Rio Icacos	Tributary	1.460	0.165	6.51	0.539	0.088	0.006	0.026	8.52	0.733	1.47	3.06	16.1
RIST11	9-Aug-01	Rio Icacos	Tributary	4.120	0.225	5.85	0.444	0.118	0.010	0.009	6.62	0.884	1.19	3.13	15.7
RIST12	9-Aug-01	Rio Icacos	Tributary	1.770	0.183	5.20	0.485	0.100	0.008	0.004	5.67	0.796	1.16	3.52	18.5
RIST13	9-Aug-01	Rio Icacos	Tributary	2.830	0.229	5.24	0.016	0.125	0.012	0.004	5.66	0.64	1.22	3.51	17.9
RIST14	9-Aug-01	Rio Icacos	Tributary	3.380	0.279	5.39	0.598	0.154	0.010	0.006	5.51	0.66	1.08	3.14	16.7
RBS2	3-Aug-01	Rio Blanco	Mainstream	4.070	0.550	20.61	1.925	0.154	0.021	0.058	21.48	6.14	20.26	10.24	12.5
RBS3	3-Aug-01	Rio Blanco	Mainstream	2.490	0.250	16.64	1.107	0.095	0.008	0.008	10.37	0.851	1.97	3.29	14.1
RBS4	3-Aug-01	Rio Blanco	Tributary	2.910	0.180	7.65	1.078	0.023	0.010	0.006	5.83	0.504	1.44	5.04	16.7
RBS5	3-Aug-01	Rio Blanco	Tributary	2.960	0.200	6.25	0.608	0.051	0.009	0.008	4.88	0.53	0.82	2.41	13.6
RBS6	3-Aug-01	Rio Blanco	Tributary	1.090	0.050	9.18	2.956	0.000	0.009	0.002	7.13	0.383	2.34	6.13	26.6
RBS7	3-Aug-01	Rio Blanco	Mainstream	3.180	1.190	6.95	0.827	0.059	0.007	0.005	5.46	0.597	1.17	3.68	13.6

Appendix B.2. Chemical parameters of water samples from the Rio Icacos-Blanco drainage system during summer 2002

Sample Name	Collection Date	Site	Subsite	NPOC mg/L	TDN mg/L	Alkalinity meq	Cl^- mg/L	SO_4^{2-} mg/L	NO_3^- mg/L	PO_4^{3-} mg/L	NH_4^+ mg/L	Na^+ mg/L	K^+ mg/L	Mg^{2+} mg/L	Ca^{2+} mg/L	SiO_2 mg/L
RIS10	8-Jul-02	Rio Icacos	Mainstream	0.321	0.324	0.538	7.24	0.49	0.313	0.039	0.007	7.45	0.65	1.51	4.31	30.5
RIS9	8-Jul-02	Rio Icacos	Mainstream	0.359	0.316	0.553	6.50	0.402	0.282	0.032	0.006	6.78	0.53	1.55	4.11	30.3
RIS8	6-Jul-02	Rio Icacos	Mainstream	0.212	0.296	0.525	6.80	0.405	0.205	0.028	0.010	7.04	0.58	1.50	3.17	30.5
RIS7	6-Jul-02	Rio Icacos	Mainstream	0.484	0.239	0.505	6.39	0.379	0.22	0.020	0.008	6.54	0.55	1.49	2.94	28.9
RIS6	6-Jul-02	Rio Icacos	Mainstream	0.507	0.184	0.488	6.57	0.353	0.164	0.016	0.009	6.42	0.43	1.38	3.70	28.0
RIS5	6-Jul-02	Rio Icacos	Mainstream	0.777	0.199	0.416	6.46	0.348	0.173	0.011	0.011	6.38	0.45	1.35	3.51	26.0
RIS4	6-Jul-02	Rio Icacos	Mainstream	1.049	0.213	0.388	6.54	0.357	0.123	0.010	0.050	6.05	0.44	1.31	3.40	23.8
RIST1	10-Jul-02	Rio Icacos	Tributary	0.780	0.192	0.278	7.03	0.378	0.14	0.007	0.009	5.78	0.43	1.12	2.62	20.3
RIST2	10-Jul-02	Rio Icacos	Tributary	1.654	0.158	0.346	6.48	0.37	0.096	0.008	0.006	5.53	0.37	1.24	3.43	21.1
RIST3	10-Jul-02	Rio Icacos	Tributary	0.367	0.165	0.316	6.83	0.346	0.133	0.007	0.014	5.94	0.54	1.12	2.14	21.5
RIST4	10-Jul-02	Rio Icacos	Tributary	0.459	0.147	0.275	6.90	0.49	0.129	0.004	0.023	5.38	0.44	1.07	2.70	18.5
RIST5	8-Jul-02	Rio Icacos	Tributary	1.255	0.121	0.325	6.26	0.485	0.083	0.010	0.007	5.20	0.45	1.12	2.97	21.4
RIST5A	10-Jul-02	Rio Icacos	Trib Transect	1.095	0.105	0.366	6.26	0.537	0.097	0.012	0.006	5.80	0.36	1.34	2.99	23.3
RIST5B	10-Jul-02	Rio Icacos	Trib Transect	1.075	0.096	0.391	5.29	0.372	0.058	0.016	0.006	4.81	0.38	0.91	2.10	23.7
RIST5C	10-Jul-02	Rio Icacos	Trib Transect	0.024	-0.001	0.421	5.94	0.506	0.07	0.013	0.003	5.77	0.42	1.33	2.84	24.9
RIST6	8-Jul-02	Rio Icacos	Tributary	0.625	0.190	0.266	6.72	0.232	0.176	0.009	0.008	5.45	0.50	0.99	2.64	20.5
RIST6A	15-Jul-02	Rio Icacos	Trib Transect	0.632	0.198	0.270	6.60	0.154	0.171	0.010	0.008	5.30	0.40	0.82	2.42	22.1
RIST6B	15-Jul-02	Rio Icacos	Trib Transect	0.537	0.220	0.287	7.61	0.191	0.196	0.011	0.005	6.11	0.36	1.04	2.57	23.1
RIST6C	15-Jul-02	Rio Icacos	Trib Transect	0.890	0.116	0.254	6.85	0.066	0.078	0.006	0.004	5.40	0.35	0.84	2.54	21.6
RIST6D	15-Jul-02	Rio Icacos	Trib Transect	0.531	0.232	0.270	7.72	0.239	0.193	0.012	0.005	6.34	0.45	0.89	2.18	23.4
RIST6E	15-Jul-02	Rio Icacos	Trib Transect	0.498	0.307	0.350	7.82	0.214	0.314	0.025	0.003	6.58	0.44	1.21	2.87	27.4
RIST6F	15-Jul-02	Rio Icacos	Trib Transect	1.303	0.123	0.262	7.47	0.111	0.105	0.015	0.006	5.82	0.40	1.27	2.52	19.5
RIST7	13-Jul-02	Rio Icacos	Tributary	0.592	0.082	0.296	4.54	0.121	0.053	0.006	0.027	3.28	0.46	0.81	2.14	15.4
RIST8	8-Jul-02	Rio Icacos	Tributary	0.483	0.143	0.378	5.83	0.256	0.135	0.012	0.014	5.48	0.59	1.14	2.34	23.6
RIST8	23-Jul-02	Rio Icacos	Trib Transect	0.769	0.163	0.357	6.21	0.267	0.137	0.009	0.010	5.49	0.49	1.21	3.77	23.0
RIST8A	23-Jul-02	Rio Icacos	Trib Transect	0.820	0.144	0.358	6.19	0.25	0.142	0.011	0.007	5.68	0.56	1.22	3.11	23.8
RIST8B	23-Jul-02	Rio Icacos	Trib Transect	0.828	0.169	0.397	4.93	0.13	0.123	0.017	0.005	4.68	0.36	0.92	3.17	25.0
RIST8C	23-Jul-02	Rio Icacos	Trib Transect	0.950	0.154	0.433	5.97	0.222	0.141	0.022	0.003	5.67	0.63	1.10	3.43	26.0
RIST9	13-Jul-02	Rio Icacos	Tributary	1.615	0.121	0.180	6.80	0.383	0.049	0.006	0.120	5.48	0.31	0.93	1.59	14.8
RIST10	8-Jul-02	Rio Icacos	Tributary	0.816	0.107	0.383	7.16	0.246	0.049	0.011	0.058	6.10	0.60	1.31	2.57	19.5

Appendix B.2. Continued.

Sample Name	Collection Date	Site	Subsite	NPOC mg/L	TDN mg/L	Alkalinity meq	Cl^- mg/L	SO_4^{2-} mg/L	NO_3^- mg/L	PO_4^{3-} mg/L	NH_4^+ mg/L	Na^+ mg/L	K^+ mg/L	Mg^{2+} mg/L	Ca^{2+} mg/L	SiO_2 mg/L
RIST11	13-Jul-02	Rio Icacos	Tributary	0.355	0.157	0.450	5.68	0.082	0.103	0.018	0.009	5.38	0.44	0.98	2.43	28.7
RIST12	8-Jul-02	Rio Icacos	Tributary	0.495	0.107	0.376	4.80	0.129	0.087	0.010	0.004	4.35	0.40	0.84	1.64	23.0
RIST13	8-Jul-02	Rio Icacos	Tributary	0.575	0.122	0.473	5.29	0.124	0.087	0.007	0.003	5.14	0.53	1.12	2.96	25.5
RIST14	8-Jul-02	Rio Icacos	Tributary	0.701	0.151	0.433	6.12	0.269	0.083	0.018	0.003	6.32	0.56	1.40	3.83	26.0
RIST14A	8-Jul-02	Rio Icacos	Trib Transect	0.511	0.173	0.476	5.90	0.257	0.083	0.022	0.002	6.21	0.57	1.54	3.69	27.2
RBS2	12-Jul-02	Rio Blanco	Mainstream	1.563	0.347	1.190	20.58	1.44	0.43	0.002	0.080	11.81	1.20	5.50	5.70	25.7
RBS3	12-Jul-02	Rio Blanco	Mainstream	1.005	0.138	0.506	7.92	0.616	0.113	0.001	0.011	7.09	0.66	1.66	4.15	26.1
RBS4	12-Jul-02	Rio Blanco	Tributary	1.139	0.091	0.661	8.44	1.457	0.041	0.002	0.007	7.40	0.59	2.14	5.09	31.2
RBS5	12-Jul-02	Rio Blanco	Tributary	1.132	0.085	0.438	7.46	0.586	0.065	0.006	0.006	6.54	0.67	1.34	4.28	27.1
RBS6	12-Jul-02	Rio Blanco	Tributary	0.884	0.029	0.600	9.49	2.523	0.019	0.007	0.002	7.58	0.20	2.70	6.25	30.4
RBS7	12-Jul-02	Rio Blanco	Mainstream	1.149	0.092	0.525	8.15	0.816	0.071	0.007	0.005	7.32	0.67	1.66	4.51	27.2
RIS10	23-Jul-02	Rio Icacos	Mainstream	2.138	0.334	0.405	7.53	0.45	0.297	0.031	0.007	6.61	0.91	1.39	5.27	23.3
RIS9	23-Jul-02	Rio Icacos	Mainstream	2.431	0.318	0.416	6.61	0.424	0.239	0.027	0.007	5.16	0.75	1.02	3.05	22.4
RIS8	23-Jul-02	Rio Icacos	Mainstream	2.403	0.327	0.391	6.78	0.488	0.244	0.029	0.008	5.48	0.72	1.14	4.33	21.0
RIS7	23-Jul-02	Rio Icacos	Mainstream	2.625	0.280	0.366	6.63	0.497	0.205	0.020	0.010	5.24	0.52	1.16	3.59	20.6
RIS6	23-Jul-02	Rio Icacos	Mainstream	2.604	0.241	0.355	6.89	0.458	0.173	0.014	0.011	5.47	0.75	1.19	3.76	20.7
RIS5	23-Jul-02	Rio Icacos	Mainstream	2.594	0.250	0.325	7.56	0.475	0.167	0.011	0.010	6.10	0.72	1.11	3.63	19.6
RIS4	23-Jul-02	Rio Icacos	Mainstream	2.371	0.219	0.307	7.32	0.488	0.166	0.020	0.141	5.81	0.66	1.28	3.92	20.2
RIST1	29-Jul-02	Rio Icacos	Tributary	1.525	0.173	0.264	7.42	0.474	0.12	0.008	0.021	5.79	0.58	1.25	3.29	18.1
RIST2	29-Jul-02	Rio Icacos	Tributary	2.136	0.133	0.280	7.21	0.425	0.077	0.007	0.008	5.37	0.64	1.31	3.23	18.2
RIST3	29-Jul-02	Rio Icacos	Tributary	0.790	0.161	0.307	6.92	0.387	0.126	0.008	0.019	5.59	0.67	1.18	3.16	20.2
RIST4	29-Jul-02	Rio Icacos	Tributary	0.770	0.127	0.255	6.96	0.485	0.095	0.003	0.028	5.15	0.72	1.06	3.00	18.1
RIST5	2-Aug-02	Rio Icacos	Tributary	0.724	0.106	0.367	6.72	0.474	0.089	0.015	0.009	5.84	0.57	1.43	3.57	23.9
RIST5A	2-Aug-02	Rio Icacos	Trib Transect	0.961	0.143	0.370	6.69	0.473	0.093	0.013	0.007	5.87	0.66	1.47	3.80	24.3
RIST5B	2-Aug-02	Rio Icacos	Trib Transect	1.121	0.115	0.405	6.24	0.602	0.073	0.011	0.007	5.81	0.54	1.51	3.08	25.3
RIST5C	2-Aug-02	Rio Icacos	Trib Transect	0.711	0.098	0.434	6.04	0.633	0.069	0.012	0.005	5.80	0.58	1.54	3.37	26.1

Appendix B.2. Continued.

Sample Name	Collection Date	Site	Subsite	NPOC mg/L	TDN mg/L	Alkalinity meq	Cl^- mg/L	SO_4^{2-} mg/L	NO_3^- mg/L	PO_4^{3-} mg/L	NH_4^+ mg/L	Na^+ mg/L	K^+ mg/L	Mg^{2+} mg/L	Ca^{2+} mg/L	SiO_2 mg/L
RIST6	31-Jul-02	Rio Icacos	Tributary	0.75	0.209	0.272	7.14	0.357	0.164	0.012	0.02	5.91	0.68	1.10	2.80	20.8
RIST6A	31-Jul-02	Rio Icacos	Trib Transect	0.73	0.123	0.290	6.93	0.348	0.157	0.01	0.01	5.54	0.56	1.07	3.19	21.6
RIST6B	31-Jul-02	Rio Icacos	Trib Transect	0.22	0.219	0.300	7.33	0.355	0.175	0.009	0.01	5.82	0.67	1.10	3.04	22.7
RIST6C	31-Jul-02	Rio Icacos	Trib Transect	1.12	0.139	0.250	7.28	0.244	0.081	0.008	0	5.50	0.48	1.02	2.72	20.3
RIST6D	31-Jul-02	Rio Icacos	Trib Transect	0.98	0.211	0.274	7.28	0.368	0.158	0.009	0	5.76	0.59	0.90	2.40	22.8
RIST6E	31-Jul-02	Rio Icacos	Trib Transect	0.75	0.297	0.338	7.70	0.342	0.274	0.017	0.01	6.28	0.52	1.25	2.62	27.1
RIST6F	31-Jul-02	Rio Icacos	Trib Transect	1.76	0.146	0.254	7.67	0.269	0.077	0.016	0.01	5.59	0.49	1.31	2.69	19.1
RIST7	23-Jul-02	Rio Icacos	Tributary	1.235	0.126	0.272	7.56	0.414	0.063	0.003	0.027	5.14	0.56	1.31	3.18	15.2
RIST8	29-Jul-02	Rio Icacos	Tributary	0.839	0.169	0.345	5.94	0.385	0.131	0.008	0.011	5.33	0.72	1.18	3.44	23.0
RIST8A	29-Jul-02	Rio Icacos	Trib Transect	0.787	0.159	0.375	6.01	0.394	0.134	0.013	0.010	5.43	0.68	1.25	3.71	24.1
RIST8B	29-Jul-02	Rio Icacos	Trib Transect	0.770	0.174	0.400	6.02	0.394	0.15	0.015	0.018	5.57	0.64	1.28	4.36	25.3
RIST8C	29-Jul-02	Rio Icacos	Trib Transect	0.908	0.182	0.425	6.09	0.39	0.141	0.027	0.007	5.67	0.69	1.26	4.10	25.8
RIST8D	29-Jul-02	Rio Icacos	Trib Transect	0.826	0.187	0.450	6.03	0.38	0.143	0.024	0.049	5.92	0.74	1.43	4.82	27.9
RIST9	23-Jul-02	Rio Icacos	Tributary	2.029	0.113	0.183	6.90	0.517	0.034	0.002	0.003	5.38	0.50	1.02	1.50	14.2
RIST10	23-Jul-02	Rio Icacos	Tributary	1.035	0.092	0.423	7.85	0.409	0.032	0.008	0.041	6.30	0.77	1.52	2.72	20.5
RIST11	23-Jul-02	Rio Icacos	Tributary	1.609	0.203	0.393	7.92	0.411	0.143	0.023	0.014	6.52	0.78	1.42	4.24	25.6
RIST12	23-Jul-02	Rio Icacos	Tributary	1.113	0.137	0.350	5.95	0.425	0.097	0.006	0.005	5.23	0.57	1.28	3.20	23.1
RIST13	23-Jul-02	Rio Icacos	Tributary	1.747	0.169	0.397	6.53	0.398	0.13	0.010	0.005	5.61	0.63	1.49	4.27	23.3
RIST14	23-Jul-02	Rio Icacos	Tributary	2.169	0.227	0.358	6.58	0.545	0.169	0.012	0.009	5.72	0.61	1.37	3.76	21.8
RIST14A	23-Jul-02	Rio Icacos	Trib Transect	8.678	1.241	0.403	9.78	0.725	0.168	0.038	0.334	9.27	2.42	1.50	4.65	24.3
RBS2	2-Aug-02	Rio Blanco	Mainstream	1.628	0.435	1.212	24.07	1.5	0.47	0.011	0.030	14.21	2.24	5.41	6.25	26.5
RBS3	2-Aug-02	Rio Blanco	Mainstream	1.145	0.128	0.480	7.68	0.669	0.103	0.008	0.009	6.89	0.66	1.56	4.52	25.1
RBS4	2-Aug-02	Rio Blanco	Tributary	1.261	0.089	0.667	8.84	1.48	0.047	0.012	0.006	7.40	0.59	2.16	5.87	30.5
RBS5	2-Aug-02	Rio Blanco	Tributary	1.481	0.092	0.434	7.45	0.696	0.072	0.007	0.006	6.59	0.64	1.34	3.60	25.7
RBS6	2-Aug-02	Rio Blanco	Tributary	0.934	0.030	0.688	9.58	2.773	0.000	0.004	0.003	7.66	0.29	3.06	5.14	28.4
RBS7	2-Aug-02	Rio Blanco	Mainstream	1.177	0.098	0.512	8.10	0.855	0.076	0.007	0.007	7.21	0.66	1.78	4.69	25.8

Appendix B. 2. Continued.

Sample Name	Collection Date	Site	Subsite	NPOC mg/L	TDN mg/L	Alkalinity meq	Cl^- mg/L	SO_4^{2-} mg/L	NO_3^- mg/L	PO_4^{3-} mg/L	NH_4^+ mg/L	Na^+ mg/L	K^+ mg/L	Mg^{2+} mg/L	Ca^{2+} mg/L	SiO_2 mg/L
RIS10	6-Aug-02	Rio Icacos	Mainstream	0.845	0.348	0.564	7.06	0.499	0.338	0.028	0.000	7.07	0.84	1.70	4.91	30.3
RIS9	6-Aug-02	Rio Icacos	Mainstream	0.829	0.328	0.533	6.98	0.467	0.316	0.024	0.005	6.91	0.80	1.68	4.76	29.9
RIS8	6-Aug-02	Rio Icacos	Mainstream	0.809	0.311	0.517	6.80	0.449	0.288	0.023	0.006	6.81	0.71	1.72	4.11	29.8
RIS7	6-Aug-02	Rio Icacos	Mainstream	0.952	0.238	0.484	6.48	0.446	0.212	0.016	0.005	6.48	0.73	1.66	5.46	28.2
RIS6	6-Aug-02	Rio Icacos	Mainstream	0.764	0.193	0.462	6.90	0.464	0.19	0.011	0.008	6.54	0.66	1.50	5.19	27.3
RIS5	6-Aug-02	Rio Icacos	Mainstream	0.880	0.169	0.425	6.77	0.449	0.167	0.006	0.008	6.10	0.69	1.46	3.02	25.6
RIS4	6-Aug-02	Rio Icacos	Mainstream	1.172	0.163	0.367	6.82	0.508	0.148	0.004	0.008	5.91	0.77	1.36	4.34	23.4

Appendix B.3. Chemical parameters of water samples from the Rio Icacos basin during winter 2005.

Sample name	Collection Date	Site	Sub-site	NPOC mg/L	TDN mg/L	Alkalinity meq	Cl^- mg/L	SO_4^{2-} mg/L	NO_3^- mg/L	PO_4^{3-} mg/L	NH_4^+ mg/L	Na^+ mg/L	K^+ mg/L	Mg^{2+} mg/L	Ca^{2+} mg/L	SiO_2 mg/L
RIS4	1-Feb-05	Rio Icacos	Mainstream	0.45	0.141	0.323	5.50	0.326	0.107	8E-04	0	5.21	0.34	1.03	3.13	16.31
RIS5	1-Feb-05	Rio Icacos	Mainstream	0.41	0.139	0.352	5.42	0.311	0.114	0.003	0.01	5.25	0.35	1.03	3.22	17.20
RIS6	1-Feb-05	Rio Icacos	Mainstream	0.40	0.155	0.396	5.47	0.321	0.118	0.003	0.01	5.45	0.39	1.07	3.17	18.25
RIS7	1-Feb-05	Rio Icacos	Mainstream	0.55	0.179	0.409	5.29	0.360	0.156	0.013	-0	5.60	0.40	1.19	3.53	18.09
RIS8	1-Feb-05	Rio Icacos	Mainstream	0.31	0.207	0.459	3.35	2.403	0.290	0.017	0	5.75	0.42	1.18	3.81	21.00
RIS9	1-Feb-05	Rio Icacos	Mainstream	0.29	0.214	0.473	5.52	0.383	0.174	0.017	0	5.80	0.41	1.23	4.40	21.50
RIS10	1-Feb-05	Rio Icacos	Mainstream	0.29	0.228	0.477	5.58	0.388	0.185	0.021	0	6.09	0.43	1.34	4.75	22.10
RIST1	2-Feb-05	Rio Icacos	Tributary	0.51	0.131	0.278	5.85	0.369	0.106	0.003	0.01	5.23	0.26	0.94	2.86	15.85
RIST2	2-Feb-05	Rio Icacos	Tributary	0.48	0.121	0.307	5.67	0.271	0.102	9E-04	0.01	5.12	0.26	1.13	3.00	16.77
RIST3	2-Feb-05	Rio Icacos	Tributary	0.34	0.128	0.291	5.98	0.304	0.112	0.004	0.01	5.41	0.45	0.98	2.84	16.41
RIST4	2-Feb-05	Rio Icacos	Tributary	0.40	0.234	0.199	6.09	0.465	0.176	5E-04	0.03	4.74	0.39	0.75	2.16	12.44
RIST5	2-Feb-05	Rio Icacos	Tributary	0.78	0.198	0.296	5.86	0.387	0.094	0.004	0	5.17	0.55	1.09	2.86	16.43
RIST6	2-Feb-05	Rio Icacos	Tributary	0.48	0.149	0.237	6.05	0.314	0.124	0.009	0.01	5.04	0.40	0.90	2.65	15.71
RIST7	2-Feb-05	Rio Icacos	Tributary	0.90	0.129	0.218	6.95	0.376	0.063	0	0.04	4.39	0.43	0.98	2.64	10.72
RIST8	3-Feb-05	Rio Icacos	Tributary	0.33	0.13	0.310	5.26	0.327	0.099	0.008	0.01	5.03	0.42	0.97	3.08	17.13
RIST9	3-Feb-05	Rio Icacos	Tributary	0.82	0.186	0.155	6.59	0.395	0.117	0	0.05	4.61	0.32	0.94	1.74	9.71
RIST10	3-Feb-05	Rio Icacos	Tributary	0.70	0.099	0.346	6.61	0.387	0.050	0.002	0.04	5.92	0.53	1.26	3.05	15.66
RIST11	3-Feb-05	Rio Icacos	Tributary	0.33	0.118	0.404	6.99	0.296	0.100	0.007	0.01	6.43	0.60	1.25	4.01	19.65
RIST12	3-Feb-05	Rio Icacos	Tributary	0.35	0.105	0.349	5.27	0.326	0.086	0.004	0.01	5.17	0.42	1.14	3.33	17.32
RIST13	3-Feb-05	Rio Icacos	Tributary	0.40	0.12	0.399	6.24	0.272	0.110	0.004	0.01	5.54	0.43	1.37	3.99	19.06
RIST14	3-Feb-05	Rio Icacos	Tributary	0.40	0.163	0.380	5.50	0.340	0.130	0.008	0	5.56	0.45	1.17	3.52	19.38
RISW1A	7-Feb-05	Rio Icacos	Groundwater	0.64	0.105	0.840	6.07	0.216	0.015	-0.060	0.09	4.67	0.35	1.30	3.01	7.13
RISW1B	7-Feb-05	Rio Icacos	Groundwater	0.58	0.092	0.097	5.92	0.565	0.007	0.002	0.04	3.19	0.37	0.90	1.75	3.70
RISW2A	7-Feb-05	Rio Icacos	Groundwater	0.58	0.097	0.633	5.04	0.334	0.006	-0.013	0.08	3.61	0.28	1.14	2.12	8.44
RISW2B	7-Feb-05	Rio Icacos	Groundwater	0.50	0.137	0.586	3.14	0.022	0.017	-0.021	0.16	2.97	0.12	0.53	1.93	7.38
RISW3A	7-Feb-05	Rio Icacos	Groundwater	0.49	0.155	1.142	4.44	0.019	0.007	-0.094	0.19	3.82	0.09	1.36	3.63	5.32
RISW3B	7-Feb-05	Rio Icacos	Groundwater	0.82	0.165	0.425	4.58	0.095	0.000	-0.025	0.08	4.16	0.35	0.71	2.08	9.04

Appendix B.3. Continued.

Sample name	Collection Date	Site	Sub-site	NPOC mg/L	TDN mg/L	Alkalinity meq	Cl^- mg/L	SO_4^{2-} mg/L	NO_3^- mg/L	PO_4^{3-} mg/L	NH_4^+ mg/L	Na^+ mg/L	K^+ mg/L	Mg^{2+} mg/L	Ca^{2+} mg/L	SiO_2 mg/L
RISW4A	7-Feb-05	Rio Icacos	Groundwater	1.56	0.219	0.460	4.18	0.08	0.008	-0.004	0.17	5.07	0.33	0.70	1.73	6.93
RISW5A	7-Feb-05	Rio Icacos	Groundwater	0.8	0.148	0.280	4.42	0.389	0	-0.008	0.11	2.82	0.27	1.03	1.93	4.24
RISW5B	10-Feb-05	Rio Icacos	Groundwater	3.64	2.157	0.700	5.16	0.097	0.014	-0.022	3.35	4.45	1.37	1.78	3.41	6.10
RISW6A	7-Feb-05	Rio Icacos	Groundwater	6.36	0.885	nd	6.73	0.589	0.045	-0.005	0.32	5.57	1.12	0.82	1.85	6.06
RISW6B	7-Feb-05	Rio Icacos	Groundwater	7.05	0.455	0.039	7.15	0.574	0.039	-0.01	0.13	3.73	0.70	0.53	1.44	2.91
RISW7A	7-Feb-05	Rio Icacos	Groundwater	1.83	0.328	0.683	3.97	0.287	0.002	-0.014	0.17	4.93	0.43	1.11	2.14	10.21
RISW7B	7-Feb-05	Rio Icacos	Groundwater	0.82	0.237	0.194	2.57	0.199	0.056	0.000	0.04	3.60	0.25	0.59	1.59	9.03
RISW8A	7-Feb-05	Rio Icacos	Groundwater	2.99	0.885	0.473	4.67	0.058	0.019	-0.008	0.57	3.68	1.86	1.05	2.67	5.63
RISSP1	8-Feb-05	Rio Icacos	Upper Source	0.27	0.091	0.428	6.14	0.537	0.059	0.0038	0.00	5.46	0.48	1.40	4.53	17.66
RISSP2	8-Feb-05	Rio Icacos	Upper Source	0.86	0.125	0.286	8.04	0.301	0.037	0	0.07	6.41	0.29	0.92	2.19	15.67
RISSP3	10-Feb-05	Rio Icacos	Upper Source	3.05	0.249	0.000	6.97	0.606	0.073	0.0031	0.15	3.82	0.44	0.43	0.85	0.96
RISSP4	10-Feb-05	Rio Icacos	Upper Source	0.38	0.282	0.089	7.85	0.537	0.276	0.0027	0.01	5.37	0.40	0.92	1.40	14.88
RISSP5	10-Feb-05	Rio Icacos	Upper Source	0.27	0.134	0.367	6.38	0.332	0.1	0.0126	0.00	6.29	0.46	0.71	3.06	20.72
RISSP6	14-Feb-05	Rio Icacos	Upper Source	1.73	0.3	0.267	10.12	0.705	0.255	0.0011	0.01	6.78	0.64	1.25	3.59	13.12
RISSP7	14-Feb-05	Rio Icacos	Upper Source	1.36	0.253	0.275	8.37	0.549	0.207	0.0042	0.03	5.61	0.54	1.12	3.79	14.01
RISSP8	14-Feb-05	Rio Icacos	Upper Source	1.44	0.228	0.331	8.78	0.551	0.174	0.0061	0.01	6.13	0.57	1.16	3.96	15.69
RISSP9	14-Feb-05	Rio Icacos	Upper Source	3.69	0.297	0.036	8.23	0.622	0.207	0	0.01	4.64	0.30	0.88	1.74	3.17
RISSP10	14-Feb-05	Rio Icacos	Upper Source	2.85	0.175	0.090	7.96	0.495	0.109	-4E-04	0.01	4.97	0.39	0.76	1.73	5.32
RISSPL1	16-Feb-05	Rio Icacos	Lower Source	0.81	0.203	0.339	6.39	0.395	0.103	0	0.09	4.28	0.50	0.93	1.71	9.93
RISSPL2	16-Feb-05	Rio Icacos	Lower Source	0.42	0.201	0.032	8.69	0.402	0.271	-1E-04	0.01	4.89	0.44	0.66	0.92	3.43
RISSPL3	17-Feb-05	Rio Icacos	Lower Source	0.61	0.165	0.102	6.91	0.377	0.094	0	0.08	3.83	0.19	0.52	0.56	2.86
RISSPL4	18-Feb-05	Rio Icacos	Lower Source	0.39	0.24	0.123	5.81	0.461	0.188	0	0.02	3.96	0.33	1.13	1.65	7.61
RISSPL5	18-Feb-05	Rio Icacos	Lower Source	0.89	0.194	0.184	6.47	0.484	0.07	0.0004	0.14	4.63	0.62	0.83	1.65	12.00
RISSPL6	18-Feb-05	Rio Icacos	Lower Source	0.41	0.431	0.000	5.37	0.361	0.35	0.0022	0.01	3.60	0.13	0.50	0.70	1.50

Appendix B.3. Continued.

Sample name	Collection Date	Site	Sub-site	NPOC mg/L	TDN mg/L	Alkalinity meq	Cl^- mg/L	SO_4^{2-} mg/L	NO_3^- mg/L	PO_4^{3-} mg/L	NH_4^+ mg/L	Na^+ mg/L	K^+ mg/L	Mg^{2+} mg/L	Ca^{2+} mg/L	SiO_2 mg/L
RISSP1	17-Feb-05	Rio Icacos	UpperSource	0.23	0.086	0.428	6.05	0.505	0.065	0.006	0.01	5.30	0.57	1.38	4.22	16.68
RISSP2	17-Feb-05	Rio Icacos	UpperSource	0.81	0.136	0.318	7.92	0.3	0.045	0.004	0.09	6.45	0.19	0.95	2.41	15.65
RISSP3	17-Feb-05	Rio Icacos	UpperSource	3.01	0.232	0.000	8.56	0.78	0.476	0	0.07	4.60	0.52	0.69	1.26	0.87
RISSP3A	17-Feb-05	Rio Icacos	UpperSource	0.48	0.576	0.016	6.66	0.474	0.551	-0	0.03	4.16	0.52	0.55	0.84	5.05
RISSP4	16-Feb-05	Rio Icacos	UpperSource	0.29	0.23	0.078	8.44	0.496	0.202	-0	0.01	5.42	0.30	0.58	1.49	13.05
RISSP4A	16-Feb-05	Rio Icacos	UpperSource	0.39	0.241	0.313	6.58	0.296	0.166	0.005	0.02	5.49	0.50	1.01	3.08	17.66
RISSP5	16-Feb-05	Rio Icacos	UpperSource	0.54	0.184	0.328	7.03	0.392	0.111	0.013	0	6.92	0.58	1.51	3.40	19.04
RISSP6	21-Feb-05	Rio Icacos	UpperSource	0.45	0.183	0.412	6.71	0.41	0.131	0.013	0.01	7.06	0.58	1.49	4.18	18.05
RISSP7	21-Feb-05	Rio Icacos	UpperSource	0.44	0.144	0.399	5.43	0.413	0.081	0.01	0.01	5.64	0.50	1.40	4.18	18.79
RISSP8	21-Feb-05	Rio Icacos	UpperSource	0.29	0.134	0.481	5.21	0.302	0.077	0.021	0.01	6.09	0.53	1.32	4.43	19.99
RISSP9	21-Feb-05	Rio Icacos	UpperSource	1.9	0.337	0.210	8.09	0.656	0.239	0.001	0.04	5.34	0.39	1.44	2.55	11.73
RISSP10	22-Feb-05	Rio Icacos	UpperSource	0.65	0.147	0.351	6.69	0.338	0.09	0.014	0.013	6.00	0.51	1.44	3.34	17.45
RISSPL1	22-Feb-05	Rio Icacos	LowerSource	0.66	0.225	0.236	6.44	0.41	0.14	-0	0.058	5.20	0.93	1.26	1.88	11.43
RISSPL2	22-Feb-05	Rio Icacos	LowerSource	1.28	0.225	0.141	2.31	0.057	0.059	0.003	0.053	0.86	0.66	0.25	0.53	11.09
RISSPL3	22-Feb-05	Rio Icacos	LowerSource	0.85	0.172	0.199	6.16	0.401	0.043	0	0.134	3.69	0.27	0.74	1.77	2.83
RISSPL4	21-Feb-05	Rio Icacos	LowerSource	0.57	0.2	0.121	5.99	0.474	0.151	0.005	0.019	3.84	0.30	0.78	1.90	7.05
RISSPL5	21-Feb-05	Rio Icacos	LowerSource	1.45	0.312	0.533	7.30	0.37	0.002	0	0.382	4.76	0.86	1.24	2.11	10.50
RISSPL6	21-Feb-05	Rio Icacos	LowerSource	0.77	0.447	0.027	5.58	0.418	0.328	0.004	0.018	3.84	0.31	0.55	0.79	1.42
RISW1A	18-Feb-05	Rio Icacos	Groundwater	0.74	0.135	0.800	7.88	0.32	0.005	-0.035	0.11	5.14	0.44	1.49	2.84	6.42
RISW1B	18-Feb-05	Rio Icacos	Groundwater	0.61	0.103	0.118	5.49	0.45	0.005	-0.006	0.07	3.25	0.39	0.99	1.78	3.85
RISW2A	18-Feb-05	Rio Icacos	Groundwater	0.47	0.11	0.701	5.22	0.283	0.106	-0.011	0.09	4.29	1.61	1.36	2.30	8.49
RISW2B	18-Feb-05	Rio Icacos	Groundwater	0.45	0.17	0.905	3.33	0.016	0.006	-0.017	0.16	3.04	0.29	0.31	1.58	7.19
RISW3A	18-Feb-05	Rio Icacos	Groundwater	0.65	0.183	1.028	8.04	0.011	0.031	0.002	0.2	3.93	0.17	1.19	4.19	4.89
RISW3B	18-Feb-05	Rio Icacos	Groundwater	0.47	0.126	0.401	5.38	0.108	0.015	0	0.06	3.83	0.25	0.56	1.78	8.05
RISW4A	18-Feb-05	Rio Icacos	Groundwater	2.08	0.513	nd	5.07	0.103	0.01	0	0.35	4.88	0.55	0.70	1.68	6.62
RISW5A	18-Feb-05	Rio Icacos	Groundwater	1.42	0.309	0.221	2.93	0.228	0.007	0.004	0.21	1.92	0.66	0.39	0.95	3.97

Appendix B.3. Continued.

Sample name	Collection Date	Site	Sub-site	NPOC mg/L	TDN mg/L	Alkalinity meq	Cl^- mg/L	SO_4^{2-} mg/L	NO_3^- mg/L	PO_4^{3-} mg/L	NH_4^+ mg/L	Na^+ mg/L	K^+ mg/L	Mg^{2+} mg/L	Ca^{2+} mg/L	SiO_2 mg/L
RISW6B	18-Feb-05	Rio Icacos	Groundwater	3.54	0.224	0.027	7.15	0.558	0.012	0	0.08	4.18	0.47	0.50	1.32	2.64
RISW7A	18-Feb-05	Rio Icacos	Groundwater	0.78	0.163	0.640	4.28	0.313	0.04	0	0.12	5.68	0.26	0.95	1.36	10.03
RISW7B	18-Feb-05	Rio Icacos	Groundwater	0.56	0.192	0.197	2.70	0.177	0.094	0	0.03	3.60	0.16	0.52	1.49	8.00
RISW8A	18-Feb-05	Rio Icacos	Groundwater	1.89	0.636	0.714	5.19	0.083	0.016	0	0.65	3.15	1.28	1.08	2.32	5.57
RISSP1	22-Feb-05	Rio Icacos	Upper Source	0.34	0.086	0.423	7.35	0.59	0.03	0.0058	0.01	5.83	0.54	1.36	4.36	16.50
RISSP2	22-Feb-05	Rio Icacos	Upper Source	1.29	0.162	0.457	9.32	0.34	0	0	0.15	7.22	0.36	1.13	2.38	15.11
RISSP3	22-Feb-05	Rio Icacos	Upper Source	3.4	0.265	0.000	9.95	0.82	0.13	-5E-04	0.13	5.15	0.60	0.72	1.45	0.90
RISSP4	22-Feb-05	Rio Icacos	Upper Source	0.54	0.221	0.092	9.54	0.58	0.16	0.0016	0.01	6.07	0.20	0.63	1.62	13.58
RISSP5	22-Feb-05	Rio Icacos	Upper Source	0.42	0.146	0.344	7.80	0.44	0.1	0.0126	0.01	7.23	0.57	0.81	3.27	20.45
RISSP6	23-Feb-05	Rio Icacos	Upper Source	0.32	0.154	0.433	5.39	0.39	0.09	0.0103	0	5.77	0.40	0.21	3.45	1.45
RISSP7	23-Feb-05	Rio Icacos	Upper Source	0.29	0.123	0.404	6.05	0.36	0.1	0.0073	0.01	5.38	0.49	1.05	3.93	17.20
RISSP8	23-Feb-05	Rio Icacos	Upper Source	0.24	0.123	0.496	5.80	0.38	0.09	0.0143	0.01	6.17	0.53	1.23	4.55	21.45
RISSP9	23-Feb-05	Rio Icacos	Upper Source	1.86	0.222	0.247	7.88	0.69	0.14	0.0044	0.01	5.91	0.32	1.34	2.89	14.07
RISSP10	24-Feb-05	Rio Icacos	Upper Source	0.54	0.189	0.352	7.23	0.38	0.1	0.0048	0.01	5.97	0.56	1.33	3.61	17.82
RISSPL1	24-Feb-05	Rio Icacos	Lower Source	0.52	0.214	0.242	7.08	0.47	0.13	0.0004	0.06	5.02	0.44	1.09	1.87	11.70
RISSPL2	24-Feb-05	Rio Icacos	Lower Source	0.51	0.369	0.136	6.89	0.27	0.24	-4E-04	0.03	4.44	0.68	0.98	1.37	10.77
RISSPL3	24-Feb-05	Rio Icacos	Lower Source	0.58	0.173	0.199	6.99	0.49	0.03	0	0.15	4.05	0.27	0.65	0.75	2.96
RISSPL4	23-Feb-05	Rio Icacos	Lower Source	0.85	0.213	0.097	7.38	0.56	0.13	0.0005	0.02	4.90	0.43	0.81	1.97	6.94
RISSPL5	23-Feb-05	Rio Icacos	Lower Source	0.73	0.218	0.226	6.58	0.41	0.09	0.0017	0.15	4.88	0.51	0.76	2.01	12.60
RISSPL6	23-Feb-05	Rio Icacos	Lower Source	0.54	0.402	0.027	5.54	0.46	0.31	0.0034	0.02	3.42	0.13	0.51	0.73	19.61

Appendix B.4. Chemical parameters of water samples from Bagmati River within Kathmandu valley during winter 2002.

Sample Name	Collection Date	Site	Sub-site	NPOC mg/L	TDN mg/L	Cl mg/L	SO_4^{2-} mg/L	NO_3^- mg/L	PO_4^{3-} mg/L	NH_4^+ mg/L	Na^+ mg/L	K^+ mg/L	Mg^{2+} mg/L	Ca^{2+} mg/L	SiO_2 mg/L
BR-1	8-Jan-02	Bagmati	Gokarna	1.9	0.381	2.49	1.61	0.0002	0.02	0.04	6.42	1.53	1.25	4.13	7.95
BR-2	8-Jan-02	Bagmati	Jorpati	4.03	1.329	6.33	3.06	0.0002	0.07	0.72	11.40	3.21	1.29	5.39	5.56
BR-3	8-Jan-02	Bagmati	Gaurighat	2.32	1.608	10.4	4.42	0.0005	0.02	0.77	12.26	3.25	2.18	10.13	8.56
BR-4	8-Jan-02	Bagmati	Sinamangal	52.5	28.02	72.3	15.19	0.0000	3.28	32.92	65.26	20.29	4.99	20.37	5.17
BR-5	8-Jan-02	Bagmati	Minbhawan	28.7	25.69	72.7	8.34	0.0000	3.32	35.20	56.77	19.86	5.47	21.99	7.93
BR-6	8-Jan-02	Bagmati	Shankhamul	26.4	23.22	48.1	5.92	0.0001	1.86	21.90	39.00	16.35	5.11	22.52	5.10
BR-7	9-Jan-02	Bagmati	Thapathali	29.1	26.17	60.2	5.57	0.0000	2.92	31.26	48.07	17.90	5.83	26.35	10.54
BR-8	9-Jan-02	Bagmati	Teku	20	21.78	45.6	4.91	0.0001	1.41	18.91	38.64	14.76	6.16	25.85	10.49
BR-9	9-Jan-02	Bagmati	Balkhu	27.2	23.59	52.4	5.81	0.0000	1.99	23.13	43.32	16.31	6.45	31.62	10.18
BR-10	9-Jan-02	Bagmati	Chhovar	27.1	23.15	55.6	5.89	0.0000	2.13	23.12	45.86	18.95	6.69	32.95	9.25

Appendix B.5. Chemical parameters of water samples from Bagmati River within Kathmandu valley during winter - summer 2003.

Sample Name	Collection Date	Site	Sub-site	NPOC mg/L	TDN mg/L	Cl^- mg/L	SO_4^{2-} mg/L	NO_3^- mg/L	PO_4^{3-} mg/L	NH_4^+ mg/L	Na^+ mg/L	K^+ mg/L	Mg^{2+} mg/L	Ca^{2+} mg/L	SiO_2 mg/L
BR-1	2-Jan-03	Bagmati	Gokarna	2.36	8.160	2.21	1.466	0.104	0.039	0.08	3.04	0.79	0.47	2.35	16.0
BR-2	2-Jan-03	Bagmati	Jorpati	1.31	7.320	2.57	2.007	0.207	0.036	0.19	3.39	1.052	0.56	2.48	16.9
BR-3	2-Jan-03	Bagmati	Gaurighat		9.970	3.57	3.016	0.200	0.046	0.68	5.03	1.166	0.89	3.48	18.2
BR-4	2-Jan-03	Bagmati	Sinamangal	4.10	24.420	19.14	7.726	0.053	2.215	23.21	32.01	5.444	1.83	6.83	5.3
BR-5	2-Jan-03	Bagmati	Minbhawan	3.59	23.380	17.13	9.695	0.000	1.791	21.28	29.78	6.002	1.66	6.62	2.4
BR-6	2-Jan-03	Bagmati	Shankhamul	4.31	21.210	19.47	7.737	0.000	1.142	14.75	27.36	5.778	2.09	8.08	22.6
BR-7	2-Jan-03	Bagmati	Thapathali	5.00	32.970	31.45	7.907	0.000	2.321	29.73	41.96	9.455	2.46	9.61	19.9
BR-8	2-Jan-03	Bagmati	Teku	4.81	26.260	33.18	7.807	0.000	1.951	24.77	37.41	8.272	2.85	10.02	29.1
BR-9	2-Jan-03	Bagmati	Balkhu	5.02	24.110	28.32	7.164	0.000	1.986	23.52	36.14	7.726	2.82	11.79	27.1
BR-10	2-Jan-03	Bagmati	Chhovar	4.79	29.140	32.81	7.539	0.864	2.498	10.64	30.45	7.978	3.09	14.19	28.9
BR-1	2-Feb-03	Bagmati	Gokarna	1.38	3.510	3.04	1.828	0.199	0.027	0.06	4.42	1.142	0.69	2.80	17.1
BR-2	2-Feb-03	Bagmati	Jorpati	1.46	3.280	2.92	3.283	0.341	0.050	0.44	4.50	0.978	0.71	3.11	17.0
BR-3	2-Feb-03	Bagmati	Gaurighat	1.91	6.870	4.02	3.776	0.381	0.040	1.20	6.29	1.732	0.96	3.86	17.0
BR-4	2-Feb-03	Bagmati	Sinamangal	4.21	9.090	16.03	7.215	0.190	0.680	6.67	21.24	5.276	1.68	7.43	20.1
BR-5	2-Feb-03	Bagmati	Minbhawan	5.83	15.610	23.07	9.012	0.021	1.794	15.24	30.91	7.43	1.89	8.24	28.0
BR-6	2-Feb-03	Bagmati	Shankhamul	4.15	11.380	19.53	7.951	0.002	0.860	10.54	23.93	5.406	2.29	10.20	20.0
BR-7	2-Feb-03	Bagmati	Thapathali	6.68	28.380	28.88	8.095	0.000	2.780	26.97	37.99	8.697	2.54	11.14	31.2
BR-8	2-Feb-03	Bagmati	Teku	5.23	18.860	19.10	7.793	0.000	1.369	17.13	28.03	6.796	2.60	10.54	19.9
BR-9	2-Feb-03	Bagmati	Balkhu	3.87	16.910	17.10	7.422	0.762	1.532	16.22	25.76	5.998	2.66	12.37	18.3
BR-10	2-Feb-03	Bagmati	Chhovar	4.68	18.110	17.44	7.801	0.765	1.546	17.64	27.08	6.557	2.81	10.42	18.8

Appendix B.5. Continued.

Sample Name	Collection Date	Site	Sub-site	NPOC mg/L	TDN mg/L	Cl^- mg/L	SO_4^{2-} mg/L	NO_3^- mg/L	PO_4^{3-} mg/L	NH_4^+ mg/L	Na^+ mg/L	K^+ mg/L	Mg^{2+} mg/L	Ca^{2+} mg/L	SiO_2 mg/L
BR-1	2-Mar-03	Bagmati	Gokarna	1.52	4.250	3.29	2.126	0.171	0.029	0.08	5.21	1.315	0.77	2.90	17.5
BR-2	2-Mar-03	Bagmati	Jorpati	1.30	0.240	2.71	2.486	0.286	0.030	0.07	3.85	0.9	0.73	2.77	17.8
BR-3	2-Mar-03	Bagmati	Gaurighat	1.73	1.110	4.15	3.211	0.846	0.062	0.08	5.62	1.298	1.05	3.59	18.2
BR-4	2-Mar-03	Bagmati	Sinamangal	5.63	18.140	25.66	8.128	0.007	2.121	15.86	33.14	7.67	1.91	5.08	30.9
BR-5	2-Mar-03	Bagmati	Minbhawan	5.36	21.360	30.33	12.16	0.000	2.683	20.81	37.43	8.643	2.29	7.99	28.6
BR-6	2-Mar-03	Bagmati	Shankhamul	3.92	15.820	32.61	6.899	1.798	1.499	0.07	17.21	5.662	2.34	11.50	18.8
BR-7	2-Mar-03	Bagmati	Thapathali	6.72	32.730	61.30	8.179	0.181	3.602	22.60	40.74	11.74	2.87	8.21	30.6
BR-8	2-Mar-03	Bagmati	Teku	4.74	24.220	56.87	7.140	1.269	2.144	1.74	23.55	7.818	2.96	13.43	30.0
BR-9	2-Mar-03	Bagmati	Balkhu	247.5	16.250	54.36	0.751	0.000	1.203	13.41	32.12	8.134	2.97	15.13	25.4
BR-10	2-Mar-03	Bagmati	Chhovar	74.76	22.550	46.45	0.769	0.013	1.906	16.17	34.70	8.284	2.95	15.31	26.9
BR-1	31-May-03	Bagmati	Gokarna	2.43	4.280	5.98	2.319	0.098	0.050	0.07	6.74	2.055	1.36	4.02	16.3
BR-2	31-May-03	Bagmati	Jorpati	2.84	4.310	6.19	9.707	0.022	0.093	1.87	12.78	2.359	1.69	5.20	19.6
BR-3	31-May-03	Bagmati	Gaurighat	3.47	7.580	28.06	2.195	0.000	0.240	7.45	42.67	8.271	4.15	10.33	16.2
BR-4	31-May-03	Bagmati	Sinamangal	8.70	32.190	75.73	19.53	0.000	4.350	27.95	110.4	22.13	5.88	10.15	29.2
BR-5	31-May-03	Bagmati	Minbhawan	7.17	30.860	85.37	15.21	0.026	5.151	30.89	114.0	25.87	6.42	12.72	16.3
BR-6	31-May-03	Bagmati	Shankhamul	9.18	40.330	89.46	4.881	0.000	5.401	36.63	119.2	26.06	7.58	16.03	14.8
BR-7	31-May-03	Bagmati	Thapathali	12.71	49.410	96.51	2.610	0.000	6.818	42.58	127.3	26.95	5.22	7.97	26.3
BR-8	31-May-03	Bagmati	Teku	14.24	50.440	122.3	2.519	0.000	6.718	41.52	134.7	29.84	6.07	6.73	27.9
BR-9	31-May-03	Bagmati	Balkhu	15.92	56.780	121.3	2.943	0.010	8.146	43.92	142.5	34.47	6.43	8.49	20.1
BR-10	31-May-03	Bagmati	Chhovar	14.23	53.010	112.5	3.136	0.000	8.679	46.55	142.4	30.73	7.14	11.38	30.9

Appendix B.6. Chemical parameters of water samples from Bagmati River within Kathmandu valley during monsoon 2004.

Sample Name	Collection Date	Site	Sub-site	NPOC mg/L	TDN mg/L	Cl^- mg/L	SO_4^{2-} mg/L	NO_3^- mg/L	PO_4^{3-} mg/L	NH_4^+ mg/L	Na^+ mg/L	K^+ mg/L	Mg^{2+} mg/L	Ca^{2+} mg/L	SiO_2 mg/L
BR-1	16-Jul-04	Bagmati	Gokarna	2.6		1.97	0.56	0.32	0.035	0.077	6.4	1.59	1.7	5.86	9.23
BR-2	16-Jul-04	Bagmati	Jorpati	2.82	0.67	2.47	1.17	0.29	0.015	0.027	7.79	1.67	1.94	5.39	7.93
BR-3	16-Jul-04	Bagmati	Gaurighat	3.72	1.1	5.75	2.1	0.34	0.031	0.467	10.3	3.02	2.25	5.65	2.66
BR-4	16-Jul-04	Bagmati	Sinamangal	4.24	2.25	11.7	2.88	0.38	0.127	1.739	16.6	3.63	2.98	6.2	9.77
BR-5	16-Jul-04	Bagmati	Minbhawan	5.11	3.52	12.4	3.06	0.26	0.238	3.04	17.7	4.96	2.9	8.21	8.94
BR-6	16-Jul-04	Bagmati	Shankhamul	4.97	3.98	11	3.49	0.6	0.247	3.07	14.7	4.41	3.52	8.14	nd
BR-7	16-Jul-04	Bagmati	Thapathali	6.47	7.11	3.8	0.91	0.14	0.618	5.858	21.2	7.21	4.49	10.88	12.2
BR-8	16-Jul-04	Bagmati	Teku	5.34	5.5	3.15	0.8	0.14	0.405	3.766	18.4	5.35	5.72	7.82	11.9
BR-9	16-Jul-04	Bagmati	Balkhu	4.93	3.75	3.66	0.76	0.18	0.129	2.212	19.2	4.31	6.05	9.14	13.6
BR-10	16-Jul-04	Bagmati	Chhovar	5.5	6.13	18.7	4.35	0.72	0.531	4.771	20.3	7.01	5.2	12.24	11.7

Appendix C.1. Dissolved carbonic species in the water samples from Rio Icacos mainstem during summer 2002.

Sample Name	Collection Date	Site	Sub-site	DIC (mmol/L)	H_2CO_3 (mmol/L)	HCO_3^- (mmol/L)	CO_3^{2-} (mmol/L)	CO_2 (mmol/L)	pCO_2 (uatm)
RIS4	6-Jul-02	Rio Icacos	Mainstream	0.390	0.090	0.300	0.00013	0.090	2407.8
RIS5	6-Jul-02	Rio Icacos	Mainstream	0.437	0.104	0.333	0.00014	0.104	2821.9
RIS6	6-Jul-02	Rio Icacos	Mainstream	0.470	0.088	0.382	0.00021	0.088	2321.0
RIS7	6-Jul-02	Rio Icacos	Mainstream	0.470	0.071	0.399	0.00027	0.071	1872.5
RIS8	6-Jul-02	Rio Icacos	Mainstream	0.534	0.088	0.446	0.00028	0.088	2286.8
RIS9	8-Jul-02	Rio Icacos	Mainstream	0.527	0.074	0.453	0.00033	0.074	1931.5
RIS10	8-Jul-02	Rio Icacos	Mainstream	0.513	0.043	0.469	0.00057	0.043	1119.4
RIS4	23-Jul-02	Rio Icacos	Mainstream	0.797	0.191	0.605	0.00020	0.191	5089.2
RIS5	23-Jul-02	Rio Icacos	Mainstream	0.748	0.189	0.559	0.00017	0.189	5052.4
RIS6	23-Jul-02	Rio Icacos	Mainstream	0.759	0.161	0.598	0.00023	0.161	4280.6
RIS7	23-Jul-02	Rio Icacos	Mainstream	0.769	0.154	0.615	0.00025	0.154	4105.4
RIS8	23-Jul-02	Rio Icacos	Mainstream	0.818	0.171	0.647	0.00025	0.171	4493.3
RIS9	23-Jul-02	Rio Icacos	Mainstream	0.850	0.145	0.705	0.00035	0.145	3784.9
RIS10	23-Jul-02	Rio Icacos	Mainstream	0.788	0.075	0.712	0.00069	0.075	1959.1
RIS4	6-Aug-02	Rio Icacos	Mainstream	nd	nd	nd	nd	nd	nd
RIS5	6-Aug-02	Rio Icacos	Mainstream	0.833	0.198	0.634	0.00027	0.198	5386.5
RIS6	6-Aug-02	Rio Icacos	Mainstream	0.980	0.216	0.764	0.00036	0.216	5703.8
RIS7	6-Aug-02	Rio Icacos	Mainstream	0.973	0.169	0.804	0.00047	0.169	4434.7
RIS8	6-Aug-02	Rio Icacos	Mainstream	1.033	0.173	0.860	0.00053	0.173	4522.2
RIS9	6-Aug-02	Rio Icacos	Mainstream	1.079	0.177	0.901	0.00056	0.177	4623.5
RIS10	6-Aug-02	Rio Icacos	Mainstream	1.345	0.121	1.222	0.00138	0.121	3126.1

Appendix C.2. Dissolved carbonic species in the water samples from tributaries and tributary transects within Rio Icacos basin during summer 2002.

Sample Name	Collection Date	Site	Sub-site	DIC (mmol/L)	H_2CO_3 (mmol/L)	HCO_3^- (mmol/L)	CO_3^{2-} (mmol/L)	CO_2 (mmol/L)	pCO_2 (uatm)
RIST1	10-Jul-02	Rio Icacos	Tributary	0.261	0.015	0.246	0.00045	0.015	382.5
RIST2	10-Jul-02	Rio Icacos	Tributary	0.320	0.084	0.236	0.00009	0.084	2211.8
RIST3	10-Jul-02	Rio Icacos	Tributary	0.333	0.134	0.199	0.00005	0.134	3564.2
RIST4	10-Jul-02	Rio Icacos	Tributary	0.322	0.139	0.184	0.00004	0.139	3723.4
RIST5	8-Jul-02	Rio Icacos	Tributary	0.341	0.082	0.259	0.00011	0.082	2170.4
RIST6	8-Jul-02	Rio Icacos	Tributary	0.285	0.080	0.205	0.00007	0.080	2106.6
RIST8	8-Jul-02	Rio Icacos	Tributary	0.414	0.186	0.228	0.00005	0.186	4910.9
RIST10	8-Jul-02	Rio Icacos	Tributary	0.450	0.125	0.325	0.00012	0.125	3398.7
RIST11	13-Jul-02	Rio Icacos	Tributary	0.399	0.085	0.314	0.00015	0.085	2238.9
RIST12	8-Jul-02	Rio Icacos	Tributary	0.360	0.101	0.259	0.00009	0.101	2667.2
RIST13	8-Jul-02	Rio Icacos	Tributary	0.425	0.103	0.322	0.00014	0.103	2678.0
RIST14	8-Jul-02	Rio Icacos	Tributary	0.383	0.045	0.338	0.00029	0.045	1173.8
RIST7	13-Jul-02	Rio Icacos	Tributary	0.374	0.226	0.148	0.00003	0.226	6157.2
RIST9	13-Jul-02	Rio Icacos	Tributary	0.190	0.064	0.126	0.00004	0.064	1807.0
RIST6	8-Jul-02	Rio Icacos	Trib Transect	0.285	0.080	0.205	0.00007	0.080	2106.6
RIST6A	15-Jul-02	Rio Icacos	Trib Transect	0.250	0.071	0.178	0.00006	0.071	1878.7
RIST6B	15-Jul-02	Rio Icacos	Trib Transect	0.265	0.043	0.221	0.00014	0.043	1139.0
RIST6C	15-Jul-02	Rio Icacos	Trib Transect	0.342	0.208	0.134	0.00002	0.208	5459.1
RIST6D	15-Jul-02	Rio Icacos	Trib Transect	0.206	0.029	0.177	0.00013	0.029	756.6
RIST6E	15-Jul-02	Rio Icacos	Trib Transect	0.267	0.017	0.250	0.00039	0.017	454.9
RIST6F	15-Jul-02	Rio Icacos	Trib Transect	0.230	0.049	0.181	0.00009	0.049	1292.8
RIST5	8-Jul-02	Rio Icacos	Trib Transect	0.341	0.082	0.259	0.00011	0.082	2170.4
RIST5A	10-Jul-02	Rio Icacos	Trib Transect	0.315	0.044	0.271	0.00020	0.044	1164.8
RIST5B	10-Jul-02	Rio Icacos	Trib Transect	0.323	0.031	0.292	0.00032	0.031	811.8
RIST5C	10-Jul-02	Rio Icacos	Trib Transect	0.324	0.035	0.289	0.00027	0.035	914.6

Appendix C.3. Dissolved carbonic species in the water samples from Rio Blanco drainage system during summer 2002.

Sample Name	Collection Date	Site	Sub-site	DIC (mmol/L)	H_2CO_3 (mmol/L)	HCO_3^- (mmol/L)	CO_3^{2-} (mmol/L)	CO_2 (mmol/L)	pCO_2 (uatm)
RBS2	12-Jul-02	Rio Blanco	Mainstream	0.497	0.080	0.417	0.0003	0.080	2495.7
RBS3	12-Jul-02	Rio Blanco	Mainstream	1.036	0.022	1.008	0.0049	0.022	675.8
RBS4	12-Jul-02	Rio Blanco	Tributary	0.435	0.008	0.425	0.0023	0.008	244.5
RBS5	12-Jul-02	Rio Blanco	Tributary	0.573	0.028	0.543	0.0012	0.028	811.4
RBS6	12-Jul-02	Rio Blanco	Tributary	0.341	0.034	0.307	0.0003	0.034	960.1
RBS7	12-Jul-02	Rio Blanco	Mainstream	0.421	0.011	0.409	0.0017	0.011	332.8
RBS2	2-Aug-02	Rio Blanco	Mainstream	2.634	0.606	2.027	0.0009	0.606	19778.5
RBS3	2-Aug-02	Rio Blanco	Mainstream	1.082	0.026	1.052	0.0047	0.026	773.1
RBS4	2-Aug-02	Rio Blanco	Tributary	1.178	0.025	1.148	0.0058	0.025	728.7
RBS5	2-Aug-02	Rio Blanco	Tributary	0.788	0.041	0.745	0.0015	0.041	1208.5
RBS6	2-Aug-02	Rio Blanco	Tributary	1.454	0.166	1.288	0.0012	0.166	4935.9
RBS7	2-Aug-02	Rio Blanco	Mainstream	1.130	0.032	1.094	0.0040	0.032	918.4

Appendix C.4. Dissolved carbonic species in the water samples from Rio Icacos mainstem during winter 2005.

Sample Name	Collection Date	Site	Sub-site	DIC (mmol/L)	H_2CO_3 (mmol/L)	HCO_3^- (mmol/L)	CO_3^{2-} (mmol/L)	CO_2 (mmol/L)	pCO_2 (uatm)
RIS4	1-Feb-05	Rio Icacos	Mainstream	0.281	0.076	0.205	0.0001	0.076	1852
RIS5	1-Feb-05	Rio Icacos	Mainstream	0.293	0.073	0.220	0.0001	0.073	1820
RIS6	1-Feb-05	Rio Icacos	Mainstream	0.319	0.072	0.247	0.0001	0.072	1782
RIS7	1-Feb-05	Rio Icacos	Mainstream	0.338	0.061	0.277	0.0002	0.061	1510
RIS8	1-Feb-05	Rio Icacos	Mainstream	0.407	0.071	0.336	0.0002	0.071	1751
RIS9	1-Feb-05	Rio Icacos	Mainstream	0.430	0.058	0.372	0.0003	0.058	1437
RIS10	1-Feb-05	Rio Icacos	Mainstream	0.415	0.034	0.381	0.0005	0.034	825

Appendix C.5. Dissolved carbonic species in the water samples from Rio Icacos tributaries at the mainstem during winter 2005.

Sample Name	Collection Date	Site	Sub-site	DIC (mmol/L)	H_2CO_3 (mmol/L)	HCO_3^- (mmol/L)	CO_3^{2-} (mmol/L)	CO_2 (mmol/L)	pCO_2 (uatm)
RIST1	2-Feb-05	Rio Icacos	Tributary	0.267	0.081	0.187	0.0001	0.081	1981
RIST2	2-Feb-05	Rio Icacos	Tributary	0.347	0.085	0.262	0.0001	0.085	2053
RIST3	2-Feb-05	Rio Icacos	Tributary	0.330	0.104	0.225	0.0001	0.104	2569
RIST4	2-Feb-05	Rio Icacos	Tributary	0.292	0.117	0.176	0.0000	0.117	2912
RIST5	2-Feb-05	Rio Icacos	Tributary	0.287	0.065	0.222	0.0001	0.065	1583
RIST6	2-Feb-05	Rio Icacos	Tributary	0.239	0.054	0.185	0.0001	0.054	1330
RIST7	2-Feb-05	Rio Icacos	Tributary	0.400	0.235	0.165	0.0000	0.235	5866
RIST8	3-Feb-05	Rio Icacos	Tributary	0.288	0.084	0.204	0.0001	0.084	2063
RIST9	3-Feb-05	Rio Icacos	Tributary	0.149	0.076	0.073	0.0000	0.076	1859
RIST10	3-Feb-05	Rio Icacos	Tributary	0.322	0.102	0.220	0.0001	0.102	2522
RIST11	3-Feb-05	Rio Icacos	Tributary	0.395	0.089	0.306	0.0001	0.089	2197
RIST12	3-Feb-05	Rio Icacos	Tributary	0.405	0.089	0.316	0.0001	0.089	2156
RIST13	3-Feb-05	Rio Icacos	Tributary	0.452	0.124	0.328	0.0001	0.124	3019
RIST14	3-Feb-05	Rio Icacos	Tributary	0.305	0.041	0.264	0.0002	0.041	986

Appendix C.6. Dissolved carbonic species in the groundwater samples from the Rio Icacos basin during winter 2005.

Sample Name	Collection Date	Site	Sub-site	DIC (mmol/L)	H_2CO_3 (mmol/L)	HCO_3^- (mmol/L)	CO_3^{2-} (mmol/L)	CO_2 (mmol/L)	pCO_2 (uatm)
RISW1A	7-Feb-05	Rio Icacos	Groundwater	2.910	2.060	0.850	0.0001	2.060	50920
RISW1B	7-Feb-05	Rio Icacos	Groundwater	1.206	1.078	0.128	0.0000	1.078	26730
RISW2A	7-Feb-05	Rio Icacos	Groundwater	2.009	1.526	0.483	0.0001	1.526	38583
RISW2B	7-Feb-05	Rio Icacos	Groundwater	2.968	2.302	0.666	0.0001	2.302	58571
RISW3A	7-Feb-05	Rio Icacos	Groundwater	3.349	1.806	1.543	0.0003	1.806	48380
RISW3B	7-Feb-05	Rio Icacos	Groundwater	2.078	1.654	0.424	0.0001	1.654	43737
RISW4A	7-Feb-05	Rio Icacos	Groundwater	1.073	0.637	0.436	0.0001	0.637	16525
RISW5A	7-Feb-05	Rio Icacos	Groundwater	1.399	1.183	0.216	0.0000	1.183	30005
RISW5B	10-Feb-05	Rio Icacos	Groundwater	0.914	0.914	0.000	0.0000	0.914	12051
RISW6A	7-Feb-05	Rio Icacos	Groundwater	nd	nd	nd	nd	nd	nd
RISW6B	7-Feb-05	Rio Icacos	Groundwater	nd	nd	nd	nd	nd	nd
RISW7A	7-Feb-05	Rio Icacos	Groundwater	2.678	1.871	0.806	0.0001	1.871	48237
RISW7B	7-Feb-05	Rio Icacos	Groundwater	1.151	0.998	0.153	0.0000	0.998	25726
RISW8A	7-Feb-05	Rio Icacos	Groundwater	0.660	0.450	0.210	0.0000	0.450	12570
RISW1A	18-Feb-05	Rio Icacos	Groundwater	2.732	1.928	0.804	0.0001	1.928	48735
RISW1B	18-Feb-05	Rio Icacos	Groundwater	2.823	2.521	0.303	0.0000	2.521	63517
RISW2A	18-Feb-05	Rio Icacos	Groundwater	3.352	2.452	0.900	0.0001	2.452	63398
RISW2B	18-Feb-05	Rio Icacos	Groundwater	5.153	3.933	1.220	0.0002	3.933	100075
RISW3A	18-Feb-05	Rio Icacos	Groundwater	4.616	2.514	2.102	0.0004	2.514	64175
RISW3B	18-Feb-05	Rio Icacos	Groundwater	3.138	2.527	0.611	0.0001	2.527	64920
RISW4A	18-Feb-05	Rio Icacos	Groundwater	nd	nd	nd	nd	nd	nd
RISW5A	18-Feb-05	Rio Icacos	Groundwater	1.688	1.388	0.301	0.0000	1.388	38024
RISW6B	18-Feb-05	Rio Icacos	Groundwater	0.868	0.829	0.039	0.0000	0.829	22864
RISW7A	18-Feb-05	Rio Icacos	Groundwater	2.488	1.906	0.582	0.0001	1.906	49279
RISW7B	18-Feb-05	Rio Icacos	Groundwater	2.661	2.207	0.454	0.0001	2.207	56526
RISW8A	18-Feb-05	Rio Icacos	Groundwater	2.877	1.580	1.297	0.0002	1.580	42883

Appendix C.7. Dissolved carbonic species in the upper source point samples within the Rio Icacos basin during winter 2005.

Sample Name	Collection Date	Site	Sub-site	DIC (mmol/L)	H_2CO_3 (mmol/L)	HCO_3^- (mmol/L)	CO_3^{2-} (mmol/L)	CO_2 (mmol/L)	pCO_2 (uatm)
RISSP1	8-Feb-05	Rio Icacos	Upper Source	0.336	0.054	0.282	0.0002	0.054	1355
RISSP2	8-Feb-05	Rio Icacos	Upper Source	1.472	1.313	0.159	0.0000	1.313	33627
RISSP3	10-Feb-05	Rio Icacos	Upper Source	0.047	0.047	0.001	0.0000	0.047	1114
RISSP4	10-Feb-05	Rio Icacos	Upper Source	0.459	0.405	0.053	0.0000	0.405	10184
RISSP5	10-Feb-05	Rio Icacos	Upper Source	0.216	0.031	0.185	0.0001	0.031	772
RISSP6	14-Feb-05	Rio Icacos	Upper Source	0.125	0.004	0.121	0.0004	0.004	94
RISSP7	14-Feb-05	Rio Icacos	Upper Source	0.297	0.047	0.250	0.0002	0.047	1126
RISSP8	14-Feb-05	Rio Icacos	Upper Source	0.231	0.029	0.202	0.0002	0.029	707
RISSP9	14-Feb-05	Rio Icacos	Upper Source	0.000	0.000	0.000	0.0000	0.000	0
RISSP10	14-Feb-05	Rio Icacos	Upper Source	0.086	0.022	0.063	0.0000	0.022	543
RISSP1	17-Feb-05	Rio Icacos	Upper Source	0.458	0.086	0.372	0.0002	0.086	2144
RISSP2	17-Feb-05	Rio Icacos	Upper Source	2.277	2.135	0.142	0.0000	2.135	54507
RISSP3	17-Feb-05	Rio Icacos	Upper Source	0.013	0.013	0.000	0.0000	0.013	323
RISSP3A	17-Feb-05	Rio Icacos	Upper Source	0.528	0.510	0.018	0.0000	0.510	12887
RISSP4	16-Feb-05	Rio Icacos	Upper Source	0.480	0.408	0.072	0.0000	0.408	10280
RISSP4A	16-Feb-05	Rio Icacos	Upper Source	0.763	0.507	0.256	0.0000	0.507	12981
RISSP5	16-Feb-05	Rio Icacos	Upper Source	0.341	0.099	0.242	0.0001	0.099	2475
RISSP6	21-Feb-05	Rio Icacos	Upper Source	0.304	0.041	0.263	0.0002	0.041	980
RISSP7	21-Feb-05	Rio Icacos	Upper Source	0.199	0.030	0.169	0.0001	0.030	725
RISSP8	21-Feb-05	Rio Icacos	Upper Source	0.227	0.054	0.174	0.0001	0.054	1298
RISSP9	21-Feb-05	Rio Icacos	Upper Source	0.172	0.052	0.121	0.0000	0.052	1234
RISSP10	22-Feb-05	Rio Icacos	Upper Source	0.316	0.080	0.236	0.0001	0.080	1924
RISSP1	22-Feb-05	Rio Icacos	Upper Source	0.208	0.112	0.096	0.0000	0.112	2777
RISSP2	22-Feb-05	Rio Icacos	Upper Source	2.441	2.064	0.377	0.0000	2.064	52522
RISSP3	22-Feb-05	Rio Icacos	Upper Source	0.055	0.054	0.001	0.0000	0.054	1289
RISSP4	22-Feb-05	Rio Icacos	Upper Source	0.368	0.328	0.040	0.0000	0.328	8059
RISSP5	22-Feb-05	Rio Icacos	Upper Source	0.291	0.194	0.097	0.0000	0.194	4854
RISSP6	23-Feb-05	Rio Icacos	Upper Source	0.366	0.070	0.297	0.0002	0.070	1673
RISSP7	23-Feb-05	Rio Icacos	Upper Source	0.344	0.083	0.261	0.0001	0.083	1994
RISSP8	23-Feb-05	Rio Icacos	Upper Source	0.465	0.123	0.341	0.0001	0.123	3000
RISSP9	23-Feb-05	Rio Icacos	Upper Source	0.190	0.040	0.150	0.0001	0.040	947
RISSP10	24-Feb-05	Rio Icacos	Upper Source	0.329	0.070	0.259	0.0001	0.070	1684

Appendix C.8. Dissolved carbonic species in the lower source point samples within the Rio Icacos basin during winter 2005.

Sample Name	Collection Date	Site	Sub-site	DIC (mmol/L)	H_2CO_3 (mmol/L)	HCO_3^- (mmol/L)	CO_3^{2-} (mmol/L)	CO_2 (mmol/L)	pCO_2 (uatm)
RISSPL1	16-Feb-05	Rio Icacos	Lower Source	1.272	1.021	0.251	0.0000	1.021	25896
RISSPL2	16-Feb-05	Rio Icacos	Lower Source	0.221	0.210	0.010	0.0000	0.210	5201
RISSPL3	17-Feb-05	Rio Icacos	Lower Source	0.268	0.233	0.035	0.0000	0.233	5643
RISSPL4	18-Feb-05	Rio Icacos	Lower Source	1.491	1.378	0.113	0.0000	1.378	34054
RISSPL5	18-Feb-05	Rio Icacos	Lower Source	0.283	0.140	0.143	0.0000	0.140	3519
RISSPL6	18-Feb-05	Rio Icacos	Lower Source	0.569	0.557	0.012	0.0000	0.557	13510
RISSPL1	22-Feb-05	Rio Icacos	Lower Source	0.766	0.740	0.026	0.0000	0.740	18538
RISSPL2	22-Feb-05	Rio Icacos	Lower Source	0.837	0.708	0.129	0.0000	0.708	18003
RISSPL3	22-Feb-05	Rio Icacos	Lower Source	0.356	0.284	0.073	0.0000	0.284	6810
RISSPL4	21-Feb-05	Rio Icacos	Lower Source	0.701	0.616	0.085	0.0000	0.616	14974
RISSPL5	21-Feb-05	Rio Icacos	Lower Source	1.702	1.290	0.412	0.0001	1.290	31772
RISSPL6	21-Feb-05	Rio Icacos	Lower Source	0.259	0.245	0.014	0.0000	0.245	5734
RISSPL1	24-Feb-05	Rio Icacos	Lower Source	0.312	0.098	0.214	0.0001	0.098	2470
RISSPL2	24-Feb-05	Rio Icacos	Lower Source	0.594	0.282	0.311	0.0001	0.282	7209
RISSPL3	24-Feb-05	Rio Icacos	Lower Source	0.416	0.351	0.065	0.0000	0.351	8479
RISSPL4	23-Feb-05	Rio Icacos	Lower Source	0.800	0.743	0.057	0.0000	0.743	18139
RISSPL5	23-Feb-05	Rio Icacos	Lower Source	0.531	0.296	0.235	0.0000	0.296	7835
RISSPL6	23-Feb-05	Rio Icacos	Lower Source	0.255	0.242	0.013	0.0000	0.242	5770

Appendix D.1. Comparison of measured and calculated carbon dioxide alkalinity in water samples from the Rio Icacos mainstem during winter 2005.

Sample Name	Collection Date	Site	Sub-site	Alkalinity (mmol/L)	CO_2 (mmol/L)	HCO_3^- (mmol/L)	CO_2 (mmol/L)
				Measured	Measured	Calculated	Calculated
RIS4	1-Feb-05	Rio Icacos	Mainstream	0.323	0.055	0.205	0.076
RIS5	1-Feb-05	Rio Icacos	Mainstream	0.352	0.084	0.220	0.073
RIS6	1-Feb-05	Rio Icacos	Mainstream	0.396	0.072	0.247	0.072
RIS7	1-Feb-05	Rio Icacos	Mainstream	0.409	0.042	0.277	0.061
RIS8	1-Feb-05	Rio Icacos	Mainstream	0.459	0.041	0.336	0.071
RIS9	1-Feb-05	Rio Icacos	Mainstream	0.473	0.030	0.372	0.058
RIS10	1-Feb-05	Rio Icacos	Mainstream	0.477	0.001	0.381	0.034

Appendix D.2. Comparison of measured and calculated carbon dioxide alkalinity in water samples from the tributaries in the Icacos mainstem during winter 2005.

Sample Name	Collection Date	Site	Sub-site	Alkalinity (mmol/L)	CO_2 (mmol/L)	HCO_3^- (mmol/L)	CO_2 (mmol/L)
				Measured	Measured	Calculated	Calculated
RIST1	2-Feb-05	Rio Icacos	Tributary	0.278	0.069	0.187	0.081
RIST2	2-Feb-05	Rio Icacos	Tributary	0.307	0.063	0.262	0.085
RIST3	2-Feb-05	Rio Icacos	Tributary	0.291	0.104	0.225	0.104
RIST4	2-Feb-05	Rio Icacos	Tributary	0.199	0.084	0.176	0.117
RIST5	2-Feb-05	Rio Icacos	Tributary	0.296	0.032	0.222	0.065
RIST6	2-Feb-05	Rio Icacos	Tributary	0.237	0.032	0.185	0.054
RIST7	2-Feb-05	Rio Icacos	Tributary	0.218	0.188	0.165	0.235
RIST8	3-Feb-05	Rio Icacos	Tributary	0.310	0.112	0.204	0.084
RIST9	3-Feb-05	Rio Icacos	Tributary	0.155	0.104	0.073	0.076
RIST10	3-Feb-05	Rio Icacos	Tributary	0.346	0.125	0.220	0.102
RIST11	3-Feb-05	Rio Icacos	Tributary	0.404	0.055	0.306	0.089
RIST12	3-Feb-05	Rio Icacos	Tributary	0.349	0.053	0.316	0.089
RIST13	3-Feb-05	Rio Icacos	Tributary	0.399	0.064	0.328	0.124
RIST14	3-Feb-05	Rio Icacos	Tributary	0.380	0.002	0.264	0.041

Appendix D.3. Comparison of measured and calculated carbon dioxide alkalinity in groundwater within the Icacos basin during winter 2005.

Sample Name	Collection Date	Site	Sub-site	Alkalinity (mmol/L)	CO_2 (mmol/L)	HCO_3^- (mmol/L)	CO_2 (mmol/L)
				Measured	Measured	Calculated	Calculated
RISW1A	7-Feb-05	Rio Icacos	Groundwater	0.840	2.065	0.850	2.060
RISW1B	7-Feb-05	Rio Icacos	Groundwater	0.097	0.939	0.128	1.078
RISW2A	7-Feb-05	Rio Icacos	Groundwater	0.633	1.519	0.483	1.526
RISW2B	7-Feb-05	Rio Icacos	Groundwater	0.586	2.175	0.666	2.302
RISW3A	7-Feb-05	Rio Icacos	Groundwater	1.142	2.525	1.543	1.806
RISW3B	7-Feb-05	Rio Icacos	Groundwater	0.425	2.455	0.424	1.654
RISW4A	7-Feb-05	Rio Icacos	Groundwater	0.460	0.603	0.436	0.637
RISW5A	7-Feb-05	Rio Icacos	Groundwater	0.279	1.275	0.216	1.183
RISW5B	10-Feb-05	Rio Icacos	Groundwater	0.700	1.068	0.000	0.914
RISW6A	7-Feb-05	Rio Icacos	Groundwater	0.000	nd	nd	nd
RISW6B	7-Feb-05	Rio Icacos	Groundwater	0.039	nd	nd	nd
RISW7A	7-Feb-05	Rio Icacos	Groundwater	0.683	2.257	0.806	1.871
RISW7B	7-Feb-05	Rio Icacos	Groundwater	0.194	1.108	0.153	0.998
RISW8A	7-Feb-05	Rio Icacos	Groundwater	0.473	0.727	0.210	0.450
RISW1A	18-Feb-05	Rio Icacos	Groundwater	0.800	2.809	0.804	1.928
RISW1B	18-Feb-05	Rio Icacos	Groundwater	0.118	2.787	0.303	2.521
RISW2A	18-Feb-05	Rio Icacos	Groundwater	0.701	3.315	0.900	2.452
RISW2B	18-Feb-05	Rio Icacos	Groundwater	0.905	3.960	1.220	3.933
RISW3A	18-Feb-05	Rio Icacos	Groundwater	1.027	3.021	2.102	2.514
RISW3B	18-Feb-05	Rio Icacos	Groundwater	0.401	3.388	0.611	2.527
RISW4A	18-Feb-05	Rio Icacos	Groundwater	0.000	nd	nd	nd
RISW5A	18-Feb-05	Rio Icacos	Groundwater	0.221	1.692	0.301	1.388
RISW6B	18-Feb-05	Rio Icacos	Groundwater	0.027	0.679	0.039	0.829
RISW7A	18-Feb-05	Rio Icacos	Groundwater	0.640	2.095	0.582	1.906
RISW7B	18-Feb-05	Rio Icacos	Groundwater	0.197	1.812	0.454	2.207
RISW8A	18-Feb-05	Rio Icacos	Groundwater	0.714	1.850	1.297	1.580

Appendix D.4. Comparison of measured and calculated carbon dioxide alkalinity in upper and lower source points within the Icacos basin during winter 2005.

Sample Name	Collection Date	Site	Sub-site	Alkalinity (mmol/L)	CO_2 (mmol/L)	HCO_3^- (mmol/L)	CO_2 (mmol/L)
				Measured	Measured	Calculated	Calculated
RISSP1	8-Feb-05	Rio Icacos	Upper Source	0.428	0.054	0.282	0.054
RISSP2	8-Feb-05	Rio Icacos	Upper Source	0.286	0.538	0.159	1.313
RISSP3	10-Feb-05	Rio Icacos	Upper Source	0.000	0.032	0.001	0.047
RISSP4	10-Feb-05	Rio Icacos	Upper Source	0.089	0.311	0.053	0.405
RISSP5	10-Feb-05	Rio Icacos	Upper Source	0.367	0.026	0.185	0.031
RISSP6	14-Feb-05	Rio Icacos	Upper Source	0.267	0.018	0.121	0.004
RISSP7	14-Feb-05	Rio Icacos	Upper Source	0.275	0.021	0.250	0.047
RISSP8	14-Feb-05	Rio Icacos	Upper Source	0.331	0.019	0.202	0.029
RISSP9	14-Feb-05	Rio Icacos	Upper Source	0.036	0.000	0.000	0.000
RISSP10	14-Feb-05	Rio Icacos	Upper Source	0.090	0.000	0.063	0.022
RISSPL1	16-Feb-05	Rio Icacos	Lower Source	0.339	0.854	0.251	1.021
RISSPL2	16-Feb-05	Rio Icacos	Lower Source	0.032	0.196	0.010	0.210
RISSPL3	17-Feb-05	Rio Icacos	Lower Source	0.102	0.135	0.035	0.233
RISSPL4	18-Feb-05	Rio Icacos	Lower Source	0.123	0.966	0.113	1.378
RISSPL5	18-Feb-05	Rio Icacos	Lower Source	0.184	0.305	0.143	0.140
RISSPL6	18-Feb-05	Rio Icacos	Lower Source	0.000	0.658	0.012	0.557
RISSP1	17-Feb-05	Rio Icacos	Upper Source	0.428	0.023	0.372	0.086
RISSP2	17-Feb-05	Rio Icacos	Upper Source	0.318	2.334	0.142	2.135
RISSP3	17-Feb-05	Rio Icacos	Upper Source	0.000	0.000	0.000	0.013
RISSP3A	17-Feb-05	Rio Icacos	Upper Source	0.016	0.413	0.018	0.510
RISSP4	16-Feb-05	Rio Icacos	Upper Source	0.078	0.460	0.072	0.408
RISSP4A	16-Feb-05	Rio Icacos	Upper Source	0.313	0.432	0.256	0.507
RISSP5	16-Feb-05	Rio Icacos	Upper Source	0.328	0.047	0.242	0.099
RISSP6	21-Feb-05	Rio Icacos	Upper Source	0.412	0.029	0.263	0.041
RISSP7	21-Feb-05	Rio Icacos	Upper Source	0.399	0.034	0.169	0.030
RISSP8	21-Feb-05	Rio Icacos	Upper Source	0.481	0.037	0.174	0.054
RISSP9	21-Feb-05	Rio Icacos	Upper Source	0.210	0.000	0.121	0.052
RISSP10	22-Feb-05	Rio Icacos	Upper Source	0.351	0.014	0.236	0.080
RISSPL1	22-Feb-05	Rio Icacos	Lower Source	0.236	0.585	0.026	0.740
RISSPL2	22-Feb-05	Rio Icacos	Lower Source	0.141	1.272	0.129	0.708
RISSPL3	22-Feb-05	Rio Icacos	Lower Source	0.199	0.197	0.073	0.284
RISSPL4	21-Feb-05	Rio Icacos	Lower Source	0.121	0.564	0.085	0.616
RISSPL5	21-Feb-05	Rio Icacos	Lower Source	0.533	0.788	0.412	1.290
RISSPL6	21-Feb-05	Rio Icacos	Lower Source	0.027	0.207	0.014	0.245

Appendidx D.4. Continued.

Sample Name	Collection Date	Site	Sub-site	Alkalinity (mmol/L)	CO_2 (mmol/L)	HCO_3^- (mmol/L)	CO_2 (mmol/L)
				Measured	Measured	Calculated	Calculated
RISSP1	22-Feb-05	Rio Icacos	Upper Source	0.423	0.027	0.096	0.112
RISSP2	22-Feb-05	Rio Icacos	Upper Source	0.457	1.692	0.377	2.064
RISSP3	22-Feb-05	Rio Icacos	Upper Source	0.000	0.092	0.001	0.054
RISSP4	22-Feb-05	Rio Icacos	Upper Source	0.092	0.362	0.040	0.328
RISSP5	22-Feb-05	Rio Icacos	Upper Source	0.344	0.037	0.097	0.194
RISSP6	23-Feb-05	Rio Icacos	Upper Source	0.433	0.002	0.297	0.070
RISSP7	23-Feb-05	Rio Icacos	Upper Source	0.404	0.033	0.261	0.083
RISSP8	23-Feb-05	Rio Icacos	Upper Source	0.496	0.038	0.341	0.123
RISSP9	23-Feb-05	Rio Icacos	Upper Source	0.247	0.017	0.150	0.040
RISSP10	24-Feb-05	Rio Icacos	Upper Source	0.352	0.138	0.259	0.070
RISSPL1	24-Feb-05	Rio Icacos	Lower Source	0.242	0.141	0.214	0.098
RISSPL2	24-Feb-05	Rio Icacos	Lower Source	0.136	0.428	0.311	0.282
RISSPL3	24-Feb-05	Rio Icacos	Lower Source	0.199	0.238	0.065	0.351
RISSPL4	23-Feb-05	Rio Icacos	Lower Source	0.097	0.629	0.057	0.743
RISSPL5	23-Feb-05	Rio Icacos	Lower Source	0.226	0.275	0.235	0.296
RISSPL6	23-Feb-05	Rio Icacos	Lower Source	0.027	0.196	0.013	0.242