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Synoptic Survey of Surface Water Isotopes and Nutrient Concentrations, Páramo High-Elevation Region, Antisana Ecological Reserve, Ecuador*

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Abstract

Here we provide baseline information on water isotopes and nutrient concentrations for channelized streams and wetlands from a páramo ecosystem in Antisana Ecological Reserve, Ecuador. Water samples were collected from wetland areas and compared to the nearby Rio Tumiguina. Stream water samples were also collected downstream from glacial source areas for 7 km (Rio Tumiguina) and 10 km (Rio Antisana). Water samples from the gauging station on the Rio Tumiguina ($n = 4$) and nearby wetlands ($n = 4$) showed significant differences for some nutrients and little difference for other nutrients. Nitrate (NO_3-N) concentrations were below 14 $\mu g\ L^{-1}$ (1 $\mu mol\ L^{-1}$) at both sites and not significantly different. Concentrations of ammonium (NH_4-N) in both stream water and wetlands were much higher than NO_3-N concentrations. For example, NH_4-N concentrations in stream water of 195 $\mu g\ L^{-1}$ (14 $\mu mol\ L^{-1}$) were 17 times that of NO_3-N concentrations. In contrast to NO_3-N and NH_4-N, there was a significant difference ($P < 0.001$) between concentrations of soluble reactive phosphate (SRP), with concentrations of SRP in the Rio Tumiguina of about 263 $\mu g\ L^{-1}$ (8.2 $\mu mol\ L^{-1}$) and below detection limits in wetlands. Dissolved organic carbon (DOC) concentrations in the Rio Tumiguina of 0.4 mg L^{-1} were quite low compared to the 23 mg L^{-1} of DOC from the páramo wetlands. At both stream transects, the $\delta^{18}O$ values decreased from glacial signatures of about $-17‰$ near the glacial terminus to $-13‰$ at distances of 7 to 10 km. Nitrate concentrations were at or below detection limits at all sampling sites. Ammonium concentrations were higher than NO_3-N concentrations in all samples. Concentrations of dissolved organic phosphorus (DOP) were almost as high as dissolved organic carbon (DOC) near the glacial outlets. Concentrations of dissolved organic nitrogen (DON) and DOC were near detection limits near the glacial outlets and then increased downstream.

Introduction

Areas of high tropical mountains above treeline are generally termed páramo. The páramo *sensu stricto* occurs in disjunct plateaus along the Andean Cordillera in Venezuela, Colombia, Ecuador, and northern Peru (Monasterio and Vuilleumier, 1986). The term páramo has also been applied to other areas in Latin America, such as the "Brazilian páramo" or campos de altitude of the southeastern Brazilian Highlands (Safford, 1999). Páramos have been described as high mountain grasslands, in general dominated physiognomically by the presence of bunch grass (Gramineae) (Monasterio and Vuilleumier, 1986). In addition to grasslands, páramo ecosystems have other floristic associations, including woody shrubs (Keating, 2000), herbaceous perennials (Black, 1982), and cushion plants (Diemer, 1996). Within páramo ecosystems, well-drained grasslands alternate with wetland-type areas characterized by mosses and other vegetation covering a thick, well-developed soil layer (Monasterio and Vuilleumier, 1986; Sarmiento, 1986).

Although "alpine-like" in some of their characteristics, Sarmiento (1986) has suggested that the páramo of high tropical mountains differ in important aspects from alpine biota in temperature latitudes of North America, Europe, and Asia. Temperature and precipitation at high elevations in intertropical regions generally have much less annual variation than at temperate latitudes. Consequently, Sarmiento (1986) believes that páramo ecosystems tend to have a greater species richness than alpine areas in temperate latitudes, because of the unproductive and snow-covered winter period at temperate latitudes. However, Diemer (1996) has suggested that, aside from the duration of the growing season, similar abiotic selection pressures operate in the Ecuadorean páramo and European Central Alps.

While there has been research on the geography and biota of páramo ecosystems (e.g., Grubb, 1970; Black, 1982; Monasterio and Vuilleumier, 1986; Sklenar and Jorgensen, 1999), to our knowledge there has been little, if any, research on the hydrology, nutrient cycling, and biogeochemistry of páramo areas. There is some urgency to understanding the hydrology and nutrient status of páramo ecosystems. Quito, the capital of Ecuador, now obtains about one-third of its municipal and industrial water from diversion structures within the Antisana Ecological Reserve. How these water diversions have affected the hydrology and biogeochemistry of páramo ecosystems is unknown. The success of the Antisana water diversion has resulted in proposals

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to expand existing uses of surface water and a call for additional water diversions and hydroelectric power in this area. The cumulative effect of additional water withdrawals on the biogeochemistry of páramo ecosystems cannot be evaluated without an understanding of the current biogeochemical status.

Glacial systems throughout the tropical Andes are undergoing massive retreat (Kaser, 1999). Ablation rates and glacial recession on Cerro Antisana over the last decade are three to five times greater than the previous three decades (Francou et al., 2000). The importance of glacial runoff to the hydrology of downstream páramo ecosystems is unknown. Therefore understanding links between glacial hydrology and downstream páramo ecosystems is important for evaluating how future glacial retreat, in combination with potential water diversions, may alter the hydrology and nutrient status of páramo regions.

Here we present results from a synoptic survey of water isotopes and nutrient concentrations from streams and wetlands draining the Antisana massif in the Antisana Ecological Reserve. Our primary objective is to obtain baseline data for an ecosystem under pressure from development. Specific questions we attempt to answer include: (1) What are the nutrient concentrations in wetlands and streams? (2) Do nutrient concentrations differ between wetlands and streams? (3) Can water isotopes provide information on source waters for wetlands? (4) Do water isotopes in streams change with downstream distance from glacial source areas? (5) Can water isotopes provide information on the importance of evaporation? (6) How do concentrations of nutrients change with distance downstream from the Antisana massif? (7) Will this baseline data set be helpful in developing more directed questions and testable hypotheses?

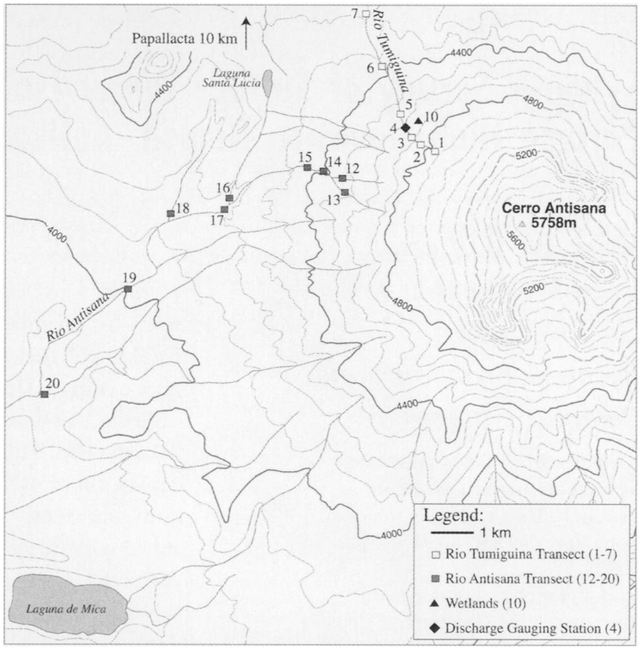

FIGURE 1. Topographic map of the study area along the west side of Cerro Antisana. Stream water samples were collected along an elevational transect at the Rio Tumiguina (sites 1–7) which flows north and Rio Antisana (sites 12–20) which flows south. Wetlands were sampled near site 10. Laguna de Mica is a water diversion for the city of Quito, Ecuador. Dashed contour lines indicate glacierized area.

Site Description

Ranging from high Andean páramo to primary and secondary forest ecosystems, the 131,000-ha Antisana Ecological Reserve is home to rare and threatened species such as the Andean Condor, the spectacled bear, and the dwarf deer. The Reserve is also the principal watershed that provides potable water for the Ecuadorian capital city, Quito, and numerous surrounding inter-Andean communities. Due to its proximity to the capital city and years of exposure to various pressures on its natural resources, the Reserve's ecology and natural resources are seriously threatened (Nature Conservancy, 2001).

As with most páramo areas in Ecuador, the Antisana Ecological Reserve contains an active glacial system located on an active volcano. Cerro Antisana is 5758 m in elevation and located at 0°28′30″S latitude and 78°08′55″W longitude (Fig. 1). Although its last eruption was in 1802, Cerro Antisana is still considered active. Rocks of Antisana are mainly basic proxenandesites with olivine and hypersthen. The Antisana massif rises directly from the Amazon basin and forms the crest of the Continental Divide that separates drainage systems that flow into the Pacific Ocean to the west and the Atlantic Ocean to the east.

We collected water samples in streams and wetlands draining the western side of the Antisana massif (Fig. 1). The hydrology and nutrient cycling is of particular interest because the Empresa Municipal de Alcantarillado y Agua Potable de Quito has proposed to harvest water from Rio Tumiguina and Rio Antisana. Currently, the water agency harvests surface water at Papallacta (about 10 km from the northern border of Fig. 1) and at Laguna de Mica (3,700 m) on the southwestern side of Cerro Antisana (Fig. 1). The high quality of these water sources allows the water to be piped directly to domestic users in Quito and surrounding communities without treatment of any kind.

The closest meteorological station to the Antisana Ecological Reserve is Izobamba, located 30 km away at an elevation of 3058 m. Mean annual temperature is 11.5°C and the yearly amplitude is less than 1°C (Sarimiento, 1986). There is no seasonal trend in air temperature; diurnal changes in air temperature are greater than annual changes in air temperature. Annual precipitation at Izobamba is 1361 mm (Sarimiento, 1986). There is no seasonal trend in precipitation and the most rainy month may occur at any time from February to October. Only November–January includes a period of decreasing precipitation, which corresponds to the veranillo or little summer.

The páramos around Antisana are a private land with reserve status and thus do not have the population pressures of other páramo ecosystems such as the Chimborazo area. However, parts of the páramo ecosystem in the Antisana Ecological Reserve have been extensively burned and grazed in the past (Grubb, 1970) and such activities continue to a limited extent today. Personal observation (B. Francou) has shown no agricultural activity and little grazing over the last five years in the area we sampled (Fig. 1), most likely because of the high elevation and the reserve status of the area.

Methods

Surface water samples were collected on a synoptic basis from 16 to 20 October 1999. Water samples (n = 4) were collected from wetland areas (site 10) at an elevation of 4500 m. We compare these wetland samples to water samples from the headwaters of the Rio Tumiguina, collected 100 m from site 10 at a gauging station (site 4) installed and maintained by the the Institut de Recherche pour le Developpement and also located at an elevation of 4500 m. Here we present mean concentrations (n = 4) from water samples collected at the gauging station on

17 October 1999 at 0900, 1200, 1500, and 1800. Stream water samples were collected along an elevational transect from two streams. The Rio Tumiguina flows north to Papallacta; samples were collected at sites 1 to 7 which ranged in elevation from 4600 to 4000 m. The Rio Antisana flows south towards Laguna de Mica; samples were collected at sites 12 to 20 which ranged in elevation from 4800 to 4200 m (Fig. 1). Additionally, we collected 30 snow and ice samples on and around Cerro Antisana for isotopic analyses to develop a local meteoric water line.

Water samples from streams and wetlands were collected as grab samples. Water samples for chemical analyses of major solutes were collected in polyethylene bottles soaked with DI water overnight and then rinsed copiously five times; bottles were further rinsed three times with sample water at the time of collection. Samples collected for chemical analyses were immediately filtered in the field through ashed, prerinsed (300 ml), 47-mm Gelman A/E glass fiber filters with ca. 1-μm pore size. A second, filtered sample was collected for organic C, N, and P in precombusted, amber-colored glass bottles with teflon-lined caps. Water isotopes were collected in unfiltered, 30-ml glass bottles with a conical polyseal cap specifically developed for water isotopes; care was taken to make sure there was no head space in the bottle. All samples were kept cool at about 5°C and shipped within 1 wk to the United States for analyses.

Chemical and nutrient analyses were conducted using the protocols in Seibold (2001) and Williams et al. (1996). Nitrate was analyzed using a Dionex DX 500 ion chromatograph with an IonPac AS4A-SC Analytical Column. The detection limit was 0.42 μg L^{-1} (0.03 μmol L^{-1}) and precision was 1.1%. Ammonium was measured on a Lachat QuikChem 8000 Flow Injection Analyzer using a method based on the Berthelot reaction. The detection limit was 4.62 μg L^{-1} (0.33 μmol L^{-1}) and precision was 0.91% (Seibold, 1995). Total dissolved N (TDN) was determined on filtered samples using potassium persulfate digestion to oxidize all forms of N into NO_3-N. Nitrate was then measured on Lachat QuikChem 4000 Flow Injection Analyzer. The detection limit for TDN was 9.8 μg L^{-1} (0.17 μmol L^{-1}) and precision was 1.62% (Seibold, 1995). Soluble reactive phosphate was analyzed using a Lachat QuikChem 8000 Flow Injection Analyzer. Total dissolved phosphorus (TDP) was determined on filtered samples using potassium persulfate digestion and 3.75 N NaOH to release phosphorus from combination with organic matter. Detection Limits for SRP were 1.3 μg L^{-1} (0.04 μmol L^{-1}) and for TDP were 0.9 μg L^{-1} (0.03 μmol L^{-1}). Dissolved organic N and DOP were calculated from filtered samples as the difference between total dissolved inorganic and organic concentrations.

Oxygen isotopes were analyzed using the CO_2 equilibration method of Epstein and Mayeda (1953) at the Institute of Arctic and Alpine Research (INSTAAR). The deuterium (D) isotope of hydrogen (H) in water was also analyzed at INSTAAR following the protocol in Vaughn et al. (1998). The δ^{18}O and D values are expressed in the conventional delta () notation as the per mil (‰) difference relative to the international Vienna-Standard Mean Ocean Water (VSMOW) standard:

$$\delta(‰) = (Rx/Rs - 1) \times 1000$$

where R denotes the ratio of heavy to light isotope in a sample Rx and the standard Rs.

Results

HEADWATER STREAMS AND WETLANDS

There were striking differences in the visual appearances of Rio Tumiguina and the wetland sites. The Rio Tumiguina drains Glacier 15 of the Antisana massif. Stream water was turbid, contained glacier flour, and was whitish in color. In contrast, water from the wetlands was clear, appeared to contain no sediments, and was characterized by a dark tea color.

TABLE 1

Páramo wetlands compared to streams: Nutrient concentrations and water isotopes

		Stream		Wetlands	
	Units	Mean	SD	Mean	SD
NH_4–N	μg L^{-1}	195	±135	41.2	±8.13
NO_3–N	μg L^{-1}	11.1	±1.21	5.9	±7.32
SRP	μg L^{-1}	263	±74.8	0	±0
DOC	mg L^{-1}	0.46	±0.07	23.6	±0.98
DON	μg L^{-1}	341	±148	172	±13.2
DOP	μg L^{-1}	522	±352	0	±0
δ^{18}O	‰	−16.95	±0.11	−13.49	±1.02
D	‰	−124.02	±0.67	−107.50	±5.65

Water samples from the gauging station on the Rio Tumiguina (n = 4) and nearby wetlands (n = 4) showed significant differences for some nutrients and little difference for other nutrients. Nitrate concentrations were below 14 μg L^{-1} (1 μmol L^{-1}) at both sites (Table 1). A t-test showed no significant difference between sites (P = 0.28). We are not aware of similar measurements for high-elevation areas of the Andes. Tropical streams in South America tend to have much higher NO_3-N concentrations than we measured at the Antisana Ecological Reserve. The 10 μg L^{-1} of NO_3-N we measured was about 15% of the 65 μg L^{-1} reported by Lewis (1986) from the Caura River in Venezuela, a low-elevation, tropical moist forest. Nitrate concentrations in a headwater basin of Lake Calado in the Central Amazon Rain Forest of about 150 μg L^{-1} were 15 times our concentrations (Lesack, 1993).

Surprisingly, NH_4-N concentrations in both stream water and wetlands were much higher than NO_3-N concentrations. NH_4-N concentrations in stream water of 195 μg L^{-1} (14 μmol L^{-1}) were 17 times that of NO_3-N concentrations (Table 1). Similarly, NH_4-N concentrations of 42 μg L^{-1} from wetlands were about eight times that of the NO_3-N concentrations of 5.8 μg L^{-1} from wetlands. There was no significant difference in NH_4-N concentrations between stream water and wetlands (P = 0.11). In most mountain ecosystems, concentrations of NH_4-N are at or below detection limits (e.g., Williams et al., 1995; Psenner et al., 1989; Coats and Goldman, 2001). For the tropical Caura River in Venezuela, Lewis (1986) reports NH_4-N values of 35 μg L^{-1} or 5 times less than our páramo streams. Similarly, Lesack (1993) reports NH_4-N concentrations from a stream draining a headwater catchment to Lake Calado in the central Amazon were generally less than 14 μg L^{-1} (1 μmol L^{-1}).

In contrast to NO_3-N and NH_4-N, there was a significant difference ($P < 0.001$) between SRP concentrations in the Rio Tumiguina and the wetlands. Concentrations of SRP in the Rio Tumiguina of about 263 μg L^{-1} (8.2 μmol L^{-1}) are quite high with respect to most ecosystems. For comparison, the Caura River in Venezuela had mean SRP concentrations of 2.5 μg L^{-1} (Lewis, 1986) and the Lake Calado catchment in the central Amazon had mean SRP concentrations of 1 μg L^{-1} (0.03 μmol L^{-1}) (Lesack, 1993). In contrast to mean SRP concentrations of 263 μg L^{-1} (8.2 μmol L^{-1}) in the Rio Tumiguina, SRP concentrations in wetlands were always below detection limits of 1.3 μg L^{-1} (0.04 μmol L^{-1}).

Concentrations of DOC differered significantly between

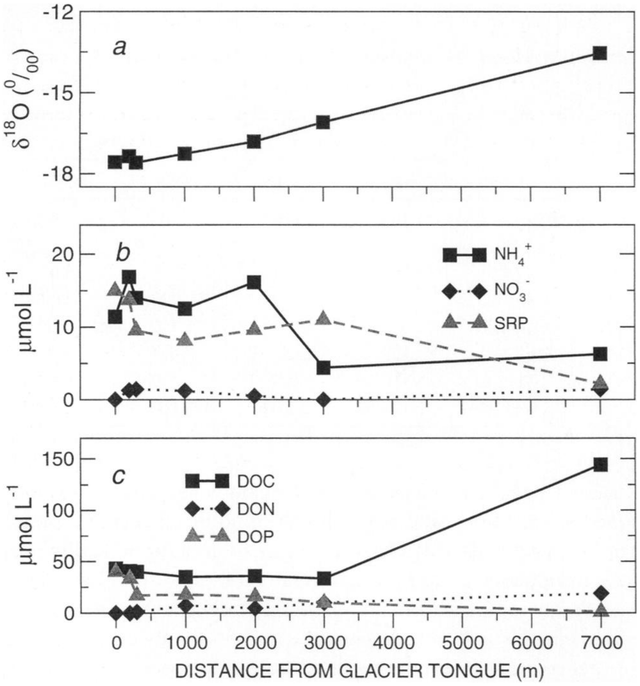

FIGURE 2. Water isotopes and nutrient concentrations along the Rio Tumigunia, which drains Glacier 15 on Cerro Antisana. The Rio Tumigunia flows into the Papallacta intake for the city of Quito. The upper panel (a) is $\delta^{18}O$, the middle panel (b) is inorganic nutrient concentrations in mol L^{-1}, and the lower panel (c) is organic nutrient concentrations in $\mu mol\ L^{-1}$.

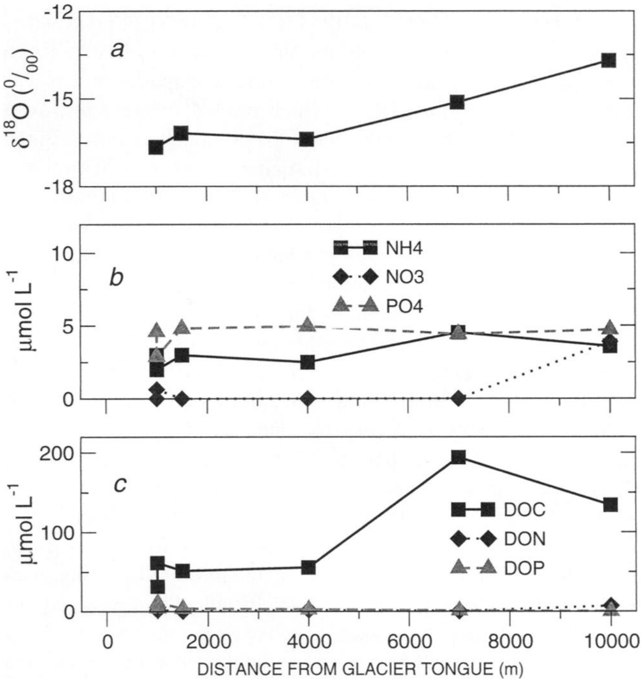

FIGURE 3. Water isotopes and nutrient concentrations along the Rio Antisana. The Rio Antisana flows into Laguna de Mica, the water diversion for the city of Quito. The upper panel (a) is $\delta^{18}O$, The middle panel (b) is inorganic nutrient concentrations in $\mu mol\ L^{-1}$, and the lower panel (c) is organic nutrient concentrations in $\mu mol\ L^{-1}$.

stream water and wetlands ($P < 0.001$) and appear to bracket the range of DOC found in surface waters worldwide. Dissolved organic carbon concentrations in the Rio Tumiguina of 0.4 mg L^{-1} (Table 1) were low compared to the 2 mg L^{-1} typical of high-elevation streams in the Rocky Mountains of the U.S.A. (McKnight et al., 1997), and comparable to the lowest values reported for alpine streams (Spitzy and Leenheer, 1991). In contrast, the 23 mg L^{-1} of DOC from the páramo wetlands (Table 1) is within the range of DOC concentrations reported from streams and rivers draining swamps and wetlands (Thurman, 1983), and much greater than typical river concentrations which range from 2 mg L^{-1} for tundra streams to 8 mg L^{-1} for wet tropics (Table 9.1, Spitzy and Leenheer, 1991). The 23 mg L^{-1} of DOC measured in the wetlands was also much greater than black-water rivers in South America such as the Rio Negro in Brazil, which have DOC concentrations of about 10 to 12 mg L^{-1} (Leenheer, 1980; Richey et al., 1990), half what we report for the páramo wetlands.

Mean concentrations of DON in the Rio Tumiguina were 341 $\mu g\ L^{-1}$ (24 $\mu mol\ L^{-1}$) and in the wetlands were 172 $\mu g\ L^{-1}$ (12 $\mu mol\ L^{-1}$), and did not differ significantly between the two water bodies ($P = 0.36$). These concentrations of DON were similar in magnitude to those reported from high-elevation areas of the Sierra Nevada (Coats and Goldman, 2001). In an exhaustive analysis of N data from tropical ecosystems in South America, Lewis et al. (1999) estimated mean DON concentrations from 25 rivers as 162 $\mu g\ L^{-1}$, quite similar to the mean DON concentration of 172 $\mu g\ L^{-1}$ from our wetland sites. The concentrations of DON measured in páramo streams and wetlands appear typical of many streams and rivers worldwide.

As with SRP, there was a significant difference in DOP concentrations between Rio Tumiguina and wetlands ($P < 0.001$). Mean concentrations of DOP in Rio Tumiguina were 522 $\mu g\ L^{-1}$ (16 $\mu mol\ L^{-1}$), while all measurements of DOP in the wetlands were below detection limits (Table 1). Both Lesack (1993) and Lewis (1986) report DOP concentrations similar to our detection limits. Thus, it appears that DOP concentrations in páramo wetlands are similar to some tropical streams in South America, while DOP concentrations in Rio Tumiguina are elevated compared to these same streams.

Water isotopes differed from surface waters and wetlands located 100 m apart. Oxygen isotopes in wetlands of −13.49‰ were significantly ($P = 0.006$) enriched by 3.46‰ compared to the −16.95‰ of Rio Tumiguina (Table 1). Similarly, deuterium values of −107.50‰ for the wetlands were significantly ($P = 0.009$) enriched compared to the −124.02‰ for the Rio Tumiguina.

LONGITUDINAL STREAM TRANSECTS

Water isotopes became enriched with distance downstream of the glacier source areas. On both stream transects, the $\delta^{18}O$ values decreased from glacial signatures of about −17‰ near the glacial terminus to −13‰ at distances of 7 to 10 km (Figs. 2a, 3a). Deuterium values showed a similar enrichment with downstream distance from the glacial source areas (data not shown). Evaporation rates may be large in these streams and wetlands because of shallow water depths and high daytime temperatures. High evaporation rates may result in enrichment of oxygen isotopes downstream from glacial sources. We evaulated the possibility of evaporation by comparing the D-$\delta^{18}O$ relationship of surface waters (both streams and wetlands) to that of the local meteoric water line. Empirical results have shown that hydrogen and isotopic values in precipitation co-vary and are generally described by the relationship (Craig, 1961) (Fig. 4).

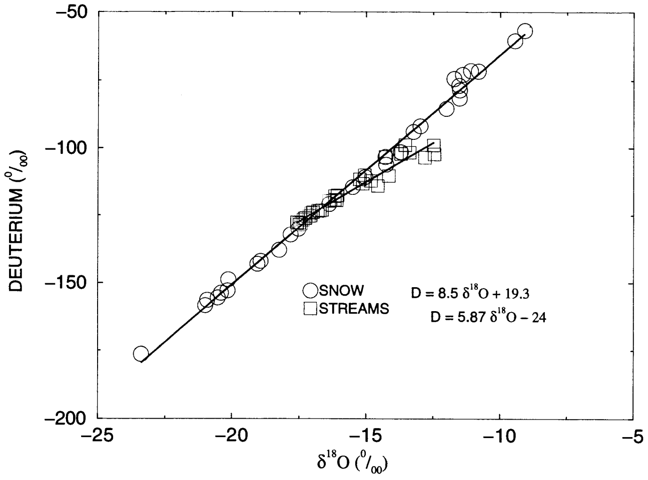

FIGURE 4. Potential evaporation line of water isotopes from surface waters compared to the local meteoric water line derived from snow and ice samples on and near Cerro Antisana.

$$\delta D = 8\ \delta^{18}O + 10 \qquad (1)$$

which is defined as the global meteoric water line. Evaporation of surface and soil water under conditions of low humidity preferentially remove the lighter isotopes, resulting in a lower slope than the local meteoric water line (Sami, 1992).

Our local meteoric water line had a similar slope but a different *y*-intercept (or deuterium excess value) compared to the global meteoric water line:

$$\delta D = 8.5\ \delta^{18}O + 19. \qquad (2)$$

The similar values in slope between our results (8.5) and the global meteoric water line (8.0) suggests an absence of complex kinetic fractionation processes affecting precipitation. However, the enriched deuterium excess value of 19 at Antisana compared to the global mean of 10 suggests that some of the water vapor that formed precipitation was derived from evaporation of localized water sources, such as the nearby Amazon basin (Grootes et al., 1989).

The D-$\delta^{18}O$ relationship of surface waters was significantly different than that of precipitation ($P < 0.05$ for both slope and *y*-intercept):

$$\delta D = 5.9\ \delta^{18}O - 24. \qquad (3)$$

The significant difference in slope indicates that water isotopes in precipitation were modified before contributing to stream flow. Both inorganic (Figs. 2b, 3b) and organic nutrient (Figs. 2c, 3c) concentrations changed along the longitudinal sampling transects. Concentrations of SRP and NH_4-N at Rio Tumiguina were highest at or near the glacial outlet and then decreased with distance downstream (Fig. 2b). Concentrations of SRP decreased from 15 μmol L^{-1} (465 μg L^{-1}) at the glacial outlet to 2 μmol L^{-1} (62 μg L^{-1}) at the lowest-elevation sampling point. Concentrations of NH_4-N were as high as 18 μmol L^{-1} (252 μg L^{-1}) near the glacial outlet and decreased to 6 μmol L^{-1} (84 μg L^{-1}) at the lowest downstream site. Concentrations of SRP and NH_4-N along the Rio Antisana transect (Fig. 3b) paralleled the longitudinal pattern of the Rio Tumiguina. On both stream transects, NO_3-N concentrations were near or below detection limits, except for the lowest downstream site.

Concentrations of DOC increased more than four-fold with distance downstream along both stream transects, from about 35 μmol L^{-1} (0.4 mg L^{-1}) near the glacial outlets to about 160 μmol L^{-1} (1.9 mg L^{-1}) at the lowest sampling points (Figs. 2c, 3c). Similarly, DON increased from about detection limits near the glacial outlets to 7–18 μmol L^{-1} (0.10–0.25 mg L^{-1}) at the lowest sampling points. In contrast to DOC and DON, concentrations of DOP decreased from the glacial outlet downstream.

Discussion

The unique geology of Cerro Antisana may have contributed in part to the high SRP and DOP concentrations that we measured in stream waters. High concentrations of SRP are unusual in high-elevation catchments. For example, SRP concentrations from 73 lakes in the European Alps were below 18 μg L^{-1} for all but one lake (Psenner, 1989). Measurements of SRP in granitic, high-elevation catchments in North America are usually below detection limits (Williams and Melack, 1991). The SRP concentrations of 263 μg L^{-1} we measured at the gauging station of the Rio Tumiquina are similar to the the 200 μg L^{-1} SRP concentrations reported by Triska et al. (1993) for the geothermally fed Salto River in Costa Rica. The Salto River drains volcanoes formed from similar tectonic processes as those at Cerro Antisana. The andesites from the Salto River contain an average P content of 0.22 wt% P_2O_5 (Pringle et al., 1993). While we did not conduct geochemical analyzes of bedrock on Antisana, it is possible that the andesitic rock typical of Cerro Antisana may also contain appreciable amounts of inorganic P in bedrock. Our longitudinal transects showed that maximum concentrations of SRP occurred at the glacial outlet and decreased with distance downstream (Figs. 2b, 3b), consistent with a lithographic source of SRP.

DOC and DON concentrations increased downstream, consistent with an increase in biological activity downstream from glacial source areas. In contrast, DOP concentrations decreased downstream from glacial source areas. The inverse behavior in concentrations of DOP and DOC/DON downstream from glacial source areas suggest that DOP may have a different origin than DOC and DON. Glacial processes in high-mountain catchments enhance rates of chemical weathering and denudation (Sharp et al., 1995). Active volcanism may alter the solute composition of stream waters by processes occurring outside of the surficial catchment, such as degassing of hot magma followed by condensation and absorption of magmatic gases into groundwater and subsequent fluid-rock interactions (Pringle et al., 1993). Cerro Antisana contains both active glaciers and active volcanism. The SRP and DOP concentrations that we measured in our synoptic survey may have been influenced to an unknown extent by these two processes in combination with lithographic sources of inorganic P.

Our measurements of SRP and DOP suggest several research questions. Does the bedrock of Cerro Antisana contain appreciable amounts of inorganic P? Does the enhancement of mechanical weathering from glacier activity in combination with geothermal activity accelerate weathering of newly extruded andesitic rocks and provide inorganic P in glacial meltwaters? Are concentrations of SRP and DOP in glacial runoff biologically available, or are they bound to glacial sediments and biologically unavailable?

The low NO_3-N values we report are similar to pristine mountain areas around the world, which generally have NO_3-N concentrations less than 1 μmol L^{-1} (Psenner et al., 1989). Aber et al. (1989, 1998) have developed a number of indicators to evaluate the N status of ecosystems. In general, water bodies with NO_3-N concentrations near 1 μmol L^{-1} are considered N-limited ecosystems (Stoddard, 1994; Williams et al., 1995; Williams and Tonnessen, 2000). The low NO_3-N concentrations that we report are consistent with their definitions of an N-limited ecosystem. The reason for the elevated NH_4-N concentrations we report is unknown and bears further research. Hedin et al. (1995) report higher NH_4-N concentrations than NO_3-N concentrations for 35 pristine mountain catchments in Chile. They suggest that streams that drain ecosystems that are highly N-limited may be characterized by having NH_4-N concentrations greater than NO_3-N concentrations. As mentioned previously, the low NO_3-N concentrations we measured are consistent with an N-limited ecosystem. The high NH_4-N concentrations and low NO_3-N concentrations we report are consistent with a heavily N-limited ecosystem as defined by Hedin et al. (1995).

A lithographic source for the high NH_4-N concentrations that we report may be worth investigating. Dahlgren (1994) has reported that ammonium-bearing rocks may be an important source of inorganic N in some situations. Holloway et al. (1998) have shown that metavolcanic bedrock can contain appreciable amounts of N (385 mg N kg^{-1}) and have suggested that the idea that geologic N can act as a source of inorganic N in soils and surface waters needs to be re-evaluated. Moreover, geothermal waters can be high in NH_4-N, particularly near their source (Cooper, 1983). Pringle et al. (1993) report NH_4-N concentrations of 20–80 μg L^{-1} from volcanic streams in Costa Rica. Since the Antisana massif is active, it may be worth investigating whether the combination of geologic N in volcanic rock and enhanced weathering caused by geothermal activity may be a source of NH_4-N. In contrast to our results, Pringle et al. (Table 2, 1993) report greater NO_3-N concentrations than NH_4-N concentrations at all of their sites.

The D-δ^{18}O relationship of stream waters was significantly different than that of precipitation at the Antisana Ecological Reserve. In contrast, the D-δ^{18}O relationship of stream waters in high-elevation catchments from mid-latitude areas is generally not significantly different than precipitation (Brown, 1998; Sueker et al., 2000). The slope of 5.9 from this high-elevation area is similar to the slope of 5.4 that Sami (1992) reports for the evaporation line for the arid eastern Cape in South Africa, where there is extensive evaporation. Evaporation of surface waters in this tropical, high-elevation area appears to be important to the local hydrology. The D-δ^{18}O relationship of surface waters draining the Antisana massif is consistent with surface waters that have undergone large amounts of evaporation. Thus, evaporation rates in this tropical, high- elevation ecosystem may be large when compared to mid-latitude, high-elevation areas.

Our isotopic data are insufficient to determine whether the enrichment of surface waters downstream from glacial source areas was because of mixing with isotopically enriched rain, evaporation, or some combination of the two. The enrichment in oxygen isotopes by about 4‰ within 7 km downstream from source areas is quite large when compared to temperate mid-latitude areas (Sueker et al., 2000). More research is needed to determine the importance of glacial runoff to stream flow in páramo ecosystems.

Water isotopes and quality suggest that glacial runoff was not the source waters for wetlands in our research area. Oxygen isotopes in wetlands of -13‰ were enriched by 3‰ in δ^{18}O compared to the -16‰ of the nearby Rio Tumiguina. The high DOC in wetlands compared to streams and the low DOP in wetlands compared to streams are consistent with glacier runoff not being the water source for wetlands. The high DOC concentrations measured suggest that páramo wetlands appear to be analogous to marshes, which are characterized as saturated areas with grasses and sedges as the dominant plant type (Thurman, 1985). Visual observations showed that on clear days water depth in wetlands decreased several cm per day, while water levels were replenished after rain events. A possible mechanism for the formation of páramo wetlands is that they are formed from perched water tables that are recharged by local precipitation and not hydrologically connected to the regional water table.

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