The Impact of Land Use Practices on Nutrients in Freshwater Streams, Guanacaste, Costa Rica

Lindsay Hagamen

This thesis is submitted in partial fulfillment of the Bachelor of Science degree in Environmental Science

Brown University
December, 2008

This thesis has been accepted in partial fulfillment of the Bachelor of Science degree in Environmental Science, with Honors distinction.

Principle Advisor: Stephen Porder

Reader: Heather Leslie

Reader: Jeremy Rich

Table of Contents

List of Tables

List of Figures

ABSTRACT

Agricultural intensification, specifically the applications of nitrogen (N) fertilizer to crop fields in temperate climates, has dramatically increased yields and helped to feed a growing global population. At the same time, however, N additions have had cascading and deleterious effects on downstream aquatic ecosystems, where nutrient loading drives eutrophication. Intensive, high nitrogen agriculture is now rapidly expanding in the tropics, but its effects on tropical streams have not been nearly as well documented as in temperate zones. In this study, I sampled streams from 12 subwatersheds in the Tempisque River Basin, in northwestern Costa Rica, that drain markedly different land use types (> 50% agriculture, forest, or pasture). There was no significant difference between N concentrations in pasture and forest streams. Ammonia (NH_4^+-N), nitrate (NO_3^-–N), and dissolved organic nitrogen (DON) all increased linearly as the fraction of agriculture within the watershed increased, and land use within 1km upstream from the sampling site best described the variation in nitrogen concentrations (R^2=0.49, 0.52, 0.59 respectively), compared to land use within 500m, 2000m, 5000m upstream or within the entire watershed. High rates of N fertilization (rice 140-180 kg N/ha-yr; sugarcane 100-150 kg N/ha-yr) may be increasing the N availability in streams draining agricultural fields throughout the Tempisque River Basin, potentially driving eutrophication. More research is necessary to establish annual nutrient fluxes and to understand the impacts of changing nutrient availability on stream ecology and downstream aquatic ecosystems.

INTRODUCTION

Modern changes in global land-use patterns are altering the functioning of ecosystems worldwide (Freckman *et al.* 1997; Vitousek *et al*. 1997; Chapin *et al*. 1998). While deforestation directly impacts ecosystem goods and services such as biodiversity, carbon balance and water cycling, (Sala *et al.* 2000; Hansen *et al.* 2008), the land use decisions that follow deforestation strongly impact the trajectory of these effects. In the tropics, land is commonly cleared for use as pasture, but increasingly, the conversion of pasture and forest to intensive crop agriculture is becoming more common (Matson and Vitousek 1990; Matthews *et al.* 1994; Brown *et al.* 2008). Agricultural intensification often includes a substantial increase in the rates of nitrogen (N) fertilizer application, which both improves yields and has deleterious consequences for downstream aquatic systems, where nutrient loading can drive eutrophication (Howarth *et al*. 1996; Vitousek *et al*. 1997; Boesch *et al.* 2001; Jenkinson 2001; Kemp and Dodds 2001; Tillman *et al.* 2001; Turner *et al.* 2003; Beman *et al.* 2005). While much of the developing world could benefit from modest increases in fertilizer use (Sánchez, 2002), large-scale intensive agriculture continues to apply large amounts of N fertilizer to maximize yields despite the consequences of excess N in downstream ecosystems (Vitousek *et al.* 1997).

While the effects of nitrogen loading in temperate aquatic systems have been extensively documented, the impacts on tropical systems have received considerably less attention (Downing *et al*. 1999; Ahrens *et al.* 2008). Nevertheless, tropical ecosystems are experiencing the beginning of what will be a significant increase in available nitrogen (Asner *et al*. 2001; Matson *et al.* 2002; Sanchez *et al.* 2007), and substantial alterations in aquatic systems are occurring in those tropical regions already under intensive agricultural production (Filoso *et al*. 2003; Harrison and Matson 2003; Beman *et al.* 2005; Ahrens *et al.* 2008). Exploring the impacts of these land use practices on the streams most immediately affected by this shift is fundamental to understanding potential alterations to aquatic ecosystems further downstream and in guiding land use decisions.

The relatively few studies of the effects of land use change on tropical streams have been focused on small pasture stream catchments in the Amazon Basin following deforestation. In the Amazon, the conversion of forest to pasture is changing the ecology and biogeochemistry of freshwater streams: riparian vegetation shifts from trees to grasses and streams widen (Bernardes *et al.* 2004; Neill *et al.* 2006), rates of surface runoff and stream discharge increase (Biggs *et al.* 2006; Chaves *et al.* 2008), the diversity of macroinvertebrate communities is reduced (Ometo *et al.* 2000), and there are large shifts in stream nutrient cycling and solute concentration (Neill *et al.* 2001; Thomas *et al.* 2004; Biggs *et al.* 2004). The conversion of tropical forests to pasture reduces nitrate (NO_3^-) and increases ammonia (NH_4^+) and dissolved organic nitrogen (DON) concentrations in pasture streams (Neill *et al*. 2006). These patterns shift with time since deforestation— an initial pulse in N loss is followed by decreased losses as pastures quickly degrade to low total ecosystem N levels (Keller *et al.* 2003; Davidson *et al.* 2007).

One would expect intensive cropping in the tropics to have a larger effect on stream nutrient cycling than grazing, as has been observed in the temperate zone, since crops typically receive significant additions of fertilizer (Jordan *et al.* 1997a). Ometo *et al.* (2000) demonstrated increases in stream nitrogen concentrations from sugarcane production in the state of Sao Paulo, Brazil and Filoso *et al.* (2003) also showed that riverine exports of total nitrogen increased with relation to the total area of sugarcane cultivation in the Piracicaba River basin in southeast Brazil. In the subtropical lowlands of the Yaqui Valley, Mexico, N from agricultural fertilizers drive high concentrations of nitrogen and increased nitrous oxide production in nearby streams and canals (Harrison and Matson 2003).

Despite this initial evidence, there have been few studies of changes in water chemistry associated with landscape-scale shifts in tropical land use, and even fewer studies outside of South America. Given wide differences in soil type, nutrient availability, and ecosystem processing of nutrients across the tropics (Townsend *et al.* 2008), this scarcity of data severely constrains our ability to understand the consequences of rapid land use change for downstream tropical ecosystems. In this context, I studied 12 streams in the Tempisque River Basin in northwestern Costa Rica with stream catchments that varied substantially in land use. I asked whether stream water chemistry varied with land use, and whether local or regional land use better explained the patterns I observed. I hypothesized that nitrogen concentrations would be highest in streams draining agricultural catchments, lower in forests, and lowest in pasture-dominated landscapes. Further, I reasoned that nutrient concentrations would be more impacted by land use practices immediately upstream than throughout the entire watershed.

METHODS

STUDY REGION

This project focused on the effects of land use on stream water chemistry in the Tempisque River Basin (5,948 km^2) in the Guanacaste Province of Costa Rica (10°28'N; 85°20'W; Fig. 1). Europeans settlers cleared much of the dry tropical forest in the region in the 1800s for grazing land. Throughout the first half of the 20th century, cattle ranching dominated the regional economy, producing for both domestic and international markets. However, in the 1980s livestock prices fell dramatically (Jimenez *et al.* 2001; Daniels and Cumming 2008), and many landowners shifted management strategies to intensive crop agriculture, particularly rice and sugarcane, and more recently, melons (Jimenez *et al*. 2001; Daniels 2004; Daniels and Cumming 2008). A government-funded hydroelectric/irrigation project (Arenal Tempisque Irrigation Project) facilitated this shift by constructing an extensive canal and aqueduct network, that enabled farmers to irrigate crops during the dry season and almost doubled rice and sugarcane yields (Jimenez *et al.* 2001; Daniels 2004). N fertilizer additions have also enabled farmers to maximize yields (recommended N inputs for rice are 140-180kg N $ha^{-1}yr^{-1}$ (Perez 2002) and are 100-150kg N $ha^{-1}yr^{-1}$ for sugarcane (Chaves 1999)). Since the mid 1970s crop agriculture has replaced most of the lowland pastures, which now remain in a patchwork throughout the largely agricultural lowlands and forested upland slopes, while continuous forest cover is rare except within boundaries of protected parks (Daniels 2006; pers. obs).

Given the landscape-level shift towards intensive crop agriculture (Daniels, 2004), nutrient pollution is of increasing concern (Loaiciga and Robinson 1995; Jimenez *et al.* 2001). Government officials, regional ecologists, and local farmers are developing an integrated watershed management plan with the hope of maintaining the health of the aquatic ecosystems while providing for the human and agricultural needs of the region (Jimenez *et al.* 2001).

SUB-WATERSHED SELECTION

I selected 12 subwatersheds located throughout the Tempisque River Basin, draining sub-basins ranging in size from 6.5- 81.8 km^2 (Table 1). I chose these catchments because they are dominated (>50%) by one of three land use categories: forest, pasture/grassland, or agriculture. Agriculture in the watersheds includes rice, sugarcane and some melon production, for each of which the recommended application of N fertilizers is 100-180kgN/ha-yr (Perez 2002; Chaves 1999). The average slope for the subwatersheds ranges from 1°-15°. Stream catchments located in the uplands contain Quaternary and Cretaceous volcanic bedrock while the bedrock of the lowland subwatersheds originated from alluvial deposits of these volcanic sediments (Centro Nacional de Información Geográfica (CNIG), *Geology of Costa Rica,* digitized and georeferenced by OTS Palo Verde). Soils range from Mollisols, Vertisols and Alfisols to less developed Inceptisols and Entisols (Ministerio de Agricultura y Ganadería (MAG), *Suelos de Costa Rica,* digitized and georeferenced by OTS Palo Verde) (Fig. 1). This region of northwestern Costa Rica receives ~1800 mm/yr rainfall (Mateo-Vega, 2001), most of which falls from May-November, with five months receiving less than 100mm of rain. Mean temperature for the region is 27.5°C and the elevation of the sampling sites ranges from 5m to 310m above sea level, and the maximum elevation in the catchments ranges from 16-850m (Mateo-Vega, 2001; USGS, SRTM path 19, row 10). The natural vegetation consists of dry deciduous tropical forest, with mangrove forests and seasonal wetlands near the coast ((Jimenez *et al.* 2001); seasonal variations in rainfall drive changes in dissolved oxygen levels and algal populations in dry tropical forest streams (Chapman and Kramer 1991).

GIS, FIELD AND LABORATORY ANALYSIS

I used SRTM elevation data and the hydrology toolset in ArcGIS 9.2 ("flow accumulation" and "watershed") to define subwatersheds in the region drained by 1st-3rd order streams. Land use classifications (for regions upstream from my sampling points) were based on GIS-based land use maps (OTS, *Land use 2000,* unpublished data). The initial year 2000 land use/land cover data identified 12 land use categories: sugarcane, melon, rice, prepared fields, disturbed soil, pasture/grassland, forest, mangrove, wetlands, water, urban and volcanic slopes. Due to the spatial heterogeneity of agricultural activities and crop type within the watersheds, I grouped sugarcane, rice, melon, prepared fields and disturbed soils under "agriculture," creating three prominent land use categories— forest, pasture and agriculture— that describe >95% of the land use within the subwatersheds. From this land use data, I identified sampling points that drained catchments with >50% of the land area covered in forest, pasture or agriculture. Due to the non-random spatial relationship between remaining forest cover in the uplands and agricultural cultivation in the flat lowlands there is some bias in the physical characteristics of the stream catchments that could not be corrected for in this experimental design.

I did not have access to more recent remotely sensed images with the appropriate spectral bands for land cover classification. In order to update the land use/land cover data for the subwatersheds, I overlaid the year 2000 land use polygons onto imagery available from Google Earth for 2005-6 and reclassified and modified the shape and size of polygons in which observable changes had occurred. I only altered polygons for which I was confident that land use change had occurred and I could clearly define the land cover. I acknowledge that if more recent and appropriate remotely sensed images were available, defining land cover using spectral properties would be a preferable method, but given the rapid land use change I felt it was better to do this semi-quantitative correction than no correction at all. While I was able to detect land use changes from year 2000 to 2005-6, which included the expansion of crop agriculture into former pasture in the lowlands and some forest regeneration in highland pastures, the changes did not substantially alter total percentages in each category.

To evaluate the scale of influence of land use practices on stream water nutrients, I calculated the fraction of the subwatershed area in each land use category within the following distances: 500m, 1000m, 2000m, and 5,000m upstream of each sampling site as well as within the entire watershed.

I collected stream water samples and made field measurements during the first week of December 2007 and January 2008, which mark the first two months of a five month dry season.

At each site, I chose two cross-stream transects, 18m apart, and characterized stream channel morphology by measuring the total stream width and stream depth at ¼, ½ and ¾ distance across the stream channel. I estimated stream velocity using the float method (with an orange), and using the velocity and measured cross sectional area of the stream, I calculated discharge using the methods described in Gore (1996). I measured dissolved oxygen, conductivity, water temperature and salinity (YSI, Model 85/10) and pH (IQ Scientific Instruments), and filtered water samples using pre-rinsed syringes through .45um PVDF membranes (not pre-rinsed) into 60mL acid washed polyethylene containers. I immediately placed the samples in an iced cooler for transport, and transferred the samples to a freezer as soon as possible, never more than 4-5 hours after sampling. I shipped the samples, packed in dry ice, back to Brown University for laboratory analysis. The samples remained frozen until lab analysis, which I performed within five months after sampling. I treated all the samples similarly from field collection until lab analysis, thawing samples as needed for analysis.

I measured ammonia (NH_4^+-N) and nitrate (NO_3^-–N + NO_2^-–N) through flow-injection analysis with a QuickChem® QC8500 Automated Ion Analyzer (Lachat Instruments, Hach Company, USA) (method 31-107-06-1-B) and DON by the difference in nitrogen concentration between persulfate digested samples and NO_3^-–N analysis using cadmium reduction (method 31-107-04-1-C). I derived digestion efficiencies for the DON method by digesting known concentrations of glutamic acid. Conversion efficiencies were generally higher at lower concentrations, and measured values were corrected for conversion efficiency using a quadratic equation derived from glutamic acid recoveries ($[DON_{corrected}] = 0.1063*[DON_{measured}]^2 + 1.193*[DON_{measured}] + 0.0346$; $R^2=0.995$). I used inductively coupled plasma atomic emission spectroscopy (JY Horiba 2000) to measure [Mg^{2+}], [Ca^{2+}], [K^{+}] and [Na^{+}] (See Appendix A for all further discussion of cations).

Procedural blanks for NO_3^-- N and NH_4^+ - N were < 0.05umol N/L, below the detection limit for both methods (0.35umol N/L and 5 umol N/L, respectively). Nitrogen duplicates all ran within 5% of each other with a mean difference of 2%; for NO_3^-–N, known standards deviated less than 4% from expected values and 3% from expected for NH_4^+-N values.

STATISTICAL ANALYSIS

I calculated the percentage of land area covered by agriculture, pasture or forest within 500m, 1000m, 2000m and 5,000m upstream of the sampling point, as well as for the entire sub-watershed. I arrayed the 12 subwatersheds along a continuum of land use for each radius, and analyzed results using a linear regression with the chemical analytes as the dependent variable and percent of forest, pasture, or agriculture as the independent variable. I averaged samples taken during the same month from the same stream (n=2), but kept the December and January sampling dates to check for consistency between sampling dates. I used a one-way ANOVA to calculate the significance of the difference between the slope of the regression lines and zero.

RESULTS

PHYSICAL CHARACTERISTICS OF STREAMS AND STREAM CATCHMENTS

Stream water temperature was consistent across all the land use gradients, averaging 25.3° C (± 1.3) for all agricultural, pasture and forested streams. Cross sectional area of the stream increased as forest cover in the entire watershed decreased, indicating that broader streams were further downslope where there was more agriculture and greater deforestation (R^2=0.45; $p=0.02$) (Table 1). However, discharge rate did not vary with land use (p=.80) (Table

1). At all but one of the sampling locations there was at least a 10m riparian zone (at *Reventado* stream sugarcane cultivation reached to within a few meters of the stream and there was no tree cover).

Stream catchment size varied between 6.5km^2 and 81.8km^2 . Watershed size did not correlate with land use practices or elevation, however agricultural cultivation was the dominant land use type in the two largest and lowest watersheds. Forest cover, pasture and crop agriculture were the only three dominant land use types within the 12 watersheds; urban settlement represented 7% of land area in the *Florentina* stream catchment and 0.7% in the *Honda* stream catchment, while the other 10 catchments had no urban cover. Wetlands and mangroves combined to cover 5% and .6% of land area in the *Reventado* and *Bejarano* stream catchments, respectively, but neither were present in any other sub-watershed. Agricultural catchments had high percentages of land under cultivation near the sampling sites (average 83% agriculture within 500m) but less so if the whole sub-watershed was considered (63% agricultural cover). Since deforestation was most intense in the lowlands, forest cover increased as more of the upstream catchment was included in the analysis, with an average of 56% forest cover within 500m of the sampling point, and an average of 75% forest cover for the whole of the "forest" watersheds. Finally, in pasture-dominated watersheds, the fraction of land covered with pasture also increased as more of the stream catchment was included, from an average of 47% in pasture within 500m to an average of 70% in pasture for the whole watershed.

Variation in soil type and parent material largely coincided with variation in land use (Fig 1), preventing the analysis of the influence of these landscape characteristics on stream nutrients. Forested watersheds contained primarily Alfisols, while Entisols and Vertisols were the dominant soils types in pasture watersheds. The agricultural catchments were the most heterogeneous, both within watersheds and between watersheds, with Entisols, Inceptisols, Mollisols, Vertisols, and Alfisols each representing at least 18% of the soil in one of the watersheds. Parent material within the watersheds all originated from volcanic rock, but of different ages. All four pasture watersheds sat atop primarily (>75%) Quaternary volcanic bedrock and volcanically derived alluvium. Two of the forested watershed sat entirely atop Tertiary volcanically-derived alluvium, and two were classified as Cretaceous volcanic sediment (>80%) (Fig. 2). Finally, three of the agricultural catchments had primarily (>80%) Quaternary volcanic sediment and alluvium bedrock, while the fourth contained 60 percent Quaternary volcanic sediment and alluvium and 40 percent Tertiary volcanic sediment.

Since deforestation is more pronounced in the lowlands, there was a correlation between elevation of sampling site and land use ($r = 0.63$, p=0.03) from forest to pasture to agriculture (Table 1). Intensive agriculture is only located in the broad, flat river floodplains, whereas most catchments with a significant amount of remaining forest cover are at higher elevations. Similarly, average slope for the forested catchment was significantly higher (9.7°) than for agricultural catchments (1.06°) (p=.01).

CHEMICAL CHARACTERISTICS OF STREAM WATER

There were no trends in dissolved oxygen level or pH (Table 1). Concentrations of NO_3^-–N, NH_4^+-N, and DON all increased with increasing agricultural cultivation in the watershed (Fig. 2). The percent of land in agricultural cultivation within 1000m upstream of the sampling site best explained variation in NO_3^-–N (Dec: R^2= 0.19, p = 0.15; Jan: R^2= 0.61, p = 0.003), NH_4^+-N (Dec: R^2= 0.48, p = 0.01; Jan:R^2= 0.48, p= .01) and DON (Dec: R^2= 0.65, p = 0.001; Jan:R^2= 0.49, p=.001). NO_3^-–N decreased with increasing forest cover within the entire watershed (Fig. 2; Table 3). The fraction of NO_3^-–N, NH_4^+-N, or DON in total nitrogen did not vary as a function of land use; nor did the ratio of DIN/DON (%forest: R^2= 0.05, *p*= 0.48; %agriculture: R^2= 0.06, *p*= 0.43). NH_4^+-N consistently contributed the least amount of nitrogen to total stream nitrogen across all land use gradients (Fig. 3). There were no significant differences in nitrogen concentrations between pasture and forested watersheds, and percent pasture within the watershed did not correlate with any of the measured variables (Table 3). There were no systematic differences in nitrogen concentrations between December and January samples.

DISCUSSION

INFLUENCE OF LAND USE ON NITROGEN CONCENTRATIONS

The nitrogen concentrations in streams flowing from predominantly agricultural watersheds are similar to those reported in previous studies in the Tempisque watershed. Loaciciga and Robinson (1995) sampled from streams draining rice paddies and found NO_3^-–N concentrations between 3.6 and 36.6umol/L and NH_4^+-N that ranged between .5-27.9umol/L during the dry season (December), which are comparable to the lowest concentrations measured in this study. In 2006, Murillo *et al* (unpublished data) measured NO_3^-–N concentrations of 52.8-71.4umol/L and .36-11.5umol/L for NH_4^+-N in canals draining rice fields. The concentrations of NO_3^-–N and DON in forest streams are similar to those measured in undisturbed Costa Rican forests that receive more rainfall (Triska *et al*. 1993; Newbold *et al*, 1995), as well as to those measured in primary tropical forests in the Amazon during the dry season (Neill *et al*. 2001). However, NH_4^+-N concentrations are four times greater than that measured by Triska *et al*. (1993) in premontane moist forests in Costa Rica, yet half that measured by Neill *et al.* (2001) in Amazonian forests, perhaps reflecting soil differences that influence the retention of NH_4^+.

NH_4^+-N and DON in Tempisque River Basin pasture streams were similar to Amazonian pasture streams, but NO_3^-–N concentrations were ten times greater (Neill *et al*. 2001), possibly due to higher levels of dissolved oxygen.

Similar to croplands in temperate regions, the rice and sugarcane fields in the Tempisque watershed receive significant nitrogen inputs to maintain soil fertility, and show a positive relationship between [NO_3^-–N], [NH_4^+-N] and [DON] in stream water and the percent of cropland in the stream catchment (Correll *et al*. 1992; Jordan *et al*. 1997). During the dry season rice plantings receive 140-180kgN ha^{-1} over the course of approximately two months (Perez, 2002)**,** and sugarcane fields receive 100-150kg N ha^{-1} yr^{-1} (Chaves, 1999), providing additional sources of all three forms of N to streams flowing near agricultural fields. In contrast, the absolute concentrations of NO_3^-–N measured in streams draining many North American agricultural fields are greater than those in the Tempisque River Basin (Jordan *et al.* 1997a and 1997b; Inwood *et al*. 2005; Morgan *et al*. 2006), perhaps reflecting both greater and longer-term N additions within these North American stream catchments. In contrast to N exports from fertilized wheat fields in the Yaqui Valley, Mexico were inorganic nitrogen accounts for most of the increase in TDN (Ahrens *et al.* 2008), the elevated nitrogen concentrations in streams draining these tropical agricultural fields can be attributed to increases in exports of both organic and inorganic nitrogen.

There were no differences in NO_3^-–N, NH_4^+-N and DON concentrations between pasture and forest watersheds in the Tempisque River Basin. In contrast, both Neill *et al*. (2001) and Thomas *et al*. (2004) found lower NO_3^-–N and higher NH_4^+-N in Amazonian pasture streams than in streams nearby in undisturbed forest. They hypothesized that grasses growing in the pasture stream beds created low dissolved oxygen levels (.1mg/L) from decomposition, inhibiting nitrification, favoring denitrification, and allowing NH_4^+ to accumulate. However, I found limited support for the hypothesis that dissolved oxygen moderated the [NH_4^+-N]:[NO_3^-–N] ratio. All the streams in this study, except for one catchment containing a high percentage of cropland and vegetation in the stream (*Bejarano)*, had dissolved oxygen levels between 6-9mg/L, which is typical of small tropical forested streams (Thomas *et al*. 2004; Neill *et al*. 2006). *Bejarano* stream had dissolved oxygen levels of 1.5 mg/L, and a higher [NH_4^+-N]:[NO_3^-–N] ratio (0.86) than two of the other agricultural sites (*Florentina* 0.18; *Sin Nombre* 0.09). However, one other agricultural stream, *Reventado,* had a high [NH_4^+-N]:[NO_3^-–N] ratio (1.09), dissolved oxygen levels of 8.8 mg/L, high [DON] and [DON]:[DIN] (Fig. 3, Table 2). *Reventado* stream had no in-stream vegetation, but is the only site which had no forest riparian zone; all other sites had forest riparian zones of at least 10m in width. Trees in forest riparian zones take in NO_3^- traveling in subsurface drainage, removing NO_3^- from soil solutions and decreasing the amount that enters streams (Jordan *et al*.1993; Williams *et al*. 1997; Jordan *et al*.1997). The lack of a forest riparian zone at *Reventado,* may allow for increased amounts of organic matter to reach the stream and be mineralized into NH_4^+-N, leading to higher relative NH_4^+-N concentrations.

Reventado stream is also the only site where there were significant differences between the nitrogen concentration in December and January (December: NO_3^-–N = 5.6; NH_4^+-N = 7.2; DON = 44.3 umol/L; January: NO_3^-–N = 74.4; NH_4^+-N = 75.7; DON = 426.4 umol/L; Fig. 2). *Reventado* is a second order stream but receives waters directly from irrigation canals draining rice and sugarcane fields. Of the subwatersheds sampled in this study, the *Reventado* catchment is the only one without a riparian buffer, and has the largest total area in agricultural cultivation. It is possible that the high N concentrations measured in January were part of a nitrogen pulse caused by a recent nearby fertilizer application followed by irrigation, which could drive the loss of mobile soil nitrogen (Riley *et al.* 2001; Harrison and Matson 2003). Additionally, the direct input of agricultural runoff into *Reventado* stream from canals may minimize the amount of in-stream nitrogen processing that can remove excess N (Filoso *et al*. 2003).

The extent of the upstream catchment included in land use calculations was an important variable in describing the variation in stream nitrogen concentrations, with land use within 1km upstream of the sampling site consistently having the strongest predictive power for stream water nitrogen (Table 3). The same mechanisms of dilution and soil retention that reduce disturbance signals in larger watersheds (Thomas *et al.* 2004; Biggs *et al.* 2004) may reduce the contribution of land use activities more than 1km upstream to stream nitrogen concentrations. This is consistent with the work from Buck *et al.* (2004) that suggests that local land use is more relevant for stream chemistry in smaller order streams whereas upland land use becomes more important as a predictor of stream quality in larger streams. Furthermore, Dodds and Oakes (2006) found that the vegetation in the riparian zone of headwater prairie streams better correlated with total nitrogen and nitrate in streams than land cover in the entire stream catchment.

LIMITATIONS OF STUDY DESIGN AND FUTURE RESEARCH

The narrow temporal distribution of data in this study and the lack of precise information about fertilizer application in the agricultural sub-watersheds limit what can be inferred from these results. These initial findings that agricultural activities are significantly increasing the total nitrogen concentrations in adjacent streams need to be substantiated with a more rigorous sampling scheme that captures both the rainy and dry seasons and identifies N fertilizer application rates and timing for surrounding fields. Additionally, some of the observed increase in nitrogen concentrations in streams near agricultural fields relative to streams in pastures and forests may be due to irrigation waters that increase rates of surface runoff and leaching in agricultural soils while forested and pasture sub-watersheds received no precipitation during the sampling months. However, this additional water source did not significantly increase the flow rate in streams draining agricultural fields, perhaps due to differing stream morphologies. Additionally, the irrigation waters are sourced from the Caribbean side of the Continental Divide and may have different background N concentrations than streams in the Tempisque watershed. While the variation in landscape characteristics (e.g. soils, parent material, slope) between the stream catchments prevent isolating the influence of these state factors on stream water chemistry, this variation does provide data about N concentrations in multiple streams in a heterogeneous landscape.

In addition to establishing annual N fluxes in streams in the Tempisque watershed, future research could examine if riparian buffers or agricultural management practices explain variation in stream water nutrients. Also, understanding the role denitrification and in-stream processing play in removing N from these streams is important for evaluating how much N from agricultural runoff reaches downstream aquatic ecosystems. Finally, evaluating the impacts of nutrient loading on stream communities as well as biologically sensitive ecosystems downstream (Palo Verde wetlands and the fisheries in the Gulf of Nicoya) may inform land management decisions.

ECOLOGICAL IMPLICATIONS OF ELEVATED NITROGEN

The limited scope of these data prevent making conclusions about the landscape level implications of elevated stream nitrogen concentrations for nitrogen cycling and regional ecology within the Tempisque watershed. However, perhaps placing these data within the context of the extensive work examining the fate and transformation of N fertilizer in intensively managed agricultural systems in the lowland subtropical Yaqui Valley in Mexico (Ahrens *et al.*

2008) provides the most appropriate parallel for understanding the potential implications of these data within the Tempisque watershed. Irrigated wheat fields in the Yaqui Valley receive approximately 250kg N/ha-yr, about 60% more than that recommended for sugarcane and rice in the Tempisque watershed, with 14-26% of N applied to farmer's fields leaching beyond the rooting zone of plants (Riley *et al.* 2001). Irrigation drives N losses from soils, leading to pulses in high concentrations of nitrogen in canals and waterways immediately draining fields and can be linked to phytoplankton blooms in the Gulf of California (Harrison and Matson 2003; Beman *et al.* 2005). Also, higher stream water oxygen concentrations at night significantly reduce denitrification rates, increasing the amount of N discharged from the stream (Harrison *et al.* 2005). However, <4% of total N inputs are exported through surface waters to the coast (Ahrens *et al.* 2008), indicating the importance of in-stream processing and denitrification in removing N, and suggesting that short pulses of high N can still make nutrient limited downstream systems vulnerable to eutrophication. Matson *et al.* (1998) recommend better matching the timing of fertilizer application with crop demand and using site specific nutrient management as two methods demonstrated to decrease N inputs into waterways, save farmers money, and do not reduce crop yields.

CONCLUSION

Considering the scarcity of N data, especially DON, for this region's fresh waterways, these data provide valuable information and a necessary starting point in understanding the impacts of N intensive crop production on the waters of the Tempisque River Basin. These results suggest that agricultural activities, including fertilizer application, are increasing nutrient availability in adjacent streams, which can potentially stimulate plant growth, modify dissolved oxygen levels and alter benthic communities.

More research is necessary to fully inform land management decisions, but low cost precautionary measures to minimize nitrogen inputs into streams may be appropriate. The results from this study indicate the relevance of local, rather than regional, land use practices on stream water nitrogen, that irrigation may drive pulses of high nitrogen concentrations, and that direct inputs from agricultural canals may minimize in-stream N processing, allowing for increases in stream N concentrations. This study provides further evidence that agricultural intensification in the tropics may have similar deleterious impacts on freshwater streams as N intensive agriculture in temperate climates. As agricultural intensification proceeds in the tropics, land managers and policy makers may want to consider the potential for these downstream effects and implement strategies to minimize the environmental and social costs of N fertilization in watershed management plans.

ACKNOWLEDGMENTS

This work was supported with funding from the Royce Fellowship granted by Brown University. The Organization for Tropical Studies (OTS) provided GIS data for land use, bedrock and soil within the Tempisque River Basin. Stephen Porder and Joaquin Chaves provided extensive help throughout the project. Dave Murray, Lara Reichman and Joe Orchardo assisted with lab work, and Lynn Carlson helped with GIS analysis. Heather Leslie and Jeremy Rich offered comments that helped to improve the manuscript.

References

Ahrens, T. D., Beman, J. M., Harrison, J. A., Jewett, P. K. & Matson, P. A. A synthesis of nitrogen transformations and transfers from land to the sea in the Yaqui Valley agricultural region of Northwest Mexico. *Water Resources Research* 44, 13, (2008).

Asner, G. P. *et al.* Physical and biogeochemical controls over terrestrial ecosystem responses to nitrogen deposition. *Biogeochemistry* 54, 1-39 (2001).

Beman, J. M., Arrigo, K. R. & Matson, P. A. Agricultural runoff fuels large phytoplankton blooms in vulnerable areas of the ocean. *Nature* 434, 211-214, (2005).

Bernardes, M. C. *et al.* Riverine organic matter composition as a function of land use changes, Southwest Amazon. *Ecological Applications* 14, S263-S279 (2004).

Biggs, T. W., Dunne, T. & Martinelli, L. A. Natural controls and human impacts on stream nutrient concentrations in a deforested region of the Brazilian Amazon basin. *Biogeochemistry* 68, 227-257 (2004).

Biggs, T. W., Dunne, T. & Muraoka, T. Transport of water, solutes and nutrients from a pasture hillslope, southwestern Brazilian Amazon. *Hydrological Processes* 20, 2527-547, (2006).

Boesch, D. F., Brinsfield, R. B. & Magnien, R. E. Chesapeake Bay eutrophication: Scientific understanding, ecosystem restoration, and challenges for agriculture. *Journal of Environmental Quality* 30, 303-320 (2001).

Buck, O., Niyogi, D.K., & Townsend, C.R. Scale-dependence of land use effects on water quality in streams in agricultural catchments. *Environmental Pollution* 130, 287-299 (2004).

Centro Nacional de Información Geográfica (CNIG) 1984**,** *Geology of Costa Rica.* Georeferenced by Organization for Tropical Studies, Palo Verde Biolgoical Station. Centro Nacional de Información Geográfica, San José.

Chapin, F. S. *et al.* Ecosystem consequences of changing biodiversity - Experimental evidence and a research agenda for the future. *Bioscience* 48, 45-52 (1998).

Chapman, L. J. & Kramer, D. L. Limnological observations of an intermittent tropical dry forest stream. *Hydrobiologia* 226, 153-166 (1991).

Chaves, J. *et al.* Land management impacts on runoff sources in small Amazon watersheds. *Hydrological Processes* 22, 1766-1775, (2008).

Chaves, M. Nutrición y fertilización de la cana de azucar en Costa Rica. *IX Congreso Nacional Agronónomico, III Congreso Nacional de Suelos.* (1999).

Correll, D. L., Jordan, T. E. & Weller, D. E. Nutrient flux in a landscape - effects of coastal land-use and terrestrial community mosaic on nutrient transport to coastal waters. *Estuaries* 431-442, (1992).

Creed, I. F. *et al.* Regulation of nitrate-N release from temperate forests: A test of the N flushing hypothesis. *Water Resources Research* 32, 3337-3354 (1996).

Daniels, A.E. Incorporating domain knowledge and spatial relationships into land use cover classifications: a rule based approach. *International Journal of Remote Sensing* 27, 2049-2975, (2006).

Daniels, A.E. Protected Area Management in the Watershed Context: A Case Study of Palo Verde National Park, Costa Rica. Masters of Science. Thesis, University of Florida. (2004).

Daniels, A. E. & Cumming, G. S. Conversion or conservation? Understanding wetland change in northwest Costa Rica. *Ecological Applications* 18, 49-63 (2008).

Davidson, E. A. *et al.* Recuperation of nitrogen cycling in Amazonian forests following agricultural abandonment. *Nature* 447, 995-U996, (2007).
Dodds, W. K. & Oakes, R. M. Controls on nutrients across a prairie stream watershed: Land use and riparian cover effects. *Environmental Management* 37, 634-646, (2006).
Downing, J. A. *et al.* The impact of accelerating land-use change on the N-cycle of tropical aquatic ecosystems: Current conditions and projected changes. *Biogeochemistry* 46, 109-148 (1999).
Filoso, S. *et al.* Land use and nitrogen export in the Piracicaba River basin, Southeast Brazil. *Biogeochemistry* 65, 275-294 (2003).
Freckman, D. W. *et al.* Linking biodiversity and ecosystem functioning of soils and sediments. *Ambio* 26, 556-562 (1997).
Galloway, J. N., Schlesinger, W. H., Levy, H., Michaels, A. & Schnoor, J. L. Nitrogen-fixation anthropogenic enhancement-environmental response. *Global Biogeochemical Cycles* 9, 235-252 (1995).
Gore, J. Discharge Measurements and Streamflow Analysis *In* R. Haurer and G. Lamberti (eds.). Methods in Stream Ecology. Academic Press: New York. (1996).
Hansen, M. C. *et al.* Humid tropical forest clearing from 2000 to 2005 quantified by using multitemporal and multiresolution remotely sensed data. *Proceedings of the National Academy of Sciences of the United States of America* 105, 9439-9444, (2008).
Harrison, J. & Matson, P. Patterns and controls of nitrous oxide emissions from waters draining a subtropical agricultural valley. *Global Biogeochemical Cycles* 17, 13, (2003).
Howarth, R. W. *et al.* Regional nitrogen budgets and riverine N&P fluxes for the drainages to the North Atlantic Ocean: Natural and human influences. *Biogeochemistry* 35, 75-139 (1996).
Inwood, S. E., Tank, J. L. & Bernot, M. J. Patterns of denitrification associated with land use in 9 midwestern headwater streams. *Journal of the North American Benthological Society* 24, 227-245 (2005).
Jenkinson, D. S. The impact of humans on the nitrogen cycle, with focus on temperate arable agriculture. *Plant and Soil* 228, 3-15. (2001).
Jimenez, J.A., King, J., Scatena, F., Bach, L., & Rojas, M. Plan Estratégico para el Manejo Integrado del Recurso Hídrico en la Cuenca el Rió Tempisque. *Organization for Tropical Studies.* (2001).
Jordan, T. E., Correll, D. L. & Weller, D. E. Nutrient interception by a riparian forest receiving inputs from adjacent cropland. *Journal of Environmental Quality* 22, 467-473 (1993).
Jordan, T. E., Correll, D. L. & Weller, D. E. Effects of agriculture on discharges of nutrients from coastal plain watersheds of Chesapeake Bay. *Journal of Environmental Quality* 26, 836-848 (1997a).
Jordan, T. E., Correll, D. L. & Weller, D. E. Nonpoint source discharges of nutrients from Piedmont watersheds of Chesapeake Bay. *Journal of the American Water Resources Association* 33, 631-645 (1997b).
Kemp, M. J. & Dodds, W. K. Spatial and temporal patterns of nitrogen concentrations in pristine and agriculturally-influenced prairie streams. *Biogeochemistry* 53, 125-141 (2001).
Kress, N., Coto, S.L., Brenes, C.L., Brenner, S., & Arroyo, G. Horizontal transport and seasonal distribution of nutrients, dissolved oxygen and chlorophyll-a in the Gulf of Nicoya, Costa Rica: a tropical estuary. *Continental Shelf Research* 22, 51-66, (2002).
Loaiciga, H. A. & Robinson, T. H. Sampling of agrochemicals for environmental assessment in

rice paddies - dry tropical wetlands, Costa-Rica. *Ground water monitoring and remediation* 107-118. (1995).
Mateo-Vega, J. Caracteristicas Generales de la Cuenca del Río Tempisque. *Organization for Tropical Studies* (2001).
Matson, P. A. & Vitousek, P. M. Ecosystem approach to a global nitrous-oxide budget. *Bioscience* 40, 667-671 (1990).
Matson, P., Lohse, K. A. & Hall, S. J. The globalization of nitrogen deposition: Consequences for terrestrial ecosystems. *Ambio* 31, 113-119 (2002).
Matthews, E. Nitrogenous fertilizers - global distribution of consumption and associated emissions of nitrous-oxide and ammonia. *Global Biogeochemical Cycles* 8, 411-439 (1994).
McGlynn, B. L. & McDonnell, J. J. Quantifying the relative contributions of riparian and hillslope zones to catchment runoff. *Water Resources Research* 39, (2003).
McGlynn, B. L. & Seibert, J. Distributed assessment of contributing area and riparian buffering along stream networks. *Water Resources Research* 39, (2003).
Ministerio de Agricultura y Ganadería (MAG) *Suelos de Costa Rica.* Digitized and georeferenced by Palo Verde Biological Station, Organization for Tropical Studies. Ministerio de Agricultura y Ganadería, San José, (1984).
Morgan, A.M., Royer, T.V., David, M.B. &Gentry, L.E. Relationships among nutrients, chlorophyll-alpha, and dissolved oxygen in agericultural streams in Illinois. *Journal of Environmental Quality* 35, 1110-1117, (2006).
Murillo, R.S. *et al.* Water samples from Rice Irrigation Canals, Bagatzi-Bagaces. Universidad Nacional de Costa Rica. Unpublished. (2006).
Neill, C., Deegan, L. A., Thomas, S. M. & Cerri, C. C. Deforestation for pasture alters nitrogen and phosphorus in small Amazonian Streams. *Ecological Applications* 11, 1817-1828 (2001).
Neill, C. *et al.* Deforestation alters the hydraulic and biogeochemical characteristics of small lowland Amazonian streams. *Hydrological Processes* 20, 2563-2580, (2006).
Newbold, J. D., Sweeney, B. W., Jackson, J. K. & Kaplan, L. A. Concentrations and export of solutes from 6 mountain streams in northwestern costa-rica. *Journal of the North American Benthological Society* 14, 21-37 (1995).
Ometo, J. *et al.* Effects of land use on water chemistry and macroinvertebrates rates in two streams of the Piracicaba river basin, south-east Brazil. *Freshwater Biology* 44, 327-337 (2000).
Organization for Tropical Studies, Palo Verde Biological Station. *Land Use 2000,* unpublished.
Osland, M. Personal communication. (2008).
Palter, J., Coto, S. L.,& Ballestero, D. The distribution of nutrients, dissolved oxygen and chlorophyll a in the upper Gulf of Nicoya, Costa Rica, a tropical estuary. *Revista de Biología Tropical* 55, 427-436 (2007).
Pérez, J. El cultivo de arroz en Costa Rica y en el proyecto de Riego Arenal-Tempisque. *Editorial OET,* 1-21, (2002).
Riley, W. J., Ortiz-Monasterio, I. & Matson, P. A. Nitrogen leaching and soil nitrate, nitrite, and ammonium levels under irrigated wheat in Northern Mexico. *Nutrient Cycling in Agroecosystems* 61, 223-236 (2001).
Sala, O. E. *et al.* Biodiversity - Global biodiversity scenarios for the year 2100. *Science* 287, 1770-1774 (2000).

Sanchez, P. Soil Fertility and Hunger in Africa. *Science* 295, 2019-2020, (2002).
Sanchez, P. *et al.* Poverty and hunger special feature: The African millennium villages (vol 104, pg 16775, 2007). *Proceedings of the National Academy of Sciences of the United States of America* 104, 19656-19656, (2007).
Thomas, S. M. *et al.* Influences of land use and stream size on particulate and dissolved materials in a small Amazonian stream network. *Biogeochemistry* 68, 135-151 (2004).
Tilman, D. *et al.* Forecasting agriculturally driven global environmental change. *Science* 292, 281-284 (2001).
Townsend, A.R. The biogeochemical heterogeneity of tropical forests. *Trends in Ecology and Evolution* 23, 424-431, (2008).
Triska, F. J., Pringle, C. M., Zellweger, G. W., Duff, J. H. & Avanzino, R. J. Dissolved inorganic nitrogen composition, transformation, retention, and transport in naturally phosphate-rich and phosphate-poor tropical streams. *Canadian Journal of Fisheries and Aquatic Sciences* 50, 665-675 (1993).
Turner, R. E. & Rabalais, N. N. Linking landscape and water quality in the Mississippi river basin for 200 years. *Bioscience* 53, 563-572 (2003).
Uhl, C. & Jordan, C. F. Succession and nutrient dynamics following forest cutting and burning in amazonia. *Ecology* 65, 1476-1490 (1984).
USGS (2004), Shuttle Radar Topography Mission, 1 Arc Second scene SRTM_u03_n019e010, Unfilled Unfinished 2.0, Global Land Cover Facility, University of Maryland, College Park, Maryland, February 2000.
Vitousek, P. M. *et al.* Human alteration of the global nitrogen cycle: Sources and consequences. *Ecological Applications* 7, 737-750 (1997).
Vitousek, P. M., Mooney, H. A., Lubchenco, J. & Melillo, J. M. Human domination of Earth's ecosystems. *Science* 277, 494-499 (1997).
Williams, M. R. & Melack, J. M. Solute export from forested and partially deforested catchments in the central Amazon. *Biogeochemistry* 38, 67-102 (1997).

Tables and Figures

Table 1. Physical Characteristics of the Streams and Stream Catchments. Altitude of sampling point and slope were calculated from SRTM elevation data in GIS; subwatershed area was also calculated in GIS. All other characteristics are directly based on field measurements made in December and January, the beginning of the dry season

Table 2. Dissolved Oxygen, Conductivity and pH in study streams
Measurements are averages from results from December and January

Table 3. Correlation of local and watershed-scale land use on nitrogen concentrations.
R^2 and *p* values are generated from averages of December and January samples. Bolded figures indicate the scale which provides the most significant correlation

Table A1. Cation concentrations
Values are averages of December and January samples. Errors represent 1 standard error.

Table A2. Correlation of local and watershed-scale land use on cation concentrations.
R^2 and *p* values are generated from averages of December and January samples. Bolded figures indicate the scale which provides the most significant correlation

Figure 1. Map of the Tempisque River Basin and the 12 stream catchments with land-use categories represented within the catchment area and soil and bedrock type in the pie charts.

Figure 2. Influence of Land Use on Nitrogen Concentrations.
A) DON B) NH_4^+-N and C) NO_3^--N versus percent agricultural land cover within 1km upstream of sampling sites. Concentrations, R^2 and p values are shown for December and January samples separately. Error bars represent one standard error from the mean.

Figure 3. Hydrologic losses of Nitrogen
A) Total N and N species in the twelve watersheds, arranged in increasing order of percent agriculture within the whole watershed B) relative amounts of different N forms arranged in increasing order of percent agriculture within the entire watershed. Values reported are averages of December and January samples

Figure A1. Influence of Land Use on Ca^{2+} and Na^+ Concentrations
Influence of catchment-wide land use on Ca^{2+} and Na^+ concentrations. Reported as the mean of samples taken in January and December.

Table 1

Study Site	Subwatershed area (km^2)	Fractions of Sub-watershed area in each Land Use	Stream Order	Altitude (m)	Slope (°)	Mean cross sectional area (m^2)	Discharge (m^3/s)	Water Temperature (°C)
Palmira	21.2	A:0%; P:66%; F:34%	2^{nd}	212	5.5	2.13	4.73	24
Cangrejal	6.5	A:0%; P: 23%;F:76%	2^{nd}	98	10.4	0.18	0.05	25.7
SantaRosa	13.4	A:0%; P:25%; F:69%	2^{nd}	91	4.5	0.42	0.1	25.8
Lechuza	13.4	A:0%; P:12%; F:88%	2^{nd}	104	15.1	0.64	0.74	24.8
Diria	7.7	A:0%; P:30%; F:52%	3^{rd}	81	9	1.06	2.61	25.5
Campero	12.6	A:2%; P:68%; F:30%	2^{nd}	51	3.6	1.48	0.95	26.2
Amores	8.3	A:3%; P:69%; F:28%	1^{st}	44	2	0.98	0.28	23.3
Honda	14.1	A:4%; P:81%; F:14%	1^{st}	34	1.3	1.09	0.37	24.9
Reventado	81.8	A:51%;P14%; F:3%	2^{nd}	3	3.3	NA	NA	28.7
Sin Nombre	8.2	A:56%;P:39%;F:5%	1^{st}	33	1.7	0.85	0.66	24.2
Florentina	11.3	A:63%;P:25%;F:32%	2^{nd}	19	1.2	2.72	3.57	25
Bejarano	46.1	A:84%;P:10%;F:7%	2^{nd}	10	1.1	2.32	0.69	24.7

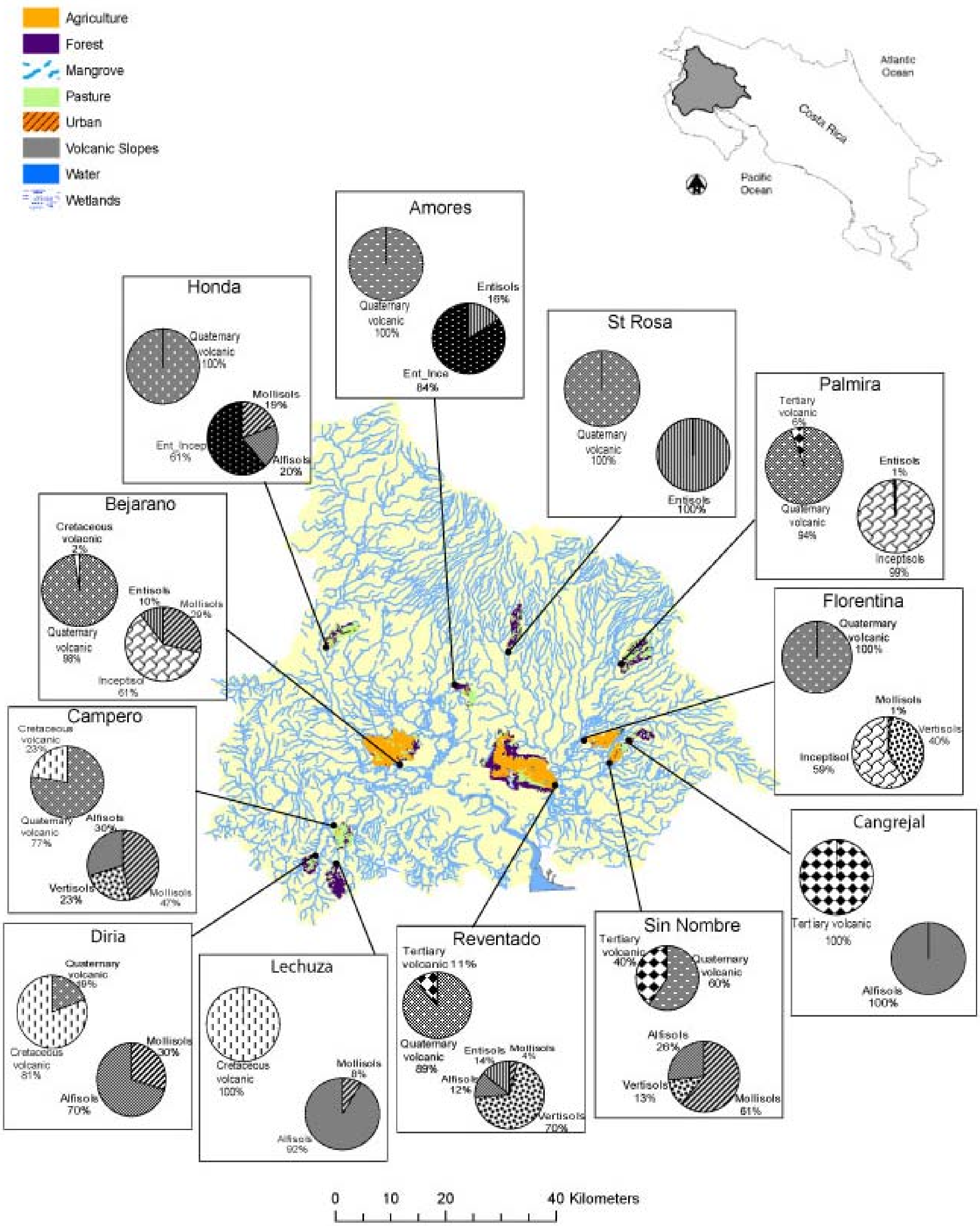
Table 2

Study Site	Dissolved O_2 (mg/L)	Conductivity (uS)	pH
Palmira	8.5±0.9	229.8±7.9	7.6±0.2
Cangrejal	6.3±0.6	270.3±48.4	7.2±0.3
SantaRosa	7.1±2.4	157.9±1.7	6.9±0.2
Lechuza	7.6±3.4	315.1±12.1	7.4±0.2
Diria	9.4±2.4	318.6±30.6	7.6±0.08
Campero	5.6±0.7	465.3±0.7	7.6±0.09
Amores	9.8±4.3	180.1±3.9	7.4±0.05
Honda	7.2±3.7	193.6±5.1	6.9±0.06
Reventado	8.4±0.06	365.7±163.6	6.6±0.6
SinNombre	8.2±1.7	215.7±18.8	7.3±0.01
Florentina	6.6±0.3	151.9±20.0	6.8±0.3
Bejarano	1.5±0.07	630.0±86.3	7.5±0.1

Table 3

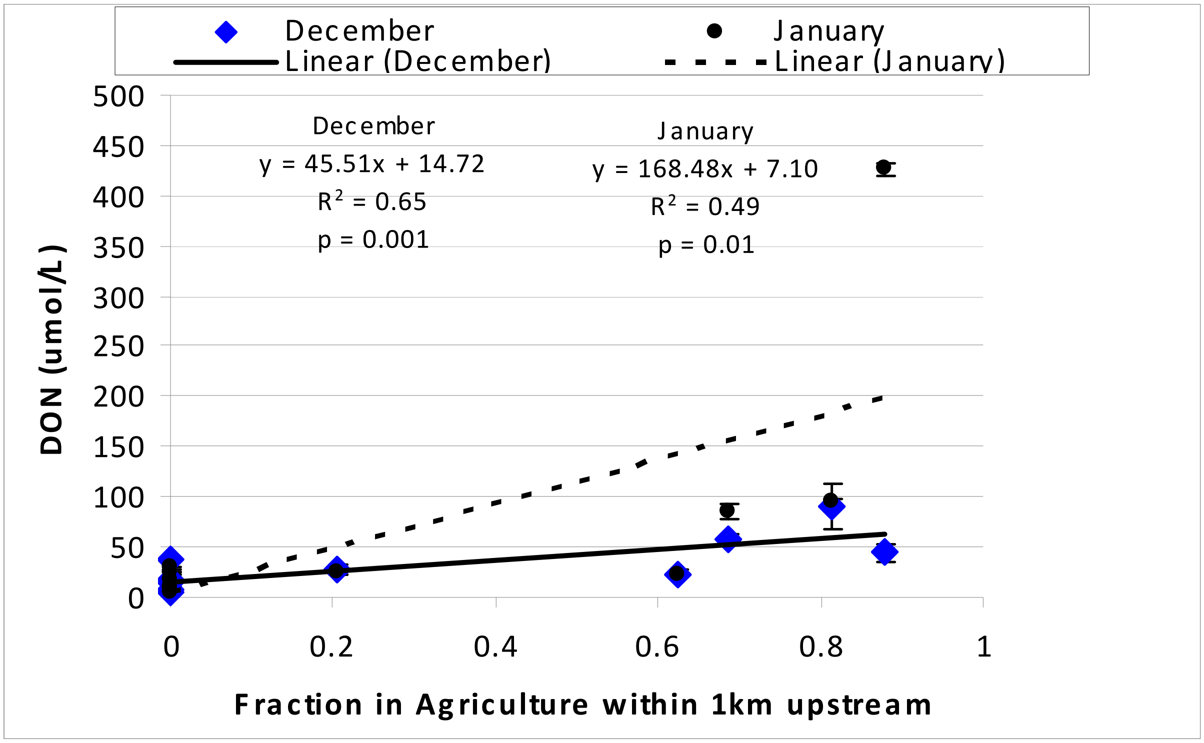
Analyte	Distance Upstream (m)	% Forest R^2	% Forest p	% Agriculture R^2	% Agriculture p	% Pasture R^2	% Pasture p
NO_3^-	500	0.37	0.04	0.28	0.08	0.00	0.85
	1000	0.48	0.01	**0.49**	**0.01**	0.01	0.71
	2000	0.46	0.01	0.39	0.03	0.04	0.51
	5000	0.36	0.04	0.47	0.01	0.01	0.82
	watershed	0.35	0.04	0.35	0.04	0.01	0.79
NH_4^+	500	0.04	0.55	0.36	0.04	0.29	0.07
	1000	0.13	0.26	**0.52**	**0.01**	0.28	0.08
	2000	0.12	0.28	0.39	0.03	0.30	0.07
	5000	0.22	0.12	0.42	0.02	0.15	0.22
	watershed	0.12	0.27	0.32	0.05	0.10	0.31
DON	500	0.15	0.22	0.39	0.03	0.14	0.22
	1000	0.25	0.10	**0.59**	**0.004**	0.19	0.15
	2000	0.19	0.16	0.45	0.02	0.29	0.07
	5000	0.18	0.17	0.47	0.01	0.19	0.15
	watershed	0.10	0.32	0.34	0.05	0.15	0.22

Figure 1



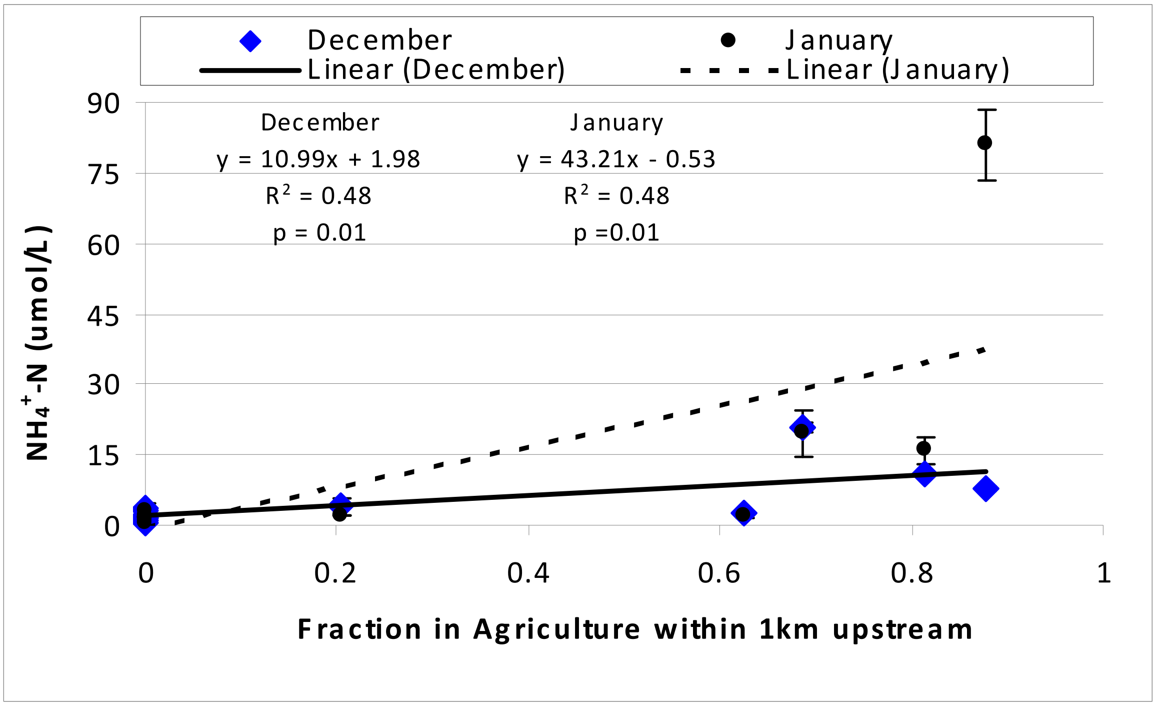
Agriculture
Forest
Mangrove
Pasture
Urban
Volcanic Slopes
Water
Wetlands
Atlantic Ocean
Costa Rica
Pacific Ocean
Amores
Quaternary volcanic 100%
Entisols 16%
Ent_Ince 84%
Honda
Quaternary volcanic 100%
Mollisols 19%
Ent_Incep 61%
Alfisols 20%
St Rosa
Quaternary volcanic 100%
Entisols 100%
Palmira
Tertiary volcanic 6%
Quaternary volcanic 94%
Entisols 1%
Inceptisols 99%
Bejarano
Cretaceous volcanic 2%
Quaternary volcanic 98%
Entisols 10%
Mollisols 29%
Inceptisol 61%
Florentina
Quaternary volcanic 100%
Mollisols 1%
Vertisols 40%
Inceptisol 59%
Campero
Cretaceous volcanic 23%
Quaternary volcanic 77%
Alfisols 30%
Vertisols 23%
Mollisols 47%
Cangrejal
Tertiary volcanic 100%
Alfisols 100%
Diria
Quaternary volcanic 19%
Cretaceous volcanic 81%
Mollisols 30%
Alfisols 70%
Lechuza
Cretaceous volcanic 100%
Mollisols 8%
Alfisols 92%
Reventado
Tertiary volcanic 11%
Quaternary volcanic 89%
Entisols 14%
Mollisols 4%
Alfisols 12%
Vertisols 70%
Sin Nombre
Tertiary volcanic 40%
Quaternary volcanic 60%
Alfisols 26%
Vertisols 13%
Mollisols 61%
0 10 20 40 Kilometers

Figure 2
A.



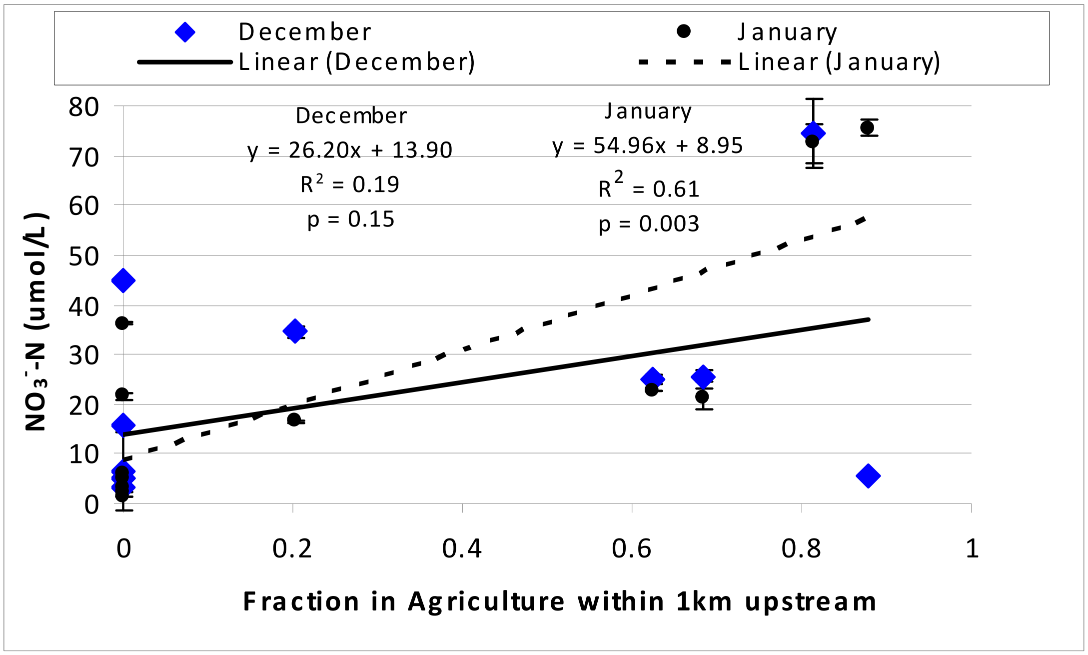
December
January
Linear (December)
Linear (January)
December
y = 45.51x + 14.72
R² = 0.65
p = 0.001
January
y = 168.48x + 7.10
R² = 0.49
p = 0.01
500
450
400
350
300
250
200
150
100
50
0
0
0.2
0.4
0.6
0.8
1
DON (umol/L)
Fraction in Agriculture within 1km upstream

B.



December
January
Linear (December)
Linear (January)
December
y = 10.99x + 1.98
R² = 0.48
p = 0.01
January
y = 43.21x - 0.53
R² = 0.48
p =0.01
NH4+-N (umol/L)
90
75
60
45
30
15
0
0
0.2
0.4
0.6
0.8
1
Fraction in Agriculture within 1km upstream

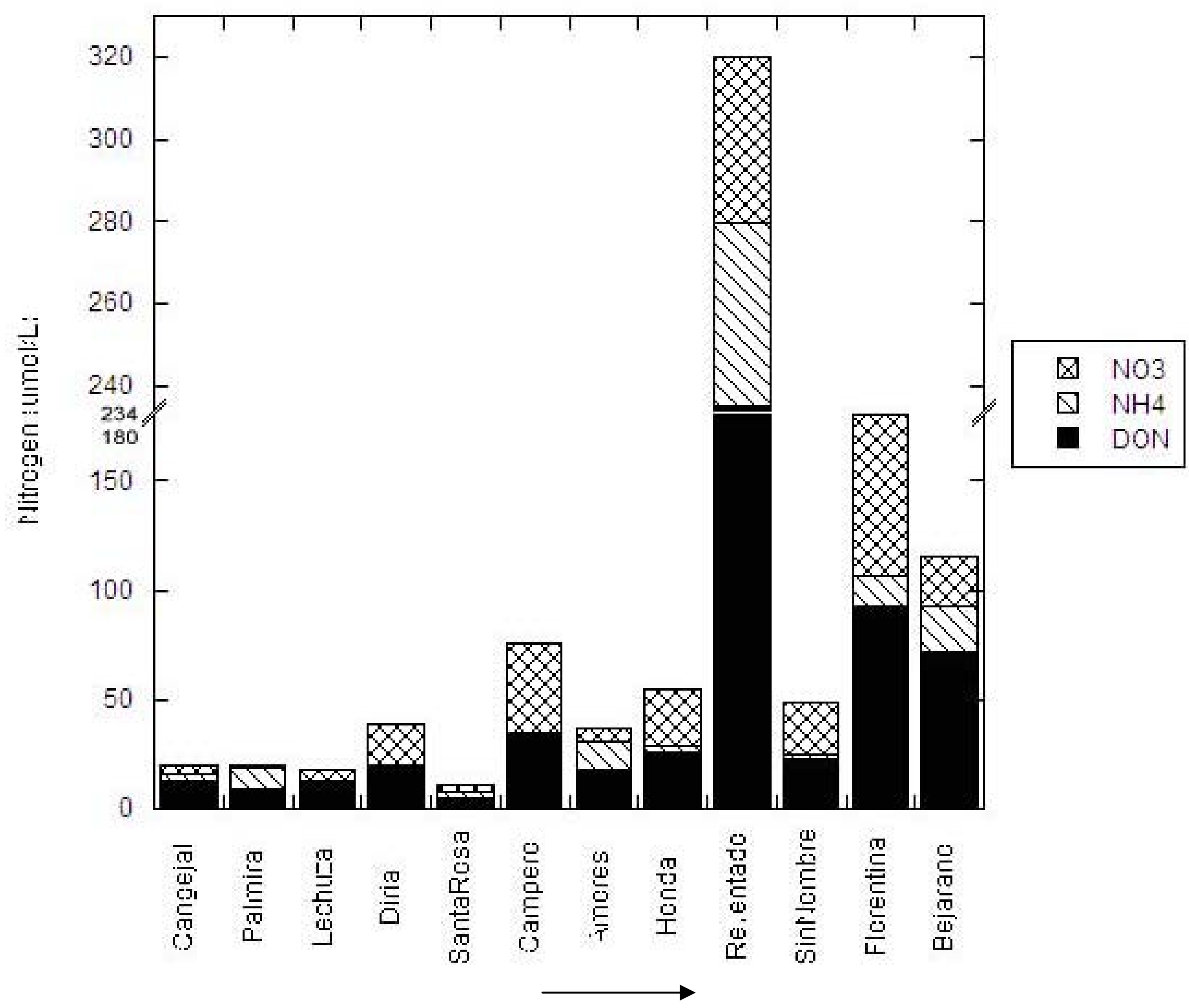
C.



December
January
Linear (December)
Linear (January)
December
y = 26.20x + 13.90
R^2 = 0.19
p = 0.15
January
y = 54.96x + 8.95
R^2 = 0.61
p = 0.003
NO_3^--N (umol/L)
0
10
20
30
40
50
60
70
80
0
0.2
0.4
0.6
0.8
1
Fraction in Agriculture within 1km upstream

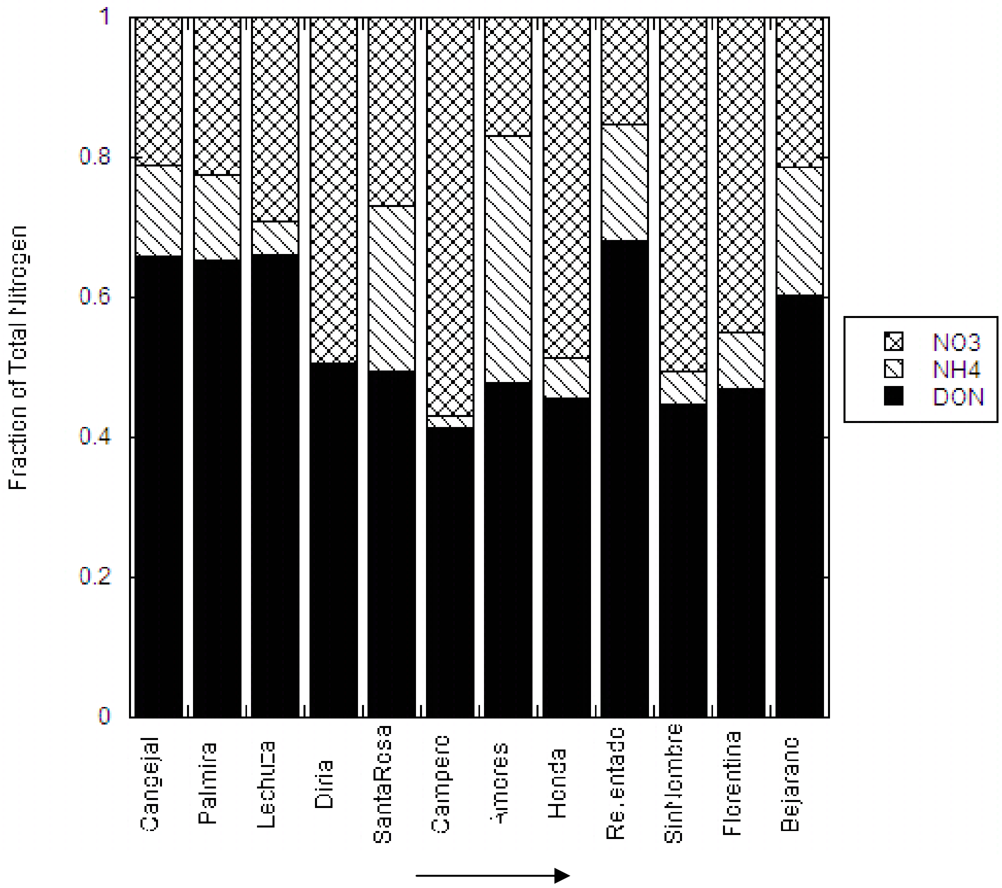
Figure 3.

A.



Nitrogen (umol/L)
320
300
280
260
240
234
180
150
100
50
0
NO3
NH4
DON
Cangejal
Palmira
Lechuza
Diria
SantaRosa
Campero
Amores
Honda
Reventado
SinNombre
Florentina
Bejarano

B.


Fraction of Total Nitrogen
0
0.2
0.4
0.6
0.8
1
NO3
NH4
DON
Cangejal
Palmira
Lechuza
Diria
SantaRosa
Campero
Honda
Re.entado
SinNombre
Florentina
Bejarano

Appendix A:
Methods and Discussion of Cation Concentrations

METHODS

I used inductively coupled plasma atomic emission spectroscopy (JY Horiba 2000) to measure [Mg^{2+}], [Ca^{2+}], [K^+] and [Na^+] Cation blanks ranged from 0.3mg/L K^+, 0.27mg/L Na^+, 0.27mg/L Ca^{2+}, and 0.08mg/L Mg^{2+}, all were near the detection limit for the method (0.3ug/L K^+,0.29mg/L Na^+, 0.1mg/L Ca^{2+}, 0.3ug/L Mg^{2+}). Known standards for Mg^{2+}, Ca^{2+}, K^+ and Na^+ deviated by a mean of 5%, 5%, 4%, and 2% from expected values, respectively.

DISCUSSION

INFLUENCE OF LAND USE ON CATION CONCENTRATIONS

Ca^{2+}, Na^+ and Mg^{2+} concentrations correlated positively with conductivity (R^2=0.72, p=0.0004; R^2=0.47, p=0.01; R^2=.88, p=6x10^{-6}, respectively). Concentrations of Ca^{2+} and Na^+ increased with agricultural cultivation (R^2=.39, p=.03; R^2=.38, p=.03) (Fig. A1), but did not vary according to forest cover or pasture. The percent of land area in agricultural cultivation for the entire watershed, and not immediately upstream from the sampling point, best described the variation in Ca^{2+} and Na^+ concentrations. Mg^{2+} and K^+ did not vary along either land use gradient (Table A2).

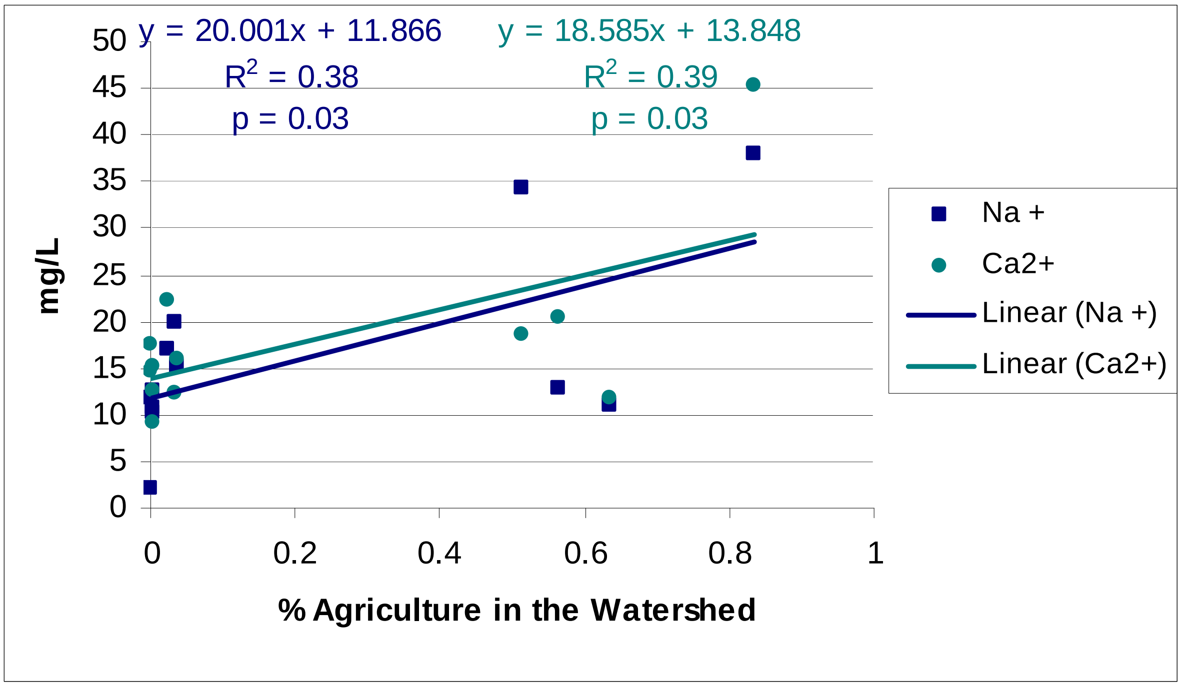
Table A1

Study Site	**Ca^{2+} (mg/L)**	**Na^{+} (mg/L)**	**K^{+} (mg/L)**	**Mg^{2+} (mg/L)**
Palmira	19.8±0.9	14.6±0.4	2.2±0.4	10.4±0.3
Cangrejal	17.6±5.7	11.8±1.5	3.3±0.8	11.3±1.5
SantaRosa	9.1±1.1	12.6±0.7	6.8±0.3	4.8±0.2
Lechuza	16.4±2.5	10.3±0.6	0.5±0.0	15.3±0.0
Diria	12.6±2.6	10.2±0.2	0.6±0.2	15.0±0.6
Campero	22.1±13.9	17.1±1.8	0.7±0.0	20.5±0.0
Amores	12.2±0.0	19.9±0.6	7.2±0.9	3.9±0.6
Honda	16.1±2.8	15.1±0.2	5.2±0.9	5.1±0.4
Reventado	18.6±2.7	34.3±7.7	6.7±3.5	9.3±1.8
Sin Nombre	20.3±0.7	12.7±0.8	1.8±0.2	7.5±0.1
Florentina	11.8±1.5	10.9±1.7	2.9±0.1	5.3±0.5
Bejarano	45.3±3.4	37.9±7.8	8.3±0.8	25.5±2.8

Table A2

Analyte	Distance Upstream (m)	% Forest R^2	% Forest p	% Agriculture R^2	% Agriculture p	% Pasture R^2	% Pasture p
Ca^{2+}	500	0.22	0.12	0.22	0.12	0.01	0.79
	1000	0.18	0.27	0.15	0.22	0.02	0.66
	2000	0.22	0.12	0.23	0.12	0.05	0.49
	5000	0.16	0.19	0.24	0.10	0.09	0.34
	watershed	0.16	0.20	**0.39**	**0.03**	0.07	0.40
Na^{+}	500	0.32	0.05	0.32	0.05	0.07	0.42
	1000	0.09	0.35	0.36	0.04	0.25	0.10
	2000	0.09	0.34	0.32	0.05	0.28	0.08
	5000	0.17	0.18	0.34	0.05	0.17	0.19
	watershed	0.12	0.26	**0.38**	**0.03**	0.12	0.27
K^{+}	500	0.01	0.75	0.01	0.75	0.16	0.20
	1000	0.01	0.80	0.02	0.64	0.01	0.74
	2000	0.12	0.34	0.01	0.79	0.00	0.94
	5000	0.06	0.45	0.02	0.67	0.01	0.71
	watershed	0.09	0.35	0.02	0.64	0.02	0.64
Mg^{2+}	500	0.09	0.36	0.02	0.70	0.08	0.37
	1000	0.01	0.74	0.01	0.81	0.01	0.82
	2000	0.01	0.80	0.02	0.63	0.03	0.59
	5000	0.00	0.92	0.04	0.56	0.18	0.17
	watershed	0.01	0.80	0.08	0.38	0.17	0.19

Figure A1


y = 20.001x + 11.866
R2 = 0.38
p = 0.03
y = 18.585x + 13.848
R2 = 0.39
p = 0.03
mg/L
50
45
40
35
30
25
20
15
10
5
0
0
0.2
0.4
0.6
0.8
1
% Agriculture in the Watershed
Na +
Ca2+
Linear (Na +)
Linear (Ca2+)