CHEMICAL AND BIOLOGICAL WATER QUALITY IN TROPICAL CLOUD FOREST STREAMS UNDER DIFFERENT LAND-USE

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PRESENTED BY
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1 Introduction

1.1 Introduction to cloud forests

“There is, however, one natural feature of this country, the interest and grandeur of which may be fully appreciated in a single walk: it is the “virgin forest”. Here no one who has any feeling of the magnificent and the sublime can be disappointed.”

Alfred Russel Wallace 1823-1913

Alfred Russel Wallace commented with these words on the wonders of the rain forest covering the Amazon Basin. If he had travelled further up, right to the origins of the Amazon, to the far-off places of Andean headwater streams, he would have encountered a forest ecosystem even more wondrous and unique – the montane cloud forest (Figure 1-1). The Merriam Webster dictionary defines cloud forests rather shortly as “wet tropical mountain forests at an altitude usually between 3000 and 8000 feet (1000 and 2500 meters) that are characterized by a profusion of epiphytes and the presence of clouds even in the dry season” (Merriam-Webster 2003). During the first international symposium on cloud forests in Puerto Rico in 1993, a more explicit collection of characteristics was put together (Hamilton et al. 1993). Here, the ecosystem is defined as having:

- a distinctly floristic and structured form
- an atmospheric environment with persistent cloud cover
- reduced solar radiation
- suppressed evapotranspiration
- enhanced net throughfall input due to the stripping of clouds by the tree canopies
- reduced canopy heights and gnarled tree trunks at higher altitudes
- a large epiphyte biomass
- wet and frequently waterlogged soils with a high organic content
- extremely high biodiversity
- a high amount of endemism (a so-called hotspot)

Cloud forests are found all around the world (see Figure 1-2), far inland or on islands, and at altitudes ranging from as low as 500 m up to 3500 m (Hostettler 2002). Although only 2.5 % of the world’s tropical forests are cloud forests (Bubb et al. 2004) they are outstandingly important for sustaining life on our planet. A myriad of plants have evolved depending upon the constant fog and hundreds of animals have evolved to depend on these plants. Numerous plant species have been found to possess medicinal qualities and contribute to the health of a multitude of people each year. For example quinine, the cure
for malaria, is extracted from the bark of the Cinchona tree, which was first discovered in the montane cloud forests of Peru (Régnier 2007).

Other essential ecosystem services provided by cloud forests are the formation of soil, carbon sequestration, the cycling of nutrients and recreation among others (Costanza et al. 1997). The key function of cloud forest, though, is the provision of high amounts of good quality freshwater. Downstream populations depend on this provision of drinking and irrigation water, an important part of which is captured by the stripping of clouds by tree canopies. Even during drier periods, pristine cloud forests supply a reliable stream flow by draining the water which is abundantly stored in the forest vegetation and soil. Several large tropical capitals such as Quito, Tegucigalpa and Mexico city are dependent on this water and are thus intertwined with the fate of these watersheds (Hostettler 2002). Not without reason around 90 % of the world’s cloud forest sites are included in the WWF Global200 region list with conservation priority (Aldrich et al. 2000).

Despite their importance, tropical forests all over the world are deforested at an overwhelming rate. The average annual deforestation rate for tropical forests in South America has been estimated to be 0.4 % for the year 2000. Amongst all South American countries, Ecuador has by far the highest deforestation rate with a lessening of the country’s forest cover of 1.2 % per year (FAO 2001). Reasons for deforestation are various, but are generally caused by population growth or shifts. The most widespread threat to tropical cloud forests is forest clearance for farming or pastures. In some countries hunting, forest fires and mining are also responsible for forest conversion or degradation. However, one of the most prevalent pressures on lowland rainforests, namely timber harvesting, is not such a big issue for cloud forests due to the mostly steep topography, and the reduced tree heights at these altitudes (Bubb et al. 2004).

Even though the intrinsic and economic values of cloud forests are widely acknowledged, our understanding of the drivers of ecosystem functioning is still deficient. Sadly, the scarce knowledge about these fragile systems poses a hindrance for effective conservation management and future policy decisions (McClain & Naiman 2008).
One of the first scientists writing about neotropical cloud forests probably was Alexander von Humboldt in 1807. He commented on the high mountain vegetation of Colombia and Ecuador with the following words: "[..] At these elevations between 2,500 and 3,500 metres above sea level, the traveller finds himself constantly surrounded by a dense fog. This precipitation (or this mysterious formation of water?) that could be the result of a strong electrical tension, gives the vegetation a verdant colour which is continuously renewed" (taken from Stadtmueller (1987)). In the following century, scientific reports continued to be mostly concerned with empirical studies, describing climatic and geographical characteristics or vegetational patterns (Lauer 1952; Mann 1968; Richards 1952; Ellenberg 1959). Only rather recently did we realize that our empirical perception of the ecosystem barely scratches the surface. Below this surface a tremendous number of individual processes act and interact, most of them being vital to the functioning of the forest. Process based studies have therefore nowadays largely replaced the merely empirical approaches of the past (Blume et al. 2008; Boy et al. 2008b; Burns et al. 2001; Elsenbeer & Lack 1996; Goller et al. 2005; Perrin et al. 2001). More and more, the investigations also focus on the impact of land-use change on the observed processes and on ecosystem health (Ataroff & Rada 2000; Ayub 2004; Bautista-Cruz & del Castillo 2005; Bojsen & Jacobsen 2003; Borbor-Cordova 2006; Brown & Lugo 1990; Buytaert et al. 2005; Chaves et al. 2008; Farley et al. 2004; Germer et al. 2009; Neill et al. 2001; Rhoades et al. 1998).

Water is one of the most obvious drivers of a healthy cloud forest. It is virtually everywhere, in the streams, in the soil, in and on the vegetation and even hovering in the air. But which paths does it take in cloud forests? How is its chemistry influenced and changed before it leaves the catchment? How do the processes differ between pristine and deforested sites? How do stream biota react to the differences? To answer at least some of the questions was the aim of this study. By combining descriptive approaches and process-based analyses it was attempted to obtain a more holistic view on the drivers of cloud forest functioning. This study is embedded in the interdisciplinary Research Unit FOR816.
'Biodiversity and Sustainable Management of a Megadiverse Mountain Ecosystem in South Ecuador' which is funded by the German Research Foundation DFG.

The main research questions were:

1. Which factors or processes are most important in shaping the water chemistry of cloud forest streams?
2. How do these differences translate into nutrient export? Can we derive some catchment understanding by analyzing nutrient behaviour and export between land-uses?
3. How are aquatic communities influenced by the differences in water chemistry and physical parameters between land-uses? Which parameters are most important?

Each question is first addressed in a separate chapter (chapter 2 to 4), then all questions are comprehensively discussed in chapter 5.

1.2 Study site

1.2.1 The Andes, Ecuador and the San Francisco River

Along most of its range, the Andes are two parallel chains of high mountain ridges divided by a flat tableland area called altiplano. A part of the eastern chain, which faces the Amazon basin and stretches from northern Peru to southern Colombia, is called the Cordillera Real. The present study was conducted in the San Francisco watershed (Figure 1-3), a headwater catchment of the Cordillera Real in southern Ecuador. At an altitude of 1800-3140 m above sea level, the San Francisco river drains a 75 km² cloud forest area between the province capitals of Loja and Zamora (ca. 3°58'30"S and 79°4'25"W). The catchment is deeply incised in a southwest-northeast direction and thus divided into predominantly north and south-facing slopes respectively.

1.2.2 Climate

Climatically, the Cordillera Real acts as a barrier between the humid Amazon (oriente) and the dry Inter-Andean region (altiplano). The catchment’s climate regime therefore generally originates from the east and results in three distinct local climate zones (Bendix et al. 2008). The lower part of the study area at around 2000 m exhibits a mean annual rainfall of 2050 mm, low average wind speeds and relatively little cloud cover. The uppermost part, however, shows a dramatic increase in precipitation amounts (around 4400 mm at 3140 m a.s.l) as well as wind speed and cloud cover (data from 1998-2004, Rollenbeck (2006), Bendix et al. (2008)). Lastly, a transition zone situated in moderate altitudes closes the link between
these extremes. These altitudinal differences in climatic regime apply to the whole catchment area. In general, the region is marked by two seasons, with the rainy season peaking around May and June and the dry season between October and December. Especially during the latter one, cloud and fog water input contribute significantly to total water input (Bendix et al. 2008). Because of the high humidity and rather cool temperatures, evapotranspiration is generally limited.

1.2.3 Vegetation

To the south, the catchment touches the border of the Podocarpus National Park and the slopes are covered by an almost pristine cloud forest with tree heights of up to 20 m. Dominant plant families are the Lauraceae, Euphorbiaceae, Melastomataceae and Rubiaceae. Tree ferns (*Cyathea spp.*) are common and bamboos (*Chusquea spp.*) also thrive here. Open space for new vegetation growth is naturally created by numerous landslides, most probably caused by a combination of steep slopes and the weight of the plant biomass. Around 76% of all slopes in the area are steeper than 25°, with 19% hereof even steeper than 40° (Beck et al. 2008).
On the opposite side of the catchment, the (northern) slope is almost entirely deforested in the lower parts and consists of patches of pasture (Setaria sphacelata, Schumach.), bracken fern (Pteridium aquilinum, L.), pine plantations (Pinus spp.) and secondary forest (Figure 1-3 B). On both slopes, the crest regions are covered by a neotropical alpine grass- and shrub land (páramo) and an evergreen elfin forest, both of which are adapted to higher wind speed, lower temperatures and lower nutrient availability (Beck et al. 2008).

1.2.4 Soils and Geology

Even though volcanoes are a characteristic feature of the landscape in north and central Ecuador, they are absent in the south-east of the country. In the San Francisco catchment the predominant rock types are metamorphous semipelites, phyllites and quartzites, all belonging to the Chiguinda Unit of the Zamora Series (Litherland et al. 1994).

Soils under forest range from Cambisols (below 2100 m) with a moderate organic layer, to Histosols (above 2100 m) with an increasing organic layer thickness (Wilcke et al. 2008). In the organic layer, a decrease in macronutrient concentration (N, P, K, Ca, Mg) with altitude is countered by the increasing depth of the organic layer, therefore nutrient storages per m² are similar along altitudinal gradients (Wilcke et al. 2008). In general, nutrient concentrations vary greatly between the organic layer and the A horizon, with C, Ca, Mg, N and P concentrations being higher in the organic layer, and K and Na being lower (Wilcke et al. 2008).

Under pasture, the original organic layer of the soil has been either completely lost or at least drastically reduced (Makeschin et al. 2008). As a result of the high precipitation most of the soils above 1800 m a.s.l. show Podzolic features e.g. bleaching of the A horizon. Often, reddish or black placic subsurface horizons exist which gives evidence to the occurrence of redoximorphic processes (Beck et al. 2008). Other soil properties such as saturated hydraulic conductivity and stone content among others are highly heterogeneous even at the small-scale (Huwe et al. 2008) in part probably due to the already mentioned frequent landslides along the steep slopes of the valley.
1.2 Study site

1.2.5 Altitudinal gradients

As a consequence of the strong differences in altitude (around 1300 m) within the San Francisco catchment, there are large gradients of climatic and environmental characteristics in the area. Figure 1-4 summarizes the most important gradients and their respective direction. These differences in altitude entail large variations in the hydrological, soil chemical and soil physical behaviour of the catchment.

1.2.6 Field sites and equipment

Within the DFG Research Unit FOR816 the subproject B3.2 started in April 2007. The selection of field sites, the installation of water level sensors and the initiation of the water sampling took place during April and May 2007. Water level and chemistry data are therefore not available before this date. Water level sensors were installed at 10 sites, 7 hereof in the tributaries, and 3 in the main river (Figure 1-3 A). In subcatchment F3 no water level sensors were installed because this catchment has been monitored by another subgroup of FOR816, the data of which was available. In August 2008 two monitoring stations had to be discarded (stations D1 and R2) since sound stage discharge relations could not be created in these highly dynamic transects. Discharge was measured manually at all stations as often as possible. Water chemistry data were taken weekly to biweekly and analyzed for ion, element, total organic carbon (TOC) and total nitrogen (TN) concentration. Less frequently rain water (one sample site) and various seeps and springs were sampled. The monitoring of aquatic diversity took place in 3 streams with pasture influence (P1-3) and in 3 forested streams (F1-3). The codes and not the names for the subcatchments were used in the following chapters to make it easier for the reader to identify the streams’ respective predominant land-use. More information on the subcatchments is given in Table 1-1.
Table 1.1 Additional information on all subcatchments (sampling period, catchment size, land-use). ‡ subcatchment is hydro-chemically monitored by another group within the FOR816.

<table>
<thead>
<tr>
<th>Code</th>
<th>Stream name</th>
<th>Predominant land-use</th>
<th>Location</th>
<th>start-end of sampling</th>
<th>Total area [ha]</th>
<th>% forest cover</th>
<th>% pasture/bracken cover</th>
<th>Analyzed in chapter</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>Francisco Head</td>
<td>Forest</td>
<td>Main river</td>
<td>Apr ’07 - today</td>
<td>3506</td>
<td>66.9</td>
<td>3.2</td>
<td>x x</td>
</tr>
<tr>
<td>R2</td>
<td>San Francisco</td>
<td>Mixed</td>
<td>Main river</td>
<td>Apr ’07 - Aug ’08</td>
<td>6541</td>
<td>63.1</td>
<td>21.0</td>
<td>x</td>
</tr>
<tr>
<td>R3</td>
<td>Planta</td>
<td>Mixed</td>
<td>Main river</td>
<td>Apr ’07 - today</td>
<td>7530</td>
<td>67.7</td>
<td>9.1</td>
<td>x x</td>
</tr>
<tr>
<td>P1</td>
<td>Quebrada Cruces</td>
<td>Pasture</td>
<td>N-slope</td>
<td>Sep ’07 - today</td>
<td>70</td>
<td>23.3</td>
<td>66.7</td>
<td>x x</td>
</tr>
<tr>
<td>P2</td>
<td>Quebrada Pasto</td>
<td>Pasture, Mixed</td>
<td>N-slope</td>
<td>May ’07 - today</td>
<td>342</td>
<td>68.4</td>
<td>14.4</td>
<td>x x</td>
</tr>
<tr>
<td>P3</td>
<td>Quebrada Aguirre</td>
<td>Pasture, Mixed</td>
<td>N-slope</td>
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<td>65.9</td>
<td>15.7</td>
<td>x</td>
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<tr>
<td>F1</td>
<td>Quebrada Milagro</td>
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<td>S-slope</td>
<td>Apr ’07 - today</td>
<td>128</td>
<td>90.0</td>
<td>1.5</td>
<td>x x</td>
</tr>
<tr>
<td>F2</td>
<td>Quebrada Ramón</td>
<td>Forest</td>
<td>S-slope</td>
<td>Apr ’07 - today</td>
<td>449</td>
<td>80.0</td>
<td>1.5</td>
<td>x x</td>
</tr>
<tr>
<td>F3</td>
<td>Q2</td>
<td>Forest</td>
<td>S-slope</td>
<td>‡</td>
<td>14</td>
<td>90.0</td>
<td>9.6</td>
<td>x</td>
</tr>
<tr>
<td>D1</td>
<td>Quebrada Navidades</td>
<td>Mixed, gravel</td>
<td>W-slope</td>
<td>Apr ’07 - Aug ’08</td>
<td>1015</td>
<td>67.2</td>
<td>11.3</td>
<td>x</td>
</tr>
<tr>
<td>D2</td>
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<td>Mixed, gravel</td>
<td>NW-slope</td>
<td>Apr ’07 - today</td>
<td>1140</td>
<td>73.1</td>
<td>10.1</td>
<td>x x</td>
</tr>
</tbody>
</table>
2 Identifying controls on the water chemistry of tropical cloud forests

2.1 Introduction

Tropical cloud forests are one of the most species rich ecosystems in the world, but also one of the most endangered. In contrast to lowland rain forests, a main characteristic of cloud forests is the interception of cloud moisture, which makes them unique in their watershed quality and quantity (Doumenge et al. 1995). The scarce knowledge of the functioning of these fragile systems, and the changes that result from deforestation, may hinder effective environmental management (Fedde et al. 2005). The conversion of cloud forest to pasture or crop land and the fast degradation of these ecological units thereafter is one of the big threats that tropical regions are facing nowadays (Günther et al. 2007). It is widely recognized that small-scale climate regimes, soil chemistry and hydrology, among others, are influenced by the loss of forest cover (Ataroff & Rada 2000; Neill et al. 2006), but the degree of this influence is poorly known. Both the pristine and the transformed state of the ecosystem, including inputs and outputs, should be investigated to detect changes in physical and chemical parameters of tropical forest catchments. Just as important as detecting changes is the question of why these changes occur, which is an issue of alteration in soil processes and flow paths (Burt & Pinay 2005).

One of the big unknowns of tropical cloud forest systems still is the fate of water. Which paths does it take? How is its chemistry influenced and changed before it leaves the system? How does deforestation alter the course of the water and its associated chemistry? What are the major drivers of water quality? These questions can be answered not only by subsurface flow path investigations but also via spatially distributed water quality surveys. Subsurface flow paths (infiltration, groundwater flow) and surface water quality (subcatchments, source areas) are intimately connected in a catchment (Soulsby et al. 2007; Tetzlaff & Soulsby 2007b). In remote areas though, most studies focus on only one of these fields, probably mostly due to limited time and resources.

Subsurface flow paths have been identified in the small scale by employing artificial dye tracers and excavating soil profiles after tracer irrigation (McLeod et al. 1998; Albrecht et al. 2003; Vanderborgh et al. 2002). For a larger scale, natural tracer concentrations (Cl, SiO$_2$) and isotopes (H$^3$, O$^{18}$, N$^{15}$) have been monitored to derive flow path understanding and generation of storm hydrographs (Rice & Hornberger 1998; Rodgers et al. 2005; Soulsby et al. 2006; Tetzlaff & Soulsby 2007a; Uhlenbrook et al. 2002). In tropical regions, subsurface flow path studies clearly dominate over surface water analyses (Elsenbeer et al. 1994; Elsenbeer & Lack 1996; Elsenbeer & Vertessy 2000; Goller et al. 2005; Schellekens et al. 2004; Wilcke et al. 2001).
Surface water (source area, water quality) investigations are mostly conducted by sampling different subcatchments, and either analyze bulk parameters (pH, conductivity, alkalinity) or ion and element concentrations to spatially and temporally quantify all water quality aspects of a catchment (Clow et al. 1996; Bernal & Sabater 2008; Simeonov et al. 2003). Often paired catchment approaches are used to investigate alterations in flow chemistry with land-use change (Neill et al. 2001; Ramos-Escobedo & Vázquez 2001). In the tropics mainly small watersheds were used for water quality studies, and have, according to Neill et al. (2006), played a large role in the understanding of catchment functioning. Almost all studies, however, have in common that they focus on the fate of some few nutrients or elements, such as sulphate, carbon or nitrate and nitrogen respectively, or on bulk parameters like alkalinity and conductivity (Poor & McDonnell 2007; Worrall et al. 2003). In areas with few site data, and even more so in the very ‘clear’ water of tropical headwater streams, it is questionable whether such an approach is sufficient because concentration differences are often very low in standard parameters. To overcome this problem, multi-tracer investigations represent a feasible option for getting a snap-shot on ungauged headwater basin processes. With the fast improvement in analytical techniques, trace elements such as, e.g., rare earth elements (REEs) have become popular as environmental tracers, at least in geochemical studies (Bwire Ojiambo et al. 2003; Chung et al. 2008; Viers & Wasserburg 2004). REEs encompass all elements belonging to the Lanthanides (periodic table elements 57-71), plus scandium (element 21) and yttrium (element 39). Due to their ubiquity in the earth’s crust they represent good tracers for weathering rates and for geological and pedological processes (Hannigan & Sholkovitz 2001; Hu et al. 2006).

Hydro-chemical studies that include a variety of sampling sites and analytes inevitably result in large amounts of data. The variation in the data reflects different chemical behaviour, different spatio-temporal sources, as well as different hydrologic conditions, making an interpretation of the results difficult. To derive general trends, the complexity of the data sets can be reduced to a few, more easily interpretable, components. Principal component analysis (PCA) is a statistical tool which is typically employed to reduce the number of dimensions in hydro-chemical data (Christophersen & Hooper 1992). In a PCA, the variation in data is projected on new, abstract orthogonal principal components (eigenvectors), with each principle component, or factor, describing a different source of variation for the data set. Each factor thus is derived from a set of correlated elements, which are influenced by the same underlying processes (flow paths) or environmental parameters (e.g. geology, anthropogenic disturbance, season). This correlation among elements which is specific for every factor enables the scientist to draw conclusions on the sources of this ‘collective’ variation.

Here principal component analysis is applied on water samples of a tropical montane cloud forest catchment. A set of over 30 elements and nutrients, which can be analyzed by standard laboratory methods, was investigated. The methodology is based on a paired catchment approach, with forested and deforested sites located in the same 75 km² cloud
forest catchment. Both sites are geologically as well as topographically comparable (Makeschin et al. 2008).

The objectives were to 1) generally describe the spatial and temporal variation in water quality of a mesoscale tropical cloud forest catchment using qualitative approaches and PCA, and to 2) evaluate if differences in water chemistry of subcatchments can be attributed to land-use and -management practices.

This leads to the hypotheses that

1) In remote, ungauged basins, the analysis of hydro-chemical characteristics of surface and subsurface flows can help to elucidate the sources and flow-paths of water
2) Land-use practices are the predominant controls on water chemistry in tropical montane watersheds,
3) In headwater streams, differences in water chemistry are attenuated at high flows due to rain dilution processes,
4) Water parameters commonly taken as indicators of water chemistry change (e.g. pH, EC, $SO_4$, Ca) are not sufficient to explain controls on water chemistry in the ion poor waters of tropical cloud forest catchments. Rare earth elements can be of use in these areas.

2.2 Material and Methods

2.2.1 Sampling design

A nested sampling approach was used, with a total of ten sampling sites in nine subcatchments (see Figure 2-1 and Table 2-1). The sites were chosen according to land-use characteristics and accessibility of the area, the latter one being a highly restricting factor in the steep and mostly impenetrable catchment. Thus, six sampling stations in different tributaries were located, i.e. two in forested (F1, F2), two in pasture streams (P1, P2), and two in anthropogenically disturbed sub-catchments (D1, D2). Additionally we sampled three sites in the main river (R1, R2 and R3). The forest stream F2 was sampled in two locations. Just before F2 flows into the main river, a small channel diverts stream water to a power plant downriver. We sampled before (F2a) and after (F2b) the channel diversion. After the channel diversion a spring emerging from a rock fracture enters the stream ($F_{well}$). F2b was situated after the mixing of well water with the remaining stream water.
2.2 Material and Methods

Figure 2-1 Study catchment and subcatchments with sampling points

Table 2-1 General information on the sampling sites

<table>
<thead>
<tr>
<th>No.</th>
<th>Code</th>
<th>(Land-) use</th>
<th>Station name</th>
<th>Size (km²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>R1</td>
<td>Forest</td>
<td>Francisco Head</td>
<td>35.01</td>
</tr>
<tr>
<td>2</td>
<td>R2</td>
<td>Mixed</td>
<td>San Francisco</td>
<td>65.41</td>
</tr>
<tr>
<td>3</td>
<td>R3</td>
<td>Mixed</td>
<td>Planta</td>
<td>75.28</td>
</tr>
<tr>
<td>4</td>
<td>P1</td>
<td>Extensive pasture</td>
<td>Quebrada Cruzes</td>
<td>0.69</td>
</tr>
<tr>
<td>5</td>
<td>P2</td>
<td>Extensive pasture</td>
<td>Quebrada Pasto</td>
<td>3.45</td>
</tr>
<tr>
<td>6</td>
<td>F1</td>
<td>Forest</td>
<td>Quebrada Milagro</td>
<td>1.27</td>
</tr>
<tr>
<td>7</td>
<td>F2a</td>
<td>Forest</td>
<td>Quebrada Ramón (a)</td>
<td>4.46</td>
</tr>
<tr>
<td>8</td>
<td>F2b</td>
<td>Forest</td>
<td>Quebrada Ramón (b)</td>
<td>4.49</td>
</tr>
<tr>
<td>9</td>
<td>D1</td>
<td>Mixed, disturbed</td>
<td>Quebrada Navidades</td>
<td>10.15</td>
</tr>
<tr>
<td>10</td>
<td>D2</td>
<td>Mixed, disturbed</td>
<td>Quebrada Zurita</td>
<td>11.38</td>
</tr>
</tbody>
</table>

For principal component analysis measurements of three wells were also included. One situated in the P1 catchment (P_well), one in the F2 catchment (F_well) and one entering the...
main river next to the R2 sampling station (Rwell). Rain (labelled ‘Rain’ in the PCA) was sampled on an event basis, and surface water from 2750 m altitude was taken during non-precipitation periods in pristine (sub-)páramo vegetation (labelled ‘Páramo’ in the PCA), reflecting water sources with a higher amount of fog water.

Water grab samples were taken at all stations between April 2007 and May 2008 at weekly to biweekly intervals. For each sample, two aliquots were taken, one for element analysis, collected in an acid washed PE bottle. The second sample was collected in a PE bottle rinsed with deionised water for the analysis of anions (Cl, NO$_3$, NO$_2$, PO$_4$ and SO$_4$). Water samples were filtered through 0.45 µm polypropylene membrane filters (Whatman Puradisc 25PP, Whatman Inc.) directly in the field.

Within three hours after collection, element samples were acidified to a pH<2 (using nitric acid) in the field-lab and then kept cool until analyzed. Element concentrations were determined via inductively coupled plasma-mass spectrometry (ICP-MS, Agilent 7500ce, Agilent Technologies). The Agilent 7500ce is able to perform ultra-trace measurements of complex unknown samples and therefore allowed to semi-quantitatively analyze a variety of elements over a wide concentration range. The quality of the results of the ICP-MS measurements was controlled by certified reference material (NIST 1643e and NRC-SLRS4) and via additional internal calibration standards. The following elements were considered (in alphabetical order): Al, As, Ba, Ca, Ce, Cr, Cu, Dy, Er, Fe, Fl, Gd, K, La, Li, Mg, Mn, Na, Nd, Ni, Pb, Pr, Rb, Sm, Sr, U, V, Y, Yb, Zn. Element concentrations of Co, Cd, Eu, Tb, Ho, Lu and Tm were below detection limit.

For Cl, NO$_3$, NO$_2$, PO$_4$ and SO$_4$ samples were frozen within 3 hours after collection until they were analyzed by ion chromatography (DX-120, Dionex Corporation). Every sample value represents the mean of 2 consecutive measurements.

Electric conductivity (µS cm$^{-1}$) and pH were measured directly in the field (pH/Cond 340i, WTW – Weilheim, Germany). Due to the ion poor water, the pH-electrode SenTix HW was especially chosen for these low-conductivity measurements.

Silicate could not be analyzed by our standard methods and was thus omitted in the following analysis. However, some measurements were conducted using rapid tests (Merck, Microquant 0.5-15.0 mg l$^{-1}$ SiO$_2$) with a precision of ±0.5 mg l$^{-1}$ SiO$_2$ and this data was used to discuss the origin of well water (chapter 2.3.3).

### 2.2.2 Data analysis

To be able to differentiate between variation due to land-use and variation due to hydrologic regime, water samples were classified into two flow conditions, i.e. baseflow and fast flow condition. Baseflow samples were defined as samples taken at hydrologic conditions with at least 70% baseflow (Figure 2-2). Among the many methods to differentiate between base- and fast flow, it was decided to use a numerical filter because of
the ease of use and good reproducibility. Baseflow contribution was thus derived by the recursive digital baseflow filter implemented in the WETSPRO tool (Willems 2009). WETSPRO applies a filter for exponential recessions proposed by Chapman (Chapman 1991). All samples not applying to baseflow conditions were classified as ‘fastflow samples’. Thus, between 10 and 13 baseflow and 16 and 24 fast flow samples were available for each station. At one pasture stream station (P1) though, only 6 baseflow and 10 fast flow samples were available for analysis because this sampling station was not set up until September 2007.

![Hydrograph separation and daily precipitation values (gauge at 1980m) for the outlet, R3](image)

Figure 2-2 Hydrograph separation and daily precipitation values (gauge at 1980m) for the outlet, R3

For statistical analysis, means (and standard deviation) of element baseflow concentration at all sampling stations were calculated. A comparison of means was conducted using an analysis of variance (ANOVA) and \( p = 0.05 \). If significant differences were apparent, Scheffé’s multiple pair-wise comparison of means was applied to extract differences among sampling stations for every investigated parameter (Scheffé’s PostHoc Test, \( p = 0.05 \)). The results of this comparison are summarized in chapter 2.3.1.

In a second step, for principal component analysis (PCA), all water chemistry data were converted to molar concentration units and standardized (i.e. centred by subtracting the arithmetic mean, and divided by the respective standard deviation) according to Hooper (2003). PCA was developed using the whole set of elements for baseflow samples, only excluding the elements which didn’t reveal any spatial difference in the ANOVA. Then,
subsets of ten elements were tested for factor loadings and variation explained. The set having highest loadings and best explaining the variation in the data was chosen for further analysis. To account for the heterogeneity in variances, the PCA analysis was based on a correlation matrix. All factors explaining 5% or more of the variation in the data were retained.

To elucidate differences in base- and fast flow concentration for the elements used in the PCA, we also applied an ANOVA ($p = 0.05$) comparing mean concentrations of the two flow conditions. All statistics were executed with the STATISTICA Software (StatSoft®), Version 6.0.

2.3 Results and Discussion

2.3.1 Descriptive spatial analysis of element concentration

As expected for headwater streams, concentrations of all elements and nutrients were very low. The chemical constituents of river water at baseflow condition are summarized in Tables 2-2 and 2-3 for all stations. Major cations were Na, Ca, Mg and K, major anions Cl, NO$_3$ and SO$_4$. Neither NO$_2$ nor PO$_4$ was detected. This was probably due to a relatively high detection limit of 0.5 mg l$^{-1}$ for phosphate and 0.1 mg l$^{-1}$ for nitrite. Mean ion concentrations generally were low, as reflected in the electric conductivity, which ranged from 5.9 µS cm$^{-1}$ to 31.9 µS cm$^{-1}$. The concentrations of most parameters varied much more strongly in the fast flow samples compared to the baseflow samples (compare Figures 2-3 and 2-4). Despite these low concentrations, significant differences between land-uses were apparent. Forest streams F1 and F2a were clearly separated from the other catchments by having the lowest pH values, and low NO$_3$, SO$_4$, Na, Mg, Ca, K, Sr and As concentrations. Both sites in forest stream F2 possessed significantly higher Rb concentrations, but Rb was also elevated in F1. Site F2b (after channel diversion and well water input) showed highest NO$_3$ concentrations of all streams, whereas NO$_3$ concentration at the outlet R3 was similar to forest streams F1 and F2a. SO$_4$ concentration in the uppermost river station R1 was comparable to the values found for F1 and F2a.

Pasture streams showed significantly elevated Na, Mg and Li values, with Na being about twice as high as in the other sites. Both disturbed subcatchments (D1, D2) had significantly higher SO$_4$ values and D1 exhibited higher concentrations in Mn, Dy, Er, Gd, La, Nd, Pr, Sm and Y, the latter eight elements all belonging to the rare earth elements. No spatial variation was found for the following ten elements: Al, Cl, Cr, Cu, Fe, Ni, Pb, U, Yb and Zn.

Compared to other tropical headwater catchments the study area exhibited noticeably low element concentrations (see Table 2-5). In montane watersheds of Puerto Rico, e.g. McDowell & Asbury (1994) report comparable values in K but higher concentrations in Na, Ca, Mg, Cl and SO$_4$. The same is true for a study in a volcanic headwater stream in Mexico, where Ramos-Escobedo and Vázquez (2001) encountered higher values of all cations and
anions except SO$_4$. This difference to other headwater streams can only be a consequence either of less nutrient input into the catchment via the atmosphere, of a more effective nutrient retention by the dense forest vegetation and soil, or of geological differences.

Chloride concentrations at all sampling stations also were low compared to other tropical headwater catchments (McDowell & Asbury 1994), probably due to the Andes acting as a natural barrier for atmospheric inputs from the coast and climate regimes mostly coming from the east. The overall median molar ratio of Na:Cl in the water samples was 3.1 for baseflow and 2.4 for fast flow, which differs considerably from the maritime (precipitation) ratio of 0.85. Sea spray seems therefore not to play a major role for the input of elements into the watershed, at least during the predominant easterly weather regimes (Boy & Wilcke 2008).

Seasonal changes in concentrations of solutes were only observed in NO$_3$, where higher concentrations were found in the southern hemisphere winter. No other parameter exhibited a seasonal change during our study period. Seasons were therefore not treated separately in the following analysis. The question on the possible causes of the observed nitrate seasonality is not in the scope of this chapter but will be addressed in chapter 3.

In Figures 2-3 and 2-4 land uses are directly compared for a subset of ten parameters, all of which are later on used in the principal component analysis. The box plots of the surface waters clearly reveal the distinction of concentrations for forested, disturbed and pasture catchments. During both flow conditions, Ca, Na, Mg and Sr concentrations are lowest in forest streams. However, differences between disturbed and pasture streams for Na, Mg and Sr are noticeable during baseflow but not during fast flow, where variation is higher. For Rb, concentrations are clearly higher in forested streams during both flow conditions. Páramo water chemistry was only measured during baseflow and is low in all ten parameters. This is consistent with our assumption of a predominant input of rather ion-poor fog water (Bendix et al. 2004) although other factors, like depth to bed rock and diminished organic matter turnover, might play a role, too. High rare earth element (REE) concentrations during baseflow are observed only for D1. In general, low REE concentrations and low variation during baseflow contrasts with higher REE concentrations and high variation during fast flow condition for all sites. Variation in fast flow clearly is highest in D1, R2 and R3, though. More explanations for the patterns observed between flow conditions and forested, pasture and disturbed catchments, respectively, are given in the discussion of the PCA analysis and PCA plots (chapters 2.3.2 and 2.3.4).
Table 2-2 Means and standard deviation of all streams in baseflow condition, EC in µS cm\(^{-1}\), all other concentrations in µg l\(^{-1}\), digits adapted to detection limit accuracy; bulk parameters and anions are shown first, thereafter all investigated elements in alphabetical order.

<table>
<thead>
<tr>
<th></th>
<th>D1</th>
<th>D2</th>
<th>F1</th>
<th>F2a</th>
<th>F2b</th>
<th>P1</th>
<th>P2</th>
<th>R1</th>
<th>R2</th>
<th>R3</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.26 (±0.23)</td>
<td>7.3 (±0.24)</td>
<td>6.61 (±0.22)</td>
<td>6.65 (±0.42)</td>
<td>6.94 (±0.31)</td>
<td>7.3 (±0.58)</td>
<td>7.41 (±0.27)</td>
<td>7.21 (±0.19)</td>
<td>7.33 (±0.31)</td>
<td>7.13 (±0.24)</td>
</tr>
<tr>
<td>EC</td>
<td>24 (±4)</td>
<td>25 (±2)</td>
<td>5 (±0.0)</td>
<td>8 (±3)</td>
<td>15 (±1)</td>
<td>31 (±2)</td>
<td>31 (±2)</td>
<td>13 (±1)</td>
<td>24 (±9)</td>
<td>18 (±6)</td>
</tr>
<tr>
<td>Cl</td>
<td>731 (±158)</td>
<td>785 (±195)</td>
<td>641 (±261)</td>
<td>618 (±275)</td>
<td>533 (±295)</td>
<td>551 (±305)</td>
<td>768 (±82)</td>
<td>682 (±263)</td>
<td>708 (±221)</td>
<td>593 (±282)</td>
</tr>
<tr>
<td>NO(_3)</td>
<td>768</td>
<td>861.1</td>
<td>638.8</td>
<td>600.2</td>
<td>1022.5</td>
<td>763.6</td>
<td>655.5</td>
<td>691.5</td>
<td>601</td>
<td></td>
</tr>
<tr>
<td>SO(_4)</td>
<td>1385.9</td>
<td>1043.5</td>
<td>553.3</td>
<td>527</td>
<td>717.5</td>
<td>778</td>
<td>933.3</td>
<td>644.1</td>
<td>989.5</td>
<td>768.1</td>
</tr>
<tr>
<td>Al</td>
<td>32 (±25.6)</td>
<td>29.3 (±11.3)</td>
<td>37.8 (±4.4)</td>
<td>31.8 (±7.2)</td>
<td>18.8 (±5.8)</td>
<td>29.9 (±9.6)</td>
<td>24.3 (±8.3)</td>
<td>46.3 (±49.7)</td>
<td>32.5 (±14.4)</td>
<td>28.7 (±8.6)</td>
</tr>
<tr>
<td>As</td>
<td>0.4 (±0.1)</td>
<td>0.4 (±0.0)</td>
<td>0.1 (±0.0)</td>
<td>0.1 (±0.0)</td>
<td>0.3 (±0.0)</td>
<td>0.5 (±0.1)</td>
<td>0.3 (±0.0)</td>
<td>0.3 (±0.0)</td>
<td>0.4 (±0.0)</td>
<td>0.3 (±0.0)</td>
</tr>
<tr>
<td>Ba</td>
<td>2.02 (±0.58)</td>
<td>1.47 (±0.27)</td>
<td>0.9 (±0.24)</td>
<td>0.87 (±0.29)</td>
<td>1.05 (±0.25)</td>
<td>2.46 (±0.73)</td>
<td>2.14 (±0.27)</td>
<td>1.08 (±0.28)</td>
<td>1.65 (±0.38)</td>
<td>1.21 (±0.19)</td>
</tr>
<tr>
<td>Ca</td>
<td>2049 (±200)</td>
<td>1994 (±155)</td>
<td>175 (±31)</td>
<td>244 (±52)</td>
<td>771 (±115)</td>
<td>1833 (±184)</td>
<td>1695 (±153)</td>
<td>813 (±123)</td>
<td>1685 (±263)</td>
<td>1235 (±152)</td>
</tr>
<tr>
<td>Ce</td>
<td>0.5 (±0.3)</td>
<td>0.1 (±0.0)</td>
<td>0.3 (±0.0)</td>
<td>0.1 (±0.0)</td>
<td>0.1 (±0.0)</td>
<td>0.2 (±0.0)</td>
<td>0.1 (±0.0)</td>
<td>0.2 (±0.0)</td>
<td>0.3 (±0.0)</td>
<td>0.2 (±0.0)</td>
</tr>
<tr>
<td>Cr</td>
<td>0.32 (±0.16)</td>
<td>0.31 (±0.15)</td>
<td>0.33 (±0.14)</td>
<td>0.33 (±0.24)</td>
<td>0.28 (±0.13)</td>
<td>0.36 (±0.1)</td>
<td>0.29 (±0.15)</td>
<td>0.25 (±0.15)</td>
<td>0.46 (±0.75)</td>
<td>0.39 (±0.3)</td>
</tr>
<tr>
<td>Cu</td>
<td>0.96 (±0.68)</td>
<td>0.67 (±0.36)</td>
<td>0.59 (±0.33)</td>
<td>0.64 (±0.48)</td>
<td>0.53 (±0.28)</td>
<td>0.75 (±0.39)</td>
<td>0.66 (±0.32)</td>
<td>0.71 (±0.4)</td>
<td>0.86 (±0.78)</td>
<td>0.62 (±0.29)</td>
</tr>
<tr>
<td>Dy</td>
<td>0.06 (±0.04)</td>
<td>0.01 (±0.00)</td>
<td>0.01 (±0.00)</td>
<td>0.01 (±0.00)</td>
<td>0.00 (±0.00)</td>
<td>0.01 (±0.00)</td>
<td>0.02 (±0.01)</td>
<td>0.04 (±0.01)</td>
<td>0.02 (±0.00)</td>
<td></td>
</tr>
<tr>
<td>Er</td>
<td>0.03 (±0.018)</td>
<td>0.008 (±0.001)</td>
<td>0.009 (±0.002)</td>
<td>0.008 (±0.003)</td>
<td>0.009 (±0.002)</td>
<td>0.005 (±0.002)</td>
<td>0.005 (±0.005)</td>
<td>0.009 (±0.005)</td>
<td>0.018 (±0.002)</td>
<td>0.013 (±0.002)</td>
</tr>
<tr>
<td>Fe</td>
<td>66 (±44)</td>
<td>23 (±10)</td>
<td>70 (±5)</td>
<td>49 (±45)</td>
<td>22 (±21)</td>
<td>73 (±9)</td>
<td>41 (±10)</td>
<td>62 (±93)</td>
<td>88 (±120)</td>
<td>63 (±50)</td>
</tr>
<tr>
<td>Gd</td>
<td>0.11 (±0.06)</td>
<td>0.02 (±0.00)</td>
<td>0.01 (±0.00)</td>
<td>0.01 (±0.00)</td>
<td>0.02 (±0.00)</td>
<td>0.01 (±0.00)</td>
<td>0.03 (±0.01)</td>
<td>0.06 (±0.01)</td>
<td>0.04 (±0.01)</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>317 (±54)</td>
<td>320 (±95)</td>
<td>219 (±30)</td>
<td>290 (±86)</td>
<td>372 (±69)</td>
<td>492 (±26)</td>
<td>417 (±47)</td>
<td>274 (±76)</td>
<td>366 (±63)</td>
<td>305 (±57)</td>
</tr>
</tbody>
</table>
Table 2-3. Mean values and standard deviation for all streams in baseflow condition, Table 2 continued. Concentrations in µg l⁻¹. Digits adapted to detection limit accuracy.

<table>
<thead>
<tr>
<th></th>
<th>D1</th>
<th>D2</th>
<th>F1</th>
<th>F2a</th>
<th>F2b</th>
<th>P1</th>
<th>P2</th>
<th>R1</th>
<th>R2</th>
<th>R3</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>0.5 ±0.35</td>
<td>0.1 ±0.02</td>
<td>0.05 ±0.0</td>
<td>0.05 ±0.0</td>
<td>0.06 ±0.01</td>
<td>0.1 ±0.02</td>
<td>0.08 ±0.03</td>
<td>0.13 ±0.07</td>
<td>0.36 ±0.08</td>
<td>0.2 ±0.06</td>
</tr>
<tr>
<td>Li</td>
<td>0.31 ±0.07</td>
<td>0.27 ±0.06</td>
<td>0.38 ±0.07</td>
<td>0.26 ±0.03</td>
<td>0.29 ±0.08</td>
<td>0.75 ±0.18</td>
<td>0.61 ±0.1</td>
<td>0.24 ±0.1</td>
<td>0.39 ±0.09</td>
<td>0.28 ±0.05</td>
</tr>
<tr>
<td>Mg</td>
<td>437 ±42</td>
<td>545 ±25</td>
<td>134 ±15</td>
<td>144 ±14</td>
<td>400 ±43</td>
<td>791 ±82</td>
<td>788 ±57</td>
<td>292 ±27</td>
<td>577 ±103</td>
<td>409 ±35</td>
</tr>
<tr>
<td>Mn</td>
<td>12.8 ±3.1</td>
<td>1.2 ±0.5</td>
<td>2.1 ±0.2</td>
<td>0.9 ±0.5</td>
<td>0.4 ±0.2</td>
<td>6.2 ±1.8</td>
<td>4.9 ±0.8</td>
<td>1.7 ±0.8</td>
<td>6.4 ±4.8</td>
<td>3.9 ±0.5</td>
</tr>
<tr>
<td>Na</td>
<td>1548 ±145</td>
<td>1652 ±76</td>
<td>708 ±73</td>
<td>698 ±122</td>
<td>1426 ±130</td>
<td>2654 ±205</td>
<td>2585 ±206</td>
<td>1240 ±185</td>
<td>1950 ±338</td>
<td>1550 ±111</td>
</tr>
<tr>
<td>Nd</td>
<td>0.50 ±0.30</td>
<td>0.10 ±0.00</td>
<td>0.01 ±0.00</td>
<td>0.01 ±0.00</td>
<td>0.01 ±0.00</td>
<td>0.10 ±0.00</td>
<td>0.01 ±0.00</td>
<td>0.10 ±0.00</td>
<td>0.30 ±0.00</td>
<td>0.20 ±0.00</td>
</tr>
<tr>
<td>Ni</td>
<td>0.62 ±0.91</td>
<td>0.29 ±0.14</td>
<td>0.31 ±0.1</td>
<td>1.2 ±2.42</td>
<td>0.29 ±0.09</td>
<td>0.31 ±0.08</td>
<td>0.61 ±0.99</td>
<td>0.57 ±0.88</td>
<td>1.74 ±4.09</td>
<td>1.1 ±1.63</td>
</tr>
<tr>
<td>Pb</td>
<td>0.16 ±0.10</td>
<td>0.11 ±0.09</td>
<td>0.16 ±0.13</td>
<td>0.17 ±0.08</td>
<td>0.14 ±0.10</td>
<td>0.19 ±0.09</td>
<td>0.14 ±0.09</td>
<td>0.13 ±0.11</td>
<td>0.24 ±0.29</td>
<td>0.14 ±0.10</td>
</tr>
<tr>
<td>Pr</td>
<td>0.141 ±0.105</td>
<td>0.027 ±0.007</td>
<td>0.014 ±0.005</td>
<td>0.014 ±0.003</td>
<td>0.015 ±0.007</td>
<td>0.027 ±0.006</td>
<td>0.023 ±0.008</td>
<td>0.036 ±0.023</td>
<td>0.094 ±0.023</td>
<td>0.054 ±0.017</td>
</tr>
<tr>
<td>Rb</td>
<td>0.6 ±0.06</td>
<td>0.52 ±0.06</td>
<td>0.86 ±0.07</td>
<td>1.34 ±0.17</td>
<td>1.41 ±0.14</td>
<td>0.6 ±0.03</td>
<td>0.57 ±0.07</td>
<td>0.67 ±0.14</td>
<td>0.77 ±0.09</td>
<td>0.71 ±0.07</td>
</tr>
<tr>
<td>Sm</td>
<td>0.113 ±0.07</td>
<td>0.024 ±0.006</td>
<td>0.017 ±0.004</td>
<td>0.012 ±0.003</td>
<td>0.014 ±0.002</td>
<td>0.023 ±0.004</td>
<td>0.019 ±0.007</td>
<td>0.028 ±0.016</td>
<td>0.073 ±0.018</td>
<td>0.043 ±0.013</td>
</tr>
<tr>
<td>Sr</td>
<td>13.0 ±1.5</td>
<td>14.6 ±0.9</td>
<td>1.7 ±0.2</td>
<td>2.7 ±0.2</td>
<td>8.2 ±1.2</td>
<td>16 ±1.1</td>
<td>16.7 ±0.8</td>
<td>7 ±0.7</td>
<td>13.7 ±1.9</td>
<td>9.7 ±0.9</td>
</tr>
<tr>
<td>U</td>
<td>0.008 ±0.002</td>
<td>0.005 ±0.001</td>
<td>0.007 ±0.0</td>
<td>0.004 ±0.0</td>
<td>0.003 ±0.0</td>
<td>0.008 ±0.0</td>
<td>0.005 ±0.0</td>
<td>0.003 ±0.0</td>
<td>0.007 ±0.0</td>
<td>0.006 ±0.0</td>
</tr>
<tr>
<td>V</td>
<td>0.178 ±0.018</td>
<td>0.18 ±0.015</td>
<td>0.072 ±0.014</td>
<td>0.08 ±0.024</td>
<td>0.124 ±0.015</td>
<td>0.167 ±0.038</td>
<td>0.179 ±0.025</td>
<td>0.107 ±0.066</td>
<td>0.163 ±0.07</td>
<td>0.129 ±0.018</td>
</tr>
<tr>
<td>Y</td>
<td>0.35 ±0.24</td>
<td>0.1 ±0.02</td>
<td>0.09 ±0.01</td>
<td>0.09 ±0.01</td>
<td>0.1 ±0.02</td>
<td>0.04 ±0.0</td>
<td>0.05 ±0.01</td>
<td>0.11 ±0.06</td>
<td>0.2 ±0.04</td>
<td>0.15 ±0.03</td>
</tr>
<tr>
<td>Yb</td>
<td>0.023 ±0.013</td>
<td>0.009 ±0.006</td>
<td>0.01 ±0.008</td>
<td>0.009 ±0.009</td>
<td>0.007 ±0.006</td>
<td>0.003 ±0.002</td>
<td>0.006 ±0.007</td>
<td>0.007 ±0.005</td>
<td>0.015 ±0.007</td>
<td>0.012 ±0.008</td>
</tr>
<tr>
<td>Zn</td>
<td>13.7 ±19.3</td>
<td>5.6 ±1.9</td>
<td>26.8 ±68.2</td>
<td>9.1 ±4</td>
<td>8.2 ±4.3</td>
<td>8.8 ±3.1</td>
<td>9.8 ±9.3</td>
<td>6.7 ±3</td>
<td>14.8 ±26.8</td>
<td>20.8 ±46.5</td>
</tr>
</tbody>
</table>
Figure 2-3 Boxplot comparison of surface waters at baseflow condition for the ten elements selected for principal component analysis; concentration unit is μg l⁻¹ for all elements; for forest stream F2 only the sampling station before channel diversion (F2a) is shown; for better comparison concentration ranges are the same as in Figure 2-4.
Figure 2-4 Boxplot comparison of surface waters at fast flow condition for the ten elements selected for principal component analysis; concentration unit is µg l⁻¹ for all elements.
2.3.2 Emerging spatial patterns at baseflow (PCA)

The projection of all investigated variables on 2 factors (principal components) accounted for almost 66% of the variation in the baseflow data (Figure 2-5). All rare earth elements loaded negatively on principal factor 1, meaning that they were all correlated among each other. Most of the other elements were grouped together with pH and EC, loading positively on principal component 2 and negatively on component 1 (Figure 2-5). Rb plotted contrary to these elements.

For all further analyses, a subset was chosen (as explained in section 2.2.2) consisting of Ca, Ce, Gd, K, Mg, Na, Nd, Rb, Sr and Y (Figure 2-6). For baseflow, this subset explained 78% of the variation in the data with only two factors, with Ca, Mg, Na, Sr and K grouping mostly along factor 1 (i.e. explaining the largest amount of variation) and the rare earth elements on factor 2. The remaining element Rb showed a contrary loading compared to the other elements (see Figure 2-6a).

The first two factors already accounted for 78% of variation in the data. Including the third component, this value increased to more than 90%. Factor 3 was expressed exclusively by the occurrence of Rb and K (see Figure 2-6b), two elements with similar chemical properties and some interesting implications (see below, this chapter).
The ordination plot, including all baseflow samples according to station, revealed a distinct pattern of five groups plus one group of scattered data (Figure 2-7a). Group A contained the pasture stream samples (P1 and P2) and plotted negatively on factor 1. Also on this axis, a second group (B) consisted of samples of a disturbed stream (D2). Group C was arranged in the middle of the ordination plot and contained almost all river samples from the catchment outlet (R3). The uppermost main river samples (R1) plotted next to the F2b forest stream samples (group D). All F2b samples also plotted close to the water samples from the spring entering the same (F_well). The rest of the forest stream samples (F1, F2a) grouped tightly together (group E), with a positive loading on factor 1 and a slightly negative loading on factor 2. Close to this group, all rain and pampa samples as well as samples from the pasture spring (P_well) could be found. Lastly a sixth, much more diffuse group (F) included samples of the other disturbed (gravel excavation) stream (D1) and most samples of the
middle main river station (R2). This last group was the only one with a strong negative loading on both, factor 1 and 2. When plotting factor 1 against factor 3 in the ordination plot (Figure 2-7b), the groupings remained relatively clear. Only sampling sites F2b and R1 (former group D) diverged.

The first component of the PCA, accounting for 45% of the variation in baseflow samples and linked to the elements Ca, Mg, Na and Sr most probably reflects changes in soil physical and chemical processes under different land-uses. It shows a clear trend for pasture streams towards higher base cation concentrations. This is most likely attributable to the history of land conversion to pasture in this region (Biggs et al. 2002; Makeschin et al. 2008; Markewitz et al. 2001). Traditionally, forests are cut down and burned before grass turfs are planted on the freshly burned soil. If pastures become overgrown, burning is repeated or pastures are abandoned. The ashes resulting from repeated burning of pastures reduce the acidity in the soil. As a consequence, concentrations of exchangeable K, Ca and Mg have been found to be augmented in the uppermost layer (0-10cm) compared to forest soil (Makeschin et al. 2008).

Our aquatic data indicate that this increase of cations in the pastures upper soils is reflected in the water chemistry and constitutes the major component of water chemistry change. If it is assumed that groundwater is similar between sites these results suggest that near-surface flow is an important factor of influence for baseflow water chemistry in the study catchment. High cation concentrations could not be due to groundwater influence because if
2.3 Results and Discussion

this was the case, baseflow chemistry would be more similar among sites (Markewitz et al. 2001).

The second principle component distinguishes a component connected to rare earth element concentrations, attributable to a second type of land-use in the study area. Here, gravel excavation might be the cause for increased amounts of rare earth elements in stream water. According to Sholkovitz (1995) an increase in rare earth element concentration can be due to the weathering of parent rock. In weathering products rare earth elements are often accumulated (Patino et al. 2003; Price et al. 2005). The sampling station with a high gravel excavation activity (D1) was distinguished quite clearly by factor 2. The middle main river station (R2) obviously was largely influenced by the water coming from D1, and therefore also plotted close to this station in the PCA ordination. Another prominent characteristic of the D1 sub-catchment is its closeness to the only semi-paved road in the area. The road virtually follows the ridge of the D1 subcatchment until it crosses the Andean depression at ‘El Tiro’ at the western limit of our study catchment (Figure 2-1). Large amounts of construction material (pebbles, stones and cement) have been and still are transported into the catchment due to frequent construction works on the landslide affected road. Therefore it can be hypothesized, that the excavation and/or input of construction material leads to an increased washing out of rare earth elements, which is eventually reflected in the water chemistry. A geologic and/or a micro-climatic explanation for an accumulation of rare earth elements might also be possible, but cannot be proven up to now. The only geologic map available for the study area does not convey differences in geology, which is also confirmed by a study of Makeschin et al. (2008). It cannot be ruled out though, that the north-western part of the area differs slightly in geological features and/or in weathering patterns. The predominantly easterly weather regime might e.g. lead to a different micro-climate on the western slopes of the catchment. More detailed studies on geologic and climatic features in a small scale are needed to fill this gap.

Lastly, the third principal component is clearly associated with the occurrence of Rb and K. As both elements also have a high loading on the first component, they seem to be partly influenced by soil physical/chemical processes. Showing the same loading on a third component though, they are an indicator of yet another reason for differences in water chemistry, which at least explains some 12% of the remaining variation. Presumably, this third component comprises a forest vegetation accumulation factor, leading to an increased level of Rb in the organic layer of forest streams, which eventually enters the river. On pasture, vegetation biomass probably is too little, pH too high or roots too shallow to increase concentrations notably. Nyholm and Tyler (2000) report a negative correlation between Rb uptake by plants and soil organisms and K availability. According to Tyler (1997), acid soil conditions favour higher biological Rb availability and therefore plant Rb uptake. Especially wood-decaying fungi may accumulate Rb according to favourable soil conditions (Tyler 1982). In growth experiments with Carex pilufera, Drobner and Tyler (1998) observed an excess uptake of Rb from acid soils, but ascribe this to secondary effects of soil acidity
2.3 Results and Discussion

(e.g. leaching losses of K, increased solubility of Al), and not directly to pH. Higher Rb concentrations in forest stream water might therefore be an indirect biologic (vegetation accumulation) result of higher Rb availability in the acid soils of forest catchments. Our finding, that Rb concentration is higher and K concentration lower in forest stream water and therefore probably also in the soil also raises the question if forest trees have to adapt to low K levels in the soil. This is answered by Soethe et al. (2008) who report foliar K deficiency at 3000 and 2400 m under forested soils in our study area.

2.3.3 Well water chemistry

As mentioned in section 2.2.1, the stream water of forest stream F2 was largely diverted into a channel, and only a fraction of this water continued on into direction of the sampling point F2b. This fraction mixed with spring water emerging from a rock fracture (Fwell). The water analysis revealed that the chemistry of Fwell was quite different from the stream water F2a, so the mixing resulted in a significant change of water chemistry at sampling point F2b. This mixing was reflected in the baseflow ordination plot (Figure 2-7a). Interestingly, well water sampled from the pasture sites (Pwell) was chemically most similar to the forest stream samples (Figure 2-7a), again indicating that geological differences among subcatchments are of minor importance for the observed differences in baseflow water chemistry. Compared to the other well waters (Fwell, Rwell) Pwell showed low concentrations of Ca, Mg and Na, slightly lower concentrations of SiO2 and similar concentrations of K. The Na/(Na+Ca) ratio, which has been used as an indicator of cation inputs by weathering (ratio <<1) or precipitation (ratio approaching 1) (Markewitz et al. 2001) is 0.87 for Pwell (0.72 for Fwell, 0.76 for Rwell). It is therefore assumed that Pwell is fed by rain and fog water and probably runs as fast sub-surface flow through cracks in the rock, where it takes up some silicate. Rwell and Fwell are similar in their Ca, Sr, Mg, K and SiO2 composition, but differ in Na (with Rwell having almost twice as much Na). For the southern slope of the study catchment Wilcke et al (2001) observed higher Na concentrations in the A and B horizon compared to the organic layer. Conversely, Mg and Ca concentrations were found to notably decrease. Thus it seems clear, that Rwell and Fwell are both subsurface flows, with Rwell probably having longer residence times as observed by the enrichment of Na. The closeness of D2 to Rwell in Figure 2-7a might hint to a higher contribution of groundwater sources for this stream. Further analysis such as 2H and 18O isotope based estimations of water mean transit times should be conducted to further explain these observations.

The first hypothesis that the analysis of hydro-chemical characteristics of surface and subsurface flows can help to elucidate sources and flow-paths of water is in agreement with the results of this study. It can also be concluded, that the differences in water chemistry are the consequence of land-use practices, and are not due to differences in geological features (second hypothesis).
2.3.4 Emerging spatial patterns at fast flow (PCA)

Compared to baseflow, the fast flow projection of factor 1 and 2 was almost identical in respect to the relation of the variables to each other and their loadings, respectively (compare Figure 2-6a and c). Ca, K, Mg, Na and Sr were still only associated with factor 1, the rare earth elements on factor 2. Rb and K again were loading on factor 3 and showed opposite loadings on factor 1 (compare Figure 2-6b and c). In general, the principal components 1 and 2 explained 80% of the variation in fast flow data (Table 2-4); principal component 3 explained an additional 12% of the variation.

The ordination plot of the fast flow data (Figure 2-7c) revealed a slightly more compressed pattern compared to the baseflow samples (Figure 2-7a). Only forest (F1, F2a) and pasture (P1, P2) streams, equivalent to groups A and E still separated relatively clearly from the other groups. However former groups B, C, D and F were mixing more or less strongly. In general, factor 1 decreased in importance during fast flow, whereas factor 2 increased (Table 2-4). Factor 1 therefore seems to be rather associated with baseflow than with fast flow conditions.

| Table 2-4 Eigenvalues of, and % variability explained by, the PCA factors. |
|-----------------------------|---------------------|---------------------|---------------------|
| Factor | Eigenvalue | Cumulative | % Total | % Cumulative |
| Baseflow | | | | |
| 1 | 4.52 | 4.52 | 45.20 | 45.20 |
| 2 | 3.29 | 7.81 | 32.98 | 78.18 |
| 3 | 1.22 | 9.04 | 12.20 | 90.38 |
| Fast flow | | | | |
| 1 | 4.34 | 4.48 | 43.42 | 43.42 |
| 2 | 3.63 | 7.97 | 36.24 | 79.67 |
| 3 | 1.24 | 9.21 | 12.43 | 92.10 |

| Table 2-5 Comparison of mean concentrations of selected parameters in tropical streams. FWM = flow weighted mean concentrations |
|-----------------------------|---------------------|---------------------|---------------------|
| | mg l⁻¹ | mg l⁻¹ (FWM) | mg l⁻¹ | mg l⁻¹ | mg l⁻¹ |
| Ca | 2.22 - 6.27 | 4.90 - 10.99 | 6.30 - 14.30 | - | 0.20 - 2.15 |
| Cl | 6.24 - 8.82 | - | 2.80 - 23.70 | - | 0.77 - 0.85 |
| K | 0.22 - 0.51 | 0.70 - 2.46 | 0.30 - 5.30 | - | 0.27 - 0.52 |
| Mg | 1.20 - 4.42 | 1.84 - 4.20 | 4.10 - 9.90 | - | 0.14 - 0.69 |
| Na | 4.36 - 7.52 | 3.56 - 7.94 | 10.80 - 21.40 | - | 0.54 - 2.36 |
| NO₃ | 0.24 - 0.29 | 0.51 - 1.23 | 2.10 - 3.00 | 0.05 - 0.68 | 0.72 - 1.11 |
| SO₄ | 2.24 - 2.67 | - | 0.10 - 1.60 | - | 0.59 - 1.37 |
Relative changes in mean element concentration between base- and fast flow condition are summarized in Table 2-6 and reveal some general patterns. For all sites, Na concentrations significantly decreased during fast flow compared to baseflow condition, which can be attributed to the mixing of stream water with less concentrated water such as rainfall (dilution pattern). However, J. Boy et al. (2008b) also report low Na concentrations in soil water of 15 and 30 cm depth (~0.5 mg l\(^{-1}\)) compared to stream water (~3 mg l\(^{-1}\)) for forest soils and microcatchments in the same study area. A dilution effect could therefore also occur through the mixing of stream water with soil water during events. In contrast to Na, rare earth element (REE) concentrations increased significantly during fast flows (flushing pattern). As mentioned earlier, REEs are mostly associated with weathering products, and therefore should be higher in soil layers containing weathered material, as for example occurring in the A and B horizon. Measurements of soil water from the southern, forested slope of the San Francisco catchment indicate that REE concentrations are higher in 30 cm soil depth compared to 15 cm soil depth (unpublished data). REE concentrations in rain, on the other hand, were at least an order of magnitude lower than stream water concentration in our data. Thus, both changes in fast flow concentration (Na decrease and REE increase) can be explained by storm flow being created by a flushing of soil water from around 30 cm depth, at least for the forested sub-catchments. For pasture sites, measurements of soil water concentration of Na and REE are still missing, so no general conclusions can be made.

Table 2-6 Comparison of base- to fast flow concentrations for the ten elements used in PCA. Arrows indicate significant concentration change (↑ means higher concentration in fast flow, and ↓ means lower concentration in fast flow, “-” indicates that no significant change was observed). Cells with a regular pattern in more than three stations are shaded in grey.

<table>
<thead>
<tr>
<th></th>
<th>Na</th>
<th>Ca</th>
<th>Mg</th>
<th>K</th>
<th>Sr</th>
<th>Rb</th>
<th>Y</th>
<th>Ce</th>
<th>Nd</th>
<th>Gd</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
</tr>
<tr>
<td>D2</td>
<td>↓</td>
<td>-</td>
<td>↓</td>
<td>-</td>
<td>↓</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
</tr>
<tr>
<td>F1</td>
<td>↓</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
</tr>
<tr>
<td>F2a</td>
<td>↓</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
</tr>
<tr>
<td>F2b</td>
<td>↓</td>
<td>↓</td>
<td>↓</td>
<td>-</td>
<td>↓</td>
<td>-</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
</tr>
<tr>
<td>P1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>↑</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>↑</td>
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<tr>
<td>P2</td>
<td>↓</td>
<td>-</td>
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<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
</tr>
<tr>
<td>R1</td>
<td>↓</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>↑</td>
<td>-</td>
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<tr>
<td>R2</td>
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</tr>
<tr>
<td>R3</td>
<td>↓</td>
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<td>↑</td>
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</tr>
</tbody>
</table>
According to the third hypothesis, stream waters should be completely mixed in the fast flow ordination plot. This was not the case. However, there was some mixing in the plot, and the formerly clearly separated groups partly converged. Rain events therefore were not capable of completely masking the chemical fingerprint of the subcatchments. This might be due to the assumed flushing of soil water during fast flow events. The fact that ion ratios are rather influenced by geographical location than by stage of stream flow has also been reported by McNeil et al. (2005) for mesoscale catchments in Queensland, Australia. It was also established, that rare earth elements are important tracers in clear headwater streams, as they are capable of conveying weathering patterns and water source areas (Chung et al. 2008; Picouet et al. 2002; Velbel & Price 2007). This confirms the fourth hypothesis, that standard parameters such as pH, EC, SO4 or Ca are not sufficient to explain controls on water chemistry in clear mountain streams.

2.4 Conclusion

Studies investigating alterations in soil processes of tropical montane forests after land-use change are rather abundant (Bautista-Cruz & del Castillo 2005; Jin et al. 2000; Rhoades et al. 2000), but the influence of these changes on the water chemistry has mostly been neglected. This study is one of the first to investigate differences in water element composition in closely related tributaries with the objective of defining the main controls on water chemistry at a catchment scale.

It was shown, that principal component analysis indeed is effective in assisting in the evaluation of spatial surveys of water chemistry change, even if concentrations of nutrients and elements are low. The inclusion of over 30 elements allowed identifying those with the highest potential to explain predominant catchment processes. Standard parameters like pH and conductivity were not sufficient to differentiate between sampling stations in detail. Only with the inclusion of rare earth element (REE) concentrations it was possible to separate more sampling stations, highlighting gravel excavation as a second important anthropogenic process influencing water chemistry in the catchment. Rare earth elements, which have been extensively used as tracers for chemical weathering, also gave insights into storm flow origin. The finding, that Rb concentration was higher and K concentration lower in forest streams support the results of other studies that forest trees have to adapt to low K levels in the soil. The inclusion of well water from the F2 sub-catchment could explain at least some of the differences between F2b and the other forest-stream stations (F1, F2a). Also a decoupling of fast and slow subsurface flow paths could be observed by analyzing the three well waters. This result highlights the importance of sampling springs and seeps in mountain catchments, as also claimed by Soulsby et al. (2007).

The central finding is that in cloud forest catchments land-use practices not only influence soil characteristics but also change water chemistry through various ways. Due to the extreme low nutrient and element concentrations in the streams, even small contributions
of ion-rich water (e.g. well water) can already change the overall water quality of streams. This high sensitivity of cloud forest catchments certainly has implications for land-use and water quality management.
3 Solute behaviour and export rates under different land-uses

3.1 Introduction

Tropical rivers are, at all scales, highly complex and multifaceted ecosystems. Unravelling their way of functioning is still a challenge to the scientific world. Most investigations focus on single aspects of tropical river ecology. There are, for example numerous studies on hydrological processes (Ataroff & Rada 2000; Bruijnzeel 2001; Bruijnzeel 2004; Buytaert et al. 2005; Perrin et al. 2001) or on biogeochemical issues (Aucour et al. 2003; Bücker et al. 2010; Elbaz-Poulichet et al. 1999; Elsenbeer et al. 1995). Others have tried to combine the effect of hydrology and biogeochemistry to gather more profound information on tropical catchment processes (Biggs et al. 2006; Borbor-Cordova 2006; Boy et al. 2008b; Bruijnzeel 1991; Elsenbeer & Lack 1996; Lesack & Melack 1996; McDowell & Asbury 1994; Salmon et al. 2001). Virtually all studies face the problem of the interplay of too many factors (climate, geology, topography, anthropogenic influence, vegetation) to derive general conclusions on the drivers of catchment functioning. In this respect, the forested mountain ranges of the Andes present an interesting opportunity for investigations on the effect of human disturbance on catchment processes. Montane headwater areas are different to other stream networks in the respect that they often lack a well-defined riparian zone. The steep, rocky relief and rather narrow valley bottoms can lead to relatively fast surface or subsurface flows (Tsujimura et al. 2001). The impact of slow, groundwater dominated processes is mostly of minor importance, and the streams are characterized by close terrestrial-aquatic linkages near to and along the soil surface. Because of these close linkages, such headwaters tend to be very sensitive to any natural or anthropogenic disturbance (Lowe & Likens 2005).

Deforestation and conversion to pasture or agriculture is one of the major disturbances for neotropical montane forests (Bubb et al. 2004). To be able to predict the impact of these disturbances on the ecosystem it is vital to investigate and quantify nutrient and water flow under different vegetation cover and land management systems. Also, according to McClain Naiman (2008), Saunders et al. (2006) and Buytaert et al. (2006) there is an urgent need to improve our knowledge on Andean solute fluxes to downstream areas, for the reason that they exert a strong influence on the ecology and productivity of amazonian lowland rivers and floodplains. Most studies reporting export values for tropical rivers are looking either at forested or at deforested sites (Biggs et al. 2006; Boy & Wilcke 2008; Liu et al. 2003; McDowell & Asbury 1994; Newbold et al. 1995; Yusop et al. 2006). Thus, there is a noteworthy shortage of studies investigating both tropical pasture and forested catchments at the same time. Only two comparative studies have been published (both from Brazil) where differences in hydrologic fluxes and solute concentrations were investigated for undisturbed forest and pasture sites (at 143 m a.s.l. and 200-500 m a.s.l) (Germer et al. 2009; Neill et al. 2001). Neill et al. (2001) detected lower concentrations of NO₃, but higher
3.2 Material and Methods

3.2.1 Sampling scheme

We sampled six subcatchments equipped with automatic gauging stations (Figure 3-1A). Two gauging stations were located in tributaries draining subcatchments in the north with mixed land-use (P1 and D2), two in tributaries draining primary forest in the south (F1, F2) and two points in the main river (R1, R3). For more information on the different subcatchments see Table 3-1.

Water samples were taken over one year (April 2007-May 2008), weekly to biweekly except for P1 where sampling began in September 2007. Analytes included \( \text{NO}_3 \), \( \text{PO}_4 \), \( \text{SO}_4 \), \( \text{NH}_4 \), total organic carbon (TOC), Ca, Mg, Na and K. Samples were taken with pre-washed PE bottles directly in the field and were immediately stored cool (Ca, Mg, Na, K) or frozen (TOC, \( \text{NO}_3 \), \( \text{PO}_4 \), \( \text{SO}_4 \)) until analyzed. We tested for ammonium directly in the field using a quick test (Aquaquant 1.4428, Merck, Darmstadt, GER) which revealed, that concentrations were below the detection limit of 0.025 mg l\(^{-1}\). Concentrations of \( \text{NO}_3 \), \( \text{PO}_4 \), \( \text{SO}_4 \) were determined by ion chromatography with detection limits of 0.1 mg l\(^{-1}\) for \( \text{NO}_3 \) and \( \text{SO}_4 \) and 0.5 mg l\(^{-1}\) for phosphate (DX-120, Dionex Corporation, CA, US). Every sample value represents the mean of two consecutive measurements of the same sample. Phosphate was found to be below the detection limit in all samples and was therefore excluded from our analysis. TOC concentrations were quantified by high temperature oxidation as requested by European DIN norms (EN1484) using a LiquiTOC analyzer (elemental analytics, Hanau, DE). Detection limit for TOC was 0.3 mg l\(^{-1}\). Lastly, element concentrations of Ca, Mg, Na and K were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS, Agilent 7500ce, Agilent Technologies, Böblingen, DE). Detection limits were 0.06, 0.01, 0.09, 0.05 mg l\(^{-1}\) for Ca, Mg, Na and K, respectively.
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Figure 3-1 Overview of the study area. Land use data from Landsat ETM+ satellite images provided by Göttlicher et al. (2009).

Table 3-1 Overview of the land-use characteristics of the study catchments. Data from Landsat ETM+ satellite images (Göttlicher et al. 2009).

<table>
<thead>
<tr>
<th>Land use [%]</th>
<th>F1</th>
<th>F2</th>
<th>P1</th>
<th>D2</th>
<th>R1</th>
<th>R3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pasture/bracken fern</td>
<td>1.1</td>
<td>1.6</td>
<td>66.7</td>
<td>10.1</td>
<td>3.2</td>
<td>9.0</td>
</tr>
<tr>
<td>Forest</td>
<td>89.7</td>
<td>79.5</td>
<td>23.4</td>
<td>73.1</td>
<td>66.8</td>
<td>67.7</td>
</tr>
<tr>
<td>(Sub)Páramo</td>
<td>8.9</td>
<td>18.7</td>
<td>9.0</td>
<td>15.6</td>
<td>29.1</td>
<td>20.9</td>
</tr>
<tr>
<td>Others</td>
<td>0.2</td>
<td>0.2</td>
<td>0.9</td>
<td>1.1</td>
<td>0.9</td>
<td>2.4</td>
</tr>
</tbody>
</table>

| Total area [ha]      | 130   | 450   | 70   | 1140 | 3500 | 7600 |

Hydrological measurements began at the same time as the sampling period. Water level sensors were installed at the outlet of the subcatchments (F1, F2, P1, D2) and in the main river (R1, R3), one of them being the outlet of the study catchment (R3). Stage data were collected every 5 min (ODYSSEY water level loggers, Dataflow Systems PTY LTD, NZ), with some exceptions due to difficulties with instruments in this remote area. At all points discharge measurements were made, with a mean of 36 measurements per gauging station, using a digital flow-meter (FLO-MATE, Marsh-McBirney Inc., Maryland, US) and a flow probe (FP101, Global Water Inc., California, US) to set up stage-discharge curves. At site P1 a V-
notch concrete weir could be installed, for the other stations the natural stream transects were used.

3.2.2 Nutrient export calculation

Because water sampling was done at a much lower frequency than discharge measurements, nutrient export had to be approximated by interpolation or regression. Schleppi et al. (2006) compared 3 possible methods, namely (1) using the mean or flow weighted mean concentration values for a distinct period, (2) using linear interpolation for the interval between measurements and (3) regression of nutrient concentration with discharge. In the same study, Schleppi et al. (2006) observed, that if concentrations were discharge dependent, methods (1) and (2) could generate strongly biased results towards under- or overestimation of nutrient export. According to them, the regression based calculation seemed to be the best approach.

To be as accurate as possible in the export calculation three possible concentration dependencies (time-, discharge- dependent, no relation) were tested separately for all measured parameters (NO$_3$, SO$_4$, TOC, Ca, Mg, Na and K) and for each stream. If concentrations were time-dependent export was calculated in a monthly time step and summed up for yearly rates. If concentrations were discharge dependent, we used the regression based export calculation method as proposed by Schleppi et al. (2006). The model uncertainties were then expressed by adding 95% confidence intervals to the regression lines.

**Nutrient export calculation - Concentration dependent on time**

In the first step of our analysis, time-dependence of nutrient concentrations was tested. For this test, samples were bulked into seven periods for each stream: (i) Apr/May’07, (ii) Jun/Jul’07, (iii) Aug/Sep’07, (iv) Oct/Nov’07, (v) Dec’07/Jan’08, (vi) Feb/Mar’08 and (vii) Apr/May’08. Two months data were aggregated for this analysis as a consequence of the sampling scheme, which implied only two to four samples per month. Means of element and nutrient concentration (with n = 4 to 8) were compared between groups using a t-test and p = 0.01. For those parameters exhibiting time dependent changes monthly and annual export was calculated by multiplying the sum of the monthly discharge with the mean of the two-monthly concentration.

**Nutrient export calculation - Concentration dependent on discharge**

For all parameters not showing time-dependent changes concentration relations with discharge were tested. These were obtained by determining instantaneous discharge at the time of sampling and regression analysis of instantaneous discharge versus instantaneous concentration. The following curve adaptations for concentration-discharge regressions

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were tested: (a) Hyperbolic function, (b) exponential function, (c) linear function with or without logarithmic transformation.

The analysis was started by testing all three fitting procedures (a), (b) and (c), narrowing it down to the one with the best adaptation, i.e. best fit ($R^2$) respectively the smallest sum of residuals. Additionally, it was tested if residuals were biased towards base-or fast flow. After finding the best adaptation for the data, the significance of the regression was tested. Only significant regression coefficients ($p = 0.01$) were retained. All statistical analyses were conducted using STATISTICA 6.0, StatSoft®.

(a) The hyperbolic function was proposed by Johnson et al. (1969) and has been used by various authors (Aulenbach & Hooper 2006; Salmon et al. 2001; Stelzer & Likens 2006). It was found to fit better than other models. It is also more process-oriented, presenting a two compartment mixing model, with:

\[
c = \frac{1}{1 + \beta \cdot Q} \cdot c_6 + c_a
\]
\[
c_6 = c_0 - c_a
\]
Where $c$ [mg l$^{-1}$] is the modelled concentration of the solute, $c_a$ [mg l$^{-1}$] is the concentration of the solute in the solution added to the prior solution, $c_0$ [mg l$^{-1}$] is the concentration of the solute in the prior solution, $c_6$ is the difference between prior and added solution, $Q$ [m$^3$ s$^{-1}$] is discharge and $\beta$ is a constant (Johnson et al. 1969). The model parameters $c_0$ and $c_a$ were adapted to obtain the best fit for the data.

(b) The exponential function has the common form:

\[
c = a \cdot e^{(b \cdot Q)}
\]
where $c$ [mg l$^{-1}$] is the modelled concentration of the solute, $Q$ [m$^3$ s$^{-1}$] is discharge and $a$ and $b$ are fitting parameters.

(c) A linear adaptation was tested with and without logarithmic transformation.

\[
c = a \cdot Q + b
\]
The common form of a linear function was taken, with $a$ and $b$ as model parameters, $c$ being the modelled concentration and $Q$ the discharge.

*Nutrient export calculation – no dependence*

If concentrations were neither time, nor discharge dependent (i.e. both the temporal analysis and the regression were not significant) export was calculated as the median concentration times the monthly discharge. The median was preferred to the mean to account for extreme values and outliers.
3.2.3 Nutrient input via precipitation

Nutrient input in montane cloud forests not only occurs by direct precipitation, but a large amount of water and nutrients also enters the forest by a process called cloud stripping (Hostettler 2002). The scarcity of qualitative rain and cloud water nutrient data in tropical mountain forests, as well as the difficulty of quantitative measurements of the amount of cloud water contribution have, with few exceptions (Boy & Wilcke 2008; McDowell & Asbury 1994) prevented researchers from calculating nutrients budgets in these ecosystems.

For a first estimation of nutrient input via precipitation, rain samples (n = 19) were collected at the lowermost precipitation gauge (Figure 3-1A) on an event basis and were analyzed for the same chemical constituents as the stream water. TOC could not be analyzed, though, because not enough rain water was available for the analysis. Quantitative total precipitation data (i.e. the sum of cloud and fog water input) was available for five stations situated in our study area at different altitudes (Figure 3-1C). This daily pluviometric data was kindly provided by Rütger Rollenbeck and Thorsten Peters on the project website database (www.tropicalmountainforest.org).

Due to the high dependence of precipitation amount on altitude, the yearly amount of rain was computed for each subcatchment by using Thiessen polygons. For this, rainfall data of four meteorological stations were used to derive precipitation lapse rates, and the average precipitation for each of the subcatchments was calculated using area weighted elevation correction. For more information on Thiessen polygons and interpolation methods see available literature (Goovaerts 2000; Hartkamp et al. 1999; Vicente-Serrano et al. 2003). Nutrient input was calculated as the median of the concentration data for rain samples multiplied by the amount of yearly precipitation in each subcatchment.

To account for concentration differences in fog and rainwater a second approach to calculate nutrient input was also tested. Literature values of fog nutrient concentration from the study area were taken (Beiderwieden et al. 2005) and the input calculation was conducted with the assumption of 80 % rainwater and 20 % fog water contribution to total precipitation based on values provided by Bruijnzeel (2004).

3.3 Results and discussion

3.3.1 Chemistry of stream water

Stream chemistry in the San Francisco catchment was clearly dominated by Na, as can be seen in Figure 3-2, where mean molar concentrations of the four investigated cations were aggregated for each sub-catchment. Under mixed land-use and in the main river, Ca was the second most abundant cation, whereas in forested streams, Ca, K and Mg were equally important. Cation concentrations in the forested streams were generally much lower than in the mixed land-use and main river catchments, although K concentrations were rather comparable between streams. NO₃ concentration was below the detection limit of 0.1 mg l⁻¹
in stream P1 (Table 3-2), and we subsequently used a hypothetical value of half the detection limit for NO$_3$ export calculations in this subcatchment. Concentrations of SO$_4$ were elevated in both, P1 and D2, but D2 had the highest values of all streams (Table 3-2).

Meybeck & Helmer (1989) tried to distinguish different stream types with respect to their dissolved major elements (SiO$_2$, Ca, Mg, K, SO$_4$) as well as pH and electric conductivity. According to their distinctions our forested waters resemble closest to pristine Amazonian clear waters. The overall median molar ratio of Na:Cl in stream water in our study area was 3.1 for baseflow and 2.4 for fast flow during 2007/2008 (Bücker et al. 2010), which differs considerably from the maritime (precipitation) ratio of 0.86 (Keene et al. 1986). The high Na concentrations in the water therefore do not seem to originate from atmospheric input (sea spray) but rather from mineral weathering. This is also confirmed by much higher Na concentrations in the A, B and C horizon compared to the organic layer, as was found for forested microcatchments located within the R1 catchment (Boy et al. 2008b).

![Stacked histograms of mean molar concentrations of the investigated cations.](image)

Table 3-2 Overview of the flow weighted mean (FWM) concentrations (mg l$^{-1}$)

<table>
<thead>
<tr>
<th></th>
<th>F1</th>
<th>F2</th>
<th>P1</th>
<th>D2</th>
<th>R1</th>
<th>R3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>0.18</td>
<td>0.22</td>
<td>1.56</td>
<td>1.57</td>
<td>0.70</td>
<td>0.94</td>
</tr>
<tr>
<td>K</td>
<td>0.21</td>
<td>0.22</td>
<td>0.51</td>
<td>0.27</td>
<td>0.23</td>
<td>0.26</td>
</tr>
<tr>
<td>Mg</td>
<td>0.13</td>
<td>0.13</td>
<td>0.65</td>
<td>0.44</td>
<td>0.26</td>
<td>0.30</td>
</tr>
<tr>
<td>Na</td>
<td>0.36</td>
<td>0.39</td>
<td>1.98</td>
<td>1.21</td>
<td>0.91</td>
<td>0.84</td>
</tr>
<tr>
<td>NO$_3$</td>
<td>0.69</td>
<td>0.54</td>
<td>n.d.</td>
<td>0.62</td>
<td>0.55</td>
<td>0.56</td>
</tr>
<tr>
<td>SO$_4$</td>
<td>0.54</td>
<td>0.48</td>
<td>0.83</td>
<td>0.85</td>
<td>0.59</td>
<td>0.72</td>
</tr>
<tr>
<td>TOC</td>
<td>6.88</td>
<td>2.54</td>
<td>4.87</td>
<td>4.55</td>
<td>3.88</td>
<td>5.44</td>
</tr>
</tbody>
</table>

n.d. = not detectable

For Mg and Ca Boy et al. (2008b) reported higher concentrations in the organic layer, compared to deeper layers. According to the same study, K concentrations are similar to Na
in that they also increase with depth, but elevated K concentrations can as well be found in throughfall and litter leachate. For Ca, Mg and K therefore a combination of atmospheric and weathering input is most likely.

Catchment P1 is primarily used as an extensive pasture, with 66.7 % of its area covered by pasture grass (*Setaria sphacellata*) or bracken fern (*Pteridium* spp.). The discovery, that tropical pasture streams exhibit lower NO$_3$ concentrations compared to forested catchments has also been published by Neill et al (2001), who attribute this to higher NO$_3$ production, connected to N mineralization and net nitrification in forest soils compared to pasture soils. Peterson et al. (2001) state that in headwater streams, NO$_3$ removal occurs either through biological assimilation or denitrification. Faster biological assimilation could occur in pasture stream P1 through algae growth, which is considerably larger in P1 due to elevated light input as noted during field observations. A third explanation for the observed NO$_3$-pattern was proposed by Biggs et al. (2006), who describe the decomposition of leaf litter as one important pathway of N input into forest catchments, a process which is clearly reduced in pasture streams. Lastly, Rhoades et al. (1998) investigated soil N availability in *Setaria* pasture on the western slope of the Andes and discovered, that *Setaria* reduces soil N concentrations to <20% of that in intact montane forests. Shading experiments with N-fixing (*Inga spec.*) and non-N-fixing (*Psidium spec.*) pasture trees revealed that the plant species was responsible for the observed changes in soil-N and not the changing climate regime. However, in the study catchment it is still not verified in how far the numbers of N-fixing organisms change with conversion to pasture (S. Setaro pers. comm.). A combination of several factors is probable, though. As far as the other disturbed subcatchment D2 is concerned, the larger size of the catchment, with a relatively minor contribution of pasture and bracken fern area of 10.1 % seems to mitigate or impede the reduction of NO$_3$ in the water, as described for P1.

SO$_4$ input can occur via atmospheric dry deposits which originate e.g. from volcano eruptions or biomass burning and via fog water (Bendix et al. 2004). As already mentioned in chapter 2, the formation of pasture land in the study area is achieved by cutting down and burning the forest trees before grass turfs are planted on the freshly burned soil (Makeschin et al. 2008). Elevated SO$_4$ concentrations are therefore expected in our mixed, pasture influenced catchments. The high value in D2 compared to P1 probably originates from a combination of higher fog water input and the input of ashes via burning. A higher fog water input in D2 is reasonable, if forest cover and therefore cloud interception is higher, as occurring here.

### 3.3.2 Time-dependent changes in stream nutrient concentration

The tests on seasonality revealed time-dependent concentration changes for NO$_3$ and SO$_4$ in all six subcatchments (Figure 3-3). SO$_4$ concentrations were constant throughout April to December 2007, with higher concentrations in catchments with mixed land-use (P1, D2) and
3.3 Results and discussion

at the outlet (R3), and the lowest in the forested streams F1 and F2. During the second half of the study period, starting in December 2007/January 2008, the concentrations started to decrease at all stations. For NO$_3$, concentrations were comparably high throughout the catchment (~1100 µg l$^{-1}$) in April/May 2007 but declined constantly down to ~300 µg l$^{-1}$ in April/May 2008.

![Figure 3-3 Seasonal changes in water chemistry during the study period for SO$_4$ (lower panel) and NO$_3$ (upper panel). In the upper panel the west wind frequency (hours per day) is shown; wind data kindly provided by T. Peters (www.tropicalmountainforest.org, FOR816 database).](image)

The decrease of SO$_4$ concentrations coincides with an increase in west wind frequency in our catchment (Figure 3-3). Atmospheric nutrient input for the study area predominantly originates from the east, namely from biomass burning and Sahara dust among others (Boy & Wilcke 2008; Boy et al. 2008a; Fabian et al. 2005). Bendix et al. (2004) state, that SO$_4$ concentrations are elevated in total precipitation during special events such as volcano eruptions or increased biomass burning in the Amazon. If these inputs are reduced by a change towards west wind dominated weather patterns, concentrations in the streams are likely declining as well. The change in wind direction pattern was probably connected to a weakening of the La Niña event, starting at the end of 2007, which caused an increase in sea surface temperature along the Niño regions 1 and 2 (i.e. the ecuadorian pacific coast).
The abruptness of the decrease in SO$_4$ concentrations in December 2007/January 2008 and contrasting to this, the steady decrease in NO$_3$ concentrations over the whole study period, are still a matter of further research, though. Additionally, longer time series are needed to more thoroughly address temporal patterns and to confirm these short-term findings.

3.3.3 Discharge dependent changes in stream nutrient concentration

The test on concentration-discharge relation was significant in 20 out of the 30 cases (i.e. 6 catchments times the remaining 5 parameters). Na and TOC were always significantly related to discharge while for Ca, Mg and K differences among the catchments occurred (Table 3-3 and Figure 3-4). Ca, Na and Mg were found to be inversely related to discharge, whereas TOC increased with discharge. For K no relation to water flows was observed, with the only exception in subcatchment P1, where K concentration increased with higher discharge. In forested streams F1 and F2 no relation to discharge for Ca, K or Mg was observed. The behaviour of the cations during storm events can also be observed in Figure 3-5, where concentration changes during a major event in June 2008 are depicted for the catchment outlet R3. Here, Na declined most strongly during storm flow, but also Ca and Mg reacted in a similar way. Only K concentration changes were ambiguous, decreasing at first and slightly increasing soon after.

| Table 3-3 Coefficients of determination for discharge-concentration relations. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                 | Ca              | K              | Mg              | Na              | TOC             |
| F1              | M               | M              | M               | Exp R$^2$=0.88  | In-In R$^2$=0.72 |
| F2              | M               | M              | M               | Exp R$^2$=0.62  | In-In R$^2$=0.44 |
| P1              | Exp R$^2$=0.30  | Hyp R$^2$=0.49 | Exp R$^2$=0.49  | Exp R$^2$=0.65  | Lin R$^2$=0.87  |
| D2              | M               | M              | Hyp R$^2$=0.38  | Exp R$^2$=0.59  | Lin R$^2$=0.41  |
| R1              | Hyp R$^2$=0.33  | M              | Hyp R$^2$=0.41  | Hyp R$^2$=0.55  | Lin R$^2$=0.57  |
| R3              | Hyp R$^2$=0.52  | M              | Hyp R$^2$=0.68  | Hyp R$^2$=0.81  | In-In R$^2$=0.77 |

Exp = exponential relation, (significant at $\alpha = 0.01$)
Hyp = hyperbolic relation, (significant at $\alpha = 0.01$)
Lin = linear relation, (significant at $\alpha = 0.01$)
In-In = linear relation with logarithmic transformation, (significant at $\alpha = 0.01$)
M = median value, taken when no other adaptation proved significant.
A variety of studies report decreases in Ca, Mg, Na concentration with increasing discharge (Anderson et al. 1997; Elsenbeer et al. 1994; Grimaldi et al. 2004; Tsujimura et al. 2001). Furthermore McDowell & Asbury (1994) and Newbold et al. (1995) describe negative relations of Ca, Na and Mg and no relation of K with discharge, as was also observed in the present study. Goller et al. (2006), Newbold et al. (1995) and Townsend-Small et al. (2007) observed clear increases in organic carbon concentration during rain events. In general, decreases in concentrations during storm flows are mostly ascribed to a dilution of stream water with less concentrated water, such as rain, whereas an increase of concentration during storm flow is ascribed to a flushing of accumulated material (Elsenbeer et al. 1994).

According to Boy et al. (2008b) Na inputs to forested streams within the R3 catchment are likely due to chemical weathering of deeper subsurface layers. Our data strongly support these findings. A decrease in the contribution of deeper water sources to total flow would therefore explain the observed pattern of decreasing concentrations during storm flow (see also Bücker et al. (2010)). This pattern applies to all investigated subcatchments and is obviously not land-use dependent. However, the reaction of Mg, K and Ca concentration varied between land-uses and might be explained by slightly different flow paths. Our conceptual understanding is, that during a rain event, storm flow in the forest originates predominantly from the organic layer (OL) and the upper soil layers, with low Na concentration but moderate Ca and Mg and high TOC concentrations. For K, Boy et al. (2008b) found, that concentrations are low in the solid phase of the OL, but that it is highly concentrated in throughfall and litter leachate. Due to the lack of an OL in the pasture, the storm flow here probably originates from the rooted surface layers and the A horizon, but a portion of the rain also enters the stream as overland flow. According to Makeschin et al. (2008) the upper 0-30 cm of pasture soil are much less concentrated with K, Mg and Ca than the OL of the forest. The decreasing concentrations of Mg and Ca in the pasture during storm flow are thus explained. High levels of K, which might be deposited on, or leached by the pasture leaves, could lead to the observed pattern of increased or steady state condition of K during high flows, even though K concentrations in the soil are not high (Elsenbeer et al. 1994).
Figure 3-4 Concentration-discharge relations of Ca, K, Mg, Na and TOC for all six study catchments.
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Figure 3-5 Behaviour of nutrient concentration during a storm in June 2008. Discharge and precipitation amount are also shown. Nutrient data from station R3.

3.3.4 Nutrient export

For the calculation of annual nutrient export we needed continuous discharge time series. Data gaps in the time series were filled by regression with other discharge stations. Gaps in R1 (65% due to a large sensor failure), P1 (50% which corresponds to the period April to September 2007), F1 (21% due to sensor failures) and F2 (12% due to sensor failures) had to be refilled by the following regressions (in the order displayed below), using ln-transformed data:

\[
\begin{align*}
    Q(F1) &= 0.67 \cdot Q(R1) - 2.14 & R^2 &= 0.63 \\
    Q(F2) &= 0.74 \cdot Q(R1) - 1.24 & R^2 &= 0.70 \\
    Q(R1) &= 0.94 \cdot Q(R3) - 1.08 & R^2 &= 0.90 \\
    Q(P1) &= 0.66 \cdot Q(R3) - 5.43 & R^2 &= 0.43
\end{align*}
\]

The large gaps in R1 were seen as critical in the further analysis, but due to the very good value for $R^2$ in the regression, the bias in the hydrograph was assumed to be small. In Figure 3-6 yearly export values with 95% confidence intervals are depicted. For Ca, Mg, K, Na, NO$_3$ and SO$_4$ annual export values and confidence limits seemed to be fairly robust. SO$_4$ and NO$_3$ export was lowest in the pasture stream P1 (0.3 kg ha$^{-1}$ year$^{-1}$), which additionally was the one with the lowest specific discharge (Figure 3-6). Although D2 also showed low specific
discharges, the export values for SO$_4$ and NO$_3$ were in the range of the other subcatchments, and for Ca, Mg and Na the export values were slightly higher. This is most likely attributable to the higher stream concentrations in D2 compared to stations F1, F2, R1 and R3. Forested streams F1 and F2 revealed notably low export values for Ca, and for Mg and Na the values were also at the lower end. At the outlet (R3) however, export of nutrients and elements was generally high. For TOC, confidence intervals were large, and export calculation therefore uncertain. No clear pattern for land-use dependence on TOC export could thus be discerned. However, the forested stream F1 showed the highest organic carbon values per ha, whereas stream P1 with predominant pasture had by far the lowest TOC export.

Figure 3-6 Histograms of calculated annual nutrient export with confidence intervals (kg ha$^{-1}$ yr$^{-1}$), and boxplots of mean daily specific discharge (m$^3$ ha$^{-1}$ d$^{-1}$), with percentiles (box), median (horizontal line), and mean value (asterisk)
3.3 Results and discussion

![Graph showing relation of NO\textsubscript{3} export and % forest cover](image)

**Figure 3-7** Relation of NO\textsubscript{3} export and % forest cover of the study catchments.

In general, nutrient export did not increase with deforestation, as was e.g. found by Likens et al. (1970) and Williams & Melack (1997). The subcatchment with the highest degree of deforestation (P1) only showed slightly higher export values for Ca compared to F1 and F2. For all other parameters export in P1 was similar to (for Mg, Na) or smaller than (for K, NO\textsubscript{3}, SO\textsubscript{4}, TOC) in the forested catchments. The refilling of discharge data for the missing period from April to August 2007 could have introduced an underestimation of export in P1. To investigate this possible underestimation, the half-yearly export for the time period where measured stage data for P1 were available (September 2007 to April 2008) was additionally calculated and compared between streams (results not shown). The same patterns as described above remained and a possible underestimation of discharge can therefore be ruled out. However, for NO\textsubscript{3}-export calculations in P1 we had to use a hypothetical value of 0.5 times the detection limit, which resulted in an extremely low NO\textsubscript{3} export value of 0.3 kg ha\textsuperscript{-1} yr\textsuperscript{-1}.

Mixed catchment D2 seemed to be special in having high Ca, Mg and Na export values. One reason for this might be that stream D2 was used for gravel excavation during the sampling period just upstream of the road, close to where water samples were taken. The excavation activity might have increased the solute load of the river and contributed significantly to the export due to the otherwise low ion concentrations of montane waters. Another possible explanation would be of course the difference in specific discharge. During September 2007 until May 2008 the specific discharge of D2 was three times higher (mean of 51.6 m\textsuperscript{3} ha\textsuperscript{-1} day\textsuperscript{-1}) compared to P1 (mean of 19.0 m\textsuperscript{3} ha\textsuperscript{-1} day\textsuperscript{-1}). With equally high nutrient concentrations in the stream water, export in D2 should therefore be roughly 3 times that of P1. Interestingly we could observe that NO\textsubscript{3} export seemed to be positively related with forest cover in our study catchment (Figure 3-7). This finding supports the already mentioned study of Rhoades et al. (1998) who state that under *Setaria* pasture soil-N is decreasing. Certainly, only extensive pastures with no application of fertilizers, as occurring here, would show this pattern. In agriculturally used areas, an increase in (intensive) pasture or cropland mostly leads to increasing levels of NO\textsubscript{3} export (Jordan et al.
1997). Although the medium forest cover values are missing in the data, the trend to higher NO₃ export with increasing forest cover seems to hold true.

In general, the values on nutrient export from forested streams F1 and F2 fall within the range reported for other (montane) forested watersheds, with the exception of McDowell & Asbury (1994) and Newbold et al. (1995) who report extremely high export values for Costa Rican and Puerto Rican montane forest catchments respectively (Table 3-4). NO₃ seems to be the only parameter for which the export is slightly elevated in the study catchment.

Table 3-4 Overview of literature values for nutrient export in tropical forests. All values were converted to kg ha⁻¹ year⁻¹ and were rounded to the nearest kg to improve readability.

<table>
<thead>
<tr>
<th>Study</th>
<th>Land-use and location</th>
<th>export in kg ha⁻¹ yr⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ca</td>
</tr>
<tr>
<td>Boy &amp; Wilcke (2008)</td>
<td>montane forest, Ecuador</td>
<td>5-13</td>
</tr>
<tr>
<td>Liu et al. (2003)</td>
<td>montane forest, China</td>
<td>34</td>
</tr>
<tr>
<td>McDowell &amp; Asbury (1994)</td>
<td>montane forest, Puerto Rico</td>
<td>44-96</td>
</tr>
<tr>
<td>Newbold et al. (1995)</td>
<td>montane forest, Costa Rica</td>
<td>133-442</td>
</tr>
<tr>
<td>Yusop et al. (2006)</td>
<td>forested, Malaysia</td>
<td>4-7</td>
</tr>
<tr>
<td>Germer et al. (2009)</td>
<td>small catchments, forested, Brazil</td>
<td>6-8</td>
</tr>
<tr>
<td>Lesack &amp; Melack (1996)</td>
<td>small catchments, forested, Brazil</td>
<td>1</td>
</tr>
<tr>
<td>This study</td>
<td>montane forest, Ecuador</td>
<td>6-8</td>
</tr>
</tbody>
</table>

*Loads which were given as NO₃-N and SO₄-S were converted to NO₃ and SO₄ loads

3.3.5 Input-output budgets

Input-output budgets of nutrients were calculated to characterize the current state of the ecosystem and to be able to evaluate the impact of land-use change on the catchment and on downstream areas. Two types of budgets were computed, one excluding, the other including the contribution of nutrient inputs to the system by fog water.

The net nutrient budget of the subcatchments calculated with only rain nutrient input was negative (= net export) for most of the parameters. For Ca, the budget was almost neutral in forest streams F1 and F2. Only for K our calculations suggested a net accumulation in all subcatchments.

Assuming a contribution of 20 % of fog water (Figure 3-8) the budget values for Ca, K, Mg and Na did not change substantially. With fog water contribution, inputs of Ca increased between 0.12-0.18 kg ha⁻¹ yr⁻¹ and for Na between 0.74-1.04 kg ha⁻¹ yr⁻¹. Mg input also
increased between 0.1-0.15 kg ha\(^{-1}\) yr\(^{-1}\) and K input decreased between 0.13-0.19 kg ha\(^{-1}\) yr\(^{-1}\). Only for NO\(_3\) and SO\(_4\), both of which were found in much higher concentrations in fog water than in rain, nutrient budgets changed visibly. For NO\(_3\) this change amounted to an additional input of 6.49-9.37 kg ha\(^{-1}\) yr\(^{-1}\) and for SO\(_4\) of 7.49-10.8 kg ha\(^{-1}\) yr\(^{-1}\). The budgets for SO\(_4\) thus changed from net export to near neutral or even to net accumulation in 5 of the 6 catchments. And for NO\(_3\) the net budget also shifted from negative (net export) to near neutral in most of the streams.

The assumption of 20 % fog water contribution to total precipitation is arguable, though. Various papers on the amount of fog water input in montane tropical forests report lower numbers. Values range between around 3 % of total precipitation in two upper montane rain forests (Hafkenscheid et al. 2001) and 9% in a Venezuelan Andean cloud forest (Ataroff 2001; Ataroff & Rada 2000) to 16 % in a Puerto Rican elfin cloud forest (Eugster et al. 2006) and 20 % or even more for wet tropical locations (Bendix et al. 2008; Bruijnzeel 2004). In the
present study, the value of 20 % was used for input calculation, because of the reportedly above-average cloudiness and the increase of fog water intake with height in the San Francisco study area (Bendix et al. 2004).

The results on K, Na and NO₃ budgets are similar to those of Lesack & Melack (1996), who describe a net accumulation of K in small forested watersheds in central Amazonia, as well as a net export of Na and NO₃. For forested catchments in Brazil, Germer et al. (2009) observed a net export in Na and K, a near neutral condition for Mg and a net accumulation in SO₄ and NO₃. In the same study, the net export of K and of Mg increased with deforestation, the latter of which coincides with our data. Boy & Wilcke (2008) reported for forested microcatchments within the R3 catchment a largely neutral to negative budget for Mg during the years 1998-2003 and positive to neutral budgets for Ca, as well as a net accumulation of K during the same period, all of which was also found for the forested catchments F1 and F2. The negative budgets for Na can be explained by weathering inputs, as was already described earlier. For Mg and Ca dry deposition inputs which are derived from Sahara dust have been proposed by Boy & Wilcke (2008) and seem the most probable explanation for the observed results.

With the assumption of 20 % fog water input to total precipitation, nutrient budgets only changed visibly for NO₃ and SO₄, both of which were found in much higher concentrations in fog water than in rain (Beiderwieden et al. 2005). Thus, for some nutrients, fog water contribution to nutrient input can play a major role in cloud forest ecosystems. This was also shown by Asbury et al. (1994) in Puerto Rican cloud forest where fog was 4 to 8 times more enriched in SO₄ and NO₃ compared to rainwater and where cloud water provided 8-30% of the total elemental wet deposition.

### 3.4 Conclusions

In this study solute dynamics and export values of pristine and disturbed tropical mountain streams were investigated. Differences in the concentration-discharge relations of forested and disturbed streams were observed and attributed to varying flow paths. By calculating nutrient input with two different methods it was shown that fog water input seems to be very important for SO₄ and NO₃ budgets in montane cloud forests. In this context, events such as El Niño and La Niña, which determine the direction of weather regime in the study area also appear to be important, as can be seen by seasonally changing SO₄ and NO₃ stream concentrations. In general, one year of data might seem too little to derive general conclusions on catchment functioning and seasonal patterns. However, the difficult and erratic nature of tropical montane catchment studies mostly impedes continuous long term data series. It is thus of utmost importance to use the available data as a solid data base for future studies, which may then be the decision basis for political and local stakeholders.
4 The influence of land-use on macroinvertebrate communities

4.1 Introduction

Tropical montane cloud forests are ranked among the most important ecosystems for sustaining life in tropical regions (Bubb et al. 2004). Not only do they host a tremendous number of plant and animal species, but they also provide essential ecosystem services, such as medicinal plants, firewood, soil formation, nutrient cycling and recreation among others (Costanza et al. 1997). Typical for montane areas are first- and second-order headwater streams, which offer another vital service to mankind, namely the storage, regulation and purification of water. Downstream populations rely on the provision of a certain amount and quality of drinking and irrigation water. However, all these services depend on a healthy functioning ecosystem, and are endangered by a degradation of the same (Doumenge et al. 1995). In the past, stream habitats have been subjected to great anthropogenic changes not only regarding the water quality, but also morphological aspects. Deforestation, river regulation, acidification, pollution and dam construction have been and still are the major factors affecting the running water ecosystems of the world (Malmqvist 2002). To counter this development and to protect the inherent ecological resources of the streams, various industrialized countries have implemented political frameworks to improve river morphology and water quality. This has not been the case in the tropics, where rates of habitat loss are high, pollution has increased and poverty of the local population exacerbates the situation (Bonell et al. 2005). Some local communities even exclusively depend on streams as a drinking water and protein source (Millenium Ecosystem Assessment 2005).

Concomitantly with the degradation of rivers, stream flora and fauna have been under increasing stress by pollution, habitat destruction, water extraction and the introduction of alien species (Meyer et al. 2007). Macroinvertebrates are particularly sensitive to changes in habitat quality and are often indicators for distinct water conditions. Taking advantage of this fact the use of macroinvertebrates as ‘bioindicators’ has become a standard method for a rapid assessment of water quality in Europe and North America. In contrast to chemical data, which only reveals a snapshot of water quality, organisms reflect the longer term condition of the stream, as they have life cycles of often more than a year and are ubiquitous (Alba-Tercedor 1996). Due to the large number of macroinvertebrate species, they offer a spectrum of responses to environmental stresses (Bode et al. 1993).

There is an urgent need to introduce a cost-effective bioindicator system for detecting water quality changes in the tropics.

In temperate regions, various systems for bioindication already exist (Saprobic Index, Belgian Biological index-BBI; Family Biotic index-FBI; Trend Biotic Index TBI, Biological Monitoring Working Party BMWP, Average Score per Taxon ASPT, Ephemeroptera-Plecoptera-Trichoptera-Index EPT). Especially for the BMWP, attempts have been made in Costa Rica, Colombia, Nicaragua and the Dominican Republic to adapt and apply this
ecological index to the Neotropics (Fenoglio et al. 2002; Guerrero-Bolano et al. 2003; Roldan 1996; Soldner et al. 2004; Stein et al. 2008). Ultimately, all biotic indices are based on the knowledge of connections between species occurrence or abundance, and the habitat or water quality of the ecosystem. This implies that information on habitat requirements of macroinvertebrate species is a prerequisite for the development of such indices.

The objective of this study was to understand how land-use influences the structure of benthic communities in tropical cloud forest streams. Multivariate statistics were used to identify those taxa and environmental variables, which are most affected by a change in land cover from forest to pasture. The central questions were:

1) Which mechanisms control macroinvertebrate occurrence and abundance in montane tropical streams?
2) What are the consequences of deforestation on macroinvertebrate communities?
3) Which groups of macroinvertebrates might be good indicators of this disturbance?

4.2 Material and Methods

4.2.1 Sampling design

6 subcatchments were sampled in the San Francisco watershed, with 4 transects in each stream and 2 sampling campaigns (November 2008 and March 2009). 3 of these subcatchments (F1-3) were located on the southern slope with predominant forest cover and largely undisturbed conditions (% forest cover: 80-90). The other 3 catchments (P1-3) showed a varying degree of disturbance, from predominant pasture cover to mixed pasture/bracken/secondary forest cover (% forest cover: 24-68). Total subcatchment size varied between 0.12 km² (F3) and 4.43 km² (F1) with a mean of 2.16 km² (Table 4-1). The sites were chosen according to land-use characteristics and accessibility of the area, the latter one being a highly restricting factor in the steep and mostly impenetrable catchment.

A transect involved the collection of hydrometric and water quality data and macroinvertebrate organisms (hereafter defined as aquatic organisms which are retained in a 500 µm mesh sized net (Hauer 2007)). Macroinvertebrate collection was accomplished by laying out a 1 m² frame into the stream at a location representative for this stream reach. All sand (< 2 mm), gravel (> 2 mm) and stones (> 2 cm) in contact with the stream water were thereafter taken out of the frame, stored in a plastic tray and searched for organisms. During the taking out of material, a D-shaped net (500 µm mesh size) was held downstream to catch possible drift and all organic material present in the frame. The organic material (leaves, branches) was also scrutinized for macroinvertebrates in the lab. Organisms were stored in 80 % Ethanol and later on identified to the lowest taxonomic level possible, mainly to genus level. Exceptions included Diptera larvae and imagines of Turbellaria, where we were only able to identify to family level or higher. Several identification keys were used (Bouchard Jr
4.2 Material and Methods

Due to the scarcity of detailed identification keys for South American species, this literature also included some keys for North American macroinvertebrates.

Figure 4-1 Study site and land-use characteristics of the area. Note that study streams P1-3 show varying degrees of deforestation whereas streams F1-3 are almost completely covered with forest.

Transects were numbered from ‘a’ to ‘d’ with ‘a’ being the most downstream transect and ‘d’ being not more than 150 m further upstream (e.g. P1a denoting the first transect in disturbed stream 1). We were not able to conduct more than four transects in each stream due to the steep terrain and a therefore rapid change in altitude and accessibility.

<table>
<thead>
<tr>
<th>Land-use cover (%)</th>
<th>P1</th>
<th>P2</th>
<th>P3</th>
<th>F1</th>
<th>F2</th>
<th>F3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Forest</td>
<td>23.5</td>
<td>67.7</td>
<td>65.9</td>
<td>89.8</td>
<td>79.7</td>
<td>90.4</td>
</tr>
<tr>
<td>Páramo</td>
<td>8.9</td>
<td>15.6</td>
<td>13.7</td>
<td>8.2</td>
<td>18.6</td>
<td>0</td>
</tr>
<tr>
<td>Pasture/bracken</td>
<td>66.7</td>
<td>15.2</td>
<td>15.7</td>
<td>1.7</td>
<td>1.5</td>
<td>9.6</td>
</tr>
<tr>
<td>Urban</td>
<td>0.5</td>
<td>0.1</td>
<td>0.1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Other</td>
<td>0.4</td>
<td>1.4</td>
<td>4.5</td>
<td>0.3</td>
<td>0.3</td>
<td>0</td>
</tr>
<tr>
<td>Total area (km²)</td>
<td>0.69</td>
<td>3.49</td>
<td>2.9</td>
<td>1.31</td>
<td>4.43</td>
<td>0.14</td>
</tr>
</tbody>
</table>
4.2 Material and Methods

4.2.2 Physical and chemical characteristics

Water chemical parameters were measured weekly to biweekly over one year in transect 'a' of each stream (exception P3 and F3 where samples were taken about once a month) to obtain a time series of stream chemical condition and minimum/maximum values. In transects b-d we measured water chemical parameters 3-6 times. Concentrations of NO₃, PO₄, SO₄ were determined by ion chromatography with detection limits of 0.1 mg l⁻¹ for NO₃ and SO₄ and a detection limit of 0.5 mg l⁻¹ for PO₄ (DX-120, Dionex Corporation, CA, US). However, as before, PO₄ concentrations were always below this detection limit and were therefore not further discussed in this chapter. Electric conductivity (EC), pH and water temperature (T) were also measured using a handheld meter (pH/Cond 340i, WTW, DE). For temperature, a 5 min time series was available for two stations (P1a, F1a), obtained by ODYSSEY temperature sensors (Dataflow Systems PTY LTD, NZ). For the other transects, stream temperatures were taken manually during the day. For all sites, O₂ concentration (in % and mg l⁻¹) and alkalinity (as mg l⁻¹ CaCO₃) were determined several times during and between sampling campaigns (Oxi320 meter with a CellOx325 sensor, WTW, DE and Alkalinity Rapid Test by Merck KGaA, DE). All other parameters (litter debris, substrate types, vegetation cover, mean stream depth and stream width) were recorded only during the time of macroinvertebrate collection. Organic material (litter debris, leaves) was oven dried for 2-3 days at 40°C and then weighed to obtain dry weight of organic matter content (detritus). Substrate type (sand/gravel/stone) and vegetation cover (% shade) was estimated using digital on-site photographs. Mean stream depth was calculated as the average of 6 measurements from inside the frame.

Water level was measured continuously every 5 min at an accuracy of ±1 mm using pressure transducer or capacitance probes (ODYSSEY Dataflow Systems PTY LTD, NZ) at the outlets of P1-P3, F1 and F2 throughout the study period. Discharge was determined using flowmeters (FP101, Global Water Instrumentation Inc., US; Flo-Mate 2000, Marsh-McBirney Inc., US). Stage-discharge curves were calculated using polynomial or power regressions. For F3 discharge time series and long term water quality data were taken from already published literature (Fleischbein et al. 2006, Wilcke et al. 2001, Wilcke et al. 2008).

4.2.3 Statistical analyses

Comparison of streams: Before comparing among streams, homogeneity of the two sampling campaigns was tested using an independent two-sided t-test with a prior test on homogeneity of variances (Levene test on equal variances, p = 0.05).

Because data on diversity indices and their applicability in tropical montane areas are rare there is no general rule which index fits best. It was therefore decided to calculate the most commonly used diversity indices to facilitate the comparison of the results to future investigations in these ecosystems: density (individuals m⁻²), richness (number of taxa m⁻²), and Shannon’s, Simpsons and Margalef’s diversity, as well as Evenness. All these indices
were calculated separately for each transect and then averaged for each stream (n = 8 for each stream, i.e. 4 transects in 2 campaigns). Biological indices (BMWP/Col (Roldan 1996) and ASPT) were calculated for each stream (n = 4 transects) and then averaged over both campaigns. The BMWP was originally used for temperate catchments. However, it was later on adapted and verified for neotropical (Colombian) watersheds by Roldan (1996), and has already been used successfully in montane tropical areas (Medellin et al. 2004; Moreno 2008). An ANOVA was used to compare the mean values of the indices among all six streams (p = 0.05).

Comparison of land-uses: For the two land-use types (forest and disturbed) abundance patterns of all taxa and EPT values were compared by grouping together all forested and disturbed streams respectively (i.e. n = 3x4x2 = 24 for each land-use type), and applying a non-parametric Kruskal Wallace test, which was chosen due to the non-normal distribution characteristics of the data. The EPT is an index which is based on the abundance of three pollution-sensitive orders (Ephemeroptera, Plecoptera and Trichoptera) of macroinvertebrates and can be used to detect macroinvertebrate community changes due to chemical pollution.

Multivariate methods: Simple regression analyses and descriptive statistics can usually not explain a complex community structure. Dependencies are multifaceted and need to be taken as such in statistical calculations. An approach often used in community analyses therefore are multivariate statistics, as they allow an inclusion of various explanatory variables. Especially ordination techniques, such as multidimensional scaling, have proven successful in identifying abundance patterns and underlying causes for species composition (Leyer & Wesche 2007).

Here we applied the two most commonly used types of multivariate analyses on our data set: canonical correspondence analysis (CCA) and non-metric multidimensional scaling (NMDS). Both multivariate analyses were conducted with the freeware statistical program R2.8.1 (R Development Core Team (2008)). For CCA we used the ‘.cca’ routine of the ‘vegan’ library (Oksanen et al. 2007), for NMDS we used the ‘metaMDS’ routine of the same library (see also Dormann & Kühn (2004)). The .cca and metaMDS routines of R have already been used several times in literature (Behan-Pelletier et al. 2008; Jurasinski & Kreyling 2007; Sedayu 2006; Valério et al. 2007) and have the advantage to be freely accessible.

CCA is used to relate environmental variables to species abundance. It combines several environmental gradients to create a synthetic gradient, which is represented as a CCA ordination axis. To evaluate the significance of the CCA axes, Monte Carlo tests are performed with 999 permutations on all constrained eigenvalues. In the ordination diagram, each taxon point represents the weighted average of the site points in which it occurs, and therefore represents the ecological niche of the taxon. Taxa which are close together in the
ordination space thus have similar niches. The arrows representing environmental parameters point to the direction of maximum change of this parameter, and the length of the arrow is proportional to the rate of change. The (0,0) point of the diagram represents the mean value of the variable. Site and taxa points can be projected on the arrow and then compared among each other regarding this particular parameter. For more information on CCA consult Braak & Verdonschot (Braak & Verdonschot 1995).

NMDS is a method which creates a distance matrix (Bray-Curtis) between the investigated objects, with increasing space between objects representing their increasing dissimilarity. Thus, groups of similar objects can be visualized and ‘goodness of fit’ of the matrix can be tested by analyzing the ‘stress’ (Kruskal’s Stress) of the ordination (after Holland (2008)). A stress of 5 to 10 can be seen as good and reliable, whereas values between 10 and 15 should already be interpreted with care (Leyer & Wesche 2007).

The advantage of using both, CCA and NMDS are apparent: CCA analyzes the relationship between measured environmental variables and macroinvertebrate assemblages, whereas NMDS enables a separation, respectively grouping, of sampling sites (transects) according to their assemblage structure. Moreover, NMDS uses a distance matrix which distorts the distances of objects much less than other ordination methods (Leyer & Wesche 2007).

To reduce the effect of large numbers in single taxa (e.g. Chironomidae), the abundance data (x) were transformed by log\(_{10}(x+1)\). The addition of 1 to each number bypasses the problem of taking the logarithm of zero abundance. Also, to avoid the unduly large influence of rare taxa in the ordination, taxa which were represented with only three or less individuals were excluded, as was proposed by Legendre & Gallagher (2001). The environmental data was normalized to a mean of ‘0’ and unit variance to eliminate the influence of units of measurement. To test the outcome and the interpretative weight of the CCA analysis, the results were compared with a simple correlation matrix (Pearson correlation coefficient), relating environmental variables to real abundance values of all taxa. All statistics were carried out using SPSS 15.0 (SPSS Inc.).

4.3 Results and discussion

Land-use has been identified to be a major factor influencing and changing aquatic communities (Benstead et al. 2003; Bojsen & Jacobsen 2003; Harding et al. 1998). There are numerous environmental variables which are directly affected by land-use change, e.g. % of canopy cover (shade), temperature, water chemistry, organic matter content, pH, conductivity, periphyton biomass and hydrologic regime among others. Many of these factors have been identified to be influencing aquatic communities (Arimoro & Ikomi 2009; Bojsen & Jacobsen 2003; Buss et al. 2004; Figueroa et al. 2003; Gower et al. 1994; Griffith et al. 2001; Ruse 1996). In this study the aim was to identify those environmental variables with the strongest influence on macroinvertebrate community structure in tropical montane streams.
### Table 4-2 Overview of taxa found.

<table>
<thead>
<tr>
<th>Order</th>
<th>Family</th>
<th>Genera</th>
<th>P1</th>
<th>P2</th>
<th>P3</th>
<th>F1</th>
<th>F2</th>
<th>F3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coleoptera</td>
<td>Elmidae</td>
<td>X X X X X X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Gyrinidae</td>
<td>X X X X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ptilodactylidae</td>
<td>X X X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Psephenidae</td>
<td>X X X X X</td>
<td></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>Diptera</td>
<td>Chironomidae</td>
<td>X X X X X</td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>Diptera spec</td>
<td>X X X X</td>
<td></td>
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<tr>
<td></td>
<td>Limonidae</td>
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</tr>
<tr>
<td></td>
<td>Simuliidae</td>
<td>X X X X</td>
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</tr>
<tr>
<td></td>
<td>Tipulidae</td>
<td>X X X X X</td>
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<tr>
<td>Ephemeroptera</td>
<td>Baetidae</td>
<td>Andesiops</td>
<td>X X X X X</td>
<td></td>
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<td></td>
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<tr>
<td></td>
<td>Baetodes</td>
<td>X X X X</td>
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<tr>
<td></td>
<td>Leptohyphidae</td>
<td>Haplohyphes</td>
<td>X X</td>
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<tr>
<td></td>
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</tr>
<tr>
<td></td>
<td>Leptophlebiidae</td>
<td>Farrodes</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
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<td>30</td>
<td>30</td>
<td>28</td>
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</tbody>
</table>
4.3.1 General observations and the influence of seasonality

A total of 5243 individuals were collected belonging to 12 invertebrate orders and 28 families. We identified 37 taxa, 30 to genera level and seven to family level (Table 4-2). 14 individuals belonging to the orders Hirudinea, Amphipoda, Hemiptera and Coleoptera were left out of the analysis due to low numbers (i.e. less than three individuals per taxon in total). According to Burneo & Gunkel (2003) and Jacobsen et al. (1997), macroinvertebrate communities of high Andean streams are mainly composed of insect families. This was confirmed by this study. Some non-insect orders seemed to be absent or very rare in our area, such as Oligochaetes, Acarina and Bivalvia. One gastropod and a few aquatic mites were encountered during a pre-sampling campaign, but due to their scarcity and their small size they were not observed during the main study. Hirudinea and Amphipoda were found in low numbers, but were not included in the analysis. There was no clear pattern in the distribution of these rare taxa.

The comparison of sampling campaigns 1 (November 2008) and 2 (March 2009) only revealed significant differences in density (ind m⁻²) in subcatchment P3. The number of taxa was not significantly different in any of the subcatchments between sampling campaigns. We therefore concluded that seasonality was not of importance here, and that the sampling campaigns could be lumped together for the following analyses.

4.3.2 Comparison of streams

Table 4-3 summarizes the environmental site parameters with means and ranges. The pH, EC and alkalinity values were significantly lower in forest sites compared to disturbed sites (ANOVA, p = 0.05). NO₃ and SO₄ concentrations were low in all streams, although disturbed sites exhibited slightly higher values in SO₄. Mean temperature was significantly lower in forest streams which probably resulted from the higher amount of shading in these sites. All other parameters did not show clear patterns between disturbed and forested catchments, and variation between transects (i.e. in-stream heterogeneity) was high, as can be seen by the parameter ranges.

To compare the macroinvertebrate community structure between streams, we calculated several biological measures. Mean density was higher in disturbed streams compared to forested ones, but this difference was only significant between disturbed stream P2 and forest streams F1-F3 and between P1 and F2. Taxa richness was comparable between P1-P3 and also differed significantly between P2 and forest streams F1 and F2. Evenness was generally higher in forest streams, but this trend was only significant between P1 and F2-F3 and between P2 and F3 (Figure 4-2). The higher density and richness in disturbed streams might be explained by mostly patchy deforestation in combination with good water quality. The amount of shading in disturbed streams was between 0-80 %, and the input of organic matter was similar across land-uses (Table 4-3). So the advantage of higher light input and its potential effect on periphyton growth, combined with the advantage of forest cover and its
resulting litter detritus input, could lead to a more diverse invertebrate community. The fact that the evenness values were lower in disturbed sites, though, already hints at negative effects of this habitat change.

Table 4-3 Means and ranges (brackets) of transects a to d for the six sampling sites and both campaigns. "Q" = discharge. *data from Wilcke et al. (2001), SO₄ was not detected (n.d.) in this study; † data taken from Fleischbein et al. (2006); ‡ estimated

<table>
<thead>
<tr>
<th></th>
<th>P1</th>
<th>P2</th>
<th>P3</th>
<th>F1</th>
<th>F2</th>
<th>F3</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.4 (6.5-7.8)</td>
<td>7.3 (6.3-7.8)</td>
<td>7.4 (6.6-7.7)</td>
<td>6.6 (5.0-7.3)</td>
<td>6.6 (5.7-7.2)</td>
<td>6.9 (5.7-7.2)</td>
</tr>
<tr>
<td>EC [μS cm⁻¹]</td>
<td>30.0 (18.0-36.0)</td>
<td>29.1 (17.0-39.0)</td>
<td>32.4 (26.0-36.0)</td>
<td>6.5 (4.0-14.6)</td>
<td>7.0 (5.0-16.0)</td>
<td>21.3 (20.0-24.0)</td>
</tr>
<tr>
<td>Alkalinity [mg L⁻¹ CaCO₃]</td>
<td>16.9 (12.0-19.0)</td>
<td>15.6 (12.0-18.0)</td>
<td>18.8 (17.5-21.0)</td>
<td>3.1 (2.0-3.5)</td>
<td>3.1 (2.0-3.5)</td>
<td>12.5 (11.0-14.0)</td>
</tr>
<tr>
<td>NO₃ [mg L⁻¹]</td>
<td>0.4 (0.4-0.4)</td>
<td>0.7 (0.2-1.3)</td>
<td>0.3 (0.3-0.3)</td>
<td>0.7 (0.3-1.3)</td>
<td>0.6 (0.1-1.1)</td>
<td>0.2*</td>
</tr>
<tr>
<td>SO₄ [mg L⁻¹]</td>
<td>0.6 (0.3-0.9)</td>
<td>0.8 (0.4-1.0)</td>
<td>0.8 (0.8-0.8)</td>
<td>0.5 (0.2-0.7)</td>
<td>0.5 (0.1-0.7)</td>
<td>n.d.*</td>
</tr>
<tr>
<td>T [°C]</td>
<td>17.0 (15.0-21.4)</td>
<td>16.0 (13.8-22.3)</td>
<td>16.1 (14.6-17.0)</td>
<td>15.1 (13.0-17.3)</td>
<td>15.4 (12.5-22.7)</td>
<td>15.5 (15.2-17.2)</td>
</tr>
<tr>
<td>O₂ [mg L⁻¹]</td>
<td>7.6 (6-11.5)</td>
<td>8 (6.1-9.6)</td>
<td>9.1 (7.8-11.2)</td>
<td>6.6 (4.1-11.6)</td>
<td>7.8 (4.5-10.9)</td>
<td>8.6 (6.9-10.4)</td>
</tr>
<tr>
<td>Q_base (Q_max) [m³ s⁻¹]</td>
<td>0.01 (0.28)</td>
<td>0.02 (3.4)</td>
<td>0.1 (4.0*)</td>
<td>0.1 (4.0)</td>
<td>0.3 (12.1)</td>
<td>0.003 (0.12)</td>
</tr>
<tr>
<td>vel_base [m² s⁻¹]</td>
<td>0.4 (0.16-0.66)</td>
<td>0.67 (0.38-1)</td>
<td>0.53 (0.25-0.98)</td>
<td>0.23 (0.04-0.38)</td>
<td>0.62 (0.08-1.2)</td>
<td>0.4 (0.19-0.6)</td>
</tr>
<tr>
<td>width [cm]</td>
<td>94 (55-110)</td>
<td>251 (180-310)</td>
<td>201 (150-290)</td>
<td>219 (150-270)</td>
<td>295 (150-540)</td>
<td>56 (5-110)</td>
</tr>
<tr>
<td>depth_max [cm]</td>
<td>13 (10-20)</td>
<td>23 (13-35)</td>
<td>21 (15-32)</td>
<td>23 (15-32)</td>
<td>31 (20-40)</td>
<td>12 (4-50)</td>
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<td>shade [%]</td>
<td>23 (0-50)</td>
<td>18 (0-50)</td>
<td>40 (10-80)</td>
<td>65 (30-90)</td>
<td>53 (30-70)</td>
<td>88 (80-90)</td>
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<tr>
<td>stones [%]</td>
<td>37 (5-70)</td>
<td>48 (30-70)</td>
<td>36 (10-60)</td>
<td>38 (10-70)</td>
<td>32 (5-70)</td>
<td>21 (0-40)</td>
</tr>
<tr>
<td>gravel [%]</td>
<td>56 (25-70)</td>
<td>49 (20-67)</td>
<td>60 (35-90)</td>
<td>57 (29-88)</td>
<td>65 (30-93)</td>
<td>63 (48-80)</td>
</tr>
<tr>
<td>sand [%]</td>
<td>7 (0-25)</td>
<td>2 (0-10)</td>
<td>3 (0-10)</td>
<td>5 (0-20)</td>
<td>3 (0-20)</td>
<td>16 (5-50)</td>
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<tr>
<td>litter detritus [g m⁻²]</td>
<td>10.5 (4.4-17.6)</td>
<td>5.1 (2.1-14.9)</td>
<td>17.2 (0.7-61.9)</td>
<td>10 (4.6-20)</td>
<td>3.8 (1.8-6.6)</td>
<td>15.9 (5.5-33.3)</td>
</tr>
</tbody>
</table>

Compared to F1 and F2, stream F3 had noticeably higher values both for richness and evenness. It also showed significantly higher values than F1 for both Shannon’s and Margalof’s diversity index (Table 4-4). F3 is not only characterized by a smaller catchment
size and therefore lower discharge rate and $Q_{\text{max}}$ compared to F1 and F2, but also by a higher amount of sandy substrate and litter detritus (Table 4-3). It might be that the combination of these factors led to the higher diversity and density in F3. From this it can be concluded, that catchment size seems to be an influential variable for macroinvertebrate community structure.

In relation to other studies at lower altitudes or in larger rivers, macroinvertebrate densities were considerably lower in the San Francisco study area (Figueroa et al. 2003; Ravera 2001; Sharma & Rawat 2009; Sponseller et al. 2001). For Ecuador, Bojsen & Jacobsen (2003) found a mean of 692 (range 343-1206) ind m$^{-2}$ in forested and 2598 (range 1498-4982) in deforested sites (at around 400 m a.s.l.) which is a much higher value compared to the present study with around 100 ind m$^{-2}$. The low densities in the San Francisco area might be the result of the predominantly hard, rocky substrates and nutrient poor water of the streams, with little to no periphyton cover nor any macrophytes. As far as species diversity is concerned, values for the 6 study streams were comparable, or even higher than the values found in other tropical studies (Arimoro & Ikomi 2009; Buckup et al. 2007; Tupinambas et al. 2007). Our values for evenness, though, were consistently lower than in most of the above mentioned studies.

In general, high numbers of individuals were found for three Ephemeroptera taxa (Andesiops, Thraulodes, Baetodes) and for the Diptera family Chironomidae, but also for some taxa of Trichoptera (Smicridea, Mortonella, Leptonema and Grumichella). The highest abundance per m$^2$ was observed in one transect of disturbed stream P2, where 148 individuals of Baetodes were collected.

Table 4-4 Comparison of diversity and biological indices between streams (mean of all transects, n = 8), different index letters denote significant differences of means (Games Howell test, p = 0.05). For BMWP/Col and ASPT we lumped together all four transects and calculated values separately only for the two sampling campaigns.

<table>
<thead>
<tr>
<th>Station</th>
<th>BMWP/Col</th>
<th>ASPT</th>
<th>Density (Ind m$^{-2}$)</th>
<th>Richness (no. taxa)</th>
<th>Evenness</th>
<th>Shannon’s Diversity</th>
<th>Margalof’s Diversity</th>
<th>Simpson’s Diversity</th>
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<tr>
<td>P1</td>
<td>128.0±5.7</td>
<td>7.3±0.0</td>
<td>152.9±89.2</td>
<td>13.8</td>
<td>0.41±0.05</td>
<td>2.0±0.1</td>
<td>5.9±0.8</td>
<td>0.80±0.04</td>
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<td>P2</td>
<td>155.0±32.5</td>
<td>7.4±0.1</td>
<td>197.5±90.8</td>
<td>17.3</td>
<td>0.45±0.04</td>
<td>2.3±0.2</td>
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<td>P3</td>
<td>138.0±32.5</td>
<td>7.5±0.2</td>
<td>125.3±59.4</td>
<td>14</td>
<td>0.43±0.10</td>
<td>2.0±0.5</td>
<td>6.2±2.1</td>
<td>0.80±0.15</td>
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<td>F1</td>
<td>143.0±9.9</td>
<td>7.3±0.3</td>
<td>58.3±32.1</td>
<td>11.0</td>
<td>0.47±0.10</td>
<td>1.8±0.3</td>
<td>5.8±1.2</td>
<td>0.77±0.10</td>
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<tr>
<td>F2</td>
<td>101.5±24.7</td>
<td>7.2±0.3</td>
<td>47.8±12.4</td>
<td>11.0</td>
<td>0.51±0.06</td>
<td>2.0±0.3</td>
<td>5.9±1.8</td>
<td>0.81±0.05</td>
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<tr>
<td>F3</td>
<td>170.5±7.8</td>
<td>7.6±0.4</td>
<td>71.1±24.9</td>
<td>16.3</td>
<td>0.55±0.07</td>
<td>2.3±0.2</td>
<td>8.3±1.4</td>
<td>0.86±0.04</td>
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</table>
According to Roldan (1996) the values for BMWP/Col indicated good (101-120) or excellent (>120) water quality for all streams. This is most probably due to the fact that the chemical quality of the water was good even in the disturbed streams, and therefore no taxa were found which would signal serious pollution. But the results reveal the difficulty for the BMWP/Col to address the heterogeneity and low taxa abundance of the forest streams: for the first campaign in F2, the BMWP/Col score was 84 (119 in campaign 2). A score of 84 would merely classify as “acceptable water quality” with “slightly polluted water” (Roldan 1996). The chemical water quality of stream F2, though, differed in no ways between the two campaigns. So although the BMWP/Col score has been used successfully in tropical montane areas (Medellin et al. 2004; Moreno 2008), it cannot be drawn upon in areas, where factors other than water quality influence the macroinvertebrate community structure. The Average Score Per Taxon was similar for all streams (Table 4-4).

Figure 4-2 Boxplots of density, richness and evenness of the six streams (n = 8 for each stream). Extreme values are depicted as circles.
4.3 Results and discussion

4.3.3 Comparison between land-uses

To derive information on community shifts with deforestation, the abundance of all taxa were compared between land-uses (disturbed-forested). Eight taxa showed significantly larger abundances in disturbed streams (Kruskal-Wallis, *p = 0.05, **p = 0.01): Elmidae (**), Simuliidae (*), Andesiops (**), Baetodes (**), Haplohyphes (**), Thraulodes (**), Anacroneuria (**), Mortionella (**), Helicopsyche (**), and Smicridea (**). Five taxa were found in significantly higher numbers in forested streams, namely Phylloicus (**), Atanatolica (**), Grumichella (*), Polythore (**), and Planariidae (*). The EPT values (numbers of Ephemeroptera, Plecoptera and Trichoptera families) on the other hand were similar in all streams. They ranged between 9 and 10 for disturbed sites and between 8 and 10 for forested sites (transects combined).

4.3.4 Multivariate analyses

The CCA revealed that 45% of the variation in the data can be explained by our environmental parameters. In total 6 axes were extracted out of 12 environmental parameters. All 6 axes were significant at p = 0.001 (R-Permutation Test, Pseudo-F value = 2.64). Substrate type, % of shading and stream width were the most influential factors for axis 1, while EC, temperature and pH were closely associated with axis 2 (Table 4-6). The first axis seems to be predominantly connected to the physical habitat characteristics whereas the second axis is more linked to the chemical characteristics of the habitat, accounting for 18% and 9% of the data variation, respectively. In the ordination diagram (Figure 4-3) transects sampled in disturbed streams clearly separated from those sampled in forested sites. Transects in stream F3 grouped together and streams F1 and F2 were rather spread out. In contrast to that, the majority of transects in disturbed streams grouped together.

According to the CCA ordination, the abundances of Atanatolica, Phylloicus, Grumichella, Marilia and some other taxa were positively correlated with % of sand in the habitat. The shading intensity seemed to be decisive for the abundance of Polythore species, and stream depth for Chironomidae abundance. For taxa which are associated with disturbed streams (Smicridea, Leptohyphes, Thraulodes, Baetodes) single explaining factors were harder to find, due to the various environmental influences in this part of the ordination space (pH, EC, temperature, velocity, alkalinity). Cernotina was located far away from all other taxa and therefore has a very distinct ecological niche according to the CCA analysis.
Table 4-5 Correlations between taxa abundance and environmental parameters (Pearson’s correlation coefficient). (*) = significant for p=0.05, (**) = significant for p= 0.01. N = number of transects with finds. (N<sub>total</sub> = 48; 6 streams x 4 transects x 2 campaigns)

<table>
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<tr>
<th>Taxa</th>
<th>pH</th>
<th>EC</th>
<th>alkal</th>
<th>T</th>
<th>O&lt;sub&gt;2&lt;/sub&gt;</th>
<th>vel</th>
<th>width</th>
<th>depth</th>
<th>shade</th>
<th>stone</th>
<th>gravel</th>
<th>sand</th>
<th>detritus</th>
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<td>.36</td>
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To test the outcome of the CCA analysis, we applied a simple correlation between environmental parameters and taxa abundances. The results are summarized in Table 4-5, where only taxa with significant correlations are shown. The abundance of *Andesiops, Polythore, Phylloicus* and *Atanatolica* correlated significantly with % of sand in the habitat. Individuals of *Atanatolica* were only found in 5 transects, though, so sample size probably was too low to make any general conclusion. As also found in the CCA ordination, *Polythore* species were positively correlated with % of shade. A significant relation of Chironomidae abundance and stream depth was not confirmed here. Parameters most often associated significantly with taxa abundance were pH (9 times), width of stream (7 times) and % of shade (7 times), whereas O₂ concentration and % of gravel in the habitat correlated only with Chironomidae and *Anacroneuria* abundance respectively. No correlations were found for the following taxa: *Anchytarsus, Tipulidae, Farrodes, Mortionella, Atopsyche, Leptonema* and *Triplectes*, which means that these taxa were either widespread, or that they only occurred in a narrow environmental range.

The CCA results show, that the percentages of shade and of substrate type were the most important factors influencing macroinvertebrate communities in the study catchment (Table 4-6). Even in the analysis of covariance, % of shade was one of the three parameters (the other ones being pH and stream width) which correlated most often with the abundance of distinct species. Interestingly, temperature did not play an equally large role in the CCA plot and correlation analysis which leads to the conclusion that higher stream temperatures are not the most important direct consequence of lower vegetation cover. Rather it was observed in the field that periphyton growth increased with decreasing canopy cover which most probably entails an increase in food supply for scrapers and collectors.

The influence of pH and, related to that, of alkalinity on the community structure has already been suggested in other studies (Fjellheim & Raddum 1992; Guerold et al. 2000; Lepori et al. 2003). The difference in pH between forested and disturbed streams was significant, and can be attributed to the history of land conversion in the area. The ashes resulting from repeated burning of pastures reduced the soil acidity (Makeschin et al. 2008). It can be assumed, that the naturally low pH and the poor buffering capacity during high flows, which resulted in a lowering of the pH value below 6 (Table 4-3), prevented acid-sensitive species from gaining a foothold in the forested streams (Lepori et al. 2003).

Guerold et al. (2000) observed a strong positive correlation between pH and the abundance of Ephemeroptera, Plecoptera, Trichoptera, Coleoptera and some Diptera taxa, although e.g. Diptera of the families Limoniidae, Simuliidae and Chironomidae were acid-tolerant. In general the authors showed a trend for higher richness values with increasing pH (pH values up to 7.5). The positive relation between taxa richness and pH holds also true in the present study (Pearson’s correlation coefficient = 0.362, N = 48, p = 0.01). Taxa which were not or scarcely found in the F1 and F2 transects (*Anchytarsus, Haplohyphes, Leptohyphes, Smicridea, Leptonema*) therefore might be intolerant of low pH values. This assumption is confirmed by the results of the correlation analysis (Table 4-5), which shows significant
relations between pH and abundance of Elmidae, Thraulodes, Anacroneuria, Andesiops, Haplohyphes, Leptohyphes, Smicridaea, Cernotina and Marilia (the latter two being negative).

Table 4-6 Correlations between CCA axes and environmental parameters.

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As far as the oxygen concentration of stream water is concerned, Jacobsen et al. (2003) proposed that in the high altitudes of Andean headwater streams, solubility of oxygen could be a restricting factor shaping aquatic communities. However, oxygen concentrations were close to saturation or even supersaturated (% saturation not shown in Table 4-3), possibly because the turbulence in these high gradient streams re-oxygenated the water. In the correlation analysis, oxygen concentrations did not exhibit any influence on macroinvertebrate community structure. It was neither related to overall density or richness, nor to the abundance of any specific taxa other than Chironomidae. Although the data showed, that oxygen concentration was similar among sites, it has to be considered that the oxygen data in this study might not be representative of the true conditions: The omnipresent bubbles in the water might have influenced the measurements.
4.3 Results and discussion

The input of organic matter in the form of litter detritus proved not to be a strongly decisive factor in the CCA ordination. As already mentioned earlier, the reason for this might be that organic matter input was comparable in both, disturbed and forested streams.

In the NMDS ordination, species and sites spread according to their dissimilarity. The stress of the ordination indicates the quality of this spread. In Figure 4-4 (left) the stress values are shown in relation to the dimensions retained for the analysis. With 4+ dimensions, the stress value falls below 10, which is an acceptable value.

The stress plot in Figure 4-4 on the right shows the stress values of each transect as a circle. The larger the circle, the larger the stress of this particular site, i.e. the location of the site is not optimal in the plot. It can be seen that there are few large circles, three of them belonging to forested sites which have been located near to disturbed sites (Figure 4-4 right, in the centre of the plot).
4.3 Results and discussion

In the NMDS ordination plot 3 groups could clearly be distinguished. One group including all transects from forest stream F3, one rather scattered group with transects from streams F1 and F2, and one group containing all transects of disturbed streams. Species directly associated with stream F3 were *Phylloicus*, *Polythore*, *Anchytarsus* and *Grumichella*. All Ephemeroptera taxa with the exception of *Farrodos* plotted close to disturbed streams. Some taxa appeared as outsiders on the borders of the plot, e.g. *Atanatolica*, *Sialis*, *Hetaerina* and *Cernotina*.

The NMDS plot not only separated all disturbed from forested transects, but also grouped together all transects of stream F3, set apart from the other forest streams. This indicates that natural (forested) conditions promote heterogeneity in macroinvertebrate communities whereas deforestation creates much more uniform community structures. To support this finding we tested for higher variances in the evenness values in forested compared to disturbed sites using the Brown-Forsythe test. This test confirmed that variance in evenness values, and thus heterogeneity of macroinvertebrate community structure between transects, is significantly higher in forested streams (p = 0.05).

The results support the good applicability of NMDS in this study. Taxa, which were uniformly distributed in all samples were found in the centre of the plot (e.g. *Farrodos*, Tipulidae), whereas taxa which exhibited higher abundances in a specific stream or land-use type were found close to the respective transects. The four taxa which were at the outer edges of the plot (*Atanatolica*, *Sialis*, *Haeterina* and *Cernotina*) were taxa only found in forested streams.
4.3 Results and discussion

4.3.5 Indicators

Several clear patterns of macroinvertebrate community composition could be found which could help as an indication for in-stream changes. Trichoptera were equally or more abundant than Ephemeroptera, which was clearly reversed in disturbed catchments. Some Ephemeroptera taxa, such as *Baetodes*, *Haplohyphes*, and *Leptohyphes* were predominantly or exclusively found in disturbed streams. Others, like *Cernotina*, *Atanatolica*, and *Sialis* seemed only to occur in pristine sites. Only one specimen of Odonata (*Polythore*) was encountered in a disturbed transect, compared to 72 specimens (*Polythore* and *Haeterina*) in forested streams. This implies that deforestation might strongly affect Odonata communities in tropical mountain ecosystems, which has also been shown for other tropical regions of the world, for example in Borneo by Sodhi et al. (2010) or in Uganda by Kasangaki et al. (2008).
4.4 Conclusion

The principal aim of this study was to understand how land-use influences the structure of benthic communities in tropical cloud forest streams. In deforested areas, streams showed higher taxa density, lower evenness values and shifts in specific abundances of certain taxa (e.g. more Ephemeroptera, less Odonata) as compared to forested areas. As was shown in the canonical correspondence analysis, the differences in percentage of shade, substrate type and pH were the variables responsible for shaping the community structure. However, the abundance of the aquatic stages could also be influenced by environmental factors affecting the non-aquatic imago stages of the taxa. Odonata imagines for example might be missing raised hides for hunting or mating along disturbed streams. Future studies should therefore also include an analysis of the influence of land-use on imago stages, to determine their role in the shaping of aquatic communities.

In clear contrast to the terrestrial part of the cloud forest ecosystem, we observed that in the aquatic realm, some amount of disturbance, i.e. patchy deforestation, increased macroinvertebrate density and richness. However, there was a strong shift in community structure from forested to disturbed sites, and many taxa disappeared in deforested areas. Deforestation also led to a more homogeneous community structure compared to the highly heterogeneous nature of forested streams. In this respect, an analysis of functional feeding groups would give more insights into the direction of the community shift. If the assumptions are right, one would expect to find more grazers and scrapers in disturbed streams.

Because data on biological indices and their applicability in tropical montane areas are rare, various indices for the stream community data were calculated. We showed that if the water quality is good under both land-uses, the BMWP/Col, the ASPT and the EPT score can not be used to detect changes in community structure occurring between forested and disturbed montane streams. In this study, an analysis of the abundance of single taxa provided better information on in-stream changes. These results demonstrate that more focus has to be put on the improvement of biological indices for tropical montane regions. Site explicit scores have to be developed, so that the community structure of a specific site (e.g. tropical montane stream) can be compared to and evaluated with respect to the ecological conditions at reference sites. The present study is a first step to improve the understanding of tropical montane streams and their response to land-use change and can therefore provide a basis for future developments of biological assessment methods.
5 Summarizing discussion

The fate of water in cloud forests was the central issue of this work. An attempt was made to answer the following three questions: 1. Which factors or processes are most important in shaping the water chemistry of cloud forest streams? 2. How do these differences translate into nutrient export and can we derive some catchment understanding by analyzing nutrient behaviour and export between land-uses? 3. How are aquatic communities influenced by the differences in water chemistry and physical parameters between land-uses and which of these parameters are most important?

By means of three closely connected studies, which were presented and discussed in three separate chapters, it became possible to answer the above mentioned questions and to improve the scientific knowledge on water flow-paths, on factors changing water chemistry and on the consequences of these changes for stream biota. This information will hopefully contribute to the conservation and sustainable management of tropical cloud forest ecosystems.

To investigate the controls on water chemistry of pristine and disturbed south Ecuadorian cloud forest catchments, water samples were screened for differences in electric conductivity, pH, anion, as well as element composition. A principal component analysis served to reduce dimensionality of the data set and extract major factors explaining variation in the data. Three main sources influencing the water chemistry in cloud forests were derived. Land-use practice, i.e. deforestation and conversion to pasture, was by far the most predominant influence on water chemistry, increasing pH and stream cation concentrations. In a deforestation experiment in the Bavarian Alps, Bäumler & Zech (1999) also detected an increase in stream solutes after the removal of 40 % forest cover and attributed this to the removal of the trees and a reduced ion uptake by roots. For four years Martin et al. (1986) monitored the effects of the clearcutting of northern montane hardwood ecosystems, and observed a strong increase in stream solute concentrations and pH in the first year after clearcutting with a gradual decline to almost natural levels after four years. Without giving a direct explanation, the authors name several possible reasons, namely increased soil temperature, reduced transpiration, increased mineralization and nitrification and increased exchange of ions in the soil (Martin et al. 1986). In the present study the pastures have been created about 12-30 years ago (Werner et al. 2005), and still solute concentrations and pH are elevated compared to forested streams. The most probable explanation for this finding is the continuing burning of overgrown pasture areas and a therefore increased nutrient input into the soil in these catchments. However, the soil physical and chemical factors mentioned by Martin et al. (1986) might play a role, too.

In the PCA analysis, the second factor changing water chemistry was the influence of other anthropogenic disturbances such as road construction or gravel excavation. In more populated regions, the impact of road maintenance on nearby stream water chemistry has
already been proven, though this mostly was connected to road salting (Demers & Sage 1990; Mason et al. 1999). Although in the San Francisco catchment, the change in water chemistry due to road construction or gravel excavation was not yet influencing the water quality of the respective subcatchments, the results highlight this pathway as a possible source of water pollution. In other words, we should be aware that the water chemistry in the San Francisco catchment is closely connected to the decisions made and actions taken for this road which connects the province capitals Loja and Zamora.

In general the PCA analysis revealed that tracer studies in montane streams with low ion and element content can favour the use of rare earth elements, which not only enable to trace weathering patterns, but can also highlight some distinct sources of anthropogenic disturbances. Although it ought to be a logical consequence of the remarkably low element and ion content of montane streams (with ECs of 5-35 µS cm⁻¹) the extreme susceptibility of cloud forest water quality to any kind of disturbance has not been noted adequately until now. Even small inputs of pollutants might result in an override of the natural stream chemistry. This could, e.g. have negative effects on the native stream flora and fauna, which have adapted to the low pH and ion content of the water (Lepori et al. 2003).

The results of the second study confirmed the assumptions of the first that sub-surface water contributes significantly to storm flow in the San Francisco catchment. A detailed analysis of nutrient behaviour during events shed light on the predominant processes and nutrient flow paths occurring during slow flow and fast flow respectively. It was discovered that in the San Francisco study area Na concentration decreased during high flows independently of land-use. Na in the study area mainly originates from weathering, i.e. from deeper soil layers (Boy et al. 2008b). By this and other observations it was inferred that under forest, storm flow is predominantly derived from the organic layer and the A horizon, with moderate Mg and Ca concentrations and low Na concentrations (Wilcke et al. 2001). The behaviour of the solute concentration during rain events consequently hints to a larger contribution of ‘old’, i.e. pre-event water to storm flow. The same was found in undisturbed, forested catchments in the Chilean Andes (Blume et al. 2008) and for microcatchments within the San Francisco catchment in Ecuador (Boy et al. 2008b). But then again, various authors also highlight the important contribution of fast flow-paths during storm flow in tropical forest catchments (Bonell & Gilmour 1978; Elsenbeer et al. 1995; Elsenbeer 2001; Hensel & Elsenbeer 1997). This issue definitely deserves a closer look in future studies.

In the present study, Mg and Ca concentrations clearly decreased with increasing discharge under pasture, which could be attributed to largely faster shallow subsurface flow paths combined with some overland flow during heavy rains. The change to a larger contribution of overland flow and thus ‘new’ water with deforestation is in accordance with the results of Germer et al. (2010) for undisturbed forest and pasture catchments in the
Amazon Basin in Brazil. In the San Francisco watershed, however, more research on water flow paths and mean residence time is needed to confirm these findings.

Both, nitrate and sulphate, exhibited a seasonal behaviour during the study period, with constantly decreasing concentrations of nitrate, and a more erratic decrease of sulphate concentrations. Although this phenomenon could not be explained in detail it can be assumed that it is connected to a changing climate regime with decreasing easterly winds and increasing westerly winds at the end of 2007. These changes are most probably due to a weakening of the La Niña event at this time, which caused an increase in sea surface temperature along the Ecuadorian Pacific coast. Observations made by Savoie et al. (1989) at Barbados support this hypothesis. They detected significant correlations of both nitrate and non sea-salt sulphate concentrations with those of Saharan dust, demonstrating that substantial fractions of both can be transported by easterly winds across the tropical North Atlantic in association with the dust.

Because differences in water quality between forested and disturbed streams might not necessarily entail differences in nutrient and element export in these sites, nutrient fluxes were calculated and compared between subcatchments. Nutrient export values in the San Francisco watershed were comparable to the values found in literature for tropical streams. They amounted to 6-8 kg ha$^{-1}$ yr$^{-1}$ for Ca, 7-8 kg ha$^{-1}$ yr$^{-1}$ for K, 4-5 kg ha$^{-1}$ yr$^{-1}$ for Mg, 11-14 kg ha$^{-1}$ yr$^{-1}$ for Na, 19-22 kg ha$^{-1}$ yr$^{-1}$ for NO$_3$ (i.e. 4.3-5.0 kg ha$^{-1}$ yr$^{-1}$ NO$_3$-N) and 17 kg ha$^{-1}$ year$^{-1}$ for SO$_4$. As can be seen in Table 5-1 nutrient export values of watersheds from all over the world can vary some orders of magnitude, depending on the proximity to the coast and thus differences in atmospheric inputs, on the geology (weathering patterns) and on evaporation/concentration processes (McDowell 2002).

<table>
<thead>
<tr>
<th></th>
<th>Ca</th>
<th>K</th>
<th>Mg</th>
<th>Na</th>
<th>NO$_3$-N</th>
<th>SO$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SE Australia$^1$</td>
<td>5</td>
<td>4</td>
<td>10</td>
<td>16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Suisse Alpes$^2$</td>
<td>460-838</td>
<td>9-17</td>
<td>25-48</td>
<td>19-31</td>
<td>4-8</td>
<td>94-178</td>
</tr>
<tr>
<td>Malaysia$^3$</td>
<td>4-7</td>
<td>7-11</td>
<td>4-6</td>
<td>3-4</td>
<td>2-6</td>
<td>1-2</td>
</tr>
<tr>
<td>USA$^4$</td>
<td>5-123</td>
<td>2-10</td>
<td>3-9</td>
<td>7-53</td>
<td>&gt;1</td>
<td></td>
</tr>
<tr>
<td>Costa Rica$^5$</td>
<td>133-442</td>
<td>21-64</td>
<td>53-137</td>
<td>104-339</td>
<td>4-6</td>
<td></td>
</tr>
<tr>
<td>Puerto Rico$^6$</td>
<td>44-96</td>
<td>5-17</td>
<td>28-63</td>
<td>96-161</td>
<td>1-3</td>
<td></td>
</tr>
<tr>
<td>Indonesia$^7$</td>
<td>29</td>
<td>22</td>
<td>31</td>
<td>27</td>
<td></td>
<td></td>
</tr>
<tr>
<td>This study</td>
<td>6-8</td>
<td>7-8</td>
<td>4-5</td>
<td>11-14</td>
<td>4-5</td>
<td>17</td>
</tr>
</tbody>
</table>

$^1$ (Hopmans et al. 1987)
$^2$ (Keller et al. 1989)
$^3$ (Yusop et al. 2006)
$^4$ (Likens et al. 1977; Campbell et al. 2000; Swank & Waide 1988; Sollins et al. 1980)
$^5$ (Newbold et al. 1995)
$^6$ (McDowell & Asbury 1994)
$^7$ (Bruijnzeel 1983)
In the present study, export values did not increase with deforestation, as has been found for example by Likens et al. (1970), Martin et al. (1986) and Williams & Melack (1997). The most logical reason for this is the low specific discharge observed in disturbed sites. Mostly, higher baseflow discharges due to reduced transpiration or higher storm flow discharge due to compaction of the soil under pasture lead to increases in annual discharge and nutrient export volume (Bruijnzeel 2001; Germer et al. 2009; Williams & Melack 1997). The low specific discharge in disturbed sites in the San Francisco watershed are probably due to higher evaporation losses or less water input (via rain or cloud stripping). Interestingly, a clear positive correlation of nitrate export and % forest cover was observed, which might be explained by higher N-need of pasture grasses (Rhoades et al. 1998) and by the fact that no fertilizers were applied on the extensively used pastures.

The objective of the third study was to understand how land-use influences habitat structure and macroinvertebrate communities in cloud forest streams of southern Ecuador. We evaluated these relationships in streams with variable land cover, using multivariate statistics to identify relationships between key habitat variables and assemblage structure, and to resolve difference in composition among sites. Results show that shading intensity, substrate type and pH were the environmental parameters most closely related to variations in community composition observed among sites. As also noted in other tropical montane studies, macroinvertebrate density and partly diversity was lower in forested sites (Bojsen & Jacobsen 2003). One explanation for this phenomenon might be the lowering of pH values to almost 5 during spates in forested streams (Lepori et al. 2003). Additionally, it was observed, that the increasing light input, probably combined with increasing nutrient concentration in disturbed streams lead to greater algae growth, which most probably brought about severe changes in the food web structure (Bojsen & Jacobsen 2003). It is to be expected, that the occurrence of generalist species increases in disturbed sites, whereas especially adapted, stenoeocius species disappear (Benstead et al. 2003). This finding highlights the extreme susceptibility of the native aquatic cloud forest fauna to deforestation. Even with partial deforestation, many taxa will disappear. However, classical bioindication systems, such as BMWP/Col, despite having been successfully used in montane tropical areas (Medellin et al. 2004; Moreno 2008), were not able to detect changes in assemblage structure between disturbed and forested streams in the San Francisco watershed. This was probably due to the overall good water quality even in disturbed streams. The difficulty of biotic indices to detect smaller changes in species associations has received little attention up to now (Ravera 2001). Another central finding of this study was that deforestation strongly affects Odonata communities in tropical cloud forest ecosystems. The susceptibility of Odonata species to deforestation has already been observed in other tropical regions such as Borneo and Uganda (Kasangaki et al. 2008; Sodhi et al. 2010), but still needs to be investigated further. In general, the results indicate that tropical montane headwater streams are complex and heterogeneous ecosystems with low invertebrate densities. It was also discovered that some
amount of disturbance, e.g. patchy deforestation, can lead at least initially to an increase in macroinvertebrate taxa richness of these streams.

Three years of hard work have left more questions than answers. There is still a lot to do! Both for the hydrological and for the biogeochemical monitoring longer time series are needed to detect long term trends and refine the calculations. A closer look has to be taken at the influence of el Niño/la Niña conditions on weather patterns and therefore on rain and cloud water nutrient input. Also, with the use of stable isotopes it might be possible to calculate water mean transit time and derive more understanding on the water flow paths in cloud forests (Asano et al. 2002). It is to be expected that the mean transit time is much higher than previously thought for steep mountainous catchments. Further understanding of different base and storm flow contributions of watershed components might be gained by applying end member mixing analysis (EMMA) (Hooper 2003). In general, little is known about extreme events and their role in nutrient and element export. Connected to this, sediment fluxes (i.e. particulate loads) still need to be calculated to be able to compare dissolved and solid nutrient export (Sammori et al. 2004). As far as the biology of the streams is concerned, an analysis of imagines certainly has to be included, to distinguish if other factors than the ones concerning the larvae are important (Smith & Collier 2005). Some imagines, e.g. might need hiding places, others might need branches or trunks to deposit their eggs, both of which are not abundant in deforested sites. An analysis of larval feeding guilds may provide better insight into a possible alteration of the food chain, e.g. from detritus feeders in forest to grazers and collectors in pasture sites (Bojsen & Jacobsen 2003). Extreme events are also of interest with regard to the aquatic communities (Buss et al. 2004), and little is published on the recolonization of rivers and streams after high flows in montane regions. One of the challenges for the coming macroinvertebrate analyses will be the identification down to species level at least for the biologically most interesting taxa Ephemeroptera, Trichoptera and Plecoptera.

In an appeal to the scientific community to move headwater streams to the head of the class, Lowe & Likens (2005) wrote about the intrinsic values of headwater streams, about their conservation challenges and the opportunities arising hereof. The following quotation is a part of their declaration:

“*There is no doubt that it is important to safeguard lowland sites, but it is difficult to see how any conservation action with a goal of protecting the long-term ecological integrity and ecosystem services of natural systems, whether aquatic or terrestrial, can succeed without a foundation of intact and functional headwaters.*”
6 Danksagung

Irgendwann hat ein weiser Mann mal gesagt „ein Kampf der sich wirklich lohnt, ist der Blick über den Tellerrand“. Das klingt simpel, wird aber heutzutage viel zu oft nicht beachtet. Durch meine Doktorarbeit hatte ich nun drei Jahre die Gelegenheit, einen Blick auf ein fremdes und wundersames Ökosystem zu werfen, und dafür bin ich vielen Menschen wirklich dankbar:

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7 References

Alba-Tercedor J (1996) Macroinvertebrados acuáticos y calidad de las aguas de los ríos. IV Simposio del Agua en Andalucía (SIAGA) 2 203-213


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Climate Prediction Center/NCEP/NWS (2008) El niño southern oscillation (ENSO) diagnostic discussion. Camp Springs, MD


Hamada N, Couceiro SRM (2003) An illustrated key to nymphs of Perlidae (Insecta, Plecoptera) genera in Central Amazonia, Brazil. Revista Brasileira de Entomologia 47 477-480


References


Likens GE, Bormann FH, Pierce RS, Eaton JS, Johnson NM (1977) Biogeochemistry of a forested ecosystem. Springer Verlag, New York


References


Nyholm NEI, Tyler G (2000) Rubidium content of plants, fungi and animals closely reflects potassium and acidity conditions of forest soils. For Ecol Manage 134(1-3): 89-96


Price JR, Velbel MA, Patino LC (2005) Allanite and epidote weathering at the Coweeta Hydrologic Laboratory, western North Carolina, USA. Am Miner 90 101-114


Ravera O (2001) A comparison between diversity, similarity and biotic indices applied to the macroinvertebrate community of a small stream: the Ravella river (Como Province, Northern Italy). Aquatic Ecology 35 97-107


Richards PW (1952) The tropical rain forest. Cambridge University Press,


Roldan G (1996) Guia para el estudio de los macroinvertebrados acuaticos del departamento de Antioquia. 2da edicion. Fondo FENColombia-Colciencias-Universidad de Antioquia, Bogota, Colombia


