Preliminary evaluation of the runoff processes in a remote montane cloud forest basin using Mixing Model Analysis and Mean Transit Time

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Abstract:
In this study, the Mean Transit Time and Mixing Model Analysis methods are combined to unravel the runoff generation process of the San Francisco River basin (73.5 km²) situated on the Amazonian side of the Cordillera Real in the southernmost Andes of Ecuador. The montane basin is covered with cloud forest, sub-páramo, pasture and ferns. Nested sampling was applied for the collection of streamwater samples and discharge measurements in the main tributaries and outlet of the basin, and for the collection of soil and rock water samples. Weekly to biweekly water grab samples were taken at all stations in the period April 2007–November 2008. Hydrometric data, Mean Transit Time and Mixing Model Analysis allowed preliminary evaluation of the processes controlling the runoff in the San Francisco River basin. Results suggest that flow during dry conditions mainly consists of lateral flow through the C-horizon and cracks in the top weathered bedrock layer, and that all subcatchments have an important contribution of this deep water to runoff, no matter whether pristine or deforested. During normal to low precipitation intensities, when antecedent soil moisture conditions favour water infiltration, vertical flow paths to deeper soil horizons with subsequent lateral subsurface flow contribute most to streamflow. Under wet conditions in forested catchments, streamflow is controlled by near surface lateral flow through the organic horizon. Exceptionally, saturation excess overland flow occurs. By absence of the litter layer in pasture, streamflow under wet conditions originates from the A horizon, and overland flow. Copyright © 2011 John Wiley & Sons, Ltd.

KEY WORDS mixing model analysis; mean transit time; tracers; hydrological processes; Andean cloud forest; Ecuador

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INTRODUCTION
According to Myers et al. (2000), the tropical Andes belongs to the 25 hotspots of biodiversity on earth; cloud forests being ranked as one of the most species-rich ecosystems. The geochemistry, biology and ecology of these ecosystems are strongly controlled by the water that passes through (Neill et al., 2006; Boy et al., 2008). Disturbance of the hydrology of these ecosystems will therefore directly affect all water-dependent processes. In this regard, understanding of the hydrology is essential to conserve in a more effective way these ecosystems. Despite scarce funding and the poor accessibility, several research groups recently deployed considerable efforts in collecting data in pristine Andean basins. Most studies have been carried out on micro-catchments of less than 10 km² with a monotonic landuse and cover (Buytaert, 2004; Goller et al., 2005; Fleischbein et al., 2006; Buytaert et al., 2007; Boy et al., 2008). However, to examine the effect of anthropogenic pressures requires studying the hydrology of larger basins where people converted forested areas into productive agricultural land and/or partly urbanised pristine areas for living. The highly spatial variability of climate, topography and other catchment properties on small scales, typical for the Andean region, prohibits extrapolation of findings obtained at the scale of micro-catchments with monotonic landuse to basins with different types of landuses. In addition, the hydrology of larger, medium or even small basins might be governed by other processes than the processes controlling the rainfall-runoff at small basin scale, justifying the need to analyse the hydrological processes at the scale of medium to large catchments (Mortatti et al., 1997; Célleri, 2007; Bücker et al., 2010). Hydrological processes here are defined as the processes controlling the conversion of precipitation into streamflow. This definition encompasses questions such as: (i) Which hydrological components contribute to streamflow (overland, soil, subsoil, shallow and deep aquifers)?, (ii) How are the different storage reservoirs interconnected?, (iii) What is the residence time of the water in the different hydrologic components?, and (iv) To what extent reflect water in the different reservoirs the geochemical composition of the source area?. For
inference of the hydrological processes, multiple techniques are used, such as hydrometric data (e.g. Kirkby, 1978; McDonell, 1990; Bonell, 1993; Montanari et al., 2006), isotropical tracers (e.g. Dincer et al., 1970; Niemi, 1977; Payne and Schroeter, 1979; Sklash and Farvolden, 1979; Maloszewski et al., 1983; Turner et al., 1987; Buttle, 1994; Mortatti et al., 1997), chemical tracers (e.g. Christophersen et al., 1990; Hooper et al., 1990; Robson and Neal, 1990; Hensel and Elsenbeer, 1997), modeling (e.g. Stephenson and Freeze, 1974; Beven and Kirkby, 1977; Dunne, 1983; Beven et al., 1995; Beven, 2001; Buytaert and Beven, 2011) or a combination of previous methods (e.g. Pearce, 1990; Wels et al., 1991; Giusti and Neal, 1993; Bonell and Fritsch, 1997; Kendall and McDonnell, 1998). Buytaert (2004); Buytaert et al. (2007) and Célleri (2007) analysed the rainfall-runoff process of Andean highland ecosystems using solely hydrometric data. Research of Payne and Schroeter (1979); Schellekens et al. (2004); Goller et al. (2005); Blume et al. (2008); Chaves et al. (2008) and Bücker (2010) demonstrated that combining different techniques leads to a more accurate understanding of the rainfall-runoff process. The main advantage of monitoring the isotope and geochemical composition in different compartments of the hydrological cycle is that in a relative short period on the basis of a limited amount of data, a fairly accurate reconstruction can be made of the water contributing areas and flow paths under variable rainfall conditions and landuses.

In line with previous, the authors’ objective was deriving a preliminary impression of the streamflow generating processes in the San Francisco River basin (South Ecuador) using hydrometric, hydrochemistry and isotopic measurements. The underlying hypotheses were: (i) use of multi-approach techniques allows the tentative identification of the principal hydrological processes and permits identification of the main sources of water, (ii) the mean transit time (MTT, McGuire and McDonnell, 2006) of the streamwater in the San Francisco basin is short and not influenced by deep water contribution, (iii) the subsurface lateral flow through the organic horizon dominates the runoff generation during wet conditions, and (iv) monitoring of the isotope and geochemical composition of water samples in different parts of a basin, yields in a relative quick and inexpensive way for the features of the hydrology of ungauged or poorly gauged basins.

MATERIALS AND METHODS

Study area

The San Francisco River basin is located in on the Amazonian side of the Cordillera Real between 1800 and 3250 m above sea level (a.s.l.) in the southernmost Andes of Ecuador, latitude 03°58′ S and longitude 79°04′ W (Figure 1). The study basin is 75.3 km² and drains into the Amazon basin. The catchment is divided into a northern and a southern zone with distinct landuses. Natural forest in the north is replaced by extensive grazeland (Setaria sphacelata) (Werner et al., 2005), which when abandoned is replaced by ferns (Pteridium aquilinum, L). The southern basin area is covered with pristine montane cloud forest with trees up to 20 m high. The dominant plant species belong to the families Lauraceae, Euphorbiaceae, Melastomataceae and Rubiaceae (Homeier et al., 2002). At the highest crest of the basin (3250 m a.s.l.), the vegetation mainly consists of a sub-páramo shrub land and an evergreen elfin forest, both of which are adapted to higher wind speed, lower temperatures and nutrient availability (Beck et al., 2008). Land cover distribution

![Figure 1. Location of the study area and nested subcatchments. 1 = PL, Planta (catchment outlet), 2 = SF, Rio San Francisco, 3 = FH, Rio San Francisco headwater, 4 = QR1, Quebrada Ramon 1, 5 = QR2, Quebrada Ramon 2, 6 = QM, Quebrada Milagro, 7 = QZ, Quebrada Zurita, 8 = QN, Quebrada Navidades, 9 = QP, Quebrada Pastos, 10 = QC, Quebrada Cruces, OL = soil water sampled in organic layer, AL = soil water sampled in A horizon layer, W = rock water](Image: Figure 1. Location of the study area and nested subcatchments. 1 = PL, Planta (catchment outlet), 2 = SF, Rio San Francisco, 3 = FH, Rio San Francisco headwater, 4 = QR1, Quebrada Ramon 1, 5 = QR2, Quebrada Ramon 2, 6 = QM, Quebrada Milagro, 7 = QZ, Quebrada Zurita, 8 = QN, Quebrada Navidades, 9 = QP, Quebrada Pastos, 10 = QC, Quebrada Cruces, OL = soil water sampled in organic layer, AL = soil water sampled in A horizon layer, W = rock water)
of the monitored subbasins is summarised in Table I. Anthropogenic impacts in the north mainly consist of extensive wood cutting, river bed gravel mining, the existence and extension of gravel roads and grazeland, while a hydropower plant is located in the southern zone of the basin.

The climate is controlled by Amazonian air masses (Beck et al., 2008). The precipitation pattern is unimodal with moderate to low inter-annual variability. The main wet season is from April to September, and the dry season from October to December (Fleischbein et al., 2006). According to Rollenbeck (2006), precipitation is strongly positively correlated with altitude, and intensities based on 5-min data are low with 90% of all monitored precipitation rates less than 10 mm h⁻¹. Precipitation is primarily caused by advective orographical clouds. In the period 1964–2008, annual precipitation varied between 900 and 4300 mm (Instituto Nacional de Meteorología e Hidrología) with an average of 2200 mm at an altitude of 1960 m; wind speeds being low and cloud cover less dense at this elevation. Annual average rainfall increases to 4700 mm (monitoring period 1994–2004) at the Cerro del Consuelo station located at the border of the catchment (3200 m a.s.l.) (Rollenbeck, 2006) and up to 6700 mm when taken horizontal rain and fog deposition into account (Bendix et al., 2008). Horizontal rain and cloud/fog water deposition contributes considerably to the total water input representing up to 41.2% of the basin water yield at 3180 m a.s.l.; below 2270 m a.s.l., water input consists only of vertical rain (Bendix et al., 2008). The mean annual temperature at 1952 m a.s.l. is 15.2 °C. The coldest months are June and July, with a mean temperature of 14.4 °C; the warmest month is November with a mean temperature of 16.1 °C. The average temperature gradient between the station at 1952 m and 2927 m a.s.l. is 0.66 °C per 100 m and the mean humidity is 86% (Fleischbein et al., 2006).

The geology of the San Francisco catchment corresponds to the Chiguinda unit, which is composed of Paleozoic metamorphic rocks such as semipelite, phyllite and quartzite (Litherland et al., 1994; Hungerbühler, 1997). As stated by Makeschin et al. (2008) the geology and soil mineralogy are fairly uniform in the basin. To the knowledge of the authors, no information on the rock permeability is available. The main chemical characteristics of the weathered and non-weathered rocks are listed in Table II (derived from the website of the DFG Research Unit FOR816, www.tropicalmountainforest.org). Generally, weathered rocks have lower concentration of all elements except Al of which the concentration is almost the same as in non-weathered rocks.

The main soil types in the basin are Histosols, Regosols, Cambisols and Stagnasols (FAO/ISRIC/ISSS, 1998). The soil distribution per subbasin is summarised in Table I (Ließ et al., 2009). Histosols typically contain a high fraction of non-decomposed plant fibers (Beck et al., 2008), are located in the sub-páramo under cloud forest and are the most common soil in the basin (Wilcke et al., 2002). The higher situated Histosols are on average 90 cm deep while Histosols under cloud forest are less deep (Wilcke et al., 2002; Makeschin et al., 2008). The area of Regosols and Cambisols decreases, while the Stagnasol soil area increases with altitude (Ließ et al., 2009). Landslides are due to the steepness of the terrain (slopes varying between 48% and 61%), the shallowness of the soils, the aboveground biomass and the plentiful precipitation year round. Open spaces in the landscape with time are covered by secondary forests.

Table I. Main characteristics of the San Francisco basin and subbasins. Acronyms of the subcatchments are explained in Figure 1

| Subcatchment | PL | SF | FH | QR1 | QR2 | QM | QZ | QN | QP | QC |
|--------------|----|----|----|-----|-----|----|----|----|----|----|
| Topography   | Units |               |               |     |     |     |     |     |     |     |
| Area         | km²  | 75.3 | 64.2 | 34.8 | 4.6 | 4.6 | 4.6 | 1.3 | 11.3 | 10.0 | 3.4 | 0.8 |
| Slope        | %    | 55   | 55   | 55   | 61  | 61  | 48  | 55  | 53   | 59   | 49  |
| Min elevation| m    | 1742 | 1910 | 1900 | 1743| 1872| 1869| 2025| 2050 | 1914 | 1829 |
| Max elevation| m    | 3250 | 3250 | 3250 | 3150| 3150| 3150| 2650| 3075 | 3025 | 2900 |
| Hydro-meteorology |               |               |     |     |     |     |     |     |     |     |     |
| Mean precipitation | mm year⁻¹ | 3396 | 3200 | 3372 | 3799| 3820| 3423| 2972| 2962 | 2760 | 2760 |
| Mean discharge | mm year⁻¹ | 2634 | 2378 | 2734 | 3090| 3078| 2764| 2217| 2307 | 2041 | 2050 |
| Runoff coefficient |               | 0.78 | 0.74 | 0.81 | 0.81| 0.81| 0.78| 0.75| 0.78 | 0.74 | 0.76 |
| Geology      | Palaeozoic metamorphic rocks |               |     |     |     |     |     |     |     |     |     |
| Landuse      |                  |               |     |     |     |     |     |     |     |     |     |
| Forest       | %    | 68   | 65   | 67   | 80  | 80  | 90  | 72  | 65   | 63   | 63   |
| Sub-páramo   | %    | 21   | 21   | 29   | 18  | 19  | 9   | 15  | 17   | 10   | 10   |
| Pasture/Bracken | %   | 9    | 12   | 3    | 1.8 | 0.8 | 0.8 | 12  | 16   | 26   | 67   |
| Others       | %    | 2    | 2    | 1    | 0.2 | 0.2 | 0.2 | 1   | 2    | 1    | 1    |
| Histosols    | %    | 66   | 74   | 74   | 70  | 66  | 57  | 70  | 71   | 62   | 54   |
| Regosols     | %    | 16   | 15   | 15   | 18  | 18  | 25  | 18  | 16   | 21   | 24   |
| Cambisols    | %    | 11   | 7    | 7    | 8   | 10  | 13  | 8   | 8    | 11   | 14   |
| Stagnasol    | %    | 7    | 4    | 4    | 4   | 6   | 5   | 4   | 5    | 6    | 8    |
| Horizon       | Horizon thickness (cm) | Ks (mm h\(^{-1}\)) | pH | C  | Al | Ca  | Fe  | Mg  | Mn  | K   | Na  |
|---------------|------------------------|---------------------|----|----|----|-----|-----|-----|-----|-----|-----|
| Forest        |                        |                     |    |    |    |     |     |     |     |     |     |
| O             | 10-20                  | 166                 | 4.7 | 466 | 5.6 | 5.3 | 3.6 | 1.8 | 0.40 | 2.5 | 0.37 |
|               |                        |                     | 4.7 | (3.4-6.7) | (0.2-37.5) | (0.2-29.8) | (0.02-46.9) | (0.2-10.2) | (0.01-2.3) | (0.7-14.4) | (0.01-6.0) |
| A             | 10-20                  | 92                  | 3.6 | 48.1 | 23.2 | 0.03 | 18.9 | 1.04 | 0.29 | 8.5 | 0.30 |
|               |                        |                     | 3.6 | (3.3-4.1) | (12.7-44.1) | (0.02-0.18) | (11.7-34.6) | (0.5-1.9) | (0.21-0.4) | (3.9-15.7) | (0.16-0.55) |
| B             | 10-80                  | 11                  | 3.9 | 34.2 | 30.1 | 0.05 | 22.9 | 1.23 | 0.30 | 10.2 | 0.33 |
|               |                        |                     | 3.6 | (3.6-4.5) | (10.7-55.8) | (0.02-0.12) | (11.5-38.2) | (0.5-2.3) | (0.4-0.18) | (4.8-16.9) | (0.16-0.58) |
| C             | 30-50                  | 17.9                | 4.1 | 10.5 | 33.2 | 0.06 | 24.8 | 1.36 | 0.29 | 11.4 | 0.36 |
|               |                        |                     | 4.1 | (3.7-4.8) | (13.7-79.1) | (0.02-0.11) | (13.8-41.3) | (0.5-2.3) | (0.16-0.4) | (3.9-17.6) | (0.19-0.57) |
| Sub-páramo    |                        |                     |    |    |    |     |     |     |     |     |     |
| O             | 10-20                  | 135                 | 4.7 | 446 | 5.5 | 4.2 | 2.6 | 1.3 | 0.68 | 2.3 | 0.17 |
|               |                        |                     | 4.7 | (3.7-5.9) | (0.3-24.1) | (0.2-11.2) | (0.14-12.1) | (0.2-3.1) | (0.06-2.2) | (1.02-8.1) | (0.03-0.4) |
| A             | 10-40                  | 91                  | 4.2 | 89.3 | 20.6 | 0.17 | 13.6 | 1.1 | 0.15 | 6.8 | 0.23 |
|               |                        |                     | 4.4 | (3.9-4.5) | (3.3-45.2) | (0.05-0.9) | (6.6-24.9) | (0.2-2.1) | (0.1-0.3) | (0.6-14.0) | (0.1-0.4) |
| B             | 30-60                  | 11                  | 4.4 | 44.3 | 26.1 | 0.08 | 17.3 | 1.4 | 0.15 | 8.1 | 0.24 |
|               |                        |                     | 4.4 | (4.2-4.7) | (3.1-53.0) | (0.02-0.33) | (6.9-29.8) | (0.1-2.8) | (0.09-0.3) | (0.6-16.7) | (0.08-0.5) |
| C             | 20-50                  | 4.7                 | 16.2 | 33.5 | 0.04 | 24.3 | 1.7 | 0.15 | 11.2 | 0.28 |
|               |                        |                     | 4.7 | (4.5-5.1) | (1.7-55.3) | (0.02-0.10) | (6.9-41.2) | (0.2-3.3) | (0.09-0.3) | (0.3-18.6) | (0.08-0.4) |
| Pasture/Shrubs|                        |                     |    |    |    |     |     |     |     |     |     |
| A             | 10-50                  | 14                  | 5.0 | 50.3 | 45.6 | 4.3 | 31.2 | 3.1 | 0.41 | 9.8 | 0.63 |
|               |                        |                     | 5.0 | (4.1-7.5) | (13.1-102.9) | (0.04-63.6) | (2.4-119.1) | (0.4-19.6) | (0.02-2.2) | (2.3-21.3) | (0.17-2.3) |
| B             | 30-60                  | 17                  | 4.9 | 37.6 | 38.4 | 0.21 | 26.2 | 1.5 | 0.24 | 11.3 | 0.67 |
|               |                        |                     | 4.9 | (3.9-5.9) | (14.2-70.4) | (0.03-1.35) | (7.7-46.5) | (0.3-4.2) | (0.39-0.17) | (4.5-22.9) | (0.19-2.6) |
| C             | 20-50                  | 30                  | 5.0 | 14.6 | 41.7 | 0.15 | 27.9 | 1.7 | 0.24 | 12.0 | 0.70 |
|               |                        |                     | 5.0 | (4.2-6.1) | (20.0-81.4) | (0.04-1.3) | (10.1-48.1) | (0.6-3.8) | (0.16-0.4) | (3.3-22.5) | (0.17-2.6) |
| Rocks         |                        |                     |    |    |    |     |     |     |     |     |     |
| Weathered     | -                      | -                   | -  | -   | -   | -   | -   | -   | -   | -   | -   |
|               |                        |                     |    |    |    |     |     |     |     |     |     |
| Non-weathered | -                      | -                   | -  | -   | -   | -   | -   | -   | -   | -   | -   |
|               |                        |                     |    |    |    |     |     |     |     |     |     |
Table II presents the main soil properties per landuse and horizon (data provided by the DFG Research Unit FOR816). The reader is referred to Makeschin et al. (2008) for a description of the laboratory analyses used. As depicted in Table II, C, Ca, Mn and the saturated hydraulic conductivity (Ks) decrease with depth (from the O to the C horizon), but slightly increase under pasture and shrubland. It is noticed that the saturated hydraulic conductivity under pasture and shrub is considerably smaller than under zero anthropogenic interference (Huwe et al., 2008). As stated by Wilcke et al. (2008) Al, Fe and K increase with depth, while Mg, Na and pH are very uniform throughout the soil profile. The O horizon significantly reduces under shrubs or ferns and disappears under pasture (Makeschin et al., 2008). Sub-páramo and forest soils are very similar. According to these authors, frequent burning of pasture results in a slight increase of hydraulic conductivity (Huwe et al., 2008) for a description of the laboratory analyses used.

Field sampling and laboratory analysis

A nested sampling approach was used for the collection of streamwater (Table I and Figure 1), with eight sampling points (subbasins) in the main tributaries, one in the main river (SF) and the outlet (PL) of the San Francisco River basin. The selection of the sites was restricted by landuse, land cover and accessibility. Four of the ten subbasins are representative for cloud forest (FH, QR1, QR2 and QM), two subbasins are covered mainly with pasture (QP and QC), and two subbasins show clear anthropogenic interference (QN and QZ). The gully Ramon (QR) is monitored at two locations, QR1 and QR2, respectively. QR2 is located just before the intake channel of the hydropower plant and QR1 downstream of the intake (Figure 1).

Precipitation was sampled for the characterisation of the chemical composition in the lower part of the catchment at 1940 m a.s.l., using polyethylene bottles installed at 1.2 m above the surface. At higher altitudes (2825 m a.s.l.), the chemical signature of precipitation was reconstructed using historical information collected between 2003 and 2005 by Beiderwieden et al. (2005) and Rollenbeck et al. (2005).

At three locations in the catchment, two in forest (OL1 and OL3) and one in sub-páramo (OL2), soil water samples in the O horizon were collected using zero-tension lysimeter devices consisting of 0.2 × 0.2 m plastic boxes covered with a polyethylene net. Soil water data of the A horizon (AL1) were derived from Boy et al. (2008), who used mullite suction cups with an average pore size diameter of 0.1 μm. Both, O and A horizon water samples are an average of several samples collected in Histosols and Regosols. Soil water of the organic horizon in sub-páramo sites was sampled from the free draining water. Due to admittance refusal by landowners’ soil water samples in pastures/ferns sites, the subcatchments FH and QZ could not be collected. The authors however assume that the monitored sites are representative for the basin given the relative uniform soil distribution.

Rock water samples were collected in two places of the catchment directly from springs emerging from rock fractures. Despite the effort to find more springs, it was not possible due to the inaccessibility of the terrain. One sampling site is located just below the QR2 site, while the second site is close to SF (Figure 1). These two points are considered representative for the area given the fairly uniformity of the geology. Piezometers for sampling the water in the underground could not be installed because of the compactness of the underlying rock formation.

Weekly to biweekly water grab samples were collected at all sites in the period April 2007–November 2008. In line with the availability of historic water quality data, water grab samples of precipitation, streams, soil and rock were analysed on the following chemical elements: Al, Ca, Fe, Mg, Mn, K and Na. All water samples were filtered in the field using 0.45-μm polypropylene membrane filters (Paradise 25 PP Syringe Filters, Whatman Inc.) and stored in acid washed PE bottles. Samples were acidified to a pH < 2 within 3 h after collection using nitric acid, were frozen and transported to Germany. Element concentrations were determined at the Institute for Landscape Ecology and Resource Management of the Justus-Liebig Universität Gießen with an inductive coupled plasma-mass spectrometer (ICP-MS, Agilent 7500ce, Agilent Technologies). The quality of ICP-MS measurements was frequently checked using certified samples (NIST 1643e and NRC-SLR4) and additional internal calibration procedures. The pH and electrical conductivity (EC) were measured in the field using a WTW pH Cond340i handheld meter (Weilheim, Germany).

The 18O/16O ratio was determined on streamwater samples, collected in tightly closed amber glass bottles (Th. Geyer GmbH & Co. KG, Germany) and analysed in Gießen using a direct-inject liquid-water isotope analyser (DLT100, Los Gatos Research, Mountain View, CA, US), with an analytical precision of ± 0.2%. Ratios of 18O/16O are expressed in delta units, δ18O (%o, parts per mille). δ18O was not measured in precipitation throughfall samples because Goller et al. (2005) reported extreme small differences between the δ18O concentration in rainfall and throughfall. Since δ18O was not measured in precipitation, precipitation δ18O data was reconstructed in two ways. First, δ18O data collected in the Estación Científica San Francisco (ECSF), situated in the study basin, in the period August 2000–August 2001 were derived from Wagner (2002) and Goller et al. (2005). Secondly, the online isotopes in precipitation calculator (OIPC) (www.watersisotopes.org) was used to estimate the δ18O precipitation amplitude at different altitudes, as a basis for the analysis of the altitude influence (McGuire et al., 2005). The OIPC results were validated in the ECSF station δ18O precipitation measurements. In Ecuador, 20 climate stations are controlled by the International Atomic Energy Agency/World Meteorological Organization Global Network for isotopes with altitudes ranging from 6 to 3150 m a.s.l. δ18O is calculated using the Bowen and Wilkinson (2002) algorithm, refined by Bowen and Revenaugh (2003).
Hydrometric measurements

The water level at the outlet of the basin and each subbasin was recorded with an accuracy of $\pm 1$ mm with a 5 min interval using pressure transducers and capacitance probe gauges (Odyssey Capacitance Probes and Odyssey Pressure Data Recorder, Dataflow Systems PTY Ltd, NZ). All river cross sections with exception of the QC outlet section were stable. In this section, a Thompson (V-notch) weir (90°/C14 section) was installed. Discharge versus stage measurements were made frequently with a Flo-Mate 2000 device (Marsh-McBirney Inc., MD, US) and a Flow Probe 101 (Global Water Instrumentation Inc., CA, US). Power or polynomial stage–discharge relationships were developed. For the QC station, the Kingdawater–Shen relation (US Bureau of Reclamation, 2001) was used to convert water level data to flow rate data. Precipitation data (rainfall and fog) were provided by Bendix and Richter (personal communication) of the DFG Research Unit FOR816. A detailed description of the setup of the meteorological stations is given by Bendix et al. (2008). Four meteorological stations were used to derive volume-weighted element values.

Due to harsh environmental conditions, equipment failure occurred several times but never lasted longer than a few days. Hence, data gap filling for precipitation and discharge was applied. Hourly rainfall gap filling was conducted applying regression analyses with other station data and bulked weekly rainfall measurements. Discharge gaps were filled using the relationship between rainfall and discharge data from neighboring catchments. Discharge data of October and November 2008 were not used because an extreme flood event changed the geometry of the measuring cross section. Hourly fog deposition data series were estimated based on fixed monthly ratios between rainfall and fog deposition.

Mixing model analysis

A Mixing Model Analysis technique based on the procedure outlined by Hooper et al. (1990) was used for the evaluation of the contribution of rainfall, soil water and rock water to streamflow, considered in this study as the three principal sources. End-members were selected using two-dimensional (2-D) plots, called mixing diagrams, plotting one solute against another solute for all possible combinations of selected elements. If the different water sources mix conservatively, most of the streamwater samples lie inside the triangle formed by the three selected end-members (Christophersen et al., 1990). Given the vastness of data, only the element combinations that gave better results are presented. Whereas in many studies, the tracer technique is used to quantify the contribution of the different water sources or to separate subflow events (Elsenbeer et al., 1995; Chaves et al., 2008; Soulsby et al., 2003; Mortatti et al., 1997; Robson and Neal, 1990; among others), in this study due to the inaccessibility of the basin, the technique is used to identify the source areas contributing to streamflow. The authors recognise the uncertainty associated to the approach, but anticipate that using multiple techniques reduce the uncertainty on the findings. Furthermore, the results in this study will be used for the design and setting up of a more detailed and effective monitoring scheme leading to more conclusive results.

Mean Transit Time estimation

An exponential piston-flow model (EPM) using a simple sine-wave approach (Malozewski et al., 1983; DeWalle et al., 1997), was used to estimate the MTT at basin scale (McGuire and McDonnell, 2006; Soulsby et al., 2006). The model assumes that the decrease in the $\delta^{18}O$ amplitude of streamwater relative to precipitation provides a basis for determining the transit time (Unnikrishna et al., 1995). The model evaluation process described by McGuire and McDonnell (2006) was used for the parameter identification. The model optimisation was performed using Monte Carlo simulations. The precipitation amplitude was estimated using the sine-wave function given in Equation (1):

$$\delta^{18}O = X + \text{Az}1[\cos(ct - \theta)]$$

where $\delta^{18}O$ is the predicted $\delta^{18}O$, $X$ the mean annual $\delta^{18}O$, $\text{Az}1$ the annual amplitude of $\delta^{18}O$ for precipitation, $c$ the angular frequency constant (2$\pi$/365), $t$ the time in days after an arbitrary date and $\theta$ the phase lag or time of the annual peak $\delta^{18}O$ in radians. Amplitudes for precipitation at different altitudes were estimated; however, minor to no difference was found between values.

The amplitude ($\text{Az}2$) and phase lag ($\theta$) for streamflow were estimated using the Equations (2) and (3), respectively:

$$\text{Az}2 = \text{Az}1 \left(1 + \frac{c^2MTT^2}{\eta^2}\right)^{-1/2}$$

$$\theta = cMTT \left(1 - \frac{1}{\eta}\right) - \arccos \left[\left(1 + \frac{c^2MTT^2}{\eta^2}\right)^{-1/2}\right]$$

where $c$ is the angular frequency constant (2$\pi$/365) and $\eta$ is a parameter describing the piston flow portion of the model. $\eta$ is equal to the total volume of water in the system divided by the volume with an exponential distribution of transit times. For $\eta = 1$, the model is equivalent to an exponential model, while for $\eta \rightarrow \infty$, the model approaches pure piston flow.

The MTT of water leaving the subcatchment or catchment is calculated by Equation (4):

$$MTT = c^{-1}\eta \left[\frac{\text{Az}2}{\text{Az}1} \right]^{-2} \left[\left(\frac{\text{Az}2}{\text{Az}1} \right) - 1\right]^{1/2}$$

Since water samples were collected on a weekly to biweekly interval, high flow samples are poorly represented with the consequence that the estimation of MTT corresponds to basically low (base and intermittent) runoff conditions. Evident samples collected during storm conditions were excluded, analogous to the approach followed by Soulsby et al. (2006). Due to the simplicity of the used model and the data limitation, the results presented herein could contain high uncertainty and
should therefore be considered as a first approximation of the MTT (Maloszewski and Zuber, 1993; McGuire and McDonnell, 2006). However, given the objectives of the study, the MTT value could be considered as a reference for identifying deep water contribution.

RESULTS AND DISCUSSION

Rainfall-runoff

Annual precipitation in the subbasins in the observation period April 2007–November 2008 varied between 2700 and 3820 mm year\(^{-1}\). As mentioned, the precipitation pattern has low inter-annual variability. Figure 2 depicts the seasonality in precipitation and streamflow of the PL station located at the outlet of the San Francisco basin. A similar behavior is found in all subbasins. A fast response of discharge to rainfall is noticed. As depicted in Table I, the average water yield of the subbasins varies between 204 and 3090 mm year\(^{-1}\), representing 76% to 81% of precipitation. Small differences are found mainly due to the spatial variability of rainfall depth and fog interception. Chaves et al. (2008) analyzing rainfall-runoff of a small rainforest catchment in Rancho Grande, Brazil, found similar values. Analysis of the rainfall timeseries reveals that the rainfall intensity of most events is less than the saturated hydraulic conductivity of the top layer, with average values ranging between 91 and 166 mm h\(^{-1}\) for forest and sub-páramo soils and 14 to 17 mm h\(^{-1}\) for pasture soils (Table II). In general, 90% of the rainfall intensities are less than 10 mm h\(^{-1}\) (Rollenbeck, 2006). Given the overall low rainfall intensities, Horton overland flow is unlikely to occur under forest and sub-páramo vegetation. However, on grazeland infiltration, excess overland flow is likely to occur during storm events given the low value of the saturated hydraulic conductivity of the top horizon. Future research in the study area is needed to identify its importance and to verify if re-infiltration of excess overland flow occurs. Fleischbein et al. (2006), in a study conducted in a micro-catchment of the San Francisco basin cover with forest close to the gauging stations QM and FH (Figure 1), excluded the occurrence of saturation excess overland flow (see also Boy et al., 2008; Bucker, 2010). Bogner et al. (2008), in a study conducted on slopes inside the QC subbasin, close to the QM gauging station, observed using dye tracers preferential flow close to the surface of pasture plots as a consequence of compaction of the top layer, whereas under primary forest, lateral flux was deeper and more evenly distributed in the soil profile. Based on the component analysis of streamflow during storms, the authors expect that saturation excess overland flow near to the river bed takes places and that on grazeland due to a reduction of the saturated hydraulic conductivity of the top horizon temporarily and locally, saturation excess overland flow occurs.

Hydrochemistry

As depicted in Table III, precipitation has low solute concentration compared to the other water sources. The pH is acid, and EC is low. Both are relatively constant in all water sources ranging between 4.37 to 7.51, and 2 to 35 µS cm\(^{-1}\), respectively. Al concentration is highest in soil water of the A horizon with an average concentration of 526 µg l\(^{-1}\) followed by the O horizon with 311 µg l\(^{-1}\). Instead of increasing with depth, the Al concentration is considerably lower in the rock water sources with averages of 10 and 19.4 µg l\(^{-1}\) for W1 and W2, respectively. From this, it can be concluded that Al is less mobile in mineral layers and, as stated by Makeschin et al. (2008), most likely to be retained by secondary minerals. Highest concentration of Ca and Mg was found in the soil water samples collected in the A horizon (average values of 1167 and 467 µg l\(^{-1}\)) and rock water (average values of 1175–1190 µg l\(^{-1}\) and 527–654 µg l\(^{-1}\)) but lower in the organic horizon with average concentrations of 135 to 685 µg l\(^{-1}\) and 176 to 302 µg l\(^{-1}\) for Ca and Mg, respectively. Na concentration is almost three times higher in rock water than in soil water sources. Water from O horizon has higher concentration of Mn than mineral layers, with average concentrations ranging between 14.0 and 52.2 µg l\(^{-1}\). K concentration is almost constant in all water types except for W1 where the concentration is nearly two orders of magnitude higher. The concentration of the major solutes in the soil and rock water samples, except Al and Ca, is very similar to the concentration trend of the elements in the solid phase. Same results were found by Boy et al. (2008) in a study conducted in three micro-catchments (8 to 13 ha) close to the San Fransisco head gauging station FH (Figure 1).

Concentration versus discharge was evaluated for all streamwater sampling stations where streamflow data were available. Only the results for the PL station for, respectively, Al and Na are shown in Figure 3. Details for the other subcatchments and solutes concentrations are listed in Bucker (2010). Results reveal that Al and Na are always significantly related to discharge, while this relation is variable and less visible for Ca, Mg, Mn and K. Na concentrations decrease with an increase in discharge, while Al increases (Figure 3). Ca and Mg behave similar to

Figure 2. Hourly timeseries of rainfall and total streamflow in mm of the San Francisco basin

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| Sample location | pH    | EC (µS cm⁻¹) | Al (mg L⁻¹) | Ca (mg L⁻¹) | Fe (mg L⁻¹) | Mg (mg L⁻¹) | Mn (mg L⁻¹) | K (mg L⁻¹) | Na (mg L⁻¹) |
|-----------------|-------|--------------|-------------|-------------|-------------|-------------|-------------|------------|-------------|
| Rainfall        | 5.7   | (4.6–6.4)    | (2–35)      | (0.6–22.0)  | (44.14–335) | (1.7–22.1)  | (4–206)     | (0.6–5.5)  | (40–303)    | (33–556)     |
| Soil water      |       |              |             |             |             |             |             |             |             |
| OL 1            | 5.1   | (4.7–5.5)    | (10–27)     | (172–423)   | (40–1939)   | (11.5–72.7) | (41–469)    | (0.5–160)  | (38–843)    | (41–579)     |
| OL 2            | 5.5   | (5.2–5.8)    | (7–9)       | (165–209)   | (30–168)    | (183–216)   | (255–352)   | (3.5–25.5) | (64–219)    | (59–740)     |
| OL 3            | 4.6   | (4.4–4.9)    | (18–23)     | (297–359)   | (103–229)   | (450–660)   | (144–189)   | (10.5–28.2)| (66–376)    | (67–452)     |
| AL              |       |              |             |             |             |             |             |             |             |
| Rock water      |       |              |             |             |             |             |             |             |             |
| W1              | 5.94  | (5.7–6.8)    | (19–22)     | (1.2–49.1)  | (913–4147)  | (0.6–68.3)  | (465–738)   | (0.4–4.1)  | (383–2020)  | (1367–3034)  |
| W2              | 6.44  | (6.2–7.5)    | (21–27)     | (7.6–49.1)  | (921–2149)  | (7.7–58.5)  | (575–760)   | (0.5–15.1) | (177–474)   | (2254–3093)  |
| Streamwater     |       |              |             |             |             |             |             |             |             |
| PL              | 7.1   | (5.5–7.5)    | (7–36)      | (7.6–358)   | (815–3228)  | (26.7–574)  | (279–1241)  | (2.7–336)  | (210–2446)  | (629–2339)   |
| SF              | 7.2   | (6.8–7.7)    | (3.34)      | (5.5–707)   | (883–2809)  | (34.5–832)  | (240–813)   | (2.1–192)  | (253–1209)  | (508–2776)   |
| FH              | 7.1   | (6.4–7.5)    | (7–22)      | (17.3–762)  | (624–1664)  | (18.8–1223) | (236–551)   | (1.6–49)   | (178–807)   | (407–1580)   |
| QR1             | 6.90  | (5.7–7.7)    | (4–37)      | (2.1–268)   | (252–1052)  | (6.1–182)   | (134–526)   | (0.1–5.7)  | (175–628)   | (183–1785)   |
| QR2             | 6.7   | (6.2–6.8)    | (5–8)       | (56.2)      | (231)       | (46.6)      | (143)       | (0.6)      | (225)       | (449–616)    |
| QM              | 6.5   | (6.2–6.8)    | (5–8)       | (95.7)      | (242.74)    | (124)       | (176)       | (4)        | (317)       | (673)        |
| QZ              | 7.21  | (4.9–7.7)    | (4–15)      | (12.3–327)  | (129–910)   | (53.5–424)  | (109–441)   | (1.5–17.2) | (143–2012)  | (156–1909)   |
| QN              | 7.1   | (6.1–7.6)    | (13–31)     | (6–413)     | (1350–8559) | (11.8–611)  | (394–745)   | (0.7–17.7) | (225–1206)  | (812–2616)   |
| QP              | 7.3   | (6.4–7.6)    | (13–36)     | (9.9–294)   | (1147–3316) | (36–6989)   | (270–2528)  | (7.4–150)  | (256–1548)  | (567–1813)   |
| QC              | 7.5   | (6.2–8.2)    | (17–39)     | (10–349)    | (1393–6360) | (28.7–306)  | (530–941)   | (2.6–17)   | (301–840)   | (1109–3104)  |
Na, decreasing with discharge. However no relation with water flow was found for the subcatchments QZ, QN, QM and QR. Concentrations of Mg in QM and QR are invariably related to discharge. For K, no relation to water flow was observed, with exception in the subbasins QC and QP where K concentration increases with discharge. Observations are generally in line with what several studies report, namely a decline in Ca, Mg and Na concentration when flow rate increases (Elsenbeer et al., 1994; Anderson et al., 1997; Tsujimura et al., 2001; Grimaldi et al., 2004). Also, McDowell and Asbury (1994) and Newbold et al. (1995) derived negative relations for Ca, Na and Mg with discharge and no relation for K as observed in the present study. On the other hand, Lorieri and Elsenbeer (1997) report that Al and Mn concentrations increase with discharge. In general, drops in concentrations during storm flows are attributed to a dilution of streamwater, whereas an increase of concentration during storm flow is ascribed to a flushing of accumulated material (Elsenbeer et al., 1994). The analysis revealed that Al and Na are the only solutes with the same hydrochemical behavior in all monitored catchments, and therefore suitable tracers for defining the hydrograph component composition using mixing model analysis.

**Isotopic tracers and mean transit time**

The mean, maximum and minimum values of $\delta^{18}O$ concentration in precipitation and streamwater are listed in the Table IV and presented in Figure 4. Given the similarity in streamflow isotopic composition between stations, Figure 4 shows only the $\delta^{18}O$ values of six out of ten streamwater sampling sites together with the fitted sine curve. The seasonal $\delta^{18}O$ pattern for the two sources of precipitation data used in this study is depicted at the top of Figure 4, with both data sets being representative for the same location. Each of them shows a seasonal pattern typical for the Andean mountain range, more diluted in the wet season and a higher $\delta^{18}O$ concentration in the dry season, with values ranging between $-12.6 \rightarrow -1.2\%_o$, $-12.8 \rightarrow -5.6$, $-13.9 \rightarrow -6.1$ and $-14.3 \rightarrow -6.3$ for stations located at 1957, 2270, 2669 and 2825 m a.s.l. Goller et al. (2002) and Goller et al. (2005)

| Sampling location | $\delta^{18}O$ measured | $n$ | Mean (‰) | Min (‰) | Max (‰) | Amplitude (‰) | $\eta$ | $R^2$ | Mean Transit Time (days) |
|------------------|-------------------------|----|-----------|---------|---------|---------------|------|------|-------------------------|
| Precipitation OIPC |                         |    |           |         |         |               |      |      |                          |
| 1957 m.a.s.l.    |                         | 12 | -6.08     | -12.60  | -1.20   | 3.00          | 0.85 |      |                          |
| 2270 m.a.s.l.    |                         | 12 | -8.80     | -12.80  | -5.60   | 3.00          | 0.82 |      |                          |
| 2669 m.a.s.l.    |                         | 12 | -9.54     | -13.90  | -6.10   | 3.10          | 0.87 |      |                          |
| 2825 m.a.s.l.    |                         | 12 | -9.80     | -14.30  | -6.30   | 3.10          | 0.80 |      |                          |
| Wagner (2002)    |                         | 24 | -6.08     | -1.20   | -12.6   | 3.20          | 0.45 |      |                          |
| and Goller et al. (2005) Streams |             |    |           |         |         |               |      |      |                          |
| PL               |                         | 35 | -7.97     | -9.82   | -6.71   | 1.01          | 2.02 | 0.41 | 330                     |
| SF               |                         | 35 | -8.02     | -9.55   | -6.29   | 0.98          | 1.71 | 0.56 | 285                     |
| FH               |                         | 30 | -7.91     | -9.49   | -6.23   | 0.79          | 1.47 | 0.35 | 313                     |
| QR1              |                         | 30 | -7.59     | -8.82   | -6.67   | 0.64          | 1.34 | 0.38 | 354                     |
| QR2              |                         | 27 | -7.83     | -9.10   | -6.97   | 0.66          | 1.78 | 0.47 | 263                     |
| QM               |                         | 27 | -7.42     | -8.22   | -6.23   | 0.93          | 1.52 | 0.36 | 269                     |
| QZ               |                         | 27 | -8.20     | -9.79   | -6.83   | 1.00          | 2.06 | 0.53 | 336                     |
| QN               |                         | 27 | -8.10     | -9.44   | -6.87   | 1.05          | 1.87 | 0.35 | 288                     |
| QP               |                         | 30 | -7.92     | -9.73   | -6.21   | 0.93          | 1.52 | 0.32 | 267                     |
| QC               |                         | 26 | -7.80     | -10.05  | -6.43   | 0.73          | 1.20 | 0.40 | 276                     |

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et al. (2005), based on the correlation between the δ¹⁸O concentration of rainfall and the synoptic wind directions, stated that variations in δ¹⁸O values are due to the influence of air masses originating from different source regions. The values of the δ¹⁸O concentration generated with OIPC are slightly lower, and the peak is situated 50 days earlier than the peak using the Wagner (2002) and Goller et al. (2005) data for a station located at 1957 m a.s.l. The difference in the position of the regressions is likely the consequence of the high variation in intra-annual precipitation and because data cover different periods.

The seasonal pattern of δ¹⁸O concentration in streamwater of the San Francisco basin and subbasins is similar to the δ¹⁸O pattern of precipitation water. Throughout the observation period, i.e. from April 2007 to November 2008, only small variations in δ¹⁸O concentration of streamwater were measured ranging between −10.05 and −6.21‰. Difference in δ¹⁸O pattern between the subbasins is small, as shown in Figure 4. The streamwater isotopic composition measured at 1980 m a.s.l. is more diluted than the isotopic composition of precipitation water, suggesting a contribution of water with lower isotopic composition from higher altitudes in the basin. Goller et al. (2005) report similar δ¹⁸O values for streamwater ranging between −8.7 and −5.8‰. Streamwater isotope values for all catchments are more damped and less responsive to precipitation likely because (i) the low temporal sampling resolution that prevented registration of all extreme values, and/or (ii) the piston flow type of response, i.e. precipitation pushes the old water out of the system that then is recorded as streamwater.

A first approximation of the MTT is derived using a model optimisation performed using Monte Carlo simulations. The amplitude for precipitation water varies between 3 and 3.2‰ with values for R² of 0.80 and 0.85 for the data derived with the OIPC calculator for stations with altitudes in the range 1957 and 2825 m a.s.l, while the amplitude using Wagner (2002) and Goller et al. (2005) data is 3.2‰ at 1957 m a.s.l. The results show that OIPC data yield similar results as the data collected by Wagner (2002) and Goller et al. (2005). Based on the similarity between both data sets, the authors used the OIPC data for the calculation of the MTT for the different subbasins. Due to the similar estimated precipitation amplitudes at different altitudes, a value of 3.0‰ was selected for all the subbasins to estimate MTT. The amplitude and η values and the correlation coefficient for streamwater are listed in the Table IV, with amplitudes ranging between 0.64 and 1.05 ‰, η values from 1.20 to 2.06 and R² values between 0.32 and 0.56.

Figure 5 shows the results of the Monte Carlo simulations for the estimation of the MTT for six of the ten subbasins. Results show for each subbasin a rapid decrease of the mean absolute error for values below the optimum estimation (solid diamond in Figure 5), while for values above, the uncertainty in the estimation of MTT increases, mainly due to the short length of the available data series (McGuire and McDonnell, 2006). As an initial estimate, given the complexity of the study basin, the authors believe that the obtained results are quite acceptable and in line with the output of similar studies. It is evident that the found MTT values in the range of 263 to 354 days (Table IV) need to be interpreted with care.

QR1 has the highest MTT value with 354 days. The MTT value for PL, SF, FH, QZ and QN subbasins vary from 285 to 336 days, while for QR2, QM, PQ and QC subbasins, MTT fluctuates between 263 and 276 days. Our study shows no correlation between MTT and basin area (R² < 0.1) suggesting that MTT is controlled by subsurface contact time and not by basin scale transport (Wolock et al., 1997). Some studies show a positive correlation between basin area and MTT (DeWalle et al., 1997; McDonell et al., 1999) while others report that basin area is not related to MTT (McGuire et al., 2002; McGuire...
Due to the similarity in geology, differences in MTTs between basins are attributable to the contribution of water from different sources. Although QR1 and QR2 are located relatively close to each other with an altitudinal difference of 129 m, MTTs are different with 354 and 263 days, respectively, suggesting that QR1 is receiving water from deeper horizons with longer contact time. As stated by Bücker (2010), spring rock water (W1) downstream QR2 is influencing QR1 during low flow conditions. Less deep rock water contribution is observed in QR2, QZ, QM, QP and QC.

Similarity in derived MTTs, independent of the vegetation cover of the subbasin, suggests that during low flows, landuse does not or minimally affects runoff generation. This assumption is supported by the low correlation observed between the percentage of forest and MTT ($R^2 < 0.05$). Notwithstanding the uncertainty on the derived MTT values, it can be concluded that during low flow conditions, subsurface flow from rock layers and/or C soil horizon is the main contributor to streamflow.

End-member identification

The chemical characteristics of soil, rock and streamwater are listed in Table IV, and the correlation between Al and Na concentration measured in water extracted from the O and A soil horizon as well as from bed rock for different flow rates are shown in Figure 4. For the application of mixing analysis, the chemical components Al and Na were selected because of their representativeness for the hydrochemistry of the San Francisco basin as mentioned in Section 3.2. In addition, the analysis revealed that the combination of Al and Na provides the best separation of water sources in the two-dimensional mixing plots. In the analysis, the chemical signature of rainfall was used given the similarity of Al and Na concentration between precipitation and throughfall (Boy et al., 2008). The chemical signature of precipitation represents also the chemical composition of infiltration excess overland flow. The Al and Na concentration in precipitation is low and therefore selected as one end-member in Figure 6. This end-member point is situated in the origin of each graph presented in this figure.

Given the similarity in soil distribution of Histosols and Regosols in the study basin, it is correct stating that the water samples collected at the sites OL1, OL2 and OL3 are representative for the study basin and the water flow through the litter layer, also called the organic near-surface flow and/or the saturation excess overland flow. High concentration of Al and the absence or the low concentration of Na is typical. The water samples collected in OL1 and OL3 have similar Al and Na signatures,
whereas the water samples in OL2 have a lower Al and higher Na content. The latter suggests that the organic near surface water flow in OL2 seeps through soils with higher mineral content. Water samples collected in the AL site are representative for the lateral flow through the A horizon and in general for the A horizon in the basin. These samples are rich in Al and poor in Na. According to Boy et al. (2008) and Lorieri and Elsenbeer (1997), Al is mobilised and transported as organometallic complex, typical for near surface flow in litter and subsurface flow in topsoil with high organic matter content.

Rock water samples collected at the W1 and W2 sites represent the flow through the mineral C horizon and cracks in the top layer of the bedrock. As explained in Section 3.3, this flow is the major contributor to streamflow under dry conditions and based on the long MTT, it is likely that the infiltrating rainfall replaces old water in the C horizon and the cracks in the top layer of the bedrock. The end-member of rock water is characterised by a high concentration of Na and zero to low concentration of Al. Boy et al. (2008) state that the origin of Na in the rock water is chemical weathering of the deeper subsurface layers. Our data strongly support this finding. Reduction in the contribution of deeper water sources to total flow, as happens during storm flow, would explain the observed pattern of decreasing concentrations during storm flow (see also Bücker et al., 2010). The Na concentration in the water samples collected at W1 is higher than in the water samples taken at W2 suggesting that the W2 rock water represents the flow through deeper rock layers with higher Na content.

**Mixing model analysis**

As shown in Figure 6, the Al and Na concentrations of streamflow of the selected subbasins are well bounded by the chemical signature of the end-member precipitation, organic soil water and rock water with exception of the subbasins QP and QC (data not shown because the similarity with QP) where the A horizon is considered instead of the organic soil water. The studied basin and subbasins could be divided in three groups based on the end-member analysis. The station located at the outlet (PL) the main river (SF) and the subcatchments (FH, QR1, QZ, QN) belong to Group 1, the subbasins QR2 and QM from Group 2 and Group 3 consist of the subbasins QC and QP.

The chemical signature of the subbasins in Group 1 during low flow conditions is strongly related to the Al and Na load of the rock water collected in site W1, which is representative for the water seeping through shallow weathered rock with high density of shallow cracks. It is supported by the MTT values varying between 285 and 354 days. The subbasin QR1 is clearly more influenced by rock water contribution than the other subbasins. When the wetness of the soil increases, the chemical signature of streamflow samples of the subbasins in Group 1 tends to be more oriented towards the chemical composition of the soil water in the O and A horizons. During storm events or when the soil profile is close to saturation, the chemical fingerprint of streamwater is closely related to the chemical signature of the water flowing laterally through the organic soil horizons. Under those conditions, the concentration of Ca decreases in favour of an increase of the Al concentration, as confirmed by Bücker et al. (2010). Given the high hydraulic conductivity of the litter layer and organic horizons, infiltration excess overland flow does not occur in the subbasins of Group 1.

The chemical fingerprint of the streamwater of the two subbasins in Group 2 is less similar to rock water at site W1 suggesting that streamflow under dry conditions is dominated by water from the C horizon and/or superficial weathered rock layers. This finding is in concordance with the lower value for MTT than the values found for the subbasins in Group 1, 263 and 269 days for QR2 and QM, respectively. As discharge increases the contributing water is coming from the same source areas, the upper soil horizons, as in the subbasins of Group 1. For the subbasins in Group 1 and 2, the chemical signature of streamwater during storm events is dominated by the water flowing through the litter and organic horizons. Here too, there is no evidence of infiltration excess overland flow in these subbasins.

The two subbasins in Group 3, QP and QC, have the largest area grazeland, varying between 26 and 67% of the total subbasin area. Mixing diagrams reveal that during low flow conditions, the streamflow samples are apparently more related to deeper rock water contribution (W2). However, lower MTT values were registered in these catchments. This apparent contradiction could be explained by the increase of Al and Na concentrations in soils under pastures as a consequence of burning. Verification shows an increase of Al and Na of nearly 100 to 700% with respect to the Al and Na content of the A horizons under forest. Similarly, an increase of the Al and Na content in the B and C horizons was observed but to a lower degree for Al (Makeschin et al., 2008). Although soil water and rock water samples in grazeland could not be collected by refusal of trespassing by the landowners, the mixing diagram (QP in Figure 6) suggests that during low flow, the chemical signature of streamwater is dominated by lateral subsurface flow through the C horizon and the superficial weathered rock layers. When discharge increases, due to the degradation of the O horizon, the chemical signature is increasingly controlled by the water lateral seeping through the A horizon. It is believed that the top soil horizons mainly contribute to the runoff generation by increasing discharge and that during storm events, lateral flow through the A horizon is dominant. However, when the discharge increases, most of the streamwater samples fall outside the mixing domain determined by the three selected end-members. This can be the consequence that the authors were not able to sample soil and bedrock water at the pasture sites, and/or that all potential end-members were not successfully sampled. The mixing domain reveals that infiltration excess overland flow is not occurring. This is in concordance with the results of the study conducted by Zimmermann (2007) in the same area using hydrometric data at plot scale. However, due to the limitations in the data, no strong conclusion can be drawn, justifying the need for further research.
CONCLUSIONS

The study revealed that the collection of hydrometric data, the chemical signature of water samples and isotopic tracers, and mixing model analysis provide crucial information on the processes dominating the runoff generation at basin scale in cloud forested areas, as stated in hypothesis 1 of this study. The applied nested approach showed to be a relevant method for the determination of the spatial variability of the processes. A combination of the methods enabled reducing the limitation of each technique, and when used together, results provided a more exact and coherent picture of the hydrological system. Furthermore, tracers in contrast with hydrometric data lead to a considerable reduction in the length of the monitoring period and associated costs. The approach offers promising possibilities for the hydrological analysis of ungauged or poorly gauged basins, as projected in hypothesis 4. In addition, the study suggests that more research on the geochemistry, complemented with the analysis of biological processes, in connection with the traditional hydrological approaches might provide far more reaching knowledge on the functioning of complex tropical ecosystems in a shorter period and at less cost.

The mixing diagrams and MTT values suggest that in the studied basin, deep water contributes significantly to streamflow, and that these contributions are relatively unaffected by landuse or topography in contradiction with the hypothesis 2. The streamflow of all subbasins is mainly composed by subsurface flow. The analysis revealed that saturation excess overland flow does not, or only exceptionally occurs in grazeland. The inclusion of spring water samples in the analysis enabled to identify differences in deep water contribution along the subbasins. As such, it highlighted the relevance of including spring, seep and well water in tracer studies of tropical mountainous areas (Souslby et al., 2007; Bücker et al., 2010).

The 3rd hypothesis, which states that under wet conditions, the runoff generation process is controlled by subsurface lateral flow through the organic horizons notwithstanding the steep topography, is confirmed by the analysis. The small differences in the generally long MTTs between catchments suggest that old water in the different storages of the basin is pushed out when new water enters.

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