Identification of the runoff generation processes in a montane cloud forest combining hydrometric data and mixing model analysis

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ABSTRACT

Field observations of runoff generation in pristine montane cloud forests are scarce. However, this knowledge is important for a sustainable natural resources management. Here we report results of a study carried out in the San Francisco River basin (75,3 km^2) located on the Amazonian side of the Cordillera Real in the southernmost Andes of Ecuador. The basin is mainly covered with cloud forest, sub-páramo, pasture and ferns. A nested sampling approach was used for the collection of stream water samples and discharge measurements in the main tributaries and outlet of the basin. Additionally, soil and rock water samples were collected. Weekly to biweekly water grab samples were taken at all stations in the period April 2007 to November 2008. Hydrometric, mean residence time and mixing model approaches allowed identifying the main hydrological processes that control the runoff generation in the basin. Results clearly reveal that flow during dry conditions mainly consists of lateral flow through the C-horizon and cracks in the top weathered bedrock layer. The data shows that all catchments 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 favor water infiltration, vertical flow paths to deeper soil horizons with subsequent lateral sub-surface flow contributes most to streamflow. Under wet conditions in forested catchments streamflow is controlled by near-surface lateral flow through the organic horizon, and it is unlikely that Horton overland flow occurs during storm events. By absence of the litter layer in pasture streamflow under wet conditions primarily originates from the rooted surface layers and the A horizon, and Hortonian overland flow during extreme events.

Keywords: Mixing model analysis, mean residence time, chemical tracers, hydrological processes, Andean cloud forest, Ecuador.

RESUMEN

Mediciones de campo de los procesos que controlan la generación de escorrentía en áreas prístinas de bosques tropicales de neblina son escasas. Sin embargo, este conocimiento es importante para un manejo sustentable de los recursos naturales. En este trabajo presentamos los resultados de un estudio levado a cabo en la cuenca del río San Francisco (75,3 km^2) ubicada en el lado Amazónico de la cordillera real en la parte Andina del Ecuador. La cuenca está cubierta principalmente por bosque nublado, sub-páramo, pastos y helechos. Para recolectar las muestras de agua y estimar el caudal de los ríos y quebradas se uso el método de muestreo anidado. Adicionalmente, se colectaron muestras de agua del suelo y la roca. Las muestras de agua fueron tomadas en el periodo de Abril del 2007 a Noviembre del 2008 con una periodicidad semanal o quincenal. Las técnicas usadas, como fueron la hidrométrica, tiempo de residencia promedio y modelo de mezcla, permitieron identificar los principales procesos hidrológicos que controlan la generación de escorrentía en la cuenca. Los resultados revelan claramente que el caudal durante condiciones secas consiste principalmente de flujo lateral a través del horizonte C y de las grietas en la parte superior de la capa meteorizada de roca. Los datos analizados muestran que el caudal, en todas las cuencas de estudio, tiene una importante contribución de aguas profundas, sin importar si dichas cuencas son prístinas o deforestadas. Durante el periodo de lluvias con intensidades normales o bajas, o cuando la humedad del suelo antecedente favorece la infiltración vertical, la dirección del flujo de agua es vertical hacia horizontes de suelo más profundos y el caudal subsecuentemente está compuesto por flujos laterales sub-superficiales. Durante condiciones húmedas el caudal en las cuencas forestadas está principalmente controlado por flujo lateral cerca de la superficie a través del horizonte orgánico, donde es improbable la existencia de flujo Hortoniano durante eventos extremos. Debido a la ausencia del horizonte de hojarasca en áreas bajo pasto, el caudal en épocas húmedas se origina principalmente de los horizontes de suelo superficiales con alta cantidad de raíces y horizonte A, y el flujo Hortoniano durante eventos extremos.

Palabras clave: Modelo de mezcla, tiempo de residencia promedio, trazadores químicos, procesos hidrológicos, bosque Andino de neblina, Ecuador.

1. INTRODUCTION

The tropical Andes belongs to the 25 hotspots of biodiversity on earth (Myers *et al.*, 2000), and cloud forests are ranked as one of the most species rich ecosystems. Unfortunately these ecosystems are unlikely to stay intact as a consequence of increasing anthropogenic pressures such as deforestation, mining, road construction, grazing and so on. According to the FAO (2006) South America suffered the largest net loss of forests between 2000 and 2005 with around 4,3 million hectares per year, followed by Africa, which lost 4,0 million hectares annually; with Ecuador experiencing the highest deforestation net rate (Henderson *et al.*, 1991; Mosandl *et al.*, 2008). Notwithstanding the importance of their socio-economic and environmental services, knowledge of the functioning of these endangered Andean ecosystems is scarce to non-existent, hindering the effective and sustainable management of these ecological very important ecosystems (Bruijnzeel, 2000; Feddema *et al.*, 2005).

According to Neill *et al.* (2006) and Boy *et al.* (2008) water passing through the ecosystems controls the geochemical, biological and ecological processes, and many of the environmental services. Disturbance of the hydrological functioning therefore directly affects all water dependent processes. In this respect, understanding the hydrology of the high Andean montane forest systems is an essential step in the more sustainable natural resources management. Lamentably, these ecosystems are ungauged or poorly gauged, which explains why the hydrology and eco-hydrology of the high Andean ecosystems is still not satisfactorily understood. Additionally, many other factors strongly inhibit progress in South America’s hydrologic research such as short timeseries of hydrological data, data gaps, poor quality data and lack of research funding.

Despite the scarce funding and the poor accessibility of those remote ecosystems, some research groups recently deployed considerable efforts in collecting data in a limited number of pristine Andean basins. Most studies have been carried out on micro-basins of less than 10 km^2 (Buytaert, 2004; Goller *et al.*, 2005; Fleischbein *et al.*, 2006; Buytaert *et al.*, 2007; Boy *et al.*, 2008; Chaves *et al.*, 2008). To examine the effect of anthropogenic pressures on pristine areas requires studying the hydrology of larger basins where people settled, converted forested pristine areas into productive agricultural land and/or partly urbanized pristine areas for living. The highly spatial variability of climate, topography and other catchment properties, typical for the Andean region, prohibits extrapolation of findings obtained at the scale of mirco-catchments to medium and large sized basins. In addition, the hydrology of larger basins might be governed by other processes than the processes controlling the rainfall-runoff at small basin scale, justifying the need to analyze in detail the hydrological processes at the scale of medium to large catchments (Mortatti *et al.*, 1997; Célleri, 2007; Buecker *et al.*, 2010).

With hydrological processes is understood the processes controlling the conversion of precipitation into streamflow, it is in which compartments of the basin (soil, subsoil, shallow and deep aquifers) water is stored and for how long, how the different reservoirs are interconnected and release water, and to what extent sources of water reflect the geochemical composition of the source area. To infer the hydrological processes multiple techniques have been used as hydrometric data (e.g. Kirkby, 1978; McDonell, 1990; Montanari *et al.*, 2006; Célleri, 2007), isotopical tracers (e.g. Sklash and Farvolden, 1979; Mortatti *et al.*, 1997; Soulsby *et al.*, 2000), hydrochemical tracers (e.g. Christophersen *et al.*, 1990; Hensel and Elsenbeer, 1997; Soulsby *et al.*, 2003), modeling (Blume, 2008; Vazquez *et al.*, 2008; Buytaert and Beven 2009) or a combination of previous methods (Bonell and Fritsch, 1997; Tanaka and Tsujimura, 1999; Biggs *et al.*, 2002; Blume *et al.*, 2008; Chaves *et al.*, 2008; Wenninger *et al.*, 2008).

The principal objective of this study is indentifying how streamflow is generated in the San Francisco River basin (South Ecuador) in response to precipitation using a combination of hydrometric, hydrochemistry and isotopic methods at basin scale and its tributaries The hypotheses laying at the basis of the study were: (i) use of multi-approach techniques allow better identification of the hydrological processes, (ii) land cover and land use practices predominantly control the runoff generation processes, (iii) notwithstanding the steep topography of the study basin is the runoff generation process during wet conditions limited to the subsurface lateral flow through the permeable organic horizons beneath the soil surface, and (iv) the mean residence time of the stream water in the San Francisco basin is short not influenced by deep water contribution.

2. MATERIALS AND METHODS

2.1. Study area

The San Francisco River basin is located on the Amazonian side of the Cordillera Real between 1800 and 3250 m.a.s.l. in the southernmost Andes of Ecuador, latitude 03°58’ S and longitude 79°04’ W (Figure 1). The study basin 75,3 km^2 large drains into the Amazon basin. The catchment is divided into a northern and a southern zone with distinct land uses. Natural forests in the north is replaced by extensive pastures (Setaria sphacelata) (Werner *et al.*, 2005) which after several years are abandoned and replaced by ferns (Pteridium aquilinum, L). The southern portion of the basin 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 subpáramo 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 for each monitored subbasin is summarized in Table 1. Anthropogenic impacts in the north mainly consist of extensive wood cutting, river bed gravel mining, a gravel road and extensive grassland, while in the south a hydropower plant is situated fed by basin water.

The climate is controlled by Amazonian air masses (Beck *et al.*, 2008) characterized by a unimodal precipitation pattern with relative constant seasonality and moderate to low inter-annual variability. The main wet season is from April to September with a maximum of 10 days without rain, while the dry season is between October and December (Fleischbein *et al.*, 2006). According to Rollenbeck (2006) precipitation is strongly correlated with altitude, and intensities 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 (INAMHI) with an average of 2200 mm at an altitude of 1960 m; wind speeds being low and cloud cover less dense at this elevation. 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; 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% (period 1998 to 2004) (Fleischbein *et al.*, 2006).

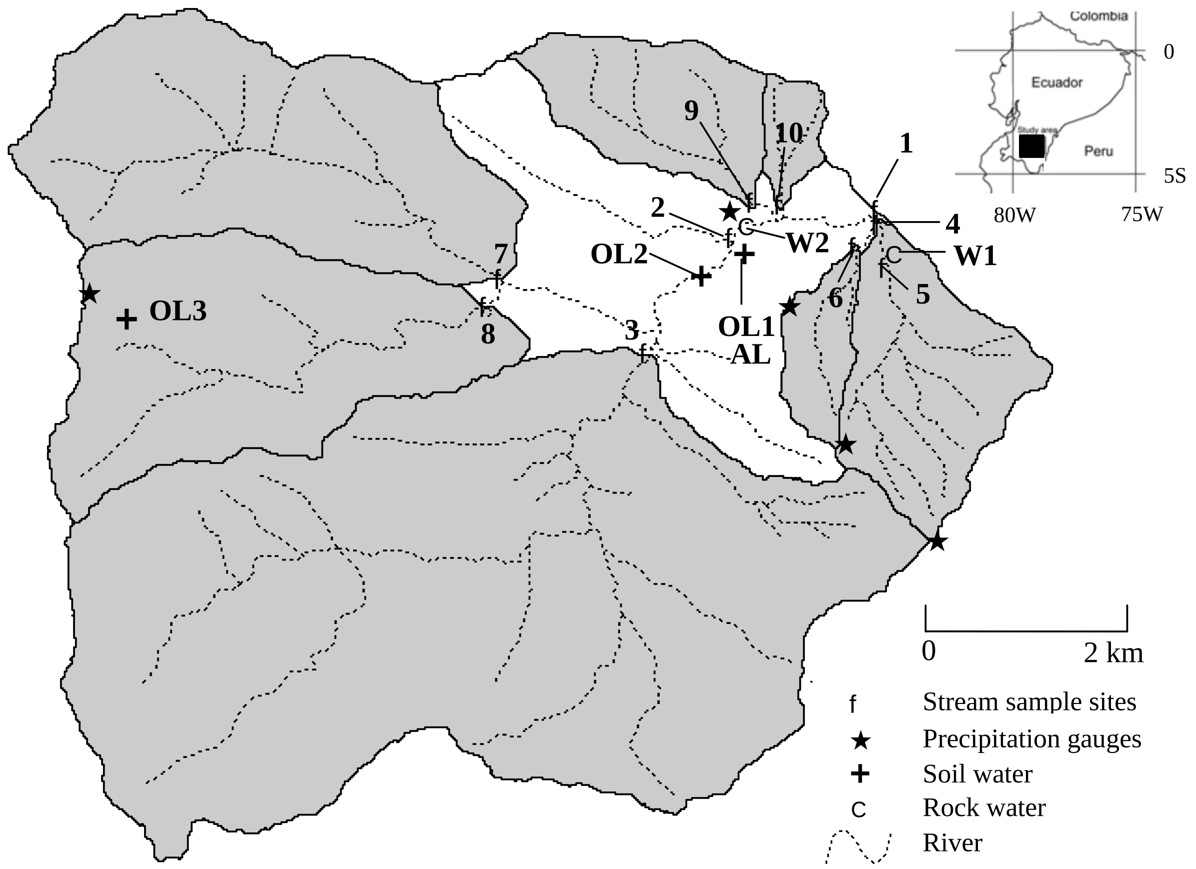

Figure 1. Location of the study area, the division of the San Francisco basin in subbasins (1 = PL, 2 = SF, 3 = FH, 4 = QR1, 5 = QR2, 6 = QM, 7 = QZ, 8 = QN, 9 = QP and 10 = QC) and field sampling network.

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; Bendix *et al.*, 2008). As stated by Makeschin *et al.* (2008) the geology and soil mineralogy are fairly uniform. 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 2. Generally, weathered rocks have lower concentration of all elements except Al of which the concentration is almost the same.

The main soil types in the study area are Histosols, Regosols, Cambisols and Stagnasols (FAO/ISRIC/ISSS, 1998). The soil map is not presented herein because the data are still unpublished. The soil distribution per subbasin is summarized in Table 1. Histosols typically contain a high fraction of non-decomposed plant fibers (Beck *et al.*, 2008), are located in the subpáramo under cloud forest and are the most common soil in the study area (Wilcke *et al.*, 2002). The higher situated Histosols are on average 90 cm deep while Histosols under cloud forest are less deep (Makeschin *et al.*, 2008; Wilcke *et al.*, 2002). The area of Regosols and Cambisols decreases with altitude while Stagnasol soils increase with altitude (Liess *et al.*, 2009). Small-scale heterogeneity is according to Huwe *et al.* (2008) dominant present most probably as a consequence of the high frequency of landslides. Landslides are due to the steepness of the terrain (slopes varying between 48 and 61%), the shallowness of the soils and the plentiful precipitation year round. Open spaces in the landscape are with time covered with secondary forest growth.

Table 1. Main characteristics of the San Francisco basin and subbasins.

	Units	PL	SF	FH	QR1	QR2	QM	QZ	QN	QP	QC
Catchment properties											
Area	[km²]	75,3	64,2	34,8	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.a.s.l	1742	1910	1900	1743	1872	1869	2025	2050	1914	1829
Max elevation	m.a.s.l	3250	3250	3250	3150	3150	2650	3075	3025	2900	2550
Hydro-meteorological characteristics											
Mean precipitation	mm y^{-1}	3396	3200	3372	3799	3820	3423	2972	2962	2760	2700
Mean discharge	mm y^{-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					Palaezoic metamorphic rocks						
Land use											
Forest	%	68	65	67	80	80	90	72	65	63	22
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
Soils											
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

Legend: PL = station located at the outlet of San Francisco river basin, SF = station in the main river, FH, QR1, QR2, QM, QZ, QN, QP and QC = stations located in the main tributaries

Table 2 presents per land use and horizon the main soil properties. The reader is referred to Makeschin *et al.* (2008) for a description of the laboratory analyses used for the determination of the soil properties. As depicted in Table 2 C, Ca, Mn and the saturated hydraulic conductivity (Ks) decrease with depth (from the O to the C horizon) except under pasture and shrub where Ks slightly increases. 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). Subpáramo and forest soils are very similar. According to these authors, frequent burning of pasture results in a slight increase of the pH and a more significant increase in Al, Na, Fe, Mg and K.

2.2. Field sampling and laboratory analysis

A nested sampling approach was used for the collection of stream water (Table 1 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 land use, land cover and accessibility. Four of the ten sampling points are representative for cloud forest (FH, QR1, QR2 and QM), two sites are covered mainly with pasture (QP and QC) and two sites are with anthropogenic interference (QN and QZ). The subbasin 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).

Table 2. Properties (average value and range) per horizon of the main soils in the studied catchment.

Horizon	Horizon thickness (cm)	Ks (mm h^{-1})	pH	C	Al	Ca	Fe	Mg	Mn	K	Na
				(g kg^{-1})							
Forest											
O	10-20	166	4,7 (3,4-6,7)	466,4	5,57 (0,2-37,5)	5,34 (0,2-29,8)	3,60 (0,02-46,9)	1,84 (0,2-10,2)	0,40 (0,01-2,3)	2,45 (0,7-14,4)	0,37 (0,01-6,0)
A	10-20	92	3,6 (3,3-4,1)	48,1	23,17 (12-7-44,1)	0,03 (0,02-0,18)	18,91 (11,7-34,6)	1,04 (0,5-1,9)	0,29 (0,21-0,4)	8,49 (3,9-15,7)	0,30 (0,16-0,55)
B	10-80	11	3,9 (3,6-4,5)	34,2	30,12 (10,7-55,8)	0,05 (0,02-0,12)	22,94 (11,5-38,2)	1,23 (0,5-2,3)	0,30 (0,4-0,18)	10,15 (4,8-16,9)	0,33 (0,16-0,58)
C	30-50	17,9	4,1 (3,7-4,8)	10,5	33,15 (13,7-79,1)	0,06 (0,02-0,11)	24,77 (13,8-41,3)	1,36 (0,5-2,3)	0,29 (0,16-0,4)	11,44 (3,9-17,6)	0,36 (0,19-0,57)
Sub-páramo											
O	10-20	135	4,7 (3,7-5,9)	446,6	5,54 (0,3-24,1)	4,22 (0,2-11,2)	2,56 (0,14-12,1)	1,30 (0,2-3,1)	0,68 (0,06-2,2)	2,32 (1,02-8,1)	0,17 (0,03-0,4)
A	10-40	90,96	4,2 (3,9-4,5)	89,3	20,55 (3,3-45,2)	0,17 (0,05-0,9)	13,58 (6,6-24,9)	1,11 (0,2-2,1)	0,15 (0,1-0,3)	6,38 (0,6-14,0)	0,23 (0,1-0,4)
B	30-60	11,23	4,4 (4,2-4,7)	44,3	26,05 (3,1-53,0)	0,08 (0,02-0,33)	17,26 (6,9-29,8)	1,35 (0,1-2,8)	0,15 (0,09-0,3)	8,13 (0,6-16,7)	0,24 (0,08-0,5)
C	20-50	-	4,7 (4,5-5,1)	16,2	33,48 (1,7-55,3)	0,04 (0,02-0,10)	24,25 (6,9-41,2)	1,71 (0,2-3,3)	0,15 (0,09-0,3)	11,21 (0,3-18,6)	0,28 (0,08-0,4)
Pasture/Shrubs											
A	10-50	14	5,0 (4,1-7,5)	50,3	45,58 (13,1-102,9)	4,25 (0,04-63,6)	31,22 (2,4-119,1)	3,06 (0,4-19,6)	0,41 (0,02-2,2)	9,78 (2,3-21,3)	0,63 (0,17-2,3)
B	30-60	17	4,9 (3,9-5,9)	37,6	38,44 (14,2-70,4)	0,21 (0,03-1,35)	26,23 (7,7-46,5)	1,54 (0,3-4,2)	0,24 (0,39-0,17)	11,28 (4,5-22,9)	0,67 (0,19-2,6)
C	20-50	30	5,0 (4,2-6,1)	14,6	41,69 (20,0-81,4)	0,15 (0,04-1,3)	27,90 (10,1-48,1)	1,69 (0,6-3,8)	0,24 (0,16-0,4)	12,04 (3,3-22,5)	0,70 (0,17-2,6)
Rocks											
Weathered	-	-	-	-	52,47 (9,2-112,3)	0,15 (0,02-1,19)	19,13 (7,4-34,4)	2,88 (0,2-6,2)	0,19 (0,07-0,5)	17,65 (2,9-36,1)	0,75 (0,19-2,9)
Non-weathered	-	-	-	-	53,85 (15,2-85,6)	0,80 (0,08-1,54)	27,56 (8,3-47,3)	5,61 (0,7-13,2)	0,29 (0,05-0,9)	22,29 (5,5-43,6)	9,49 (1,2-17,2)

Precipitation was sampled during events in the lower part of the catchment, more in particular 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 (2006).

At three locations in the catchment, two in forest (OL1 and OL3) and one in subpáramo (OL2), soil water samples of the O horizon were collected using zero-tension lysimeter devices consisting of 20 cm x 20 cm x 0,05 cm 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. Soil water of the organic horizon in subpáramo sites was collected from the free drainage water in dry periods. Due to admittance refusal by landowners' soil water samples in pastures/ferns sites could not be collected.

Rock water samples were collected in two places of the catchment directly from springs emerging from rock fractures. One is located just behind the QR2 site, while the second site is close to SF. These two points are considered representative for the area given the uniformity of the geology as stated before. Piezometers for sampling the water in the underground could not be installed due to the compactness of the 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 analyzed on the following chemical elements: Al, Ca, Fe, Mg, Mn, K and Na. Water samples in soils and rocks were taken in dry periods, whereas precipitation during rainfall events. All water samples were filtered in the field using 0,45 μm polypropylene membrane filters (Puradisc 25 PP Syringe Filters, Whatman Inc.) and stored in acid washed PE bottles. Samples were acidified to a pH < 2 within three hours after collection using nitric acid and kept in a cold storage room until transport to Germany. Element concentrations were determined at the Institute for Landscape Ecology and Resource Management of the Justus-Liebig Universität Gieβen 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 directly in the field, using a WTW pH Cond340i handheld meter (Weilheim, Germany).

Only, stream water samples were analyzed for the $^{18}O/^{16}O$ ratio. Samples were collected in tightly closed amber glass bottles (Th. Geyer GmbH & Co. KG, Germany) and analyzed in Gieβen using a direct-inject liquid-water isotope analyzer (DLT100, Los Gatos Research, Mountain View, CA, US), with an analytical precision of ± 0,2%. Ratios of $^{18}O/^{16}O$ are expressed in delta units, $\delta^{18}O$ (‰, parts per mille). Since $\delta^{18}O$ was not measured in precipitation samples, precipitation $\delta^{18}O$ data were reconstructed in the following two ways. First, $\delta^{18}O$ data collected in the same location in the period August 2000 - August 2001 were derived from Wagner (2002) and Goller *et al.* (2005). Secondly, the online isotope in precipitation calculator (OIPC) was used to estimate the $\delta^{18}O$ precipitation amplitude at different altitudes. The OIPC consists of a simple HTML form allowing users to estimate $\delta^{18}O$ for different locations and altitudes based on global data of the International Atomic Energy Association/World Meteorological Organization Global Network for Isotopes in Precipitation. In Ecuador the mentioned network has 20 stations which altitude ranging between 6 and 3150 m.a.s.l. $\delta^{18}O$ is calculated according to an algorithm developed by Bowen and Wilkinson (2002) and refined by Bowen and Revenaugh (2003). Goller *et al.* (2005) report very small differences between rainfall and throughfall $\delta^{18}O$ concentration.

2.3. Hydrometric measurements

The water level with an accuracy of ± 1 mm was recorded with an interval of 5 minutes using pressure transducers and capacitance probe gauges (Odyssey Capacitance Probes and Odyssey Pressure Data Recorder, Dataflow Systems PTY Ltd, NZ) installed at the outlet of each subbasin and basin. The river cross sections in all limnigraphic stations are stable with the exception of the QC outlet section, where a

Thompson (V-notch) weir (90°) 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 empirically developed for all stations, with the exception of the QC limnigraphic station. For this station the Kindsvater-Shen relation (USDI Bureau of Reclamation, 2001) was used to convert water level data to flow rate data.

Precipitation data (rainfall + fog) were provided by Bendix and Richter of the DFG Research Unit (www.tropicalmountainforest.org). A detailed description of the set up of the meteorological stations is given by Bendix *et al.* (2008). Four meteorological stations were used to derive volume weighted element values.

Due to the harsh environmental conditions equipment failure occurred several times but never lasted longer than a couple of days. Hence, data gap filling for precipitation and discharge timeseries was necessary. 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. Hourly fog deposition data series were estimated based on fixed monthly ratios between rainfall and fog deposition.

2.4. Mixing model analysis

A mixing model analysis according to the procedure outlined by Hooper *et al.* (1990) was applied to identify the contribution of rainfall, soil water and rock water to streamflow. End-members were selected using two dimensional (2-D) plots, called mixing diagrams, plotting one solute against another solute for all possible combinations of the selected elements. If the different water sources mix conservatively most of the stream water 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.

2.5. Mean residence time estimation

A simple sine-wave approach, based on a steady-state well mixed model (Maloszewski *et al.*, 1983; DeWalle *et al.*, 1997), was used to estimate the mean residence time (T) at basin scale (Soulsby *et al.*, 2006). The model assumes that the decrease in the $\delta^{18}O$ amplitude of stream water relative to precipitation provides a basis for determining the residence time (Unnikrishna *et al.*, 1995). Seasonal trends in $\delta^{18}O$ were modeled using a trial and error technique to fit sine curves to seasonal variation in rainfall and stream water, as defined by Eq. (1):

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

where $\delta^{18}O$ is the predicted $\delta^{18}O$, X the mean annual $\delta^{18}O$, A the annual amplitude of $\delta^{18}O$, c the angular frequency constant ($2\pi/365$), t the time in days after an arbitrary date and θ the phase lag or time of the annual peak $\delta^{18}O$ in radians. The residence time (T) of water leaving the subcatchment or catchment is calculated by Eq. (2):

$$T = c^{-1}\left[\left(\frac{Az2}{Az1}\right)^{-2} - 1\right]^{0.5} \qquad (2)$$

where Az1 and Az2 are the amplitudes of precipitation and stream water respectively, and c is the angular frequency constant. Since water samples were collected on a weekly to biweekly interval high flow samples are poorly represented with the consequence that the estimation of T correspond to basically slow (base + intermittent) runoff conditions. Evident samples collected during storm conditions were excluded, analogue 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 should be considered as a preliminary approximation of T (Maloszewski and Zuber, 1993; McGuire and McDonell, 2006). As more data become available more elaborated models will be applied to estimate the mean residence time.

3. RESULTS AND DISCUSSION

3.1. Rainfall-runoff

Annual precipitation in the observation period, April 2007 - November 2008, varied between 2700 and 3820 mm y^{-1}. As mentioned the pattern of precipitation 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. Similar behavior is found in all subbasins. In the PL and each subbasin the fast response of discharge to rainfall is noticed. As depicted in Table 1, the average water yield of the subbasins varies between 2041 and 3090 mm y^{-1}, representing 76 to 81% of the precipitation. Small differences are found mainly due to the spatial variability of the total precipitation (rainfall depth + fog interception). Chaves *et al.* (2008) analyzing rainfall-runoff of a small rainforest catchment in Rancho Grande, Brazil, found similar values.

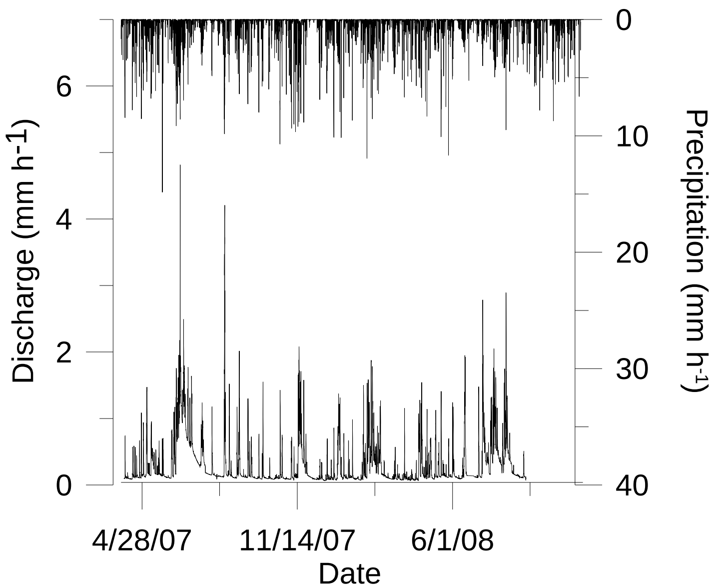

Figure 2. 1-hourly timeseries of rainfall (mm hr^{-1}) and total streamflow (mm h^{-1}) of the San Francisco basin.

Analysis of the rainfall timeseries reveals that the rainfall intensity of most events is less than the saturated hydraulic conductivity of the top layer, which value varies between 11 and 166 mm h^{-1} (Table 2). 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 very unlikely. Only saturation excess overland flow near to the river bed is expected. Apparently, because the reduction of the Ks in the top horizon of soils under pastures, it is not unrealistic to assume that Hortonian flow during storm events on grazing land occurs. Fleischbein *et al.* (2006) in a study conducted in a small tributary of San Francisco basin also excluded the occurrence of Hortonian overland flow (see also Boy *et al.*, 2008; Bücker, 2010).

3.2. Hydrochemistry

As depicted in Table 3 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 horizons with an average concentration of 526 µg l^{-1} followed by the O horizons with 311 µg l^{-1}. Instead of increasing with depth, the Al concentration is considerably lower in the two 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 Al is retained by secondary minerals. Highest concentration of Ca and Mg are found in A horizon soil water (average values of 1166,7 and 466,7 µg l^{-1}) and rock water (average values of 1175,64 - 1190,39 µg l^{-1} and 527 - 654 µg l^{-1}) but lower in the organic horizon with average concentrations of 134,88 to 684,78 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 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 microcatchments (8 to 13 ha) affluent of PL.

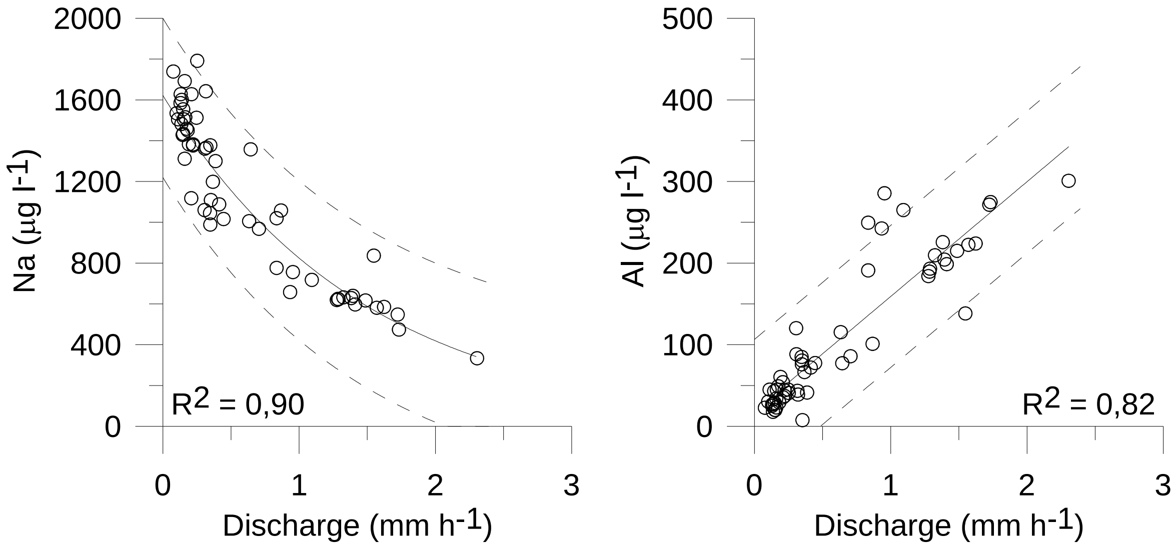

Figure 3. Relation between discharge and Na and Al concentration at the outlet of the San Francisco basin.

Concentration versus discharge relations were tested (Figure 3) for all stream water sampling stations where discharge values were available. Only the results for the PL station for Al and Na are showed, details for the other subcatchments and solutes concentrations are found in Bücker (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 increase of discharge, while Al increases (Figure 3). Ca and Mg behave similar to Na; decreasing with discharge. However no relation with water flow was found for the subcatchments QZ, QN, QM and QR. Concentrations of Mg are in QM and QR invariably

Table 3. Chemical characteristics (average value and range) of rainfall (volume weighted), rock and stream water.

	No Samples	pH	EC ($\mu S\ cm^{-1}$)	Al	Ca	Fe	Mg	Mn	K	Na
				($\mu g\ l^{-1}$)						
Rainfall	35	5,73 (4,6-6,35)	8 (2-35)	6,4 (0,6-22,0)	142,96 (44,14-335)	5,5 (1,7-22,1)	21 (4-206)	1,9 (0,6-5,5)	123 (40-303)	113 (33-556)
Soil water										
OL 1	14	5,06 (4,68-5,5)	16 (10-27)	311 (172-423)	684,78 (39,6-1938,5)	34,7 (11,5-72,7)	302 (41-469)	52,2 (0,5-159,8)	299 (38-843)	120 (41-579)
OL 2	10	5,47 (5,19-5,8)	8 (7-9)	185 (165-209)	140,04 (30-167,8)	197,7 (182,7-216)	293 (255-352)	14 (3,5-25,5)	198 (64-219)	627 (591-740)
OL 3	10	4,64 (4,37-4,9)	19 (18-23)	321,4 (297-359)	134,88 (102,9-229,2)	559,6 (450,4-659,8)	176 (144-189)	17,9 (10,5-28,2)	153 (66-376)	202 (67-452)
AL	-	-	-	526 (250-1000)	1166,7 (200-2000)	-	466,7 (400-1500)	9 (4-15)	201 (75-700)	465 (270-500)
Rock water										
W1	24	5,94 (5,7-6,8)	20 (19-22)	10 (1,2-49,1)	1175,64 (913,3-4147)	10,2 (0,6-68,3)	527 (465-738)	2,9 (0,4-4,1)	502 (383-2020)	1640 (1367-3034)
W2	14	6,44 (6,22-7,51)	24 (21-27)	19,4 (7,6-49,1)	1190,39 (921,3-2149)	29 (7,7-58,5)	654 (575-760)	3,9 (0,5-15,1)	277 (177-474)	2495 (2254-3093)
Stream water										
PL	56	7,12 (5,51-7,51)	16 (7-36)	80,4 (7,6-357,6)	1297,46 (814,9-3228)	103,6 (26,7-574,1)	414 (279-1241)	18,2 (2,7-336)	375 (210-2446)	1383 (629-2339)
SF	54	7,22 (6,5-7,68)	21 (3-34)	94,8 (5,5-707,4)	1608,59 (883-2809)	132,5 (34,5-831,7)	511 (240-813)	16,4 (2,1-192,1)	398 (253-1209)	1646 (508-2776)
FH	47	7,08 (6,43-7,47)	13 (7-22)	93,3 (17,3-761,6)	886,36 (624,2-1663,5)	136,5 (18,8-1223)	314 (236-551)	31,8 (1-649)	308 (178-807)	1139 (407-1580)
QR1	41	6,90 (5,66-7,7)	12 (4-37)	55,3 (2,1-268,2)	638,53 (251,6-1052)	44,8 (6,1-182)	339 (134-526)	1,2 (0,1-5,7)	368 (175-628)	1134 (183-1785)
QR2	52	6,65 (6,2-6,84)	6 (5-8)	56,2 (25-161,6)	230,58 (194,7-334,7)	46,6 (23,1-114)	143 (125-185)	0,6 (0,4-1,1)	225 (187-250)	616 (449-616)
QM	51	6,54 (4,94-7,65)	6 (4-15)	95,7 (12,3-327)	242,74 (129,3-909,7)	124,1 (53,5-424,2)	176 (109-441)	4 (1,5-17,2)	317 (143-2012)	673 (156-1909)
QZ	45	7,21 (6,61-7,59)	23 (13-31)	77,9 (6-412,9)	2059,19 (1349,5-8559)	69,6 (11,8-611)	532 (394-745)	3 (0,7-17,7)	401 (225-1206)	1579 (812-2616)
QN	43	7,14 (6,42-7,61)	24 (13-36)	79,8 (9,9-293,7)	2064,34 (1147-3315,5)	278,2 (36-6898)	487 (270-2528)	20,2 (7,4-150,4)	386 (256-1548)	1471 (567-1813)
QP	52	7,32 (6,15-8,24)	28 (17-39)	67,9 (10-349,2)	1907,02 (1392,5-6360)	88,4 (28,7-306,2)	794 (530-941)	5,7 (2,6-17)	469 (301-840)	2441 (1109-3104)
QC	40	7,47 (6,05-8,43)	29 (18-36)	71,7 (10-361,3)	1843,32 (1080-2813,5)	120,4 (29,8-435)	784 (464-948)	8,3 (2,5-22,3)	605 (416-934)	2617 (1245-3295)

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. The solute discharge relations reveal that Al and Na are the only solutes with the same hydrochemical behavior in all monitored catchments, and therefore representative for the entire San Francisco basin.

Several studies report 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 and discharge as observed in the present study. At the other hand Lorieri and Elsenbeer (1997) reports that Al and Mn concentrations increase with discharge. In general, drops in concentrations during storm flows are mostly attributed to a dilution of stream water, whereas an increase of concentration during storm flow is ascribed to a flushing of accumulated material (Elsenbeer *et al.*, 1994).

3.3. Isotopic tracers and mean residence time

The mean, maximum and minimum values of $\delta^{18}O$ concentration in precipitation and stream water are listed in the Table 4 and presented in Figure 4.

Table 4. Mean, maximum and minimum $\delta^{18}O$ values, modeled amplitude and mean residence times of the San Francisco basin and subbasins.

	N° samples	$\delta^{18}O$ measured				R^2	Residence Time days
		Mean ‰	Min ‰	Max ‰	Amplitude ‰		
Precipitation	12-24	-6,08	-12,6	-1,2	3,0-3,2	0,34-0,85	
Stream water							
PL	35	-7,97	-9,82	-6,71	0,60	0,38	285
SF	35	-8,02	-9,55	-6,29	0,65	0,30	262
FH	30	-7,91	-9,49	-6,23	0,60	0,35	285
QR1	30	-7,59	-8,82	-6,67	0,55	0,38	311
QR2	27	-7,83	-9,1	-6,97	0,70	0,45	242
QM	27	-7,42	-8,22	-6,23	0,75	0,40	225
QZ	27	-8,2	-9,79	-6,83	0,60	0,43	285
QN	27	-8,1	-9,44	-6,87	0,65	0,36	262
QP	30	-7,92	-9,73	-6,21	0,72	0,32	252
QC	26	-7,8	-10,05	-6,43	0,73	0,40	232

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. Solid points correspond to the data derived from Wagner (2002) and Goller *et al.* (2005) while the open dots stand for the isotope values derived with the OIPC; both data sets are representative for the same location. Either 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 and -1,2‰. Goller *et al.* (2005) stated, based on the correlation between the $\delta^{18}O$ concentration of rainfall and the synoptic wind directions that variations in $\delta^{18}O$ values are due to the influence of air masses originating from different source regions. The values of the $\delta^{18}O$ 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. The difference in the position of the regressions is likely due to the high variation of intra-annual precipitation and because data cover different periods.

The seasonal pattern of $\delta^{18}O$ concentration in stream water of the San Francisco basin and subbasins is similar to the $\delta^{18}O$ pattern of precipitation water. Throughout the observation period, i.e. from April 2007 to November 2008, only small variations in $\delta^{18}O$ concentration of stream water were measured ranging between -10,05 and -6,21‰. Difference in $\delta^{18}O$ pattern between the subbasins was small as well, as shown in Figure 4. The stream water 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 $\delta^{18}O$ values for stream water ranging between -8,7 and -5,8‰. Stream water isotope values for all catchments are more damped and less responsive to precipitation, most probably the consequence that the applied weekly to biweekly sampling scheme unlikely capture extreme values during storm events.

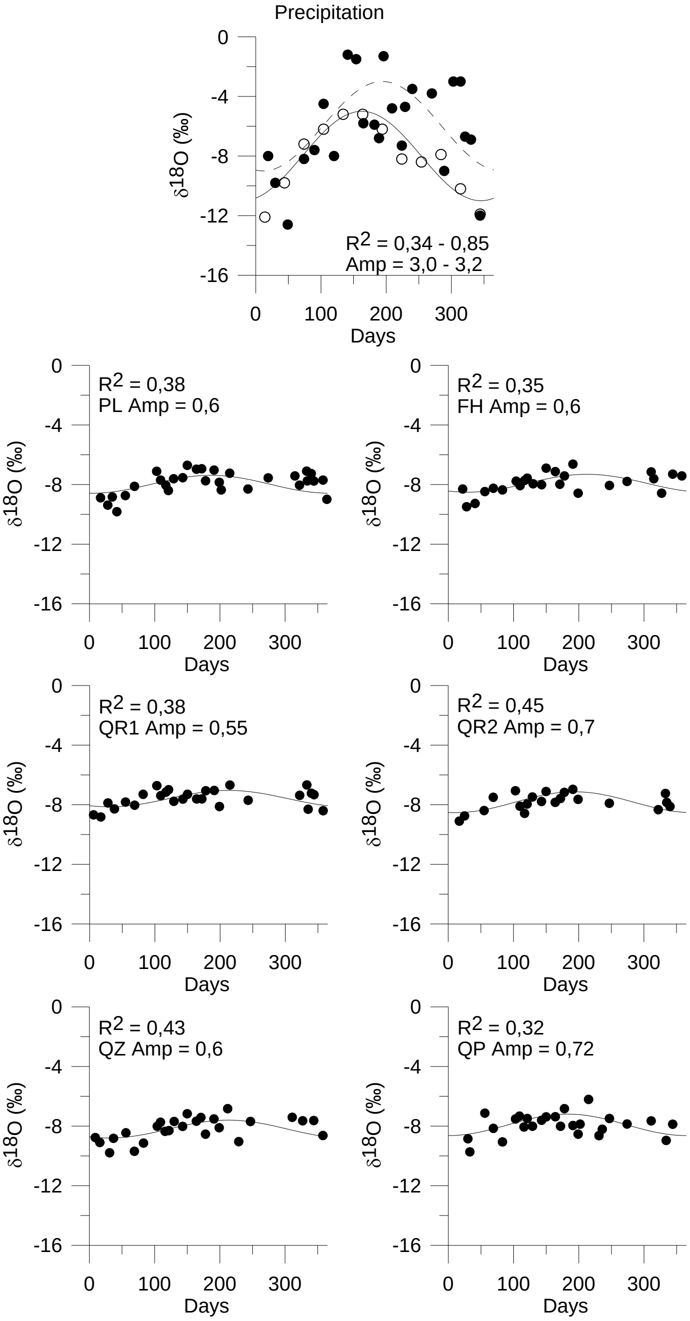

Figure 4. Fitted annual regression models to $\delta^{18}O$ for precipitation (dashed regression line for the Goller *et al.* (2005) data and solid regression line for the OICP data) and stream water for the San Francisco basin and subbasins.

For reason of the similitude in isotopic composition of stream water at some stations, Figure 4 shows only the $\delta^{18}O$ values of 6 out of the 10 stream water sampling sites together with the fitted sine curve. A first approximation of the mean residence time is derived using the amplitude and phase shift of the fitted sine curve. The amplitude for precipitation water varies between 3 and 3,2‰ with correlation values of 0,34 and 0,85 for the Wagner (2002) and Goller *et al.* (2005) data and the data derived with OIPC, respectively. Given the observed similitude the authors concluded to use the Wagner (2002) and Goller *et al.* (205) data to simulate the seasonality of $\delta^{18}O$ in precipitation and estimate the mean residence time (T). Amplitude values and the correlation coefficient for stream water are listed in the Table 4, with amplitudes ranging between 0,55 and 0,75‰ and R^2 values between 0,30 and 0,45.

According to a preliminary estimate T values are in the range 225 to 311 days. QR1 has the highest value with 311 days. The T value for PL, SF, FH, QZ and QN subbasins vary from 262 to 285 days, while for QR2, QM, QP and QC subbasins T fluctuates between 225 and 242 days. Our study shows no correlation between T and basin area ($R^2 < 0,1$) suggesting that T 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 T (DeWalle *et al.*, 1997; McDonell *et al.*, 1999) while others report that basin area is not related to T (McGuire *et al.*, 2002; McGuire *et al.*, 2005; Rodgers *et al.*, 2005). Due to the similarity in geology, differences in T values 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, T values are different, 311 and 242 days respectively, suggesting that QR1 is receiving water from deeper horizons with higher contact time. As stated by Bücker (2010) spring rock water (W1) downstream QR2 is influencing directly QR1 during slow flow conditions. Less influence of deep rock water contribution is observed in QR2, QM, QP and QC.

Similar T values were derived for the different subbasins independent the vegetation cover suggesting that during slow flows landuse in the studied subbasins does not affect runoff generation. This assumption is supported by the low correlation observed between the percentage of forest and T ($R^2 < 0,05$). Based on the calculated T values it can be concluded that subsurface flow from rock layers and/or C soil horizons is dominant during slow flow conditions, with minimal effect of landuse. The fast hydrological response to rainfall, the permeability of the soil and the presence of cracks in the top layer of the rock are the main factors conditioning the runoff generation during slow flow. The estimated T values are surprisingly high given the steepness of the slopes and the shallowness of the soils from which it is concluded that during slow flow new water is pushing out old water retained in the rock layers and/or C soil horizon.

3.4. End-members identification

The chemical characteristics of soil, rock and stream water are listed in Table 3 and the correlation between Al and Na concentration measured in water extracted from the O and A horizon, and bed rock for different flow rates are shown in Figure 5. For the application of the mixing model analysis the chemical components Al and Na were selected because of their representativeness for the hydrochemistry of the San Francisco basin as mentioned earlier. 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 similitude of the 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 end-member in the 6 graphs presented in Figure 5. This end-member point is situated in the origin of each graph.

The water samples collected at the sites OL1, OL2 and OL3 are representative for the water flow though the litter layer, also called the organic near-surface flow and/or the saturation excess overland flow in zones where the soil is saturated. High concentration of Al and the absence or the low concentration of Na is typical for the second end-member. The water samples collected in OL1 and OL3 have similar Al and Na signature, 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. These samples are rich in Al and poor in Na. According to Boy *et al.* (2008) and Lorieri and Elsenbeer (1997) Al is mobilized and transported as organic-complex, typical for near surface flow in litter and subsurface flow in topsoil with high organic matter content.

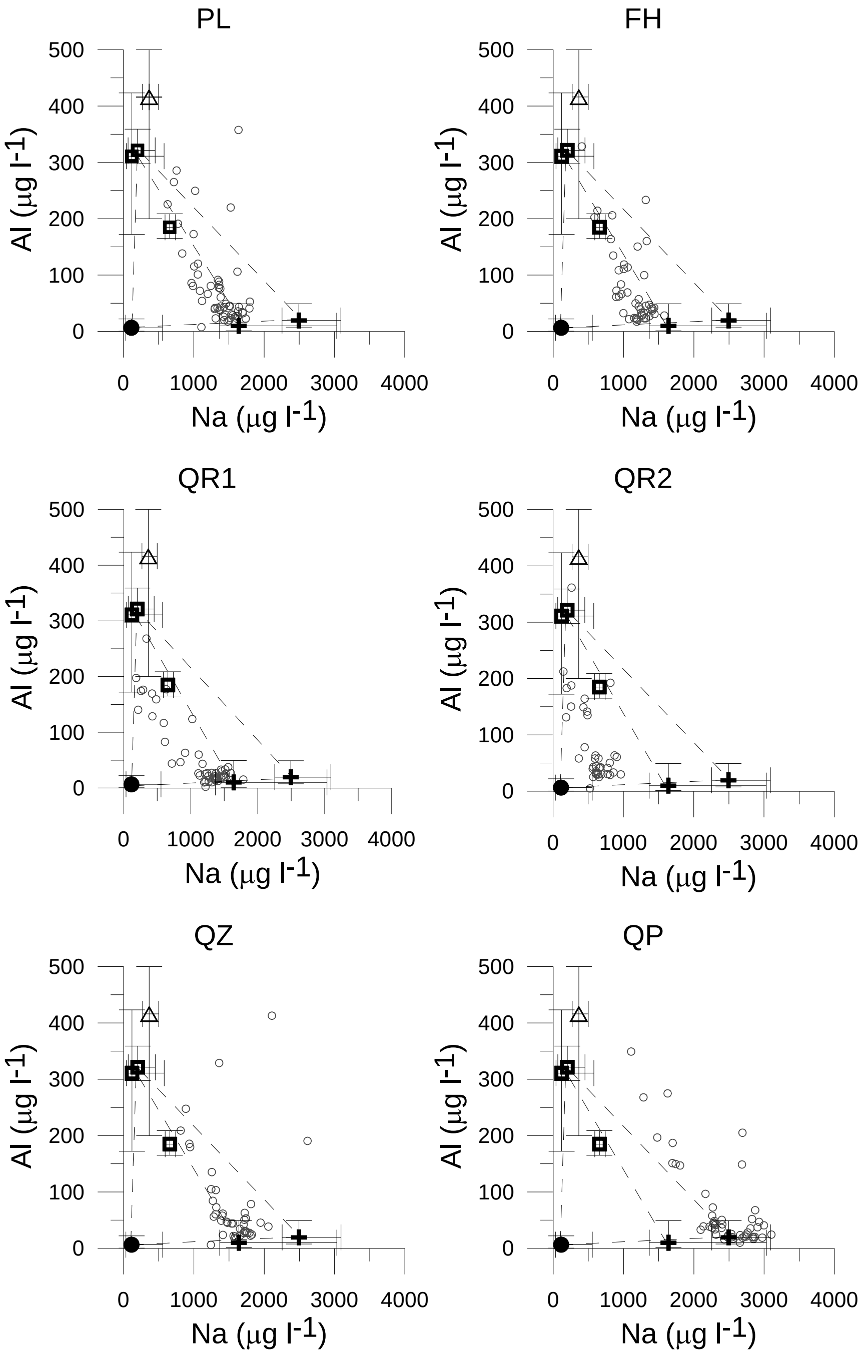

Figure 5. Mixing diagrams for the tracer Na and Al for the San Francisco basin and subbasins. Circle = precipitation; square = O horizon soil water; triangle = A horizon soil water; and cross = rock water.

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 large value of T 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 characterized by a high concentration of Na and zero to low concentration of Al. Boy *et al.* (2008b) states 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 (Bücker *et al.*, 2010). The Na concentration in the water samples collected at W2 is higher than in the water samples taken at W1 suggesting that the W2 rock water represents the flow through deeper rock layers with higher mean residence time.

3.5. Mixing model analysis

As shown in Figure 5 is the Al and Na concentration of streamflow of the selected subbasins well bounded by the chemical signature of the end-members precipitation, organic soil water and rock water with exception of the subbasin QP and QC where the A horizon water exceeds 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 form Group 2 and Group 3 consists of the subbasins QC and QP.

The chemical signature of the subbasins in Group 1 is during slow flow conditions 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 undeep cracks. It is supported by the T values varying between 262 and 311 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 tend to be more oriented towards the chemical composition of the soil water in the O and A horizon. During storm events or when the soil profile is close to saturation the chemical load of stream water is closely related to the chemical signature of the water flowing lateral through the organic horizons. Under those conditions the concentration of Ca decreases in favor 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 load of the stream water of the two subbasins in Group 2 is less influenced by 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. Deep rock water is less contributing to streamflow. This finding is in concordance with the lower value for T than the values found for the subbasins in Group 1, 242 and 225 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. Similarly in the subbasins in Group 1 during storm events it is the water flowing through the litter and organic horizons that is dominating the chemical signature of stream water of the subbasins in Group 2. Hereto, there is no evidence of infiltration excess overland flow.

The two subbasins in Group 3, QP and QC, have the largest area under pasture, varying between 26 and 67% of the total subbasin area. Mixing diagrams reveal that during slow flow conditions the streamflow samples are apparently more related to deeper rock water contribution (W2). However, lower T 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 the pasture sites could not be collected due to the refusal of access by the landowners, the mixing diagram (QP in Figure 5) suggests that during low flow the chemical signature of stream water is dominated by lateral subsurface flow through the C horizon and the superficial weathered rock layers. When the discharge is increasing, most of the stream water samples fall outside the mixing domain determined by the three selected end-members. 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. The mixing domain reveals that infiltration excess overland flow is not happening. This is in concordance with the results of the study conducted by Zimmermann (2007) in the same area using hydrometric data at plots scale.

4. CONCLUSIONS

The study reveals that the simultaneous application of multiple techniques such as hydrometric data, mean residence time and mixing model analysis provide crucial information on the processes dominating the runoff generation at basin scale in cloud forested areas. The applied nested approach showed to be suitable for the determination of the spatial variability of the processes. Combination of the methods enabled reducing the limitation of each technique and when used together results provided a more exact and comprehensive picture of the system. Furthermore, tracers in contradiction to hydrometric data permit, additionally to a considerable reduction in the period and cost of data collection, reaching consistent conclusions.

The mean residence time values and the mixing diagrams showed that in all studied subbasins, no matter whether pristine or deforested and how steep the topography, deep water contributes to streamflow. The streamflow of all subbasins is mainly composed by subsurface flow, except in subbasins where pasture cover dominates. The loss of the litter layer and the compaction of the top layer under grass cover are responsible for the occurrence of Hortonian flow during storm events. The inclusion of spring water samples in the analysis enabled to identify differences in deep water contribution along the subbasins, and as such highlighted the relevance of including in tracer studies in mountain areas the sampling of spring, seep and well water (Soulsby *et al.*, 2007; Buecker *et al.*, 2010). Results also showed that land use and vegetation cover do not control the runoff generation processes as hypothesized, indicating that runoff is mainly controlled by soil and subsoil properties.

The third 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 completely confirmed by the conducted analyses. The small differences in the high mean residence time values between catchments suggests that old water in the different pools of the basin are pushed out when new water enters. The study also 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 ecosystems in a shorter period at less cost.

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REFERENCES

Anderson, S., W. Dietrich, R. Torres, D. Montgomery, K. Loague, 1997. Concentration-discharge relationships in runoff from a steep, unchanneled catchment. *Water Resour. Res.*, 33(1), 211-225.

Beck, E., F. Makeschin, F. Haubrich, M. Richter, J. Bendix, C. Valarezo, 2008. The Ecosystem (Reserva Biológica San Francisco). In: Beck, E., J. Bendix, I. Kottke, F. Makeschin and R. Mosandl (Eds.), Gradients in a Tropical Mountain Ecosystem of Ecuador. *Springer,* Berlin, 281-290.

Beiderwieden, E., T. Wrzesinsky, O. Klemm., 2005. Chemical characterization of fog and rain water collectied at the eastern Andes cordillera. *Hydro. Earth Syst. Sc.*, 9, 185-191

Bendix, J., R. Rollenbeck, P. Fabian, P. Emck, M. Richter, E. Beck, 2008. Climate. In: Beck, E., J. Bendix, I. Kottke, F. Makeschin, R. Mosandl (Eds.), Gradients in a Tropical Mountain Ecosystem of Ecuador. *Springer,* Berlin, 63-74.

Biggs, T.W., T. Dunne, T.F. Domingues, L.A. Martinelli, 2002. Relative influence of natural watershed properties and human disturbance on stream solute concentrations in the southwestern Brazilian Amazon basin. *Water Resour. Res.*, 38(8), 25.

Blume,T., 2008. Hydrological processes in volcanic ash soils - Measuring, modelling and understanding runoff generation in an undisturbed catchment, *Ph.D. dissertation*, University of Potsdam, Potsdam, Germany, 153 pp.

Blume, T., E. Zehe, D.E. Reusser, A. Iroumé, A. Bronstert, 2008. Investigation of runoff generation in a pristine, poorly gauged catchment in the Chilean Andes I: A multi-method experimental study, *Hydrol. Proc., 22*(18), 3661-3675.

Bogner, C., S. Engelhardt, J. Zelinger, B. Huwe, 2008. Visualization and analysis of flow patterns and water flow simulation in disturbed and undisturbed tropical soils. In: Beck, E., J. Bendix, I. Kottke, F. Makeschin, R. Mosandl (Eds.), Gradients in a Tropical Mountain Ecosystem of Ecuador. *Springer,* Berlin, 403-412.

Bonell, M., J.M. Fritsch, 1997. Combining hydrometric-hydrochemistry methods: a challenge for advancing runoff generation process research. *Hydrochemistry,IAHS Publ. no. 244*, 227-234.

Bonell, M., 2005. Runoff generation in tropical forest. In: Bonell, M., L.A. Bruijnzeel (Eds.), Forest, Water and People in the Humid Tropics, *Cambridge University Press: Cambridge*, 314-406.

Boy, J., C. Valarezo, W. Wilcke, 2008. Water flow paths in soil control element exports in an Andean tropical montane forest. *Eur. J. Soil Sci.*, 59(6), 1209-1227.

Bowen, G.J., B. Wilkinson, 2002. Spatial distribution of δ^{18}O in meteoric precipitation. *Geology,* 30(4), 315-318.

Bowen G.J., J. Revenaugh, 2003. Interpolating the isotopic composition of modern meteoric precipitation. *Water Resour. Res.*, 39(10), 1299, doi:10.129/2003WR002086.

Bruijnzeel, L.A., 2000. An ecohydrological perpective of mountain cloud forest. In: Gladwell, J.S. (Ed.). Proceedings of the second international colloquium on hydrology and water management in the humid tropics*, UNESCO, Paris and CATHALAC, Panama*, 329-359.

Bücker, A., 2010. Chemical and biological water quality in tropical cloud forest streams under different land-use. *Ph.D. Dissertation*, Justus-Liebig Universität Gießen, Giessen, Germany, 93 pp.

Bücker, A., P. Crespo, H.G. Frede, K. Vaché, F. Cisneros, L. Breuer, 2010. Identifying controls on water chemistry of tropical cloud forest catchments - combining descriptive approaches and multivariate analysis, *Aquat. Geochem*., doi: 10.1007/s10498-009-9073-4.

Buytaert, W., 2004. The properties of the soils of the south Ecuadorian páramo and the impact of land use changes on their hydrology, *Ph.D. dissertation*, Katholieke Universiteit Leuven, Leuven, Belgium, 228 pp.

Buytaert, W., V. Iniguez, B. De Bièvre, 2007. The effects of afforestation and cultivation on water yield in the Andean páramo, *Forest Ecol. Manag.*, *251*, 22-30.

Buytaert, W., B. Beven, 2009. Regionalisation as a learning process. *Water Resour. Res.*, 45, W11419.

Célleri, R., 2007. Rainfall variability and rainfall-runoff dynamics in the Paute river basin - southern Ecuadorian Andes, *Ph.D. dissertation*, Katholieke Universiteit Leuven, Leuven, Belgium, 125 pp.

Chaves, J., C. Neill, S. Germer, S. G. Neto, A. Krusche, H. Elsenbeer, 2008. Land management impacts on runoff sources in small Amazon watersheds. *Hydrol. Process.*, 22, 1766-1775.

Christophersen, N., C. Neal, R.P. Hooper, R.D. Vogt, S. Andersen, 1990. Modelling streamwater chemistry as a mixture of soilwater end-members - a step towards second generation acidification models. *J. Hydrol.*, 116, 307-320.

DeWalle, D.R., P.J. Edwards, B.R. Swistock, R. Aravena, R.J. Drimmie, 1997. Seasonal hydrology of three Appalachian forest catchments. *Hydrol. Process.*, 11, 1895-1906.

Elsenbeer, H., D. Lorieri, M. Bonell, 1995. Mixing model approaches to estimate storm flow sources in an overland flow-dominated tropical rain forest catchment. *Water resource and research*, 31(9), 2267-2278.

Elsenbeer, H., A. Lack, 1996. Hydrometric and hydrochemical evidence for fast flowpaths at La Cuenca, western Amazonia. *J. Hydrol.*, 180(1-4), 237-250.

Elsenbeer, H., A. West, M. Bonell, 1994. Hydrologic Pathways and Stormflow Hydrochemistry at South Creek, Northeast Queensland. *J. Hydrol.*, 162(1-2), 1-21.

Elsenbeer, H., 2001. Hydrologic flowpaths in tropical rainforest soilscapes - a review. *Hydrol Process.*, 15(10), 1751-1759.

FAO, 2006. Global forest resources assessment 2005: Progress towards sustainable forest management. *Forestry Paper 147*, 320 pp.

FAO/ISRIC/ISSS, 1998. World Reference Base for Soil Resources. *World Soil Resources Report 84*, 88 pp.

Feddema, J.J., K.W. Oleson, G.B. Bonan, L.O. Mearns, L.E. Buja, G.A. Meehl, W.M. Washington, 2005. The importance of land-cover change in simulation future climates. *Science*, 210, 1674-1678.

Fleischbein, K, W. Wilcke, J. Boy, C. Valarezo, W. Zech, K. Knoblich, 2005. Rainfall interception in a lower montane forest in Ecuador: effects of canopy properties. *Hydrol. Process.*, 19, 1355-1371.

Fleischbein, K., W. Wilcke, C. Valarezo, W. Zech, K. Knoblich, 2006. Water budgets of three small catchments under montane forest in Ecuador: experimental and modelling approach. *Hydrol. Process.*, 20(12), 2491-2507.

Goller, R., W. Wilcke, M.J. Leng, H.J. Tobschall, K. Wagner, C. Valarezo, W. Zech, 2005. Tracing water paths through small catchments under a tropical montane rain forest in south Ecuador by an oxygen isotope approach. *J. Hydrol.*, 308, 67-80.

Grimaldi, C, M. Grimaldi, A. Millet, T. Bariac, J. Boulegue, 2004. Behaviour of chemical solutes during a storm in a rainforested headwater catchment. *Hydrol. Process.*, 18(1), 93-106.

Henderson, A., S.P. Churchill, J.L. Luteyn, 1991. Neotropical plant diversity. *Nature*, 351, 21-22.

Hensel, D., H. Elsenbeer, 1997. Stormflow generation in tropical rainforest: a hydrochemical approach. *Hydrochemistry,IAHS Publ. no. 244*, 227-234.

Homeier, J., H. Dalitz, S.W. Breckle, 2002. Waldstruktur und Baumartendiversität im montanen Regenwald der Estacón Cientíca San Franscisco in Südecuador. *Ber. d. Reinh. Tüxen-Ges.*, 14, 109-118.

Hooper, R.P., N. Christophersen, N.E. Peters, 1990. Modelling streamwater as a mixture of soilwater end-members - an application to the Panola mountain catchment, Georgia, USA. *J. Hydrol.*, 116, 321-343.

Hungerbühler, D., 1997. Tertiary basins in the Andes of southern Ecuador (3°00´-4°20´): Sedimentary evolution, deformation and regional tectonic implications, *Ph.D. dissertation*, Institute of Geology, ETH Zürich, Switzerland, 182 pp.

Huwe, B., B. Zimmermann, J. Zeilinger, M. Quizhpe, H. Elsenbeer, 2008. Gradients and patterns of soil physical parameters at local, field and catchment scales. In: Beck, E., J. Bendix, I. Kottke, F. Makeschin, R. Mosandl (Eds.), Gradients in a Tropical Mountain Ecosystem of Ecuador. *Springer,* Berlin, 391-402.

Johnson, M.S., J. Lehmann, E.G. Couto, J.P. Filho, S.J. Riha, 2006. DOC and DIC in flowpaths of Amazonian headwater catchments with hydrologically contrasting soils. *Biogeochemistry*, 81(1), 45-57.

Kirkby, M.J., 1978. Hillslope hydrology. *Wiley*, Chichester, 389 pp.

Liess, M., B. Glaser, B. Huwe, 2009. Digital soil mapping in southern Ecuador. *Erdkunde*, 63(4), 309-319.

Litherland, M., J.A. Aspden R.A. Jemielita, 1994. The metamorphic belts of Ecuador. *Br. Geol. Surv., Overseas Memoir N° 11*. 147 pp.

Lorieri, D., H. Elsenbeer, 1997. Aluminium, iron and manganese in near-surface waters of a tropical rainforest ecosystem. *Sci. Total Environ.*, 205(1), 13-23.

Makeschin, F., F. Haubrich, M. Abiy, J.I. Burneo, T. Klinger, 2008. Pasture management and natural soil regeneration. In: Beck, E., J. Bendix, I. Kottke, F. Makeschin, R. Mosandl (Eds.), Gradients in a Tropical Mountain Ecosystem of Ecuador. *Springer,* Berlin, 431-441.

Maloszewski, P., W. Rauert, W. Stichler, A. Herrmann, 1983. Application of flow models in a alpine catchment area using tritium and deuterium data, *J. Hydrol.*, 66, 319-330.

Maloszewski, P., A. Zuber, 1993. Principles and practice of calibration and validation of mathematical models for interpretation of environmental tracer data in aquifers. *Adv. Water Resour.*, 16, 173-190.

McDonell, J.J., 1990. A rationale for old water discharge through macropores in a steep, humid catchment. *Wat. Resour. Res*., 26, 2821-2832.

McDonell, J., L.K. Rowe, M.K. Stewart, 1999. A combined tracer-hydrometric approach to assess the effect on catchment scale on water flow path, source and age. In: Leibundgut, C., J. McDonell, G. Schults (Eds.), Integrated Methods in Catchment Hydrology-Tracers, Remote Sensing and New Hydrometric Techniques, *IAHS Publ.*, 258, 265-273.

McDonell, W., C.E. Asbury, 1994. Export of Carbon, Nitrogen, and Major Ions from 3 Tropical Montane Watersheds. *Limnol. Oceanogr.*, 39(1), 111-125.

McGuire, K.J., D.R. DeWalle, W.J. Gburek, 2002. Evaluation of mean residence time in subsurface water using oxygen-18 fluctuations during drought conditions in the mid-Appalachians. *J. Hydrol.*, 261, 132-149.

McGuire, K.J., J.J. McDonell, M. Weiler, C. Kendall, B.L. McGlynn, J.M. Welker, J. Seibert, 2005. The role of topography on catchment-scale water residence time. *Water Resour. Res.*, 41, W05002.

McGuire, K.J., J.J. McDonell, 2006. A review and evolution of catchment transit time modeling. *J. Hydrol.*, 330(3-4), 543-563.

Montanari, L., M. Sivapalan, A. Montanari, 2006. Investigation of dominant hydrological processes in a tropical catchment in a monsoonal climate via the downward approach. *Hydrol. Earth Syst. Sci*., 10, 769-782.

Moraes, J.M., A.E. Schuler, T. Dunne, R.O. Figueredo, R. Victoria, 2006. Water storage and runoff processes in plinthic soils under forest and pasture in eastern Amazonia. *Hydrol. Process.*, 20, 2509-2526.

Mortatti, J., J.M. Moraes, R.L. Victoria, A. Martinelli, 1997. Hydrograph separation of the Amazon river: A methodological study. *Aquat. Geochem*., *3*, 117-128.

Mosandl, R., S. Günter, B. Stimm, M. Weber, 2008. Ecuador suffers the highest deforestation rate in South America. In: Beck, E., J. Bendix, I. Kottke, F. Makeschin, R. Mosandl (Eds.), *Gradients in a tropical mountain ecosystem of Ecuador*, Ecological Studies, Springer Verlag, Berlin, Germany, 431-441.

Myers, N., R.A. Mittermeier, C.G. Mittermeier, G.A.B. da Fonseca, J. Kent, 2000. Biodiversity hotspots for conservation priorities. *Nature*, 403, 853-858.

Neill, C., H. Elsenbeer, A.V. Krusche, J. Lehmann, D. Markewitz, R.D. Figueiredo, 2006. Hydrological and biogeochemical processes in a changing Amazon: results from small watershed studies and the large-scale biosphere-atmosphere experiments. *Hydol. Process.*, 20(12), 2467-2476.

Newbold, J.D, B.W. Sweeney, J.K. Jackson, L.A. Kaplan, 1995. Concentrations and Export of Solutes from 6 Mountain Streams in Northwestern Costa-Rica. *J. N. Am. Benthol. Soc.*, 14(1), 21-37.

Rodgers, P., C. Soulsby, S. Waldron, D. Tetzlaff, 2005. Using stable isotope tracers to assess hydrological flow paths, residence times and landscape influences in a nested mesoscale catchment. *Hydro. Earth Syst. Sc.*, 9, 139-155.

Rollenbeck R, P. Fabian, J. Bendix, 2005. Precipitation dynamics and chemical properties in tropical mountain forests of Ecuador. *Adv. Geosci.*, 6, 1-4.

Rollenbeck, R., 2006. Variability of precipitation in the Reserva Biologica San Francisco/Southern Ecuador. *Lyonia*, 9, 43-51.

Rollenbeck, R., J. Bendix, P. Fabian, J. Boy, H. Dalitz, P. Emck, M. Oesker, W. Wilcke, 2007. Comparison of different techniques for the measurement of precipitation in tropical montane rain forest regions. *J. Atmos. Ocean. Tech.*, 24, 156-168.

Schellekens, J., F.N. Scatena, L.A. Bruijnzeel, A.I.J.M. van Dijk, M.M.A. Groen, R.J.P. van Hogezand, 2004. Stormflow generation in a small rainforest catchment in the Luquillo experimental forest, Puerto Rico. *Hydrol. Process.*, 18(3), 505-530.

Sklash, M.G., R.N. Farvolden, 1979. The role of groundwater in storm runoff. *J. Hydrol*., 43, 45-65.

Soulsby, C.D., R. Malcolm, R. Helliwell, R.C. Ferrier, A. Jenkins, 2000. Isotope hydrology of Allt a' Mharcaidh catchment, Cairngorms, Scotland: implications for hydrological pathways and residence times. *Hydrol. Process*., 14, 747-762.

Soulsby, C., P. Rodgers, R. Smart, J. Dawson, S. Dunn, 2003. A tracer-based assessment of hydrological pathways at different spatial scales in a mesoscale Scottish catchment. *Hydrol. Prosses*., 17, 759-777.

Soulsby, C., D. Tetzlaff, P. Rodgers, S. Dunn, S. Waldron, 2006. Runoff processes, stream water residence times and controlling landscape characteristics in a mesoscale catchment: An initial evaluation. *J. Hydrol.*, 325, 197-221.

Soulsby C, D. Tetzlaff, N. van den Bedem, I.A. Malcolm, P.J. Bacon, A.F. Youngson, 2007. Inferring groundwater influences on surface water in montane catchments from hydrochemical surveys of springs and streamwaters. *J. Hydrol.*, 333(2-4), 199-213.

Tanaka, T., M. Tsujimura, 1999. Integration of tracer techniques and hydrometric approaches in catchment hydrology: research on hydrological processes in the Kawakami experimental basin, central Japan. In: Leibundgut, C., J. McDonell, G. Schultz (Eds.), Integrated methods in catchment hydrology - tracers, remote sensing and new hydrometric techniques. *IAHS*, 258, 135-142.

Tsujimura, M, Y. Onda, J. Ito, 2001. Stream water chemistry in a steep headwater basin with high relief. *Hydrol. Process.*, 15(10), 1847-1858.

Unnikrishna, P.V., J.J. McDonnell, M.L. Stewart, 1995. Soil water isotope residence time modeling. In: Trudgill, S. T. (Ed.), Solute modeling in catchment systems. *Wiley*, Chichester, 237-260.

US Bureau of Reclamation, 2001. Water measurement manual, US Department of the Interior, USA, *Tech. Rep.*, 317 pp.

Vázquez, R.F., P. Willems, J. Feyen, 2008. Improving the predictions of a MIKE SHE catchment-scale application by using a multi-criteria approach. *Hydrol. Process.*, 22(13), 2159-2179.

Wagner, K., 2002. Fractionation of oxygen and hydrogen isotopes in waters of microcatchments in an tropical mountain rain forest of Southern Ecuador, *M.Sc. thesis*, Friedrich Alexander University of Erlanen, Nürnberg, Germany, 58 pp.

Wennibger, J., S. Uhlenbrook, S. Lorentz, C. Leibundgut., 2008. Identification of runoff gerneration processes using combined hydrometric, tracer and geophysical methods in a headwater catchment in South Africa. *Hydrol. Sci. J.*, 53(1), 65-80.

Werner, F., J. Homeier, R. Gradstein, 2005. Diversity of Vascular epiphytes on isolated remnant trees in the montane forest belt of Southern Ecuador. *Ecotropica*, 11, 21-40.

Wilcke, W., S. Yasin, U. Abramowski, C. Valarezo, W. Zech, 2002. Nutrient storage and turnover in organic layers under tropical montane rain forest in Ecuador. *Eur. J. Soil Sci.*, 53, 15-27.

Wilcke, W., S. Yasin, S., Schmitt, C., Valarezo, W. Zech, 2008. Soils along the altitudinal transect and in catchments. In: Beck, E., J. Bendix, I. Kottke, F. Makeschin, R. Mosandl (Eds.), Gradients in a Tropical Mountain Ecosystem of Ecuador. *Springer,* Berlin, 75-86.

Wolock, D.M., J. Fan, G.B. Lawrence, 1997. Effects of basin size on low-flow stream chemistry and subsurface contact time in the Neversink River watershed, New York. *Hydrol. Process.*, 11, 45-57.

Zimmermann, B., 2007. Spatial and temporal variability of the soil saturated hydraulic conductivity in gradients of disturbance. *Ph.D. Dissertation*, Potsdam University, Potsdam, Germany, 106 pp.