

Reply to Referee #2

In the following please find the corrections and comments to the referee's response. For clarity, the comments of the referee were copied in black and our comments are in blue.

The scope of this paper addresses a need for more hydrologic studies and stable isotope measurements of precipitation in tropical, mountainous environments. The topic fits within the scope of HESS. However, there are significant revisions that need to be made before it can be accepted for publication. Special attention to organization of argument and corroboration of observations with additional data sets would improve the paper. Some of the larger-scope issues are presented below.

1. The paper attributes an observed shift toward lower isotope values to a seasonality of weather patterns, and it distinguishes this seasonality from "the amount effect" on isotopic composition, when in fact these two things are related. Orographic rainfall associated with trade winds may experience limited rainout, yielding heavier stable isotopic compositions, whereas other precipitation systems may be derived from already depleted air masses, thus producing lighter isotopic compositions. Therefore, different prevailing weather systems and the amount effect on isotopic composition are linked. The paper could benefit from added discussion that elaborates and explains its reasoning behind causes of the seasonality, and two the heavily referenced publications in the paper (Rhodes et al., 2006 and Scholl et al., 2009) can help with thinking through a restructured discussion.

The seasonality and the amount effect are, as described, linked together and presented within the history of arriving air masses. The amount effect we tried to distinguish here is the rain out effect on-site yielding lighter isotopic compositions in the course of strong rain events compared to light rain events with small amounts of precipitation. To clarify this we added the following section to the introduction and rephrased the "amount effect" to "on-site amount effect":

"In general the isotopic composition of the incoming precipitation is inherently shaped by its history, e.g. by the source of the moisture and the amount effect due to rain out along the path taken by the air mass. As we cannot distinguish between the factors shaping the history of the incoming air mass by looking at on-site measurements, we restricted our analysis to the dependency of the isotopic signature of the precipitation on the prevailing weather conditions, the source of the incoming air masses, the spatial dependency within the study area and the on-site amount effect due to a discrimination of light isotopes during rainout in the course of a single event. For the on-site amount effect we assume that events with a higher amount of precipitation with the same history will yield an overall lighter isotopic composition than events with smaller amounts of rainfall. However, recent studies give rise to the assumption that other factors than the amount of precipitation or the origin of the air masses play an important role in controlling seasonal patterns of isotope signatures (Breitenbach et al., 2010; Feng et al., 2009; Kebede and Travi, 2011; Lee et al., 2009; Peng et al., 2010; Rhodes et al., 2006; Risi et al., 2008a, 2008b; Scholl et al., 2009; Villacís et al., 2008; Vimeux et al., 2005, 2011)." For example, Rhodes et al. (2006) and Scholl et al. (2009) concluded that orographic precipitation during the trade wind dominated dry season is enriched compared to the mostly convective precipitation type during the wet season occurring e.g. in Costa Rica and Puerto Rico, respectively. Vimeux et al. (2005) reported that moisture transport history is another important factor controlling the seasonal variation of isotope signatures in the Andes."

We furthermore slightly restructured the discussion and concentrated, as mentioned above, on the analysis of the influence of the prevailing weather conditions, the source of the incoming air masses, the spatial dependency within the study area and the on-site amount effect.

2. The data set represents only 3.5 months of data. Describing a “strong” seasonal isotopic signal is over stated given the limited data set. Are there other data sets in the region collected over longer time spans that could corroborate the observed pattern? More discussion of the “Amaluza” data, or other data sets if they exist, could help here. In addition, the interpretation of the “seasonality” of the data needs to be connected better to changes in prevailing air masses that bring precipitation to the study area. If wind direction, shown in Figure 5, is not clearly defined after Mid-October, then I am confused as to the “prevailing” air mass that is responsible for the lighter isotope compositions after Mid-October. The introduction section implies that the Pacific Westerlies prevail during this time. Is Figure 5 at odds with this description, or are the wind directions significantly different? How do the authors know that wind direction data are linked to a change in larger-scale prevailing air masses that bring precipitation to the region? The authors should be able to find other data sets to firm up this interpretation.

In general we agree with the reviewer that the dataset covering a 3 month period is not extraordinary extensive to identify seasonality. However, we found it still suitable to explore the spatial and temporal dependency of the isotopic composition of precipitation with respect to the prevailing weather conditions and the origin of the air masses. This is especially the case as the shifts in weather patterns are more than evident during the study period.

We especially strengthened the line of reasoning regarding the influence of the origin of the air masses by adapting figures and deploying the HYSPLIT model suggested by the other reviewer to identify the source of the precipitation measured within the study area. We also improved the discussion by taking a closer look at the trajectories taken by the air masses responsible for the measured rainfall to delineate a) the period characterized by trade winds and b) to visualize the travel distance above the Amazonas. See the new Figure 2 and 5 that shows the influence of origin of air masses on stable isotope signatures in precipitation.

3. Discussion of the deuterium excess data (section 3.3) needs to be improved. The paper describes an “abrupt decrease [in deuterium excess] in mid-October,” yet Figure 6 shows differences in this shift between the four sample sites, and the decrease seems more gradual than abrupt at the “El Tiro” location. Make sure the written descriptions carefully describe the observations. The discussion of effects of relative humidity vs. recycled water on deuterium excess needs to be explained further within the context. Additionally, the discussion in Section 3.3 is confusing about whether lower deuterium excess is attributed to changes in moisture recycling during the year, or differences in the proportion of recycled water within certain air masses that bring precipitation to the study area. The picture of what the authors interpret as happening at this location needs to be improved.

We agree with the reviewer that the phrase “abrupt decrease” overstates the measured effect. Taking a closer look at the isotope signature and the local climate data we could delineate an intermediate stage in mid October explaining the downward trend in the isotope signatures. This period at the end of the trade wind dominated period is characterized by low wind velocities and no clear wind direction. The source of the moisture during this transition phase is still the Amazonas region. We assume that the remaining moisture becomes more and more depleted in the course of several rain out events until it reaches the study area leading to a rather smooth than abrupt change in the isotopic composition. We therefore changed the discussion (see below) and adapted figure 2, which now combines the climate data and the isotopic composition for all events and shows the 3 periods in different colors.

“All 3 periods represent a distinct weather period. Before 18 October local climate measurements at the El Tiro climate station showed 91% east to southeasterly winds and an average wind velocities of $9.2 \text{ m}\cdot\text{s}^{-1}$ thereafter only 32% and an average wind velocities of $2.5 \text{ m}\cdot\text{s}^{-1}$ (26 October – 24 December). The high wind

speed and steady wind direction of the first period are typical for trade wind dominated periods. Without the SE trade winds the period after the 26 October shows no dominant wind direction. The transition phase is characterized by the lowest wind velocities of $1.3 \text{ m}\cdot\text{s}^{-1}$ on average and no clear wind direction. HYSPLIT results (Fig. 5) confirmed the different sources of the air masses. In the first phase of the investigation period all monitored rain events passed with the trade winds over the Amazonas region. During the transition phase the air parcels responsible for the recorded precipitation traveled for over 12 days above the Amazonas region close to the study area with a relative low pace, indicating that the arriving air masses may become continuously depleted in heavy isotopes in the course of ongoing rain fall events before they reach the study area. After mid October the backward trajectories show no clear pattern delivering moisture to the study area from the Pacific as well as from the Gulf of Mexico and the Amazonas. ... To further investigate and strengthen our assumption that recycled moisture from the Amazon Basin is responsible for the high isotopic composition during trade wind related precipitation events we used the deuterium excess parameter to assess the actual amount of recycled moisture (Araguas-Araguas et al., 2000; Bowen and Revenaugh, 2003; Froehlich et al., 2002; Gat, 2000; Liu et al., 2007; Njitchoua et al., 1999; Peng et al., 2010; Victoria et al., 1991)."

4. One source is not cited properly, which brings suspicion that other miscitations exist. Scholl et al. (2009) do not describe a seasonality in deuterium excess, as is stated on p. 8437, lines 7-8. Rhodes et al. (2006) do, but this is not mentioned. Also, the interpretations presented on p. 8436, lines 3-15 are similar to findings of Rhodes et al. (2006).

Indeed the source from Scholl et al. (2009) only deals with the seasonality of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ and not of deuterium excess. We therefore deleted the reference from the according section and checked our paper for any other possible miscitations. We also added the reference of Rhodes et al., 2006 to the observed seasonality of the deuterium excess. Our findings presented in p. 8436, lines 3-15 are maybe somewhat similar to the findings presented by Rhodes et al. (2006) as far as they both deal with the influence of seasonality (especially trade winds) on the isotopic signature, but we intend to depict the settings unique to our study area in this section and therefore see no need to include any further reference. Furthermore, there is no reason why not to confirm and publish observations made by others before.

5. Figures 2 and 6 need to be presented differently. The graphs need to show that each sample represents a discrete event. Therefore, the isotope data must be represented as points rather than as a continuous curve. Each sample represents an average isotopic composition for a particular event, and it is unknown how the composition may be changing over the sampling interval (yet the curves imply that this is known). The individual points need to be shown, and some indication of sampling interval would be helpful. Additionally, the x-axes do not show a linear representation of time; instead, the dates are categorical. Because time is a variable, the spacing of tick marks on the x-axis needs to represent an equal number of days.

The figure was changed in accordance to the suggestion of the reviewer. Furthermore we merged figures 2 and 6 into one figure. To ease the separation of the different station for the deuterium excess we added a dashed line to implicate that the course of the signature between the events is not know but still allows following the trend between the points.

6. Figure 1 needs a locator map within South America, not just the watershed delin-eation. Presenting a broader view of the study area will help communicate interpretations of the results within the context of large-scale wind patterns and regions that could supply recycled water to the study area.

We added an overview map as suggested, and included the location of the Amaluza GNIP station and latitude and longitude values for the study area.

7. The paper's interpretations of the "altitude effect" and lapse rate from the stable isotope data are reasonable for the data presented.

Okay.

8. The grammar and writing generally is good. I did catch a few typos. Others may exist. a) p. 8427, line 24: add a comma after citation, and change "Though" to "though". b) p. 8428, line 21: add "s" after "dominate." c) p. 8432 line 9, ($p < 0.05$): The p-value should be "greater than" 0.05 to be not significant.

We checked the text ones more for errors and corrected the given sections.

9. Other sections needing clarity:

a) p. 8429, hypothesis 1: This first hypothesis isn't specifically addressed in the discussion.

The old hypothesis 1: "There is no dominant effect (amount, altitude, continental, seasonal) responsible for the depletion of the stable water isotope signal of precipitation" was meant to serve as a base line assumption (no effect), which will be tested positive in the case that hypotheses 2-4 fail. It was not discussed in any detail as hypotheses 2-4 tested positive and it became obsolete. For conciseness we now abandoned hypotheses 1 and concentrate on the remaining three.

b) p. 8429, first paragraph: Clarify altitude changes for sampling sites in addition to the region.

We added the following sentence to the description of the study area to clarify the terrain of the region:

"As a part of the Amazon basin, close to the border of the watershed, the terrain of the region surrounding the study area is characterized by a more or less continuous decline to the east and a relatively high mountain range to the west."

c) p. 8431, lines 1-11: Are the Pacific westerlies the dominant wind pattern for Oct-Dec? What brings moisture to region if not the trade winds?

To further investigate the source of the precipitation during the investigated period we deployed the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPPLIT) model developed by Draxler and Rolph (2012) to calculate the 12days-backward trajectories for the 26 events. The simulation results showed, that during the Oct-Dec period most of the precipitation came from the Gulf of Mexico or from the Pacific, rather than coming from the Amazonas area. To clarify the source of the precipitation we decided to replace figure 5 (showing wind direction and velocity) with a new figure 5 showing the trajectories calculated by HYSPPLIT. The also added the following text for further clarification:

"... After mid October the backward trajectories show no clear pattern delivering moisture to the study area from the Pacific as well as from the Gulf of Mexico and the Amazonas (Fig. 5)."

d) p. 8433, line 22: Rozanski et al. (1993) have a more updated global meteoric water line than Craig (1961).

We added the reference to the GMWL reported by Rozanski et al. (1993) to the

according section. Because of its past importance and its unbroken prominence, we decided to keep the reference GMWL reported by Craig (1961). The section now reads as follows:

"In comparison to the global meteoric water line ($\delta^2H = 8 \times \delta^{18}O + 10\%$ defined by Craig (1961a) or more recently $\delta^2H = 8.13 \times \delta^{18}O + 10.8\%$ defined by Rozanski et al. (1993) the local meteoric water line for all 26 events ($\delta^2H = 8.31 \times \delta^{18}O + 14.47\%$) shows a slightly higher slope, which is still in good agreement with the slope expected under equilibrium conditions represented by the GMWL."

e) p. 8434, lines 22-24: Clarify differences in the temperature ranges in the study area versus those referenced. It's not clear from the text that the lapse rates for the other mentioned studies are also in the tropics and might experience similar temperature changes with elevation(although reading the reference list clarifies that a little bit).

To clarify the similarities in the temperature dependency of our study area and the study area of the mentioned studies we added the following sentence:

"Both studies were also carried out in tropical environment with a similar altitudinal air temperature gradient ($0.61^\circ\text{C } 100 \text{ m}^{-1}$ in our study area; Gonfiantini et al. (2001) $0.42\text{-}0.55^\circ\text{C } 100 \text{ m}^{-1}$; Peng et al. (2010) $0.53\text{-}0.65^\circ\text{C } 100 \text{ m}^{-1}$)."

f) p. 8435, lines 9-11: Connection between times of SE trade winds and changes in stable isotope composition is not clear in Figure 2. Make relationship between the timing of the seasonal precipitation patterns and changes in the data more clear.

We changed figure 2 by adding the climate data directly to the figure and a color code to separate the different periods (trade wind vs. no trade wind).

g) p. 8437, line 23: Sentence "Elevated deuterium excess values..." is missing a verb.

Replaced "evidence" with "indicate":

"Elevated deuterium excess values indicate that recycled moisture from the Amazon Basin is an important flux for orographic precipitation attributed to southeasterly trade winds."

h) p. 8438, line 7-8: "...but still revealed no significant effect" This point is unclear as presented.

We adapted the section which now reads as follows:

"Calculations were therefore conducted separately for the different wind conditions (SE trade winds, transition phase and post trade wind period with no clear wind direction), but still revealed no significant effect."

i) p. 8438, lines 12-19: The paper would be better off stating this information up front. Acknowledge that the monitoring period was short at the beginning, and strengthen the argument through elaboration with other data sets.

We strengthened our argumentation by adding additional proof for the interpretation of the source of the air masses responsible for the recorded precipitation events. We also added the following section to the introduction:

“As a monitoring period of around 3 month is not sufficient to identify the seasonality in the isotopic compositions of precipitation we rather investigate the dependency of isotopic composition on weather conditions and the origin of air masses responsible for the rainfall. Origin of air masses go along with a change in seasons in our research area (Bendix et al. 2008) and dominate not only hydrological fluxes but also many other ecosystem processes such as plant respiratory activity (Zach et al. 2010).”

Revised manuscript

**Impact of elevation and weather patterns on the isotopic composition of
precipitation in a tropical montane rainforest**

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Abstract

This study presents the spatial and temporal variability of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ isotope signatures in precipitation of a south Ecuadorian montane cloud forest catchment (San Francisco Catchment). From 02 September to 25 December 2010, event sampling of open rainfall was conducted along an altitudinal transect (1,800 m asl to 2,800 m asl) to investigate possible effects of altitude and weather conditions on the isotope signature.

The spatial variability is mainly affected by the altitude effect. The event based $\delta^{18}\text{O}$ altitude effect for the study area averages $-0,22\text{‰} \times 100 \text{ m}^{-1}$ ($\delta^2\text{H}$: $-1,12\text{‰} \times 100 \text{ m}^{-1}$). The temporal variability is mostly controlled by prevailing air masses. Precipitation during the times of prevailing southeasterly trade winds is significantly enriched in heavy isotopes compared to precipitation during other weather conditions. In the study area, weather during austral winter is commonly controlled by southeasterly trade winds. Since the Amazon Basin contributes large amounts of recycled moisture to these air masses, trade wind-related precipitation is enriched in heavy isotopes. We used deuterium excess to further evaluate the contribution of recycled moisture to precipitation. Analogously to the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values, deuterium excess is significantly higher in trade wind related precipitation. Consequently, it is assumed that evaporated moisture is responsible for high concentrations of heavy isotopes during austral winter.

1. Introduction

Stable water isotopes have been widely used as tracers in catchment hydrology, e.g. to validate hydrological models (Birkel et al., 2009; Koivusalo et al., 2000; Liebming et al., 2007; Rodgers et al., 2005b), identify areas of groundwater recharge (Cortés et al., 1997; Gonfiantini et al., 2001; Kattan, 2006), investigate flow paths (Barthold et al., 2011; Goller et al., 2005; Rodgers et al., 2005a) or to calculate the Mean Transit Time (MTT) of water

(Garvelmann et al., 2012; Kabeya et al., 2007; McGuire et al., 2002, 2005; Rodgers et al., 2005b).

All these approaches require a detailed knowledge of the composition of the isotopic input signal, i.e. precipitation (Darling and Talbot, 2003). But the isotopic composition of this precipitation signal varies temporally and spatially due to the depletion of isotopes caused by the temperature, amount (or rainout), continental, elevation (or altitude) and prevailing weather conditions, mostly expressed by a seasonal effect (Dansgaard, 1964; Gat, 1996; Siegenthaler and Oeschger, 1980). On catchment scales, the altitude effect is an important measure for the spatial variability, especially in mountainous catchments that cover high altitudinal ranges. It has therefore been the topic of various studies conducted around the world (Cortés et al., 1997; Garcia et al., 1998; Gonfiantini et al., 2001; Kattan, 2006; McGuire et al., 2005; Peng et al., 2010; Scholl et al., 2009; Siegenthaler and Oeschger, 1980; Vimeux et al., 2005, 2011; Vogel et al., 1975; Yurtsever and Gat, 1981). Most of the reported lapse rates for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ lie in ranges of -0.1 to -0.6‰ 100 m^{-1} and -0.5 to -4‰ 100 m^{-1} , respectively. The altitude effect is usually less pronounced in the tropics (Sturm et al., 2007) though information for tropical montane rainforest ecosystems is limited. We are aware of only one study in Puerto Rico where a gradient of -0.12‰ 100 m^{-1} for $\delta^{18}\text{O}$ and -0.6‰ 100 m^{-1} for $\delta^2\text{H}$ has been found (Scholl et al., 2009).

In addition to the altitudinal effect the temporal variability of isotope signatures in precipitation can be substantial. In many ecosystems a clear seasonality is observed, which is attributable to the amount effect, with precipitation being depleted in heavy isotopes during wet seasons (Dansgaard, 1964; Garcia et al., 1998; Gonfiantini et al., 2001; Lachniet and Patterson, 2006, 2009; Liu et al., 2007; Rietti-Shati et al., 2000; Rozanski et al., 1992), though seasonal differences tend to be smaller in the tropics than at higher latitudes (Scholl et al., 2011). In general the isotopic composition of the incoming precipitation is inherently shaped by its his-

tory, e.g. by the source of the moisture and the amount effect due to rain out along the path taken by the air mass. As we cannot distinguish between the factors shaping the history of the incoming air mass by looking at on-site measurements, we restricted our analysis to the dependency of the isotopic signature of the precipitation on the prevailing weather conditions, the source of the incoming air masses, the spatial dependency within the study area and the on-site amount effect due to a discrimination of light isotopes during rainout in the course of a single event. For the on-site amount effect we assume that events with a higher amount of precipitation and the same history will yield an overall lighter isotopic composition than events with smaller amounts of rainfall. However, recent studies give rise to the assumption that other factors than the amount of precipitation or the origin of the air masses play an important role in controlling seasonal patterns of isotope signatures (Breitenbach et al., 2010; Feng et al., 2009; Kebede and Travi, 2011; Lee et al., 2009; Peng et al., 2010; Rhodes et al., 2006; Risi et al., 2008a, 2008b; Scholl et al., 2009; Villacís et al., 2008; Vimeux et al., 2005, 2011). For example, Rhodes et al. (2006) and Scholl et al. (2009) concluded that orographic precipitation during the trade wind dominated dry season is enriched compared to the mostly convective precipitation type during the wet season occurring e.g. in Costa Rica and Puerto Rico, respectively. Vimeux et al. (2005) reported that moisture transport history is another important factor controlling the seasonal variation of isotope signatures in the Andes. The Amazon Basin is known to contribute large amounts of recycled moisture to the air masses transported by trade winds (Martinelli et al., 1996; Salati et al., 1979; Valletcoulomb et al., 2008). This contribution of recycled moisture to precipitation can be traced by the deuterium excess parameter (Araguas-Araguas et al., 2000; Froehlich et al., 2002; Gat, 2000; Kabeya et al., 2007; Njitchoua et al., 1999; Victoria et al., 1991). Since southeasterly (SE) trade winds prevail in our research area in the tropical montane forests of Southern Ecuador during austral winter (Emck, 2007), we assume that a large share of the air masses responsible for rainfall

85 during this period originates from the Amazon. Consequently, we expect higher isotope signa-
86 tures and higher values of deuterium excess during the period dominated by SE trade winds.

87 Our work focuses on improving the understanding of the hydrological processes responsible
88 for the rainfall-runoff generation in a remote tropical montane rainforest catchment of Ecua-
89 dor. Previous work in micro-catchments in the study area by Goller et al. (2005) focused on
90 the temporal variability of isotope signatures in rainfall, throughfall, and streamwater. They
91 found that near-surface event water dominates runoff in these pristine rainforest-covered mi-
92 cro-catchments. In contrast, groundwater dominated fluxes tend to govern runoff generation
93 on larger scales as revealed by geogenic tracer analyses (Bücker et al., 2010; Crespo et al.,
94 2012). Surprisingly, Crespo et al. (2012) derived MTTs of up to 260 to 350 days, despite the
95 very responsive, flashy hydrographs that tend to react within a few hours to precipitation in-
96 puts. The uncertainty of this estimate remains unknown, given the limited information of sta-
97 ble isotopes in precipitation that the authors used.

98 This study presents a more detailed investigation of the temporal and spatial variations in
99 $\delta^{18}\text{O}$ and $\delta^2\text{H}$ isotope signatures of precipitation and paves the ground for further research. As
100 a monitoring period of around 3 month is not sufficient to identify the seasonality in the iso-
101 topic compositions of precipitation we rather investigate the dependency of isotopic composi-
102 tion on weather conditions and the origin of air masses responsible for the rainfall. However,
103 origin of air masses go along with a change in seasons in our research area (Bendix et al.
104 2008) and thus can be seen as a proxy for seasonality. The identification of processes causing
105 the variation in the isotopic composition will establish a tool for understanding the interde-
106 pendencies among climate, hydrology, ecology and water resources in future research
107 (Rhodes et al., 2006). Knowledge about the spatial variability of isotope signatures in precipi-
108 tation will enable researchers to better identify flow paths and draw conclusions about the
109 contribution of precipitation from different altitudes to discharge (Cortés et al., 1997;

Gonfiantini et al., 2001; Kattan, 2006). Tracing isotopes through the hydrological cycle further allows calculations of the MTT in the catchment. The objective of this paper therefore is to investigate the following hypotheses, which are based on findings reported in the previous sections:

(1) The concentration of heavy isotopes decreases with increasing altitude.

(2) Precipitation during SE trade wind dominated periods is enriched in heavy isotopes compared to precipitation during other weather conditions.

(3) Precipitation during SE trade wind dominated periods shows significantly higher deuterium excess values.

2. Material and Methods

2.1. Location and climate of the study area

The study area is located on the eastern slopes of the Andes (S Ecuador) in the San Francisco valley. As part of the Amazon basin, close to the border of the watershed, the terrain of the region surrounding the study area is characterized by a more or less continuous decline to the east and a comparatively high mountain range to the west. The highest point of the study area is the *Cerro El Consuelo*, coll. *Antenas* at 3,155 m asl. The lowest point is at 1,720 m asl. Fig. 1 shows the topography of the study area and the location of sampling sites and climate stations. The topography of the San Francisco catchment allows the investigation of a large altitudinal gradient within a relatively small horizontal distance. Valleys in the study area are deeply incised. The southern part of the catchment is mainly vegetated by primary forest. In the northern part, the natural forest has been replaced by extensive pastures in parts and is further characterized by a mix of shrubs, reforestation sites and sub-paramo (Göttlicher et al., 2009).

Average annual sums of precipitation, for the period 2002 to 2008, amount to 1,500 to 4,900 mm a⁻¹ with a large spatial variability (Rollenbeck and Bendix, 2011). Moreover, there is a significant input of fog to the ecosystem, which accounts for 5 to 35% of precipitation and enhances the total water input up to 6,500 mm a⁻¹ at the highest altitudes (Rollenbeck et al., 2011). According for Rollenbeck et al. (2011) the designated fog input increases with altitude and amount of rainfall, comprising various forms of horizontal precipitation like the actual fog, drizzle and other wind driven rain. Along a N to S transect investigated by Bendix et al. (2008), an altitudinal increase of precipitation (lapse rate) of 220 mm 100 m⁻¹ was observed. However, spatial observations of radar based precipitation inputs do not indicate that this altitudinal effect is valid for the whole study area, especially in an E-W direction (Rollenbeck and Bendix, 2011). Along the E-W transect that was investigated in the present study (Fig. 1) climate stations have also not shown an altitudinal increase of incoming precipitation. Precipitation at the highest point investigated in this study (*El Tiro*, 2,800 m asl) amounts to 1,500 mm a⁻¹, whilst at the lowest point (ECSF, 1,800 m asl) it is 2176 mm a⁻¹ (Bendix et al., 2006; Emck, 2007). This demonstrates the high spatial variability of precipitation amounts occurring in the study area.

The weather within the study area is dominated by easterly trade winds. From January to April, northeasterly trade winds are prevailing. Southeasterly trade winds dominate weather in the study area from April to mid-October (Emck, 2007). From June to September, the proportion of trade winds is close to 100%. For the rest of the year, it is still more than 50%. The temporal variability of isotope signatures in the present study was, for the most part, expected to be determined by the prevailing air masses. During the investigation period, southeasterly tropical trade winds were prevailing from September to mid-October. In that period, wind direction was hardly changing and wind speeds were high (5 to 15 m s⁻¹). From mid-October on, as trade winds weakened, wind direction was much less clear defined and lower wind speeds were measured. The observed change in weather patterns at that time of the year is

consistent with long term climate records for the study area (Bendix et al., 2008; Emck and Richter, 2008). Since tropical trade winds travel at altitudes below 3,000 m (Scholl et al., 2002), the Andes form a topographic barrier which leads to a rainout of air masses. The *Cordillera Real* serves as a climate divide between the humid Amazon Basin and the dry Inter Andean Region. From mid-October on, when trade winds weaken in their intensity and frequency, other wind directions and lower wind speeds are observed. However, precipitation originating from pacific westerlies hardly reaches the study area, since most of these air masses rain out at the western slopes of the Andes (Bendix et al., 2008; Emck, 2007).

The main factor influencing air temperature in the study area is elevation. Mean annual temperature ranges from 12°C (at 3260 m asl) to 22°C (at 1600 m asl). The average gradient of air temperature is 0.61°C 100 m⁻¹. As usual for tropical regions, seasonal changes in temperature are low (Bendix et al., 2008).

2.2. Experimental set up

To investigate the depletion effects on isotope signatures in precipitation, a transect along an altitudinal gradient of 1,000 m was investigated. An event sampling was conducted at four sampling sites along this altitudinal gradient: ECSF at 1,800 m asl, *Loma Chamusquín* at 2070 m asl, *Quebrada Navidades* at 2,460 m asl and *El Tiro* at 2,800 m asl (Fig. 1).

Each site consisted of three collectors made from 1 L glass bottles prepared with circular funnels of 0.10 m in diameter. Bottles were placed in white polyethylene tubes to avoid heating and tubes were screwed to wooden pales and installed 1 m aboveground. A table tennis ball was placed into each funnel to prevent the sample from evaporating. According to IAEA standard procedures, samples were filled and stored in 2 ml brown glass vials covered by silicone septa (Mook, 2000).

Prior to field sampling the reliability of the table tennis ball to prevent evaporation losses was tested in the laboratory. During a 21 d period the effect of four different climatic conditions simulated in climate chambers (30°C/15°C and 15°C/10°C in a 12 h day-night cycle each at 50% and 90% relative humidity) on the isotopic composition was tested. Collectors with table tennis balls were stored under these different climate conditions and water samples were withdrawn in intervals of three days. Even under the most unfavorable conditions in the climate chambers (temperature 30°C/15°C and relative humidity 50%) the enrichment of heavy isotopes was either not significant ($p>0.05$) or, in the case of scenario 4, within the measuring inaccuracy of the analytical device of 0.2‰ for $\delta^{18}\text{O}$ and 0.6‰ for $\delta^2\text{H}$ (Tab. 1). During the field experiment not more than one day passed between the precipitation event and sample collection. We therefore exclude a measurable effect of the sampling procedure on the isotopic compositions of the samples.

Total precipitation sums between each event sampling were also measured in the collectors. Climate data from stations near ECSF and *El Tiro* were also used to investigate the influence of climatic parameters (relative humidity (%), air temperature (°C), rainfall amount and intensity (mm h^{-1}) and wind direction (°) and speed (m/s)) on the isotopic composition of the samples. The wind direction of air masses moving over the study area was measured at the *El Tiro*. In addition to the on-site climate measurements we used the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model developed by Draxler and Rolph (2012) to calculate for each event the backwards trajectories for the previous 12 days (288 hours) of the air masses responsible for rainfall reaching the study area in an elevation of 1,500 m above ground level. For the analyses in our study, the HYSPLIT model was operated with meteorological input from the Global Data Assimilation System (GDAS) reanalysis data set. To account for interannual variability of climate conditions we sampled in a period during which a shift in the prevailing wind conditions was most likely to occur (Emck, 2007). Therefore samples were taken from September to December 2010.

2.3. Analysis and statistics

Isotope signatures of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ were analyzed according to the IAEA standard procedure (Newman et al., 2009) using a Los Gatos Research DLT-100-Liquid Water Isotope Analyzer (Los Gatos Research Inc., Mountain View, US). Water samples are vaporized and analyzed via near infrared absorption spectroscopy to simultaneously quantify the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ isotope signatures in an optical cell. Isotope ratios are reported in per mil (‰) relative to an international acknowledged reference standard, the *Vienna Standard Mean Ocean Water* or VSMOW (Craig, 1961b). Precision of the method is 0.2‰ for $\delta^{18}\text{O}$ and 0.6‰ for $\delta^2\text{H}$, resulting in a quadratic error of 1.7‰ for deuterium excess (LGR, 2012).

Data preparation was conducted by excluding outliers from the repetitive measurements of $\delta^{18}\text{O}$ and $\delta^2\text{H}$. Results were considered as outliers if the standard deviation from the average was larger than one. Not more than one out of three samples per event and sampling point was allowed to be excluded. If two out of three results had a standard deviation larger than one, no outlier was excluded. On average the three samples per event and sampling point showed a fairly similar standard derivation of 0.27‰ for $\delta^{18}\text{O}$ (ranging from 0.03‰ to 0.87‰) and 0.58‰ for $\delta^2\text{H}$ (ranging from 0.01‰ to 1.66‰) for all four sites. Mean values of the remaining results built the dataset from here on. All deviations are given as mean error. Statistical evaluation was performed using SPSS Statistics (Version 16.0; SPSS Inc. Chicago, IL, US). For a comparison of our results, isotope precipitation data from the IAEA-GNIP station Amaluza, Ecuador was used (IAEA, 2012). Amaluza is located about 170 km north of the study area and the dataset comprises monthly means starting from May 1992 – July 1994 (27 values).

3. Results and Discussion

In this study, 26 events were sampled at four altitudinal levels in a period from 2 September to 25 December 2010 (during all events we recorded precipitation at all four altitudes). Isotopic compositions of open rainfall range from -16.5 to 2.7‰ for $\delta^{18}\text{O}$ and from -120.2 to 30.8‰ for $\delta^2\text{H}$ (see Tab. 2 for more details). Compared to the study of Goller et al. (2005) and the data from Amaluza, isotope signatures presented in this study cover a relatively wide range. This fact can be attributed to the event-based sampling design where there is no mixing of events with extreme values, as compared to sampling in defined intervals which often produces a narrower range of values. The range is also in good agreement with the daily precipitation values reported by Villacis et al. (2008) for lower parts of the Ecuadorian Amazonas in the north east of the country ranging from -15.51‰ to 1.56‰ for $\delta^{18}\text{O}$.

In comparison to the global meteoric water line ($\delta^2\text{H} = 8 \times \delta^{18}\text{O} + 10\text{‰}$ defined by Craig (1961a) or more recently $\delta^2\text{H} = 8.13 \times \delta^{18}\text{O} + 10.8\text{‰}$ defined by Rozanski et al. (1993)) the local meteoric water line for all 26 events ($\delta^2\text{H} = 8.31 \times \delta^{18}\text{O} + 14.47\text{‰}$) shows a slightly higher slope, which is still in good agreement with the slope expected under equilibrium conditions represented by the GMWL. The higher intercept (deuterium excess) of the local meteoric water line is most likely attributable to re-evaporated/recycled precipitation reaching the study area during the investigation period. Fig. 2a shows the $\delta^{18}\text{O}$ isotope signatures of all sampled events ($\delta^2\text{H}$ shows the same course (data not shown), any difference between $\delta^2\text{H}$ and $\delta^{18}\text{O}$ is expressed by the deuterium excess shown in Fig. 2b). Spatial variability, i.e. the difference between the four sampling sites, is relatively low compared to the temporal variability, which points to a distinct dependency of isotope signatures on the prevailing weather conditions and the origin of the air masses.

3.1. Altitude effect

To separate the altitude effect from the temporal variation, the altitude effect was calculated for each event separately (Fig. 3). Event lapse rates (δ versus altitude) calculated by linear regression show that the concentration of heavy isotopes in the precipitation samples generally decreases with altitude (Fig. 3 and Fig. 4). On average, the $\delta^{18}\text{O}$ altitude effect is $-0.22\text{‰} \times 100\text{m}^{-1}$ and for $\delta^2\text{H}$ it amounts to $-1.12\text{‰} \times 100\text{m}^{-1}$ (standard error 0.2‰ for $\delta^{18}\text{O}$ and 1.39 for $\delta^2\text{H}$). As usual for tropical regions (Sturm et al., 2007), it lies within the lower part of the ranges reported in literature (Tab. 3). Most $\delta^{18}\text{O}$ event lapse rates of the present study are between -0.1 and $-0.4\text{‰} \times 100\text{m}^{-1}$ ($\delta^2\text{H}$: -0.8 to $-1.5\text{‰} \times 100\text{m}^{-1}$). However, three out of 26 events do not show a negative lapse rate for both $\delta^{18}\text{O}$ and $\delta^2\text{H}$ (Fig. 4; dates 06.09., 01.10. and 21.10.). Overall linear regression of the data showed that the altitude effect of $\delta^{18}\text{O}$ is significant ($p < 0.05$), while for $\delta^2\text{H}$ it is insignificant ($p = 0.19$). Nevertheless, using a one-tailed t-test, it could be shown that the event lapse rates deviate significantly from zero for both $\delta^{18}\text{O}$ and $\delta^2\text{H}$ ($p < 0.01$). Consequently, we generally assume that concentrations of heavy isotopes decrease with altitude.

The deuterium excess also shows a significant spatial variability, i.e. an increase with altitude of $0.6\text{‰} \times 100\text{m}^{-1}$ ($p < 0.01$) (Fig. 3). Gonfiantini et al. (2001) report that the increase of deuterium excess with altitude is predominantly present at high relative humidity, which is prevailing in the study area. However, there must be additional factors to explain the altitude effect of deuterium excess (Gat et al., 2000).

In the studies presented by Gonfiantini et al. (2001) and Peng et al. (2010), a seasonality of the altitude effect is reported. Both studies were also carried out in tropical environment with a similar altitudinal air temperature gradient ($0.61^\circ\text{C } 100\text{m}^{-1}$ as in our study area; Gonfiantini et al. (2001) $0.42\text{--}0.55^\circ\text{C } 100\text{m}^{-1}$; Peng et al. (2010) $0.53\text{--}0.65^\circ\text{C } 100\text{m}^{-1}$). The authors explain this by the larger lapse rate (temperature vertical gradient) during rainy months. During

the investigation period, no such temporal effect on the altitude effect is observed in our study area. Furthermore, a multiple regression analysis of event lapse rates revealed no significant influence of temperature, relative humidity and precipitation amount or intensity on the altitude effect. However, one factor that might enhance the altitude effect is the so-called pseudo-altitude effect (Moser and Stichler, 1971), which leads to an evaporative enrichment of heavy isotopes in falling raindrops. Due to the larger altitudinal difference between cloud base and surface, this enrichment is more pronounced at lower altitudes (Gat et al., 2000), and can be almost excluded in tropical montane cloud forests where the cloud base is often at the same level as the sampling sites.

3.2. Impact of prevailing air masses

The temporal variability of isotope signatures in tropical precipitation is to a large degree attributed to the origin of air masses that prevail during different times of the year (Liu et al., 2007; Rhodes et al., 2006). Isotope signatures of precipitation in the study area are significantly higher during the times of SE trade winds (02 September – 18 October) than for the rest of the investigation period (26 October – 24 December) with no clear wind direction and lower wind velocities (Fig. 2). Between these two periods a transition in the origin and consistence of the source of the prevailing air masses takes place (19 October – 25 October). This transition phase at the end of the trade wind period is characterized by abating wind velocities and intermediate isotope signatures (Fig. 2d). Concentrations of $\delta^{18}\text{O}$ range between -8.3 to +2.7‰ for trade wind related events, -7.2 to -4.6‰ for events during the transition phase and -16.5 to -3.6‰ for other events ($\delta^2\text{H}$: -55.3 to 30.8‰, -51.2 to -27.5‰ and -120.2 to -27.0‰, respectively). Mean values of $\delta^{18}\text{O}$ are -3.0‰ for trade wind related precipitation, -6.3‰ for events during the transition phase and -9.9‰ for other precipitation events ($\delta^2\text{H}$: -8.8‰, -40.3‰ and -69.5‰).

302 All three periods represent a distinct weather period. Before 18 October local climate meas-
303 urements at the El Tiro climate station showed 91% east to southeasterly winds and average
304 wind velocities of 9.2 m s^{-1} , and thereafter, only 32% and an average wind velocities of 2.5 m
305 s^{-1} (26 October – 24 December). The high wind speed and steady wind direction of the first
306 period are typical for trade wind dominated periods. Without the SE trade winds the period
307 after the 26 October shows no dominant wind direction. The transition phase is characterized
308 by the lowest wind velocities of 1.3 m s^{-1} on average and no clear wind direction. HYSPLIT
309 results (Fig. 5) confirmed the different sources of the air masses. In the first phase of the in-
310 vestigation period all monitored rain events passed with the trade winds over the Amazonas
311 region. During the transition phase the air parcels responsible for the recorded precipitation
312 traveled for over 12 days across the Amazonas region close to the study area with a relative
313 low velocity. This potentially indicates that the arriving air masses become continuously de-
314 pleted in heavy isotopes in the course of ongoing rain fall events before reaching the study
315 area. After mid October the backward trajectories show no clear pattern delivering moisture to
316 the study area from the Pacific as well as from the Gulf of Mexico and the Amazonas (Fig. 5).

317 Since most of the precipitation in the study area is trade wind related orographic precipitation,
318 which is the main driving factor behind the observed altitude effect, it is important to under-
319 stand the impact of trade winds on the isotopic composition of precipitation in the study area.
320 Tropical trade winds move at altitudes below 3,000 m asl and take up large amounts of recy-
321 cled moisture over the Amazon Basin when coming from the SE. This moisture is enriched in
322 heavy isotopes and shows a higher deuterium excess due to the discrimination of heavy iso-
323 topes during fractionation processes like evaporation. Reaching the Andes, the air masses are
324 orographically lifted and thus subject to rainout (Scholl et al., 2002). Thus, trade wind related
325 precipitation in the study area is enriched in heavy isotopes. From mid-October to the end of
326 December, when trade winds weaken, other air masses, partly originating from the Pacific,
327 influence the climate in the investigated area (Fig. 5, Bendix et al., 2008; Emck, 2007) and

precipitation contains significantly less heavy isotopes. Despite being of orographic nature as well, this precipitation is not characterized by recycled moisture.

To further investigate and strengthen our assumption that recycled moisture from the Amazon Basin is causing the high isotopic composition during trade wind related precipitation events we used the deuterium excess parameter to assess the actual amount of recycled moisture (Araguas-Araguas et al., 2000; Bowen and Revenaugh, 2003; Froehlich et al., 2002; Gat, 2000; Liu et al., 2007; Njitchoua et al., 1999; Peng et al., 2010; Victoria et al., 1991). For trade wind related precipitation events, deuterium excess averages 14.9‰ and hence, is significantly higher than for other events ($d = 9.6\text{‰}$). The temporal variability of event deuterium excess in the study area shows a similar trend compared to the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values, including the decrease after mid-October (Fig. 2b). These observations confirm the assumption that intense moisture recycling takes place when precipitation is attributed to SE trade winds. Goller et al. (2005) report an annual mean deuterium excess of 11.1‰ for their site at the lower part of the same investigation area, pointing to the assumption that moisture recycling might not be high all year long. Since they did not measure both $\delta^2\text{H}$ and $\delta^{18}\text{O}$ for all samples, no temporal variability of deuterium excess was reported. Mean annual deuterium excess at the GNIP station Amaluza was 15.5‰. Highest values were measured from July to October (18.4 to 19.2‰), i.e. the time of the year when SE trade winds prevail in the study area. Lowest values were measured from March to May (10 to 12.5‰) and in November (11.9‰).

Some studies report an amount effect (Bony et al., 2008) or a seasonality (Henderson-Sellers et al., 2010; Liu et al., 2007; Rhodes et al., 2006) of deuterium excess, showing higher values during the dry season. For the present study, a linear regression of event deuterium excess with precipitation amount showed no significant influence ($p=0.56$). The temporal variability therefore should, analogously to the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values, rather be attributed to the influence

of SE trade winds bringing precipitation to the study area that contains large amounts of recycled moisture.

4. Conclusions

The stable isotopic composition of precipitation collected in the San Francisco catchment showed strong temporal variations consistent with differences in weather conditions and the origin of air masses. Elevated deuterium excess values indicate that recycled moisture from the Amazon Basin is an important flux for orographic precipitation attributed to southeasterly trade winds. Rainfalls following these trade winds are enriched in heavy isotopes compared to precipitation during other weather conditions. We further found decreasing concentrations of heavy isotopes with altitude.

In general, the presented findings are in good agreement with the underlying theoretical concepts and have highlighted the need to account for spatial and temporal variation. Comparison to studies conducted in the same research area and in comparable ecosystems showed that the variability of the isotopic composition in the study area is rather governed by the prevailing air masses than by a local amount effect due to rainout. As in the case of the altitude effect, any on site amount effect is overshadowed by the temporal variability. Calculations were therefore conducted separately for the different wind conditions (SE trade winds, transition phase and post trade wind period with no clear wind direction), but still revealed no significant effect. However, longer term measurements will be needed to rule out the impact of the amount effect, and of other air masses with certainty (particularly NE trade winds that prevail in the study area from January to March).

The presented findings build a solid base showing the range of the spatial temporal variability isotopic composition in the study area. Though the monitoring period was relatively short, the extensive monitoring set up captured the complete range of climate conditions within the

study area (e.g. trade winds and precipitation patterns) on a fine temporal and spatial scale. In combination with the long term monitoring currently conducted at ECSF further insight will be gained about inter-annual variability (Vimeux et al., 2011) and the effect of El Niño and La Niña on the isotopic signature of the incoming precipitation in the study area.

Combining seasonal and spatial variations of δ and deuterium excess can provide an effective tool for tracing moisture through the hydrological cycle. Further work will use these data to validate hydrological models identifying the actual pathways of the water in the catchment and calculate mean transit times. Moreover, the data can serve as a contribution to the global data set on isotopic composition of precipitation which is used in climate modeling.

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Tab. 1 Results of the validation experiment. Temperature and relative humidity during the validation experiment. Day- and nighttime temperatures were programmed in 12-hour-cycles.

scenario	daytime temperature [°C]	nighttime temperature [°C]	Relative humidity [%]	slope $\delta^2\text{H}$ [‰ d ⁻¹]	p	slope $\delta^{18}\text{O}$ [‰ d ⁻¹]	p
1	30	15	50	0.031	0.084	0.044	0.796
2	30	15	90	-0.013	0.697	0.135	0.171
3	15	10	50	-0.037	0.529	-0.12	0.098
4	15	10	90	0.025	0.354	0.024	0.029*

* denotes that the regression is significant on the 0.05 level.

Tab. 2 Descriptive statistic of all 26 events sampled

	Loactation	min	mean	max	range
$\delta^2\text{H}$ [‰]	all stations	-120.2	-27.6	30.8	151.0
	ECSF (1800 m a.s.l.)	-92.9	-22.0	30.8	123.7
	Chamusquin (2070 m a.s.l.)	-95.0	-25.0	26.9	121.8
	Navidade (2460 m a.s.l.)	-101.7	-30.6	9.2	110.9
	El Tiro (2800 m a.s.l.)	-120.2	-32.9	14.0	134.2
$\delta^{18}\text{O}$ [‰]	all stations	-16.5	-5.1	2.7	19.2
	ECSF (1800 m a.s.l.)	-12.1	-4.0	2.7	14.8
	Chamusquin (2070 m a.s.l.)	-12.7	-4.6	1.8	14.4
	Navidade (2460 m a.s.l.)	-14.3	-5.7	-0.9	13.4
	El Tiro (2800 m a.s.l.)	-16.5	-6.1	0.1	16.5

Tab. 3 Altitude effect of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ in precipitation from various sites around the world.

Author	$\delta^2\text{H}$ [‰ 100 m ⁻¹]	$\delta^{18}\text{O}$ [‰ 100 m ⁻¹]	Location
Yurtsever & Gat (1981)	-1.5 to -4	-0.15 to -0.5	GNIP-data, worldwide
Gonfiantini et al. (2001)	-	-0.15 to -0.24	Mount Cameroon, Bolivia
Scholl et al. (2009)	-0.6	-0.12	Cloud forest, Puerto Rico
Peng et al. (2010)	-	-0.17 to -0.22	Taiwan
Garcia et al. (1998)	-	-0.17	Ecuador
Siegenthaler & Oeschger (1980)	-	-0.25	Switzerland (<2000m)
Siegenthaler & Oeschger (1980)	-	-0.09	Switzerland (>2000m)
Hou et al. (2003)	-	-0.12 to -0.29	Himalaya
McGuire et al. (2005)	-	-0.15	Oregon, USA
Aravena et al. (1999)	-	-1	Chile
Saylor et al. (2009)	-1.5	-0.18	Colombia
Cortés et al. (1997)	-	-0.2	Mexico
Vogel et al. (1975)	-	-0.1 to -0.6	Argentina
Kattan (2006)	-1.1	-0.14	Syria
Vimeux et al. (2005)	-1.7	-	Bolivia
Vimeux et al. (2011)	-1.5	-	Bolivia, event-based
This study	-1.12	-0.22	Ecuador, event-based

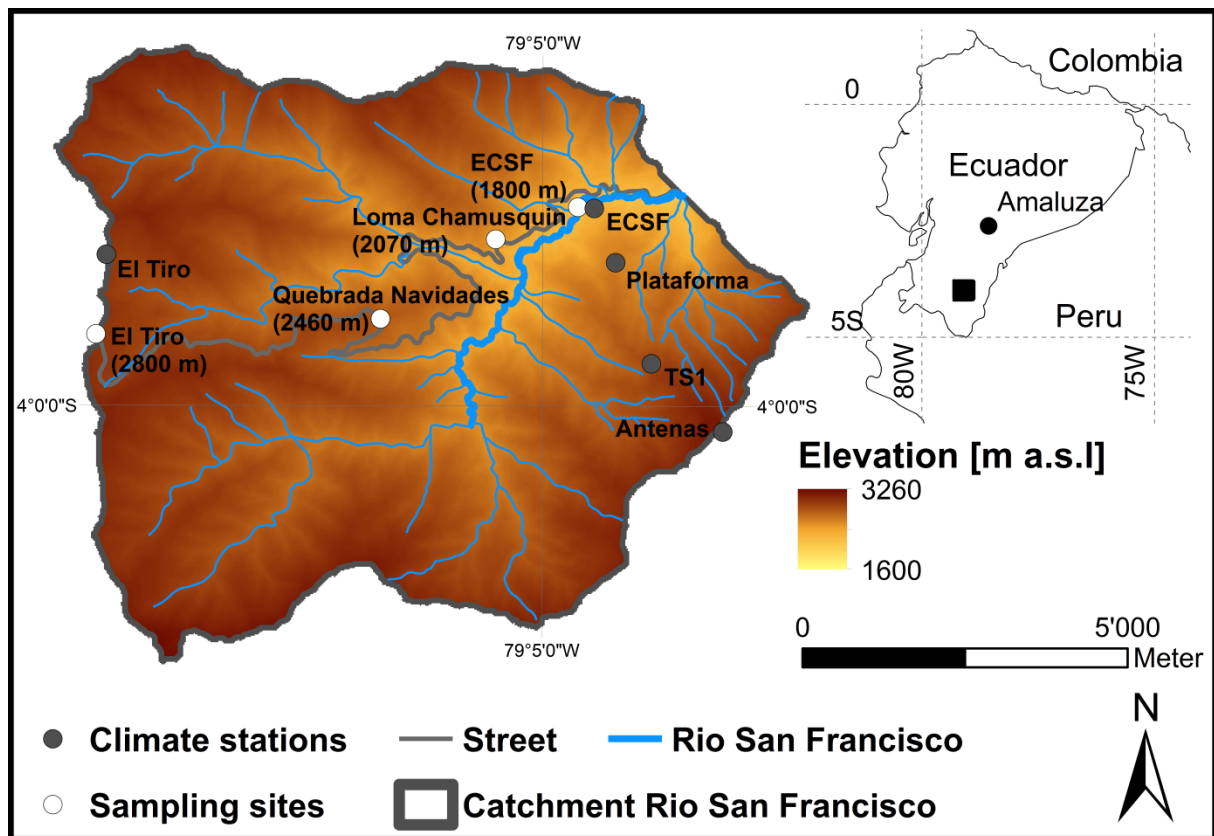


Fig. 1. Investigation area with sampling sites and climate stations

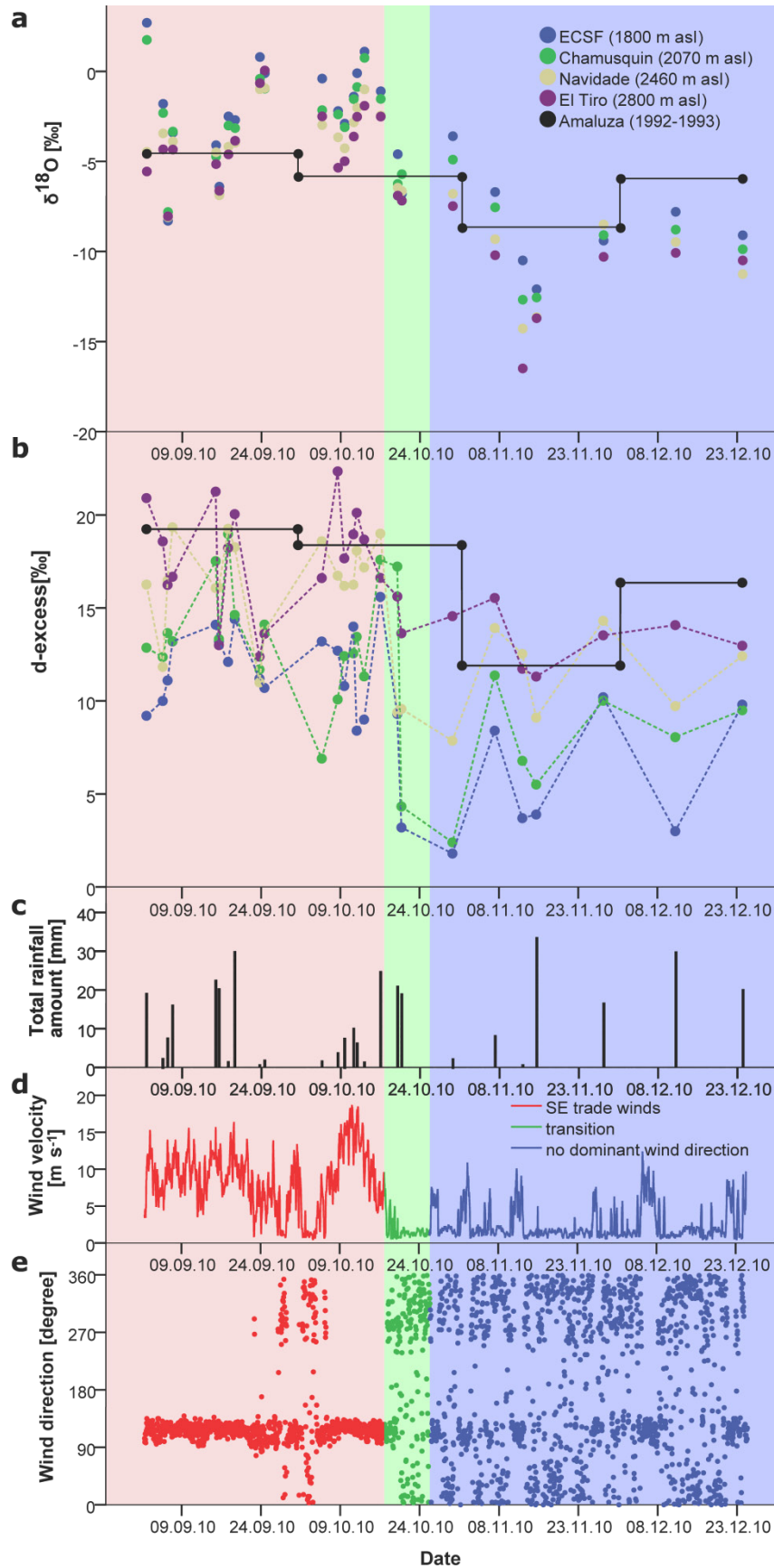


Fig. 2. Results of the 26 events sampled. **a** $\delta^{18}\text{O}$ isotope signatures, **b** deuterium excess of all sampled events compared to weighted monthly means from GNIP station Amaluza from 1992-1993, **c** total amount of rainfall for each event, **d** wind velocity and **e** wind direction for the investigated period recorded at the El Tiro climate station. For **a** and **b** the different measurement stations are color coded. For **d** and **e** the colors indicate the 3 different climate periods.

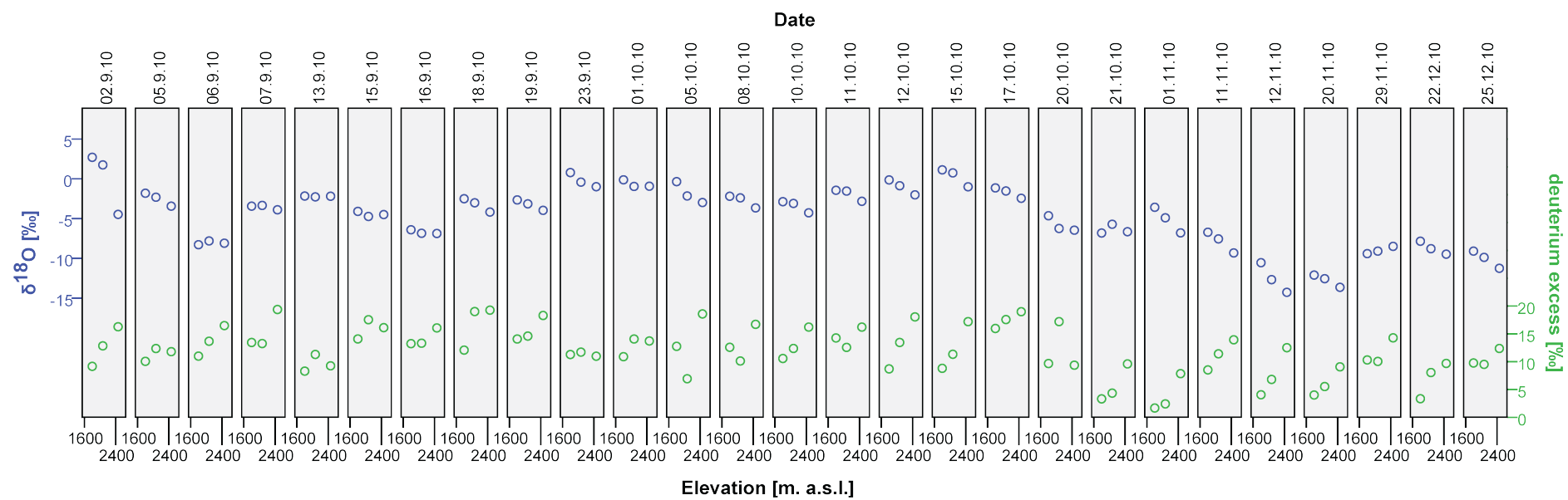


Fig. 3. Altitude effect and temporal variation of $\delta^{18}\text{O}$ isotope signature and the deuterium excess in precipitation.

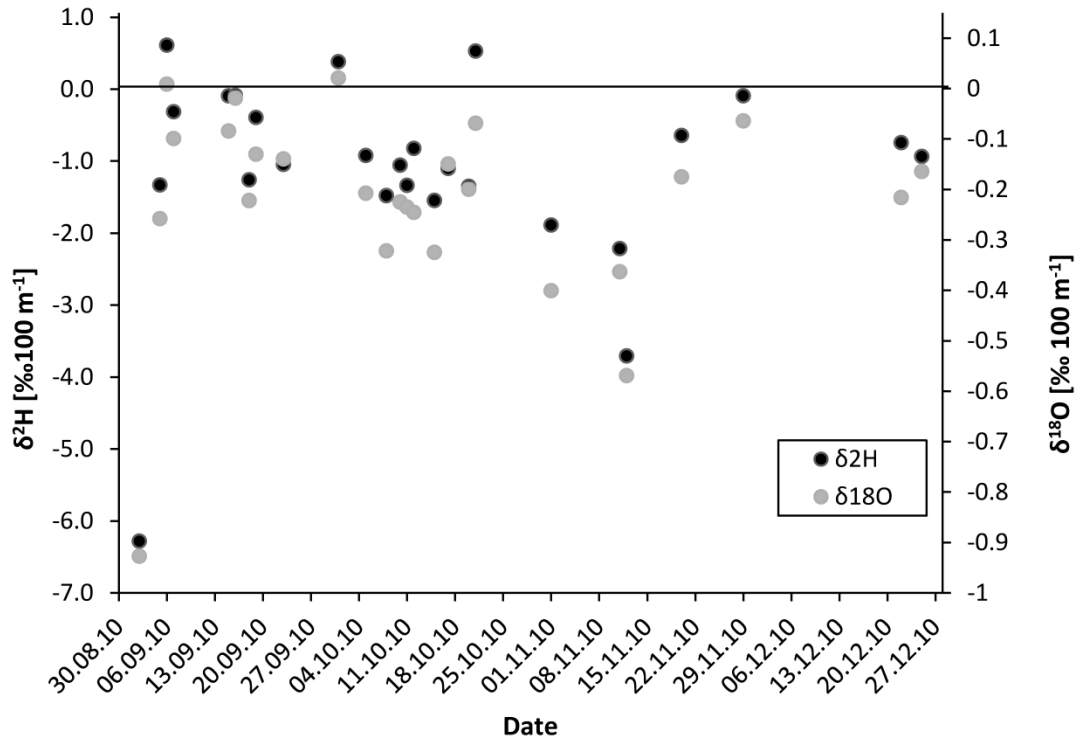


Fig. 4. Event based altitude effect of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ isotope signatures in precipitation. The majority of the events show a depletion of heavy isotopes with altitude (i.e. a negative lapse rate). Only during 3 events for ^2H and 2 events for ^{18}O out of 26 events an enrichment of heavy isotopes with altitude was recorded.

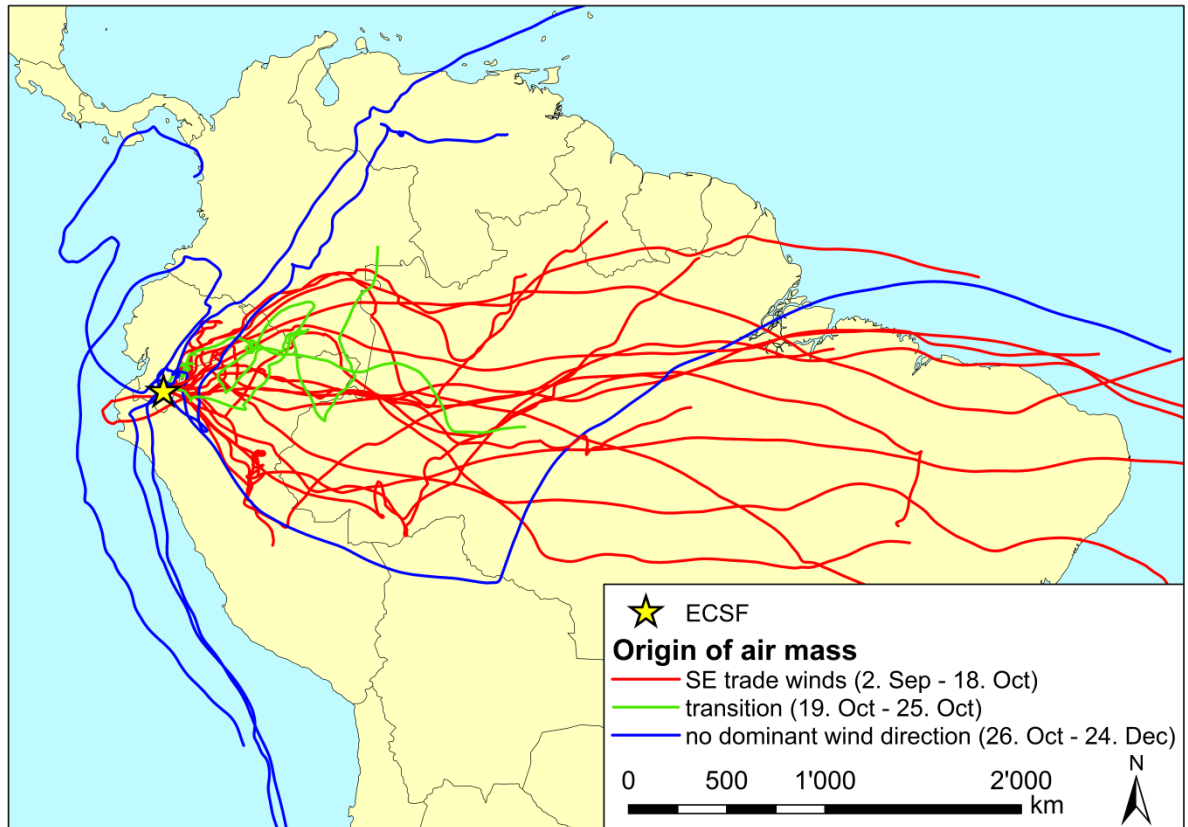


Fig. 5. 12 days back trajectories for the 26 rain events calculated with the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model developed by Draxler and Rolph, (2012).

Revised manuscript
(showing changes)

Impact of elevation and weather patterns on the isotopic composition of precipitation in a tropical montane rainforest

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Abstract

This study presents the spatial and temporal variability of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ isotope signatures in precipitation of a south Ecuadorian montane cloud forest catchment (San Francisco Catchment). From 02 September to 25 December 2010, event sampling of open rainfall was conducted along an altitudinal transect (1,800 m asl to 2,800 m asl) to investigate possible effects of altitude and weather conditions on the isotope signature.

The spatial variability is mainly affected by the altitude effect. The event based $\delta^{18}\text{O}$ altitude effect for the study area averages $-0,22\text{‰} \times 100\text{ m}^{-1}$ ($\delta^2\text{H}$: $-1,12\text{‰} \times 100\text{ m}^{-1}$). The temporal variability is mostly controlled by prevailing air masses. Precipitation during the times of prevailing southeasterly trade winds is significantly enriched in heavy isotopes compared to precipitation during other weather conditions. In the study area, weather during austral winter is commonly controlled by southeasterly trade winds. Since the Amazon Basin contributes large amounts of recycled moisture to these air masses, trade wind-related precipitation is enriched in heavy isotopes. We used deuterium excess to further evaluate the contribution of recycled moisture to precipitation. Analogously to the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values, deuterium excess is significantly higher in trade wind related precipitation. Consequently, it is assumed that evaporated moisture is responsible for high concentrations of heavy isotopes during austral winter.

1. Introduction

Stable water isotopes have been widely used as tracers in catchment hydrology, e.g. to validate hydrological models (Birkel et al., 2009; Koivusalo et al., 2000; Liebming et al., 2007; Rodgers et al., 2005b), identify areas of groundwater recharge (Cortés et al., 1997; Gonfiantini et al., 2001; Kattan, 2006), investigate flow paths (Barthold et al., 2011; Goller et al., 2005; Rodgers et al., 2005a) or to calculate the Mean Transit Time (MTT) of water

(Garvelmann et al., 2012; Kabeya et al., 2007; McGuire et al., 2002, 2005; Rodgers et al., 2005b).

All these approaches require a detailed knowledge of the composition of the isotopic input signal, i.e. precipitation (Darling and Talbot, 2003). But the isotopic composition of this precipitation signal varies temporally and spatially due to the depletion of isotopes caused by the temperature, amount (or rainout), continental, elevation (or altitude) and [prevailing weather conditions, mostly expressed by a](#) seasonal effect (Dansgaard, 1964; Gat, 1996; Siegenthaler and Oeschger, 1980). On catchment scales, the altitude effect is an important measure for the spatial variability, especially in mountainous catchments that cover high altitudinal ranges. It has therefore been the topic of various studies conducted around the world (Cortés et al., 1997; Garcia et al., 1998; Gonfiantini et al., 2001; Kattan, 2006; McGuire et al., 2005; Peng et al., 2010; Scholl et al., 2009; Siegenthaler and Oeschger, 1980; Vimeux et al., 2005, 2011; Vogel et al., 1975; Yurtsever and Gat, 1981). Most of the reported lapse rates for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ lie in ranges of -0.1 to -0.6‰ 100 m^{-1} and -0.5 to -4‰ 100 m^{-1} , respectively. The altitude effect is usually less pronounced in the tropics (Sturm et al., 2007) though information for tropical montane rainforest ecosystems ~~isare~~ [isare](#) limited. We are aware of only one study in Puerto Rico where a gradient of -0.12‰ 100 m^{-1} for $\delta^{18}\text{O}$ and -0.6‰ 100 m^{-1} for $\delta^2\text{H}$ has been found (Scholl et al., 2009).

In addition to the altitudinal effect the temporal variability of isotope signatures in precipitation can be substantial. In many ecosystems a clear seasonality is observed, which is attributable to the amount effect, with precipitation being depleted in heavy isotopes during wet seasons (Dansgaard, 1964; Garcia et al., 1998; Gonfiantini et al., 2001; Lachniet and Patterson, 2006, 2009; Liu et al., 2007; Rietti-Shati et al., 2000; Rozanski et al., 1992). ~~Though~~ [Though](#) seasonal differences tend to be smaller in the tropics than at higher latitudes (Scholl et al., 2011). [In general the isotopic composition of the incoming precipitation is inherently shaped by its his-](#)

tory, e.g. by the source of the moisture and the amount effect due to rain out along the path
taken by the air mass. As we cannot distinguish between the factors shaping the history of the
incoming air mass by looking at on-site measurements, we restricted our analysis to the de-
pendency of the isotopic signature of the precipitation on the prevailing weather conditions,
the source of the incoming air masses, the spatial dependency within the study area and the
on-site amount effect due to a discrimination of light isotopes during rainout in the course of a
single event. For the on-site amount effect we assume that events with a higher amount of
precipitation and the same history will yield an overall lighter isotopic composition than
events with smaller amounts of rainfall. However, recent studies give rise to the assumption
that other factors than the amount of precipitation or the origin of the air masses play an im-
portant role in controlling seasonal patterns of isotope signatures (Breitenbach et al., 2010;
Feng et al., 2009; Kebede and Travi, 2011; Lee et al., 2009; Peng et al., 2010; Rhodes et al.,
2006; Risi et al., 2008a, 2008b; Scholl et al., 2009; Villacís et al., 2008; Vimeux et al., 2005,
2011). For example, Rhodes et al. (2006) and Scholl et al. (2009) concluded that orographic
precipitation during the trade wind dominated dry season is enriched compared to the mostly
convective precipitation type during the wet season occurring e.g. in Costa Rica and Puerto
Rico, respectively. Vimeux et al. (2005) reported that moisture transport history is another
important factor controlling the seasonal variation of isotope signatures in the Andes. The
Amazon Basin is known to contribute large amounts of recycled moisture to the air masses
transported by trade winds (Martinelli et al., 1996; Salati et al., 1979; Valletcoulomb et al.,
2008). This contribution of recycled moisture to precipitation can be traced by the deuterium
excess parameter (Araguas-Araguas et al., 2000; Froehlich et al., 2002; Gat, 2000; Kabeya et
al., 2007; Njitchoua et al., 1999; Victoria et al., 1991). Since southeasterly (SE) trade winds
prevail in our research area in the tropical montane forests of Southern Ecuador during austral
winter (Emck, 2007), we assume that a large share of the air masses responsible for rainfall
during this period originates from the Amazon. Consequently, we expect higher isotope signa-

tures and higher values of deuterium excess during the period dominated by SE trade winds and a less pronounced impact of the amount effect.

Our work focuses on improving the [understanding of the](#) hydrological processes [responsible for the](#) rainfall-runoff generation in a remote tropical montane rainforest catchment of Ecuador. Previous work in micro-catchments in the study area by Goller et al. (2005) focused on the temporal variability of isotope signatures in rainfall, throughfall, and streamwater. They found that near-surface event water dominates runoff in these pristine rainforest-covered micro-catchments. In contrast, groundwater dominated fluxes tend to govern runoff generation on larger scales as revealed by geogenic tracer analyses (Bücker et al., 2010; Crespo et al., 2012). Surprisingly, Crespo et al. (2012) derived MTTs of up to 260 to 350 days, despite the very responsive, flashy hydrographs that tend to react within a few hours to precipitation inputs. The uncertainty of this estimate remains unknown, given the limited information of stable isotopes in precipitation that the authors used.

This study presents a more detailed investigation of the temporal and spatial variations in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ isotope signatures of precipitation and paves the ground for further research. [As a monitoring period of around 3 month is not sufficient to identify the seasonality in the isotopic compositions of precipitation we rather investigate the dependency of isotopic composition on weather conditions and the origin of air masses responsible for the rainfall. However, origin of air masses go along with a change in seasons in our research area \(Bendix et al. 2008\) and thus can be seen as a proxy for seasonality.](#) The identification of [seasonal-processes causing the](#) variation in the isotopic composition will establish a tool for understanding the [interdependencies](#) among climate, hydrology, ecology and water resources in future research (Rhodes et al., 2006). Knowledge about the spatial variability of isotope signatures in precipitation will enable researchers to better identify flow paths and draw conclusions about the contribution of precipitation from different altitudes to discharge (Cortés et al., 1997;

Gonfiantini et al., 2001; Kattan, 2006). Tracing isotopes through the hydrological cycle further allows calculations of the MTT in the catchment. The objective of this paper therefore is to investigate the following hypotheses, which are based on findings reported in the previous sections:

~~(1) There is no dominant effect (amount, altitude, continental, seasonal) responsible for the depletion of the stable water isotope signal of precipitation.~~

~~(2)~~(1) The concentration of heavy isotopes decreases with increasing altitude.

~~(3)~~(2) Precipitation during SE trade wind dominated periods is enriched in heavy isotopes compared to precipitation during other weather conditions.

~~(4)~~(3) Precipitation during SE trade wind dominated periods shows significantly higher deuterium excess values.

2. Material and Methods

2.1. Location and climate of the study area

The study area is located on the eastern slopes of the Andes (S Ecuador) in the San Francisco valley. As part of the Amazon basin, close to the border of the watershed, the terrain of the region surrounding the study area is characterized by a more or less continuous decline to the east and a comparatively high mountain range to the west. The highest point of the study area is the *Cerro ~~de~~El Consuelo*, coll. *Antenas* at 3,155 m asl. The lowest point is at 1,720 m asl. Fig. 1 shows the topography of the study area and the location of sampling sites and climate stations. The topography of the San Francisco catchment allows the investigation of a large altitudinal gradient within a relatively small horizontal distance. Valleys in the study area are deeply incised. The southern part of the catchment is mainly vegetated by primary forest. In the northern part, the natural forest has been replaced by extensive pastures in parts and is

further characterized by a mix of shrubs, reforestation sites and sub-paramo (Göttlicher et al., 2009).

Average annual sums of precipitation, [for the period 2002 to 2008](#), amount to 1,500 to 4,900 mm a⁻¹ with a large spatial variability (Rollenbeck and Bendix, 2011). Moreover, there is a significant input of fog to the ecosystem, which accounts for 5 to 35% of precipitation and enhances the total water input up to 6,500 mm a⁻¹ at the highest altitudes (Rollenbeck et al., 2011). [According for Rollenbeck et al. \(2011\) the designated fog input increases with altitude and amount of rainfall, comprising various forms of horizontal precipitation like the actual fog, drizzle and other wind driven rain.](#) Along a N to S transect investigated by Bendix et al. (2008), an altitudinal increase of precipitation (lapse rate) of 220 mm 100 m⁻¹ was observed. However, spatial observations of radar based precipitation inputs do not indicate that this altitudinal effect is valid for the whole study area, especially in an E-W direction (Rollenbeck and Bendix, 2011). Along the E-W transect that was investigated in the present study (Fig. 1) climate stations have also not shown an altitudinal increase of incoming precipitation. Precipitation at the highest point investigated in this study (*El Tiro*, 2,800 m asl) amounts to 1,500 mm a⁻¹, whilst at the lowest point (ECSF, 1,800 m asl) it is 2176 mm a⁻¹ (Bendix et al., 2006; Emck, 2007). This demonstrates the high spatial variability of precipitation amounts [occurring](#) in the study area.

The weather within the study area is dominated by easterly trade winds. From January to April, northeasterly trade winds are prevailing. Southeasterly trade winds dominate weather in the study area from April to mid-October (Emck, 2007). From June to September, the proportion of trade winds is close to 100%. For the rest of the year, it is still more than 50%. The temporal variability of isotope signatures in the present study was, for the most part, expected to be determined by the prevailing air masses. During the investigation period, southeasterly tropical trade winds were prevailing from September to mid-October. In that period, wind

direction was hardly changing and wind speeds were high (5 to 15 m s⁻¹). From mid-October on, as trade winds weakened, wind direction was much less clear defined and lower wind speeds were measured. The observed change in weather patterns at that time of the year is consistent with long term climate records for the study area (Bendix et al., 2008; Emck and Richter, 2008). Since tropical trade winds travel at altitudes below 3,000 m (Scholl et al., 2002), the Andes form a topographic barrier which leads to a rainout of air masses. The *Cordillera Real* serves as a climate divide between the humid Amazon Basin and the dry Inter Andean Region. From mid-October on, when trade winds weaken in their intensity and frequency, other wind directions and lower wind speeds are observed. However, precipitation originating from pacific westerlies hardly reaches the study area, since most of these air masses rain out at the western slopes of the Andes (Bendix et al., 2008; Emck, 2007).

The main factor influencing air temperature in the study area is elevation. Mean annual temperature ranges from 12°C (at 3260 m asl) to 22°C (at 1600 m asl). The average gradient of air temperature is 0.61°C 100 m⁻¹. As usual for tropical regions, seasonal changes in temperature are low (Bendix et al., 2008).

2.2. Experimental set up

To investigate the depletion effects on isotope signatures in precipitation, a transect along an altitudinal gradient of 1,000 m was investigated. An event sampling was conducted at four sampling sites along this altitudinal gradient: ECSF at 1,800 m asl, *Loma Chamusquín* at 2070 m asl, *Quebrada Navidades* at 2,460 m asl and *El Tiro* at 2,800 m asl (Fig. 1).

Each site consisted of three collectors made from 1 L glass bottles prepared with circular funnels of 0.10 m in diameter. Bottles were placed in white polyethylene tubes to avoid heating and tubes were screwed to wooden pales and installed 1 m aboveground. A table tennis ball was placed into each funnel to prevent the sample from evaporating. Accord-

ing to IAEA standard procedures, samples were filled and stored in 2 ml brown glass vials covered by silicone septa (Mook, 2000).

Prior to field sampling the reliability of the table tennis ball to prevent evaporation losses was tested in the laboratory. During a 21 d period the effect of four different climatic conditions simulated in climate chambers (30°C/15°C and 15°C/10°C in a 12 h day-night cycle each at 50% and 90% relative humidity) on the isotopic composition was tested. Collectors with table tennis balls were stored under these different climate conditions and water samples were withdrawn in intervals of three days. Even under the most unfavorable conditions in the climate chambers (temperature 30°C/15°C and relative humidity 50%) the enrichment of heavy isotopes was either not significant ($p \geq 0.05$) or, in the case of scenario 4, within the measuring inaccuracy of the analytical device of 0.2‰ for $\delta^{18}\text{O}$ and 0.6‰ for $\delta^2\text{H}$ (Tab. 1). During the field experiment not more than one day passed between the precipitation event and sample collection. We therefore exclude a measurable effect of the sampling procedure on the isotopic compositions of the samples.

Total precipitation sums between each event sampling were also measured in the collectors. Climate data from stations near ECSF and *El Tiro* were also used to investigate the influence of climatic parameters (relative humidity (%), air temperature (°C), rainfall amount and intensity (mm h^{-1}) and wind direction (°) and speed (m/s)) on the isotopic composition of the samples. The wind direction of air masses moving over the study area was measured at the *El Tiro*. [In addition to the on-site climate measurements we used the Hybrid Single-Particle Lagrangian Integrated Trajectory \(HYSPLIT\) model developed by Draxler and Rolph \(2012\) to calculate for each event the backwards trajectories for the previous 12 days \(288 hours\) of the air masses responsible for rainfall reaching the study area in an elevation of 1,500 m above ground level. For the analyses in our study, the HYSPLIT model was operated with meteorological input from the Global Data Assimilation System \(GDAS\) reanalysis data set.](#)

To account for interannual variability of climate conditions we sampled in a period during which a shift in the prevailing wind conditions was most likely to occur (Emck, 2007). Therefore samples were taken from September to December 2010.

2.3. Analysis and statistics

Isotope signatures of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ were analyzed according to the IAEA standard procedure (Newman et al., 2009) using a Los Gatos Research DLT-100-Liquid Water Isotope Analyzer (Los Gatos Research Inc., Mountain View, US). Water samples are vaporized and analyzed via near infrared absorption spectroscopy to simultaneously quantify the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ isotope signatures in an optical cell. Isotope ratios are reported in per mil (‰) relative to an international acknowledged reference standard, the *Vienna Standard Mean Ocean Water* or VSMOW (Craig, 1961b). Precision of the method is 0.2‰ for $\delta^{18}\text{O}$ and 0.6‰ for $\delta^2\text{H}$, [resulting in a quadratic error of 1.7‰ for deuterium excess](#) (LGR, 2012).

Data preparation was conducted by excluding outliers from the repetitive measurements of $\delta^{18}\text{O}$ and $\delta^2\text{H}$. Results were considered as outliers if the standard deviation from the average was larger than one. Not more than one out of three samples per event and sampling point was allowed to be excluded. If two out of three results had a standard deviation larger than one, no outlier was excluded. [On average the three samples per event and sampling point showed a fairly similar standard derivation of 0.27‰ for \$\delta^{18}\text{O}\$ \(ranging from 0.03‰ to 0.87‰\) and 0.58‰ for \$\delta^2\text{H}\$ \(ranging from 0.01‰ to 1.66‰\) for all four sites.](#) Mean values of the remaining results built the dataset from here on. All deviations are given as mean error. Statistical evaluation was performed using SPSS Statistics (Version 16.0; SPSS Inc. Chicago, IL, US). For a comparison of our results, isotope precipitation data from the IAEA-GNIP station Amaluza, Ecuador was used (IAEA, 2012). Amaluza is located about 170 km north of the study area [and the dataset comprises monthly means starting from May 1992 – July 1994 \(27 values\).](#)

3. Results and Discussion

In this study, 26 events were sampled at four altitudinal levels in a period from 2 September to 25 December 2010 ([during all events we recorded precipitation at all four altitudes](#)). Isotopic compositions of open rainfall range from -16.5 to 2.7‰ for $\delta^{18}\text{O}$ and from -120.2 to 30.8‰ for $\delta^2\text{H}$ ([see Tab. 2 for more details](#)). Compared to the study of Goller et al. (2005) and the data from Amaluza, isotope signatures presented in this study cover a relatively wide range. This fact can be attributed to the event-based sampling design where there is no mixing of events with extreme values, as compared to sampling in defined intervals which often produces a narrower range of values. [The range is also in good agreement with the daily precipitation values reported by Villacis et al. \(2008\) for lower parts of the Ecuadorian Amazonas in the north east of the country ranging from -15.51‰ to 1.56‰ for \$\delta^{18}\text{O}\$.](#)

In comparison to the global meteoric water line ($\delta^2\text{H} = 8 \times \delta^{18}\text{O} + 10\text{‰}$ [defined by Craig \(1961a\) or more recently \$\delta^2\text{H} = 8.13 \times \delta^{18}\text{O} + 10.8\text{‰}\$ defined by Rozanski et al. \(1993\)](#)) the local meteoric water line for all 26 events ($\delta^2\text{H} = 8.31 \times \delta^{18}\text{O} + 14.47\text{‰}$) shows a slightly higher slope, which is still in good agreement with the slope expected under equilibrium conditions represented by the GMWL. The higher intercept (deuterium excess) of the local meteoric water line is most likely attributable to re-evaporated/[recycled](#) precipitation reaching the study area during the investigation period. ~~Taking into account annual data presented by Goller et al. (2005) for the same study area, the mean deuterium excess of 11.1‰ is again in close proximity to deuterium excess of the global meteoric water line.~~ Fig. 2a shows the $\delta^{18}\text{O}$ ~~and $\delta^2\text{H}$~~ isotope signatures of all sampled events ([\$\delta^2\text{H}\$ shows the same course \(data not shown\), any difference between \$\delta^2\text{H}\$ and \$\delta^{18}\text{O}\$ is expressed by the deuterium excess shown in Fig. 2b\).](#) Spatial variability, i.e. the difference between the four sampling sites, is relatively low compared to the temporal variability, which points to a distinct [seasonality dependency](#) of isotope signatures [on the prevailing weather conditions and the origin of the air masses](#).

3.1. Altitude effect

To separate the altitude effect from the temporal variation, ~~it~~the altitude effect was calculated for each event separately (Fig. 3). Event lapse rates (δ versus altitude) calculated by linear regression show that the concentration of heavy isotopes in the precipitation samples generally decreases with altitude (Fig. 3 and Fig. 4). On average, the $\delta^{18}\text{O}$ altitude effect is $-0.22\text{‰} \times 100\text{m}^{-1}$ and for $\delta^2\text{H}$ it amounts to $-1.12\text{‰} \times 100\text{m}^{-1}$ (standard error 0.2‰ for $\delta^{18}\text{O}$ and 1.39 for $\delta^2\text{H}$). As usual for tropical regions (Sturm et al., 2007), it lies within the lower part of the ranges reported in literature (Tab. 3). Most $\delta^{18}\text{O}$ event lapse rates of the present study are between -0.1 and $-0.4\text{‰} \times 100\text{m}^{-1}$ ($\delta^2\text{H}$: -0.8 to $-1.5\text{‰} \times 100\text{m}^{-1}$). However, three out of 26 events do not show a negative lapse rate for both $\delta^{18}\text{O}$ and $\delta^2\text{H}$ (Fig. 4; dates 06.09., 01.10. and 21.10.). Overall linear regression of the data showed that the altitude effect of $\delta^{18}\text{O}$ is significant ($p < 0.05$), while for $\delta^2\text{H}$ it is insignificant ($p = 0.19$). Nevertheless, using a one-tailed t-test, it could be shown that the event lapse rates deviate significantly from zero for both $\delta^{18}\text{O}$ and $\delta^2\text{H}$ ($p < 0.01$). Consequently, we generally assume that concentrations of heavy isotopes decrease with altitude.

The deuterium excess also shows a significant spatial variability, i.e. an increase with altitude of $0.6\text{‰} \times 100\text{m}^{-1}$ ($p < 0.01$) (Fig. 3). Gonfiantini et al. (2001) report that the increase of deuterium excess with altitude is predominantly present at high relative humidity, which is prevailing in the study area. However, there must be additional factors to explain the altitude effect of deuterium excess (Gat et al., 2000).

In the studies ~~presented by~~Gonfiantini et al. (2001) and Peng et al. (2010), a seasonality of the altitude effect is reported. Both studies were also carried out in tropical environment with a similar altitudinal air temperature gradient ($0.61^\circ\text{C } 100\text{m}^{-1}$ as in our study area; Gonfiantini et al. (2001) $0.42\text{--}0.55^\circ\text{C } 100\text{m}^{-1}$; Peng et al. (2010) $0.53\text{--}0.65^\circ\text{C } 100\text{m}^{-1}$). The authors explain this by the larger lapse rate (temperature vertical gradient) during rainy months. During

the investigation period, no such ~~seasonal~~ temporal effect on the altitude effect is observed in our study area. Furthermore, a multiple regression analysis of event lapse rates revealed no significant influence of temperature, relative humidity and precipitation amount or intensity on the altitude effect. However, one factor that might enhance the altitude effect is the so-called pseudo-altitude effect (Moser and Stichler, 1971), which leads to an evaporative enrichment of heavy isotopes in falling raindrops. Due to the larger altitudinal difference between cloud base and surface, this enrichment is more pronounced at lower altitudes (Gat et al., 2000), and can be almost excluded in tropical montane cloud forests where the cloud base is often at the same level as the sampling sites.

3.2. Impact of prevailing air masses

The temporal variability of isotope signatures in tropical precipitation is to a large degree attributed to the origin of air masses that prevail during different times of the year (Liu et al., 2007; Rhodes et al., 2006). Isotope signatures of precipitation in the study area are significantly higher during the times of SE trade winds (02 September – 18 October) than for the rest of the investigation period (26 October – 24 December) with no clear wind direction and lower wind velocities (Fig. 2). Between these two periods a transition in the origin and consistence of the source of the prevailing air masses takes place (19 October – 25 October). This transition phase at the end of the trade wind period is characterized by abating wind velocities and intermediate isotope signatures (Fig. 2d). Concentrations of $\delta^{18}\text{O}$ range between -8.3 to +2.7‰ for trade wind related events, -7.2 to -4.6‰ for events during the transition phase and -16.5 to -3.6‰ for other events ($\delta^2\text{H}$: -55.3 to 30.8‰, -51.2 to -27.5‰ and -120.2 to -27.0‰, respectively). Mean values of $\delta^{18}\text{O}$ are -3.0‰ for trade wind related precipitation, -6.3‰ for events during the transition phase and -9.9‰ for other precipitation events ($\delta^2\text{H}$: -8.8‰, -40.3‰ and -69.5‰).

All three periods represent a distinct weather period. Before 18 October local climate measurements at the El Tiro climate station showed 91% east to southeasterly winds and average wind velocities of 9.2 m s^{-1} , and thereafter, only 32% and an average wind velocities of 2.5 m s^{-1} (26 October – 24 December). The high wind speed and steady wind direction of the first period are typical for trade wind dominated periods. Without the SE trade winds the period after the 26 October shows no dominant wind direction. The transition phase is characterized by the lowest wind velocities of 1.3 m s^{-1} on average and no clear wind direction. HYSPLIT results (Fig. 5) confirmed the different sources of the air masses. In the first phase of the investigation period all monitored rain events passed with the trade winds over the Amazonas region. During the transition phase the air parcels responsible for the recorded precipitation traveled for over 12 days across the Amazonas region close to the study area with a relative low velocity. This potentially indicates that the arriving air masses become continuously depleted in heavy isotopes in the course of ongoing rain fall events before reaching the study area. After mid October the backward trajectories show no clear pattern delivering moisture to the study area from the Pacific as well as from the Gulf of Mexico and the Amazonas (Fig. 5).

~~Rhodes et al. (2006) and Scholl et al. (2009) related high isotope signatures in the dry seasons in Costa Rica and Puerto Rico to the enhanced influence of trade winds during these times. These findings are in good agreement with the temporal variability observed in the present study. In contrast to the findings of many studies on the seasonality of isotope signatures in the tropics (e.g. Depetris et al., 1996; Garcia et al., 1998; Gonfiantini et al., 2001; Lachniet and Patterson, 2006, 2009; Rietti-Shati et al., 2000), this variability cannot be attributed to the amount effect since in the study area SE trade winds occur mostly in the wetter season. The influence of prevailing air masses is further revealed by the simultaneity of ebbing trade winds and decreasing isotope signatures in mid-October, as can be seen in Fig. 2 and Fig. 5. The isotope ratios for trade wind related events cover a similar (although somewhat wider) range compared to the reported values by Liu et al. (2007) ($\delta^{18}\text{O}$: -7.0 to 0.3‰) and Rhodes et~~

~~al. (2011) ($\delta^{18}\text{O}$: -3.9 to -1.3‰) for dry seasons. Analogously, values for the period from mid-October to December are similar to those measured for rainy seasons by the quoted authors.~~

Since most of the precipitation in the study area is trade wind related orographic precipitation, which is the main driving factor behind the observed altitude effect, it is important to understand the impact of trade winds on the isotopic composition of precipitation in the study area. Tropical trade winds move at altitudes below 3,000 m asl and take up large amounts of recycled moisture over the Amazon Basin when coming from the SE. This moisture is enriched in heavy isotopes and shows a higher deuterium excess due to the discrimination of heavy isotopes during fractionation processes like evaporation. Reaching the Andes, the air masses are orographically lifted and thus subject to rainout (Scholl et al., 2002). Thus, trade wind related precipitation in the study area is enriched in heavy isotopes. From mid-October to the end of December, when trade winds weaken, other air masses, partly originating from the Pacific, influence the climate in the investigated area (Fig. 5, Bendix et al., 2008; Emck, 2007) and precipitation contains significantly less heavy isotopes. Despite being of orographic nature as well, this precipitation is not characterized by recycled moisture.

3.3. Deuterium excess

~~We used the deuterium excess parameter d~~ To further investigate and strengthen our assumption that the influence of recycled moisture from the Amazon Basin is causing the high isotopic composition ~~of during trade wind related~~ precipitation events we used the deuterium excess parameter to assess the actual amount of recycled moisture (Araguas-Araguas et al., 2000; Bowen and Revenaugh, 2003; Froehlich et al., 2002; Gat, 2000; Liu et al., 2007; Njitchoua et al., 1999; Peng et al., 2010; Victoria et al., 1991). For trade wind related precipitation events, deuterium excess averages 14.9‰ and hence, is significantly higher than for other events ($d = 9.6\text{‰}$). The temporal variability of event deuterium excess in the study area shows a similar trend compared to the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values, including the ~~abrupt~~ decrease

~~after~~ mid-October (Fig. 2b). These observations confirm the assumption that intense moisture recycling takes place when precipitation is attributed to SE trade winds. Goller et al. (2005) report an annual mean deuterium excess of 11.1‰ for their site at the lower part of the same investigation area, pointing to the assumption that moisture recycling might not be high all year long. Since they did not measure both $\delta^2\text{H}$ and $\delta^{18}\text{O}$ for all samples, no temporal variability of deuterium excess was reported. Mean annual deuterium excess at the GNIP station Amaluza was 15.5‰. Highest values were measured from July to October (18.4 to 19.2‰), i.e. the time of the year when SE trade winds prevail in the study area. Lowest values were measured from March to May (10 to 12.5‰) and in November (11.9‰).

Some studies report an amount effect (Bony et al., 2008; ~~Scholl et al., 2009~~) or a seasonality (Henderson-Sellers et al., 2010; Liu et al., 2007; ~~Rhodes et al., 2006; Scholl et al., 2009~~) of deuterium excess, showing higher values during the dry season. For the present study, a linear regression of event deuterium excess with precipitation amount showed no significant influence ($p=0.56$). The temporal variability therefore should, analogously to the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values, rather be attributed to the influence of SE trade winds bringing precipitation to the study area that contains large amounts of recycled moisture.

~~In addition to the temporal variability, deuterium excess in the present study also shows a significant spatial variability, i.e. an increase with altitude of $0.6\text{‰} \times 100\text{m}^{-1}$ ($p<0.01$). Gonfiantini et al. (2001) report that the increase of deuterium excess with altitude is predominantly present at high relative humidity, which are prevailing in the study area. However, there must be additional factors to explain the altitude effect of deuterium excess (Gat et al., 2000).~~

4. Conclusions

The stable isotopic composition of precipitation collected in the San Francisco catchment showed strong temporal variations consistent with differences in weather conditions and the origin of air masses. Elevated deuterium excess values ~~evidence indicate~~ that recycled moisture from the Amazon Basin is an important flux for orographic precipitation attributed to southeasterly trade winds. Rainfalls following these trade winds are enriched in heavy isotopes compared to precipitation during other weather conditions. We further found decreasing concentrations of heavy isotopes with altitude.

In general, the presented findings are in good agreement with the underlying theoretical concepts and have highlighted the need to account for spatial and temporal variation. Comparison to studies conducted in the same research area and in comparable ecosystems ~~has shown~~ that the ~~seasonality variability~~ of the isotopic composition in the study area is ~~probably~~ rather governed by the prevailing air masses than by ~~the a local~~ amount effect ~~due to rainout~~. As in the case of the altitude effect, any ~~on site~~ amount effect is overshadowed by the temporal variability. Calculations were therefore conducted separately for the different wind conditions (~~SE trade winds, transition phase and post trade wind period with no clear wind direction~~), but still revealed no significant effect. However, longer term measurements will be needed to rule out the impact of the amount effect, and of other air masses with certainty (particularly NE trade winds that prevail in the study area from January to March).

The presented findings build a solid base showing the range of the spatial temporal variability isotopic composition in the study area. Though the monitoring period was relatively short, the extensive monitoring set up ~~was designed to capture~~ the complete range of climate conditions within the study area (e.g. trade winds and precipitation patterns) on a fine temporal and spatial scale. In combination with the long term monitoring currently conducted at ECSF further insight will be gained about inter-annual variability (Vimeux et al., 2011) and the effect

of El Niño and La Niña on the isotopic signature of the incoming precipitation in the study area.

Combining seasonal and spatial variations of δ and deuterium excess can provide an effective tool for tracing moisture through the hydrological cycle. Further work will use these data to validate hydrological models identifying the actual pathways of the water in the catchment and calculate mean transit times. Moreover, the data can serve as a contribution to the global data set on isotopic composition of precipitation which is used in climate modeling.

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Tab. 1 Results of the validation experiment. Temperature and relative humidity during the validation experiment. Day- and nighttime temperatures were programmed in 12-hour-cycles.

scenario	daytime temperature [°C]	nighttime temperature [°C]	Relative humidity [%]	slope $\delta^2\text{H}$ [‰ d ⁻¹]	p	slope $\delta^{18}\text{O}$ [‰ d ⁻¹]	p
1	30	15	50	0.031	0.084	0.044	0.796
2	30	15	90	-0.013	0.697	0.135	0.171
3	15	10	50	-0.037	0.529	-0.12	0.098
4	15	10	90	0.025	0.354	0.024	0.029*

* denotes that the regression is significant on the 0.05 level.

Tab. 2 Descriptive statistic of all 26 events sampled

	<u>Loactation</u>	<u>min</u>	<u>mean</u>	<u>max</u>	<u>range</u>
<u>$\delta^2\text{H}$ [‰]</u>	<u>all stations</u>	<u>-120.2</u>	<u>-27.6</u>	<u>30.8</u>	<u>151.0</u>
	<u>ECSF (1800 m a.s.l.)</u>	<u>-92.9</u>	<u>-22.0</u>	<u>30.8</u>	<u>123.7</u>
	<u>Chamusquin (2070 m a.s.l.)</u>	<u>-95.0</u>	<u>-25.0</u>	<u>26.9</u>	<u>121.8</u>
	<u>Navidade (2460 m a.s.l.)</u>	<u>-101.7</u>	<u>-30.6</u>	<u>9.2</u>	<u>110.9</u>
	<u>El Tiro (2800 m a.s.l.)</u>	<u>-120.2</u>	<u>-32.9</u>	<u>14.0</u>	<u>134.2</u>
<u>$\delta^{18}\text{O}$ [‰]</u>	<u>all stations</u>	<u>-16.5</u>	<u>-5.1</u>	<u>2.7</u>	<u>19.2</u>
	<u>ECSF (1800 m a.s.l.)</u>	<u>-12.1</u>	<u>-4.0</u>	<u>2.7</u>	<u>14.8</u>
	<u>Chamusquin (2070 m a.s.l.)</u>	<u>-12.7</u>	<u>-4.6</u>	<u>1.8</u>	<u>14.4</u>
	<u>Navidade (2460 m a.s.l.)</u>	<u>-14.3</u>	<u>-5.7</u>	<u>-0.9</u>	<u>13.4</u>
	<u>El Tiro (2800 m a.s.l.)</u>	<u>-16.5</u>	<u>-6.1</u>	<u>0.1</u>	<u>16.5</u>

Tab. 3 Altitude effect of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ in precipitation from various sites around the world.

Author	$\delta^2\text{H}$ [‰ 100 m ⁻¹]	$\delta^{18}\text{O}$ [‰ 100 m ⁻¹]	Location
Yurtsever & Gat (1981)	-1.5 to -4	-0.15 to -0.5	GNIP-data, worldwide
Gonfiantini et al. (2001)	-	-0.15 to -0.24	Mount Cameroon, Bolivia
Scholl et al. (2009)	-0.6	-0.12	Cloud forest, Puerto Rico
Peng et al. (2010)	-	-0.17 to -0.22	Taiwan
Garcia et al. (1998)	-	-0.17	Ecuador
Siegenthaler & Oeschger (1980)	-	-0.25	Switzerland (<2000m)
Siegenthaler & Oeschger (1980)	-	-0.09	Switzerland (>2000m)
<u>Hou et al. (2003)</u>	<u>-</u>	<u>-0.12 to -0.29</u>	<u>Himalaya</u>
McGuire et al. (2005)	-	-0.15	Oregon, USA
Aravena et al. (1999)	-	-1	Chile
Saylor et al. (2009)	-1.5	-0.18	Colombia
Cortés et al. (1997)	-	-0.2	Mexico
Vogel et al. (1975)	-	-0.1 to -0.6	Argentina
Kattan (2006)	-1.1	-0.14	Syria
Vimeux et al. (2005)	-1.7	-	Bolivia
Vimeux et al. (2011)	-1.5	-	Bolivia, event-based
This study	-1.12	-0.22	Ecuador, event-based

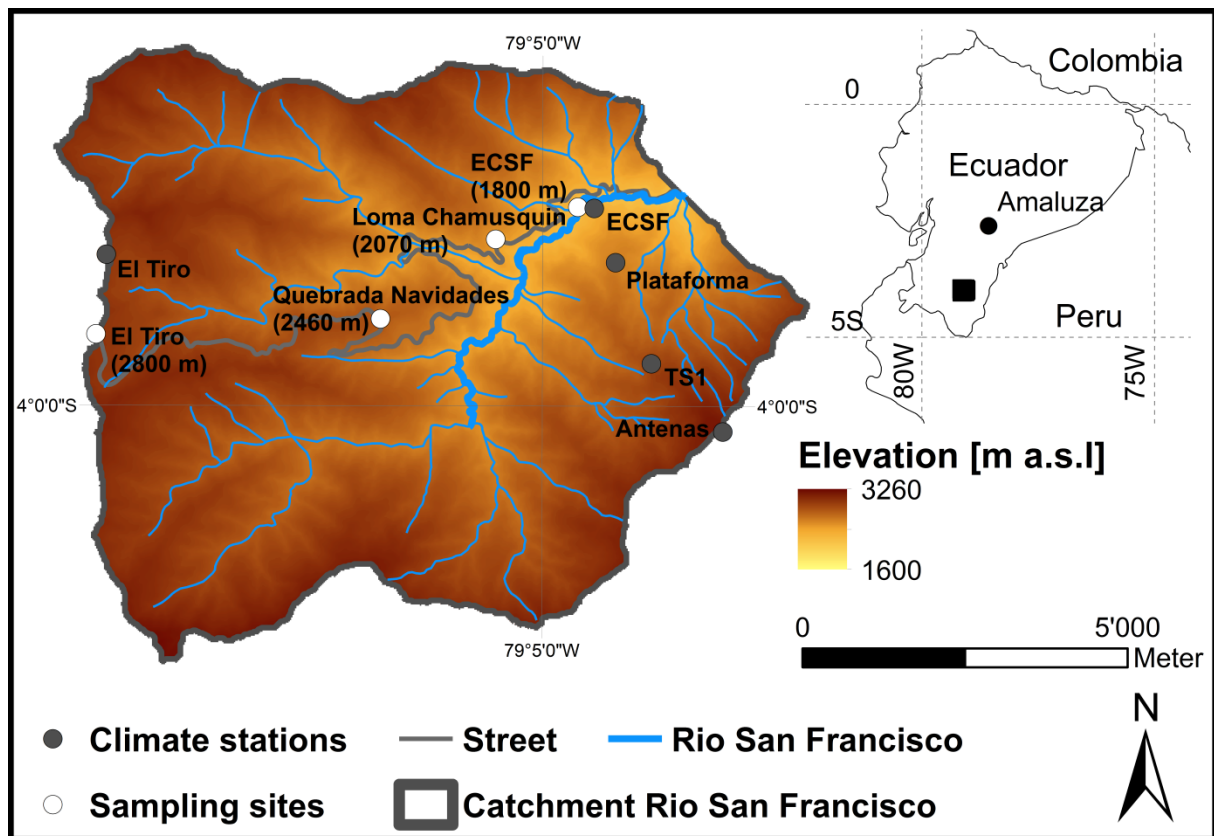


Fig. 1. Investigation area with sampling sites and climate stations

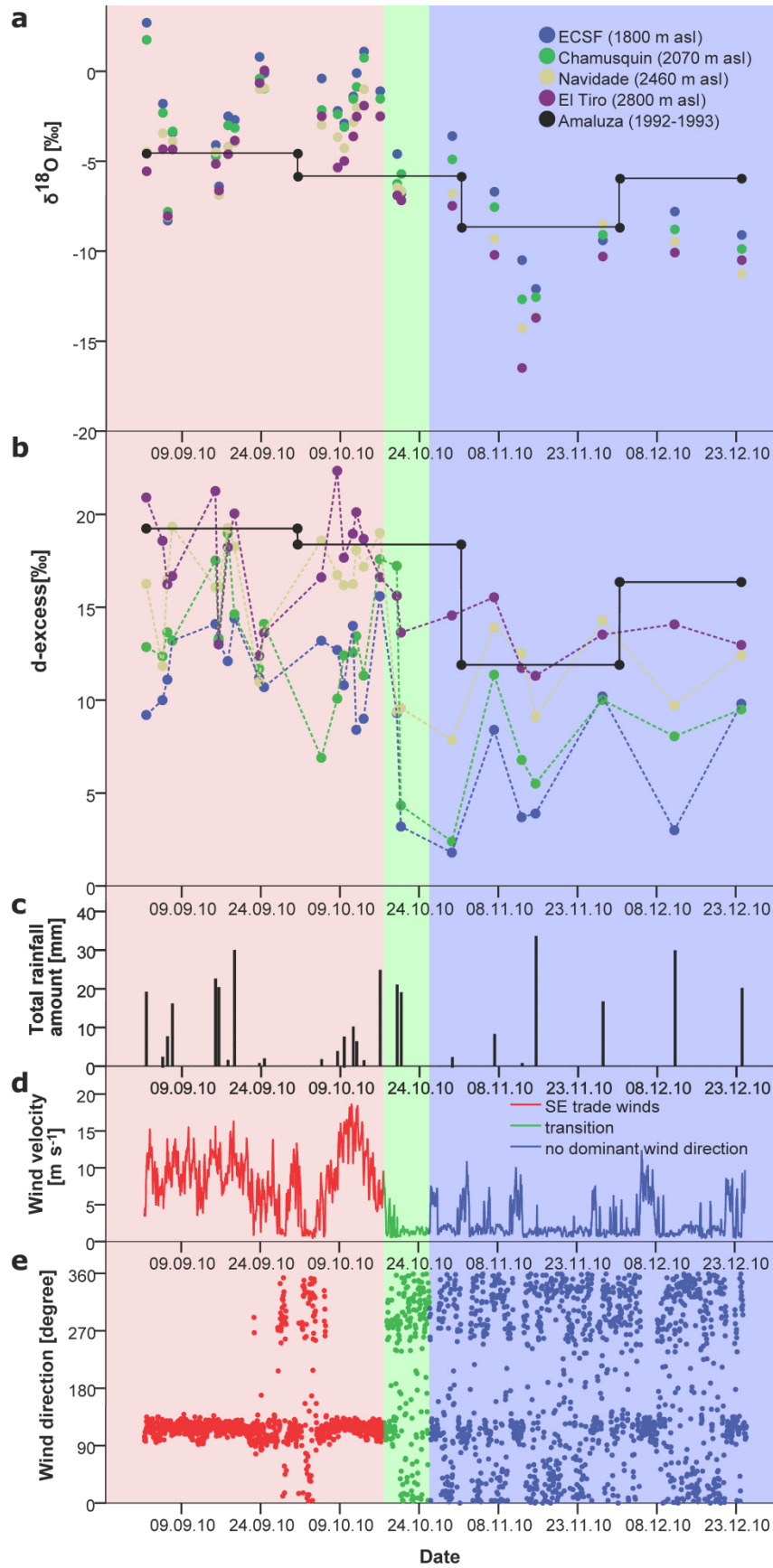


Fig. 2. Results of the 26 events sampled. **a** $\delta^{18}\text{O}$ isotope signatures, **b** deuterium excess of all sampled events compared to weighted monthly means from GNIP station Amaluza from 1992-1993, **c** total amount of rainfall for each event, **d** wind velocity and **e** wind direction for the investigated period recorded at the El Tiro climate station. For **a** and **b** the different measurement stations are color coded. For **d** and **e** the colors indicate the 3 different climate periods.

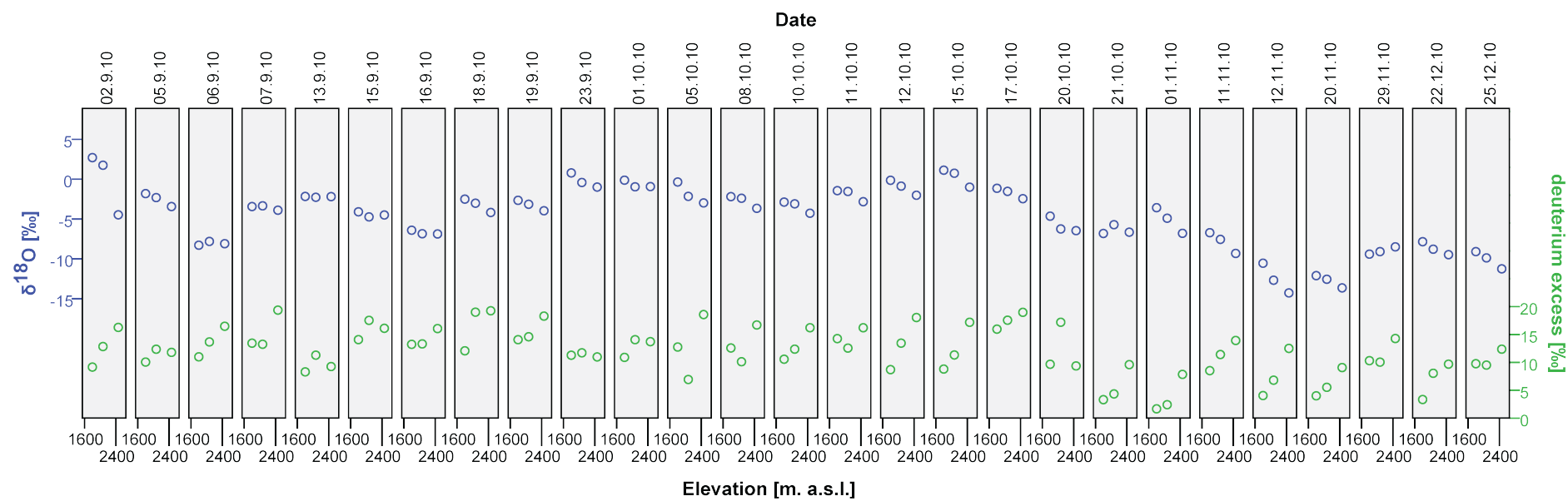


Fig. 3. Altitude effect and temporal variation of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ isotope signature and the deuterium excess in precipitation.

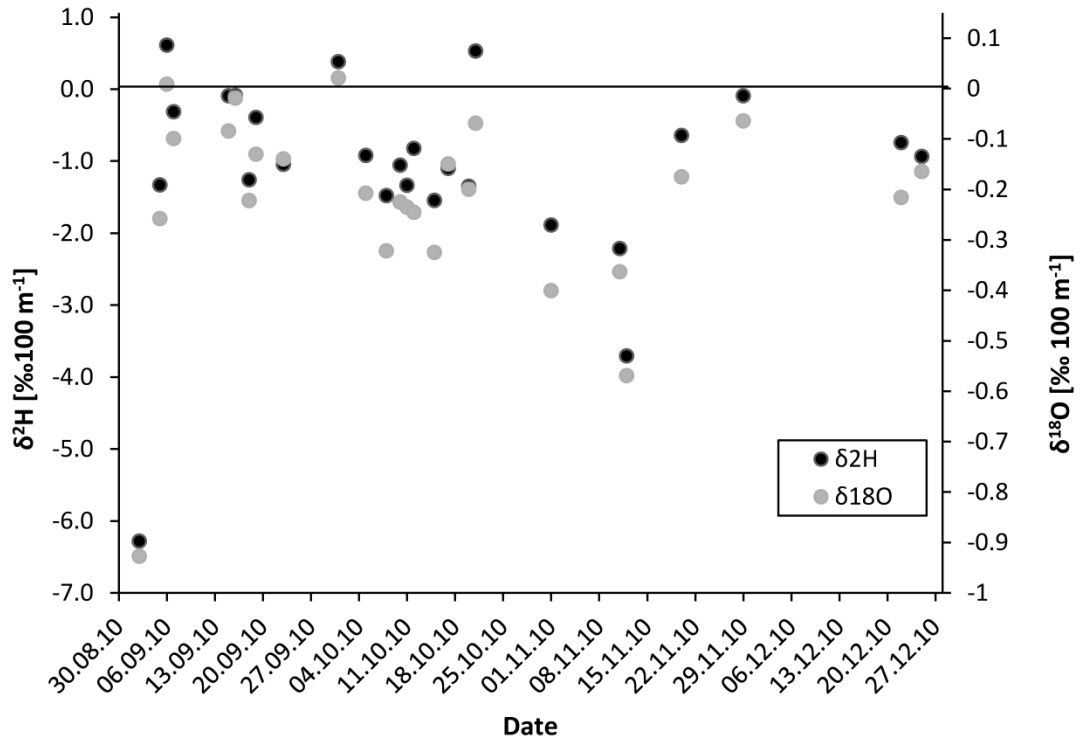


Fig. 4. Event based altitude effect of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ isotope signatures in precipitation. The majority of the events show a depletion of heavy isotopes with altitude (i.e. a negative lapse rate). Only during 3 events for ^2H and 2 events for ^{18}O out of 26 events an enrichment of heavy isotopes with altitude was recorded.

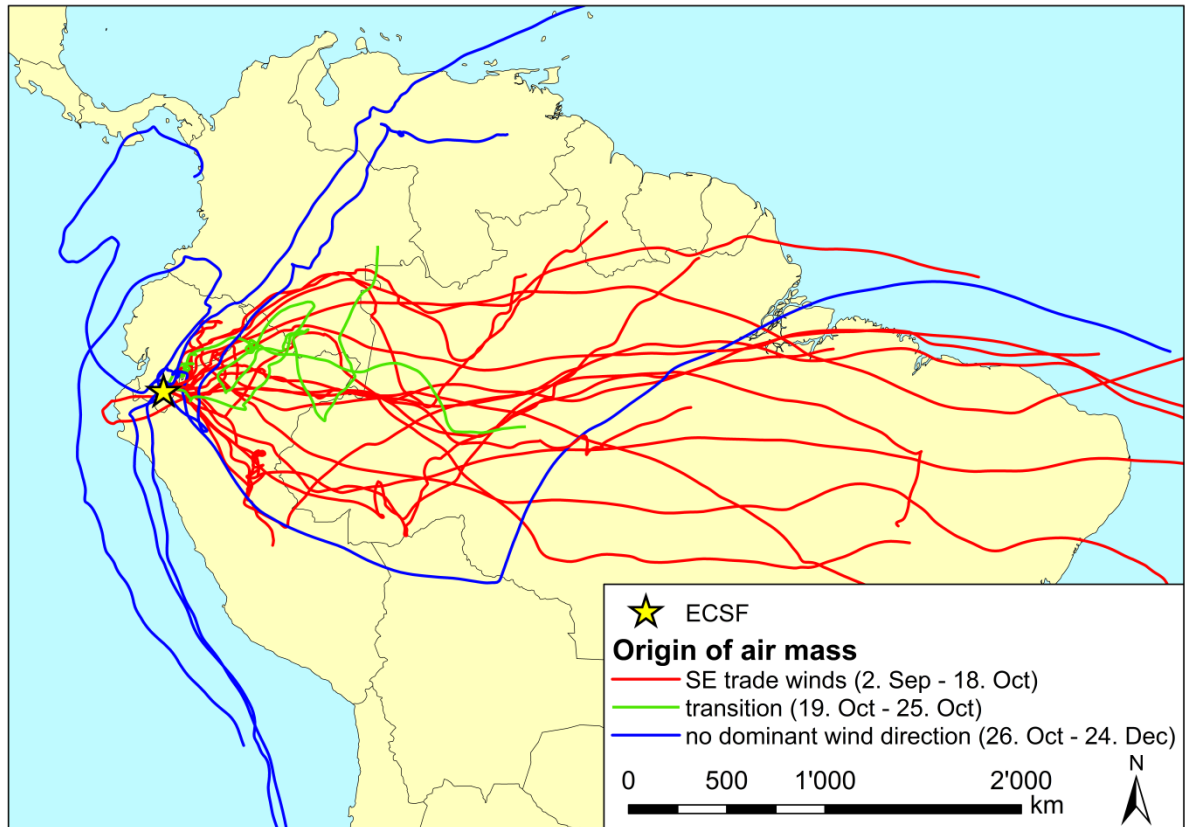


Fig. 5. 12 days back trajectories for the 26 rain events calculated with the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model developed by [Draxler and Rolph, \(2012\)](#).