## Reply to Referee #1

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.

General comment: This paper deals with the isotopic composition of precipitation in the San Francisco valley, along the eastern slope of the Andes in Ecuador. The authors explore two potential effects on the isotopic composition of precipitation: the altitude effect and the influence of air masses origin. The paper is well written although there are numerous repetitions from one section to another and important details are missing both in the text and on the Figures (see moderate to minor comments). Though the importance of the topic can be understood, their analyses are based on only 26 rain events (from September to December) which is questionable to draw a robust conclusion. Regardless, the authors reliably discuss the altitude effect. However, my main concern deals with the impact of prevailing air masses. One of the major conclusions of the paper is that a specific isotopic signature of precipitation can be found during the times of SE trade winds. I find this conclusion highly speculative in respect to their poor analysis. Indeed, the authors claim that the isotopic composition of precipitation (deuterium and deuterium excess) in the investigation area is significantly higher when air masses originate from the Southeast. However, the authors do not demonstrate this relationship. Where is it shown that there is a robust link between SE trade winds and isotopic signature? Figure 5 is highly confusing (see my suggestions at the end). In addition, it seems to me that some SE trade winds are still recorded for some of the rain events after mid-October: do those rain events exhibit high deuterium excess, high isotopic composition (maybe the trend should be removed)? Thus, I strongly suggest calculating back trajectories (for example, HYSPLIT model can be use online at http://ready.arl.noaa.gov/HYSPLIT.php) to investigate the potential relationship between isotopic composition and air masses origin. Then, a robust point-by-point analysis could be done by examining the isotopic signature of each event regarding the air mass origin. Actually, my feeling is that the high isotopic composition from September to mid-October and the decreasing trend from mid-October could be also related to other factors such as an increase in precipitation amount upstream the sites of collection. With this these regards, I don't think the manuscript is at the level of publication in HESSD in the present form and major to minor comments will have to be addressed in a revised version.

General replies:
We gratefully acknowledge the recommendations of the reviewer. In general we agree with the reviewer that the dataset covering a 3 month period is not very extensive to identify seasonality's. However, we still found it 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. These two parameters, however, reflect the seasonality in the research area very well.. Nevertheless, we improved the manuscript as suggested, turned away from the analyses of seasonality, focused more general on the impact of weather patterns and added some new analysis. 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 as suggested by the reviewer to identify the source of the precipitation measured within the study area (supported by an additional figure we included). Within the following section we will point by point summarize the changes we made in accordance with the comments of the reviewer.

Moderate to minor comments:

**Page 8429**
Hypothesis 1 is unclear. It assumes that there is no dominant effect responsible for the depletion of the water stable isotopes signal. Which depletion is concerned by this assumption? Is it the isotopic depletion of air masses originating from the Atlantic Ocean or is it the isotopic depletion of air masses observed along Andean slopes? Or is it the isotopic

depletion from mid-October?

The former hypothesis 1 “There is no dominant effect (amount, altitude, continental, seasonal) responsible for the depletion of the stable water isotope signal of precipitation“ was mend to be a base line assumption, 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. To clarify this we now abandoned hypotheses 1 and concentrate on the remaining three.

**Page 8430**
-Lines 7-8: over which period precipitation amount are given?

The reference period was added to the section and now reads as follows:

> *“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).”*

-Lines 9-10: the fog input is not clear. How does it form? What is the water origin? Does the fog input exhibit seasonality?

The following sentences were added to the section:

> *“As for Rollenbeck et al. (2011) the designated fog input increases with altitude and amount of rainfall and comprises various forms of horizontal precipitation including the actual fog, drizzle and other wind driven rain.”*

**Page 8433**
-Line 3: please mention that these precisions lead to a quadratic uncertainty of 1.7 per mil for deuterium excess.

The respective sentence was adapted as follows:

> *“Precision of the method is 0.2‰ for $\delta^{18}O$ and 0.6‰ for $\delta^{2}H$, resulting in a quadratic error of 1.7 for deuterium excess (LGR, 2012).”*

-Lines 4-14: 3 precipitation collectors are set up at each site. I am wondering about the scattering of the isotopic composition of the 3 precipitation samples for one site for each rain event. Can the authors mention some information (for example one sigma per event and per site, the mean sigma for the 26 events for one site)?

As the presentation of the precision (standard derivation σ) of the 3 repetitions at each site for all events and would be too extensive and the scattering of the $\delta^{18}O$ and $\delta^{2}H$ values between the sites showed no significant differences (see following figure), we added the following sentence:

> *“On average the three samples per event and sampling point showed a fairly similar standard derivation of 0.27‰ for $\delta^{18}O$ (ranging from 0.03‰ to 0.87‰) and 0.58‰ for $\delta^{2}H$ (ranging from 0.01‰ to 1.66‰) for all 3 sites.”*

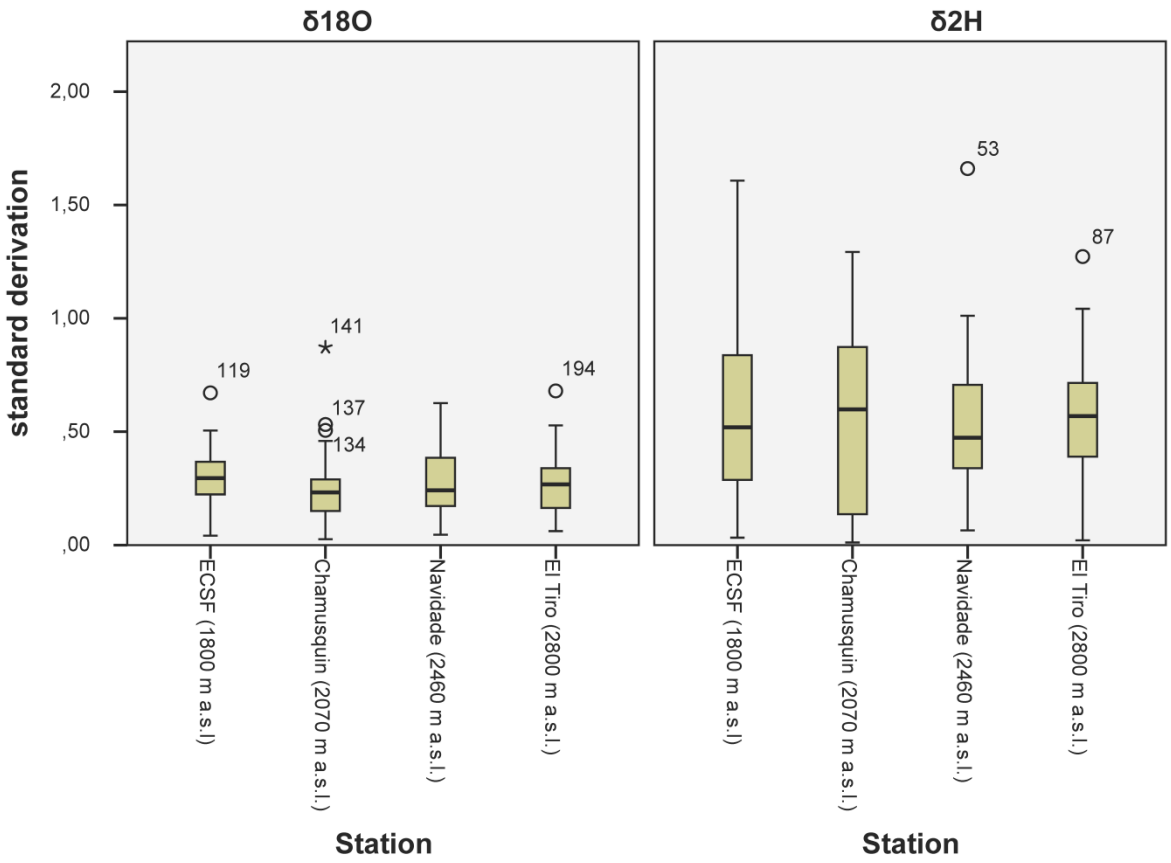


**Figure** Boxplots of the standard derivation for all 4 sites. (not included in the manuscript)

-Section 3: If I understand well, there were only 26 common events between the 4 sites, right? But how many samples were collected at the lowest station compared with the highest station?

The rainfall for all 26 events extended over the whole research area and contributed precipitation to all sampling sites resulting in an equal sample numbers for each site (26 times 3). For clarification, we added the following:

> *"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)."*

-First paragraph of section 3: please, give the range of the isotopic composition for each site. The -16.5 to 2.7 per mil range for oxygen 18 is comparable with the range of isotopic values found by Villacís et al. (2008) at Nuevo Roca Fuerte, upstream the San Francisco valley. Please mention this study (M. Villacís et al., Analysis of the climate controls on the isotopic composition of precipitation (d18O) at Nuevo Rocafuerte, 74.58W, 0.98S, 250 m, Ecuador, C. R. Geoscience 340, 2008).

Thanks for providing the additional, helpful reference, which we were not aware of, and which we added to the paper:

> *"The range is also in good agreement with the daily precipitation values reported by Villacís 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 $\delta^{18}O$."*

We also added the following table to the according section in the text to describe the

underlying dataset.

**Tab. 2** Descriptive statistic of all 26 events

| | Loactation | min | mean | max | range |
|---|---|---|---|---|---|
| $\delta^2H$ [‰] | 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 |
| $\delta^{18}O$ [‰] | 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 |

-Please show on Figure 2 precipitation amount at each site.

We added the total amount of rainfall for each event to Figure 2.

-Please discuss the relationship between precipitation and the isotopic composition of precipitation. The authors can also investigate the role of rainout upstream following the method done by Villacís et al. (2008).

We found the size of our dataset unsuitable to investigate the role of rainout upstream following the method done by Villacís et al. (2008). Calculating a grid based covariance between the monthly mean (only 3 values) would be very error-prone and first test on event based data revealed no clear dependency.

-Line 18: where is the Amaluza GNIP station? How many isotopic data are available from 1992 to 1994 over the September-December periods (is it a continuous record)?

The location of the Amaluza station from the GNIP network was added to Fig. 1. The data set comprises monthly means starting from May 1992 – July 1994 (27 values). For comparison the mean value of the reference period September-December was used within figures 2 and 6.

-Line 27: high intercept can also be a signature of arrivals of recycled air masses in the valley

For us “recycled air masses” refer to the change in the isotopic signature due to (re-)evaporation. To clarify the sentences we added the word “recycled”. The sentence now reads as follows:

> *“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.”*

**Page 8434**
-Lines 1-3 are not useful.

We discarded the respective sentences.

-Line 12: please give one sigma for deuterium and oxygen 18 mean altitude effect. Indeed, according to Figure 3, the altitude effect is significantly different from one event to another.

Without any doubt, the altitude effect changes from one event to another (see Figure 4) and due to the high variability the standard error is relatively high (1.39 for $\delta^2H$ and 0.2 for $\delta^{18}O$). We added the standard error to the according section, which now reads as follows:

> *"On average, the $\delta^{18}O$ altitude effect is -0.22‰ × 100 $m^{-1}$ and for $\delta^2H$ it amounts to -1.12‰ × 100 $m^{-1}$ (standard error 0.2‰ for $\delta^{18}O$ and 1.39 for $\delta^2H$)."*

-Lines 15-17: Regarding the 3 dates for which a negative lapse rate is shown: it is possible that different air masses precipitate at the different sampling sites, isn't it?

We assume the reviewer refers to the positive lapse rates rather than to the expected negative lapse rates.
The positive lapse rate of the 3 events cannot be explained by the different origin of the air masses. All 3 events with a positive lapse rate occurred during the time of southeasterly trade winds which was confirmed by the local climate measurements and the HYSLPIT simulations (see figure below).
We further verified the homogenous source of the air masses responsible for the positive lapse rates by calculating the backward trajectories with HYSPLIT for several elevations above ground level for these events and found all events could best be described by the trajectories in 1500 m above ground level (trajectories not explicitly shown in Figure 5)".
The source of the positive lapse rates could not be detected by taking a closer look at possible different air masses and still remains unresolved.

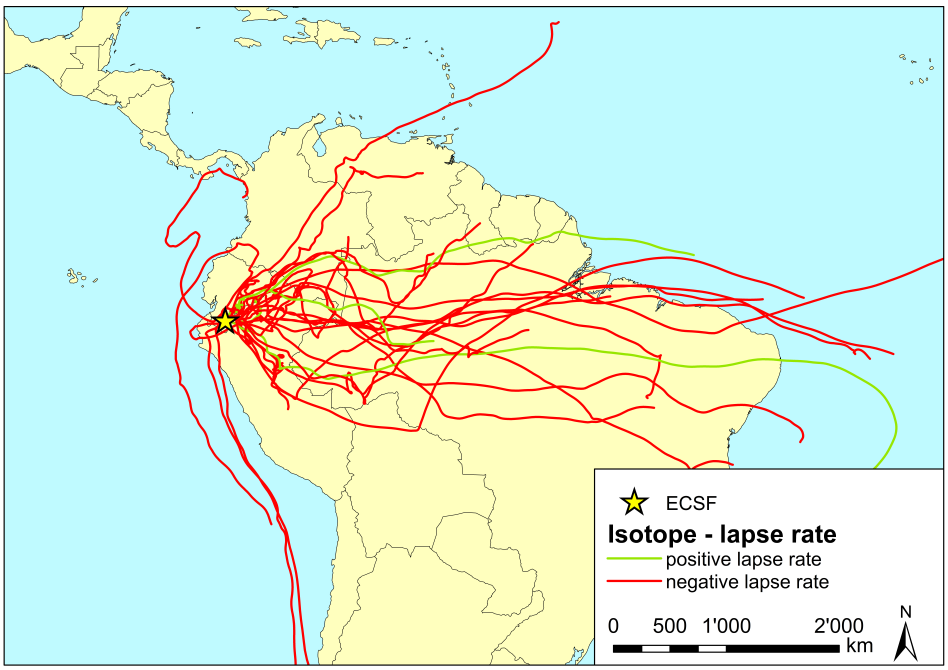


**Figure** Backward trajectories calculated with HYSPLIT for events with positive and negative lapse rates for all 26 events (figure not included in the manuscript).

-According to Figure 4, an altitudinal effect is seen on deuterium excess. Can the authors mention and discuss it here instead of at the end of section 3-3? In general, I would include the discussion of section 3-3 in sections 3-1 and 3-2.

The discussion of the deuterium excess - altitude effect was shifted to section 3.1. In general we agree with the reviewer that section 3.2 and 3.3 show the same things based on different aspects. We therefore combined the two sections and adjusted the reasoning.

-Start of section 3-2: Geographic origin of air masses is one of the potential controls on the isotopic composition of precipitation. But, other factors can be involved. For example, in the recent study done by Vimeux et al. (2011), no significant relationship between air masses origin and isotopic composition of precipitation was found at the event-scale in a similar valley in the Andes.

We included this remark into the introduction. The section in the introduction now reads as follows:

> *"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)."*

**Page 8435**
-Line 11: is the associated figure, figure 2?

Yes. Figure 2a and 2b show the course of the isotope concentration in precipitation over time. To clarify the meant period we change the section as follows:

> *"Isotope signatures of precipitation in the study area are significantly higher during the times of SE trade winds (02 September – 16 October) than for the rest of the investigation period (01 November – 24 December) (Fig. 2a and 2b)."*

**Page 8436**
-Lines 8-13: The seasonal effect on deuterium excess mentioned in those studies is a seasonal effect. I mean that those studies do not claim that there is a relationship between deuterium excess and precipitation at the event-based scale.

The citation in the section (P. 8436 L. 8-13) by Scholl et al. (2002) was not meant to refer to any seasonality. It describes the concept of enrichment of precipitation due to orographic lifting of air parcels and thus rainout.

**Figures and Tables**
-Table 2: the study done by Shugui et al. (2003) in EPSL could be added.

We added the following information to the table:

| Author | $\delta^2H$ [‰ 100 m-1] | $\delta 18O$ [‰ 100 m-1] | Location |
|---|---|---|---|
| Hou et al. (2003) | - | -0.12 to -0.29 | Himalaya |

-Figure 1: please locate the investigation area by indicating longitudes and latitudes.

We added an overview map, the location of the Amaluza GNIP station and the longitudes and latitudes for the research area to figure 1.

-Figure 2: there is no need to show both deuterium and oxygen 18. The authors could only show one isotope and add deuterium excess (Figure 4) on Figure 2. This could allow the reader to see if any relationship exists between deuterium and deuterium excess for

example. Please also add on this Figure precipitation amount for each site. Please mention in the caption where is the Amaluza GNIP station and how many data are available for each month.

We combined figure 2 and 6 to allow the direct comparison between δ18O, deuterium excess and the amount of rainfall. Added dashed lines to ease the separation of the different stations for 2b. We added the total amount of rainfall fallen for each event recorded at the El Tiro climate station. Showing the intensities [mm/h] during each event or the amount of rainfall fallen at each site would be to complex.
The location of the Amaluza GNIP station was added to figure 1 and the dataset of Amaluza was described in section 2.3 which ends now as follows:

> *"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)."*

-Figure 3: please add deuterium excess on this Figure to illustrate the altitude effect mentioned at the end of section 3-3.

Converted continuous line to points and added the deuterium excess to illustrate its altitude dependency rather than showing the $\delta^2H$ values.

-Figure 5: This figure is highly confusing and should be improved. For example, the authors could mention which direction corresponds to southeasterly winds and use a different color for this case. They could also indicate only the mean wind directions during one rain event, separating the different climate stations (so for example, we will see only 4 markers on the Figure for one rain event, with a specific color for SE origin and a specific code to distinguish the climate stations).

Instead of showing the wind direction and velocity we now show the 12-days-backward trajectories for the 26 rain events calculated with the HYSPLIT model.

# 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 $\delta^{18}O$ and $\delta^{2}H$ 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 $\delta^{18}O$ altitude effect for the study area averages -0,22‰ × 100 $m^{-1}$ ($\delta^{2}H$: -1,12‰ × 100 $m^{-1}$). 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 $\delta^{18}O$ and $\delta^{2}H$ 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; Liebminger 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 $\delta^{18}O$ and $\delta^{2}H$ 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 $\delta^{18}O$ and -0.6‰ 100 $m^{-1}$ for $\delta^{2}H$ 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-

60 tory, e.g. by the source of the moisture and the amount effect due to rain out along the path
61 taken by the air mass. As we cannot distinguish between the factors shaping the history of the
62 incoming air mass by locking at on-site measurements, we restricted our analysis to the de-
63 pendency of the isotopic signature of the precipitation on the prevailing weather conditions,
64 the source of the incoming air masses, the spatial dependency within the study area and the
65 on-site amount effect due to a discrimination of light isotopes during rainout in the course of a
66 single event. For the on-site amount effect we assume that events with a higher amount of
67 precipitation and the same history will yield an overall lighter isotopic composition than
68 events with smaller amounts of rainfall. However, recent studies give rise to the assumption
69 that other factors than the amount of precipitation or the origin of the air masses play an im-
70 portant role in controlling seasonal patterns of isotope signatures (Breitenbach et al., 2010;
71 Feng et al., 2009; Kebede and Travi, 2011; Lee et al., 2009; Peng et al., 2010; Rhodes et al.,
72 2006; Risi et al., 2008a, 2008b; Scholl et al., 2009; Villacís et al., 2008; Vimeux et al., 2005,
73 2011). For example, Rhodes et al. (2006) and Scholl et al. (2009) concluded that orographic
74 precipitation during the trade wind dominated dry season is enriched compared to the mostly
75 convective precipitation type during the wet season occurring e.g. in Costa Rica and Puero
76 Rico, respectively. Vimeux et al. (2005) reported that moisture transport history is another
77 important factor controlling the seasonal variation of isotope signatures in the Andes. The
78 Amazon Basin is known to contribute large amounts of recycled moisture to the air masses
79 transported by trade winds (Martinelli et al., 1996; Salati et al., 1979; Valletcoulomb et al.,
80 2008). This contribution of recycled moisture to precipitation can be traced by the deuterium
81 excess parameter (Araguas-Araguas et al., 2000; Froehlich et al., 2002; Gat, 2000; Kabeya et
82 al., 2007; Njitchoua et al., 1999; Victoria et al., 1991). Since southeasterly (SE) trade winds
83 prevail in our research area in the tropical montane forests of Southern Ecuador during austral
84 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 $\delta^{18}O$ and $\delta^{2}H$ 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

159 consistent with long term climate records for the study area (Bendix et al., 2008; Emck and
160 Richter, 2008). Since tropical trade winds travel at altitudes below 3,000 m (Scholl et al.,
161 2002), the Andes form a topographic barrier which leads to a rainout of air masses. The *Cor-*
162 *dillera Real* serves as a climate divide between the humid Amazon Basin and the dry Inter
163 Andean Region. From mid-October on, when trade winds weaken in their intensity and fre-
164 quency, other wind directions and lower wind speeds are observed. However, precipitation
165 originating from pacific westerlies hardly reaches the study area, since most of these air
166 masses rain out at the western slopes of the Andes (Bendix et al., 2008; Emck, 2007).

167 The main factor influencing air temperature in the study area is elevation. Mean annual tem-
168 perature ranges from 12°C (at 3260 m asl) to 22°C (at 1600 m asl). The average gradient of
169 air temperature is 0.61°C 100 $m^{-1}$. As usual for tropical regions, seasonal changes in tempera-
170 ture are low (Bendix et al., 2008).

171 **2.2. Experimental set up**

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

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

182 Prior to field sampling the reliability of the table tennis ball to prevent evaporation losses was
183 tested in the laboratory. During a 21 d period the effect of four different climatic conditions
184 simulated in climate chambers (30°C/15°C and 15°C/10°C in a 12 h day-night cycle each at
185 50% and 90% relative humidity) on the isotopic composition was tested. Collectors with table
186 tennis balls were stored under these different climate conditions and water samples were
187 withdrawn in intervals of three days. Even under the most unfavorable conditions in the cli-
188 mate chambers (temperature 30°C/15°C and relative humidity 50%) the enrichment of heavy
189 isotopes was either not significant ($p>0.05$) or, in the case of scenario 4, within the measuring
190 inaccuracy of the analytical device of 0.2‰ for $\delta^{18}O$ and 0.6‰ for $\delta^{2}H$ (Tab. 1). During the
191 field experiment not more than one day passed between the precipitation event and sample
192 collection. We therefore exclude a measurable effect of the sampling procedure on the isotop-
193 ic compositions of the samples.

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

## 2.3. Analysis and statistics

Isotope signatures of $\delta^{18}O$ and $\delta^{2}H$ 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 $\delta^{18}O$ and $\delta^{2}H$ 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 $\delta^{18}O$ and 0.6‰ for $\delta^{2}H$, 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 $\delta^{18}O$ and $\delta^{2}H$. 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 $\delta^{18}O$ (ranging from 0.03‰ to 0.87‰) and 0.58‰ for $\delta^{2}H$ (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 $\delta^{18}O$ and from -120.2 to 30.8‰ for $\delta^{2}H$ (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 Villacís 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 $\delta^{18}O$.

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. 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 $\delta^{18}O$ isotope signatures of all sampled events ($\delta^{2}H$ shows the same course (data not shown), any difference between $\delta^{2}H$ and $\delta^{18}O$ 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 $\delta^{18}O$ altitude effect is -0.22‰ × 100m$^{-1}$ and for $\delta^{2}H$ it amounts to -1.12‰ × 100 m$^{-1}$ (standard error 0.2‰ for $\delta^{18}O$ and 1.39 for $\delta^{2}H$). As usual for tropical regions (Sturm et al., 2007), it lies within the lower part of the ranges reported in literature (Tab. 3). Most $\delta^{18}O$ event lapse rates of the present study are between -0.1 and -0.4‰ × 100 m$^{-1}$ ($\delta^{2}H$: -0.8 to -1.5‰ × 100 m$^{-1}$). However, three out of 26 events do not show a negative lapse rate for both $\delta^{18}O$ and $\delta^{2}H$ (Fig. 4; dates 06.09., 01.10. and 21.10.). Overall linear regression of the data showed that the altitude effect of $\delta^{18}O$ is significant ($p<0.05$), while for $\delta^{2}H$ 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 $\delta^{18}O$ and $\delta^{2}H$ ($p<0.01$). 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‰ × 100 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°C 100 m$^{-1}$ as in our study area; Gonfiantini et al. (2001) 0.42-0.55°C 100 m$^{-1}$; Peng et al. (2010) 0.53-0.65°C 100 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 $\delta^{18}O$ 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 ($\delta^{2}H$: -55.3 to 30.8‰, -51.2 to -27.5‰ and -120.2 to -27.0‰, respectively). Mean values of $\delta^{18}O$ are -3.0‰ for trade wind related precipitation, -6.3‰ for events during the transition phase and -9.9‰ for other precipitation events ($\delta^{2}H$: -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).

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

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

330 To further investigate and strengthen our assumption that recycled moisture from the Amazon
331 Basin is causing the high isotopic composition during trade wind related precipitation events
332 we used the deuterium excess parameter to assess the actual amount of recycled moisture
333 (Araguas-Araguas et al., 2000; Bowen and Revenaugh, 2003; Froehlich et al., 2002; Gat,
334 2000; Liu et al., 2007; Njitchoua et al., 1999; Peng et al., 2010; Victoria et al., 1991). For
335 trade wind related precipitation events, deuterium excess averages 14.9‰ and hence, is sig-
336 nificantly higher than for other events (d = 9.6‰). The temporal variability of event deuteri-
337 um excess in the study area shows a similar trend compared to the $\delta^{18}O$ and $\delta^{2}H$ values, in-
338 cluding the decrease after mid-October (Fig. 2b). These observations confirm the assumption
339 that intense moisture recycling takes place when precipitation is attributed to SE trade winds.
340 Goller et al. (2005) report an annual mean deuterium excess of 11.1‰ for their site at the
341 lower part of the same investigation area, pointing to the assumption that moisture recycling
342 might not be high all year long. Since they did not measure both $\delta^{2}H$ and $\delta^{18}O$ for all samples,
343 no temporal variability of deuterium excess was reported. Mean annual deuterium excess at
344 the GNIP station Amaluza was 15.5‰. Highest values were measured from July to October
345 (18.4 to 19.2‰), i.e. the time of the year when SE trade winds prevail in the study area. Low-
346 est values were measured from March to May (10 to 12.5‰) and in November (11.9‰).

347 Some studies report an amount effect (Bony et al., 2008) or a seasonality (Henderson-Sellers
348 et al., 2010; Liu et al., 2007; Rhodes et al., 2006) of deuterium excess, showing higher values
349 during the dry season. For the present study, a linear regression of event deuterium excess
350 with precipitation amount showed no significant influence (p=0.56). The temporal variability
351 therefore should, analogously to the $\delta^{18}O$ and $\delta^{2}H$ 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 $\delta^2H$ [‰ $d^{-1}$] | p | slope $\delta^{18}O$ [‰ $d^{-1}$] | 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 |
|---|---|---|---|---|---|
| **$\delta^2H$ [‰]** | 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 |
| **$\delta^{18}O$ [‰]** | 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 $\delta^2H$ and $\delta^{18}O$ in precipitation from various sites around the world.

| Author | $\delta^2H$ [‰ 100 $m^{-1}$] | $\delta^{18}O$ [‰ 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 |

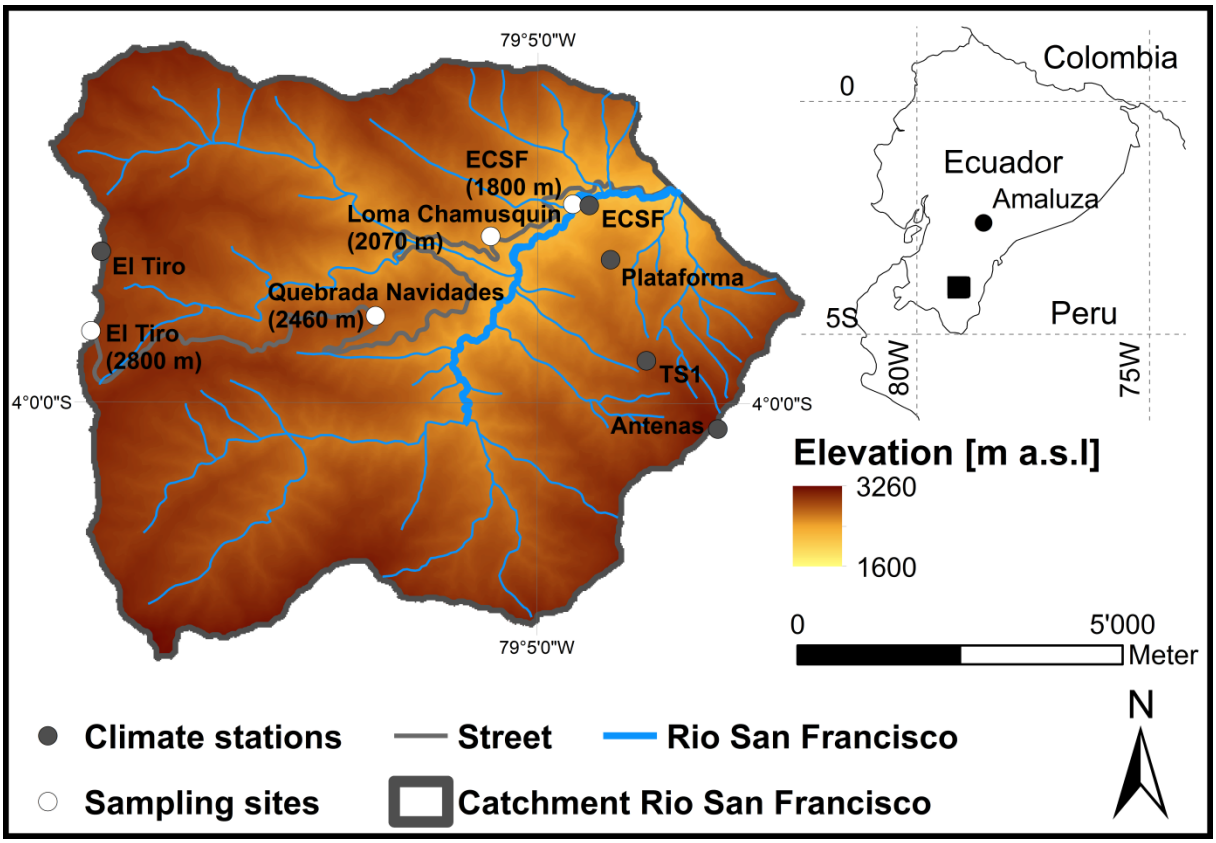


**Fig. 1.** Investigation area with sampling sites and climate stations

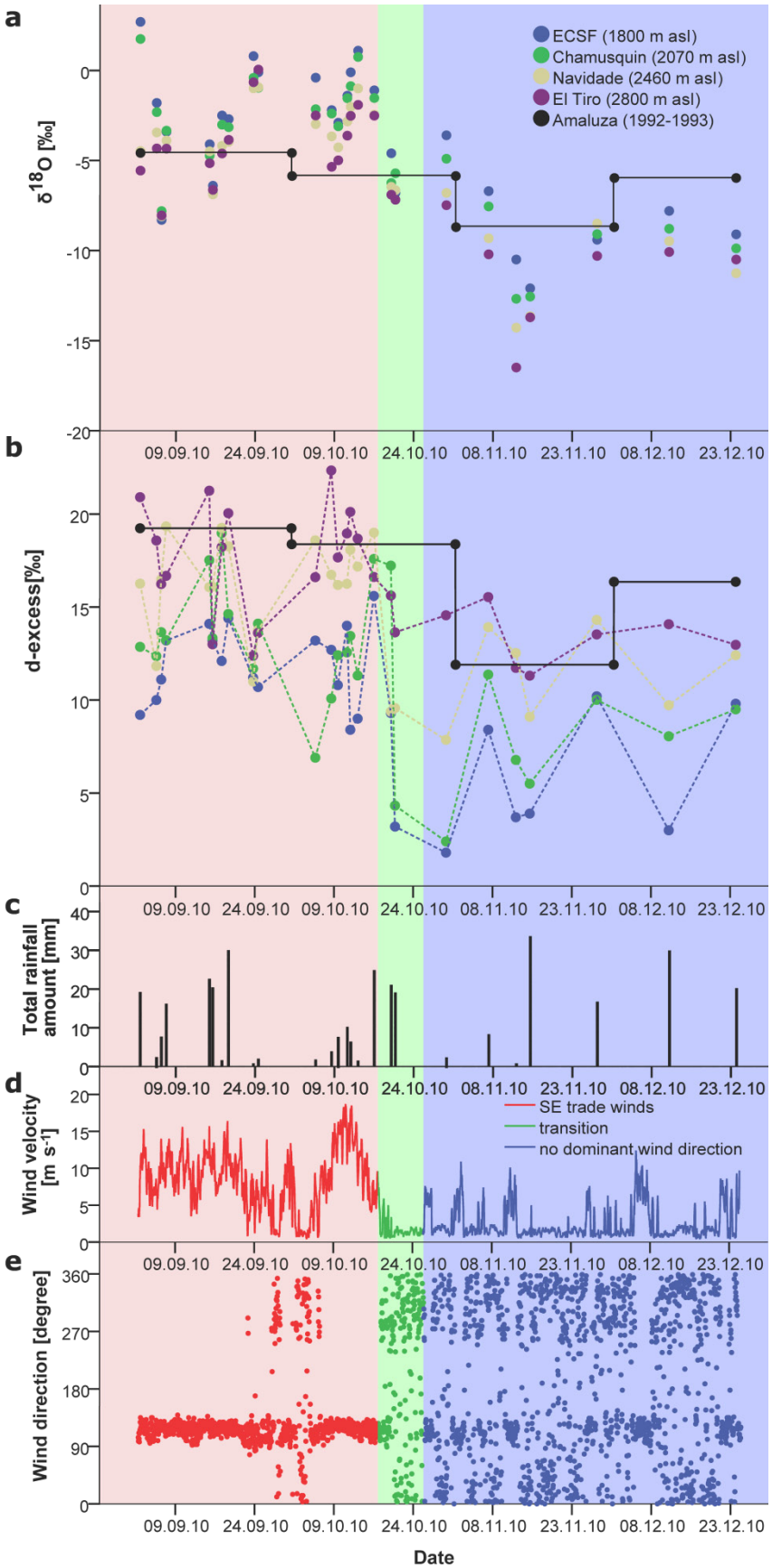


**Fig. 2.** Results of the 26 events sampled. **a** $\delta^{18}O$ isotope signatures, **b** deuterium excess of all sampled events compared to weighted monthly means from GNIP station Amaluza from 1992-1993, **c** total amount of rainfall for each event, **d** wind velocity and **e** wind direction 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.

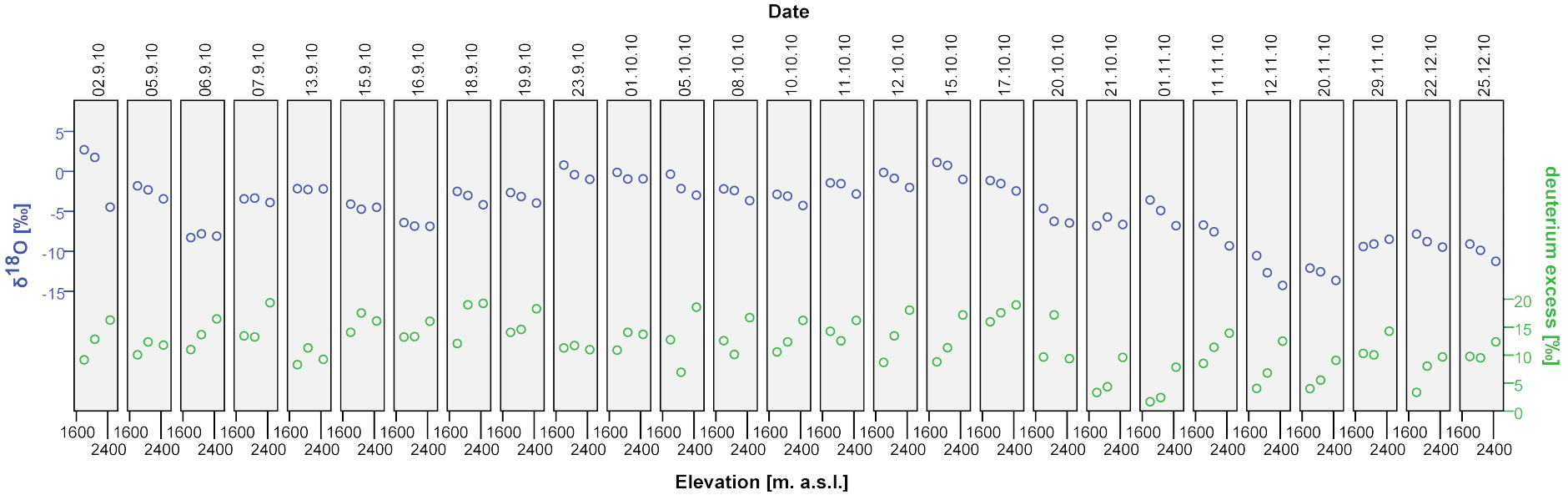


**Fig. 3.** Altitude effect and temporal variation of $\delta^{18}O$ isotope signature and the deuterium excess in precipitation.

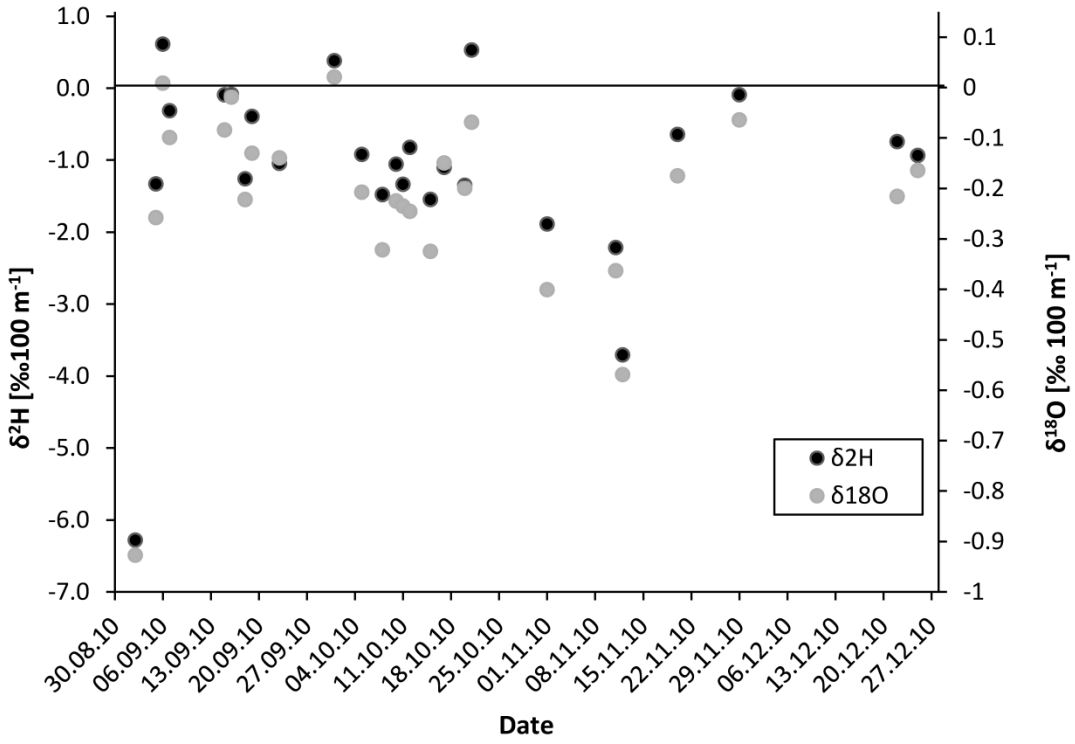


**Fig. 4.** Event based altitude effect of $\delta^{18}O$ and $\delta^{2}H$ isotope signatures in precipitation. The majority of the events show a depletion of heavy isotopes with altitude (i.e. a negative lapse rate). Only during 3 events for $^{2}H$ and 2 events for $^{18}O$ out of 26 events an enrichment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

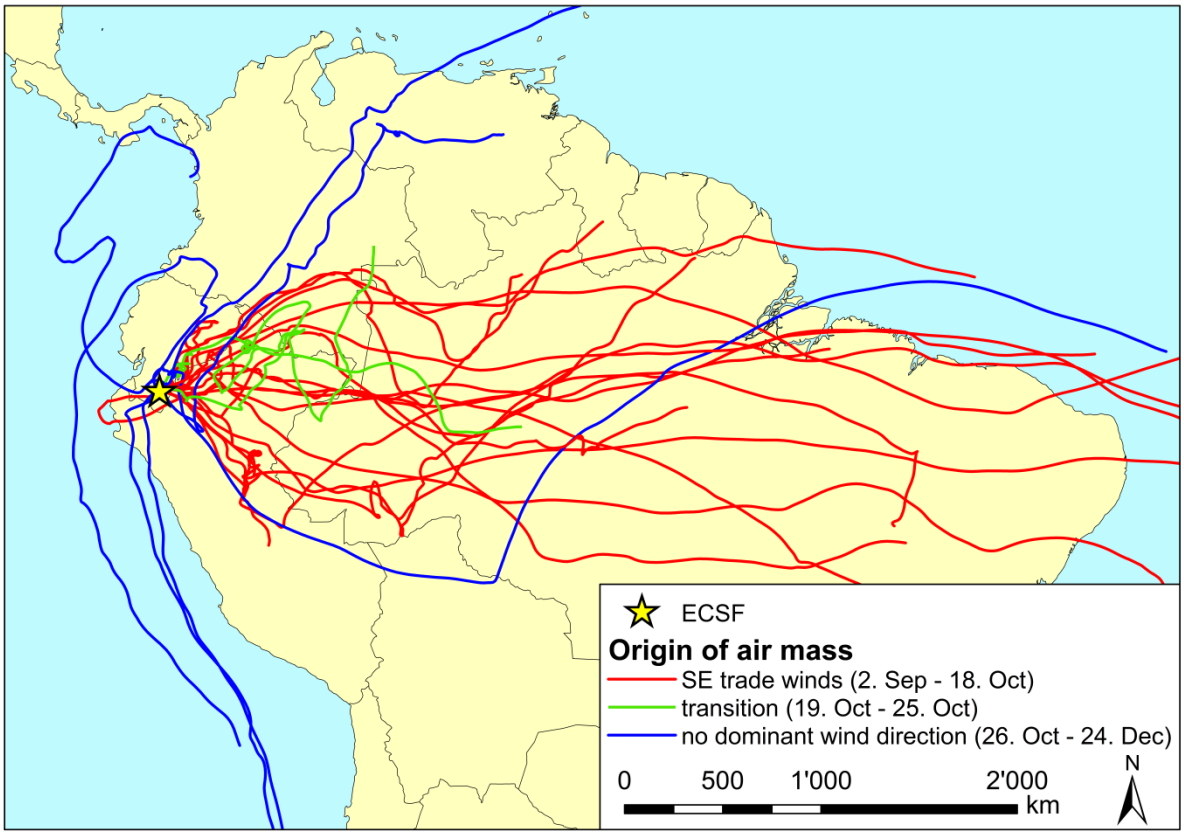


**Fig. 5.** 12 days back trajectories for the 26 rain events calculated with the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model developed by Draxler and Rolph, (2012).

# 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 $\delta^{18}O$ and $\delta^{2}H$ 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 $\delta^{18}O$ altitude effect for the study area averages -0,22‰ × 100 $m^{-1}$ ($\delta^{2}H$: -1,12‰ × 100 $m^{-1}$). 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 $\delta^{18}O$ and $\delta^{2}H$ 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; Liebminger 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 $\delta^{18}O$ and $\delta^{2}H$ 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~~are~~ limited. We are aware of only one study in Puerto Rico where a gradient of -0.12‰ 100 $m^{-1}$ for $\delta^{18}O$ and -0.6‰ 100 $m^{-1}$ for $\delta^{2}H$ 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)., t~~T~~hough 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 locking 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 Puero 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 $\delta^{18}O$ and $\delta^{2}H$ 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

134 further characterized by a mix of shrubs, reforestation sites and sub-paramo (Göttlicher et al.,
135 2009).

136 Average annual sums of precipitation, for the period 2002 to 2008, amount to 1,500 to 4,900
137 mm $a^{-1}$ with a large spatial variability (Rollenbeck and Bendix, 2011). Moreover, there is a
138 significant input of fog to the ecosystem, which accounts for 5 to 35% of precipitation and
139 enhances the total water input up to 6,500 mm $a^{-1}$ at the highest altitudes (Rollenbeck et al.,
140 2011). According for Rollenbeck et al. (2011) the designated fog input increases with altitude
141 and amount of rainfall, comprising various forms of horizontal precipitation like the actual
142 fog, drizzle and other wind driven rain. Along a N to S transect investigated by Bendix et al.
143 (2008), an altitudinal increase of precipitation (lapse rate) of 220 mm 100 $m^{-1}$ was observed.
144 However, spatial observations of radar based precipitation inputs do not indicate that this alti-
145 tudinal effect is valid for the whole study area, especially in an E-W direction (Rollenbeck
146 and Bendix, 2011). Along the E-W transect that was investigated in the present study (Fig. 1)
147 climate stations have also not shown an altitudinal increase of incoming precipitation. Precipi-
148 tation at the highest point investigated in this study (*El Tiro*, 2,800 m asl) amounts to 1,500
149 mm $a^{-1}$, whilst at the lowest point (ECSF, 1,800 m asl) it is 2176 mm $a^{-1}$ (Bendix et al., 2006;
150 Emck, 2007). This demonstrates the high spatial variability of precipitation amounts occur-
151 ring in the study area.

152 The weather within the study area is dominated by easterly trade winds. From January to
153 April, northeasterly trade winds are prevailing. Southeasterly trade winds dominate weather in
154 the study area from April to mid-October (Emck, 2007). From June to September, the propor-
155 tion of trade winds is close to 100%. For the rest of the year, it is still more than 50%. The
156 temporal variability of isotope signatures in the present study was, for the most part, expected
157 to be determined by the prevailing air masses. During the investigation period, southeasterly
158 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 ~~heading~~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-

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

185 Prior to field sampling the reliability of the table tennis ball to prevent evaporation losses was
186 tested in the laboratory. During a 21 d period the effect of four different climatic conditions
187 simulated in climate chambers (30°C/15°C and 15°C/10°C in a 12 h day-night cycle each at
188 50% and 90% relative humidity) on the isotopic composition was tested. Collectors with table
189 tennis balls were stored under these different climate conditions and water samples were
190 withdrawn in intervals of three days. Even under the most unfavorable conditions in the cli-
191 mate chambers (temperature 30°C/15°C and relative humidity 50%) the enrichment of heavy
192 isotopes was either not significant ($p \leq 0.05$) or, in the case of scenario 4, within the measur-
193 ing inaccuracy of the analytical device of 0.2‰ for $\delta^{18}O$ and 0.6‰ for $\delta^{2}H$ (Tab. 1). During
194 the field experiment not more than one day passed between the precipitation event and sample
195 collection. We therefore exclude a measurable effect of the sampling procedure on the isotop-
196 ic compositions of the samples.

197 Total precipitation sums between each event sampling were also measured in the collectors.
198 Climate data from stations near ECSF and *El Tiro* were also used to investigate the influence
199 of climatic parameters (relative humidity (%), air temperature (°C), rainfall amount and inten-
200 sity (mm $h^{-1}$) and wind direction (°) and speed (m/s)) on the isotopic composition of the sam-
201 ples. The wind direction of air masses moving over the study area was measured at the *El*
202 *Tiro*. In addition to the on-site climate measurements we used the Hybrid Single-Particle
203 Lagrangian Integrated Trajectory (HYSPLIT) model developed by Draxler and Rolph (2012)
204 to calculate for each event the backwards trajectories for the previous 12 days (288 hours) of
205 the air masses responsible for rainfall reaching the study area in an elevation of 1,500 m
206 above ground level. For the analyses in our study, the HYSPLIT model was operated with
207 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 $\delta^{18}O$ and $\delta^{2}H$ 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 $\delta^{18}O$ and $\delta^{2}H$ 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 $\delta^{18}O$ and 0.6‰ for $\delta^{2}H$, 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 $\delta^{18}O$ and $\delta^{2}H$. 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 $\delta^{18}O$ (ranging from 0.03‰ to 0.87‰) and 0.58‰ for $\delta^{2}H$ (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 $\delta^{18}O$ and from -120.2 to 30.8‰ for $\delta^{2}H$ (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 Villacís 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 $\delta^{18}O$.

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. 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 $\delta^{18}O$ ~~and $\delta^{2}H$~~ isotope signatures of all sampled events ($\delta^{2}H$ shows the same course (data not shown), any difference between $\delta^{2}H$ and $\delta^{18}O$ 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 $\delta^{18}O$ altitude effect is -0.22‰ × 100m$^{-1}$ and for $\delta^{2}H$ it amounts to -1.12‰ × 100 m$^{-1}$ (standard error 0.2‰ for $\delta^{18}O$ and 1.39 for $\delta^{2}H$). As usual for tropical regions (Sturm et al., 2007), it lies within the lower part of the ranges reported in literature (Tab. 3). Most $\delta^{18}O$ event lapse rates of the present study are between -0.1 and -0.4‰ × 100 m$^{-1}$ ($\delta^{2}H$: -0.8 to -1.5‰ × 100 m$^{-1}$). However, three out of 26 events do not show a negative lapse rate for both $\delta^{18}O$ and $\delta^{2}H$ (Fig. 4; dates 06.09., 01.10. and 21.10.). Overall linear regression of the data showed that the altitude effect of $\delta^{18}O$ is significant ($p<0.05$), while for $\delta^{2}H$ 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 $\delta^{18}O$ and $\delta^{2}H$ ($p<0.01$). 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‰ × 100 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~~of~~ 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°C 100 m$^{-1}$ as in our study area; Gonfiantini et al. (2001) 0.42-0.55°C 100 m$^{-1}$; Peng et al. (2010) 0.53-0.65°C 100 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 $\delta^{18}O$ 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 ($\delta^{2}H$: -55.3 to 30.8‰, -51.2 to -27.5‰ and -120.2 to -27.0‰, respectively). Mean values of $\delta^{18}O$ are -3.0‰ for trade wind related precipitation, -6.3‰ for events during the transition phase and -9.9‰ for other precipitation events ($\delta^{2}H$: -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) ($\delta^{18}O$: -7.0 to 0.3‰) and Rhodes et~~

~~al. (2011) ($\delta^{18}$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 t~~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‰). The temporal variability of event deuterium excess in the study area shows a similar trend compared to the $\delta^{18}O$ and $\delta^{2}H$ values, including the ~~abrupt~~ decrease

after~~in~~ 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 $\delta^2H$ and $\delta^{18}O$ 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 $\delta^{18}O$ and $\delta^2H$ 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‰ × 100m$^{-1}$ ($p<0.01$). 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~~ showed~~n~~ 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~~ 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

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

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

412

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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 $\delta^2H$ [‰ $d^{-1}$] | p | slope $\delta^{18}O$ [‰ $d^{-1}$] | 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 |
|---|---|---|---|---|---|
| $\delta^2H$ [‰] | 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 |
| $\delta^{18}O$ [‰] | 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 $\delta^2H$ and $\delta^{18}O$ in precipitation from various sites around the world.

| Author | $\delta^2H$ [‰ 100 $m^{-1}$] | $\delta^{18}O$ [‰ 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 |

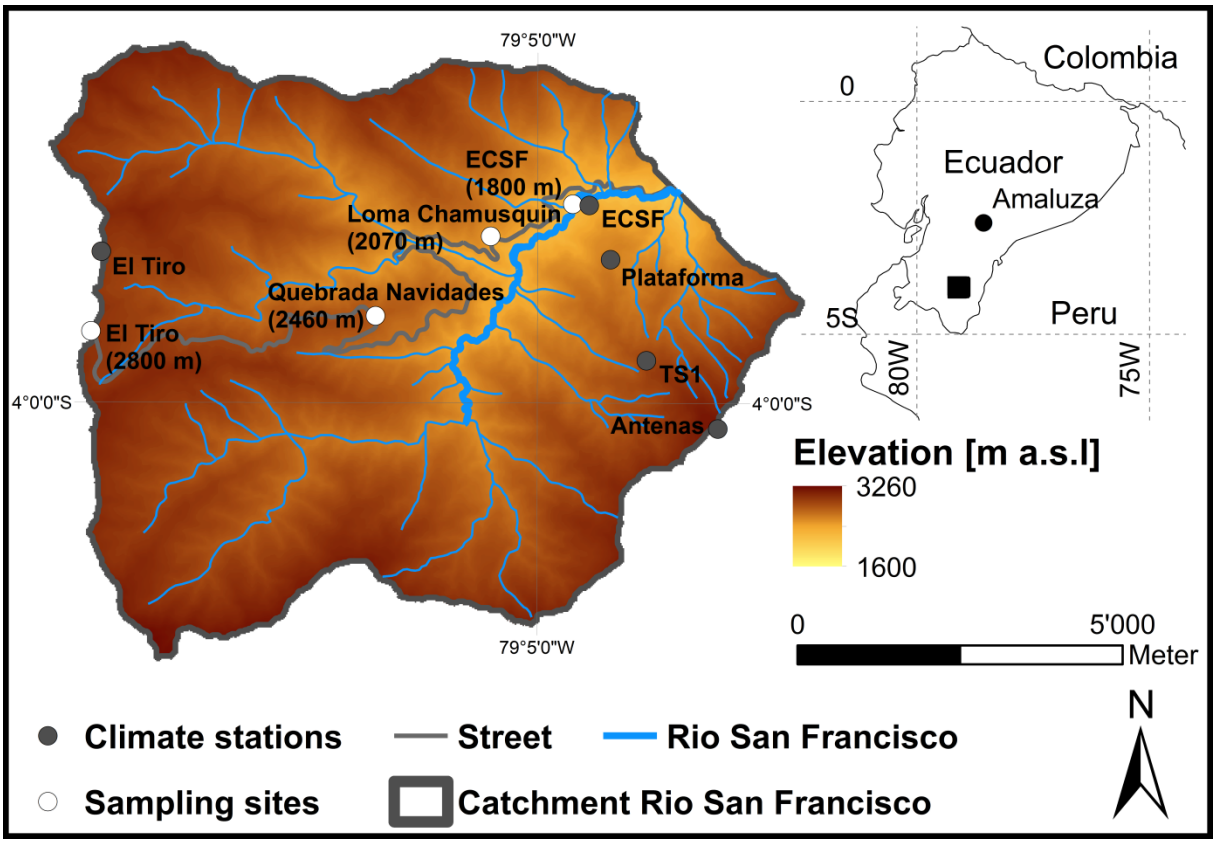


**Fig. 1.** Investigation area with sampling sites and climate stations

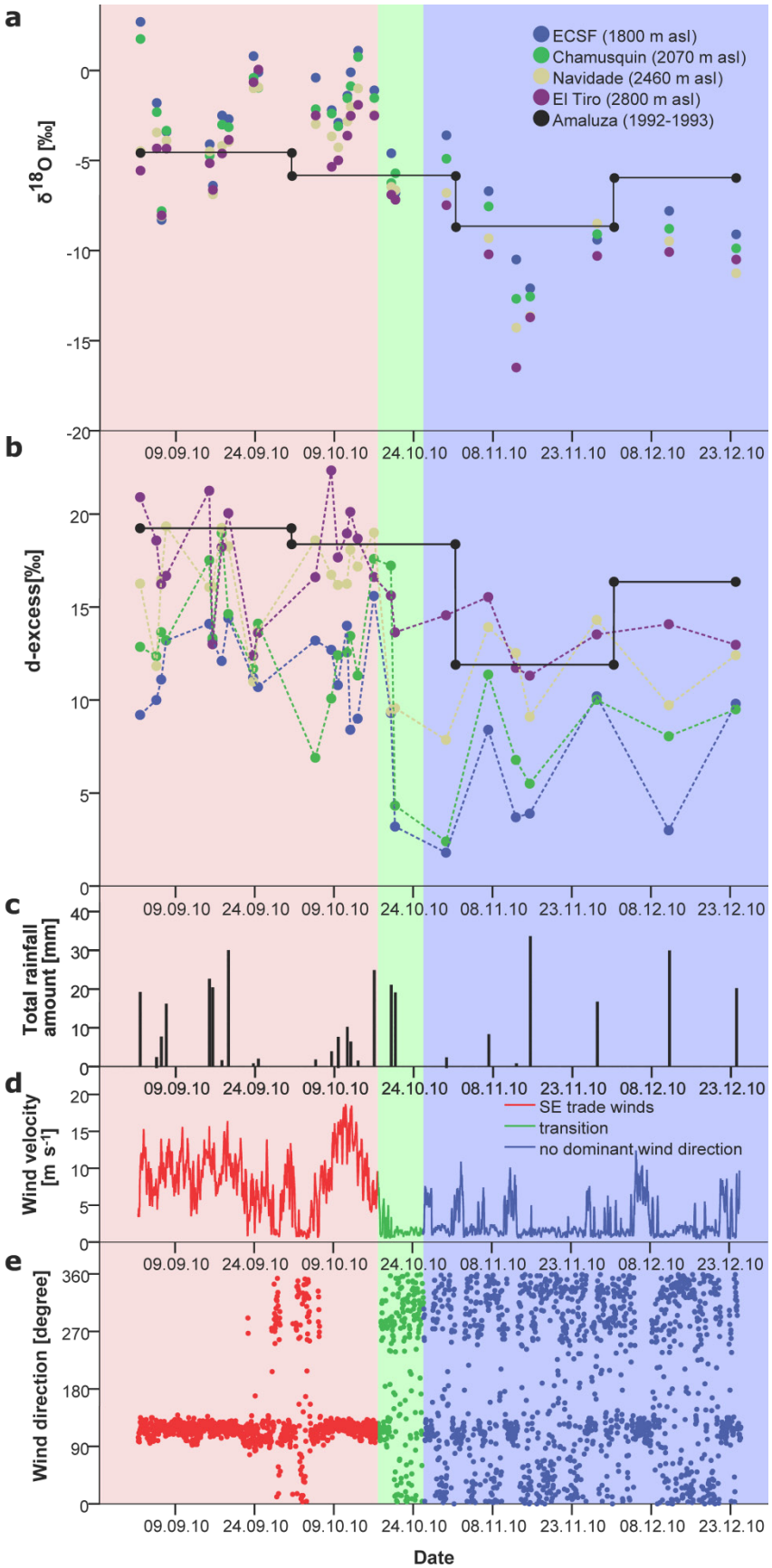


**Fig. 2.** Results of the 26 events sampled. **a** $\delta^{18}O$ isotope signatures, **b** deuterium excess of all sampled events compared to weighted monthly means from GNIP station Amaluza from 1992-1993, **c** total amount of rainfall for each event, **d** wind velocity and **e** wind direction 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.

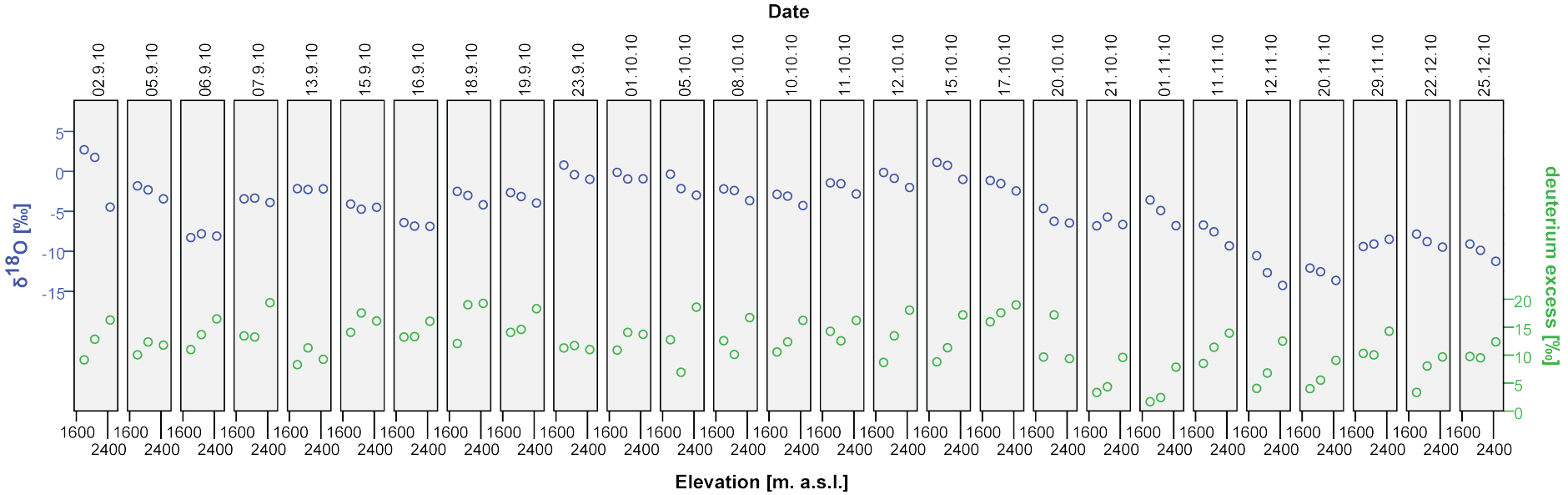


**Fig. 3.** Altitude effect and temporal variation of ~~δ²H and~~ $\delta^{18}O$ isotope signature and the deuterium excess in precipitation.

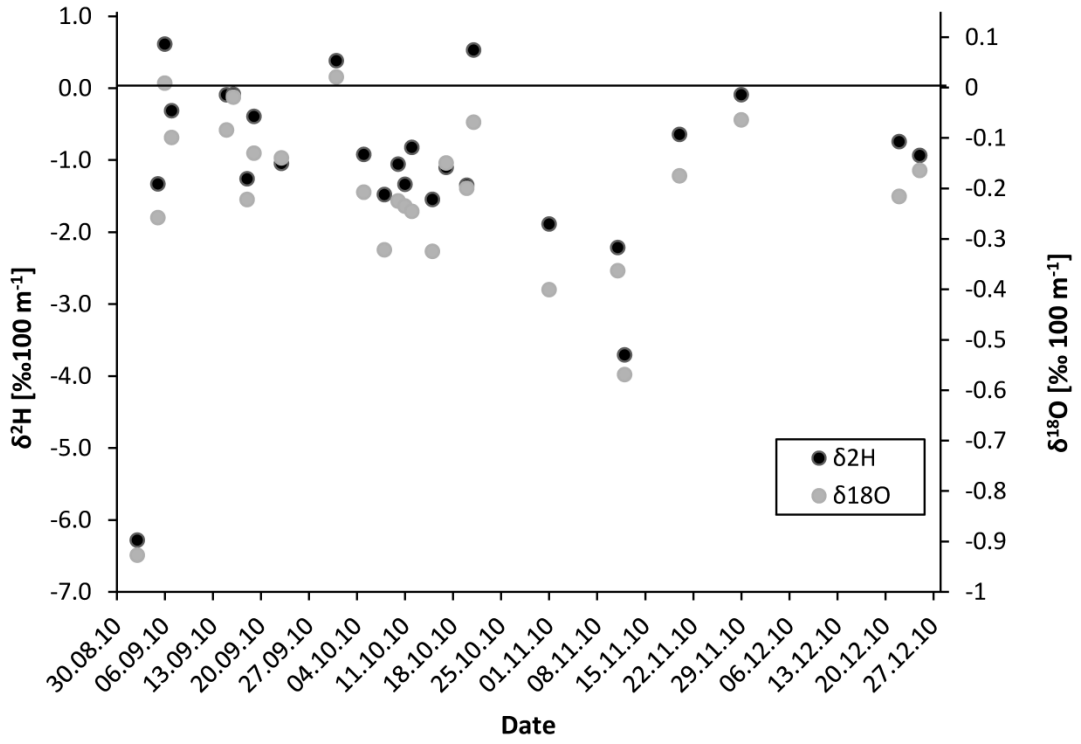


**Fig. 4.** Event based altitude effect of $\delta^{18}O$ and $\delta^{2}H$ isotope signatures in precipitation. The majority of the events show a depletion of heavy isotopes with altitude (i.e. a negative lapse rate). Only during 3 events for $^{2}H$ and 2 events for $^{18}O$ out of 26 events an enrichment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

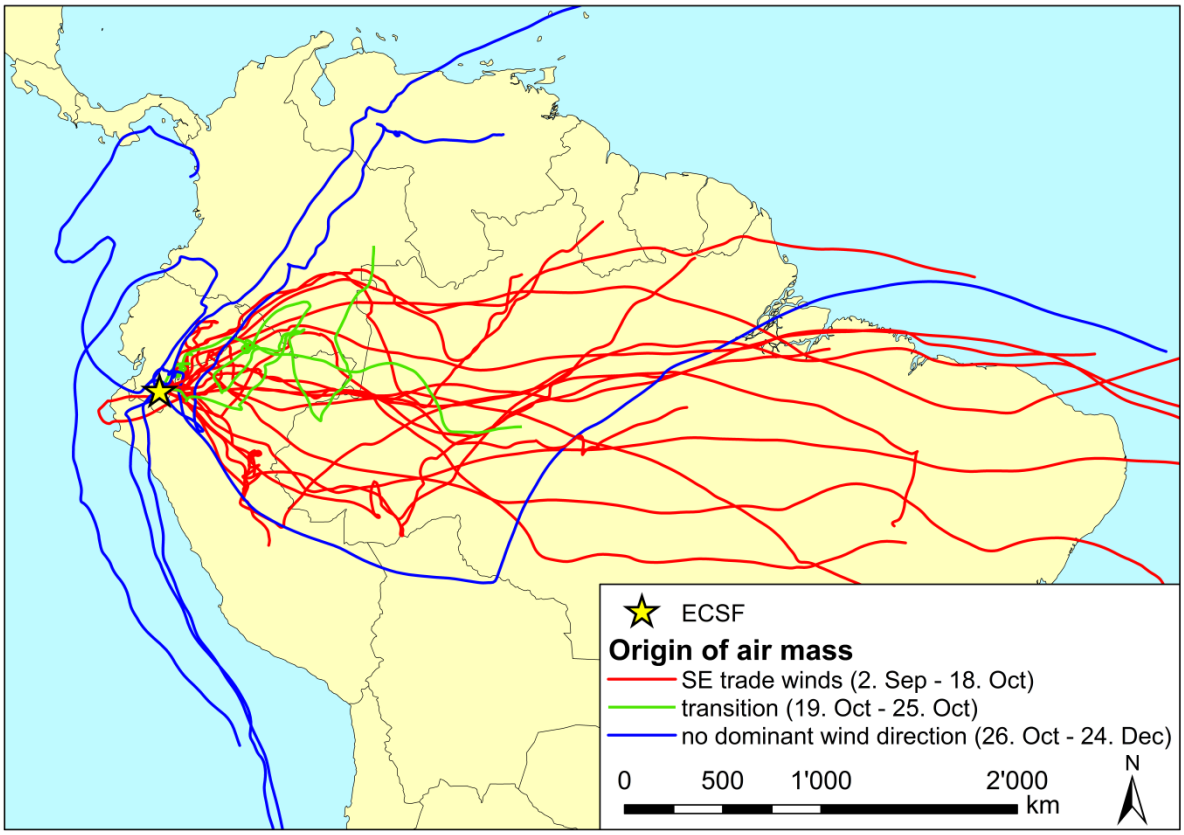


**Fig. 5.** 12 days back trajectories for the 26 rain events calculated with the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model developed by Draxler and Rolph, (2012).