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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 2 September to 25 December 2010, event sampling of open rainfall was conducted along an altitudinal transect (1800 m a.s.l. to 2800 m a.s.l.) 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 $-0.22‰ \times 100\,m^{-1}$ ($\delta^{2}H$: $-1.12‰ \times 100\,m^{-1}$). 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

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Transit Time of water (MTT) (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 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 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). Though seasonal differences tend to be smaller in the tropics than at higher latitudes (Scholl et al., 2011). However, recent studies give rise to the assumption that other factors than the amount of precipitation 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, b; Scholl et al., 2009; Villacís et al., 2008; Vimeux et

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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 signatures 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 hydrological process understanding of 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 dominate 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.

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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. The identification of seasonal variation in the isotopic composition will establish a tool for understanding the interconnections 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. The concentration of heavy isotopes decreases with increasing altitude.
3. Precipitation during SE trade wind dominated periods is enriched in heavy isotopes compared to precipitation during other weather conditions.
4. 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. The highest point of the area is the *Cerro de Consuelo*, coll. *Antenas* at 3155 m a.s.l. The lowest point is at 1720 m a.s.l. Figure 1 shows the topography of the study area and the location of sampling sites and climate stations. The topography

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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 amount to 1500 to 4900 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 6500 mm a^{-1} at the highest altitudes (Rollenbeck et al., 2011). 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 observation 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*, 2800 m a.s.l.) amounts to 1500 mm a^{-1}, whilst at the lowest point (ECSF, 1800 m a.s.l.) it is 2176 mm a^{-1} (Bendix et al., 2006; Emck, 2007). This demonstrates the high spatial variability of precipitation amounts 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,

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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 3000 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 to 22° C. 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 1000 m was investigated. An event sampling was conducted at four sampling sites along this altitudinal gradient: ECSF at 1800 m a.s.l., *Loma Chamusquín* at 2070 m a.s.l., *Quebrada Navidade* at 2460 m a.s.l. and *El Tiro* at 2800 m a.s.l. (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 and tubes were screwed to wooden pales and installed 1 m above-ground. A table tennis ball was placed into each funnel to prevent the sample from evaporating. According to IAEA standard procedures, samples were filled and stored in 2 ml brown glass vials covered by silicone septa (Mook, 2000).

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

Total precipitation sums between each event sampling were also measured in the collectors. Climate data from stations near ECSF and *El Tiro* were also used to investigate the influence of climatic parameters (relative humidity (%), air temperature (°C), rainfall amount and intensity (mm h^{-1}) and wind direction (°) and speed (m s^{-1})) on the isotopic composition of the samples. The wind direction of air masses moving over the study area was measured at the *El Tiro*. 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 δ^{18}O and δ^{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 δ^{18}O and δ^{2}H isotope signatures in an optical cell. Isotope ratios are

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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 δ^{18}O and 0.6‰ for δ^{2}H (LGR, 2012).

Data preparation was conducted by excluding outliers from the repetitive measurements. 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. 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 70 km southwest of the study area.

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. Isotopic compositions of open rainfall range from −16.5 to 2.7‰ for δ^{18}O and from −120.2 to 30.8‰ for δ^{2}H. 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.

In comparison to the global meteoric water line ($\delta^{2}\mathrm{H} = 8 \times \delta^{18}\mathrm{O} + 10$‰) defined by Craig (1961) the local meteoric water line for all 26 events ($\delta^{2}\mathrm{H} = 8.31 \times \delta^{18}\mathrm{O} + 14.47$‰) shows a slightly higher slope, which is still in good agreement with the slope expected under equilibrium conditions represented by the GMWL. The higher intersect (deuterium excess) of the local meteoric water line is most likely attributable to re-evaporated precipitation reaching the study area during the investigation period.

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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. Figure 2 shows the $\delta^{18}O$ and $\delta^{2}H$ isotope signatures of all sampled events. 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 of isotope signatures.

3.1 Altitude effect

To separate the altitude effect from the temporal variation, it 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 (Figs. 3 and 4). On average, the $\delta^{18}O$ altitude effect is -0.22 ‰ $\times$ 100 m^{-1} and for $\delta^{2}H$ it amounts to -1.12 ‰ $\times$ 100 m^{1}. As usual for tropical regions (Sturm et al., 2007), it lies within the lower part of the ranges reported in literature (Table 2). Most $\delta^{18}O$ event lapse rates of the present study are between -0.1 and -0.4 ‰ $\times$ 100 m^{-1} ($\delta^{2}H$: -0.8 to -1.5 ‰ $\times$ 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 6 September, 1 October and 21 October). 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.

In the studies of Gonfiantini et al. (2001) and Peng et al. (2010), a seasonality of the altitude effect is reported. The authors explain this by the larger lapse rate (temperature vertical gradient) during rainy months. During the investigation period, no such seasonal 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

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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 than for the rest of the investigation period (Fig. 2). Concentrations of δ^{18}O range between −8 to +2 ‰ for trade wind related events and −16.5 to −3.6 ‰ for other events (δ^{2}H: −55 to 30 ‰ and −120.2 to −27 ‰, respectively). Mean values of δ^{18}O are −2.9 ‰ for trade wind related precipitation and −9.1 ‰ for other precipitation events (δ^{2}H: −8.8 ‰ and −63 ‰).

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 Figs. 2 and 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) (δ^{18}O: −7.0 to 0.3 ‰) and Rhodes et al. (2011) (δ^{18}O: −3.9 to −1.3 ‰) for dry seasons. Analogously, values for the period

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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 3000 m a.s.l. and take up large amounts of recycled moisture over the Amazon Basin when coming from the SE. This moisture is enriched in heavy isotopes. Reaching the Andes, the air masses are orographically lifted and thus subject to rainout (Scholl et al., 2002). Hence, 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 (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 to investigate the influence of recycled moisture from the Amazon Basin on the isotopic composition of precipitation events (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 14.6 ‰ and hence, is significantly higher than for other events (d = 9.8 ‰). 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 in mid-October (Fig. 6). 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

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be high all year long. Since they did not measure both δ^2H and δ^{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; 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 δ^{18}O and δ^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 ‰ × 100 m^{-1} ($p < 0.01$). Gonfiantini et al. (2001) report that the increase of deuterium excess with altitude is predominantly present at high relative humidity, which are prevailing in the study area. However, there must be additional factors to explain the altitude effect of deuterium excess (Gat et al., 2000).

4 Conclusions

The stable isotopic composition of precipitation collected in the San Francisco catchment showed strong temporal variations consistent with differences in weather conditions and the origin of air masses. Elevated deuterium excess values evidence 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.

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

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

Combining seasonal and spatial variations of δ and deuterium excess can provide an effective tool for tracing moisture through the hydrological cycle. Further work will use the 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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Table 1. Results of the validation experiment. Temperature and relative humidity during the validation experiment. Day- and nighttime temperatures were programmed in 12-h-cycles.

scenario	daytime temperature [°C]	nighttime temperature [°C]	Relative humidity [%]	slope δ^2H [‰ d^{-1}]	p	slope δ^{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.

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Table 2. Altitude effect of δ^2H and δ^{18}O in precipitation from various sites around the world.

Author	δ^2H ‰ 100 m^{-1}	δ^{18} ‰ 100 m^{-1}	Location
Yurtsever and 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 and Oeschger (1980)	–	−0.25	Switzerland (< 2000 m)
Siegenthaler and Oeschger (1980)	–	−0.09	Switzerland (> 2000 m)
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

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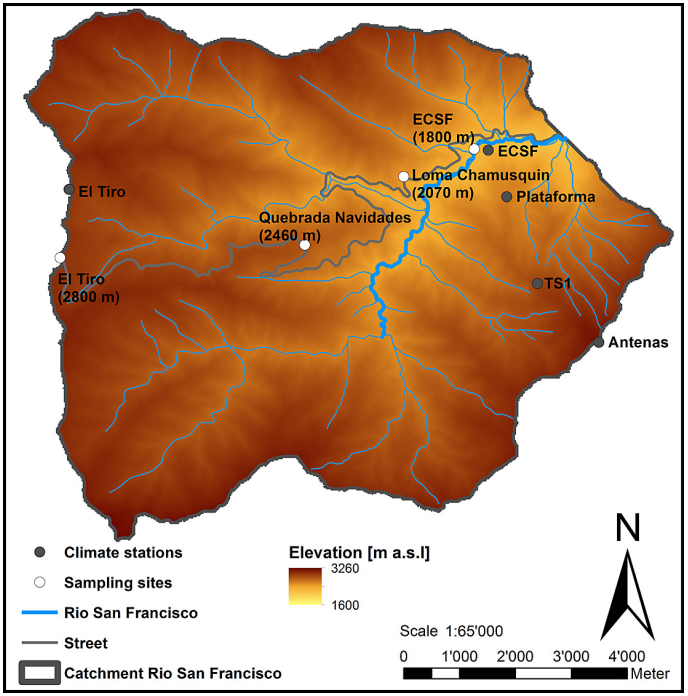

Fig. 1. Investigation area with sampling sites and climate stations.

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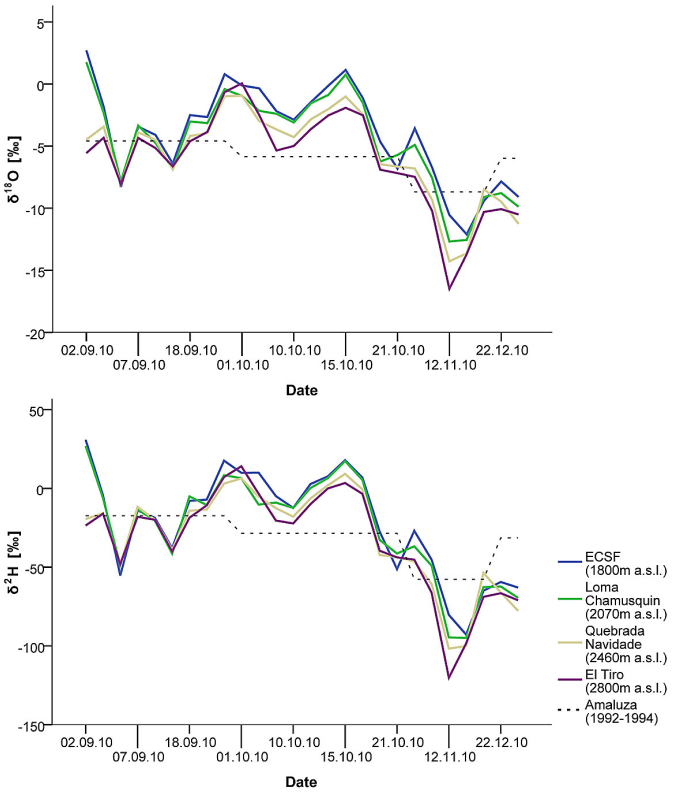

Fig. 2. $\delta^{18}O$ and $\delta^{2}H$ isotope signatures of all sampled events compared to weighted monthly means from GNIP station Amaluza.

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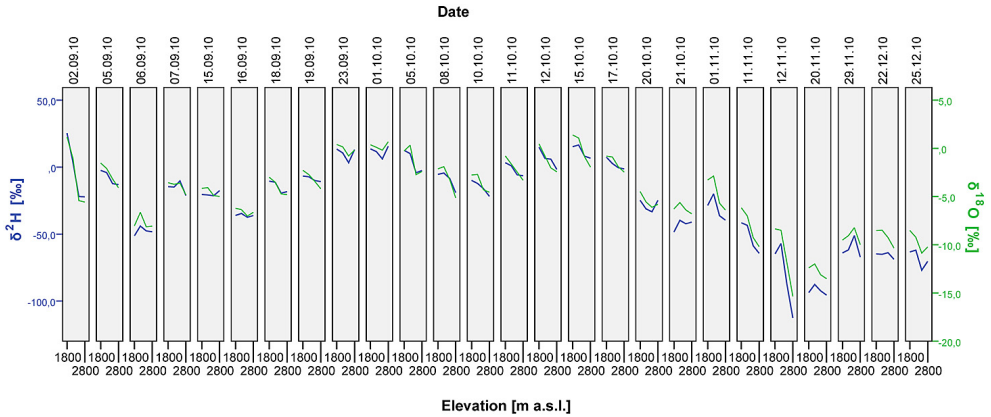

Fig. 3. Altitude effect and temporal variation of δ^2H and δ^{18}O isotope signature in precipitation.

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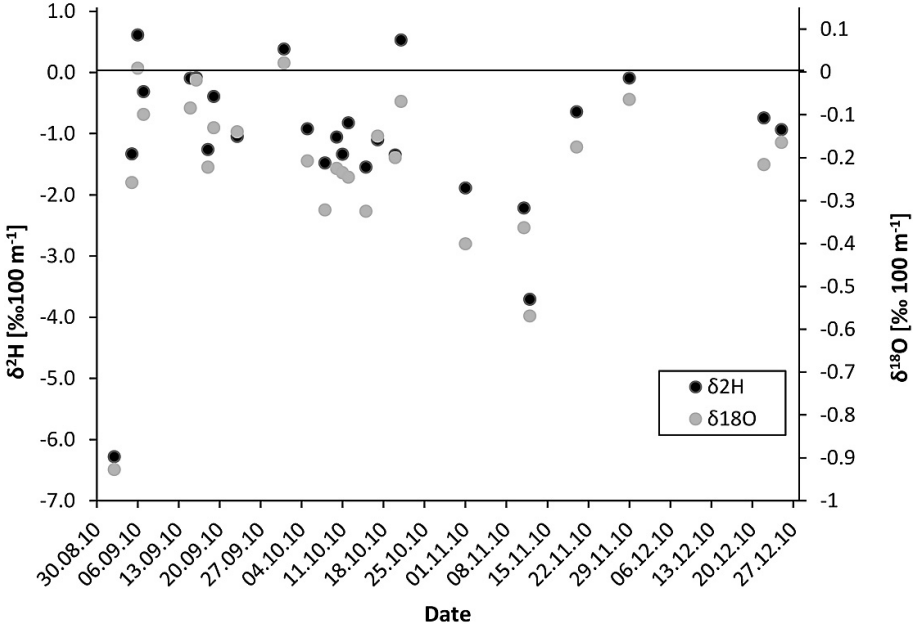

Fig. 4. Event based altitude effect of $\delta^{18}O$ and $\delta^{2}H$ isotope signatures in precipitation. The majority of the events show a depletion of heavy isotopes with altitude (i.e. a negative lapse rate). Only during 3 events for ^{2}H and 2 events for ^{18}O out of 26 events an enrichment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

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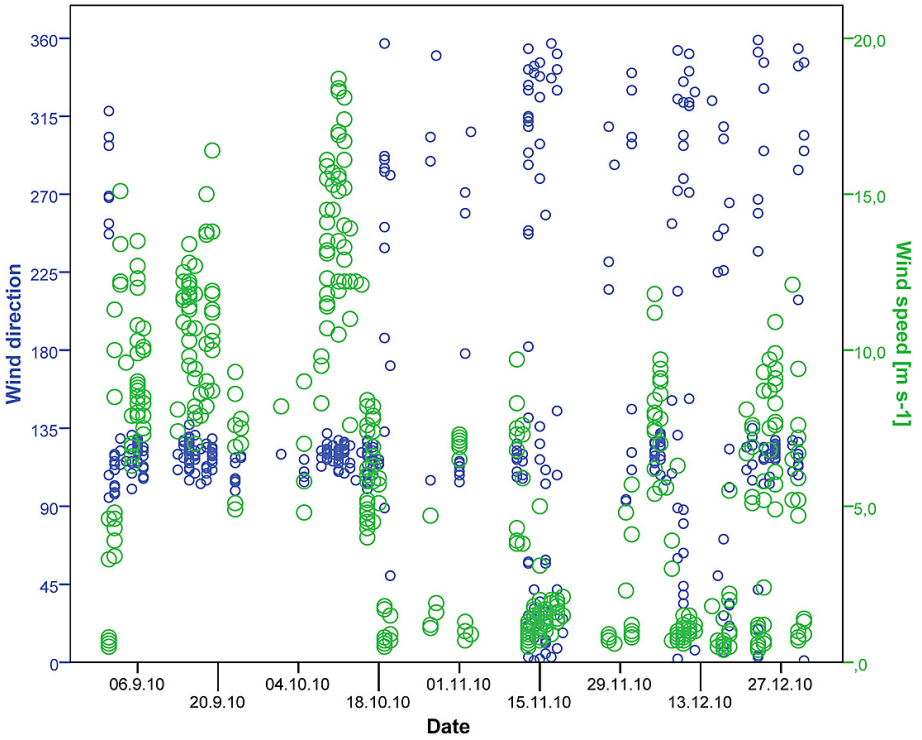

Fig. 5. Wind direction and wind speed during precipitation events at *El Tiro* climate station. From Mid-October on, when trade winds are ebbing, wind direction is less clearly defined and windspeeds are lower.

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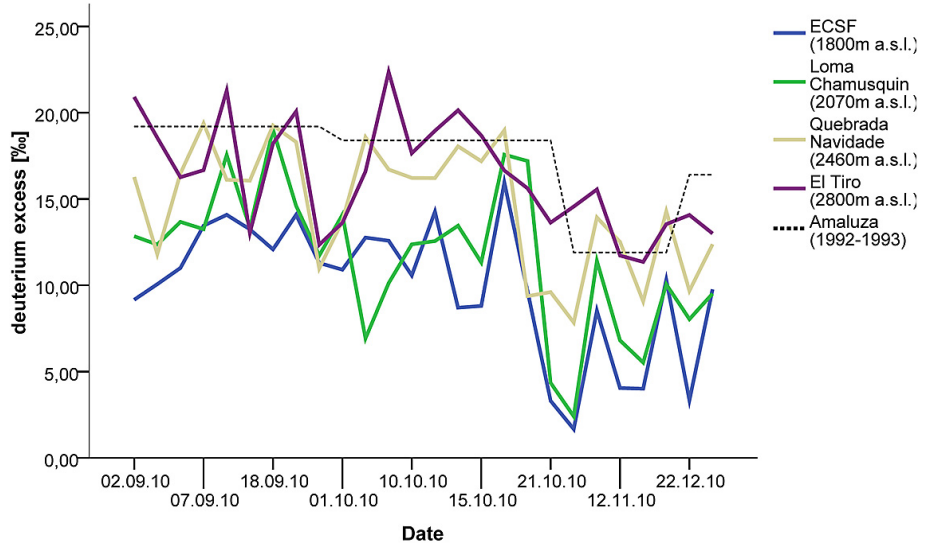

Fig. 6. Deuterium excess of precipitation events at the four sampling sites compared to monthly mean deuterium excess at GNIP station Amaluza.

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