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1 **Isotopic equilibrium between raindrops and water vapor during the onset**  
2 **and the termination of the 2005-2006 wet season in the Bolivian Andes**

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19

20 **Abstract**

21 The isotopic equilibrium state between precipitation and low-level water vapor is a common  
22 assumption in numerous paleoclimate and atmospheric studies based on water stable isotopes.  
23 However, the paucity of field observations limits the validation of this assumption. This study  
24 examines the isotopic equilibrium state from event-based precipitation and daily near-surface  
25 water vapor samples collected during the onset and the termination of the 2005-2006 wet  
26 season in the Bolivian Andes (Zongo valley, 16°09'S, 68°07'W). Our observations show that  
27 the observed isotopic composition of precipitation ( $\delta D_p$ ) deviates from the theoretical isotopic  
28 composition of precipitation at equilibrium with water vapor ( $\delta D_{p\_eq}$ ). Disequilibriums  
29 ( $\Delta D_{p\_eq} = \delta D_p - \delta D_{p\_eq}$ ) are mostly negative (73%), indicating that precipitation is more  
30 depleted than a condensate that would have been formed from surface water vapor, and half  
31 of them are between -10 and +10‰. They are significantly correlated to  $\delta D_p$  ( $r^2=0.30$ ,  $n=70$ ,  
32  $p<0.001$ ) suggesting that controls on  $\delta D_p$  also impact  $\Delta D_{p\_eq}$ . Although equilibrium state does  
33 not prevail at the individual rain event scale, a strong relationship is observed between  $\delta D_p$   
34 and  $\delta D_{p\_eq}$  over the whole period of field samplings ( $r^2=0.86$ ,  $n=70$ ,  $p<0.001$ ). The review of  
35 possible causes to explain the disequilibriums shows that below-cloud rain evaporation and  
36 diffusive exchanges are little involved. Other local processes such as rain type, condensation  
37 conditions and surface water recycling appear as better candidates to explain  $\Delta D_{p\_eq}$ . Lastly,  
38 we explore how local processes affect  $\delta D_p$ . We show that large-scale dynamic along air  
39 masses history is dominant (nearly 80%) to explain  $\delta D_p$  whereas local effects are dominant to  
40 explain deuterium excess in precipitation. In consequence, we conclude that  $\delta D_p$  is a correct  
41 candidate to examine and to reconstruct large-scale atmospheric processes from past to  
42 present time scales.

43 **Keywords:**

44 Water stable isotopes, isotopic equilibrium, below-cloud processes, Bolivia, Andes.  
45

46

## 47 **1-Introduction**

48 Stable isotopes of precipitation and water vapor are increasingly cited as a useful tool  
49 to explore a range of atmospheric processes (Galewsky et al., 2016 for a recent review).  
50 Stable isotopes of precipitation are also widely recognized to reconstruct past environment  
51 and climate. Usually, the isotopic composition of water is defined as follows in per mill (‰):

$$52 \quad \delta^{18}\text{O} \text{ or } \delta\text{D} (\text{‰}) = \left( \frac{R_{\text{sample}}}{R_{\text{SMOW}}} - 1 \right) \cdot 1000 \quad (1)$$

53 Where R is the isotopic ratio between heavy ( $\text{H}_2^{18}\text{O}$  for  $\delta^{18}\text{O}$  and  $\text{HD}^{16}\text{O}$  for  $\delta\text{D}$ ) and  
54 light ( $\text{H}_2^{16}\text{O}$ ) molecules in rain or water vapor and SMOW (Standard Mean Ocean Water) is  
55 the international standard for water isotopic measurements (i.e.,  $\delta_{\text{SMOW}} = 0\text{‰}$  by definition).

56 In clouds, the formation of droplets by condensation of ambient water vapor follows  
57 the thermodynamic law that leads the two phases towards isotopic equilibrium. This isotopic  
58 equilibration has been first postulated and confirmed by Stewart (1975) by simulating rainfall  
59 in a chamber where saturated conditions prevailed. Then, raindrops formed in upper  
60 atmospheric levels continuously exchange water molecules with the surrounding water vapor  
61 as they fall. These exchanges tend to re equilibrate isotopically the two water phases at each  
62 atmospheric level. They are all the more effective the closer the atmosphere is to saturation. In  
63 unsaturated air, rain also partially evaporates below clouds. In addition to the aforementioned  
64 equilibrium fractionation, the different water molecules diffusivities ( $\text{H}_2^{18}\text{O}$  and  $\text{HD}^{16}\text{O}$   
65 diffuse lower than  $\text{H}_2^{16}\text{O}$ ) induce a kinetic isotopic fractionation during water evaporation.  
66 From both  $\delta^{18}\text{O}$  and  $\delta\text{D}$ , the deuterium excess parameter is commonly calculated and used to  
67 explore processes mainly controlled by kinetic isotopic fractionation. It is defined as  
68 (Dansgard ,1964):

$$69 \quad d = \delta\text{D} - 8 \cdot \delta^{18}\text{O} \quad (2)$$

70 The balance between thermodynamic and kinetic processes (and so the isotopic  
71 equilibrium state between raindrops and ambient vapor) is influenced by below-cloud relative  
72 humidity as well as rain and cloud characteristics (height of condensation, height of melting  
73 layer, height of cloud base, droplets size and precipitation rate) (Managave et al., 2016; Wang  
74 et al., 2016; Aggarwal et al., 2016). Recycling of evapotranspired moisture from the surface  
75 can also prevent the isotopic equilibrium state (Anderson et al., 2002; Aemissegger et al.,  
76 2015; Desphande et al., 2010; Lekshmy et al., 2018).



77 As a consequence, the question of the distance to the isotopic equilibrium for  
78 precipitation and water vapor is raised (Stewart, 1975) as it is of large relevance for a set of  
79 studies:

80 - The isotopic equilibrium is an initial hypothesis in a number of modeling studies requiring  
81 the isotopic composition of water vapor ( $\delta_v$ ) as a key parameter (Craig and Gordon, 1965):  
82 because the observations of  $\delta_v$  are still few compared to the observations of the isotopic  
83 composition of precipitation ( $\delta_p$ ), the later is often used to deduce  $\delta_v$  based on the equilibrium  
84 state;

85 - The understanding of isotopic exchanges between raindrops and ambient water vapor can  
86 offer better constraints on below-cloud atmospheric processes and on the vertical structure of  
87 precipitation systems (Bony et al., 2008; Risi et al., 2008; Aemissegger et al., 2015; Lekshmy  
88 et al., 2018; Graf et al., 2019) provided that all processes influencing the rain-water vapor  
89 isotopic exchanges can be disentangled (Graf et al., 2019);

90 - Paleoclimate reconstructions based on archives of  $\delta_p$  assume that the later is a correct proxy  
91 for  $\delta_v$  (through the isotopic equilibrium), which is itself considered an integrated tracer of all  
92 climate processes along air masses trajectory. Post-condensation exchanges in the atmosphere  
93 between water vapor and precipitation thus raises the question of the representativeness of  $\delta_p$   
94 compared with  $\delta_v$ .

95 Simultaneous isotopic observations in rain and water vapor are needed to examine  
96 whether equilibrium state prevails and, if appropriate, to identify the causes inducing a  
97 departure from equilibration. Despite the recent advent of commercial laser absorption  
98 spectrometers to measure in situ water vapor isotopic ratios, simultaneous observations of  $\delta_p$   
99 and  $\delta_v$  are still limited although in progression (Tremoy et al., 2014; Aemissegger et al., 2015;  
100 Graf et al., 2019 for some recent examples). The lack of observations in both water phases is  
101 especially apparent in tropical and subtropical environments. Only a few studies have  
102 investigated the characteristics of water and rain isotopic ratios in subtropical Northern  
103 latitudes where precipitation occur in a summer monsoon context with the following  
104 characteristics: large vapor content during saturation at relatively high temperature, potential  
105 large contribution of evapotranspiration to surface water vapor, presence of convective and  
106 stratiform rains. In West Africa (13.50°N, 2.08°E), Tremoy et al. (2014) explored the rain-  
107 water vapor interaction along 74 squall lines during three monsoon seasons (2010, 2011 and

108 2012). They showed that the isotopic equilibrium state strongly varies from one rain to  
109 another and along the monsoon season: precipitation and water vapor are very close to the  
110 equilibrium state during the core of the monsoon whereas disequilibrium appears at the  
111 beginning and at the end of the rainy season. Evaporation of droplets is the main process  
112 involved in isotopic disequilibrium leading to an isotopic enrichment of water vapor at the  
113 start of the season (high level of evaporation rate, low relative humidity and enriched  
114 precipitation) and to an isotopic depletion of water vapor at the end of the monsoon (lower  
115 evaporation rate and very depleted rain). In Southern peninsular India (8.76°N, 77.12°E and  
116 11.51°N and 76.02°E), during the monsoon season, Lekshmy et al. (2018) also showed that  
117 disequilibrium between water vapor and rain varies throughout the rainy season with low  
118 disequilibrium during the pre-monsoon and the core of the monsoon and higher  
119 disequilibrium at the end of the monsoon. They attribute the equilibrium rate to the partition  
120 between stratiform and convective precipitation. They argue that during stratiform  
121 precipitation vertical mixing can be reduced and below-cloud water vapor can be enriched by  
122 transpired moisture. Further north, in Western India (23.03°N, 72.56°E), Deshpande et al.  
123 (2010) and Srivastava et al. (2015) showed that the isotopic equilibrium prevails along the  
124 2007 monsoon except during its onset and retreat. Further southeast, in the Bay of Bengal, in  
125 the maritime context of Anadaman Islands (11.66°N, 92.73°E), Sinha and Chakraborty (2020)  
126 concluded that water vapor and rain are close to the equilibrium state in average over the  
127 entire 2015 Indian monsoon season. In a case study during the 2012 summer season in  
128 Taiwan (25.02°N, 121.50°E), Laskar et al. (2014) showed that the isotopic equilibrium state is  
129 attained during a typhoon occurring in the late summer monsoon whereas rain and water  
130 vapor significantly deviate from the isotopic equilibrium during an equally large rain event  
131 earlier in the season. They incriminated long-range transport and high level of isotopic  
132 distillation as potential explanations for very depleted rains and thus for a long distance to  
133 equilibrium state. In the Chinese subtropics (28°18N, 112.93°E), Yao et al. (2018) showed  
134 that water vapor and precipitation are in or near an equilibrium state during the summer  
135 monsoon season. Although all these studies explored different tropical and subtropical regions  
136 (India, Asia and Africa) with different environment, atmospheric dynamic and climate, they  
137 all clearly showed that the isotopic equilibrium state strongly varies throughout the monsoon  
138 season and that, most of the time, the equilibrium assumption is fulfilled (or almost fulfilled)  
139 during the core of monsoon, i.e when atmospheric conditions are close to saturation with high  
140 surface temperatures (>20°C). They also suggest that a large number of processes are  
141 involved to explain the equilibrium deviation depending on the site location (type of rain,

142 below-cloud evaporation of droplets, altitude of condensation, evapotranspiration, variety of  
143 the moisture sources and distance of the site to the moisture sources).

144 To complete these previous studies and to help bridging the knowledge gap in  
145 Southern Hemisphere, we present in this paper simultaneous isotopic observations in near-  
146 surface water vapor and precipitation in the Bolivian Andes (tropical South America), on two  
147 sites at low and high elevation, at the onset and at the end of the 2005-2006 rainy season.  
148 Several studies have focused on the controls on  $\delta_p$  in this Andean region from subseasonal to  
149 interannual timescale and on the potential of  $\delta_p$  for paleoclimate reconstructions (Vimeux et  
150 al., 2005; Vuille and Wener 2005; Vimeux et al., 2011; Guy et al., 2019). They concluded that  
151 the main control of  $\delta_p$  is the degree of rainout upstream the Andes, along air masses  
152 trajectories, and that the local amount effect is a poor factor in controlling  $\delta_p$ . Vimeux et al.  
153 (2011) and Guy et al. (2019) also reported deuterium excess observations in rain ( $d_p$ ). They  
154 did not conclude on what are the meteorological controls on  $d_p$  but they noticed that no  
155 relationship appears between  $d_p$  and moisture origins and pathways. However, isotopic  
156 exchanges between rain and water vapor, their interest in examining atmospheric processes  
157 and their potential influence on the climate information contained in  $\delta_p$  have never been  
158 investigated there.

159 A description of the sites, of the instrumental setup and of isotopic analyses is done in  
160 section 2. Methodology is detailed in section 3. Section 4 describes the isotopic observations  
161 and the equilibrium state between water vapor and rain. In section 5, we explore to what  
162 extent local processes deviate rain and water vapor from the isotopic equilibrium. Further, we  
163 examine in which extent  $\delta_p$  is a correct proxy of  $\delta_v$  (section 6).

## 164 **2- Precipitation and water vapor sampling during the 2005 and 2006 field** 165 **campaigns**

### 166 **2-1 Sampling sites**

167 Water vapor and precipitation were collected simultaneously at two sites in the Zongo  
168 Valley (Bolivian Andes): at Huaji ( $16^{\circ}02'28''\text{S}$ ,  $67^{\circ}58'38''\text{W}$ , 945 m, at the base of the  
169 valley) and at Plataforma ( $16^{\circ}16'55''\text{S}$ ,  $68^{\circ}07'17''\text{W}$ , 4750 m, at the top of the valley)  
170 (Figure 1). This valley belongs to the Bolivian Company of Electric Energy (COBEE)  
171 providing electric power for La Paz (capital city of Bolivia). Pluviometers and water vapor  
172 collection systems are located nearby the hydropower plants. The distance between the two

173 stations is about 30 km as the crow flies (~40 km by road). This valley is located on the  
174 northeast side of the Bolivian Cordillera Real and links up the Amazon basin with the Andean  
175 summits at the latitude of La Paz (Figure 1). The atmospheric circulation in tropical South  
176 America is characterized by easterly trade winds which transport moisture from the Atlantic  
177 Ocean and from the central Amazon region toward the eastern Andes. The later act as a  
178 barrier and deviate the moisture flow parallel to the Andes toward the southern Amazon and  
179 the subtropical region of South America (the so-called South American Low-Level Jet  
180 (SALLJ) (Marengo et al., 2004). At the synoptic-scale, a southwesterly direction low level air  
181 flow, associated to the SALLJ structure, penetrates in the Andes through the east valleys  
182 (Vimeux et al., 2011; Junquas et al., 2018) (Figure 1). The orography of the valleys locally  
183 strengthens this moisture transport by both mechanical channelization of the moisture flux  
184 and thermally driven surface upslope flow developing along the Amazon slopes (Junquas et  
185 al., 2018). The uplift of air masses can be reduced or reversed during nighttime in the upper  
186 part of the valleys because of downslope flows induced by katabatic winds (Junquas et al.,  
187 2018). This nighttime reverse moisture flow is probably unusual in the Zongo valley during  
188 the rainy season (Junquas et al., 2018) as supported by the uniformity of the isotopic  
189 composition of precipitation along the valley regardless of rainy hours (Vimeux et al., 2011).  
190 There are however a few exceptions: some punctual isotopic discrepancies can be seen in  
191 precipitation between Huaji and Plataforma. They are attributed to a westerly flow from the  
192 Bolivian Altiplano (Vimeux et al., 2005, 2011) that can develop during weak easterly winds  
193 and reaches the top of the valley. This diurnal local atmospheric circulation is also supported  
194 by a 1 km-resolution simulation of moisture flows around the Zongo valley carried out with  
195 the WRF model (Weather Research and Forecasting model) (C. Junquas and J-P. Sierra, pers.  
196 comm.).

197 We chose to sample rain and water vapor at these two extreme locations in this valley  
198 for different reasons. First, we wanted to examine the water vapor-rain interactions at  
199 locations undergoing different meteorological conditions (temperature and relative humidity,  
200 Table 1). Indeed, the atmosphere at Huaji is always very close to saturation conditions from  
201 October to April and diffusive exchanges are expected to dominate rain-water vapor  
202 interactions. In contrast, lower relative humidity at Plataforma could promote evaporation of  
203 droplets under the cloud although temperature is very low (Table 1). Secondly, different types  
204 of surface are encountered at the two sites. Vegetation dominates at Huaji while bare soil is  
205 present at Plataforma. In addition, Huaji site is close to the Zongo stream resulting in a

206 possible secondary moisture source. As a result, an evapotranspired moisture flux could be  
207 encountered at Huaji unlike Plataforma. At Plataforma, the site is at about 130 m from the  
208 Zongo water reservoir, at the base of the Zongo glacier (16°16'S, 68°09'W, from 4900 to 6000  
209 m), in which glacier runoff is stored by COBEE. The lake reservoir can potentially evaporate  
210 and contribute to local humidity. However, given the mean temperature at this site during our  
211 field campaigns (~2°C), this water body is unlikely to be a significant source of surface water  
212 vapor relative to the ascent of moisture from the base of the valley. Then, event-based and  
213 monthly rains have been sampled at both sites for isotopic analyses since 1999 (Vimeux et al.,  
214 2005, 2011). The proximity of the COBEE hydropower plants allowed us to have dedicated  
215 observers monitoring the pluviometers since 1999, guaranteeing the quality of the  
216 observations. Thus, we only needed to set up the water vapor collection at a few meters from  
217 pluviometers. At last, the available precipitation data in this valley over several years allowed  
218 us to characterize the 2005-2006 rainy season comparatively to the other years.

219 Two field campaigns were organized at the onset (October-November) and at the  
220 termination (March-April) of the 2005-2006 wet season. We chose those transition periods as  
221 they are supposed to offer (1) a sufficient atmospheric moisture level to collect enough water  
222 vapor within ~24h for mass spectrometer analyses and (2) a balance between time periods  
223 with atmospheric conditions close to saturation within the heart of the rainy season (when  
224 diffusive exchanges are supposed to control isotopic processes leading to the equilibrium) and  
225 time periods with only a few rain events, during the start and the end of the dry season, with  
226 lower surface relative humidity (when evaporative processes under clouds are supposed to  
227 take place). During the first campaign, water vapor sampling started on October 23<sup>rd</sup>, 2005 at  
228 both stations and ended on November 21<sup>st</sup>, 2005 (November 27<sup>th</sup>, 2005) at Huaji  
229 (Palataforma). The second campaign started on March 15<sup>th</sup>, 2006 (March 11<sup>st</sup>, 2006) and  
230 ended on May 1<sup>st</sup>, 2006 (April 30<sup>th</sup>, 2006) at Huaji (Plataforma).

## 231 **2-2 Water vapor and rain collection**

232 Water vapor was collected using the cryogenic technique described for example in  
233 Yakir and Wang (1996), or Yakir and Sternberg (2000) (laser instruments based on  
234 Wavelength-Scanned Cavity Ring Down Spectroscopy (WS-CRDS) (Gupta et al., 2009) were  
235 not available in 2005-2006). The two cryogenic systems drew air from an intake at about ~2.5  
236 m above the surface through a heated PFA (perfluoroalkoxy) tubing to avoid any  
237 condensation. The length of the heated tubing between the inlet and the cold trap was about 3

238 m. The cold trap was immersed in ethanol-dry ice maintained at about -90 °C using a  
239 cryocooler (Thermo Scientific HAAKE EK 90 model). The cold trap was made up of two  
240 parts: the main trap was a Pyrex spiral double trap and a secondary Pyrex spiral single trap  
241 was placed right after to check that all water vapor was captured. The air flow-rate was  
242 regulated at ~45L/hour to avoid any ice plug at the entrance of the main trap (at Plataforma).  
243 A KNF pump (N86 KN.18 model) was placed on the outlet line. For each campaign, the two  
244 cryogenic systems used at Huaji and Plataforma were tested by simultaneously collecting  
245 water vapor during one week at Huaji before the beginning of the campaign and were  
246 validated by comparing isotopic results. In order to capture enough water vapor volume for  
247 mass spectrometer analyses, water vapor was collected during time periods from 14h to 31h  
248 with a majority of collections around 23h. All the iced water samples were recovered into  
249 liquid water on site. Water volumes varied between 1 ml (at Plataforma) up to ~20 ml (at  
250 Huaji). Precipitation was collected at the two stations on an event-based resolution,  
251 immediately after the rain event as described in Vimeux et al. (2011).

### 252 **2-3 Isotopic analyses and on site meteorological measurements**

253 In 2005, 23 (30) water vapor samples and 26 (30) precipitation events were collected  
254 at Huaji (Plataforma). The second field campaign in 2006 was longer and 42 (41) water vapor  
255 samples and 48 (40) precipitation events at Huaji (Plataforma) were collected. Both  $\delta^{18}\text{O}$  and  
256  $\delta\text{D}$  and were measured on water vapor and precipitation by mass spectrometers (Finnigan  
257 MAT 252 coupled with the usual  $\text{CO}_2\text{-H}_2\text{O}$  equilibration for  $\delta^{18}\text{O}$  and LSCE home-made  
258 mass spectrometer coupled with water reduction on 600°C-heated uranium for  $\delta\text{D}$ ) except for  
259 some water samples with volumes lower than 3 ml. In that case, we were not able to measure  
260  $\delta^{18}\text{O}$  (samples are now empty and they cannot be measured with a WS-CRDS laser analyzer  
261 requiring smaller water volumes). This situation occurred for example for a number of  
262 Plataforma water vapor samples during 2005 and 2006. The other gaps in water vapor isotopic  
263 ratios record correspond to days for which the cryogenic system had technical problems. The  
264 accuracies of measurements are of  $\pm 0.5\text{‰}$  and  $\pm 0.05\text{‰}$  for  $\delta\text{D}$  and  $\delta^{18}\text{O}$  respectively, leading  
265 to an average quadratic analytical uncertainty on d lower than  $\pm 0.7\text{‰}$  for both phases  
266 (hereafter,  $d_v$  and  $d_p$  for water vapor and precipitation respectively).

267 During both campaigns, 10-min resolution surface temperature and relative humidity  
268 were recorded using a HOBO® sensor from Onset Computer Corp at Huaji. At Plataforma,  
269 30-min surface temperature and relative humidity were recorded by a meteorological station

270 on site (TRIES-CLIMA model).

## 271 **3- Methodology**

### 272 **3-1 Calculation of the distance to the isotopic equilibrium**

273 In this paper, we explore how far from the isotopic equilibrium with surrounding water  
274 vapor are the raindrops. As a consequence, the isotopic disequilibrium ( $\Delta D_{p\_eq}$ ) is defined as  
275 the difference between the observed  $\delta D_p$  and the calculated isotopic composition of  
276 precipitation at equilibrium with water vapor ( $\delta D_{p\_eq}$ ) as:

$$277 \quad \Delta D_{p\_eq} = \delta D_p - \delta D_{p\_eq} \quad (3)$$

278 where  $\delta D_{p\_eq}$  is calculated according to:

$$279 \quad \alpha_{eq} = \frac{\delta D_{p\_eq} + 1000}{\delta D_v + 1000} \quad (4)$$

280 where  $\alpha_{eq}$  ( $>1$ ) is the precipitation-water vapor equilibrium fractionation coefficient  
281 (Majoube, 1971).

282 For each  $\delta D_v$  measurement, we examine whether rain occurred during the collection of  
283 water vapor. If this is the case,  $\alpha_{eq}$  is calculated considering the average temperature over the  
284 rain event considered, of composition  $\delta D_p$ . When several rain events occurred during the time  
285 period of water vapor collection, temperature is averaged over the different rain events to  
286 calculate  $\alpha_{eq}$  and the amount-weighted  $\delta D_p$  is used in Equation (3).

287 In addition to  $\Delta D_{p\_eq}$ , we similarly define  $\Delta d_{p\_eq}$  accounting for the disequilibrium  
288 relative to deuterium excess as:

$$289 \quad \Delta d_{p\_eq} = d_p - d_{p\_eq} \quad (5)$$

290 The definition of  $\Delta D_{p\_eq}$  offers the possibility to review processes potentially involved  
291 in departure from equilibrium state based on the sign of  $\Delta D_{p\_eq}$ : a negative disequilibrium  
292 suggests that precipitation is more depleted than a condensate that would have been formed  
293 from surface water vapor and in contrast a positive disequilibrium suggests that precipitation  
294 is more enriched than expected at equilibrium. The combination of  $\Delta D_{p\_eq}$  and  $\Delta d_{p\_eq}$  provides  
295 an original metric to discuss below-cloud atmospheric processes as used by Graf et al. (2019)

296 (see section 3-2).

### 297 **3-2 Below-cloud evaporation and diffusion processes**

298 When raindrops fall through the atmosphere in unsaturated conditions, they experience  
299 evaporation with kinetic fractionation and they partially (or fully) re equilibrate by diffusion  
300 with the ambient vapor. The isotopic exchanges that take place between falling drops and  
301 water vapor through evaporation and diffusion processes are treated in a unified manner in the  
302 Stewart's theory (Stewart, 1975).

303 We consider a droplet ( $P_0$ ) in the cloud with an initial mass  $m_{p0}$  of isotopic ratio  $R_{p0}$ , in  
304 equilibrium with cloud water vapor of isotopic ratio  $R_{v0}$ , falling into an air of isotopic ratio  $R_v$ .  
305  $R_v$  is actually the surface isotopic ratio assuming a strong mixing layer under the cloud where  
306 evaporation proceeds.  $R_{p0}$  is typically more depleted than the precipitation at the isotopic  
307 equilibrium with  $R_v$  so that  $R_{p0} < \alpha_{eq} R_v$ . As raindrop evaporation proceeds, we note  $m_p$  the rain  
308 mass and we define the residual fraction of liquid,  $f$ , as:

$$309 \quad f = \frac{m_p}{m_{p0}} \quad (6)$$

310 As a consequence, the parameter  $f$  varies from 1 (no evaporation) to 0 (total  
311 evaporation).

312 The precipitation isotopic ratio  $R_p$  is given as a function of  $f$  by Stewart et al. (1975):

$$313 \quad R_p = f^\beta \cdot R_{p0} + (1 - f^\beta) \cdot \gamma \cdot R_v \quad (7)$$

314 where  $\beta$  and  $\gamma$  coefficients are defined as:

315

$$316 \quad \beta = \frac{1 - \alpha_{eq} \cdot (1 - h) \cdot \left(\frac{D}{D'}\right)^n}{\alpha_{eq} \cdot (1 - h) \cdot \left(\frac{D}{D'}\right)^n} \quad (8)$$

$$317 \quad \gamma = \frac{\alpha_{eq} \cdot h}{1 - \alpha_{eq} \cdot (1 - h) \cdot \left(\frac{D}{D'}\right)^n} \quad (9)$$

318 where  $D/D'$  is the ratio of molecular diffusivities in air of the most ( $H_2^{16}O$ ) and less  
319 ( $H_2^{18}O$  or  $HD^{16}O$ ) abundant isotopologues (1.0285 and 1.0251 for  $H_2^{18}O$  and  $HD^{16}O$ )



320 respectively) (Merlivat, 1978),  $n$  is a parameter that modulates the water molecules diffusivity  
 321 and that depends on drop size and  $h$  is the ambient relative humidity. In our calculations, the  $n$   
 322 parameter is set to 0.58, corresponding to droplets of 1 mm in diameter (Stewart, 1975; Bony  
 323 et al., 2008).

324 The Stewart's theory assumes that all the droplets have the same size and that the  
 325 water vapor isotopic ratio is not too much affected as evaporation proceeds.

326 Some consequences arise from the Stewart's Equation (7):

327 (1) As evaporation proceeds, raindrop gets enriched and its deuterium excess decreases  
 328 (because HDO diffuses faster than  $H_2^{18}O$ ).  $R_p$  in Equation (7) tends to a target value of  
 329  $R_{p\_target} = \gamma R_v$  ( $f=0$ ). The lower the relative humidity, the higher the target value.  
 330 This implies that if evaporation and diffusive processes explain  $\Delta D_{p\_eq}$ , the later has a  
 331 maximal value of  $1000(\gamma - \alpha_{eq})R_v$  attained for  $f=0$ . The dryer the air is, the more  
 332 strongly the maximum  $\Delta D_{p\_eq}$  can take positive values. Similarly,  $d_p$  tends to a target  
 333 value for  $f=0$  (the lower the relative humidity, the lower the target value) and  $\Delta d_{p\_eq}$   
 334 has a minimal value attained for  $f=0$ .

335 (2) As evaporation proceeds, the distance of the observations to the target value is given  
 336 by  $1-f^\beta$ . For example, for  $f^\beta=0.2$ , 80% of the distance between the isotopic  
 337 composition of  $P_0$  and the one of the target precipitation ( $P_{target}$ ) is achieved. The path  
 338 to the target is traveled all the more efficiently as the evaporated fraction is strong  
 339 (weak  $f$ ) and as  $h$  is strong (in this case, diffusive exchanges are favored and  $\beta$  has  
 340 high values).

341 The quantity  $f^\beta$  in equation (7) can be written in delta notation as:

$$342 \quad f^\beta = \frac{\delta D_p - \delta D_{p\_target}}{\delta D_{p0} - \delta D_{p\_target}} \quad (10)$$

343  $f^\beta$  is calculated here considering  $\delta D$ . It can also be calculated from  $\delta^{18}O$ . The two  
 344 results are very close each other as  $f^\beta$  is mainly controlled by  $f$  and  $h$ . Under such conditions,  
 345 we assume in our study that:

$$346 \quad f^\beta = \frac{\delta D_p - \delta D_{p\_target}}{\delta D_{p0} - \delta D_{p\_target}} = \frac{d_p - d_{p\_target}}{d_{p0} - d_{p\_target}} \quad (11)$$

347 Therefore, if evaporation and diffusion are the unique processes at play, Equation (11)  
 348 applies with a unique initial precipitation  $P_0$  and  $f$  can be calculated. Consequently, in our  
 349 study, for each disequilibrium considered, we seek whether there exists a unique  $P_0$  satisfying  
 350 Equation (11). As done for example in Graf et al., (2019),  $P_0$  can be estimated in a diagram  
 351 representing  $\Delta d_{p\_eq}$  as a function of  $\Delta D_{p\_eq}$  so that the three precipitation  $P_0$  ( $f=1$ ),  $P$  (the  
 352 observation) and  $P_{target}$  ( $f=0$ ) are aligned (see Figure 2 and its legend for explanations). Then,  
 353  $f^B$  and  $f$  can be graphically deduced (or calculated).

354 The previous calculations are not defined at saturation ( $h$  of 100%, pure diffusive  
 355 case). In that case, there is virtually no evaporation and diffusive exchanges dominate  
 356 between raindrop and water vapor as to drive the two phases toward isotopic equilibrium.

### 357 **3-3 Estimation of local versus large-scale processes influence on $\delta_p$**

358 The partition between local and large-scale effects on water vapor and precipitation  
 359 isotopic ratios is examined in this paper using the Risi et al. (2010)'s methodology. It relies on  
 360 the hypothesis that the isotopic composition of water vapor further reflects large-scale  
 361 processes affecting the air masses along its trajectory (e.g. isotopic distillation, vertical mixing  
 362 induced by convection and large-scale subsidence), whereas the isotopic composition of  
 363 precipitation can be affected by local processes such as evaporation of droplets. This method  
 364 does not allow us to discuss the type of local processes involved in the  $\delta D_p$  departure from  
 365  $\delta D_v$  (or  $\delta D_{p\_eq}$ ) but it determines how much local effects affect  $\delta D_p$ . Variations of the later are  
 366 decomposed into a large-scale processes contribution ( $\delta D_v$ ) and a local processes contribution  
 367 ( $\delta D_p - \delta D_v$ ) as follows:

$$368 \quad \delta D_p = \delta D_v + (\delta D_p - \delta D_v) \quad (12)$$

369 Based on Equation (12), we can say that the contribution of large-scale processes to  
 370  $\delta D_p$  can be estimated by the slope (a) of the linear regression of  $\delta D_v$  as a function of  $\delta D_p$ :

$$371 \quad \delta D_v = a \cdot \delta D_p + b \quad (13)$$

372 Similarly, the contribution of local processes to  $\delta D_p$  can be estimated by the slope (c)  
 373 of the linear regression of  $\delta D_p - \delta D_v$  as a function of  $\delta D_p$ :

$$374 \quad \delta D_p - \delta D_v = c \cdot \delta D_p + d \quad (14)$$

375 This decomposition leads to:

376 
$$\delta D_p = a \cdot \delta D_p + c \cdot \delta D_p \quad \text{with } a + c = 1 \text{ and } b = -d \quad (15)$$

377 For example, if large-scale (local) processes fully explain  $\delta D_p$ , the value of a (c) will  
378 be 1 (0) and the value of c will be 0 (1).

379 A similar decomposition method can be applied for deuterium excess, with a large-  
380 scale processes contribution ( $d_v$ ) and a local processes contribution ( $d_p - d_v$ ).

381 As in section 3-1, in order to compare the isotopic composition of water vapor and  
382 precipitation, we have considered rain event(s) occurring within the period of water vapor  
383 sampling. When several rain events occurred during the time period of water vapor collect the  
384 amount-weighted  $\delta D_p$  is used.

## 385 **4- Results**

### 386 **4-1 Precipitation**

387 We compared monthly precipitation amount during the 2005-2006 rainy season (i.e.  
388 from October 2005 to April 2006) with monthly precipitation amount averaged over the rainy  
389 seasons from 2000 to 2011 (from October to April). For this purpose, we used data from 5  
390 monthly pluviometers well stacked from the base to the top of the Zongo valley (Figure 1 and  
391 Vimeux et al., 2005). At each station, the total precipitation from October 2005 to April 2006  
392 is higher by 1.8 to 20.0% compared to the 2000-2011 period (Figure 3a). For each month,  
393 from October 2005 to April 2006, total precipitation over the valley (sum of precipitation  
394 amount over the 5 stations) is higher by 11.0 to 46.6% compared with the mean total  
395 precipitation over 2000-2011, except in February and April 2006 where total precipitation is  
396 lower by 35% and 1% respectively (Figure 3b). Regarding the occurrence of precipitation  
397 events, the 2005-2006 rainy season exhibits a significant number of precipitation events from  
398 March to April 2006 (+190 and +360% of rain events at Huaji and Plataforma respectively  
399 compared with averaged March-April period over 2000-2011).

400 During the two campaigns, we observed orographic rains that develop along the  
401 Zongo valley slope, without convection. Consistently, precipitation rates are low (Table 1).  
402 Focusing only on the rain events that occurred during water vapor sampling, precipitation rates  
403 varied from 0.1 to 16 mm/h (80% of rain events exhibit a precipitation rate lower than 5mm/h

404 and only 4 events have rain rates higher than 10 mm/h) with a mean (median) of 3.5 (2.2)  
405 mm/h. The 68%-confidence interval is between 0.8 and 6 mm/h (precipitation rate follows a  
406 log-normal distribution).

#### 407 **4-2 $\delta D_p$ and $\delta D_v$ at Huaji and Plataforma**

408 During the 2005 and 2006 campaigns, the range of  $\delta D_v$  at Huaji (Plataforma) is -76.7  
409 to -167.4‰ (-101.6 to -233.3‰) with a mean of  $-121.9 \pm 22.6$ ‰ ( $-163.6 \pm 33.6$ ‰), whereas the  
410 range of  $\delta D_p$  is -3.5 to -131.0‰ (-9.3 to -201.7‰) with a mean of  $-63.0 \pm 32.7$ ‰ ( $-$   
411  $111.7 \pm 46.1$ ‰) (Figure 4). Distinctions between the onset and the end of the rainy season are  
412 reported in Table 1. We see that for both water phases, in average, the isotopic depletion is  
413 higher in 2006 than in 2005. This can be explained by the seasonal progressive isotopic  
414 discharge of water vapor along the rainy season due to the cumulative local and upstream  
415 rainout as shown by Vimeux et al. (2005, 2011) and Vuille and Werner (2005).

416 During the two campaigns, we collected water vapor during time periods with no rain  
417 and conversely, a few rain events occurred while the water vapor system was not operational.  
418 Therefore, 70 simultaneous observations of  $\delta D_p$  and  $\delta D_v$  are available at Huaji (37  
419 observations) and Plataforma (33 observations).  $\delta D_p$  and  $\delta D_v$  clearly evolve in parallel at both  
420 sites over the whole period: covariances ( $r^2$ ) are 0.87 (n=37) and 0.83 (n=33) respectively at  
421 Huaji and Plataforma ( $p < 0.001$ ).

#### 422 **4-3 $d_p$ and $d_v$ at Huaji and Plataforma**

423 As for deuterium, deuterium excess exhibits fluctuations both in water vapor and in  
424 precipitation during the 2005 and 2006 campaigns. The range of  $d_v$  at Huaji (Plataforma) is  
425 10.8 to 17.3‰ (12.5 to 26.1‰) with a mean of  $14.4 \pm 1.7$ ‰ ( $20.6 \pm 3.6$ ‰), whereas the range of  
426  $d_p$  is 1.6 to 15.4‰ (10.8 to 22.9‰) with a mean of  $10.2 \pm 2.9$ ‰ ( $16.6 \pm 2.7$ ‰). On both sites,  
427 we observe that averaged deuterium excess in water vapor is higher than in precipitation by  
428 ~4‰ (4.2‰ and 3.9‰ at Huaji and Plataforma respectively) (see the sign of  $d_p - d_v$  on Figure  
429 4). On both sites, we also observe that the mean  $d_p$  is slightly higher in 2005 than in 2006  
430 (Table 1). However, the mean  $d_v$  at Huaji are similar in 2005 and 2006 whereas at Plataforma,  
431 the mean  $d_v$  is lower in 2005 than in 2006 (Table 1).

432 Because of missing  $\delta^{18}O_v$  (mainly at Plataforma, see section 2), only 54 (and not 70)  
433 simultaneous observations of  $d_p$  and  $d_v$  are available at Huaji (35 observations) and

434 Plataforma (19 observations). Covariances between  $d_p$  and  $d_v$  are much lower than between  
435  $\delta D_p$  and  $\delta D_v$  and falls to 0.17 (n=35) and 0.02 (n=19) for Huaji and Plataforma respectively.  
436 However, variations of  $d_p$  reflects those of  $d_p-d_v$  with covariances of 0.65 (n=35) and 0.56  
437 (n=19) at Huaji and Plataforma respectively.

#### 438 **4-4 Comparison between Huaji and Plataforma**

439  $\delta D_v$  exhibits similar variations at Huaji and Plataforma (the slope of the linear  
440 regression between  $\delta D_v$  at Huaji and Plataforma is of 1.03,  $r^2=0.59$ , n=54,  $p<0.001$ ) except  
441 during one week in November 2005 (between November 8<sup>th</sup> and 15<sup>th</sup>), a few days in mid-  
442 March 2006 (between 13<sup>th</sup> and 18<sup>th</sup> March) and in April 2006 (between April 6<sup>th</sup> and 10<sup>th</sup>)  
443 (Figure 4). Without accounting for those periods of discrepancies, the covariance of  $\delta D_v$   
444 between the two sites increases to 0.75 (n=43,  $p<0.001$ ) with a significant difference between  
445 the onset ( $r^2=0.79$ , n=17,  $p<0.001$ ) and the termination ( $r^2=0.34$ , n=26,  $p<0.01$ ) of the wet  
446 season.

447 Similarly to  $\delta D_v$ ,  $\delta D_p$  exhibits similar variations between Huaji and Plataforma (the  
448 slope of the linear regression between  $\delta D_p$  at Huaji and Plataforma is 1.05,  $r^2=0.64$ , n=31,  
449  $p<0.001$ ). The aforementioned discrepancies on  $\delta D_v$  between Huaji and Plataforma are also  
450 recorded in  $\delta D_p$ , and by skipping those rainout events the covariance between the two sites  
451 increases up to 0.73 (n=21,  $p<0.001$ ) with again a significant difference between the onset  
452 ( $r^2=0.96$ , n=7,  $p<0.001$ ) and the termination ( $r^2=0.50$ , n=14,  $p<0.01$ ) of the wet season.

453 In this paragraph, we explore if the aforementioned isotopic discrepancies between the  
454 two sites could reflect different moisture sources at Plataforma and Huaji on these specific  
455 days. Indeed, as mentioned in section 2-1, a persistent moisture flow from the Bolivian  
456 Altiplano could impact Plataforma station and not Huaji. Interestingly, we can compare  $\delta D_p$  at  
457 Plataforma with  $\delta D_p$  of event-based precipitation collected at Layca Cota (a site located  
458 downtown La Paz on the Altiplano, at 16°30'16"S and 68°07'23"W, 3635 m, and thus on the  
459 western Andean side) where  $\delta D_p$  has been monitored since December 2001 (Figure 4). The  
460 two signals are fairly similar from November 8<sup>th</sup> to 15<sup>th</sup>, 2005 and during mid-March 2006  
461 although there are only two common days between the two isotopic series during this period  
462 (there is no precipitation at Layca Cota in April 2006). This similarity suggests that  
463 Plataforma and Layca Cota stations sample over these specific time periods similar air masses  
464 that do not attain the Huaji station. As an initial exploration, we used the HYSPLIT

465 backtrajectory model (Draxer and Rolph, 2010; Rolph, 2010) to calculate air masses pathways  
466 for those specific days. This model runs with the 1°-resolution operational NCEP-GDAS  
467 (National Centers for Environmental Prediction-Global Data Assimilation System) analyses.  
468 This resolution is too low to distinguish Palataforma and Huaji sites. However, it allows us to  
469 examine the main large-scale direction from which air masses originate and thus to  
470 distinguish a potential moisture arrivals from the Bolivian Altiplano. From November 8<sup>th</sup> to  
471 16<sup>th</sup>, 2005, the remote air parcel origin (>4 days) is located southward indicating long air  
472 masses pathways at mid-latitudes (Ronchail et al., 1989) consistent with a strong isotopic  
473 distillation ( $\delta D_p$  from November 8<sup>th</sup> to 15<sup>th</sup>, 2005 are among the most depleted values). When  
474 air masses approach the latitude of La Paz and of the Zongo valley, they are northwestward  
475 transported, certainly not overflying the low elevation of the Zongo valley. As a consequence,  
476 the periods of discrepancies in  $\delta D_p$  between Huaji and Plataforma may be due to different air  
477 masses origin and history between the two sites. Plataforma would have experienced air  
478 masses originating from the highlands, affecting the highest summits of the Cordillera and  
479 barely passing over them as already observed in this area between November and March for  
480 the very close site of Chacaltaya atmospheric platform (16°21'1.78"S, 68°8'53.44"W, 5240 m,  
481 at about 8 km from Plataforma station, Figure 1) (Andrade et al., 2016; Wiedensohler et al.,  
482 2018). This local air flow circulation between the Bolivian Altiplano, the high summits of the  
483 Cordillera Real and the top of the Zongo valley would need to be confirmed by higher  
484 resolution models. It is worth noting that deuterium excess in both precipitation and water  
485 vapor for those days does not exhibit a specific signature that could be associated to the  
486 southward moisture origin. This lack of signal in  $d_p$  for southward moisture origin has already  
487 been pointed out by Vimeux et al. (2011). Guy et al. (2019) also observed in several Bolivian  
488 and Peruvian rain isotopic ratios series in the Andes that no relationship appears between  
489 extreme  $d_p$  and large-scale moisture sources and trajectories.

490 The variations of  $d_v$  at Huaji and Plataforma show similarities although the  
491 relationship is lower than for  $\delta D_v$  (the slope is of 0.99,  $r^2=0.33$ ,  $n=19$ ,  $p<0.05$ ) whereas a less  
492 significant relationship is shown for  $d_p$  ( $r^2=0.14$ ,  $n=31$ ,  $p<0.05$ ) suggesting that local effects  
493 may affect  $d_p$ .

#### 494 **4-5 Altitudinal isotopic gradients**

495 As water vapor and rain isotope ratios are reported for two elevations, we give here the  
496 main features of the isotopic altitudinal gradient. As expected, water vapor and precipitation

497 isotopic ratios at Plataforma are more depleted than at Huaji. The mean  $\delta D_v$  difference  
498 between the two sites is of  $-38.2 \pm 16.5\text{‰}$  (this value is calculated only over common days of  
499 water vapor sampling and does not account for the aforementioned discrepancies in  $\delta D_v$   
500 between the two sites). This leads to a mean isotopic-altitude gradient of  $-1.0\text{‰}/100\text{m}$ . A  
501 similar isotopic gradient is found for precipitation ( $-1.3\text{‰}/100\text{m}$ ). Those results are consistent  
502 with previous calculations done in Vimeux et al. (2005, 2011) along the Zongo valley from  
503 monthly and event-based precipitation isotope ratios over longer periods. We observe a  
504 similar gradient in the water vapor phase at the onset and at the termination of the wet season  
505 ( $-0.8\text{‰}/100\text{m}$  in 2005 and  $-1.1\text{‰}/100\text{m}$  in 2006). This similarity is also observed on  
506 precipitation ( $-1.2$  and  $-1.3\text{‰}/100\text{m}$  in 2005 and 2006 respectively). The altitudinal isotopic  
507 gradient is commonly attributed to the orographic rainout effect along the Andean slopes. It  
508 can also arise from shallow convection that allows for free troposphere and boundary layer air  
509 masses mixing along Andean slopes, and that depletes surface water vapor at high altitude  
510 (Angert et al., 2008; Welp et al., 2012; Bailey et al., 2013; Guilpart et al., 2017). However,  
511 this last assumption is not favored here. First, the similarity of  $\delta D_p$  and  $\delta D_v$  between the base  
512 and the top of the valley (also seen in Vimeux et al., 2011) suggests that most of the time the  
513 same air mass travels and precipitates from the base to the top of the valley. Second, we  
514 clearly did not observe convection during the field campaigns.

515 We also observe a strong effect of the altitude on  $d_v$  with higher values at Plataforma  
516 than at Huaji. The mean gradient is  $+0.2\text{‰}/100\text{m}$  ( $n=19$ ). The same gradient is observed on  $d_p$   
517 ( $n=31$ ). No difference is seen between the onset and the termination of the rainy season. This  
518 gradient for deuterium excess may arise from the complete discharge of air masses as they are  
519 lifted up to the summit of the valley: as  $\delta D_v$  decreases, and in an idealized case tends to -  
520  $1000\text{‰}$  for both isotopes as the end of Rayleigh isotopic distillation,  $d_v$  tends toward  $+7000\text{‰}$   
521 per definition. In addition, vertical mixing between free troposphere and boundary layer may  
522 contribute to increase  $d_v$  in altitude. Actually, high  $d_v$  values can prevail in the upper  
523 atmosphere due to ice crystal formation (Jouzel and Merlivat, 1984) or to the influence of  
524 remote deep convection (Bony et al., 2008). However, our understanding of the local  
525 atmospheric circulation in the Zongo valley does not support the presence of intense vertical  
526 mixing of air in the upper part of the valley.

#### 527 **4-6 Isotopic disequilibriums**

528  $\Delta D_{p\_eq}$  is calculated for 70 simultaneous observations of  $\delta D_p$  and  $\delta D_v$  at Huaji (37

529 observations) and Plataforma (33 observations).  $\Delta D_{p\_eq}$  varies from -51.5 to 35.0‰.  $\Delta D_{p\_eq}$  is  
530 mostly negative (73%) and the mean of negative  $\Delta D_{p\_eq}$  is -17.5‰ (positive and negative  
531  $\Delta D_{p\_eq}$  do not follow a normal distribution and so no standard deviation is calculated, see  
532  $\Delta D_{p\_eq}$  distribution on Figure 5a and b). The positive  $\Delta D_{p\_eq}$  reflect a lower departure from the  
533 isotopic equilibrium with a mean of 4.8‰.

534 The distribution of  $\Delta D_{p\_eq}$  is significantly different at Huaji and at Plataforma (Figure  
535 5a). At Huaji (Plataforma), the mean negative  $\Delta D_{p\_eq}$  is of -9.6‰ (-24.1‰) representing 62%  
536 (85%) of the  $\Delta D_{p\_eq}$ . Plataforma also records the most negative disequilibria (100 (83)% of  
537 the  $\Delta D_{p\_eq}$  lower than -20 (-30)‰ are encountered at that site) whereas the positive  $\Delta D_{p\_eq}$  are  
538 mainly observed at Huaji (74%). This relationship between the sign of  $\Delta D_{p\_eq}$  and the two  
539 sites is significant at the 95%-confidence level according to a Chi-squared test. In addition,  
540 the mean absolute distance to the isotopic equilibrium at Huaji (Plataforma) is 7.7‰ (21.2‰)  
541 and 70% (27%) of  $\Delta D_{p\_eq}$  range from -10‰ to +10‰.  $\Delta D_{p\_eq}$  is thus more pronounced at  
542 Plataforma than at Huaji and exhibits a deviation towards negative values.

543 By examining the differences between 2005 and 2006 (Figure 5b), we note that the  
544 number of positive (negative)  $\Delta D_{p\_eq}$  is similar in 2005 and 2006 (29(71) and 26(74)%  
545 respectively) although we observe that the four most positive  $\Delta D_{p\_eq}$  (5.0‰, 7.2‰, 16‰ and  
546 35.0‰) occur in 2005 whereas the lowest  $\Delta D_{p\_eq}$  (<-50‰) can be observed during the two  
547 campaigns.

548 We captured at Huaji 17 rain events with an averaged relative humidity of 100%.  
549 Although we can expect that the equilibrium state prevails in saturation conditions,  $\Delta D_{p\_eq}$  is  
550 not equal to 0 and can be positive or negative ( $\Delta D_{p\_eq} < 0$  for 11 rain events). We observe that  
551 the mean absolute distance to isotopic equilibrium for those 17 rain events is 8.2‰, similar to  
552 the mean absolute distance over the whole dataset at this station (7.7‰).

553 Regarding how  $\Delta D_{p\_eq}$  varies along with other observations, it is worthwhile noting  
554 that:

555 (1)  $\Delta D_{p\_eq}$  and relative humidity (<100%) do not co-vary ( $r^2=0.06$ ,  $n=50$ ,  $p<0.1$ ). The  
556 correlation hardly increases up to  $r^2=0.10$  ( $n=12$ ,  $p<0.1$ ) if considering only positive  $\Delta D_{p\_eq}$   
557 ( $\delta D_p > \delta D_{p\_eq}$ ). This suggests that processes dependent on relative humidity and increasing  $\delta D_p$   
558 relatively to its value at equilibrium are not dominant;



559 (2) a significant positive relationship is observed between  $\Delta D_{p\_eq}$  and  $\delta D_p$  with a  
560 covariance of  $r^2=0.30$  ( $n=70$ ,  $p<0.001$ ) suggesting that processes enhancing the deviation from  
561 equilibrium towards negative values ( $\delta D_p < \delta D_{p\_eq}$ ) tends also to deplete  $\delta D_p$  (Figure 5c).

562  $\Delta d_{p\_eq}$  is calculated over 54 simultaneous observations of  $d_p$  and  $d_v$  at Huaji (35  
563 observations) and Plataforma (19 observations) (Figure 6). It varies from -11.3 to 2.4‰. It is  
564 mostly negative (78%) and the mean of negative  $\Delta d_{p\_eq}$  is -3.3‰. The positive  $\Delta d_{p\_eq}$  occur at  
565 Huaji (except for one  $\Delta d_{p\_eq}<0$  at Plataforma) and reflect a lower departure from the isotopic  
566 equilibrium with a mean of 0.9‰ (Figure 6). Because of missing  $\Delta d_{p\_eq}$  at Plataforma in 2005,  
567 we do not compare in details the two sites and the two campaigns. No significant correlation  
568 is found between  $\Delta d_{p\_eq}$  and other isotopic and meteorological parameters.

569 Interestingly, although deviations from isotopic equilibrium appear at the individual  
570 rain event scale, the covariance between  $\delta D_p$  and  $\delta D_{p\_eq}$  for the whole dataset is highly  
571 significant ( $r^2=0.86$  over the whole data set with  $r^2=0.85$  and  $r^2=0.83$  for Huaji and Plataforma  
572 respectively,  $p<0.001$ ). This suggests that the isotopic equilibrium is a more robust  
573 assumption at the subseasonal scale (several weeks) than for individual rain events as already  
574 pointed out by previous studies (Deshpandes et al., 2010; Srivasta et al., 2015; Lekshmy et al.,  
575 2018; Penchenat et al., 2020). The covariance between  $d_p$  and  $d_{p\_eq}$  over the whole dataset,  
576 although lower ( $r^2=0.56$ ) is also highly significant ( $p<0.001$ ).

## 577 **5- How are local processes involved in vapor-rain isotopic disequilibrium?**

578 Our observations show that equilibrium state between water vapor and rain does not  
579 prevail during our campaigns at the individual rain scale. The range and the sign of  
580 disequilibriums, as well as the different conditions of relative humidity and temperature  
581 during the two campaigns, suggest that a variety of processes are at play during isotopic  
582 exchanges between rain and water vapor. In this section, we review local processes possibly  
583 involved in the isotopic disequilibrium between rain and vapor. In a first part (section 5-1), we  
584 propose a metric to estimate the potential errors made on the calculated disequilibriums  
585 because of the different time duration in rain and water vapor collection.

### 586 *5-1 Errors on calculated disequilibriums due to water vapor sampling*

587 An important caveat in our study deals with the difference in the duration of water  
588 vapor and rain sampling periods. Water vapor was collected for time periods ranging between

589 14h to 31h, with a majority around 23h, whereas precipitation samples correspond to specific  
 590 rain event(s) never exceeding a few hours. This difference in sampling time periods was  
 591 common before the advent of laser spectrometry and is still present in a few recent studies  
 592 (Kurita et al., 2013; Lekshmy et al., 2018; Sinha and Chakraborty, 2020).

593 Before exploring physical processes that could be involved in isotopic disequilibria,  
 594 we propose in this sub section to estimate the error that may affect  $\Delta D_{p\_eq}$  ( $\epsilon_D$ ) and  $\Delta d_{p\_eq}$  ( $\epsilon_d$ )  
 595 if the isotopic composition of water vapor is different during and outside the rain event. This  
 596 estimate could thus be reused in future studies facing the same concern or for example in  
 597 studies where rain hours are not well know (Penchenat et al., 2020).

598 The isotopic composition of water vapor before and after the rain event is noted  
 599  $\delta D_{v\_out}$  and  $d_{v\_out}$ . The isotopic composition of water vapor during the rain event is noted  
 600  $\delta D_{v\_ev}$  and  $d_{v\_ev}$ . We define  $X_D$  and  $X_d$  the differences of the isotopic composition of water  
 601 vapor between inside and outside the rain event as:

$$602 \quad X_D = \delta D_{v\_ev} - \delta D_{v\_out} \quad (16)$$

$$603 \quad X_d = d_{v\_ev} - d_{v\_out} \quad (17)$$

604 If the isotopic composition of water vapor decreases during rain event then  $X_D < 0$  and  
 605 if deuterium excess increases during the rain event then  $X_d > 0$ , and conversely.

606 We define  $r$  as the fraction of the full water vapor sampling period (of composition  
 607  $\delta D_{v\_ave}$  and  $d_{v\_ave}$ ) that is during the rain event. In our manuscript, we try to estimate the  
 608 disequilibrium  $\Delta D_{p\_eq\_ev}$  ( $\delta D_p - \delta D_{p\_eq\_ev}$ ), which was not measured, by  $\Delta D_{p\_eq\_ave}$  ( $\delta D_p -$   
 609  $\delta D_{p\_eq\_ave}$ ), which was measured. In the Supplementary Material, we demonstrate that the  
 610 errors  $\epsilon_D$  ( $\Delta D_{p\_eq\_ave} - \Delta D_{p\_eq\_ev}$ ) and  $\epsilon_d$  ( $\Delta d_{p\_eq\_ave} - \Delta d_{p\_eq\_ev}$ ) can be written as:

$$611 \quad \epsilon_D = \alpha_{eq\_D} \cdot (1 - r) \cdot X_D \quad (18)$$

$$612 \quad \epsilon_d = (1 - r) \cdot ((\alpha_{eq\_D} - \alpha_{eq\_180}) \cdot X_D + \alpha_{eq\_180} \cdot X_d) \quad (19)$$

613 We note that the ratio,  $\epsilon_D/\epsilon_d$ , does not depend on  $r$  and is equal to:

$$614 \quad \frac{\epsilon_d}{\epsilon_D} = \frac{\alpha_{eq\_D} - \alpha_{eq\_180}}{\alpha_{eq\_D}} + \frac{\alpha_{eq\_180}}{\alpha_{eq\_D}} \cdot \frac{X_d}{X_D} \quad (20)$$

615 In our study, the fraction  $r$  is rather well known and about 10% (i.e. a water vapor

616 sampling period of 23h and a rain event of 2h). To quantify  $\epsilon_D$  and  $\epsilon_d$ , we also need to  
617 estimate the range of  $X_D$  and  $X_d$ . To this purpose, we would ideally need to refer to  
618 continuous high resolution water vapor isotopic observations in tropical and subtropical  
619 regions before, during and after rain events. Such observations have been published for  
620 cyclonic rains. However, this type of rain differs too much from the orographic rain  
621 encountered in the Zongo valley to be considered. Tremoy et al. (2014) in West Africa is so  
622 far the only study that has examined changes in water vapor and rain isotopic composition  
623 during rain events at a 5-minute time resolution and in a subtropical climate. Although rain  
624 events are mostly convective rain, this study offers some upper bound values for  $X_D$  and  $X_d$ .  
625 They showed that for 80% of rain events, average  $\delta^{18}O_v$  during rain interval is depleted by 1  
626 to 2‰ compared with  $\delta^{18}O_v$  averaged over the 30-min time interval preceding the rain start.  
627 The last 20% of rain events show an average increase of  $\delta^{18}O_v$  of about 0.8‰ during rain  
628 event. Tremoy et al. (2014) showed also that the average  $d_v$  over rain events is higher during  
629 all studied rain events by 0.5 to 2.3‰ compared with mean  $d_v$  over the 30-min time interval  
630 preceding the rain start. Tremoy et al. (2014) attributed this  $d_v$  increase to rain evaporation.  
631 Based on these amplitude changes for  $\delta^{18}O_v$  and  $d_v$  during rain events, we determine changes  
632 in  $\delta D_v$  during the rain event (i.e  $X_D$  varies from -15 to 10‰) and we simulate the errors  $\epsilon_D$   
633 and  $\epsilon_d$  for 3 values of  $X_d$  (0‰, 0.5‰ and 2‰) with a fraction  $r$  of 0.1. The  $\epsilon_D$  and  $\epsilon_d$  co-  
634 variation is plotted on Figure 6. We clearly see on this figure that:

635 (1) Errors on  $\Delta D_{p\_eq}$  and  $\Delta d_{p\_eq}$  positively co-vary. In the most likely case where  $X_d=0$   
636 (the deuterium excess of water vapor is the same during and outside the rain event as  
637 evaporative processes are poorly involved in our study, see section 5-2) and  $X_D<0$  (water  
638 vapor isotopic composition is lower during rain event), the  $\epsilon_D$  and  $\epsilon_d$  trajectories towards  
639 negative  $\Delta D_{p\_eq}$  and  $\Delta d_{p\_eq}$  as  $X_D$  decreases could explain part of the co-variation between  
640  $\Delta D_{p\_eq}$  and  $\Delta d_{p\_eq}$  at Plataforma. Indeed, the trajectory of  $\epsilon_D$  and  $\epsilon_d$  in the  $\Delta d_{p\_eq}/\Delta D_{p\_eq}$   
641 diagram follows a constant slope of about 0.07 (the first member in Equation (20)), similar to  
642 the slope of the linear regression for Plataforma observations (0.09). However, this cannot  
643 explain the most negative disequilibriums. It is worth noting that the co-variation of errors  
644 could also play a role at Huaji for the few cases where both disequilibriums are positive  
645 ( $X_D>0$ , Figure 6).

646 (2) Considering the most likely case of  $X_d=0‰$  and  $X_D<0$ , the upper bounds for the  
647 errors are -14.65‰ and -1.02‰ for  $\Delta D_{p\_eq}$  and  $\Delta d_{p\_eq}$  respectively.

648 *5-2 Below-cloud rain evaporation and diffusive exchanges*

649 In order to explore the influence of below-cloud evaporation and diffusion processes  
650 on the isotopic disequilibria, we first excluded observations exhibiting an average relative  
651 humidity of 100% (17 cases at Huaji) and/or a higher (lower)  $\delta D_p$  ( $d_p$ ) than  $\delta D_{p\_target}$  ( $d_{p\_target}$ )  
652 (9 cases at Huaji). We did not consider either observations for which  $\Delta d_{p\_eq}$  or  $h$  is not  
653 available (17 cases mainly at Plataforma). We therefore examined the 27 remaining cases (9  
654 at Huaji, 18 at Plataforma) following the methodology described in section 3-2. A similar  
655 figure to Figure 2 is produced for each of the 27 cases and if Equation (11) applies a value of  $f$   
656 is determined. Below-cloud evaporative and diffusive exchanges can be involved in only four  
657 cases at Huaji (October 25<sup>th</sup>, 29<sup>th</sup>, 30<sup>th</sup> and April 9<sup>th</sup>) (see for example Figure 2 done for  
658 October 29<sup>th</sup> and Table 2). The associated evaporative rates vary from 2 to 20% ( $f$  from 0.80  
659 to 0.98) pointing out that diffusive exchanges dominate relatively to evaporation (Table 2).  
660 The limited influence of evaporation and diffusive exchanges is somewhat surprising. This  
661 result must be considered with caution as it may arise from the difference in temporal  
662 resolution between water vapor and rain samplings (see section 5-1).

663 Our result deserves that evaporative effects are responsible for the mostly negative  $d_p$ -  
664  $d_v$  signal (evaporation decreases  $d_p$  and tends to increase  $d_v$  as evaporation proceeds) and  
665 other processes should explain higher deuterium excess in the surface water vapor phase.

666 For cases exhibiting a relative humidity of 100% at Huaji, in the common case of a  
667 raindrops falling in a richer environment, diffusive exchanges will enrich precipitation ( $\delta D_p$   
668 tends to  $\delta D_{p\_eq}$  with  $\Delta D_{p\_eq} \leq 0$ ) and deplete water vapor around it. The efficiency of diffusive  
669 exchanges in conditions of saturation could explain the lower negative disequilibria at  
670 Huaji than at Plataforma. However, equilibrium state does not strictly prevail in conditions of  
671 surface saturation at Huaji and disequilibrium values for such conditions are comparable to  
672 those calculated for lower relative humidity at the same site. We cannot exclude that relative  
673 humidity in upper atmospheric levels is lower than at the surface. Other processes could also  
674 offset the efficiency of diffusive exchanges as describe in following sections.

675 *5-3 Evapotranspiration from the continental surface*

676 At the first order, plants do not fractionate relative to the water taken up by the roots.  
677 They just re-inject the isotopic signal of former precipitation by transpiration in the lower  
678 atmosphere. Fast and intense recycling of this vapor, in particular in regions with numerous

679 rainfall events and therefore a permanent relaxation of  $\delta D_v$  to the isotopic composition of  
680 former rainfall events, should lead to a small negative isotopic disequilibrium. Indeed,  
681 recycling tends to increase  $\delta D_v$  and so  $\delta D_{p\_eq}$  is even more difficult to attain (the distance  
682 between  $\delta D_{p0}$ , isotopic composition of rain in equilibrium with cloud water vapor, and  $\delta D_{p\_eq}$   
683 is increased). This process could explain the small negative  $\Delta D_{p\_eq}$  at Huaji where vegetation  
684 is abundant.

685         Evaporation of surface water (soil water or stagnant water) may generate a very  
686 depleted flux toward the low-level atmosphere (Craig and Gordon, 1965; Penchenat et al.,  
687 2020). For example, using the mean conditions at Huaji for temperature, relative humidity and  
688 isotopic composition of water vapor, and considering that the water surface has the isotopic  
689 composition of the mean precipitation over the studied period, leads to an isotopic  
690 composition of the evaporative flux of  $\sim -450\text{‰}$ . This induces a depletion of the isotopic  
691 composition of near-surface water vapor so that the isotopic composition of precipitation in  
692 isotopic equilibrium with this depleted vapor could be lower than  $\delta D_p$  (Penchenat et al.,  
693 2020). This evaporative process is actually the only one that could explain the few calculated  
694 positive  $\Delta D_{p\_eq}$  (enrichment of precipitation from its expected value at equilibrium),  
695 consistently with the correlation between positive  $\Delta D_{p\_eq}$  and the highest values for  $\delta D_p$  in our  
696 observations. This process could be at play on the Huaji site (recording 74% of positive  
697  $\Delta D_{p\_eq}$ ) where the Zongo stream flows. Unfortunately, it would be very speculative to  
698 quantify this process on that site as we actually do not know the isotopic composition of  
699 surface water and its possible variation in time.

700         In this section, we do not discuss the impact of transpiration by vegetation and  
701 evaporation of surface waters on  $\Delta d_{p\_eq}$ . Indeed, the variations of  $\Delta d_{p\_eq}$  strongly depend on  
702 the isotopic composition of the advected moisture flux and the transpired or evaporated  
703 moisture flux as well as on their relative contribution for which we have no information.

#### 704 *5-4 Condensation height*

705         A negative  $\Delta D_{p\_eq}$  may also arise from a high altitude of condensation, above the  
706 melting layer. In this case, the initial raindrop is very depleted and it always exhibits lower  
707 isotope content than the value that corresponds to isotopic equilibrium with the environment.  
708 If exchanges between droplets and water vapor are reduced, the distance to equilibrium will  
709 be as large as the altitude of condensation is high. The significant positive relationship

710 between negative  $\Delta D_{p\_eq}$  and  $\delta D_p$  supports this explanation for negative  $\Delta D_{p\_eq}$ .

#### 711 *5-5 Droplet and rain types*

712 A raindrop falls through an environment more and more enriched relative to the vapor  
713 it was formed from.  $\Delta D_{p\_eq}$  will be as negative as the equilibration between the droplets and  
714 the surrounding vapor is ineffective. Therefore, a first factor we have to take into account is  
715 how much a certain raindrop is exposed to its environment. We assume that small raindrops  
716 with low falling velocities come to a more complete equilibrium with surrounding water  
717 vapor than big and fast falling raindrops produced by intense rain events (small and slow  
718 raindrops offer a larger interactive surface and a smaller terminal velocity (Houze, 1997,  
719 2014; Lee and Fung, 2008). This assumption is hardly addressable from our observations and  
720 has already been challenged by some observations in tropical India (Lekshmy et al., 2018).  
721 We thus limit the discussion to a few elements.

722 Our observations mostly capture low precipitation rates favoring the equilibration.  
723 This could explain the low disequilibriums in our study and the very significant covariance  
724 between  $\delta D_p$  and  $\delta D_{p\_eq}$ , suggesting an averaged isotopic equilibrium over the period of  
725 observations, although individual coupled rain and water show deviations from equilibrium.

726 Although there is no relationship between  $\Delta D_{p\_eq}$  and precipitation rate, we found the  
727 lowest values of  $\Delta D_{p\_eq}$  (<-30‰, 9 values) among the lowest precipitation rates (<4.1 mm/h).  
728 These lowest  $\Delta D_{p\_eq}$  are associated with highly depleted precipitation (Figure 5c). According  
729 to several recent studies (Aggarwal et al., 2016; Tharammal et al., 2017; Zwart et al., 2018;  
730 Konecky et al., 2019; Sanchez-Murillo et al., 2019),  $\delta D_p$  depletion in tropical rain could be  
731 attributed to a large proportion of stratiform rain. In such rain type, hydrometeors grow by  
732 vapor diffusion above the melting layer where moisture is relatively depleted in heavy  
733 isotopes. Such rain type is supposed to favor isotopic equilibration (low precipitation rate and  
734 small raindrop compared to convective rain rains according to Schumacher and Houze et al.  
735 (2003)). In case stratiform rain are dominant during our campaigns, our observations suggest  
736 that, because of very depleted initial rain, the distance to equilibrium state with low-level  
737 water vapor is such large that  $\Delta D_{p\_eq}$  stays mostly negative despite ideal conditions for  
738 diffusive exchanges between both water phases. Such negative disequilibriums for dominant  
739 stratiform fraction rains have already been observed by Desphande et al. (2010), Lekshmy et  
740 al. (2018) and Penchenat et al. (2020). It is worth noting that the complex orography of the

741 Zongo valley prevents us for examining in details the relationship between  $\Delta D_{p\_eq}$  and the  
742 partition between convective to stratiform rain as done in some previous studies (Lekshmy et  
743 al., 2018, for example). The use of the usual TRMM (Tropical Rainfall Measuring Mission)  
744 product to document this partition in the Zongo region would require a thorough analysis of  
745 the radar signal associated with different cloud types in this complex terrain, which requires a  
746 dedicated and significant effort beyond the scope of our study (Iguchi et al., 2009).

## 747 **6- To what extent do local processes influence $\delta D_p$ and $d_p$ ?**

748 Small  $\Delta D_{p\_eq}$  and parallel changes of  $\delta D_v$  and  $\delta D_p$  at both sites suggest that at first  
749 order  $\delta D_p$  variations reflect those of the low-level vapor and that local processes are not  
750 strong enough to offset the effect of large-scale processes on  $\delta D_p$ . Following the  
751 decomposition method explained in section 3-3, we quantify the relative contributions of local  
752 and remote processes on  $\delta D_p$ . Large-scale processes explain 79% and 77% of  $\delta D_p$  variability  
753 at Huaji and Plataforma respectively (Figure 7a). No significant difference can be seen when  
754 differentiating the onset (2005) and the termination (2006) of the rainy season (not shown).

755 In contrast, the lack of correlation between  $d_v$  and  $d_p$ , combined with a significant  
756 correlation between  $d_p$  and of  $d_p-d_v$ , suggests that variations of  $d_p$  do not reflects those in the  
757 low-level vapor and that local effects strongly affect this second order parameter. The Risi et  
758 al.'s decomposition shows that local processes explain 75% and 89% of  $d_p$  variability at Huaji  
759 and Plataforma respectively (Figure 7b). If we separate the onset and the termination of the  
760 rainy season for Huaji (no enough data at Plataforma in 2005), we observe that local  
761 processes are much stronger at the onset of the wet season (81%, n=14) than at the end of the  
762 rainy season (61%, n=21).

763 A direct conclusion of this section is that  $\delta D_p$  is mainly controlled by large-scale  
764 processes, reflecting  $\delta D_v$ , and that post-condensation processes involved as rain falls are poor  
765 factors to explain  $\delta D_p$ . This is in agreement with previous work from Vimeux et al. (2011),  
766 only based on  $\delta D_p$  observations, which showed that  $\delta D_p$  offers a spatial homogeneity along  
767 the Zongo valley despite different precipitation and different in situ post-condensation  
768 processes along the valley. This is also consistent with Vuille and Werner (2005), showing  
769 that  $\delta D_p$  in the Andes mainly depends on atmospheric processes upstream the site of  
770 collection. In contrast, our analysis suggests that local processes have a stronger influence on  
771  $d_p$ , offsetting the possibility to explore large-scale signal and moisture source trajectories from

772  $d_p$ . The influence of local processes on  $d_p$  was also suggested by Guy et al. (2019) by  
773 comparing  $d_p$  series on different stations in the Bolivian and Peruvian Andes, although no  
774 quantification of local influence on  $d_p$  were done.

## 775 **7- Conclusions**

776 In this paper, we explore whether the isotopic equilibrium state between water vapor  
777 and precipitation prevailed during the onset and the termination of the 2005-2006 wet season  
778 in the Bolivian Andes.

779 Rain and water vapor are very close to the isotopic equilibrium over the whole period  
780 of our observations (covariance between  $\delta D_p$  and  $\delta D_{p\_eq}$  is of 0.86) although for individual  
781 rain events we observed deviations from the equilibration. The distance from isotopic  
782 equilibrium is mostly small and negative but deviations can occur for some rain events (20%  
783 of disequilibriums have an absolute value higher than 20‰). The Stewart's theory, treating in  
784 a uniform manner both evaporative effects and diffusive exchanges, failed to explain major  
785 part (~85%) of our observations. Partial evaporation of falling precipitation, one of the key  
786 processes controlling tropical and subtropical tropospheric humidity (Folkins and Martin,  
787 2005) is thus, at our sites and during the sampling periods, a very secondary factor in  
788 controlling the isotopic composition of both water vapor and precipitation. This result in the  
789 Bolivian Andes is consistent with some observations in Sahel (Risi et al., 2008) and in India  
790 (Lekshmy et al., 2018). Therefore, other processes or rain characteristics are strong enough to  
791 offset below-cloud effects. The height of condensation or the type of rain can explain the  
792 negative disequilibriums. Our observations also suggest that significant inputs of  
793 evapotranspired moisture at ground level could explain some departures from the isotopic  
794 equilibrium. This influence of surface water vapor fluxes has already been suggested by  
795 previous studies (Desphande et al., 2010; Lekshmy et al., 2018). Our observations also  
796 confirm modeling studies done by Lee and Fung (2008) who simulated a high degree of rain-  
797 vapor equilibration in tropical regions on longer timescale than individual rain events (above  
798 70% (90%) for deep convective precipitation (stratiform precipitation)).

799 We also show that the isotopic composition of precipitation and near-surface water  
800 vapor closely co-vary: at first order,  $\delta_p$  is a correct tracer of  $\delta_v$  and so a correct candidate to  
801 reconstruct past large-scale atmospheric processes. In opposite, deuterium excess in  
802 precipitation is more affected by local post-condensation processes than isotopes ratio making



803 this tracer difficult to use to study moisture sources for example.

804 Our study will need to be completed and confirmed by continuous isotopic  
805 measurements in water vapor along a complete rainy season, from November to March, to  
806 capture  $\delta D_v$  and  $\delta D_p$  on the same duration. Indeed, the difference in time sampling for rain  
807 and water vapor can induce errors on  $\Delta D_{p\_eq}$  and  $\Delta d_{p\_eq}$  if the isotopic composition of water  
808 vapor largely changes during the rain event. Continuous observations over a complete season  
809 will also enable us to have more rain events and to further discuss the isotopic equilibrium on  
810 contrasted time scales (individual, sub-seasonal and seasonal scales) as well as the role of rain  
811 type (convective versus stratiform) on the equilibration. This is now possible with WS-CRDS  
812 laser technology providing continuous isotopic measurements in the water vapor phase (Lee  
813 et al., 2006; Gupta et al., 2009; Wen et al., 2010; Tremoy et al., 2011 for some examples).

814

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987 **Figure captions**

988 **Figure 1:** (a) Cross-section of the Zongo valley in the Northeast-Southwest direction with the  
989 sites of Huaji (945 m), Plataforma (4750 m) and Chacaltaya observatory (5240 m) (black  
990 rectangles). The main moisture flow along the Andean slope from the Amazon basin,  
991 associated to the South American Low Level Jet (SALLJ), is mentioned by the red arrows and  
992 (b) Google Earth map of the Zongo Valley with the location of Huaji (945 m) and Plataforma  
993 (4750 m) as well as the five pluviometers located at Harca (1480 m), Sainani (2210 m),  
994 Botijlaca (3492 m), Tiquimani (3900 m) and Zongo (4264 m) sites. The location of  
995 Chacaltaya observatory is also indicated. Red arrows represent the channelization of moisture  
996 flux inside the valley. Google Earth image (5 May 2020). Bolivia. Images CNES/Airbus,  
997 Maxar Technologies, Eye alt. 61 km, US Department of State Geographer  
998 (<https://earth.google.com/web/>).

999 **Figure 2:** Diagram showing  $\Delta d_{p\_eq}$  as a function of  $\Delta D_{p\_eq}$  for October 29<sup>th</sup>, 2005 at Huaji  
1000 ( $T=24$  °C,  $h=87.3\%$ ). Orange line is the theoretical trajectory of initial droplet  $P_0$  as  $z$  (altitude  
1001 of the droplet formation in the cloud at isotopic equilibrium with water vapor) varies from 0  
1002 to 3 km at  $T=24$  °C. The isotopic composition of the initial cloud water vapor ( $\delta D_{v0}$  and  $d_{v0}$ )  
1003 is obtained from the observed  $\delta D_v$  and  $d_v$  by applying the isotopic altitudinal gradients  
1004 calculated in section 4-5 for  $z$  varying from 0 to 3 km. The isotopic composition of the initial  
1005 precipitation  $P_0$  ( $\delta D_{p0}$  and  $d_{p0}$ ) is then calculated at equilibrium with cloud water vapor  
1006 considering a lapse rate of  $-5.1$  °C/km (Vimeux et al., 2011). The orange circle is  $P_0$  for  $z=3$   
1007 km. The theoretical isotopic equilibrium is plotted on (0,0) ( $P_{eq}$ , light blue circle) and  $P_0$  is  
1008 equal to  $P_{eq}$  for  $z=0$  km. Green line is the theoretical trajectory of  $P_{target}$  ( $f=0$ ) as  $h$  decreases  
1009 from 100% ( $P_{target} = P_{eq}$ ) at  $T=24$  °C. The green circle is  $P_{target}$  for  $h=87.3\%$ . Purple line is the  
1010 trajectory of precipitation for  $h=87.3\%$  and  $T=24$  °C as  $f$  varies from 1 ( $P_0$ ) to 0 ( $P_{target}$ ). The  
1011 intercept between the orange and purple theoretical curves is obtained for  $f=1$  and it  
1012 determines  $P_0$  (red circle) at  $z=0.6$  km for this specific day. The observations ( $P_{obs}$ , blue  
1013 square) can be explained by the Stewart's theory and corresponds to  $f=0.98$  ( $f^\beta$  can be  
1014 calculated or graphically deduced as the ratio between the distance between  $P_{obs}$  and  $P_{target}$  and  
1015 the distance between  $P_0$  and  $P_{target}$ ). In the general case, when no intercept is found between  
1016 the trajectory of precipitation (purple line) and the trajectory of initial precipitation (orange  
1017 line), the Stewart's theory does not apply.

1018 **Figure 3:** Comparison of precipitation (in mm) over the 2005-2006 (light green) rainy season



1019 with the mean 2000-2011 rainy season (dark green) in the Zongo valley for (a) 5 stations in  
1020 the Zongo valley (Harca, Sainami, Botijlaca, Tiquimani and Zongo) (precipitation for one  
1021 station is the sum of precipitation from October to April); (b) each month from October to  
1022 April (precipitation for one month is the sum of precipitation over the 5 stations).

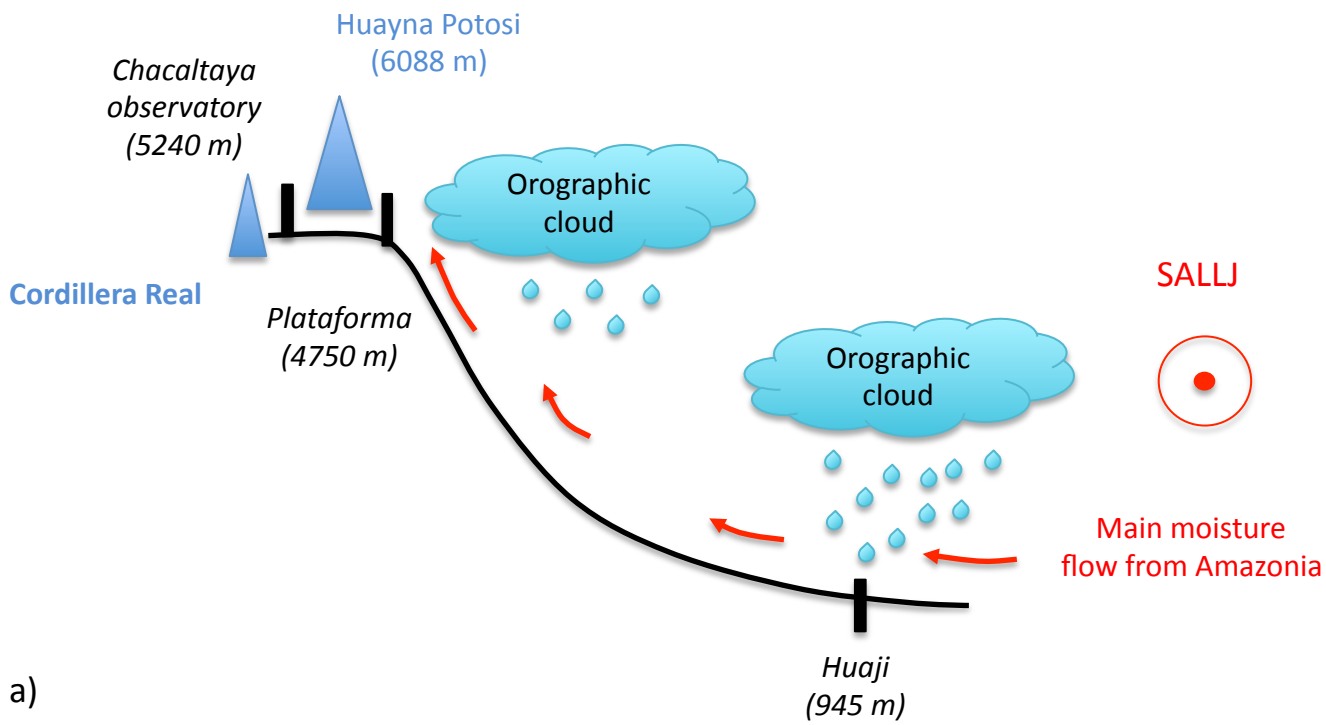
1023 **Figure 4:** Isotopic composition ( $\delta D$ , ‰ V-SMOW) and deuterium excess ( $d$ , ‰ V-SMOW)  
1024 in precipitation (stars) and water vapor (circle) at Huaji (red), (blue) and Layca Cota (green)  
1025 during the 2005 and 2006 field campaigns. When several precipitation events occur within a  
1026 day, the daily amount-weighted isotopic composition is calculated and shown here. The date  
1027 for water vapor data corresponds to the day where the vapor sample is collected. When  
1028 available in both phases, the difference of deuterium excess between rain and water vapor is  
1029 also shown (squares).

1030 **Figure 5:** Distribution of  $\Delta D_{p\_eq}$  (‰) (a) at Plataforma and Huaji and (b) in 2005 and 2006;  
1031 (c)  $\Delta D_{p\_eq}$  (‰) as a function of  $\delta D_p$  (‰) for the whole 2005-2006 time period.

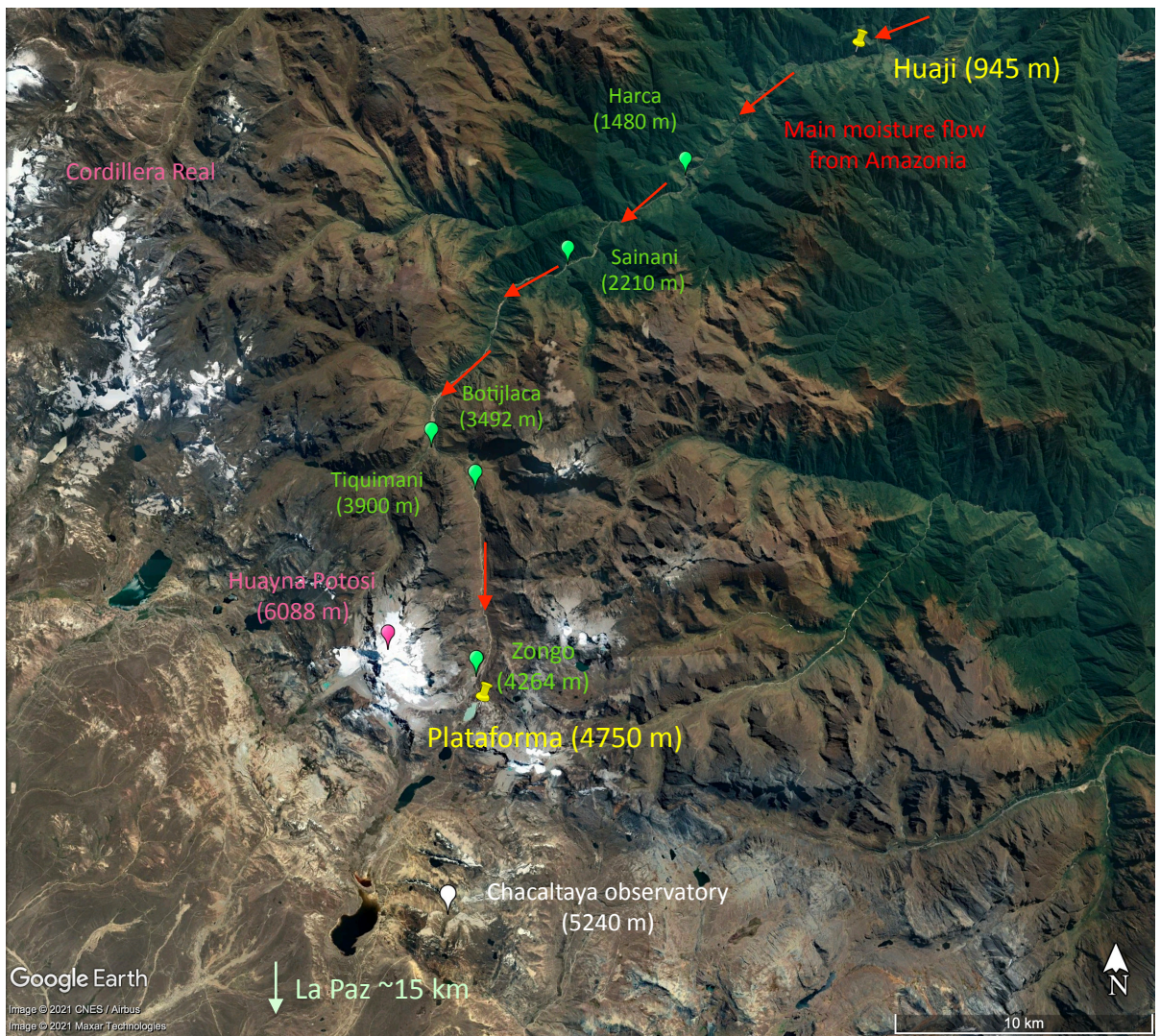
1032 **Figure 6:**  $\Delta d_{p\_eq}$  (‰) as a function of  $\Delta D_{p\_eq}$  (‰) for the 54 simultaneous deuterium and  
1033 deuterium excess disequilibriums (Huaji 2005: red circles, Huaji 2006: green circles,  
1034 Plataforma 2005: blue circles and Plataforma 2006: black circles). We also show how  $\epsilon_d$  (‰)  
1035 varies as a function of  $\epsilon_D$  (‰) for different values of  $X_D$  (from -15 to 10‰), and for three  
1036 values of  $X_d$  ( $X_d=0‰$  red arrows,  $X_d=0.5‰$  orange arrows,  $X_d=2‰$  dark yellow arrows).

1037 **Figure 7:** (a) Decomposition of  $\delta D_p$  into a large-scale signal (associated to  $\delta D_v$ , square) and a  
1038 local effect (associated to  $\delta D_p - \delta D_v$ , circle) for Huaji (red) and Plataforma (black). Those  
1039 contributions are plotted as a function of  $\delta D_p$  for the whole dataset following the  
1040 decomposition of Risi et al., (2010); (b) same as (a) but for deuterium excess.

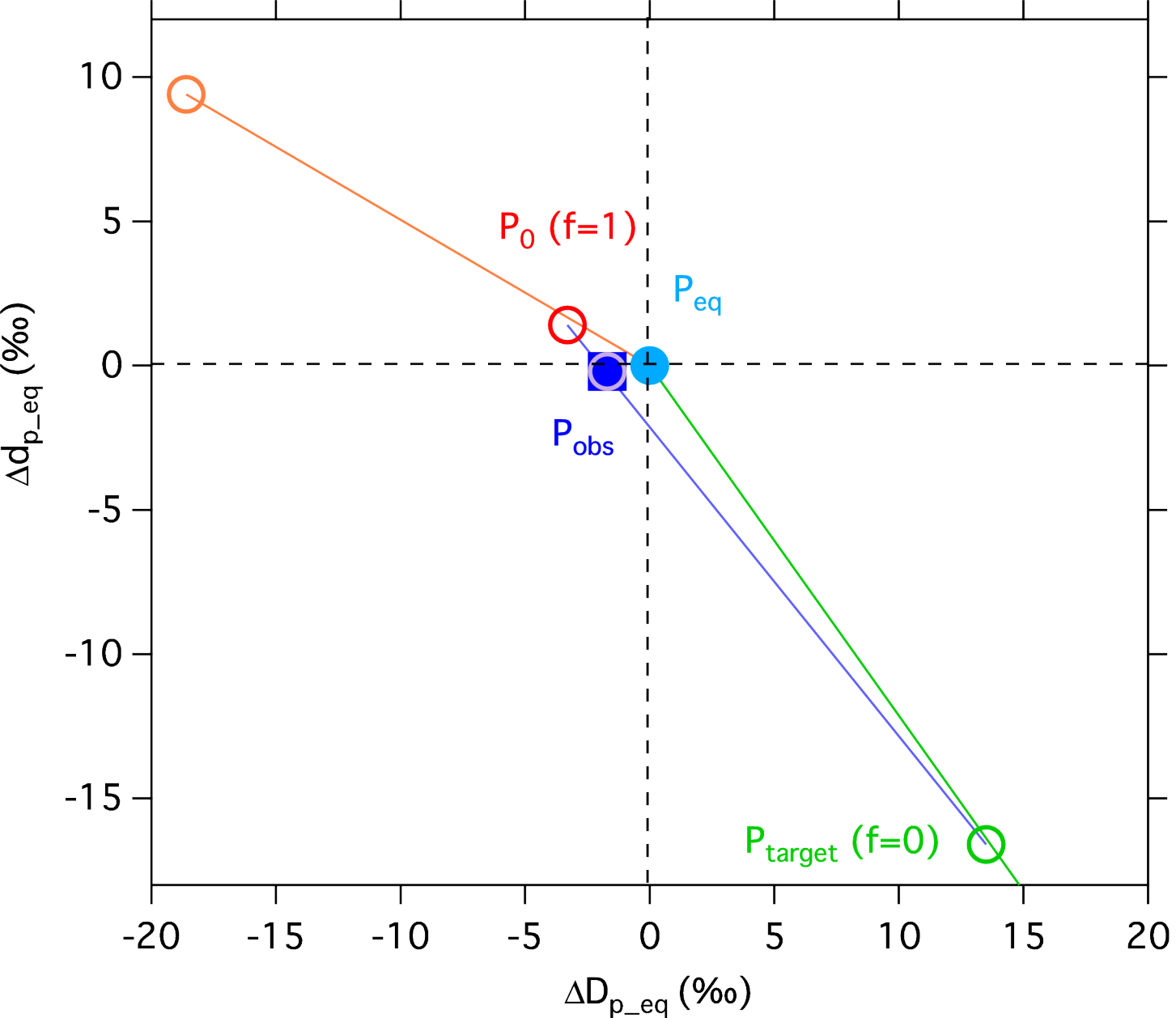
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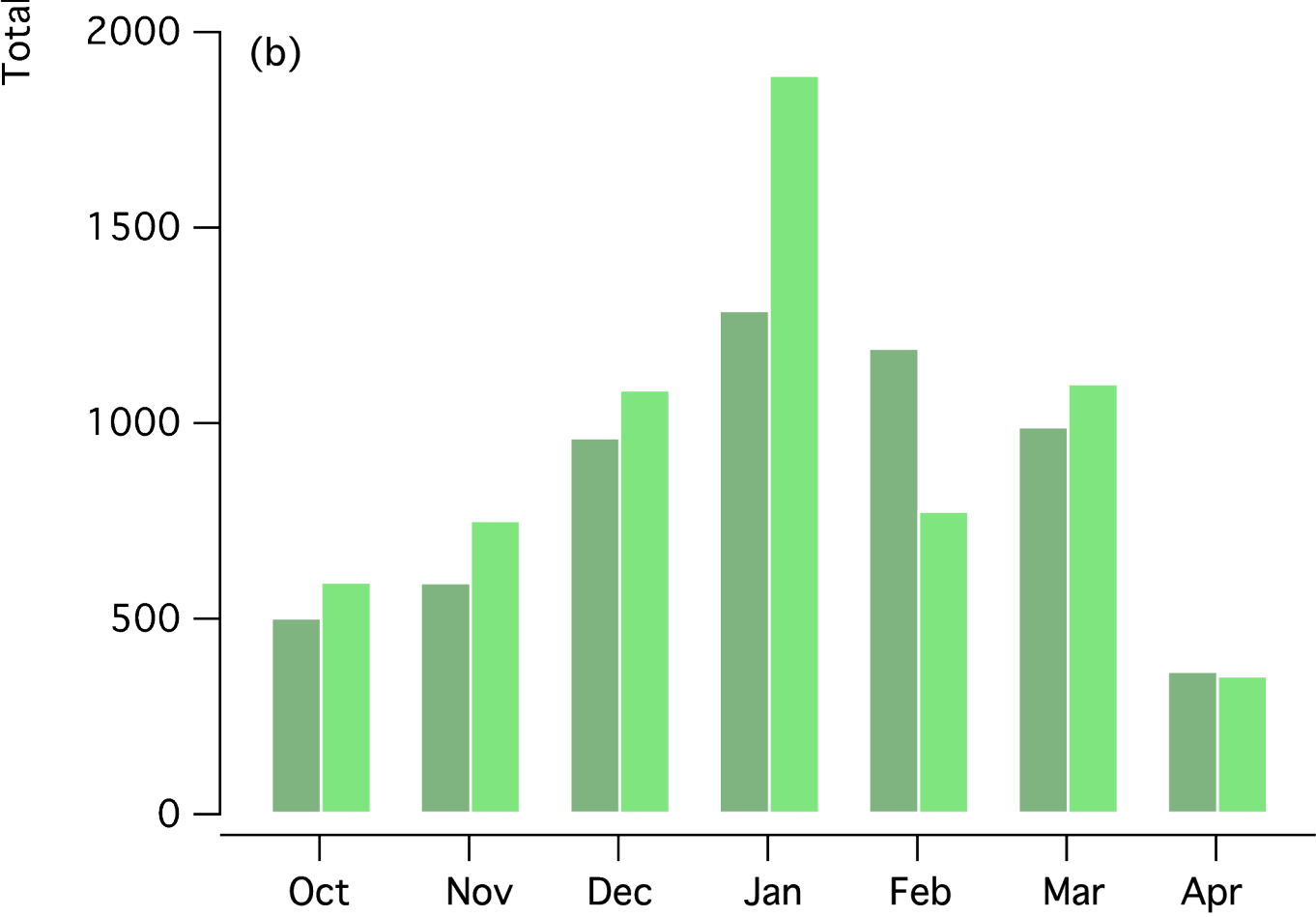
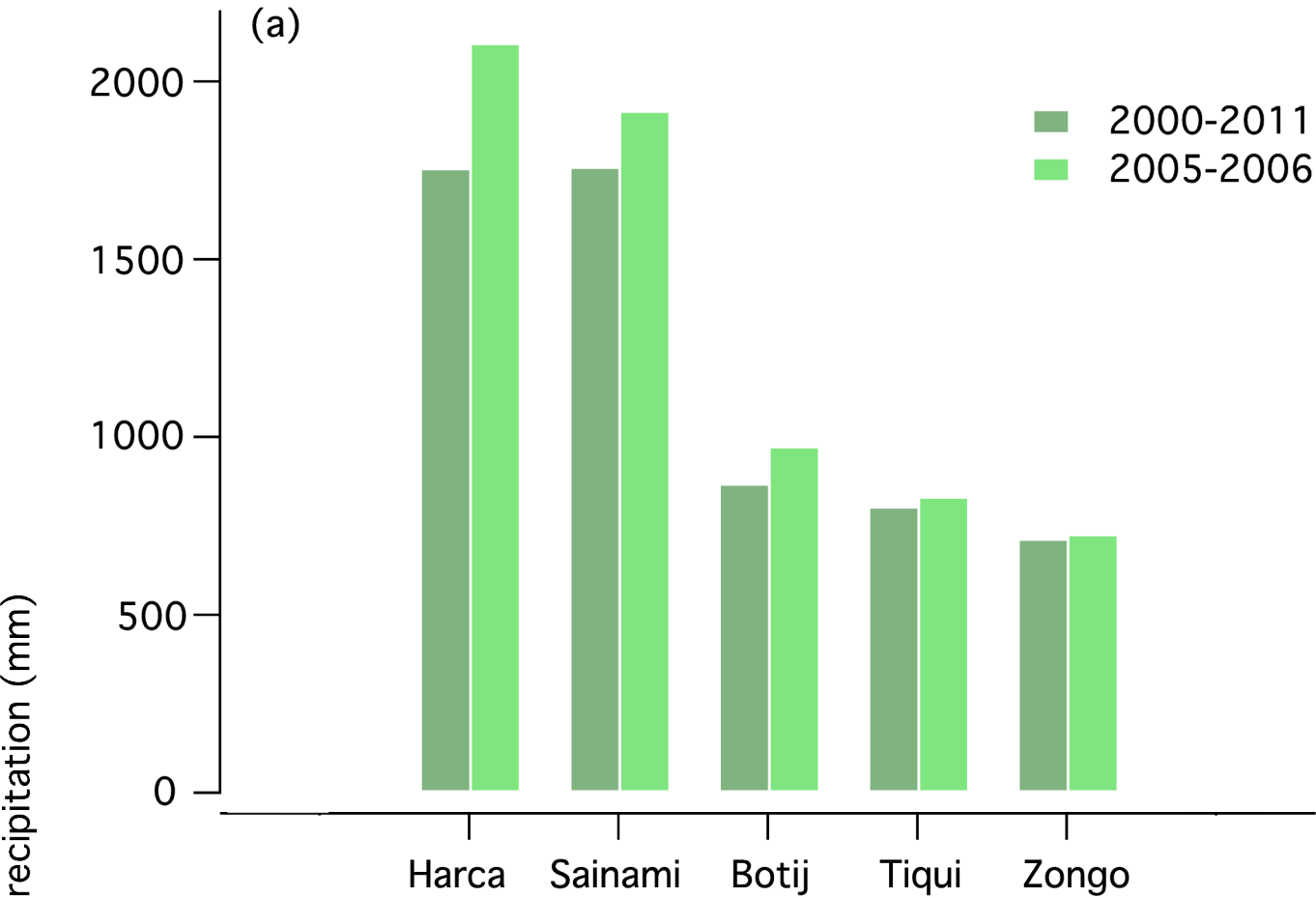
a)

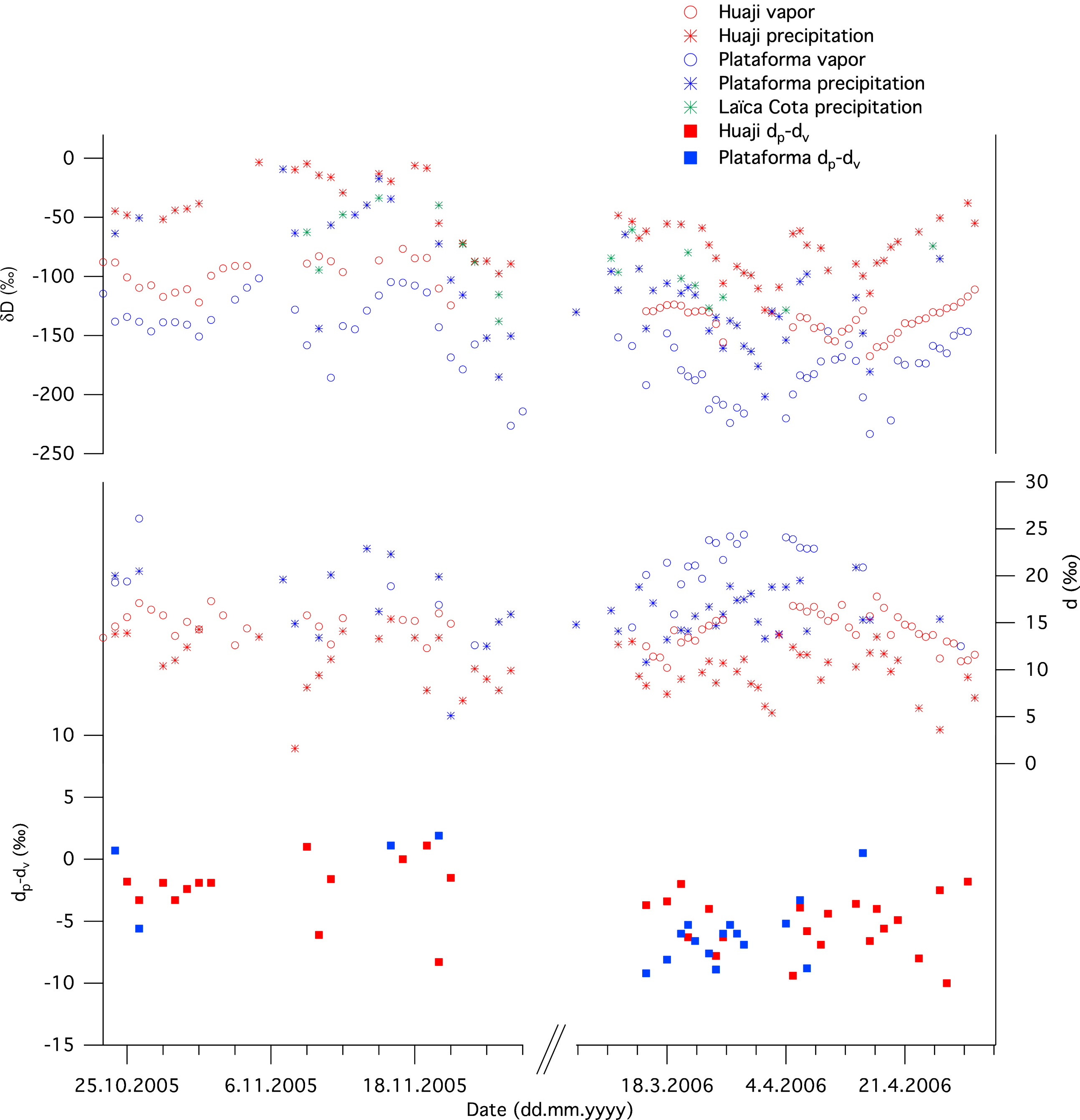


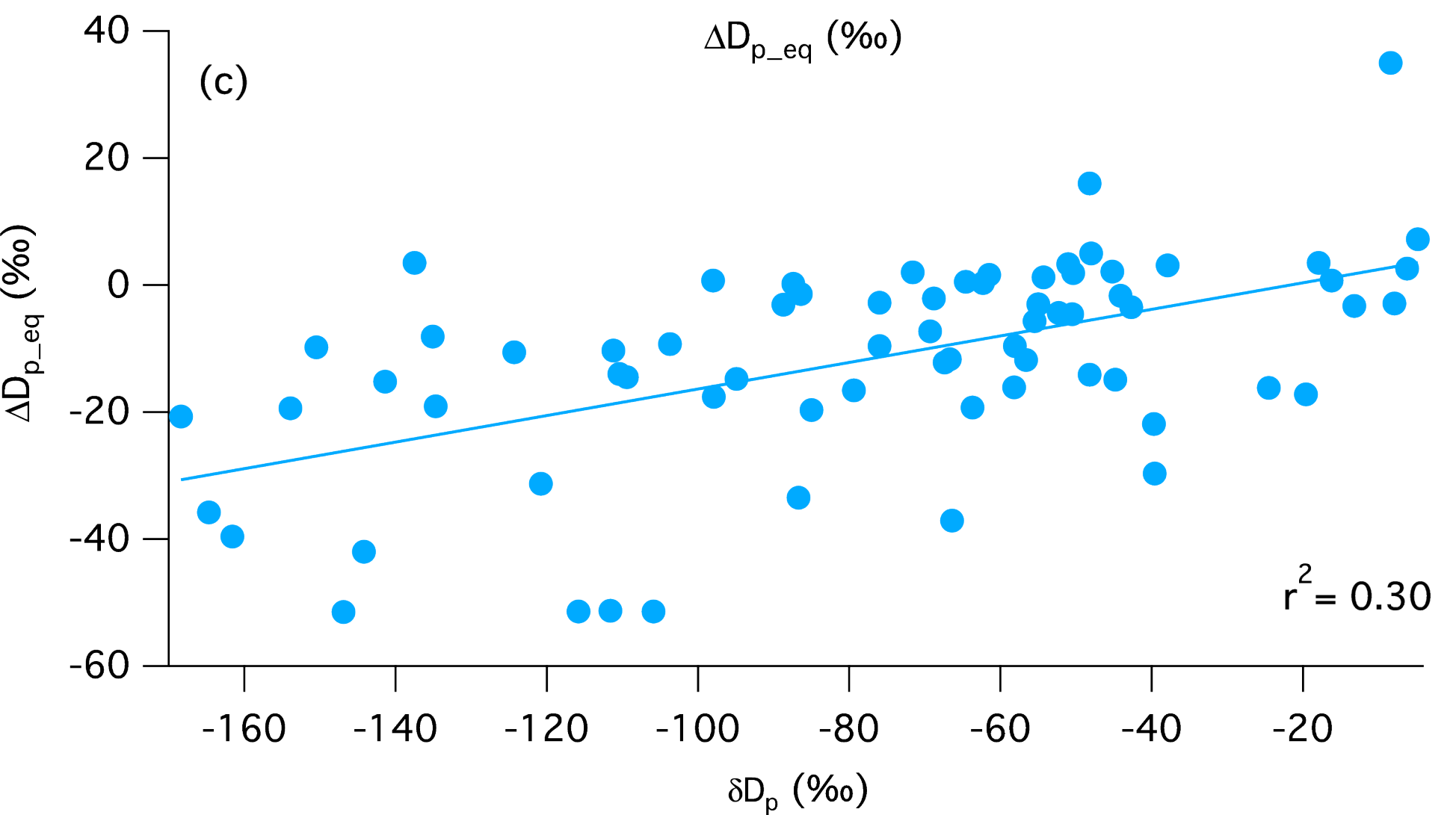
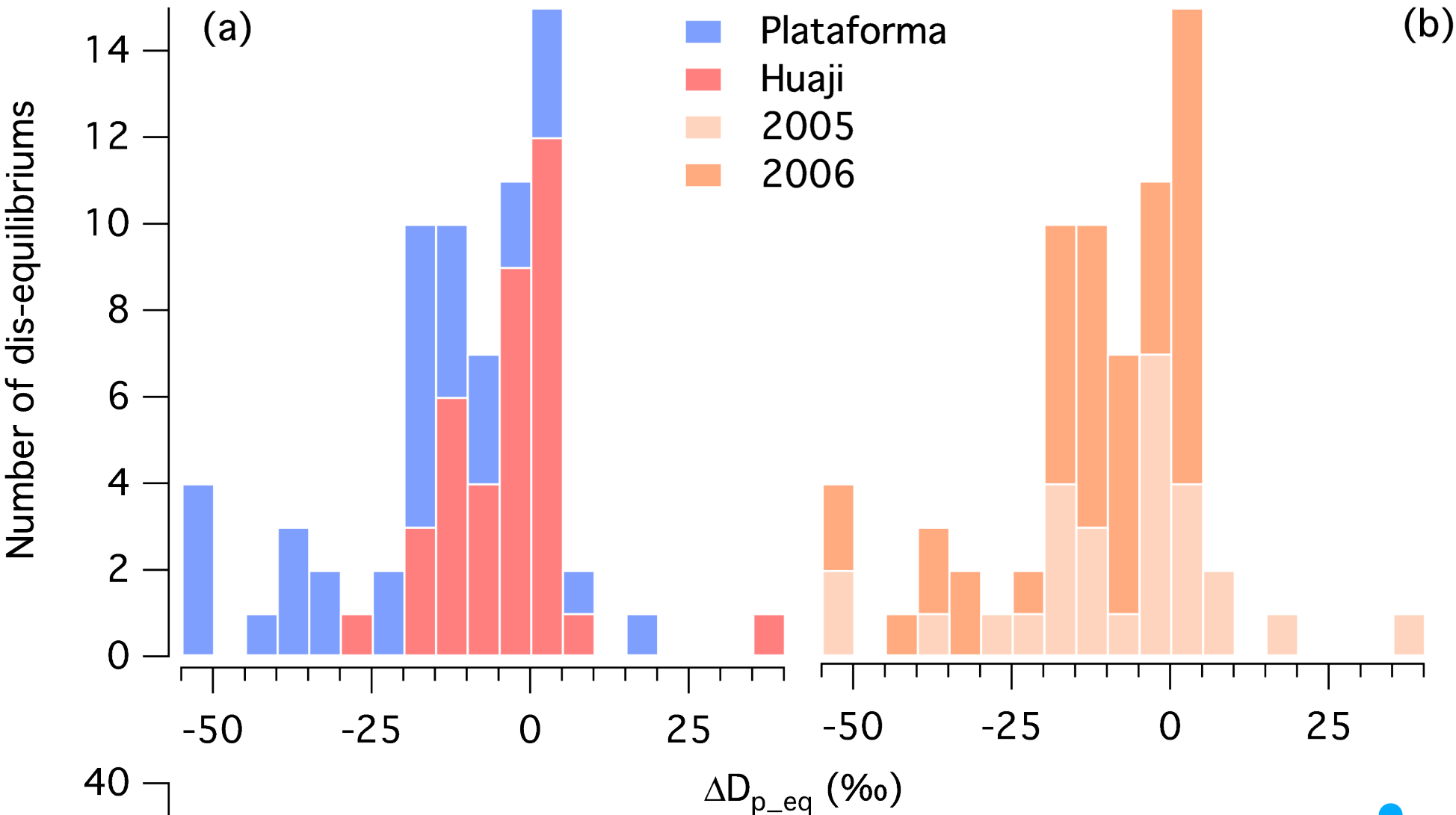
b)



- Huaji, October 29<sup>th</sup> 2005,  $T=24$  °C,  $h=87.3\%$  ( $P_{obs}$ )
- Initial precipitation ( $P_0$ ) for  $z=0$  to 3 km
- Initial precipitation ( $P_0$ ) for  $z=3$  km
- Initial precipitation ( $P_0$ ) for  $z=0.6$  km
- Target precipitation for  $h$  decreasing from 100%
- Target precipitation for  $h=87.3\%$  ( $P_{target}$ )
- Target precipitation for  $h=100\%$  ( $P_{eq}$ )
- Precipitation for  $f=1$  to 0,  $h=87.3\%$ ,  $T=24$  °C
- Precipitation for  $f=0.98$  ( $P_{obs}$ )

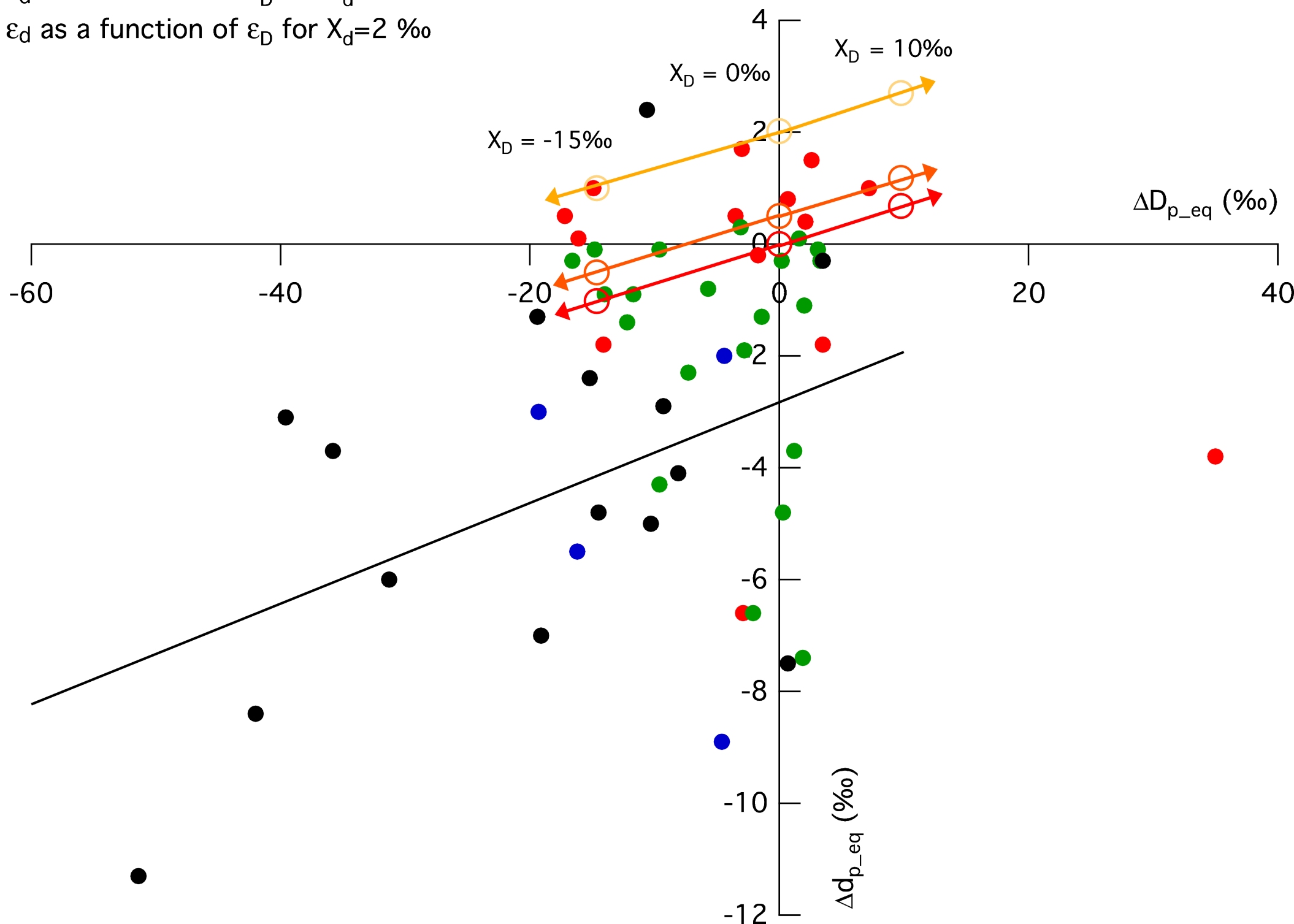


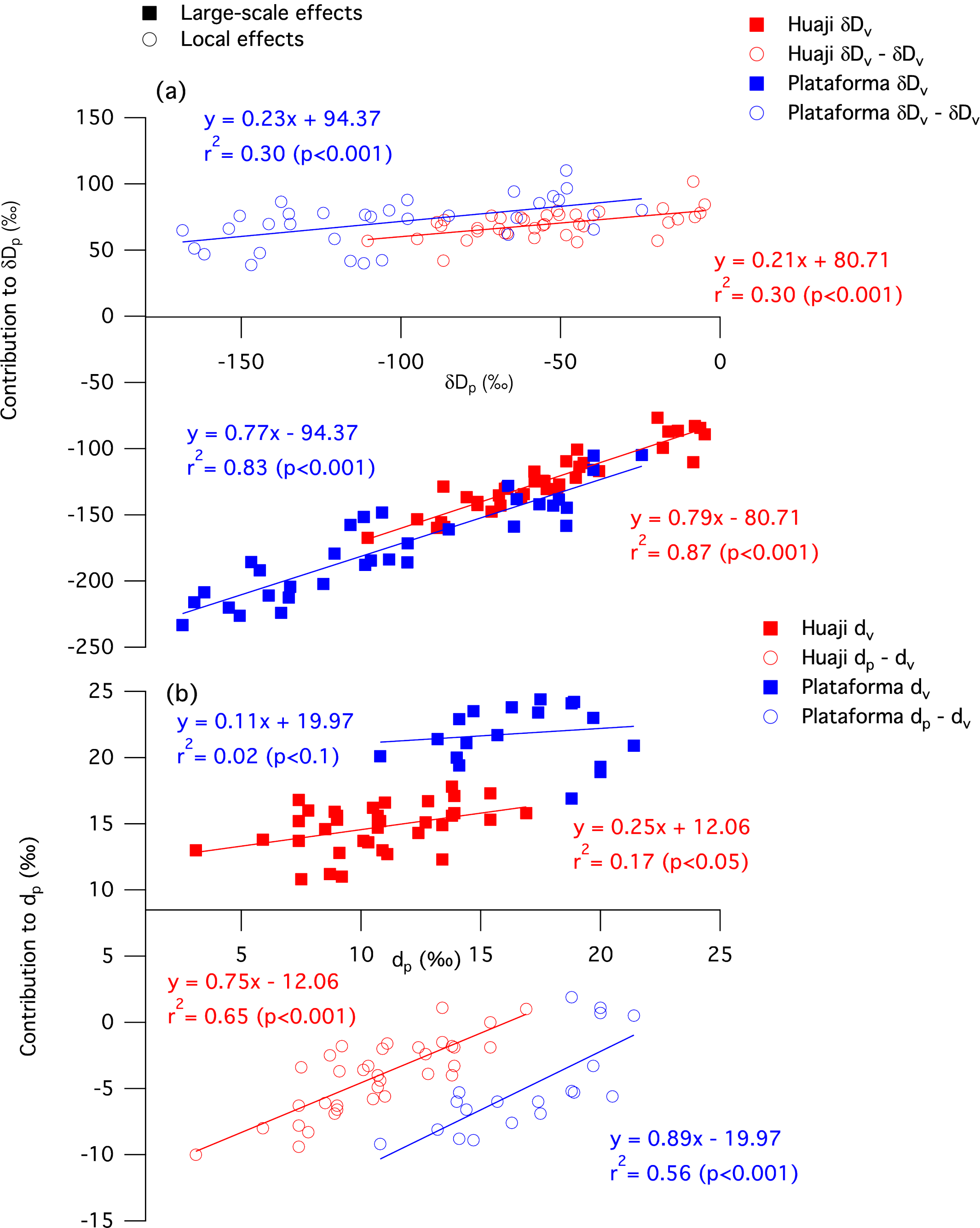






- Huaji 2005
- Huaji 2006
- Plataforma 2005
- Plataforma 2006
- Linear regression of Plataforma observations
- ○ Trajectory of  $\varepsilon_d$  as a function of  $\varepsilon_D$  for  $X_d=0$  ‰ ( $\varepsilon_d/\varepsilon_D=0.07$ )
- ○ Trajectory of  $\varepsilon_d$  as a function of  $\varepsilon_D$  for  $X_d=0.5$  ‰
- ○ Trajectory of  $\varepsilon_d$  as a function of  $\varepsilon_D$  for  $X_d=2$  ‰







**Table 1:** mean $\pm 1\sigma$  for surface relative humidity and temperature and water isotopic composition ( $\delta D_v$ ,  $\delta D_p$ ,  $d_v$ ,  $d_p$ ) and mean[68%-confidence interval] for precipitation rate (it follows a log-normal distribution) during the two field campaigns at Huaji (2005 campaign: October 23<sup>th</sup>-Nov 21<sup>st</sup>, 2006 campaign: March 15<sup>th</sup>-May 1<sup>st</sup>) and Plataforma (2005 campaign: October 23<sup>th</sup>-Nov 27<sup>th</sup>, 2006 campaign: March 11<sup>th</sup>-April 30<sup>th</sup>). All rain events occurring within the field campaigns are taken into account for the calculation of  $\delta D_p$ ,  $d_p$  and precipitation rates. The isotopic composition of precipitation is amount-weighted.

Field campaign	2005	2006
	m $\pm 1\sigma$ or m[68%-confidence interval]	m $\pm 1\sigma$ or m[68%- confidence interval]
<b>Relative humidity (%)</b>		
Huaji	88.1 $\pm 17.0$	92.7 $\pm 12.3$
Plataforma	69.6 $\pm 22.2$	68.1 $\pm 22.2$
<b>Temperature (°C)</b>		
Huaji	22.8 $\pm 4.6$	21.1 $\pm 4.0$
Plataforma	2.3 $\pm 2.7$	2.3 $\pm 2.5$
<b>Precipitation rate (mm/h)</b>		
Huaji	4.7[1.2-7.7]	4.8[1.0-8.7]
Plataforma	1.6[0.8-2.4]	1.4[0.5-2.3]
<b><math>\delta D_v</math> (‰)</b>		
Huaji	-98.0 $\pm 13.7$	-136.3 $\pm 12.3$
Plataforma	-141.1 $\pm 30.3$	-181.0 $\pm 24.6$
<b><math>\delta D_p</math> (‰)</b>		
Huaji	-40.6 $\pm 30.2$	-79.1 $\pm 24.1$
Plataforma	-82.9 $\pm 56.5$	-124.3 $\pm 34.7$
<b><math>d_v</math> (‰)</b>		
Huaji	14.9 $\pm 1.4$	14.1 $\pm 1.8$
Plataforma	18.9 $\pm 4.4$	21.1 $\pm 3.3$
<b><math>d_p</math> (‰)</b>		
Huaji	10.9 $\pm 3.4$	9.7 $\pm 2.4$
Plataforma	17.8 $\pm 3.3$	16.1 $\pm 2.2$

**Table 2:** Disequilibriums ( $\Delta D_{p\_eq}$ , ‰), temperature (T, °C), precipitation rate (P, mm/h), relative humidity (h, %) and drops evaporated fraction (1-f, %) when  $\Delta D_{p\_eq}$  can be explained by the Stewart's theory. Temperature and relative humidity are averaged over the rain period.

Site and date	$\Delta D_{p\_eq}$ (‰)	$\Delta d_{p\_eq}$ (‰)	T (°C)	P (mm/h)	h (%)	1-f (%)
Huaji October 25, 2005	-14.9	-1.0	25.5	8.0	83.3	20
Huaji October 29, 2005	-1.7	-0.2	24.0	3.0	87.3	2
Huaji, October 30, 2005	-3.4	0.5	24.0	2.5	88.0	2
Huaji, April 9, 2006	-2.8	-1.9	23.6	-	91.5	6