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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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18

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 (δD_p) deviates from the theoretical isotopic
28 composition of precipitation at equilibrium with water vapor (δD_{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 δD_p ($r^2=0.30$, $n=70$,
32 $p<0.001$) suggesting that controls on δD_p also impact ΔD_{p_eq} . Although equilibrium state does
33 not prevail at the individual rain event scale, a strong relationship is observed between δD_p
34 and δD_{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 ΔD_{p_eq} . Lastly,
38 we explore how local processes affect δD_p . We show that large-scale dynamic along air
39 masses history is dominant (nearly 80%) to explain δD_p whereas local effects are dominant to
40 explain deuterium excess in precipitation. In consequence, we conclude that δD_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 (H_2^{18}O for $\delta^{18}\text{O}$ and HD^{16}O for δD) and
54 light (H_2^{16}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 (H_2^{18}O and HD^{16}O
65 diffuse lower than H_2^{16}O) induce a kinetic isotopic fractionation during water evaporation.
66 From both $\delta^{18}\text{O}$ and δD , 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 (δ_v) as a key parameter (Craig and Gordon, 1965):
82 because the observations of δ_v are still few compared to the observations of the isotopic
83 composition of precipitation (δ_p), the later is often used to deduce δ_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 δ_p assume that the later is a correct proxy
91 for δ_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 δ_p
94 compared with δ_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 δ_p
99 and δ_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 δ_p in this Andean region from subseasonal to
149 interannual timescale and on the potential of δ_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 δ_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 δ_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 δ_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 δ_p is a correct proxy of δ_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 23rd, 2005 at
228 both stations and ended on November 21st, 2005 (November 27th, 2005) at Huaji
229 (Palataforma). The second campaign started on March 15th, 2006 (March 11st, 2006) and
230 ended on May 1st, 2006 (April 30th, 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 δD 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 δD) 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 δD 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 (ΔD_{p_eq}) is defined as
275 the difference between the observed δD_p and the calculated isotopic composition of
276 precipitation at equilibrium with water vapor (δD_{p_eq}) as:

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

278 where δD_{p_eq} is calculated according to:

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

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

282 For each δD_v measurement, we examine whether rain occurred during the collection of
283 water vapor. If this is the case, α_{eq} is calculated considering the average temperature over the
284 rain event considered, of composition δD_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 α_{eq} and the amount-weighted δD_p is used in Equation (3).

287 In addition to ΔD_{p_eq} , we similarly define Δd_{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 ΔD_{p_eq} offers the possibility to review processes potentially involved
291 in departure from equilibrium state based on the sign of ΔD_{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 ΔD_{p_eq} and Δd_{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 β and γ 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 ΔD_{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 ΔD_{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 Δd_{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 β has
 340 high values).

341 The quantity f^β 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^β is calculated here considering δD . It can also be calculated from $\delta^{18}O$. The two
 344 results are very close each other as f^β 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 Δd_{p_eq} as a function of ΔD_{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 δ_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 δD_p departure from
 365 δD_v (or δD_{p_eq}) but it determines how much local effects affect δD_p . Variations of the later are
 366 decomposed into a large-scale processes contribution (δD_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 δD_p can be estimated by the slope (a) of the linear regression of δD_v as a function of δD_p :

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

372 Similarly, the contribution of local processes to δD_p can be estimated by the slope (c)
 373 of the linear regression of $\delta D_p - \delta D_v$ as a function of δD_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 δD_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 δD_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 δD_p and δD_v at Huaji and Plataforma**

408 During the 2005 and 2006 campaigns, the range of δD_v at Huaji (Plataforma) is -76.7
409 to -167.4‰ (-101.6 to -233.3‰) with a mean of -121.9 ± 22.6 ‰ (-163.6 ± 33.6 ‰), whereas the
410 range of δD_p is -3.5 to -131.0‰ (-9.3 to -201.7‰) with a mean of -63.0 ± 32.7 ‰ ($-$
411 111.7 ± 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 δD_p and δD_v are available at Huaji (37
419 observations) and Plataforma (33 observations). δD_p and δD_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 ± 1.7 ‰ (20.6 ± 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 ± 2.9 ‰ (16.6 ± 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 δD_p and δD_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 δD_v exhibits similar variations at Huaji and Plataforma (the slope of the linear
440 regression between δD_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 8th and 15th), a few days in mid-
442 March 2006 (between 13th and 18th March) and in April 2006 (between April 6th and 10th)
443 (Figure 4). Without accounting for those periods of discrepancies, the covariance of δD_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 δD_v , δD_p exhibits similar variations between Huaji and Plataforma (the
448 slope of the linear regression between δD_p at Huaji and Plataforma is 1.05, $r^2=0.64$, n=31,
449 $p<0.001$). The aforementioned discrepancies on δD_v between Huaji and Plataforma are also
450 recorded in δD_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 δD_p at
457 Plataforma with δD_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 δD_p has been monitored since December 2001 (Figure 4). The
460 two signals are fairly similar from November 8th to 15th, 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 8th to
471 16th, 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 (δD_p from November 8th to 15th, 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 δD_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 δD_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 δD_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 δD_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 δD_p and δD_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 δD_v decreases, and in an idealized case tends to -
520 1000‰ 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 ΔD_{p_eq} is calculated for 70 simultaneous observations of δD_p and δD_v at Huaji (37

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

534 The distribution of ΔD_{p_eq} is significantly different at Huaji and at Plataforma (Figure
535 5a). At Huaji (Plataforma), the mean negative ΔD_{p_eq} is of -9.6‰ (-24.1‰) representing 62%
536 (85%) of the ΔD_{p_eq} . Plataforma also records the most negative disequilibriums (100 (83)% of
537 the ΔD_{p_eq} lower than -20 (-30)‰ are encountered at that site) whereas the positive ΔD_{p_eq} are
538 mainly observed at Huaji (74%). This relationship between the sign of ΔD_{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 ΔD_{p_eq} range from -10‰ to +10‰. ΔD_{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) ΔD_{p_eq} is similar in 2005 and 2006 (29(71) and 26(74)%
545 respectively) although we observe that the four most positive ΔD_{p_eq} (5.0‰, 7.2‰, 16‰ and
546 35.0‰) occur in 2005 whereas the lowest ΔD_{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, ΔD_{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 ΔD_{p_eq} varies along with other observations, it is worthwhile noting
554 that:

555 (1) ΔD_{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 ΔD_{p_eq}
557 ($\delta D_p > \delta D_{p_eq}$). This suggests that processes dependent on relative humidity and increasing δD_p
558 relatively to its value at equilibrium are not dominant;

559 (2) a significant positive relationship is observed between ΔD_{p_eq} and δD_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 δD_p (Figure 5c).

562 Δd_{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 Δd_{p_eq} is -3.3‰. The positive Δd_{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 Δd_{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 Δd_{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 δD_p and δD_{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 ΔD_{p_eq} (ϵ_D) and Δd_{p_eq} (ϵ_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 δD_{v_out} and d_{v_out} . The isotopic composition of water vapor during the rain event is noted
 600 δD_{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 δD_{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 ϵ_D ($\Delta D_{p_eq_ave} - \Delta D_{p_eq_ev}$) and ϵ_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, ϵ_D/ϵ_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 ϵ_D and ϵ_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 ΔD_v during the rain event (i.e X_D varies from -15 to 10‰) and we simulate the errors ϵ_D
633 and ϵ_d for 3 values of X_d (0‰, 0.5‰ and 2‰) with a fraction r of 0.1. The ϵ_D and ϵ_d co-
634 variation is plotted on Figure 6. We clearly see on this figure that:

635 (1) Errors on ΔD_{p_eq} and Δd_{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 ϵ_D and ϵ_d trajectories towards
639 negative ΔD_{p_eq} and Δd_{p_eq} as X_D decreases could explain part of the co-variation between
640 ΔD_{p_eq} and Δd_{p_eq} at Plataforma. Indeed, the trajectory of ϵ_D and ϵ_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 disequilibria. It is worth noting that the co-variation of errors
644 could also play a role at Huaji for the few cases where both disequilibria 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 ΔD_{p_eq} and Δd_{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) δD_p (d_p) than δD_{p_target} (d_{p_target})
652 (9 cases at Huaji). We did not consider either observations for which Δd_{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 25th, 29th, 30th and April 9th) (see for example Figure 2 done for
658 October 29th 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 (δD_p
668 tends to δD_{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 δD_v to the isotopic composition of
680 former rainfall events, should lead to a small negative isotopic disequilibrium. Indeed,
681 recycling tends to increase δD_v and so δD_{p_eq} is even more difficult to attain (the distance
682 between δD_{p0} , isotopic composition of rain in equilibrium with cloud water vapor, and δD_{p_eq}
683 is increased). This process could explain the small negative ΔD_{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 an
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 δD_p (Penchenat et al.,
693 2020). This evaporative process is actually the only one that could explain the few calculated
694 positive ΔD_{p_eq} (enrichment of precipitation from its expected value at equilibrium),
695 consistently with the correlation between positive ΔD_{p_eq} and the highest values for δD_p in our
696 observations. This process could be at play on the Huaji site (recording 74% of positive
697 ΔD_{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 Δd_{p_eq} . Indeed, the variations of Δd_{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 ΔD_{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 ΔD_{p_eq} and δD_p supports this explanation for negative ΔD_{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. ΔD_{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 δD_p and δD_{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 ΔD_{p_eq} and precipitation rate, we found the
727 lowest values of ΔD_{p_eq} ($<-30\text{‰}$, 9 values) among the lowest precipitation rates (<4.1 mm/h).
728 These lowest ΔD_{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), δD_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 ΔD_{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 ΔD_{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 δD_p and d_p ?**

748 Small ΔD_{p_eq} and parallel changes of δD_v and δD_p at both sites suggest that at first
749 order δD_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 δD_p . Following the
751 decomposition method explained in section 3-3, we quantify the relative contributions of local
752 and remote processes on δD_p . Large-scale processes explain 79% and 77% of δD_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 δD_p is mainly controlled by large-scale
764 processes, reflecting δD_v , and that post-condensation processes involved as rain falls are poor
765 factors to explain δD_p . This is in agreement with previous work from Vimeux et al. (2011),
766 only based on δD_p observations, which showed that δD_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 δD_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 δD_p and δD_{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, δ_p is a correct tracer of δ_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 δD_v and δD_p on the same duration. Indeed, the difference in time sampling for rain
807 and water vapor can induce errors on ΔD_{p_eq} and Δd_{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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- 986

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 Δd_{p_eq} as a function of ΔD_{p_eq} for October 29th, 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 (δD_{v0} and d_{v0})
1003 is obtained from the observed δD_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 (δD_{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^β 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).

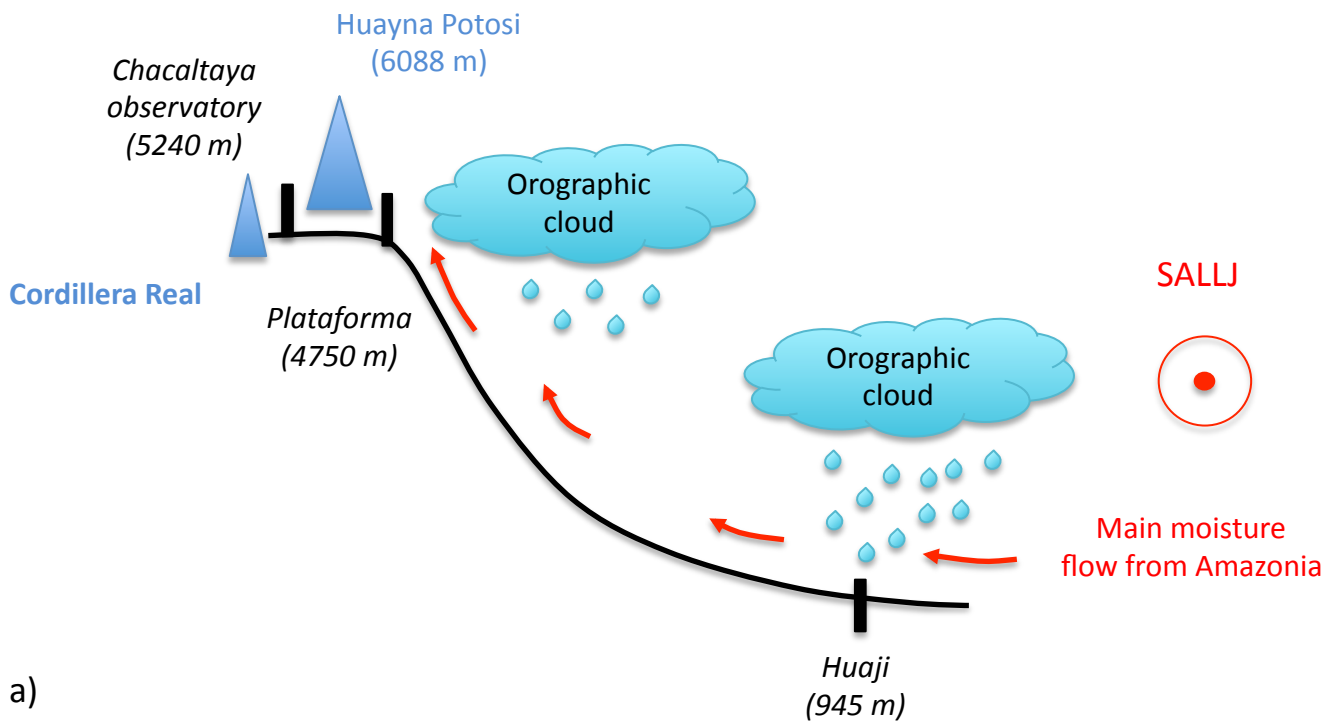
1023 **Figure 4:** Isotopic composition (δD , ‰ V-SMOW) and deuterium excess (d , ‰ V-SMOW)
1024 in precipitation (stars) and water vapor (circle) at Huaji (red), (blue) and Layca Cota (green)
1025 during the 2005 and 2006 field campaigns. When several precipitation events occur within a
1026 day, the 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 ΔD_{p_eq} (‰) (a) at Plataforma and Huaji and (b) in 2005 and 2006;
1031 (c) ΔD_{p_eq} (‰) as a function of δD_p (‰) for the whole 2005-2006 time period.

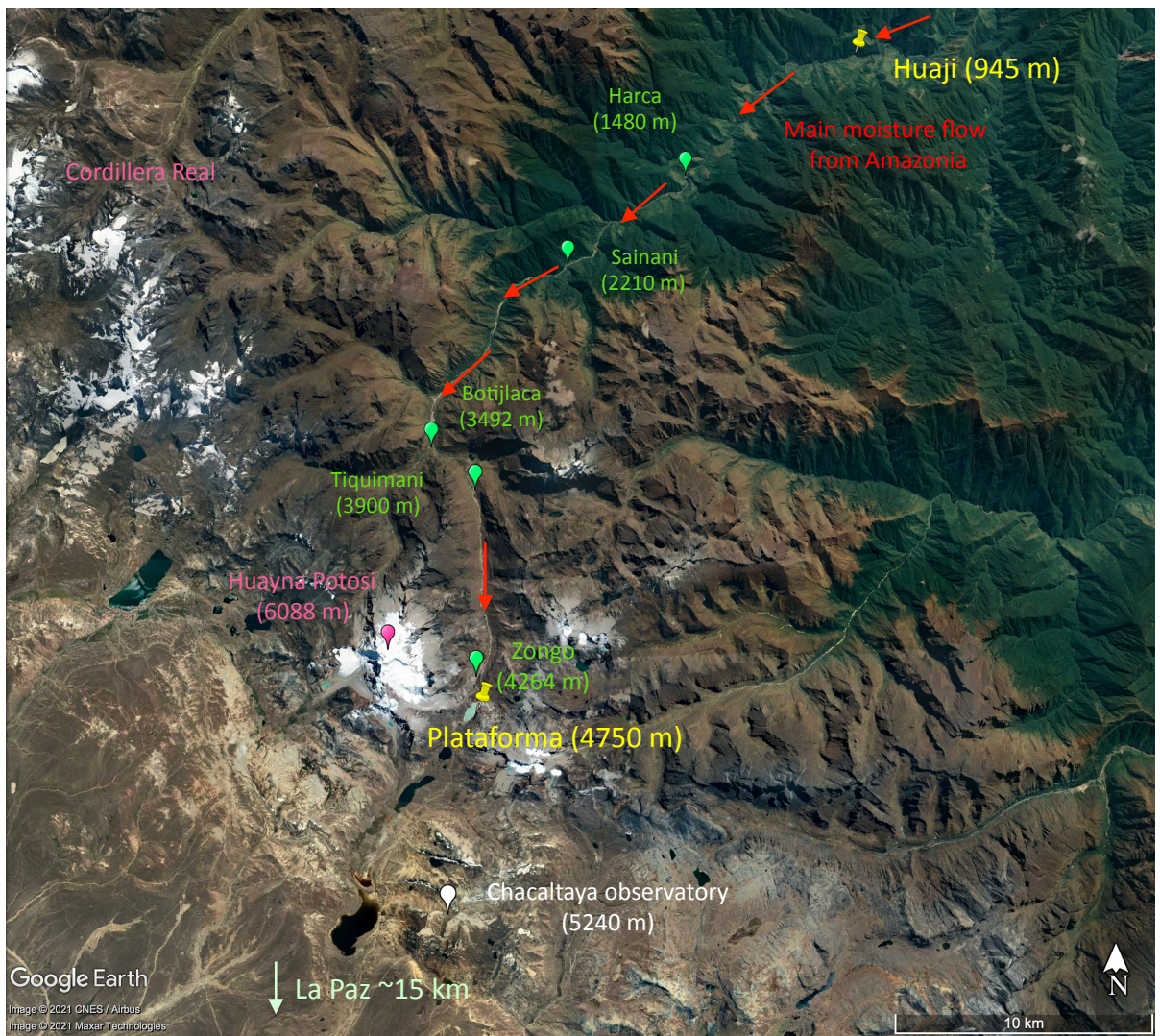
1032 **Figure 6:** Δd_{p_eq} (‰) as a function of ΔD_{p_eq} (‰) for the 54 simultaneous deuterium and
1033 deuterium excess disequilibriums (Huaji 2005: red circles, Huaji 2006: green circles,
1034 Plataforma 2005: blue circles and Plataforma 2006: black circles). We also show how ϵ_d (‰)
1035 varies as a function of ϵ_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 δD_p into a large-scale signal (associated to δD_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 δD_p for the whole dataset following the
1040 decomposition of Risi et al., (2010); (b) same as (a) but for deuterium excess.

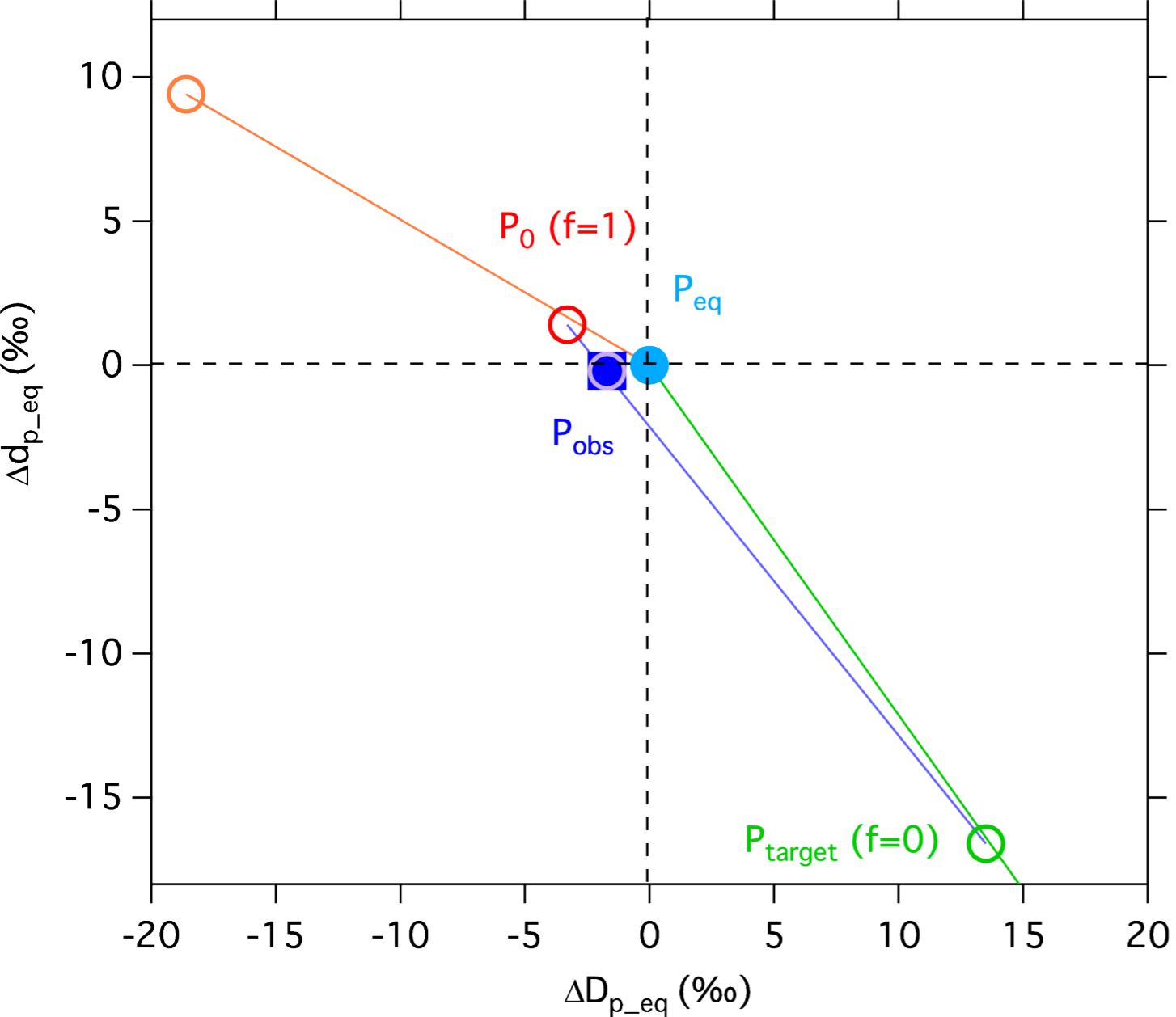
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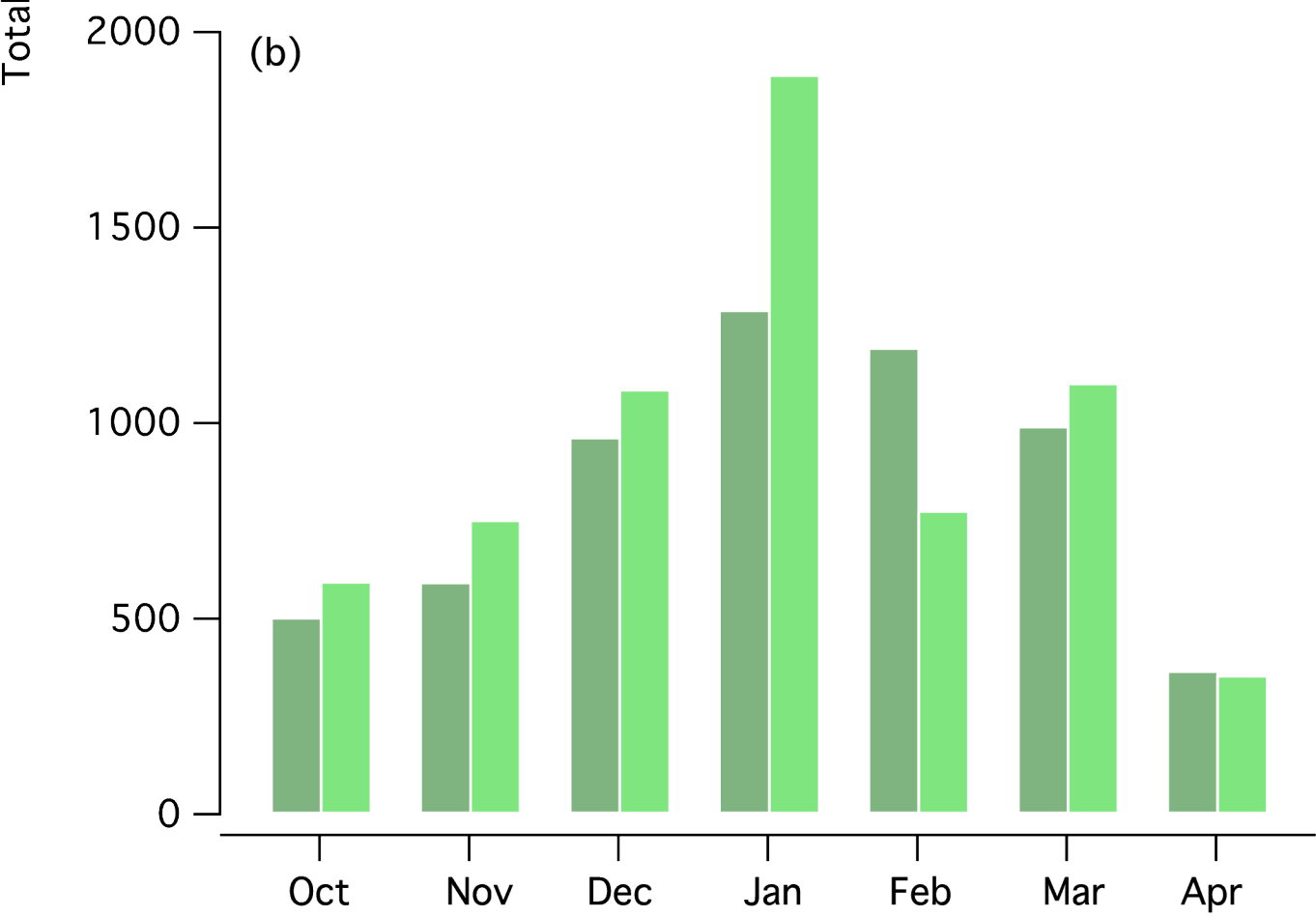
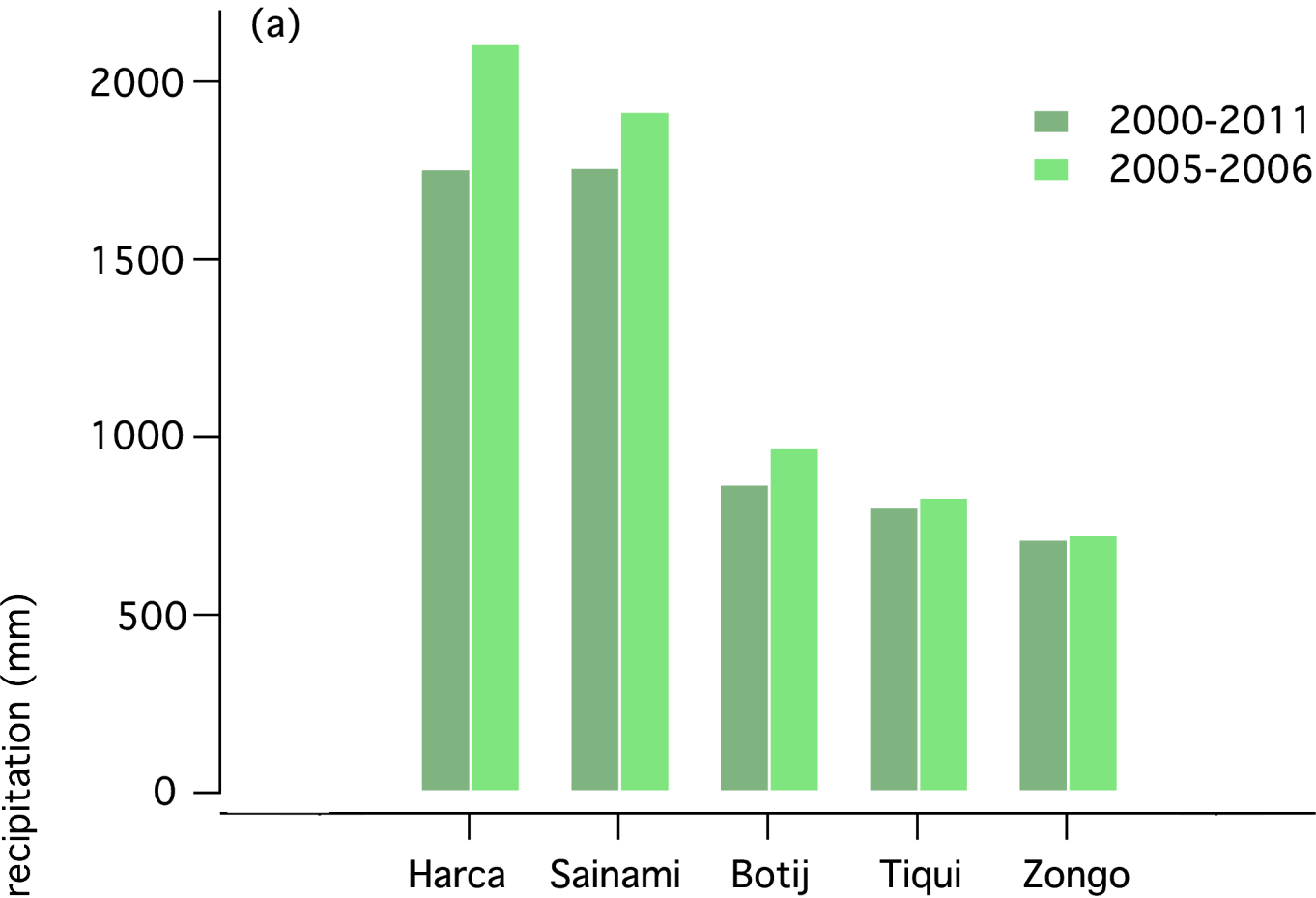
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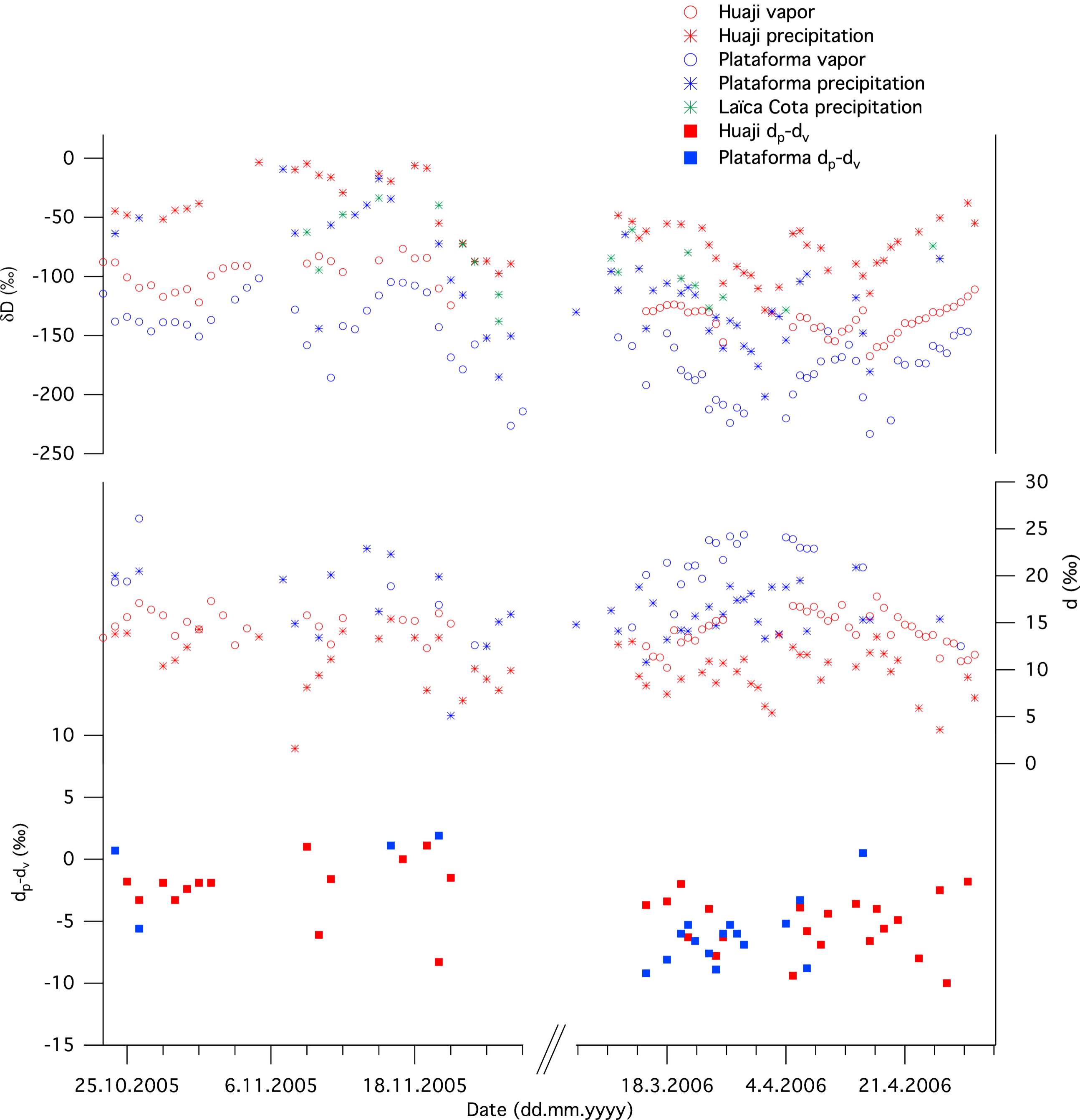


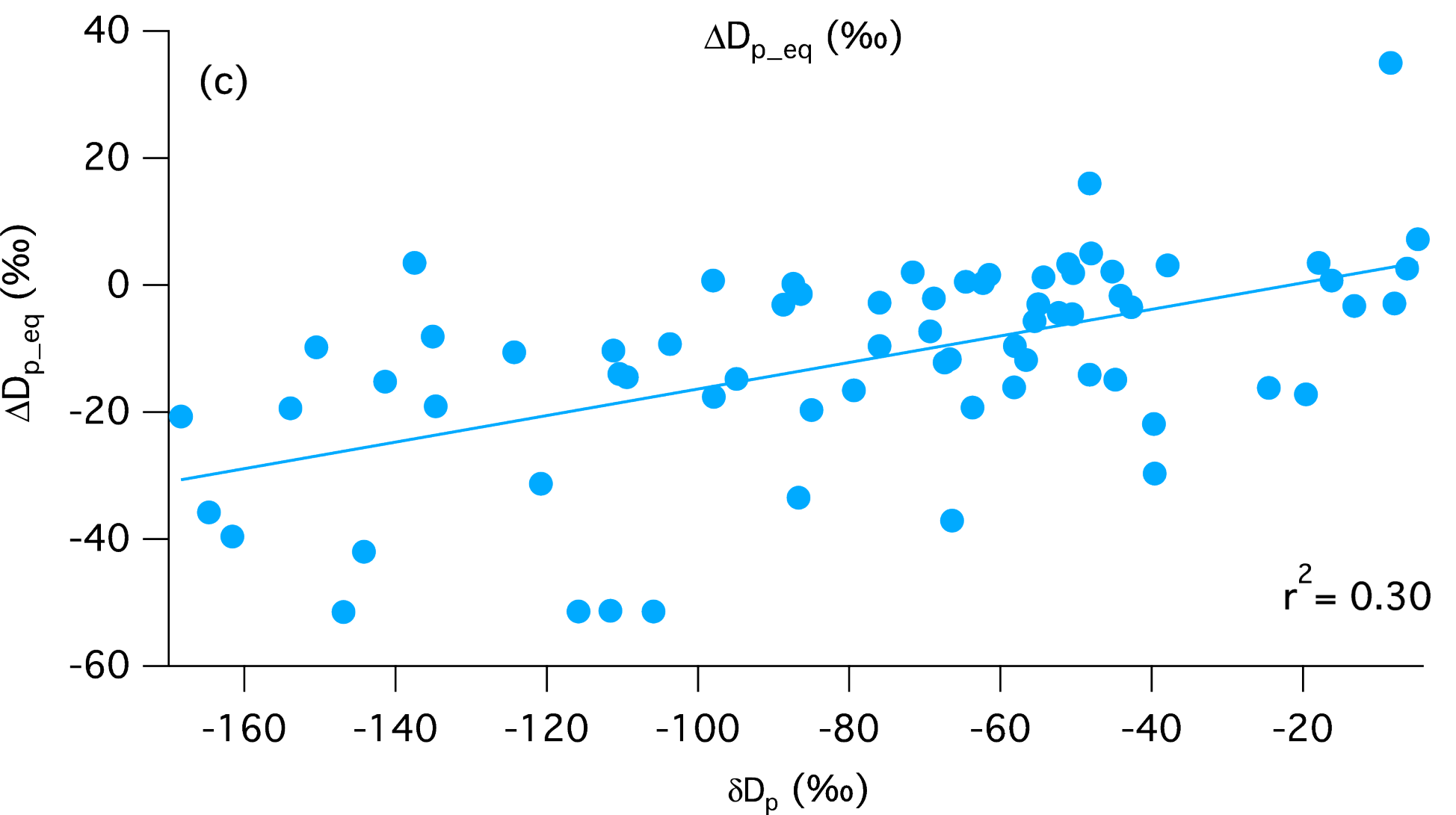
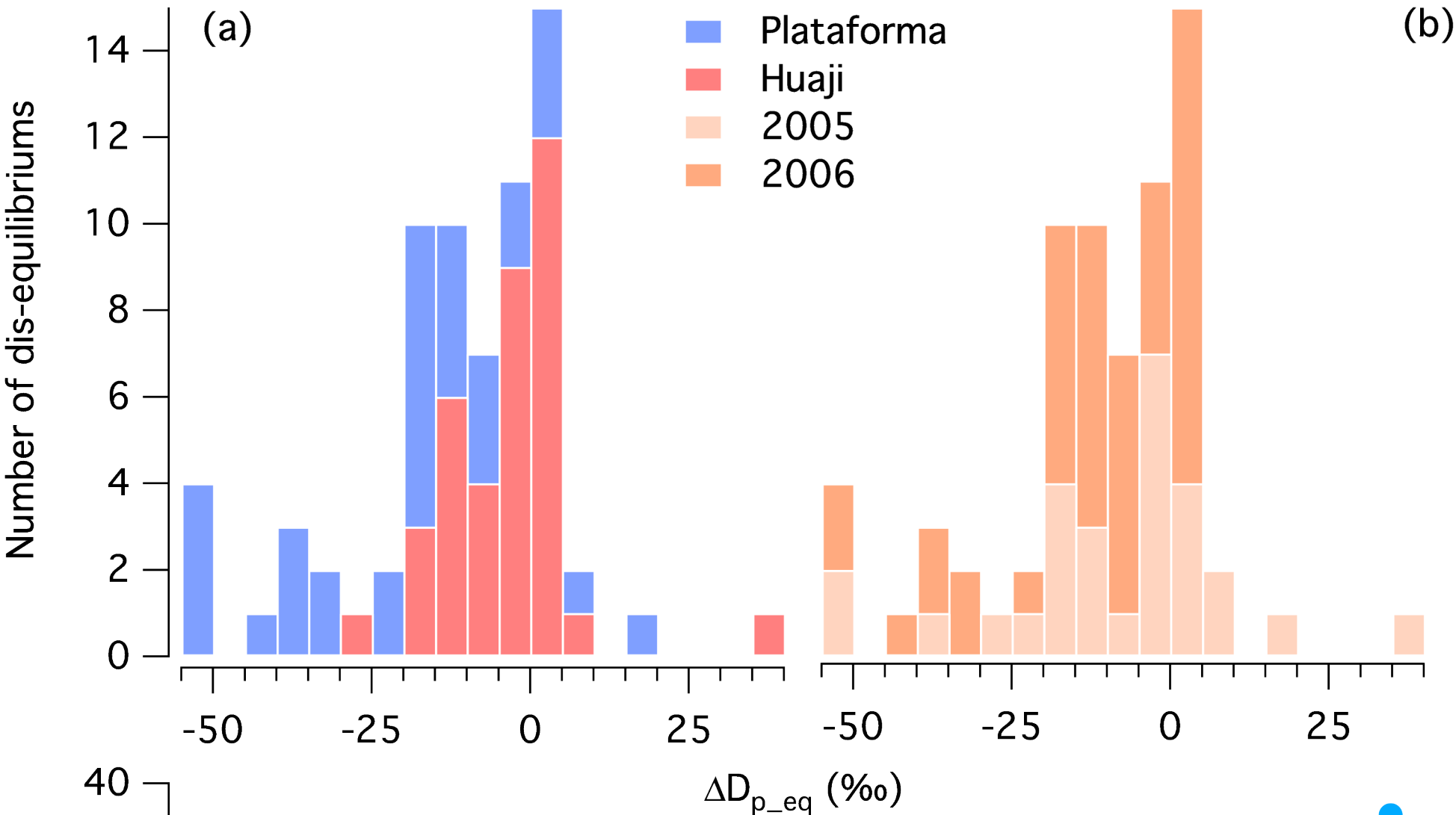
b)



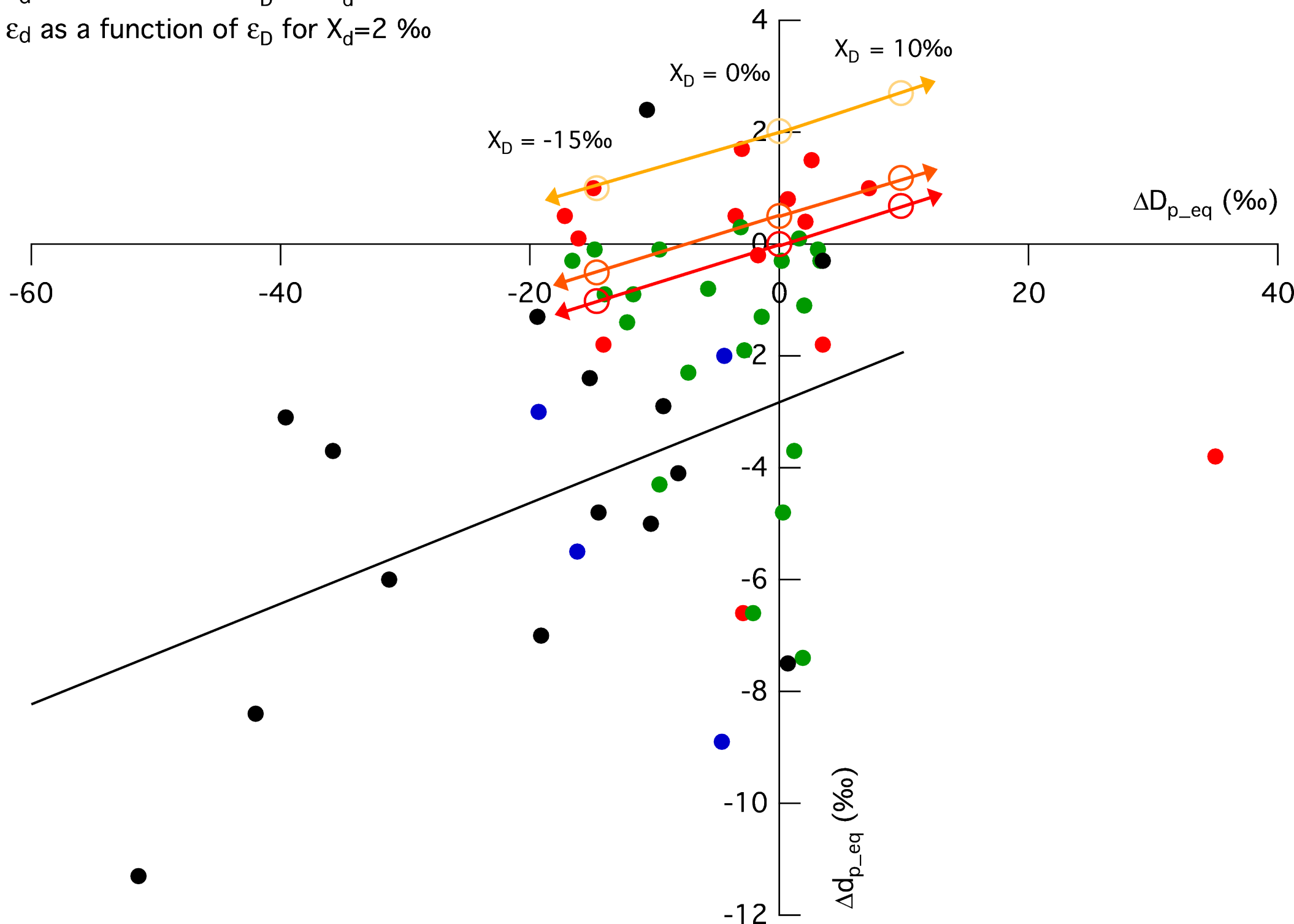
- Huaji, October 29th 2005, $T=24$ °C, $h=87.3\%$ (P_{obs})
- Initial precipitation (P_0) for $z=0$ to 3 km
- Initial precipitation (P_0) for $z=3$ km
- Initial precipitation (P_0) for $z=0.6$ km
- Target precipitation for h decreasing from 100%
- Target precipitation for $h=87.3\%$ (P_{target})
- Target 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 ε_d as a function of ε_D for $X_d=0$ ‰ ($\varepsilon_d/\varepsilon_D=0.07$)
- Trajectory of ε_d as a function of ε_D for $X_d=0.5$ ‰
- Trajectory of ε_d as a function of ε_D for $X_d=2$ ‰



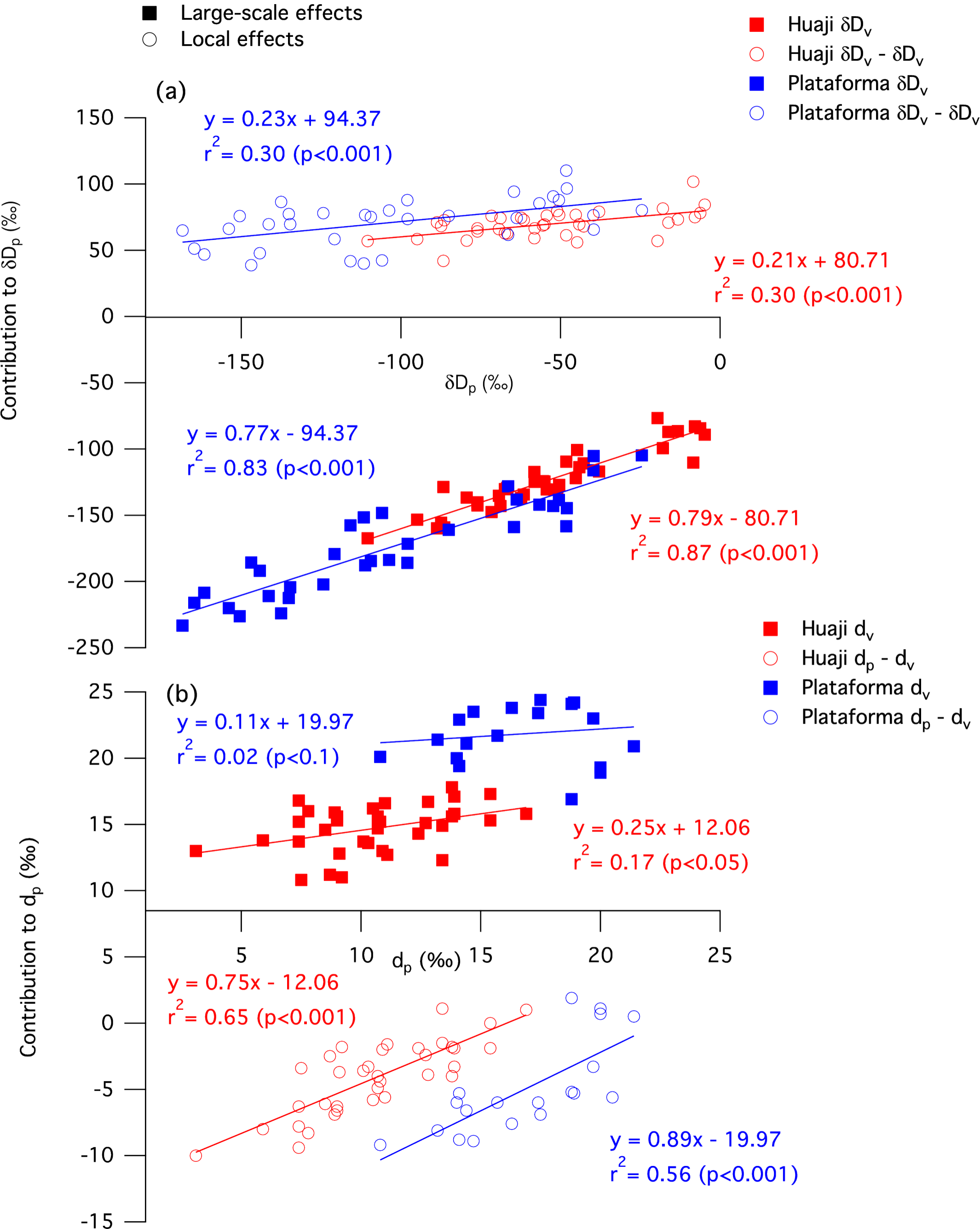


Table 1: mean $\pm 1\sigma$ for surface relative humidity and temperature and water isotopic composition (δD_v , δD_p , d_v , d_p) and mean[68%-confidence interval] for precipitation rate (it follows a log-normal distribution) during the two field campaigns at Huaji (2005 campaign: October 23th-Nov 21st, 2006 campaign: March 15th-May 1st) and Plataforma (2005 campaign: October 23th-Nov 27th, 2006 campaign: March 11th-April 30th). All rain events occurring within the field campaigns are taken into account for the calculation of δD_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]
Relative humidity (%)		
Huaji	88.1 ± 17.0	92.7 ± 12.3
Plataforma	69.6 ± 22.2	68.1 ± 22.2
Temperature (°C)		
Huaji	22.8 ± 4.6	21.1 ± 4.0
Plataforma	2.3 ± 2.7	2.3 ± 2.5
Precipitation rate (mm/h)		
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]
δD_v (‰)		
Huaji	-98.0 ± 13.7	-136.3 ± 12.3
Plataforma	-141.1 ± 30.3	-181.0 ± 24.6
δD_p (‰)		
Huaji	-40.6 ± 30.2	-79.1 ± 24.1
Plataforma	-82.9 ± 56.5	-124.3 ± 34.7
d_v (‰)		
Huaji	14.9 ± 1.4	14.1 ± 1.8
Plataforma	18.9 ± 4.4	21.1 ± 3.3
d_p (‰)		
Huaji	10.9 ± 3.4	9.7 ± 2.4
Plataforma	17.8 ± 3.3	16.1 ± 2.2

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

Site and date	ΔD_{p_eq} (‰)	Δd_{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