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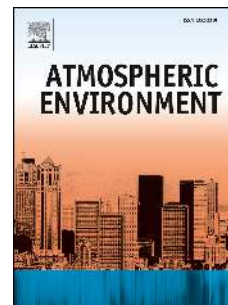
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Precipitation chemistry and wet deposition in a remote wet savanna site in West Africa: Djougou (Benin)

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Abstract.

In the framework of the IDAF (IGAC/DEBITS/AFRICA) international program, this study aims to study the chemical composition of precipitation and associated wet deposition at the rural site of Djougou in Benin, representative of a West and Central African wet savanna. Five hundred and thirty rainfall samples were collected at Djougou, Benin, from July 2005 to December 2009 to provide a unique database. The chemical composition of precipitation was analyzed for inorganic (Ca^{2+} , Mg^{2+} , Na^+ , NH_4^+ , K^+ , NO_3^- , Cl^- , SO_4^{2-}) and organic (HCOO^- , CH_3COO^- , $\text{C}_2\text{H}_5\text{COO}^-$, $\text{C}_2\text{O}_4^{2-}$) ions, using ion chromatography. The 530 collected rain events represent a total of 5706.1 mm of rainfall compared to the measured pluviometry 6138.9 mm, indicating that the collection efficiency is about 93%. The order of total annual loading rates for soluble cations is $\text{NH}_4^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$. For soluble anions the order of loading is carbonates $> \text{HCOO}^- > \text{NO}_3^- > \text{CH}_3\text{COO}^- > \text{SO}_4^{2-} > \text{Cl}^- > \text{C}_2\text{O}_4^{2-} > \text{C}_2\text{H}_5\text{COO}^-$. In the wet savanna of Djougou, 86% of the measured pH values range between 4.7 and 5.7 with a median pH of 5.19, corresponding to a VWM (Volume Weighed Mean) H^+ concentration of $6.46 \mu\text{eq.L}^{-1}$. This acidity results from a mixture of mineral and organic acids. The annual sea salt contribution was computed for K^+ , Mg^{2+} , Ca^{2+} and SO_4^{2-} and represents 4.2% of K^+ , 41% of Mg^{2+} , 1.3 % of Ca^{2+} , and 7.4 % of SO_4^{2-} . These results show that K^+ , Ca^{2+} , SO_4^{2-} , and Mg^{2+} were mainly of non-marine origin. The marine contribution is estimated at 9%. The results of the chemical composition of rainwater of

35 Djougou indicates that, except for the carbonates, ammonium has the highest VWM
36 concentration ($14.3 \mu\text{eq.L}^{-1}$) and nitrate concentration is $8.2 \mu\text{eq.L}^{-1}$. The distribution of monthly
37 VWM concentration for all ions is computed and shows the highest values during the dry season,
38 comparing to the wet season. Identified nitrogenous compound sources (NO_x and NH_3) are
39 domestic animals, natural emissions from savanna soils, biomass burning and biofuel
40 combustions. The second highest contribution is the calcium ion ($13.3 \mu\text{eq.L}^{-1}$), characteristic of
41 dust aerosols from terrigenous sources, Calcium contributes up to 46% of the precipitation
42 chemistry in Djougou. Finally, these results are compared to those obtained for other selected
43 African sites representative of other main natural ecosystems: dry savanna and forest. The study
44 of the African ecosystem transect indicates a pH gradient with more acidic pH in the forested
45 ecosystem. Nitrogenous contribution to the chemical composition of rain in Lamto, wet savanna,
46 (24%) is equivalent to the one estimated in Djougou (24%). The last contribution concerns
47 organic acidity, which represents 7% of total ionic content of precipitation at Djougou. The
48 relative particulate contribution PC and the relative gaseous contribution GC are calculated using
49 the mean chemical composition measured in Djougou for the studied period. The comparison
50 with other African sites gives 40% and 43% PC in wet savannas of Lamto (Côte d'Ivoire) and
51 Djougou (Benin) respectively, 20% PC in the equatorial forest of Zoetele (Cameroon) and 80%
52 PC in dry savanna of Banizoumbou (Niger). The results shown here indicate the existence of a
53 North-South gradients of organic, marine, terrigenous and nitrogenous contributions along the
54 transect in West and Central Africa

55

56 Keywords: Precipitation chemistry, wet deposition, neutralization factor, chemical composition.

57

58 1. Introduction

59 Atmosphere–biosphere interactions are important to understand the biogeochemical cycles of
60 atmospheric species that modulate the atmospheric composition. Anthropogenic emissions and
61 climate change play important roles in modifying atmospheric processes. In this context, wet and
62 dry- deposition of chemical species on the earth's surface play a significant role in controlling
63 the concentration of gases and aerosols in the atmosphere. The chemical composition of
64 atmospheric deposition is the product of several interacting atmospheric physical and chemical
65 processes such as: emission and source strengths; transport processes and dynamics of the
66 atmosphere; atmospheric chemical reactions and removal processes among others. Future
67 changes in atmospheric composition require information on past and present atmospheric

68 composition. In a special issue of the Atmospheric Environment journal, three overview papers
69 dealing with atmospheric composition changes emphasized that trace atmospheric constituents
70 are changing the earth's climate (IPCC, 2007), the global biodiversity (Millennium Ecosystem
71 Assessment, 2005) and the biogeochemical cycle of key atmospheric components such as
72 nitrogen, carbon, and sulfur (Laj et al., 2009; Monks et al., 2009; Fowler et al., 2009). Moreover,
73 these papers focused on the need to optimize observing systems coordinated from regional to
74 global scale to analyze and predict future atmospheric composition. The study of deposition
75 processes and their quantification thus allows for identifying the spatial and temporal evolution
76 of atmospheric chemistry and is an important way for distinguishing between natural and
77 anthropogenic influences. In regions where biogeochemical cycles are disturbed by human
78 activities, atmospheric deposition can either be a source of toxic substances or a source of
79 nutrients for the ecosystems. Having an understanding of chemical deposition fluxes is therefore
80 an essential aspect of a global interdisciplinary approach in order to develop a predictive
81 capacity for the functioning ecosystems and determining the impacts on biogeochemical cycles
82 (Brimblecombe *et al.*, 2007; Bobbink et al., 2010, Vitousek et al., 1997, Whelpdale *et al.*, 1996;
83 Pienaar, 2005).

84 Since the last three decades rainwater chemistry is subject of intensive research in many
85 countries and in different ecosystems. In 1995, the first WMO global precipitation chemistry
86 assessment provided a critical review of worldwide acidic atmospheric deposition (Whelpdale
87 and Kaiser, 1996). In the framework of WMO/GAW (World Meteorological
88 Organization/Global Atmospheric Watch), a recent assessment has presented a global overview
89 of worldwide precipitation chemistry and deposition by using quality assured measurements to
90 complement and validate available global models (Vet et al., 2014). The assessment presents
91 precipitation chemistry and deposition measurements obtained from several regional and 22
92 national monitoring networks for North America, South America, Europe, Africa, Asia Oceania,
93 and the oceans. This report demonstrates that deposition data computed from quality assured
94 measurements were limited in many regions, especially in the tropics. The IDAF project has
95 contributed to this work and has been recognized by WMO/GAW to provide a unique deposition
96 database for some African sites. DEBITS (Deposition of Biogeochemically Trace species), a
97 task of IGAC (International Global Atmospheric Chemistry) since 2005, represents one of these
98 regional networks dedicated to study atmospheric deposition in the tropics (Pienaar et al., 2005).
99 In the framework of DEBITS, the IDAF (IGAC/DEBITS/AFRICA) project started in 1994 and
100 aims to study dry and wet deposition fluxes in Africa. The goal of IDAF program is to provide a
101 long-term measuring network to study atmospheric composition and wet and dry atmospheric

102 processes and fluxes. During the Long Observation Phase of the AMMA (African Monsoon
103 Multidisciplinary Analysis) program, IDAF took an active part in investigating rainwater
104 chemistry and in determining aerosols and gas concentrations in the atmosphere over
105 West/Central Africa (AMMA/ LOP, Lebel et al., 2009; Mougouin et al., 2009; Mari et al., 2010).

106 The measuring network of the IDAF project includes 10 monitoring sites covering three types of
107 ecosystems over West and Central Africa: dry Savanna (Banizoumbou in Niger, Katibougou and
108 Agoufou in Mali, Louis – Trichardt, Amersfoort and Cape Point in South Africa), wet savanna
109 (Lamto in Ivory Coast and Djougou in Benin) and equatorial forest (Zoetele in Cameroon and
110 Bomassa in Congo).

111 Among studies performed in Africa, the works on precipitation chemistry done by Lacaux et al.,
112 1992; Sigha et al., 2003; Yoboué et al., 2005; Galy-Lacaux et al., 2009, Laouali et al., 2012,
113 Mphepya et al., 2004 and 2006 represent some synthesis papers on wet deposition fluxes
114 representative at the scale of main African ecosystems. In the present investigation, we show
115 wet only sampling and analysis of a 4 year database of rainwater chemistry, at a regional
116 representative wet savanna site in the area of Djougou in Benin. This work complements the
117 previous work of Yoboué et al. in 2005 in the wet savanna of Lamto in Côte d'Ivoire.

118 The objectives of this work are (1) to provide a background study of rainwater chemistry in
119 Benin with samples collected from 2005 to 2009, (2) to provide a better understanding of the
120 source types that contribute to the precipitation content at the scale of the year and the season,
121 (3) to analyze the inter-annual variability of rainwater composition and associated wet deposition
122 fluxes for all the different ionic species. Finally, results are compared to the results obtained for
123 other African sites of the IDAF project representative of wet, dry savannas and forest. Results
124 presented in this paper allow establishing a baseline record against which possible changes in
125 rainwater chemistry due to the changing of emissions. This study should be considered as a new
126 contribution to answer to the WMO/GAW recommendations that emphasize the scarcity of
127 deposition measurements at the scale of the African continent where a strong population growth,
128 an industrial development or agriculture intensification are observed.

129

130 **2. Study area**

131 Djougou is a village situated in Northwest Benin. The IDAF site is located in Nangatchori
132 (9°65'N, 1°74'E) near Djougou, approximately 460 km from Cotonou. The average altitude is
133 430 m. Nangatchori belongs to the wet savanna region of Benin (Figure 1). Figure 1 shows the
134 10 IDAF sites, operating in 2014, on a vegetation map of Africa (Mayaux et al., 2004).

135 The climate of Djougou is sub - Sudanese with a mean annual rainfall of 1190mm, measured
136 over 50 years (Le Barbe, 2002; Le Lay et al., 2005). It is characterized by a wet season from
137 April to October, and a dry season from November to March. These seasons are schematically
138 determined by the position of the Intertropical Convergence Zone (ITZC), the surface formed by
139 the convergence of Saharan and oceanic air masses. The wet season starts when the position of
140 the Intertropical Front reaches rather high latitudes. It allows the south air masses, loaded with
141 moisture of the Atlantic Ocean, to move northward the Saharan hot and dry air masses. This
142 moisture transport is a key factor for the monsoon system in West Africa (Lebel et al., 2009).
143 The daily mean temperatures vary from 25 °C in August to 31 °C in March. Daily amplitude of
144 temperatures achieves 20°C during the Harmattan period (January) with minimum values from
145 16°C to 19°C to maxima are about 36°C-39°C. In August, the daily amplitude of temperatures is
146 less marked with an order of magnitude around 5°C.

147 Approximately 70 % of the population of this region dedicates itself to agricultural activities
148 (<http://www.gouv.bj/>). The main cultures are yam, corn, sorghum, mil, groundnut, cowpea and
149 cotton. The relief is little bumped and represents a plateau strewn with some hills by place. It is
150 also necessary to notify that this region is just in the South of the Atakora mountain, thus
151 explaining that the rainfall amount is higher compared to more Eastern zones in Benin.

152 Vegetation is composed of a mosaic of dry forests and savannah, with dense and tall herbaceous
153 strata, mainly composed of perennial grasses, and more or less dense woody strata. In the Global
154 Land Cover Classification, our site is classified as deciduous open woodland (Mayaux et al.,
155 2004, Adon et al., 2010). Ninety-five percent of the area of the Sudanian site is on tropical
156 ferruginous soil (Seghieri et al., 2009, Kamagate et al., 2007). Most of the landscape is
157 undergoing hydric erosion.

158 We assume that the IDAF site of Djougou is rural and representative of a remote site of african
159 wet savanna.

160

161

162 **3. Material and methods**

163 **3. 1. Rain sampling**

164 Rainwater samples at Djougou were collected using an automatic precipitation collector
165 designed for the IDAF network. The principle of functioning is as follows:

- 166 - The first rain droplets order the rain detector to open the lid of the collector
- 167 - To collect rainwater, polyethylene single-use bags are used. In order to avoid any
168 contamination by aerosols and insects, the rain collector remains closed before and after the rain.

169 - Rain samples are immediately collected by a local observer after the rain event.
170 - Samples are stored in 50 ml Greiner tubes of 50 ml in a freezer -18°C (WMO-GAW report
171 n°160, 2004).
172 - After collection, samples are sent for analysis to the Laboratoire d'Aérodologie in Toulouse in the
173 strict respect of the cold chain, where they are stored in a freezer until analysis.
174
175 During all the sampling period, an automatic pluviometer has registered all rain events with a
176 time resolution from 5 min to 1 hour at the Djougou site. In addition, during the long-term
177 observation period of the AMMA program (2005-2007) 3 other rain gauges of the same type
178 were settled at the site in the framework of an hydrological project (Depreater et al., 2009). All
179 equipments were in good agreement and provided rain event depth with a maximum uncertainty
180 of 1/10 mm.
181 Table 1 shows the seasonal and annual precipitation (mm) at Djougou site for the 2005-2009
182 period. Annual precipitation varies from a minimum of 1143.5mm in 2006 to a maximum of
183 1537.2 mm in 2009. Le Barbé et al., 2002 and Le Lay et al., 2005 have measured a mean annual
184 rainfall of 1190mm (over 50 years) at Djougou in the framework of the upper Ouémé catchment
185 study. In the present study, the mean annual precipitation measured at Djougou from 2005 to
186 2009 exceeds this value with a mean annual value P_t of 1338.7 mm. The dry season, defined
187 from November to March, represents $4\pm 3\%$ (23.2 to 126 mm) of the total annual precipitation.
188 The wet season, from April to October, represents $96 \pm 3\%$ (1088.3 to 1499.7 mm) of the total
189 annual precipitation.
190 Table 2 presents the annual total precipitation (P_t) in mm, the percent total precipitation (%TP) in
191 percent and the interannual variability in % relative to the mean annual rainfall for the 2005-
192 2009 period. The percent total precipitation %TP was calculated as the ratio between the annual
193 precipitation depth P_t and the collected rain depth P_c , as defined by WMO-GAW (report n° 160,
194 2004). The Percent Coverage Length (%PCL) has been annually and quarterly calculated during
195 all the sampling period (report n° 160, 2004, Table 2). From July 2005 to December 2009, the
196 total rainfall amount is 6138 mm and the collected rain samples represent a total of 5706.1 mm
197 (530 rainy events collected). The mean collection rate is estimated at 93% and the PCL at 100%
198 (Table 2), except for 2005. The percent Total Precipitation (%TP) in 2005 is around 53%. From
199 2006 to 2009 it ranges between 92% and 95%. In this study, annual mean values of VWM and
200 WD are calculated for the 2006-2009 period when all completeness criteria were verified. In
201 2005, according to the quarterly %PCL results, only data from July to December were used for

202 the computation of monthly average of Volume Weighted Mean (VWM) and Wet Deposition
203 (WD).

204 According to all the parameters calculated in Table 2, in reference to WMO international
205 standards, we assume that the precipitation collection at Djougou is representative of the studied
206 period 2005-2009.

207

208 **3. 2. Analytical procedure**

209 The chemical analyses of the samples are performed at the Chemical Laboratory of the
210 Laboratoire d'Aérologie (LA), Toulouse, France.

211 It includes measurements of pH and conductivity and determination of the inorganic (Na^+ , NH_4^+ ,
212 K^+ , Mg^{2+} , Ca^{2+} , Cl^- , NO_3^- , SO_4^{2-}) and organic ions (HCOO^- , CH_3COO^- , $\text{C}_2\text{H}_5\text{COO}^-$, $\text{C}_2\text{O}_4^{2-}$) by
213 ion chromatography as described in Galy-Lacaux and Modi, 1998. pH is measured with an ATI
214 Orion 350 instrument with a combined electrode (ATI Orion model 9252) filled with KCl (4 M)
215 and saturated with AgCl. Two standard solutions (WTW) at pH 4.01 and 7.00 are used for its
216 calibration. The precision is 0,01pH unit.

217 The ion chromatography analyses are performed using DIONEX DX500 and ICS 1000 ionic
218 chromatographs with two automatic samplers (AS50). The eluents for anions and cations are
219 NaOH and MSA, respectively. Certified ionic standards are used for IC calibration. Carbonates
220 are analysed with the DX500, using an AS1 column with ionic exclusion and an isocratic mode
221 (100% H_2O).

222 Since 1996, the Laboratoire d'Aérologie participates to the WMO-GAW precipitation quality
223 assurance program twice a year. Results are available under the reference 700106 at the
224 following address: <http://qasac-america.org/>. Analytical performances of the Laboratoire
225 d'Aérologie for the 2005-2009 period have been published in Laouali et al., 2012 using the ring
226 diagrams representation. According to these WMO inter-comparison tests, analytical precision is
227 estimated to be 5% or better for all ions, within the uncertainties on all measured values
228 presented here.

229

230 **3.3. Data quality control**

231 To improve the quality of the IDAF dataset, the WMO quality criteria were applied to all the
232 IDAF precipitation samples. These criteria were based on the calculation of ion sum (IS) and ion
233 difference (ID) for each sample to consider the ionic balance (IB):

234

$$235 \quad IS = \sum_{\text{cations}} C_i + \sum_{\text{anions}} C_i \quad (1)$$

$$236 \quad ID = \sum_{\text{cations}} C_i - \sum_{\text{anions}} C_i \quad (2)$$

$$237 \quad IB = \left(\frac{ID}{IS} \right) * 10^2 \quad (3)$$

238 where:

239 C_i is the concentration of ion type in a specific sample, expressed in $\mu\text{eq.L}^{-1}$.

240 IS is the sum of all ion concentrations and ID is the difference between the sum of cation
 241 concentrations and the sum of anion concentrations. IS and ID are expressed in $\mu\text{eq.L}^{-1}$. IB
 242 expresses ID in percent of sum of all concentrations IS. WMO acceptance criteria are presented
 243 in the WMO-GAW report n° 160 (2004). ID criteria have been calculated for all database i.e.
 244 530 samples collected at Djougou (July 2005 - December 2009). Results indicate that 490
 245 samples, i.e. 92% of collected samples, are in the WMO acceptance range and will be considered
 246 in all the calculations presented in the result sections. 14 samples have been rejected from the
 247 database because of very low precipitation depths, preventing from pH and conductivity
 248 measurements, and chemical analysis. The final database used in this paper corresponds to 476
 249 samples on a total of 530, representing 90% of qualified samples.

250

251 4. Results and discussions

252

253 4.1. Annual volume - weighted mean precipitation concentrations and wet deposition

254 The annual volume-weighted mean concentrations (VWM) of ionic constituents in Djougou
 255 rainwater have been calculated using:

$$256 \quad \text{VMW} (\mu\text{eq.L}^{-1}) = \frac{\sum_{i=1}^N C_i P_i}{\sum_{i=1}^N P_i} \quad (4)$$

257 Where, C_i is the ionic concentration for each element in $\mu\text{eq.L}^{-1}$, P_i the precipitation amount for
 258 each rainy event in mm, and N the total number of rain events. Concentrations of H^+ were
 259 calculated from measured pH values. The annual wet deposition (WD) expressed in $\text{kg.ha}^{-1}.\text{yr}^{-1}$
 260 is calculated by multiplying the VWM in mg.L^{-1} concentrations by the annual average rainfall
 261 amount (P_t in mm) according to equation 5.

$$262 \quad \text{WD}(\text{kg.ha}^{-1}.\text{yr}^{-1}) = \text{VWM}(\text{mg.L}^{-1}) * \frac{P_t}{100} \quad (5)$$

263 VWM concentration ($\mu\text{eq.L}^{-1}$) and annual WD in precipitation over the five-year period (2005-
 264 2009) at the wet savanna site of Djougou are displayed in table 3. In 2005, samples have been

265 collected since July (after the beginning of the rainy season, May and June have not been
 266 sampled). Table 2 indicates that collected rains represent only 53 % of the 2005 pluviometry.
 267 For this reason, the year 2005 is excluded to calculate the mean characteristics of the chemical
 268 composition of rain over the study period. Table 3 presents the mean VWM and WD with
 269 associated standard deviations during the 2006-2009 period. As a matter of fact, collected
 270 samples in July, August September and October 2005 have a very good representativity with an
 271 efficiency of collection comprised between 79 and 99% for these four months of the wet season.
 272 The most important ions in Djougou rainwater samples are carbonates ions, NH_4^+ and Ca^{2+} .
 273 NH_4^+ and Ca^{2+} VWM concentrations represent 66% of the total cations VWM concentrations.
 274 The carbonates and HCOO^- VWM concentrations represent 53.6% of the total anions VWM
 275 concentrations. Afterwards, in decreasing order, we find NO_3^- , HCOO^- , CH_3COO^- , H^+ , SO_4^{2-} ,
 276 Na^+ , Cl^- , Mg^{2+} , K^+ , and $\text{C}_2\text{H}_5\text{COO}^-$. The concentration of cations follows a general pattern NH_4^+
 277 $> \text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$, while concentration of anions follows a general pattern Carbonates $>$
 278 $\text{HCOO}^- > \text{NO}_3^- > \text{CH}_3\text{COO}^- > \text{SO}_4^{2-} > \text{Cl}^- > \text{C}_2\text{O}_4^{2-} > \text{C}_2\text{H}_5\text{COO}^-$.

279

280 4.1.1. Marine and terrigenous contributions

281 In order to identify the origin of elements in rainwater, sea salt contribution and corresponding
 282 enrichment factors have been calculated according to the method suggested by many authors
 283 (Keene et al., 1986; Chao and Wong, 2002; Quiterio et al., 2004) using equations 6 and 7.

284 Enrichment factors (EF) were calculated using equation 6.

$$285 (\text{EF})_x = [\text{X}/\text{Na}^+]_{\text{rain}} / [\text{X}/\text{Na}^+]_{\text{seawater}} \quad (6)$$

286 where, EF_x is the enrichment factor of the species X, Na^+ is used as the marine reference,
 287 $(\text{X}/\text{Na}^+)_{\text{rain}}$ is the ratio of the X ion amount to Na^+ in rain, and $(\text{X}/\text{Na}^+)_{\text{seawater}}$ is the ratio of
 288 species X to Na^+ in seawater. Reference values $[\text{X}/\text{Na}]_{\text{seawater}}$ for the different ions are taken from
 289 Keene et al. (1986) to compute EF for marine contribution. EF for marine contributions are
 290 calculated from mean VWM of K^+ , Cl^- , Mg^{2+} , SO_4^{2-} , Ca^{2+} (Table 3). The sea-salt fraction (SSF)
 291 for some selected ionic components X of rainwater is calculated considering the ionic proportion
 292 to Na^+ in seawater and suggesting that Na^+ concentration represents the marine reference using
 293 equation 7 (Keene et al., 1986; Singh et al., 2008; Pauliquevis et al., 2012).

$$294 [\text{X}]_{\text{ss}} = [\text{X}/\text{Na}^+]_{\text{seawater}} \times [\text{Na}^+]_{\text{rainwater}} \quad (7)$$

295 In addition, a correlation analysis between the different ionic species has been performed using
 296 the Spearman Method for the 476 rain events in agreement with the WMO criteria (table 4).
 297 High correlation could indicate that concerned ions have the same origins or participate in a
 298 same chemical reaction. Results of sea salt fractions and enrichment factors for K^+ , Cl^- , Mg^{2+} ,

299 SO_4^{2-} , Ca^{2+} ions are given in table 5. The SSF for K^+ , Mg^{2+} , Ca^{2+} and SO_4^{2-} are estimated to be
300 around 4.2%, 41%, 1.3 % and 7.4 % respectively. $\text{EF}_{\text{marine}}$ for Cl^- is lower than 1 showing that
301 Cl^- was almost 100% marine assuming that all the sodium is from marine source (Cao et al.,
302 2009). The high correlation between Na^+ and Cl^- ($r = 0.93$) suggests that both have mainly a
303 marine origin. K^+ and Mg^{2+} are highly correlated with Na^+ ($r = 0.89$, and $r = 0.84$, respectively)
304 and with Cl^- ($r = 0.87$, and $r = 0.83$, respectively) showing that they also have a marine origin.
305 K^+ , Mg^{2+} and SO_4^{2-} are also correlated with Ca^{2+} ($r = 0.70$, $r = 0.93$, $r = 0.77$ respectively)
306 emphasizing the contribution of the crustal source. Ouafu et al., (personal communication 2014)
307 have recently studied the chemical composition of the aerosols collected at Djougou from 2005
308 to 2009. This work indicates that during the wet season, the Particulate Organic Matter is
309 predominant, followed by dust and Elemental Carbon in both sizes (PM2.5 and PM10). These
310 results point out the importance of biofuel combustion used for cooking, and biogenic emissions
311 during the wet season. This combustion source certainly explains one part of the potassium
312 signature measured in rains. The positive relationship between K^+ , Mg^{2+} , SO_4^{2-} and Ca^{2+}
313 confirms the importance of particles coming from the desert and semiarid regions in the
314 chemical composition of rainfall. The North African desert areas (Sahel and Sahara) are
315 probably the most important mineral aerosol source (Kaufman et al., 2005, Marticorena et al,
316 2010). Due to the partial dissolution of soil dust terrigenous components, rain in the wet savanna
317 of Benin is loaded with dissolved calcium and carbonates (calcite), which may account for a
318 large part of the ionic concentrations of rainwater. In addition to calcite, dolomite, and gypsum,
319 the dissolution of other key minerals such as illite, smectite, palygorskite that compose African
320 dusts, explains the enrichment of Mg^{2+} , SO_4^{2-} and K^+ (Avila et al., 1997). This result is similar
321 to that obtained in other African ecosystems and regions of the world such as in Asia (Loye-Pilot
322 et al., 1986; Sigha et al., 2003; Galy-Lacaux et al., 2009; Laouali et al., 2012, Kandler and
323 Shultz, 2007; Celle-Jeanton et al., 2009; Desboeufs et al. 2010; Kulshrestha et al., 2009).

324

325 4.1.2. Nitrogenous compounds

326 The chemical composition of rainwater at Djougou indicates that nitrogenous compound
327 concentrations represent an important contribution, about 23% of the total ionic charge.
328 Ammonium has the highest VWM concentration with $14.3 \pm 2.2 \mu\text{eq.L}^{-1}$. Nitrate concentration is
329 $8.2 \pm 0.5 \mu\text{eq.L}^{-1}$ (Table 3). These results are in accordance with data obtained at the wet savanna
330 site of Lamto where NH_4^+ and NO_3^- are $16.8 \mu\text{eq.L}^{-1}$ and $8.9 \mu\text{eq.L}^{-1}$, respectively (Yoboué et al.,
331 2005). NH_4^+ is also the main nitrogenous ion found in the rain samples at the three dry savannas

332 sites: Agoufou ($25.2 \mu\text{eq.L}^{-1}$), Banizoumbou ($17.9 \mu\text{eq.L}^{-1}$), Katibougou ($19.1 \mu\text{eq.L}^{-1}$) (Laouali
333 et al., 2012). Note that atmospheric monthly NH_3 surface concentrations (3.9 ± 1.2 ppb) measured
334 using passive sampling (Adon et al., 2010) are also higher than NO_2 (1.1 ± 0.1 ppb) at the
335 Djougou site.

336 Sigha et al., 2003 and Yoboue et al., 2005 suggested that ammonium content in precipitation
337 results from the inclusion of gaseous ammonia and particles contained in clouds and rainwater.
338 These inclusions are due to the prevailing emission sources around the studied site. Major
339 sources of NH_3 include bacterial decomposition of urea in animal excreta and emission by
340 natural or fertilized soils (Schlesinger and Hartley, 1992; Galy-lacaux and Modi, 1998). Biomass
341 burning during the dry season, domestic combustions and incomplete traffic sources all along the
342 year are the other principal sources of NH_3 (Delmas et al., 1995, Brocard et al., 1996; Lacaux et
343 Modi 1998, Laouali et al., 2012). To explain nitrate and ammonium concentration in rains, we
344 assume that nitrogenous gaseous compounds such as NO_x and NH_3 are related to main sources
345 such as biomass burning, biogenic NO emissions from soils, NH_3 volatilization and biofuel and
346 fossil fuel combustions (Junker and Liousse 2008, Delon et al., 2012, Galy-Lacaux and Delon,
347 2014, Liousse et al., 2014).

348
349 Figure 2 presents the relative contributions of each source, i.e. Biogenic NO, biofuel and
350 incomplete traffic (BF), biomass burning (BB) and volatilization processes (Vol.). Fluxes are
351 calculated at a spatial resolution of 5° by 5° around the Djougou site from 2002 to 2007 with a
352 monthly resolution. These calculations use both satellite data and simulation results, following
353 the methodology developed by Delon et al. (2012), and by Galy-Lacaux and Delon 2014.
354 Biogenic NO emissions from soils have been simulated using a parameterization developed in
355 Delon et al. 2007. The contribution of domestic fires and incomplete traffic to NO_x and NH_3
356 emissions is estimated according to the work of Junker and Liousse, 2008 and Liousse et al.,
357 (2014) based on African fuel consumption and specific emission factors. The contribution of
358 biomass burning fires is estimated according to Liousse et al., 2010, based on L3JRC burnt area
359 satellite product, Global Land Cover (GLC) vegetation map and data on burning efficiencies and
360 emission factors. No industrial sources are found in the area of Djougou. NH_3 volatilization is
361 computed from the N input by organic fertilization. Synthetic fertilization in West Africa is
362 considered as negligible (Delon et al., 2012). N input by organic fertilization is the product of N
363 release by livestock (in $\text{kgN.animal}^{-1}.\text{yr}^{-1}$), by the animal population in Benin (Food and
364 Agriculture Organization, FAO, (2009) (<http://kids.fao.org/glipha>)). For Djougou, this N input is
365 estimated to be $8 \text{ kgN.ha}^{-1}.\text{yr}^{-1}$. 30% of this value volatilized as NH_3 , the remaining 70% N stay

366 in the soil and contribute to NO biogenic emission (Delon 2012, Galy –Lacaux and Delon 2014).
367 Uncertainties in the estimation of NH₃ volatilization is 50%, as described in Galy and Delon
368 2014, and reaches 60% for NH₃ and NO_x biofuel emissions.

369 As a result, we can notice that NO in the wet savanna of Djougou is mainly produced by soil
370 emission and biomass burning (figure 2). NO is oxidized into NO₂ and HNO₃ by photochemical
371 reactions. HNO₃ is further scavenged by clouds. Simulations of biogenic NO soil emission at the
372 Djougou site during the 2002-2007 period shows mean rates of $3.2 \pm 0.6 \text{ kgN} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$ during the
373 wet season and $2.3 \pm 1.2 \text{ kgN} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$ as yearly mean (Figure 2). Biogenic NO fluxes from
374 soils strongly depend on soil humidity and are lower during the dry season, when microbial
375 activity at the origin of N formation in the soil is less active (Yienger and Levy, 1995; Meixner
376 et al., 1997, Hudman et al., 2012). NH₃ is mainly produced by volatilization processes, biofuel
377 and biomass burning at the Djougou site.

378 In terms of nitrogenous particulate content in precipitation, gaseous ammonia is transformed into
379 particulate ammonium in the atmosphere and is associated with various anions to form
380 (NH₄)₂SO₄, NH₄Cl, and NH₄NO₃. NH₄NO₃ is formed by the reaction of HNO₃ with NH₃ on
381 moist soil surfaces, partly because of the formation of un-dissociated NH₄NO₃ when relative
382 humidity is more than 62% (Singh and Mondal 2008; Saxena et al., 1996). Nitrate in rainwater
383 might be the result of homogenous and heterogeneous gas-phase transformations of NO_x to
384 HNO₃, followed by reaction with NH₃ to form NH₄NO₃. Dominance of NH₄NO₃ has been
385 reported in rainwater by many authors and reflects the influence of biodegradation and
386 agricultural activities. In this study, correlations between NH₄⁺ and SO₄²⁻ ($r = 0.82$), NH₄⁺ and
387 Cl⁻ ($r = 0.74$), and between NH₄⁺ and NO₃⁻ ($r = 0.86$) confirm that ammonium is associated in
388 multiphase reactions.

389

390 **4. 1.3. Acid contribution**

391 The measured pH values in rainwater samples collected from 2005 to 2009 are between 3.96 and
392 7.47. 86% of rain samples pH range between 4.7 and 5.7. Figure 3 shows the pH distribution
393 frequency. The median pH is 5.19 and corresponds to a mean VWM H⁺ concentration of $6,46 \pm$
394 $2,19 \mu\text{eq} \cdot \text{L}^{-1}$. During the studied period (2005-2009), 82% of rainy events had pH values less
395 than 5.60. 5.60 represents the pH value resulting from the equilibrium between atmospheric CO₂
396 and pure distilled water. This result confirms that the majority of rainy events collected in
397 African wet savannas are acidic (Lacaux et al., 1992, Galy–Lacaux et al., 2009, Yoboue et al.,
398 2005, Sigha et al., 2003). The highest pH values superior to 5.9 are essentially found in rain

399 samples with high concentration of calcium, carbonates and magnesium. This demonstrates the
400 associated basic contribution of dust present in rain composition.

401 Annual acetic, formic, propionic and oxalic volume weighed mean concentrations were
402 calculated for the 2005-2009 period excluding data of 2007 because organic ions VWM could
403 not be measured for this year. Measured VWM concentrations of organic acids are relatively
404 high. Mean HCOO^- (formic) and CH_3COO^- (acetic) concentrations are 8.6 and 6.70 $\mu\text{eq.L}^{-1}$,
405 respectively. VWM concentrations of $\text{C}_2\text{O}_4^{2-}$ and $\text{C}_2\text{H}_5\text{COO}^-$ are lower by a factor of 7 and 15
406 respectively. HCOO^- and CH_3COO^- VWM concentrations are comparable to those measured at
407 the Lamto wet savanna site, and higher than in Congo (Dimonika Forest, Lacaux et al., 1992).
408 These concentrations represent about half of organic acids VWM concentrations measured in big
409 cities of the world such as Singapore or Sao Paulo (Vet et al., 2014).

410 In terms of concentration, the more important acids in the atmosphere are acetic and formic
411 acids generally derived from the following sources: vegetation, biomass burning and bio fuel,
412 fossil fuel, agricultural emissions and soils (Paulot et al., 2011). Wet deposition is one of the
413 major sinks of organic acids. Therefore, at Djougou, the rain composition with high organic
414 acidity could be mainly explained by two strong sources: BVOC (Biogenic Volatile Organic
415 carbon) from vegetation and VOC from combustions. Saxton et al., (2007) have performed
416 BVOC measurements during the AMMA 2006 wet season at Djougou and have shown that
417 BVOC levels are high, especially for isoprene and monoterpene. For some specific species,
418 levels in Benin are higher than VOC measurements performed in a forest of the North Congo
419 (Serça et al., 1998). On the other hand, the Djougou site is also influenced by VOC emissions
420 from combustions. Ouafó et al., 2014 (personal communication) and Lioussé et al., 2010
421 demonstrate that if biomass burning remains the major source of organic aerosols during the dry
422 season in Benin, domestic fires using fuelwood, charcoal and animal waste are also important
423 sources which remain stable all over the year and thus important during the wet season.

424 To evaluate the acidic contribution to the rain, we consider SO_4^{2-} , NO_3^- and HCOO^- , CH_3COO^- ,
425 $\text{C}_2\text{O}_4^{2-}$ and $\text{C}_2\text{H}_5\text{COO}^-$ as the main acidifying components of rains, for mineral and organic
426 acidity respectively. We define the potential acidity (pA) as the sum of nitrate, sulfate, formate
427 and acetate VWM concentrations, supposing that all ions are associated with H^+ (equation 8).

$$428 \quad pA = \sum \text{anions} = [\text{SO}_4^{2-}] + [\text{NO}_3^-] + [\text{HCOO}^-] + [\text{CH}_3\text{COO}^-] + [\text{C}_2\text{H}_5\text{COO}^-] + [\text{C}_2\text{O}_4^{2-}] \quad (8)$$

429 Using pA calculations, we also calculate the Fractional Acidity FA (Balasubramanian et al.,
430 2001, Cao et al., 2009, Cheng Y. et al., 2011) according to equation (9).

431

$$\sum FA = [H^+] / \left([SO_4^{2-}] + [NO_3^-] + [HCOO^-] + [CH_3COO^-] + [C_2H_5COO^-] + [C_2O_4^{2-}] \right) \quad (9)$$

433 According to Balasubramanian et al., (2001), if FA equals to 1, the acidity generated by acids is
 434 not neutralized at all. In Djougou precipitations, the annual average of FA is 0.23 indicating that
 435 about 77% of the rain acidity is neutralized by alkaline ions. The evaluation of the relative
 436 contribution of each anion to the Potential Free Acidity (PFA) of precipitation was determined
 437 using the following formula (10) (Dos Santos et al., 2008):

$$PFA = \frac{[X]}{\sum anions} \quad (10)$$

439 where, $[X]$ is the individual VWM concentration ($\mu\text{eq.L}^{-1}$) of the concerned anion. Relative
 440 contributions of each organic and inorganic acid to the Potential Free Acidity in Djougou
 441 rainwater are presented in Table 6. Relative contributions of organic and inorganic acids are
 442 49.6% and 50.4% respectively. Assuming that all major organic and inorganic anions (NO_3^- , Cl^- ,
 443 SO_4^{2-} , $HCOO^-$, CH_3COO^- and $C_2O_4^{2-}$) measured in rainwater composition could be in the form of
 444 free acids, the pA is estimated to be $28.6 \mu\text{eq.L}^{-1}$, leading to a pH of 4.5. This pH is lower than
 445 the measured pH of 5.19. That means that a fraction of the acidity is neutralized, especially by
 446 alkaline species such as Ca^{2+} , NH_4^+ .

447 Neutralization Factor NF has also been calculated to appreciate the neutralization of rainwater by
 448 different alkaline ions NH_4^+ , Ca^{2+} , Mg^{2+} , and K^+ (Rastogi and Sarin, 2005, Celle-Jeanton et al.
 449 2009). In this study, considering the significant VWM values of CH_3COO^- and $HCOO^-$, the
 450 Neutralization Factor was calculated using equation (11):

$$NF_{x_i} = \frac{[x_i]}{[NO_3^-] + [SO_4^{2-}] + [HCOO^-] + [CH_3COO^-] + [C_2O_4^{2-}] + [C_2H_5COO^-]} \quad (11)$$

452 Where x_i are cations of interest, and all ionic concentrations are expressed in $\mu\text{eq.L}^{-1}$.
 453 The NF values for NH_4^+ , Ca^{2+} , Mg^{2+} , and K^+ are 0.499, 0.464, 0.074 and 0,070 respectively.
 454 These values represent 45%, 42%, 7% and 6% of the contribution to the neutralization process
 455 respectively. These results show that NH_4^+ and Ca^{2+} are the main neutralization ions in
 456 rainwater. The analysis of correlation coefficient shows that the acidity (H^+) is not correlated to
 457 mineral acids (NO_3^- and SO_4^{2-}) (table 4). In addition, the good correlation between Ca^{2+} and
 458 NO_3^- ($r = 0.75$) indicates the presence of heterogenous chemistry processes of neutralization
 459 between alkaline dust particles and gaseous nitric acid. Galy-Lacaux et al., 2001 have shown that
 460 this capture could be complete and could explain to a large extent the neutralization processes of
 461 the rain potential acidity. This result has been widely emphasized in other parts of the world
 462 where desert soil dust emissions influence rain chemistry, as for example in Spain or in the

463 Mediterranean basin (Avila, 1997, 1998; Herut et al., 2000), in Asia (Kulshrestha et al., 2003,
464 2005; Hu et al., 2003). H^+ is only slightly correlated with $HCOO^-$, CH_3COO^- , $C_2H_5COO^-$ and
465 $C_2O_4^{2-}$ (Table 4). One part of the organic acidity is neutralized by dissolved gases such as
466 ammonia, explaining the low remaining acidity ($6.5 \mu eq.L^{-1}$) compared to the pA ($28.6 \mu eq.L^{-1}$).
467 This result is illustrated by the correlation coefficients between NH_4^+ and all organic ions (r
468 varies from 0.55 to 0.74).

469

470 **4. 2. Monthly variation of concentrations and wet deposition of chemical constituents at the** 471 **wet savanna site of Djougou**

472 Mean monthly distribution of VWM concentrations are presented in Figure 4(a-d), for the main
473 chemical constituents grouped by sources contribution along the year, i.e: marine (4a),
474 terrigenous (4b), nitrogenous (4c) and organic (4d). Vertical bars indicate the standard deviation
475 while the mean monthly rain depth is superimposed on the monthly VWM ion concentrations.
476 Uncertainty bars for December, January and February are not plotted because of a too low
477 number of rains for these months (table 1).

478 Results show the large monthly difference in VWM concentrations for the main chemical
479 constituents in rainwater during the dry season compared to wet season. The first (January to
480 March) and last (November to December) rainfall event of a year presents very high monthly
481 VWM concentrations for the four groups of rain components. These high VWM concentration
482 values obtained during the dry season are due to dust particles in the atmosphere coming from
483 Harmattan winds and to gases emitted by biomass burning (figure 2).

484 In the core of the wet season (April to September), measured VWM concentrations are 2 to 20
485 times lower. Monthly NH_4^+ VWM varies from 230.9 in January to $9.4 \mu eq.L^{-1}$ during the wet
486 season. Monthly Ca^{2+} VWM concentrations range from 130.5 to $7.2 \mu eq.L^{-1}$; NO_3^- from 120.6 to
487 $6.1 \mu eq.L^{-1}$ and $HCOO^-$, CH_3COO^- , SO_4^{2-} , K^+ , Mg^{2+} , Cl^- and Na^+ monthly VWM concentrations
488 vary respectively from 114 to $6.0 \mu eq.L^{-1}$, from 47.8 to $3.8 \mu eq.L^{-1}$, from 52.4 to $5.4 \mu eq.L^{-1}$,
489 from 37.1 to $1.1 \mu eq.L^{-1}$, from 48.5 to $1.2 \mu eq.L^{-1}$, from 34.4 to $2.4 \mu eq.L^{-1}$ and from 21.4 to 2.5
490 $\mu eq.L^{-1}$. Seasonal VWM concentrations were calculated. Results indicates that VWM
491 concentration of major ions in Djougou rainwater are on average 5 ± 2 higher in the dry season
492 (November-March) than in the wet season (April-October). The impact of the high VWM
493 concentrations during the dry season on the annual VWM concentrations has been calculated,
494 and shows that results are species dependent. Mg^{2+} , NH_4^+ , Ca^{2+} , K^+ , NO_3^- and CH_3COO^- VWM
495 concentrations during the dry season represent 15%, 11%, 11%, 10%, 7% and 8% of the mean
496 annual VWM concentration, respectively. It represents only 2% or 3% for Na^+ , Cl^- , SO_4^{2-} and

497 carbonates. These proportions show that dry season rains, representing only 4% of the total
498 annual rain depth contributes to about 10% of the total measured chemical composition of
499 precipitation. Equation (5) is used to compute mean monthly WD for the period (Figure 5).
500 Results suggest an opposite picture compared to monthly VWM repartition. WD is maximum
501 during the wet season from July to September and increases proportionally to the rain depth
502 amount. Maximum occurs in July and August.

503

504 **4. 3 Inter-annual variability of rain chemistry**

505 At the IDAF site of Djougou, the total annual precipitation varies from 1144mm to 1539mm
506 during the sampling period (2005-2009), with a mean of 1325mm. The variability of the
507 precipitation annual amount corresponds to $\pm 16\%$. pH values range from 3.96 to 7.47 and the
508 annual mean pH is 5.19 with a maximum deviation of ± 0.15 . To investigate the inter-annual
509 variability of the rain chemical composition, the variation around the mean VWM concentrations
510 has been calculated for groups of ionic components, representative of the different contributions
511 identified in previous sections. For the marine contribution, VWM concentrations of Na^+ , Cl^- ,
512 ssCa^{2+} , ssMg^{2+} , ssSO_4^{2-} and ssK^+ are summed. For the nitrogenous and the terrigenous
513 contribution, of the sum of NO_3^- and NH_4^+ and carbonate ions, nssCa^{2+} , nssMg^{2+} , nssK^+ and
514 nssSO_4^{2-} VWM concentrations are considered, respectively. Finally, the group representing the
515 organic contribution is composed of organic ions, HCOO^- , CH_3COO^- , $\text{C}_2\text{O}_4^{2-}$ and $\text{C}_2\text{H}_5\text{COO}^-$.
516 For the acidic contribution H^+ VWM concentration is used, calculated from pH values. Results
517 show that the marine contribution varies from 5.4 to 11.5 $\mu\text{eq.L}^{-1}$ with a mean value of 8.8 ± 2.56
518 $\mu\text{eq.L}^{-1}$. The nitrogenous contributions vary from 20.3 to 25.3 $\mu\text{eq.L}^{-1}$ with a mean value of 22.5
519 ± 2.2 $\mu\text{eq.L}^{-1}$. The terrigenous contribution ranges from 36.7 to 49.8 $\mu\text{eq.L}^{-1}$ with a mean value of
520 44.0 ± 6.4 $\mu\text{eq.L}^{-1}$. The VWM concentration related to the organic source varies from 8.3 to 17.7
521 $\mu\text{eq.L}^{-1}$ with a mean value of 14.2 ± 5.1 $\mu\text{eq.L}^{-1}$. Ion H^+ VWM concentrations range from 4.5 to
522 8.9 $\mu\text{eq.L}^{-1}$ with a mean value of 6.46 $\mu\text{eq.L}^{-1}$. At Djougou, the inter-annual variation of rain
523 chemical composition, through the analysis of the different sources contribution, indicates that
524 the marine, the nitrogenous, the organic and the terrigenous contributions vary around 29%,
525 10%, 36% and 15% respectively around the mean calculated for the period 2005-2009. The
526 mean total ionic charge of rain samples is between 93.0 and 98.9 $\mu\text{eq.L}^{-1}$. Even if differences in
527 the total ionic charge are measured, with a minimum in 2007, wet deposition increases from
528 2006 to 2009 and follows the same pattern as the rainfall gradient. The total mean annual WD
529 for this period is $51.3 \text{kg.ha}^{-1}.\text{yr}^{-1}$. During the experimental period, the WD varied from $42 \text{kg.ha}^{-1}.$
530 yr^{-1} in 2006 to $59.7 \text{kg.ha}^{-1}.\text{yr}^{-1}$ in 2009. The total mean WD does not take into account data

531 from 2007 because organic ions VWM could not be measured for this year. S deposition is
532 calculated from SO_4^{2-} , and N deposition from NO_3^- and NH_4^+ (Table 3). The results show that
533 sulfur wet deposition, in $\text{kg}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$ varies from 1.28 to 1.38, with a mean value of 1.31.
534 Nitrogen wet deposition ranges from 3.4 to 4.6 $\text{kg}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$, with a mean value of $3.9 \pm 0.6 \text{ kg}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$.
535 The computation of standard deviation on VWM and WD from 2006 to 2009 indicates that
536 concentration and deposition variations never exceed 20%. WD interannual variability for dry
537 and wet season has been computed. During the dry season, Mg^{2+} , NH_4^+ , Ca^{2+} , K^+ and NO_3^-
538 present a variation of 21%, 13%, 15%, 17% and 10% respectively. Cl^- , SO_4^{2-} , HCOO^- , CH_3COO^- ,
539 $\text{C}_2\text{H}_5\text{COO}^-$, $\text{C}_2\text{O}_4^{2-}$ and carbonates vary within 9%, 7%, 15%, 14%, 13%, 16% and 4% respectively
540 during the period 2005-2009. Overall, wet deposition during the dry season months represents an
541 average of 8% of the total annual wet deposition. That means that 92% of deposition fluxes
542 occur from april to october. However, the results show that the wet deposition measured at
543 Djougou during the dry season accounts for up to 20% of the annual wet deposition for some
544 species, namely magnesium and organic acids, which is not negligible. We assume that biomass
545 burning during the dry season months affects significantly rain chemistry of the first rainy events
546 with emissions of organic compounds.

547

548 **5. Discussion and conclusions**

549

550 The results and analysis examined in the previous sections allow us to comment on several
551 aspects of rainwater chemistry in the wet savanna site of Djougou, and to make a comparison
552 with other sites on the transect dry savanna-wet savanna and forest in West and Central Africa.

553 The mean pH value of 5.19 measured in Djougou precipitation is close to results obtained in the
554 wet savanna site of Lamto in Côte d'Ivoire (5.16, Yoboué et al., 2005). The acidity in the wet
555 savanna of Djougou is the result of a mixture of inorganic and organic acids, where the organic
556 acids (HCOOH , CH_3COOH , $\text{C}_2\text{H}_5\text{COOH}$ and $\text{H}_2\text{C}_2\text{O}_4$) are responsible for 49% of the potential
557 acidity. NH_4^+ and Ca^{2+} are identified as the main neutralization ions for the acidity of rainwater
558 in Djougou. The variation of these compounds and their chemical association regulate the acidity
559 which increases from dry savanna to forest. Higher pH are measured in dry savannas at
560 Banizoumbou in Niger (5.75), at Katibougou and Agoufou in Mali (5.54) and (6.28),
561 respectively (Laouali et al., 2012). In the equatorial forest at Zoetele in Cameroon, acidic pH is
562 measured (pH=4.92), (Sigha et al. 2003). This pH is comparable to low values of pH measured
563 in the dry savannas sites of South Africa (Louis Trischart: 4.91 and Amersfoort: 4.32)
564 (Mpephya et al., 2004, 2006) affected by anthropogenic sources. To compare the mean chemical

565 characteristics of precipitation in the wet savanna of Djougou with other IDAF sites, we have
566 calculated the mean contribution of marine, nitrogenous, terrigenous and acidic species for all
567 the sites over the studied period. This calculation is done according to results published for dry
568 savannas by Galy-Lacaux et al., (2009), Laouali et al., (2012), for the wet savanna of Lamto by
569 Yoboué et al., 2005 and for the forest by Sigha et al., 2003. These papers present studies of rain
570 data collection and associated chemical analysis integrated over 4 to 10 years. Figure 6 (a, b, c,
571 d) presents the contributions of groups of species in % for the wet savanna of Djougou in Benin
572 (Figure 6a) and Lamto in Ivory Coast (Figure 6b), the dry savanna of Banizoumbou in Niger
573 (Figure 6c) and the forest of Zoetele (Figure 6d). The terrigenous contribution represents 55% of
574 the total composition at the dry savanna site of Banizoumbou whereas it represents 46% in
575 Djougou and 34% in Lamto. Nitrogenous contribution in Lamto is 24%, 23% in Djougou, 24%
576 in Zoetele and 21% in Banizoumbou. To investigate the relative contribution of particles and
577 gases in rainwater, we applied the methodology proposed by Yoboue et al., 2005 to our study.
578 We calculate the relative particulate contribution (PC) and the relative gaseous contribution (GC)
579 using the mean chemical composition measured in Djougou for the period 2006-2009. Mean GC
580 is 57% and mean PC is 43% in Djougou precipitation. For the wet savanna of Lamto, Yoboué et
581 al., 2005 indicates a GC of 58% and a PC of 42%. In the dry savanna site of Banizoumbou,
582 results give 30 % for GC and 70% for PC (Galy Lacaux et al., 2009) and for the forest of Zoetele
583 Sigha et al., 2003 report 50% of GC and 50% of PC. These results show that the gaseous
584 contribution in rainwater is more important in wet savanna and forest ecosystems than in dry
585 savanna, where particulate contributions dominates the chemical composition of rain. The
586 sources of nitrogenous compounds have been identified in this study as significative at Djougou
587 all year. The main nitrogenous sources are the biomass burning and soils during the dry season
588 and vegetation and soil sources during the wet season. The analysis of the identified
589 contributions suggests that the precipitation chemistry at Djougou is influenced by a combination
590 of sources. Four main contributions have been identified. It includes the terrigenous contribution
591 (soil and dust), the nitrogenous contribution (biomass burning, livestock, biofuel and biogenic
592 emissions), the marine and the organic contributions. The computation of the inter-annual
593 variability of wet deposition at Djougou (2005-2009) is in the range of 20 ± 7 % for marine,
594 terrigenous, organic, nitrogenous and acidic contributions respectively. The largest uncertainties
595 concern the concentrations of organic acids due to difficulties in sample preservation. The
596 seasonal analysis of the wet deposition (WD) shows that its value during the wet season
597 represents an average of 92 % of the wet annual deposition. This seasonal analysis has also
598 shown that rainy events during the dry season months are strongly affected by biomass and

599 biofuel combustion sources and charged in organic acidity, explaining 20% of the organic acids
600 measured in annual chemical composition of precipitation.

601 To conclude, this study describes 4-5 years of continuous measurement of rain chemistry in the
602 wet savanna site of Djougou in Benin. The rainwater chemistry presented in this work may be
603 considered as background estimation for Benin and responds to concerns of climate change in a
604 tropical region where limited databases are available. These data provide an ideal baseline
605 against which changes in rainwater chemistry as a result of local and regional land use may
606 occur. In this way, the IDAF project based on a long term monitoring of atmospheric deposition
607 should help to document possible trends in Africa, a continent where demographic pressure, land
608 use change and atmospheric emissions could strongly evolve in the future.

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610

611

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ACCEPTED MANUSCRIPT

1 **Table 1.** Seasonal and annual precipitation (Pt in mm) at Djougou site for the 2005-2009
 2 periods.
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		2005		2006		2007		2008		2009	
January											
February											
March		126		55.2		18.6		23.2		29.7	
April											
May											
June											
July											
August											
September											
October		1267.7		1088.3		1223.8		1345.3		1499.7	
November											
December		0		0		4.4		3.9		7.8	
Seasonal representativity to annual precipitation in %											
Dry season	Wet season	9.0%	91%	4.8%	95.2%	1.8%	98.2%	2.0%	98.0%	2.4%	97.6%
Pt		1393.7		1143.5		1246.8		1372.4		1537.2	

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26 Table 2. Rainwater collection at Djougou (2005-2009) : Annual Total Precipitation (Pt in mm),
 27 Inter-annual variability of precipitation in %, collected precipitation (Pc in mm), percent Total
 28 Precipitation (%TP) , Annual Percent Precipitation Coverage Length (%PCL) and in bracket:
 29 %PCL for each quarter (0 and 1 means 0% and 100% respectively)
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Year	2005	2006	2007	2008	2009
Pt (mm)	1393.6	1143.5	1246.8	1372.4	1537.2
Inter Annual variability (%)	+4.3%	- 4.6%	- 6.9%	+2.5%	+14.8%
Pc (mm)	735.4	1047.7	1171.1	1294.7	1457.2
%TP (%)	53	92	94	94	95
%PCL annually (%)	50	100	100	100	100
(quarterly)*	(0011)	(1111)	(1111)	(1111)	(1111)

Precipitation chemistry and wet deposition in a remote wet savanna site in West Africa- *Djougou (Benin)*53
54Table 3 Annual Volume Weighted Mean (VWM) concentrations in $\mu\text{eq.l}^{-1}$ and Wet Deposition (WD) expressed in $\text{kg.ha}^{-1}.\text{yr}^{-1}$ at Djougou during the period 2005-2009

	VWM	WD	VWM	WD	VWM	WD	VWM	WD	VWM	WD	VWM	σ_{VWM}	WD	σ_{WD}
	2005		2006		2007		2008		2009		Mean (06-09)		Mean (06-09)	
H ⁺	9.87	0.14	8.92	0.1			4.54	0.06	7.01	0.11	6.46	± 2.19	0.09	± 0.02
Na ⁺	4.8	1.54	5.5	1.44	3.4	0.98	4.2	1.32	2.15	0.76	3.8	± 1.4	1.13	± 0.31
NH ₄ ⁺	8.4	2.11	17.3	3.58	12.2	2.75	13.4	3.31	14.3	3.97	14.3	± 2.2	3.40	± 0.51
N- NH ₄ ⁺		1.64		2.78		2.14		2.57		3.09			2.64	± 0.40
K ⁺	1.8	0.96	2.4	1.10	1.9	0.92	2.2	1.16	1.5	0.92	2.0	± 0.4	1.02	± 0.12
Ca ²⁺	9.6	2.68	13.8	3.15	13.9	3.47	14.2	3.89	11.5	3.53	13.3	± 1.2	3.51	± 0.30
Mg ²⁺	1.2	0.21	2.1	0.30	2.0	0.30	2.5	0.42	1.8	0.33	2.1	± 0.3	0.34	± 0.06
NO ₃ ⁻	6.1	5.27	8.0	5.65	8.0	6.21	7.9	6.73	9.0	8.6	8.2	± 0.5	6.8	± 1.28
N- NO ₃ ⁻		0.95		1.01		1.11		1.21		1.54			1.22	± 0.23
Cl ⁻	4.2	2.06	3.7	1.52	3.7	1.65	3.8	1.86	2.3	1.27	3.4	± 0.7	1.58	± 0.25
SO ₄ ²⁻	6.9	4.63	7.3	4.04	5.9	3.53	6.1	4.03	5.6	4.13	6.2	± 0.8	3.93	± 0.27
S- SO ₄ ²⁻		1.54		1.35		1.18		1.34		1.38			1.31	± 0.09
HCOO ⁻ (HCOO*)	14.2 (13.4)	8.91	9.5 (9.0)	4.87			5.0 (4.3)	3.09	11.3 (10.7)	7.81	8.6 (8.0)	± 3.2	5.27	± 1.95
CH ₃ COO ⁻ (CH ₃ COO*)			8.8 (6.1)	5.93			3.7 (3.0)	3.04	7.7 (5.4)	7.01	6.8 (4.8)	± 2.6	5.33	± 3.15
C ₂ H ₅ COO ⁻ (C ₂ H ₅ COO*)			0.4 (0.3)	0.37			0.3 (0.2)	0.32	0.5 (0.3)	0.53	0.41 (0.28)	± 0.08	0.41	± 0.11
C ₂ O ₄ ²⁻ (C ₂ O ₄ *)	0.8 (0.7)	0.51	1.3 (1.2)	0.81			1.1 (0.9)	0.68	1.4 (1.3)	0.87	1.2 (1.1)	± 0.2	0.59	± 0.10
Carbonates			13.2	9.20	27.5	20.93	25.8	21.63	21.2	19.89	21.9	± 6.4	17.91	± 5.85
pH	5.01		5.05				5.34		5.15		5.19*			
Pt in mm	1393.7 (838.9)**		1143.5		1246.8		1372.4		1537.2		1325***			

*Median pH.

** Total precipitation during collection period in yr 2005; *** Mean Annual Precipitation

 σ_{VWM} and σ_{WD} are the standard deviation of VWM and WD respectively ; in brackets dissolved part for organic acids.55
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Table 4. Correlation coefficients between ions in rainwater (2005-2009). The “Spearman” method was used with a 1% confidence level

Variables	H ⁺	Na ⁺	NH ₄ ⁺	K ⁺	Ca ²⁺	Mg ²⁺	NO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	HCOO ⁻	CH ₃ COO ⁻	C ₂ H ₅ COO ⁻	C ₂ O ₄ ²⁻
H ⁺	1												
Na ⁺	-0.20	1											
NH ₄ ⁺	-0.03	0.73	1										
K ⁺	-0.17	0.89	0.79	1									
Ca ²⁺	-0.39	0.73	0.73	0.70	1								
Mg ²⁺	-0.33	0.84	0.81	0.82	0.93	1							
NO ₃ ⁻	-0.03	0.68	0.85	0.71	0.75	0.81	1						
Cl ⁻	-0.24	0.93	0.74	0.87	0.75	0.83	0.74	1					
SO ₄ ²⁻	-0.05	0.73	0.82	0.70	0.77	0.79	0.77	0.72	1				
HCOO ⁻	0.42	0.40	0.60	0.40	0.43	0.43	0.52	0.32	0.54	1			
CH ₃ COO ⁻	0.31	0.38	0.63	0.42	0.38	0.41	0.51	0.32	0.49	0.80	1		
C ₂ H ₅ COO ⁻	0.24	0.32	0.55	0.37	0.33	0.36	0.45	0.28	0.42	0.69	0.93	1	
C ₂ O ₄ ²⁻	0.24	0.51	0.74	0.55	0.49	0.55	0.66	0.49	0.65	0.81	0.78	0.71	1

Table 5. Comparison of sea water ratios with rain water components at Djougou.
 EF_{Marine} = Enrichment Factor, $SSF\%$ =Sea-Salt Fraction NSSF = Non Sea-Salt Fraction

	Cl/Na^+	SO_4^{2-}/Na^+	K^+/Na^+	Ca^{2+}/Na^+	Mg^{2+}/Na^+
Sea water ratios (Keene et al., 1986)	1.167	0.121	0.022	0.044	0.227
Ratios in rain	0.896	1.638	0.527	3.449	0.554
EF_{MARINE}	0.8	13.5	24.2	79.7	2.4
$SSF (\%)$	100%	7.4%	4.2%	1.3%	41%
$NSSF (\%)$	0	92.6%	95.8%	98.7%	59%

Table 6. Relative contribution of organic and mineral acidity to the total acidity measured at Djougou.

Potential Acidity	Concentration ($\mu\text{e.L}^{-1}$)	Potential Free Acidity (%)
Organic		
HCOO^-	8.0	28
CH_3COO^-	4.8	16.8
$\text{C}_2\text{H}_5\text{COO}^-$	0.3	1.0
$\text{C}_2\text{O}_4^{2-}$	1.1	3.8
Total 1	14.2	49.6
Mineral		
NO_3^-	8.2	28.7
SO_4^{2-}	6.2	21.7
Total 2	14.4	50.4
Total pA	28.6	
H^+ measured	6.5	

1 Figure captions

2
3 Figure 1. Situation of the IDAF Djougou site, vegetation and localization map of the 10
4 measurement stations of the IDAF network.

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6
7 Figure 2. Mean monthly distribution of nitrogen compounds emissions and associated uncertainties
8 in $\text{kg N}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$. BB=Biomass Burning, vol= volatilization, BF= Bio Fuel, for the Djougou site
9 (2002-2007).

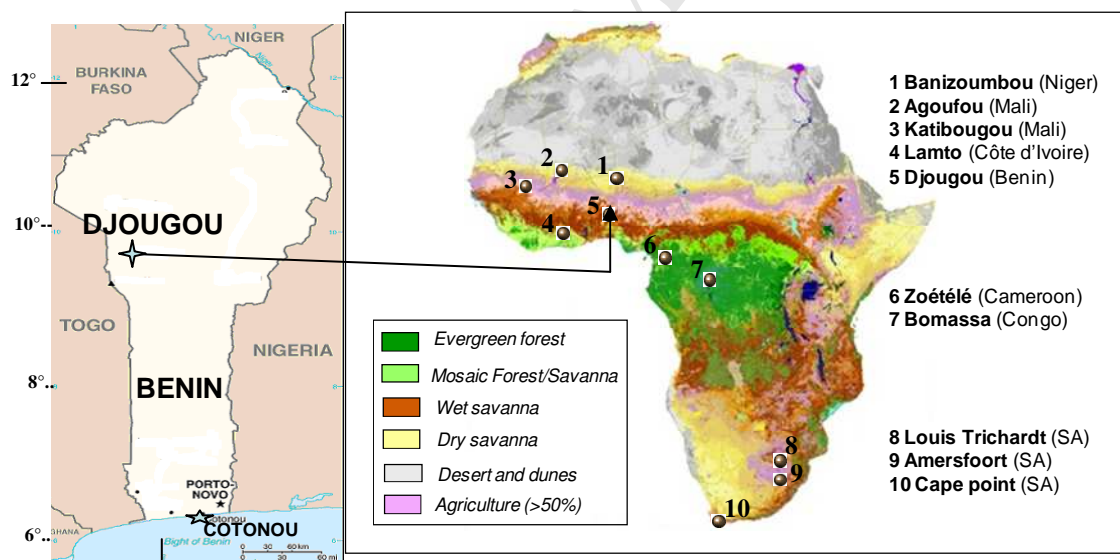
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11 Figure 3. Frequency distribution of pH.

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13 Figure 4. Distribution of monthly means VWM of major ions in rainwater ($\mu\text{eq}\cdot\text{L}^{-1}$) and mean
14 monthly precipitation depth (mm) 4- a for Na^+ ; Cl^- and K^+ ; 4-b for Ca^{2+} , Mg^{2+} and SO_4^{2-} , 4c for
15 NH_4^+ and NO_3^- ; 4-d for HCOO^- and CH_3COOH for the Djougou site (2005 -2009).
16 Vertical bars represent the standard deviation around each monthly mean.

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18 Figure 5. Distribution of monthly mean Wet Deposition of major ions in the wet savanna site of
19 Djougou (2005 -2009).

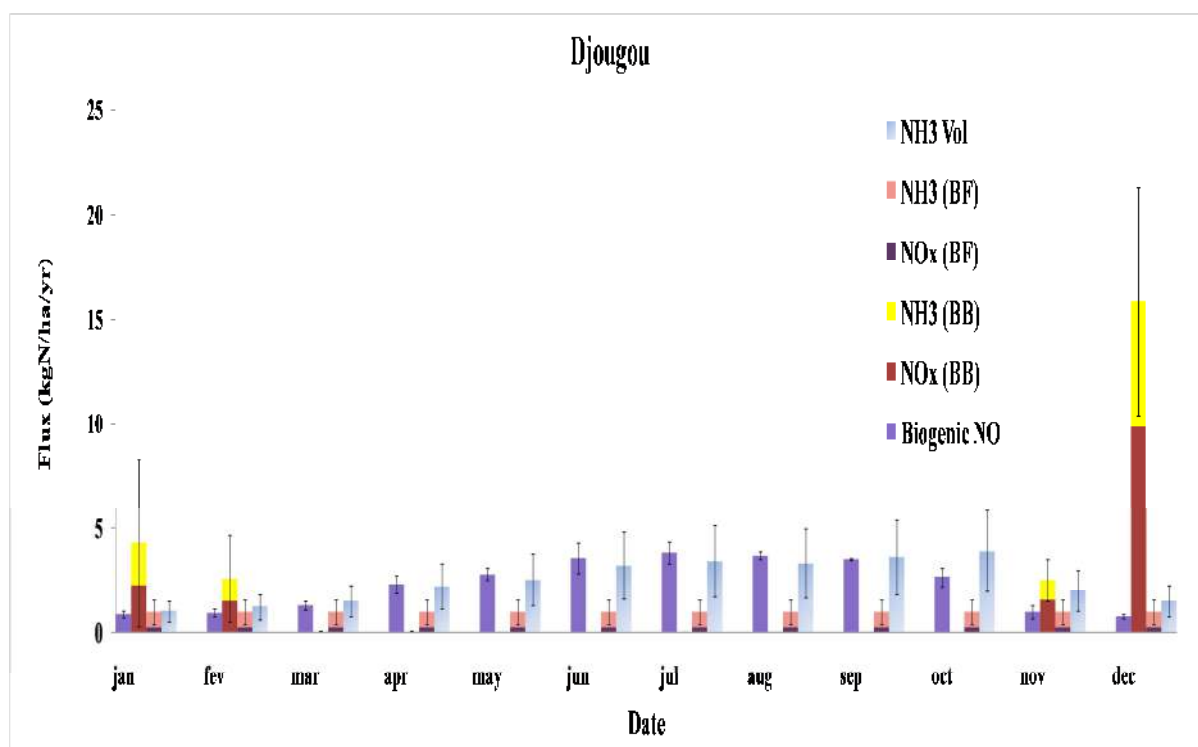
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21 Figure 6 Estimation of the marine, the nitrogenous, the organic, the acidity and the terrigenous
22 contributions to the rain chemical content along West and Central African ecosystems.

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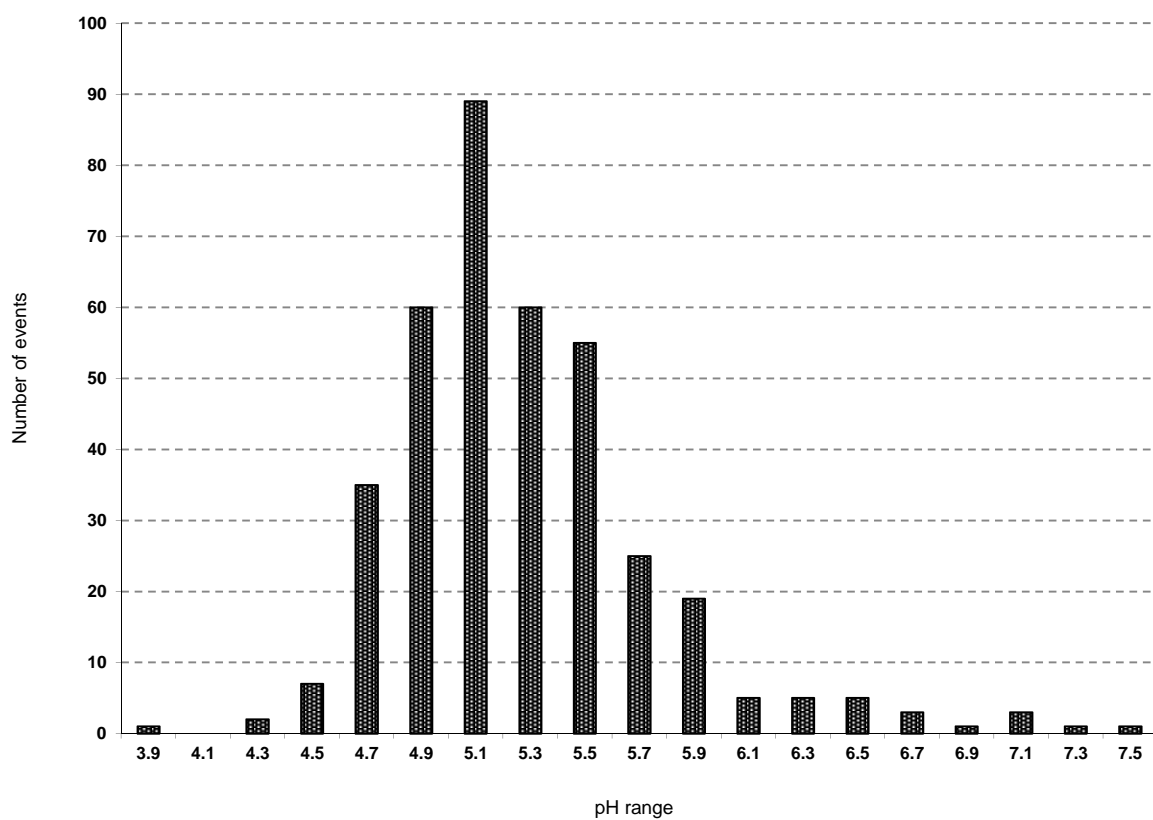
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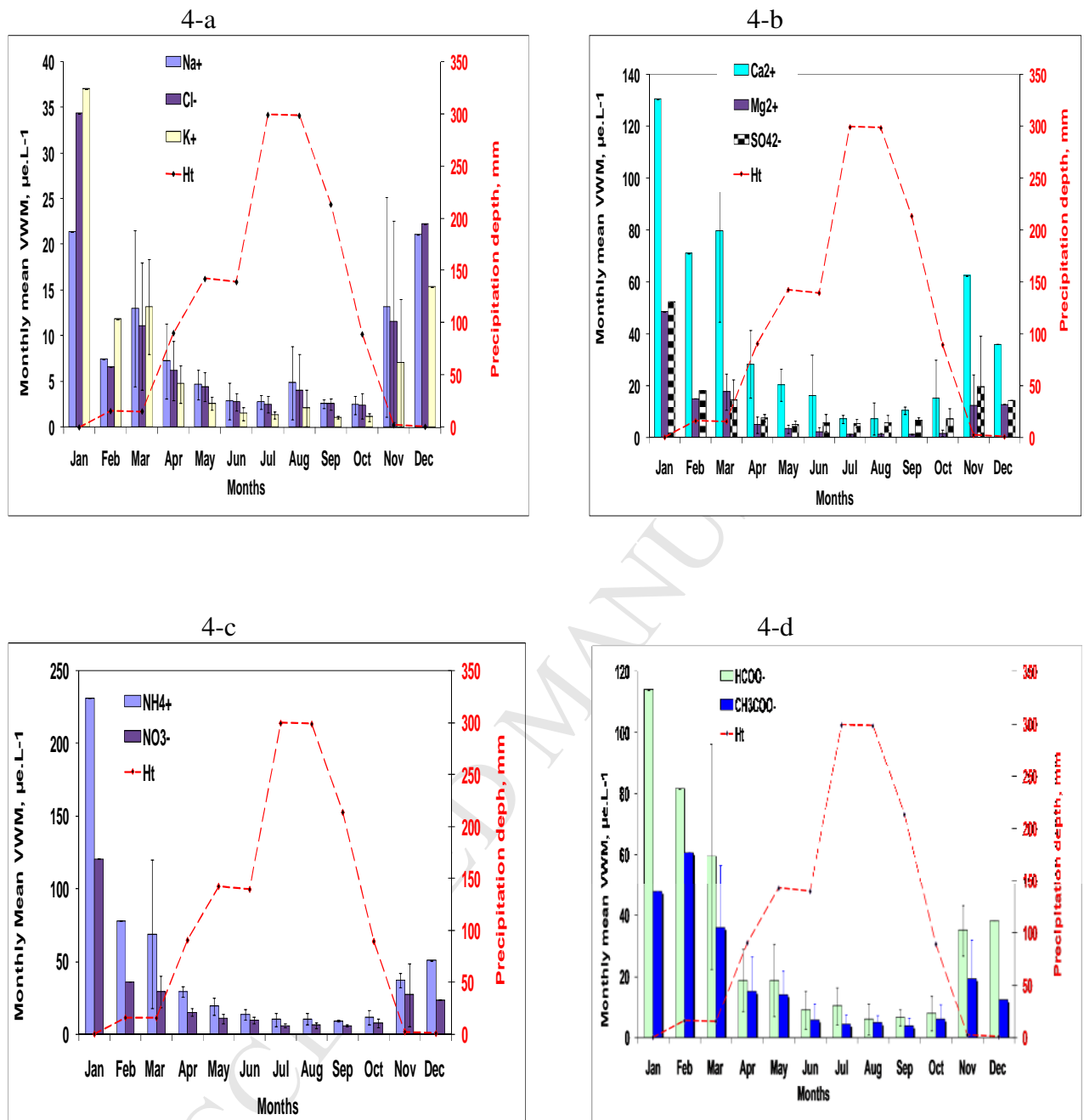
Figure 2



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Figure 3

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Figure 4

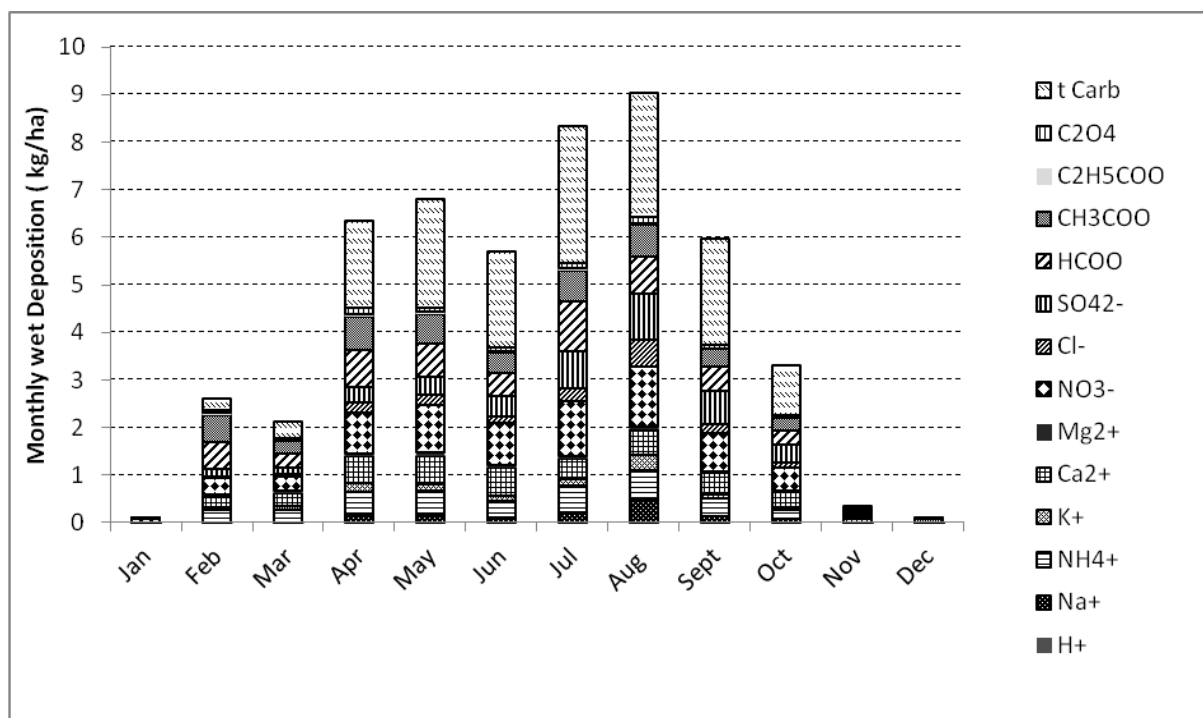
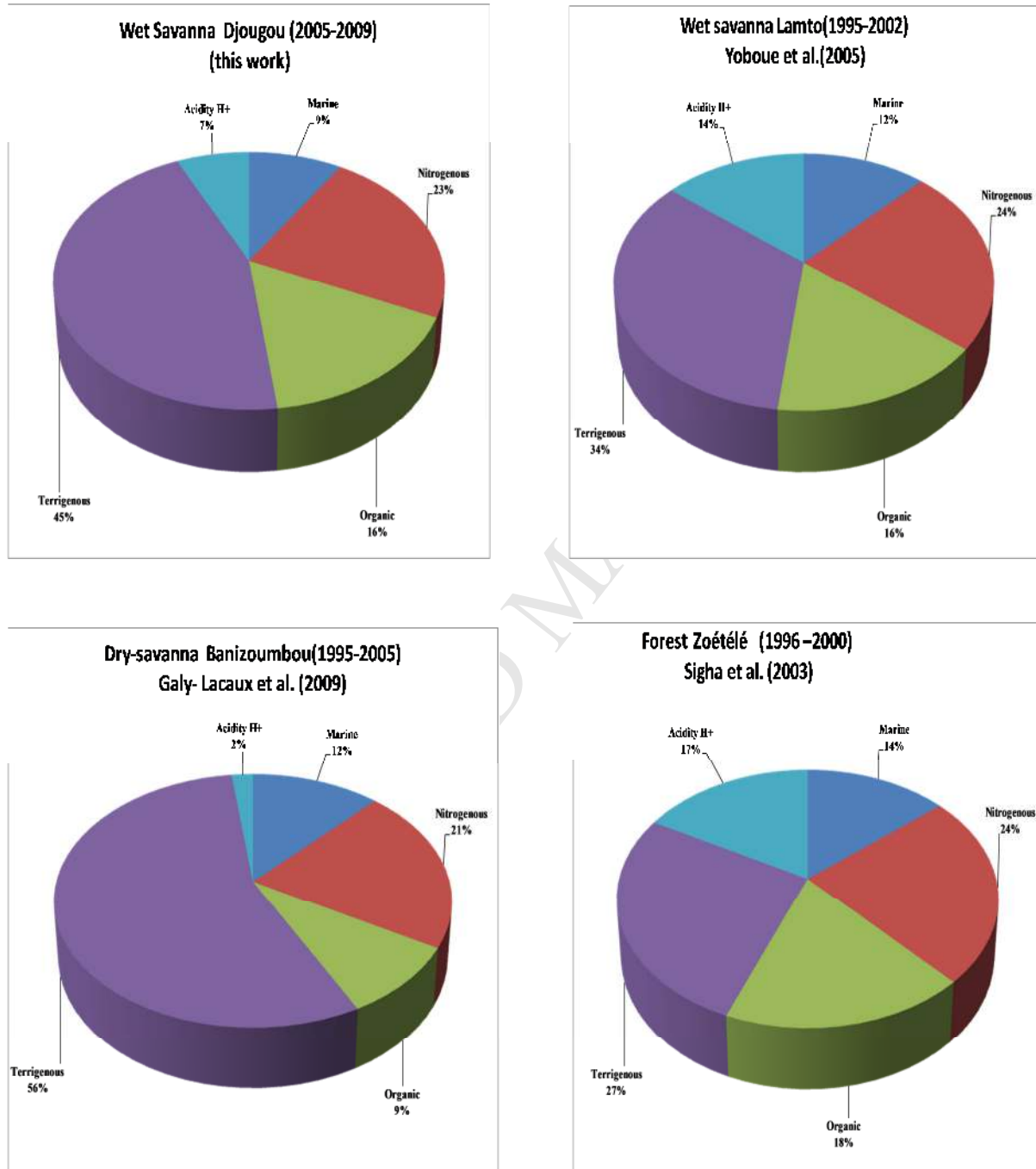
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Figure 5

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Figure 6

Highlights

1. We provide a background study of the rain chemistry of a rural wet savanna site.
2. The frequency distribution of pH of rainwater at Djougou (Benin) is computed.
3. We estimate the nitrogenous compound emitted monthly by different sources.
4. We compute the distribution of monthly means of the wet deposition of major ions.
5. We estimate the sources contributions to the rain chemical content in West Africa.