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

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HIGHLIGHTS

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

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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^{-}, $C_2H_5COO^{-}$, $C_2O_4^{2-}$) 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 NH_4^{+} > Ca^{2+} > Mg^{2+} > K^{+}. For soluble anions the order of loading is carbonates > $HCOO^{-}$ > NO_3^{-} > CH_3COO^{-} > SO_4^{2-} > Cl^{-} > $C_2O_4^{2-}$ > $C_2H_5COO^{-}$. 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 $\mu eq \cdot L^{-1}$. 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 Djougou indicates that, except for the carbonates, ammonium has the highest VWM concentration (14.3 $\mu eq \cdot L^{-1}$) and nitrate concentration is 8.2 $\mu eq \cdot L^{-1}$. The distribution of monthly VWM concentration for all ions is computed and shows the highest values during the dry season, comparing to the wet season. Identified nitrogenous compound sources (NO_x and NH_3) are domestic animals, natural emissions from savanna soils, biomass burning and biofuel combustions. The second highest contribution is the calcium ion (13.3 $\mu eq \cdot L^{-1}$), characteristic of dust aerosols from terrigenous sources, Calcium contributes up to 46% of the precipitation chemistry in Djougou. Finally, these results are compared to those obtained for other selected African sites representative of other main natural ecosystems: dry savanna and forest. The study of the African ecosystem transect indicates a pH gradient with more acidic pH in the forested ecosystem. Nitrogenous contribution

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to the chemical composition of rain in Lamto, wet savanna, (24%) is equivalent to the one estimated in Djougou (24%). The last contribution concerns organic acidity, which represents 7% of total ionic content of precipitation at Djougou. The relative particulate contribution PC and the relative gaseous contribution GC are calculated using the mean chemical composition measured in Djougou for the studied period. The comparison with other African sites gives 40% and 43% PC in wet savannas of Lamto (Côte d'Ivoire) and Djougou (Benin) respectively, 20% PC in the equatorial forest of Zoetele (Cameroon) and 80% PC in dry savanna of Banizoumbou (Niger). The results shown here indicate the existence of a North-South gradients of organic, marine, terrigenous and nitrogenous contributions along the transect in West and Central Africa.

1. Introduction

Atmosphere–biosphere interactions are important to understand the biogeochemical cycles of atmospheric species that modulate the atmospheric composition. Anthropogenic emissions and climate change play important roles in modifying atmospheric processes. In this context, wet and dry-deposition of chemical species on the earth's surface play a significant role in controlling the concentration of gases and aerosols in the atmosphere. The chemical composition of atmospheric deposition is the product of several interacting atmospheric physical and chemical processes such as: emission and source strengths; transport processes and dynamics of the atmosphere; atmospheric chemical reactions and removal processes among others. Future changes in atmospheric composition require information on past and present atmospheric composition. In a special issue of the Atmospheric Environment journal, three overview papers dealing with atmospheric composition changes emphasized that trace atmospheric constituents are changing the earth's climate (IPCC, 2007), the global biodiversity (Millennium Ecosystem Assessment, 2005) and the biogeochemical cycle of key atmospheric components such as nitrogen, carbon, and sulfur (Laj et al., 2009; Monks et al., 2009; Fowler et al., 2009). Moreover, these papers focused on the need to optimize observing systems coordinated from regional to global scale to analyze and predict future atmospheric composition. The study of deposition processes and their quantification thus allows for identifying the spatial and temporal evolution of atmospheric chemistry and is an important way for distinguishing between natural and anthropogenic influences. In regions where biogeochemical cycles are disturbed by human activities, atmospheric deposition can either be a source of toxic substances or a source of nutrients for the ecosystems. Having an understanding of chemical deposition fluxes is therefore an essential aspect of a global interdisciplinary approach in order to develop a predictive capacity for the functioning ecosystems and determining the impacts on biogeochemical cycles (Brimblecombe et al., 2007; Bobbink et al., 2010, Vitousek et al., 1997; Whelpdale and Kaiser, 1996; Pienaar, 2005).

Since the last three decades rainwater chemistry is subject of intensive research in many countries and in different ecosystems. In 1995, the first WMO global precipitation chemistry assessment provided a critical review of worldwide acidic atmospheric deposition (Whelpdale et al., 1996). In the framework of WMO/GAW (World Meteorological Organization/Global Atmospheric Watch), a recent assessment has presented a global overview of worldwide precipitation chemistry and deposition by using quality assured measurements to complement and validate available global models (Vet et al., 2014). The assessment presents precipitation chemistry and deposition measurements obtained from several regional and 22 national monitoring networks for North America, South America, Europe, Africa, Asia Oceania, and the oceans. This report demonstrates that deposition data computed from quality assured measurements were limited in many regions, especially in the tropics. The IDAF project has contributed to this work and has been recognized by WMO/GAW to provide a unique deposition database for some African sites. DEBITS (Deposition of Biogeochemically Trace species), a task of IGAC (International Global Atmospheric Chemistry) since 2005, represents one of these regional networks dedicated to study atmospheric deposition in the tropics (Pienaar, 2005). In the framework of DEBITS, the IDAF (IGAC/DEBITS/AFRICA) project started in 1994 and aims to study dry and wet deposition fluxes in Africa. The goal of IDAF program is to provide a long-term measuring network to study atmospheric composition and wet and dry atmospheric processes and fluxes. During the Long Observation Phase of the AMMA (African Monsoon Multidisciplinary Analysis) program, IDAF took an active part in investigating rainwater chemistry and in determining aerosols and gas concentrations in the atmosphere over West/Central Africa (AMMA/LOP, Lebel et al., 2009; Mougin et al., 2009; Mari et al., 2010).

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

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

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