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Study of Formic and Acetic Acids in the Air of Humid Savannah Case of Lamto (Cote d'Ivoire)

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Abstract

From January 1995 to December 2004, 860 rainwater samples were collected in the humid savannah of Lamto. Using the Henry's law, we determined the content of formic and acetic acids in the air based on their concentrations in rainwater. The annual partial pressure of both formic and acetic acids over the decade is variable. It covers a range of 0.003 (1998) to 0.21 ppbv (1996) and 0.27 (1999) to 0.47 ppbv (1996) for formic and acetic acids respectively. Also, the partial pressure in the dry season is higher than that in the wet season. This difference is related to the enrichment of the organic acid content in the air by the various sources that produce these acids. One of the main sources of increment in organic acid is biomass burning. This biomass burning contributes between 21% and 51% to the formation of the two acids in the humid savannah of Lamto. Ultimately the average annual organic acidity varies from 40% to 60% over the ten years period.

Keywords

Formic Acid, Acetic Acid, Organic Acidity, Biomass Burning

1. Introduction

Numerous field investigations of organic acids in the boundary layer and through the free troposphere have been undertaken *in situ* and remotely during isolated, time limited local as well as regional studies for more than three

decades. The results indicate that formic and acetic acids are ubiquitous components of the atmosphere [1]-[6]. They are significant contributors to rain acidity in remote environments (16% - 65%) and also regulate aqueous reactions with pH-dependence in cloud [7]-[10]. They remain an important interest for environmental researchers since they can be used as automobile pollution tracers. Formic and acetic acids can be primary pollutants from motor vehicles [11] and biomass combustion [12]. This observation led authors to suggest the use of ratio of Acetic to Formic acids as an index of pollution [6] [11]-[13]. Sources of these acids are not sufficiently understood [14]. The predominant source of formic acid (FA) and acetic acid (AA) is thought to be photochemical degradation of biogenic volatile organic compounds (VOCs), in particular isoprene and its oxidation products [15] [16]. Moreover, other sources include oxidation of anthropogenic and pyrogenic volatile organic compounds (VOCs) [9] [16] [17] and direct emissions from biomass and biofuel burning [18] [19] and terrestrial vegetation [6] [20] [21]. Ozonolysis of simple alkenes in the presence of water vapour has been identified as possible source of organic acids [22] [23]. In-cloud aqueous phase oxidation by HO radicals of acetaldehyde has been estimated to be too slow to significantly impact the formation of acetic acid over the Amazonian boundary layer [24] [25]. Possible sources, for formic acid, are ants and rocks [26] [27]. Among these sources, the contribution of savannah soils, ants, rocks, and in-cloud formation is very uncertain, but most probably minor [21].

Carboxylic acids measurement methods are numerous and various (e.g., Mist chamber technique [28]-[30], embedded measurement devices in balloons [31], in the free troposphere by aircraft measurements [32]-[34] etc.). All these measurement methods are more or less complex and require a lot of logistical and financial resources for their implementation. For this reason there are few earlier studies over Africa on these acids in the gaseous phase. However, numerous studies on the physicochemical precipitation have shown that carboxylic acids (mostly, formic and acetic acids) contribute between 30% and 70% to the total free acidity of rainwater [35]-[38]. This contribution increases from the arid savannah of Sahel to tropical forest over this continent [37]-[39]. Therefore, our study is a contribution to the understanding of the variation in levels of formic and acetic acids in the boundary layer of the humid savannah of Lamto. Thus, the main purpose of this study is to estimate and analyse the variations in levels of these two acids in the atmosphere from their concentration in rainwater. We have used Henry's law for the estimation. Subsequently, an analysis of the impact of biomass burning on this variability is also conducted.

2. Materials and Methods

2.1. Experimental Site

Lamto geophysical station is located in West Africa precisely in Côte d'Ivoire. Since 1994 it has became IDAF (IGAC/DEBITS/Africa: International Global Atmospheric Chemistry/Deposition of Biogeochemically Important Trace Species/AFrica) network experimental site, where it characterises the humid savannah ecosystem. This station is located between the Guinean savannah and tropical forest (6˚31'N latitude and 5˚02'W longitude), **Figure 1**. Previous studies [38] [40] have shown that 2 main air mass influence the chemical composition of rainfall in Lamto. Harmattan wind rich in Ca^{2+} contained in aeolian particles under gypsum ($CaSO_4$), calcite ($CaCO_3$) or dolomite ($CaMg(CO_3)$). The Cl^- are for those emanating from the maritime salts [38] [40]. Other anthropogenic sources of the main chemical components are from Coffee, Cocoa, pineapple, domestic cooking and biomass burning of the people living in the surrounding areas [38] [40]. The climate of the Lamto station is controlled by the Inter-Tropical Convergence Zone (ITCZ), boundary between the moist and hot air from ocean (Monsoon) and dry and hot air from the continent (Harmattan). Thus, Lamto has a bimodal seasonal rainfall characterised by 4 periods, 2 rainy seasons distinguished by a long dry season from December to February and rainfall recession in August, with an average of 1200 mm·year^{-1} [38] [40] [41]. The monthly mean temperature is about 27˚C and less from one season to another. At Lamto, average monthly relative humidity in the area Lamto above 50%. The values are between 65% and 83%. The months of June and July have the highest relative humidity value about 82%.

2.2. Sources of Data

For this study, we used two types of data. The meteorological data produced by Ivory Coast Meteorological Agency (SODEXAM). They have been used to determine the seasonal distribution of rainfall at Lamto during the period of study and to calculate the dryness index. Physicochemical data of rain waters have been supplied
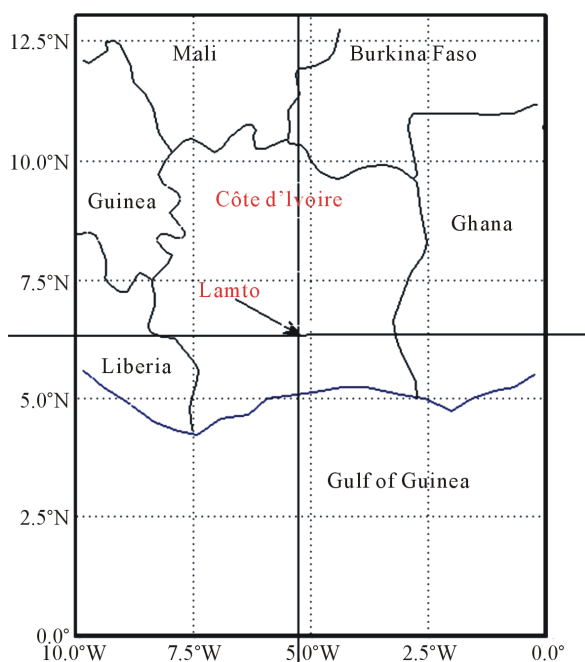
Figure 1. The Lamto station location.

by IDAF network and used to determine the partial pressures of formic and acetic acids.

2.2.1. Seasonal Distribution of Rainfall in Lamto from 1994 to 2004

The seasonal distribution of rainfall was defined based on Gaussen and Bagnouls [42] (**Table 1**) for each year. For a monthly rainfall (P in mm) and temperature (T in ˚C), a given month is consider as dry when P < 2T *i.e.* when potential evapotranspiration (PET) is greater than the rainfall [42]. Conversely, a month is assumed to be wet when P > 2T [42].

Beyond this seasonal distribution, the yearly seasonal drought is also an important parameter which should be considered in the biomass burning impact on air quality. The amount of biomass burning is dependent on the type of vegetation but also on meteorological factors such intense drought [43]. Therefore, for the purposes of considering this important factor, for each season, De Martonne [44] dryness index has been calculated based on:

$$I = \frac{12 p \text{ (mm)}}{t \text{ (˚C)} + 10}$$
(1)

where *t* is the monthly mean temperature (˚C) and *p* is monthly mean rainfall (mm).

Table 2 presents the mean indexes calculated for each season during the study period. Dryness increases when the index value decreases, a weak dryness associated to more rainfall and/or low temperature.

2.2.2. Samples Collection and Chemical Analysis

Since 1994, the chemical signature of the Lamto savannah has been monitored through rainfall, gas and aerosols samples collection. A total of 860 samples were collected and analysed during the study period. The main dissolved chemical substances (H^+, NH_4^+, Ca^{2+}, Mg^{2+}, Na^+, Cl^-, SO_4^{2-}, NO_3^-, $C_2O_4^{2-}$, HCOOH and CH_3COOH) in the rainwater collected over the study area were determined by using the high performance liquid chromatography technique . Nitrate and oxalate ions were analyzed by ionic chromatography. A full description of the determinations of these chemical species was done by previous studies [38] [41] [45]-[48] and is available at: http://idaf.sedoo.fr.

2.2.3. Determination of the Partial Pressures in Air

During cloud formation, the partial pressure of organic monoacid (HCOOH or CH_3COOH) in the air is balanced

Table 1. Seasonal distribution of rainfall in Lamto during 1994-2004.

	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004
January											
February											
March											
April											
May											
June											
July											
August											
September											
October											
November											
December											

☐ Wet season; ☐ Dry season.

Table 2. Mean dryness for dry and wet seasons during 1994-2004.

Years	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004
Dry season	0.38	0.12	0.20	0.34	0.20	0.43	0.45	0.33	0.38	0.40	0.45
Wet season	1.43	1.73	1.67	1.56	1.23	1.72	1.57	1.55	1.46	1.76	1.22

with the acid concentration on gaseous form present in the rainfall. The gas solubility balance in the aqueous phase of cloud droplet is governs by Henry law [1] [20] [35]. This law is given by:

$$P_i = C_S / H \tag{2}$$

where P_i is the gas partial pressure (atm), C_S is maximum concentration at saturation (mole/L) and H is the Henry's law constant (mole/Latm).

Considering the acid (AH):

$$AH + H_2O \rightleftarrows H_3O^+ + A^- \tag{3}$$

The partial pressure P_{gas} of the each carboxylic monoacid in equilibrium with the water cotent of cloud is calculated by:

$$P_{gaz} = \frac{X}{H\left(1 + 10^{pH - pK_a}\right)} \tag{4}$$

where P_{gas} is Gas partial pressure in the air (atm), X is the total concentration of the acid measured in the rainfall water (mole/L), H is the Henry's law constant (mole/L.atm), pH is the acidity of the rainfall sample and pKa is the pH at which half of the acid is dissociated.

3. Results and Discussions

3.1. Interannual Evolution of Partial Pressures of Formic and Acetic Acids

Over the decade (1995-2004), the annual mean partial pressures of organic monoacid (formic and acetic) have been determined. P_{gas} values vary from 0.003 (1998) ppbv to 0.21 ppbv (1996) for formic acid and from 0.27 (1999) ppbv to 0.45 ppbv (1996) for acetic acid. **Figure 2** shows P_{gas} evolution for the two acids which have
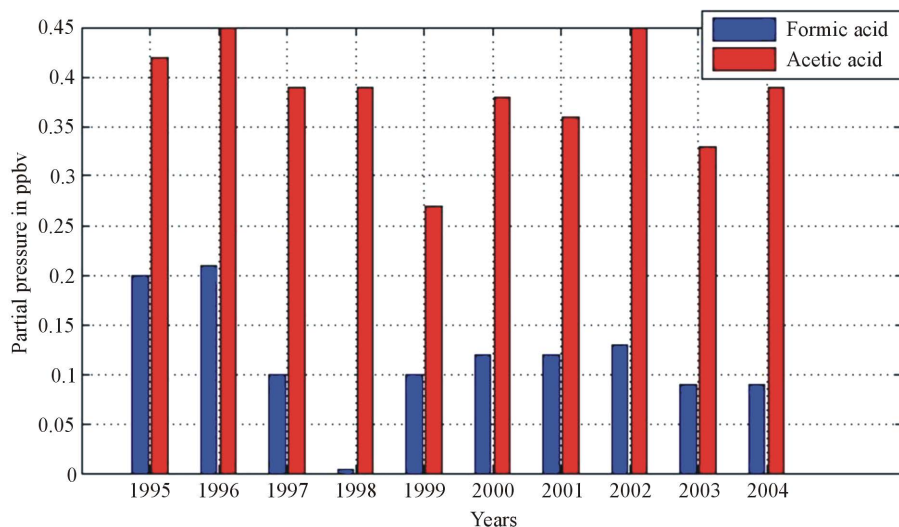
Figure 2. Interannual variability of partial pressures for formic and acetic acid in the air of humid savannah in Lamto.

similar interannual variations. However, the acetic acid appears to be less than the formic over the decade. The mean partial pressure in the air is of 0.12 ± 0.06 ppbv for a variation coefficient of 50% against 0.38 ± 0.06 ppbv with a variation coefficient of 16% for acetic acid. The decadal mean value of P_{gas} for the acetic acid is 3.2 times greater than the formic acid. The interannual variability over the decade is related to organic acid sources. The organic acid in the air is dependent on biomass burning, isoprene gaseous phase photochemical, aldehydes oxidation in liquid phase and the direct emission of acid by vegetation [6] [7] [10] [16] [19] [20] [49].

P_{gas} observed in the atmosphere of the humid savannah Lamto is within the range of values generally observed in the atmosphere of rural areas (**Table 3**). However, very low values of the order of pptv are obtained Lamto. This can be attributed either to the low contribution of the sources of these acids during that period, to a larger leaching Lamto atmosphere compared to other site. Finally, another explanation could be due to the process of neutralization of acids by Sahara dust brought by the Harmattan. Since it has been shown that this air mass influences the chemical composition of the atmosphere Lamto [38] [40].

3.2. Seasonal Evolution of Partial Pressures of Formic and Acetic Acids

P_{gas} seasonal values for the formic and acetic acid vary from 0.002 (1998) to 0.61 ppbv (1995) and 0.28 (1999) to 0.98 ppbv (1995) respectively during dry season. During wet season, these values vary between 0.003 (1998) and 0.17 ppbv (1996) for formic acid and 0.23 (1999) and 0.44 ppbv (2002) for acetic. Dry season P_{gas} values are higher than those of the wet season despite the considered acid and year. However, in 1998, the formic acid partial pressure values during the wet season were close to those of the dry season (**Figure 3(a)**). This pattern is also observed for the acetic acid which partial pressure values are slightly greater than those of dry season (**Figure 3(b)**). It would find its explanation in our distribution of seasons. Indeed, generally in the distribution of seasons the last two months of the year (November and December) are dry months. However, in 1998 these months are wet overcharged with aridity index of 1.2. In addition, N'datchoh *et al.* [54] showed that these months are part of the period of intense fires in the West African regions near the Gulf of Guinea and Lamto is located 160 km from Abidjan big city coastal.

Excluding the 1998, which is a particular year, the mean ration of P_{gas} for the organic acid during dry season over wet season was 2.5 ± 0.9 ppbv and 1.8 ± 0.6 ppbv respectively. The partial pressure of organic acid in the atmosphere of humid savannahs of Lamto increased from factor 2 from wet season to dry season. This seasonal gain is not only explained by rainfall difference between dry and wet season since there is no linearity factors between the dilution factor (24.4 ± 4.82) and P_{gas} variation of organic acid. Therefore, the seasonal variation of organic acid involves several sources with a predominance related to climatologically and meteorological conditions. However, an intensification of organic acids during dry season or additional contribution related to fires may be considered. Biomass burning fires intensification and the additional contribution of fires located far

Table 3. Levels of formic acid and acetic acid at different sites around the world (ppbv).

Location	Formic acid	Acetic Acid	References
Equatorial forest of Mayombe (Congo)	0.08	0.13	Servant *et al*. [20]
Amazonia	0.20	0.20	Talbot *et al*. [25]
Germany	0.20	0.70	Hartmann *et al*. [50]
Venezuela	0.80	0.50	Sanhueza *et al.* [51]
Hawaii	0.50	0.40	Norton [52]
Congo	0.50	0.60	Helas *et al*. [53]
Humid savannah of Lamto (Côte d'Ivoire)	0.12	0.38	Present study
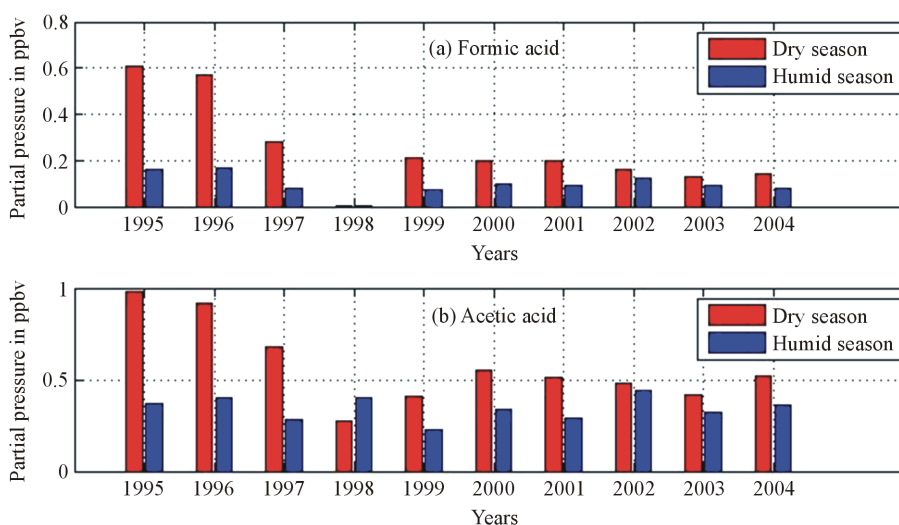
Figure 3. Seasonal partial pressures of organic acids in ppbv over humid savannah of Lamto (a) formic acid; acetic acid during 1995-2004.

away may explain this organic acid concentration increasing during dry season. Indeed, during this period, from October of the previous year to March of the following year, biomass fires are prevalent in West Africa [41] [54] [55].

The decade was not homogeneous. It is interesting to notice that maximum ratios are 3.8 and 2.7 for formic and acetic acids respectively, in 1995, while the minimum values of 1.3 and 1.1 were recorded in 2002. The low ratio obtained in 2002 could find an explanation in reducing the contributions of local fires. Indeed, from September to December 2002, the migration of the central and northern populations to the cities of the south because of the war has allowed a reduction of agriculture (slash and burn agriculture, hunting, charcoal production) and the resulting forced fallow.

3.3. Contribution of Organic Acids to Total Free Acidity (TFA) of Rainfall

In this part of work, to determine the contribution of organic acids to total free acidity (TFA), it is important to introduce oxalic acid in the calculations and the analysis. Because it is the third abundant carboxylic acids measured at Lamto [38].

So to determine organic acidity contribution to the rainfall acidity, the total acidity (TFA) was defined as:

$$TFA = 2nssSO_4^{2-} + \left[NO_3^- \right] + \left[A^- \right] \tag{5}$$

$$nssSO_4^{2-} = \left[SO_4^{2-} \right] + \left[SO_4^{2-} \right] maritime \tag{6}$$

where $\left[nssSO_4^{2-} \right]$ is the non-maritime sulfate ions concentration, $\left[SO_4^{2-} \right]_{maritime}$ is the maritime sulfate ions concentration, $\left[SO_4^{2-} \right]$ is the rainfall sulfate ion concentration, $[A^-]$ is the total concentration of organic acids contains in rainfall and $\left[NO_3^- \right]$ is the Nitrate ions concentration contains in the rainfall.

The most common method used to evaluate the contribution of maritime salt to ions concentration in precipitation is the comparison of the Cl^- to Na^+ ratio measured in the rainfall and the sea waters. It is 1.14 close to the value found by Yoboué *et al.* [38]. Over Lamto, this ratio is almost equal to that of the sea water (1.16) and was determined as:

$$[X]_{maritime} = [Na]_{rainfall} \times [X/Na]_{maritime} \quad [38]\ [56]\ [57] \tag{7}$$

The concentration of sulfate ions from maritime source was determined at Lamto. This lead to total acidity calculation.

The total acidity values (TFA) over 1998-2004 were determined. The TFA varied between 24.84 µeq·L^{-1} in 1999 and 40.28 µeq·L^{-1} in 2004 during wet season and between 42.47 µeq·L^{-1} in 1998 and 91.78 µeq·L^{-1} in 2004 during dry season. TFA mean values over the study period are 35.02 ± 5.16 and 67.32 ± 23.25 µeq·L^{-1} respectively for wet and dry seasons. TFA variation was weak during wet season but strong during dry season, where they are two times more than the wet season ones. This may be explained by the weighted concentrations during dry season which are higher than the wet season one. The mean contribution of organic acids (**Table 4**) is 48.9% for the wet season (27.6% for formic acid; 13.9% for acetic acid and 7.4 for oxalic acid) and 45% during dry season (27.1% for formic acid; 9.9% for acetic acid and 8.4% for oxalic acid). The contribution to acidity of organic acids (formic, acetic and oxalate) was stable from one season to another. This is similar for the mineral acidity which value is in the same range (40% to 60%) generally observed in Equatorial Africa [35] [36] [38] [58]. The organic acidity is in average equivalent to mineral acidity and is one of characteristic of rainfall waters in this region [58].

Comparing to studies of the tropical regions of America and Africa such as Brazil (Amazonia), Congo (Dimonika), Cameroon (Zoétélé) and in less polluted regions of North America and Australia [35] [36] [58]-[62], the contribution of organic acid to total acidity found in Lamto is in the same range as those of the above sites. As for these above cited sites, Lamto is less influenced by anthrogenic activities such as industries and stock farming. Thus the atmospheric acidity is dominated by the organic component which represents 50% to 80% of the total acidity.

3.4. Impact of Biomass Fires

In the purpose to analyse biomass fires impact, their acid formic and acetic concentration, nitrate ion have been used as chemical tracer. This choice is justified by the existence of strong correlation of this ion and organic acids of rainfall over Lamto and is considered as the best indicator of biomass fires impact on rainfall chemical composition [38] [41]. Biomass fires contribution in the organic acids is made by choosing as reference four fires plumes obtained during Atmospheric Boundary Layer Experiment (ABLE 2A) campaigns conducted in Amazonia in 1988 [35] [58]. The nitrate, formate and acetate ions content measured are summarised in **Table 5** together with those measured in Lamto for comparison purpose. For each year, the reference ratio of [X] to [Nitrate] was determined which represents biomass fires contribution in organic acids production (formic and acetic) during the dry and wet seasons in Lamto atmosphere (**Table 6**). Fires contribution to organic acids is variable from year to year. It is higher for a factor of 1.5 during wet season for acetic acid and around factor 2 in dry season. This contribution represent between 13% and 38% for formic acid and between 22% and 48% for acetic acid. In dry season, this contribution is between 17% and 38% for formic acid and 23% to 80% for acetic acid. Thus biomass fires are involved about 19% - 31% in the production of organic acids production during wet season and 26% - 51% during dry season for formic and acetic acids. Biomass fires non negligible contribution to organic monoacids during the wet season may be explained firstly by domestic fires since the African continent energy balance is dominated by biomass usage which represents 2/3 of the total energy consuming [63] [64]. In Côte d'Ivoire, firewood, charcoal, and agricultural waste remains the main source of energy. This represents 73% of house consummation and more than 95% of the Ivorian rural population use firewood or charcoal as fuel [65]-[67]. Secondly, it may come from the global pollution while general circulation insures the mixing of several air masses over the continent [41] [68] [69]. Thus during wet season in West Africa, the southern hemisphere as well as the central part of Africa are in dry season where a biomass fire occurs. Therefore, when the

Table 4. Contribution of acidity of main organic acids measured in rainfall waters in atmosphere of wet savannah of Lamto and determination of TFA during wet and dry seasons over the study period (1998-2004).

Years	Wet season				Dry season			
	%OA[a]	%FA[b]	%AA[c]	%AOX[d]	%AO[a]	%FA[b]	%AA[c]	%AOX[d]
1998	46.29	23.78	14.13	8.37	33.04	12.23	1.48	19.32
1999	37.72	20.80	12.40	4.52	36.07	25.91	5.88	4.28
2000	45.86	26 .07	12.91	6.89	51.24	32.62	12.35	6.26
2001	57.18	33.24	14.51	9.43	44.36	27.63	8.48	8.25
2002	57.48	34.40	15.93	7.15	53.51	32.31	14.80	6.40
2003	51.11	29.82	12.45	8.84	45.26	26.84	11.20	7.23
2004	47.27	25.43	15.03	6.81	54.26	31.97	15.41	6.89
Mean	48.99	27.65	13.91	7.43	45.36	27.07	9.94	8.38
Standard deviation	6.96	5.02	1.36	1.64	8.36	7.12	5.02	4.98

[a]Organic acids; [b]Formic acid; [c]Acetic acid; [d]Oxalic acid.

Table 5. Mean organic anions (fomate, acetate) and nitrate fires plumes over Amazonia forest during ABLE 2A (1998) compared with those in rainfall water during 1995-2004 in Lamto station.

Ions	Amazonia (pulme) [X], ppt	Lamto (rainfall) [X], µéq/L		Amazonia (plume) [X]/[Nitrate]	Lamto (rainfall) [X]/[Nitrate]	
	Dry	Dry	Wet	Dry	Dry	Wet
Formate	2.80	23.50	13.40	0.23	0.91	1.24
Acetate	2.00	8.50	5.70	0.16	0.33	0.53
Nitrate	302.00	25.80	10.80	1.00	1.00	1.00
Oxalate	97.00	2.80	1.70	0.32	0.11	0.16

Table 6. Biomass fires contribution estimates in organic acid production during wet end dry seasons from 1995 to 2004.

Years	Wet season		Dry season	
	Formate [%]	Acetate [%]	Formate [%]	Acetate [%]
1995	16.43	40.00	28.75	80.00
1996	17.69	40.00	28.75	80.00
1997	16.43	26.67	28.75	76.67
1998	23.00	40.00	25.56	76.67
1999	28.75	32.00	38.33	80.00
2000	20.90	32.00	17.69	32.00
2001	13.52	22.86	28.75	76.67
2002	15.33	22.86	19.17	32.00
2003	38.33	26.67	28.75	76.67
2004	32.86	26.67	17.69	22.86
1995-2004	18.56	30.32	25.30	48.56

West African monsoon is well established over the continent, south-western may transport plumes from southern hemisphere and central part of Africa towards West Africa [41] [43] [70]-[72]. Thus this may considerably impact on Lamto atmospheric chemistry since this region is close to Guinea Golf (approximately 160 km) and 41% of ozone profile obtained by Guinean troposphere radiosonde exploration during wet showed an intrusion of biomass fires plumes coming from southern hemisphere between 800 and 600 hPa [43].

Fires contribution to increase in organic acidity during the dry season compare to the wet season is about 7% and 18% for formic and acetic acid respectively. This increment may be attributed to rainfall deficit at this period of the year, which is important and leads to very weak drought indexes (0.12 to 0.45). Thus, vegetation particularly grass wither due to dryness in savannah region is favourable to biomass fires.

Dry and wet season's frequency, as well as the drought of the dry season and its length has important impact on biomass fires and organic acidity since its play an important role in biomass availability. Thus, assuming that each year with a long drought and preceded by a relative wet year, meaning with wetter days than the current year, the risk of having more and intense fire is higher than another year in the same conditions but with longer sweet dry season. As illustration, the beginning of dry season and biomass fires contribution in 1999. Generally, in Lamto, the big dry season start in November/December and end in March/April of the following year. However, in 1999, November and December 1998 were particularly wet with 1.2 as drought index, favouring vegetation growth, in opposition to January-February-March 1999 where the drought index is close to 0 (severe drought), associated more contribution of biomass fires to formic (from 23% to 26%) and acetic (from 40% to 80%) acids.

Finally, the presents results are similar to those obtained in Dominka forest in northern Congo [62] though the chemical tracer used there was oxalate. Fire contribution was assessed for formate and acetate ions to be 18% - 38% during wet season and 28% - 39% during dry season. Over the African tropical region as well as in forest or savannah regions, atmospheric chemistry is strongly influenced by biomass fires throughout the seasons.

4. Conclusion

The present study results show that formic and acetic acids in the atmosphere of Lamto from January 1995 to December 2004 confirmed the important role of two acids in the acid rainfall with a contribution estimated between 45% and 50% of the total acidity. Moreover, it is important to underline that biomass fires contribute from 18.9% to 30.3% to acid emission for formic and acetic acids respectively during wet season. During the dry season, it is estimated to be 25.3% for formic acid and 48.6% for acetic acid emission contribution from biomass fires. This aspect therefore puts a significant emphasis on the role of biomass burning in the atmospheric chemistry of African tropical regions. Ultimately, it would be interesting to carry out *in situ* measurements of organic acids and volatile organic compounds such as terpenes, isoprene and aldehydes in order of better understanding of the contributions of others sources such as vegetation and photochemical reactions.

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