Methane, Carbon Monoxide and Light Non-Methane Hydrocarbon Emissions from African Savanna Burnings During the FOS/DECAFE Experiment

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Abstract. Atmospheric samples from savanna burnings were collected in the Ivory Coast during two campaigns in January 1989 and January 1991. About 30 nonmethane hydrocarbons from C_2 to C_6, carbon monoxide, carbon dioxide and methane were measured from the background and also at various distances from the burning. Concentrations in the fire plume reached ppmv levels for C_2–C_4 hydrocarbons, and 5300, 500 and 93 ppmv for CO_2, CO and CH_4 respectively. The excess in the mixing ratios of these gases above their background level is used to derive emission factors relative to CO and CO_2. For the samples collected immediately in the fire plume, a differentiation between high and low combustion efficiency conditions is made by considering the CO/CO_2 ratio. Ethene (C_2H_4), acetylene (C_2H_2), ethane (C_2H_6) and propene (C_3H_6) are the major NMHC produced in the flaming stage, whereas a different pattern with an increasing contribution of alkanes is observed in samples typical of post flaming processes. A strong correlation between methane and carbon monoxide suggests that these compounds are produced during the same stage of the combustion. In samples collected at a distance from the fire and integrated over a period of 30 minutes, the composition is very similar to that of flaming. $\Delta NMHC/\Delta CO_2$ is of the order of 0.7%, $\Delta CH_4/\Delta CO_2$ of the order of 0.4% and $\Delta CO/\Delta CO_2$ of the order of 6.3%. From this study, a global production by African savanna fires is derived: 65 Tg of CO–C, 4.2 Tg of CH_4–C and 6.7 Tg of NMHC–C. Whereas acetylene can be used as a conservative tracer of the fire plumes, only ethene, propene and butenes can be considered in terms of their direct photochemical impact.

Key words: biomass burning, hydrocarbons, methane.

1. Introduction

The burning of biomass in the Tropics is a substantial source of reactive species which can play an important role in the chemistry and radiation balance of the troposphere. This source includes carbon monoxide and carbon dioxide, nitrogen species, methane and nonmethane hydrocarbons (NMHC), particularly in the C_2–

C_3 range (Crutzen *et al.*, 1979; Greenberg *et al.*, 1984; Crutzen *et al.*, 1985; Hao *et al.*, 1990; Crutzen and Andreae, 1990).

The impact of hydrocarbons on the tropospheric ozone budget is the consequence of their reaction with OH radicals. Oxidation of hydrocarbons by OH initiates a photochemical reaction chain which results in the formation of reactive species such as peroxy radicals, aldehydes, ketones and lead finally to a production or destruction of ozone, depending on the ambient NO concentrations. Tropospheric ozone formation due to biomass burning emissions was shown to occur over Amazonia (Kirchhoff *et al.*, 1988; Kirchhoff and Rasmussen, 1990). In the tropical belt of Africa, recent investigations have shown that a similar effect led to an ozone enriched layer at 2 or 3 km altitude, where its concentration locally reached 60 ppbv (Cros *et al.*, 1988; Marenco and Said, 1989; Cros *et al.*, 1991), and extended also over the western Indian Ocean, and the south Atlantic (Fishman and Larsen, 1987; Fishman *et al.*, 1991). The DECAFE experiment undertaken in February 1988 in the equatorial forest of the Congo has demonstrated that the production of ozone can be accounted for not only by local emissions of isoprene from trees, but also by a photochemical oxidation of hydrocarbons originating from remote savanna areas (Rudolph *et al.*, 1990). This conclusion was based on the significantly high levels of NMHC with an increasing trend versus the altitude, and in particular on the occurrence of 500 pptv of acetylene in the boundary layer indicating a long range advection from biomass burning (Bonsang *et al.*, 1988; Rudolph *et al.*, 1990).

Burnings in African savannas represents a substantial amount (nearly 50%) of the biomass burnt in the tropical belt. The aim of this paper is to characterize the composition of these emissions, in hydrocarbons and carbon monoxide, and to assess their global budget in order to further evaluate their potential impact on the tropospheric photochemistry and ozone formation.

2. Experiment

Two experiments were carried out in west Africa in order to measure the background mixing ratios of reactive gaseous species during the dry season and to determine their production by savanna burnings. These experiments were conducted from 13 to 22 January 1989, and from 9 to 15 January 1991, in the Ivory Coast at the experimental station of LAMTO (06°13′ N, 05°01′ W) located at the border of the tropical rain forest and savanna, within a large reserve of 20 km^2. The vegetation burned in this savanna region consists mainly of graminea (*Hyparrhenia displandra and Loudetia simplex*). The dry season is characterized by an east to north-east flux of dry air coming from the Sahelian regions (Harmattan), associated with the presence of a haze layer of about 2 km thickness resulting from the advection of dust particles and smoke combustion aerosols.

Samples representing the local background at ground level were collected at the station at 10 m height. Samples from the vicinity of the burning were collected during several intensive experiments on 16 and 18 January 1989 and on 9, 10, 11, 12, 14 and 15 January 1991. Two different kinds of samples were collected at ground level: Instantaneous samples (canisters samples) were collected close to the region of burning, these samples were collected by filling previously evacuated electropolished stainless steel canisters within 15 to 20 seconds. Integrated samples were collected at a distance of 50–100 m, downwind from the fires. They were obtained by filling 20 liter Tedlar bags at a constant flow rate using a portable compressor, over 20 minutes. An aliquot fraction of these samples was transferred into glass vials subsequently analysed in the laboratory. The stability of hydrocarbons in glass vials was checked in the laboratory, for high mixing ratios, typical of burning emissions. No significant variation for alkanes and alkenes was observed over two months' storage. Additionally, some grab samples were collected on board a single-engined instrumented Bonanza aircraft of the Ivory Coast army. Samples were taken in the fire plume at 300 m altitude during two intensive fires on 14 and 15 January 1991. For comparison some results of pressurized samples collected on board the french aircraft 'Caravelle' during the TROPOZ II experiment over the Ivory Coast in January 1991 are presented (Boissard, 1992).

Analysis was performed in the laboratory within one month. NMHC were measured by gas chromatography using a capillary column (AL_2O_3/KCl) and a FID detector according to a technique previously described (Bonsang and Lambert, 1985; Kanakidou *et al.*, 1989). Atmospheric samples are cryogenically enriched in a Tenax trap maintained at –120 °C, then desorbed at +140 °C and introduced onto the column where cryofocussing occurs at –80 °C. In order to remove carbon dioxide during the injection which causes interferences with ethene, a trap made with ascarite (soda/adbestos) and potassium carbonate was used. A typical chromatogram is shown in Figure 1. About 20–30 hydrocarbons including isomers of alkenes and dienes were identified. For hydrocarbons in the ppb level, the accuracy of the measurement was of 5%.

CH_4 was measured by gas chromatography, with a packed carbosphere S column, and FID detection. CO_2 was measured by FID gas chromatography after methanization, and CO was measured by gas chromatography with a 1/8″ molecular sieve column and a HgO reduction gas detector. For samples collected during the burning emissions, CH_4, CO and CO_2 standards were prepared by static dilution of a commercially available mixture of few % of these gases in nitrogen (Scotty I analysed gases). For background or aircraft samples, carbon dioxide was measured against a standard of 500 ppm CO_2 (Air Liquide), for methane, a sample of ambient air with 1.86 ± 0.013 ppmv was calibrated in KFA Jülich against a standard preparated from static dilution. For carbon monoxide a standard of 41.7 ± 1.1 ppbv was prepared by static dilution of a commercially available standard (Matheson gas products). Concerning the experiment of January 1991, 22 samples were measured at Jülich for CH_4, NMHC, CO and CO_2 using very similar procedures, including a cryogenic concentration for NMHC. Details of this analytical procedure are given by Rudolph *et al.* (1992) and Rudolph *et al.* (1995, this issue). It was previously demonstrated that both laboratories were in good agreement (less than 10%

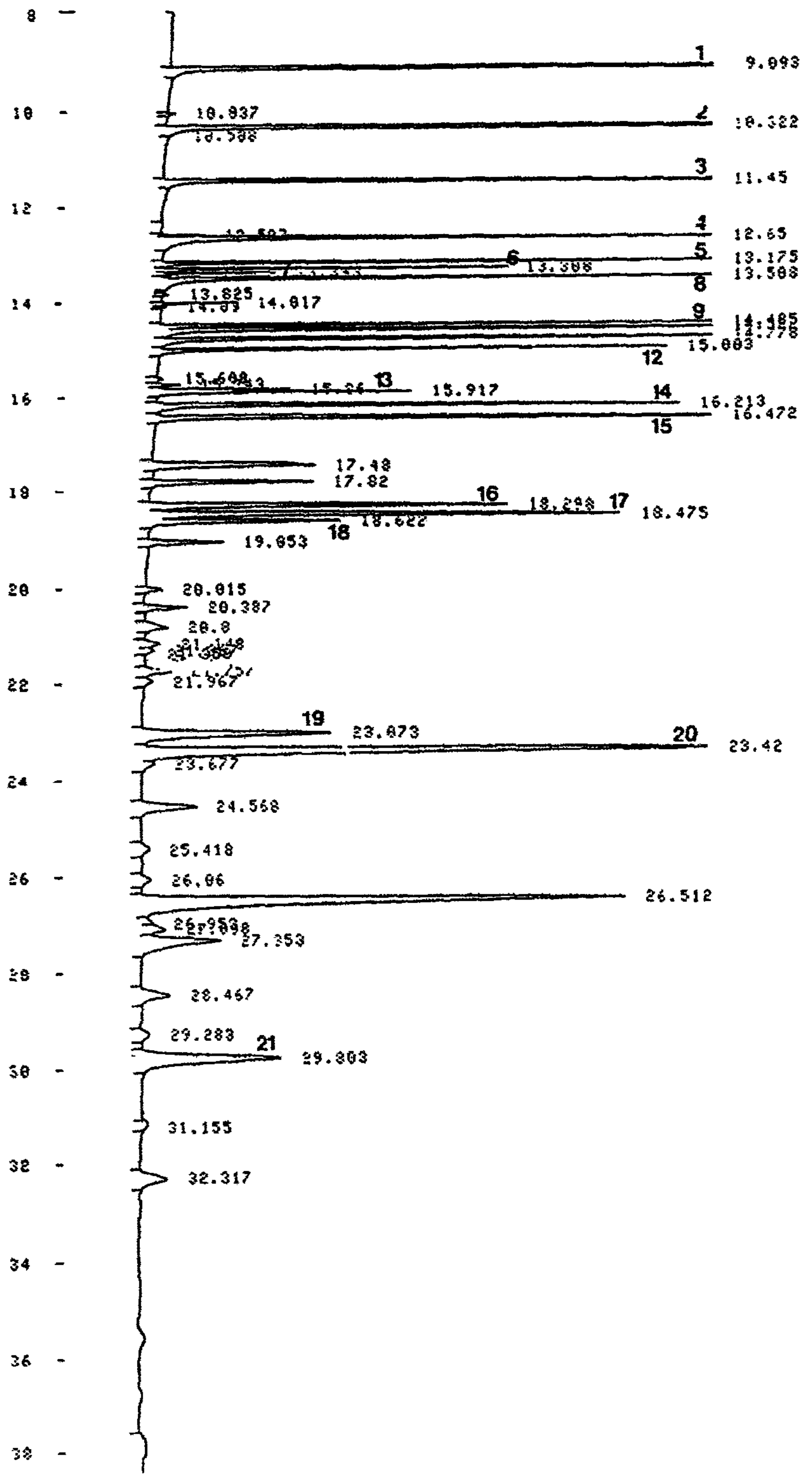

Fig. 1. Typical chromatogram of fire samples analysis by gas chromatography, showing the main species identified: 1: ethane; 2: ethene; 3: propane; 4: propene; 5: acetylene; 6: isobutane; 7: propadiene; 8: n butane; 9: trans-2 butene; 10: 1 butene; 11: iso butene; 12: cis-2 butene; 13: iso pentane; 14: n pentane; 15: 1,3 butadiene; 16: 2 methyl-2 butene; 17: 1 pentene; 18: 2-methyl-1-butene; 19: n hexane; 20: isoprene; 21: 1 hexene.

difference) for hydrocarbons analysis of samples collected over continental areas (Rudolph *et al.*, 1992).

3. Results

3.1. COMPARISON OF BIOMASS BURNING DATA WITH BACKGROUND CONDITIONS

Table I reports the mixing ratios measured for the different compounds in the background troposphere and over the Ivory Coast. At 10° N, results for the marine boundary layer are taken from Rudolph and Ehhalt (1981) and Rudolph and Johnen (1990), and for the free troposphere from Marenco *et al.* (1989). The tropospheric background over the Ivory Coast below 1000 m, and above 2500 m (i.e. below and above the haze layer) was measured during the TROPOZ II flight (Marenco, 1992; Boissard, 1992) for the area located between 5–10° N and 3–8° W. The background at the Lamto station and the range of mixing ratios measured in the fire plume were measured during the two campaigns in 1989 and 1991. Ground level background methane concentrations at Lamto were of the order of 1.65–1.75 ppmv in 1989 and 1.80–1.82 ppmv in 1991. For CO they were of the order of 300–420 ppbv during both campaigns. The range of concentration for some major NMHCs measured during background conditions at Lamto during the burnings period are significantly larger than the background concentrations measured at the same latitude over the Atlantic Ocean. Despite the fact that the ocean is also a source of NMHC (Bonsang *et al.*, 1988), these high concentrations denote a significant influence of emissions from the continent. In particular, acetylene concentrations are about ten times higher than the background at those latitudes, and similar to the concentrations previously observed during the DECAFE experiment in the boundary layer of the equatorial forest over the Congo (Bonsang *et al.*, 1988; Rudolph *et al.*, 1992). Concentrations in the free troposphere above the haze layer drop to values much closer to the background level for that latitude (i.e. 129 ppbv for CO, 1.82 ppmv for CH_4 in 1991, 0.2 ppbv for C_2H_2, 1.1 ppbv for C_2H_6, 0.7 ppbv for C_2H_4 and 0.33 ppbv for C_3H_8). NMHC concentrations during fire emissions reached several ppbv to several ppmv, simultaneously CO concentrations reached 500 ppmv, CO_2 5300 ppmv and CH_4 93 ppmv.

3.2. EMISSION FACTORS

The difference between the mixing ratios in the fire samples and the samples representative of the background level at Lamto, enabled us to derive the excess mixing ratio attributed to the biomass burning contribution

$$\Delta x = [x]_{\text{in fire plume}} - [x]_{\text{background}} , \qquad (1)$$

[x] being the mixing ratio of CO, CO_2 or hydrocarbons expressed in carbon. Emission factors were then derived relative to CO_2 and CO and expressed as: $\Delta[x]/\Delta CO_2$ or $\Delta[x]/\Delta CO$.

TABLE I. Tropospheric background of VOC's in the tropical belt and in Ivory Coast

	Tropospheric background at 10° N	Tropospheric background over Ivory Coast		Background at Lamto	Mixing ratio in the fire plume
		below 1000 m(c)	above 2500 m(c)		
CO ppbv	70(a)	182	129	300–420	3×10^3 to 500×10^3
CO_2 ppmv	340	–	–	350–400	414 to 5300
CH_4 ppmv					
in 1989	1.64(a)	–	–	1.65	
in 1991	1.77–1.81(b, c)	1.844	1.826	1.820	1.9 to 93.2
C_2H_2 ppbv	0.05–0.15(b)	0.382	0.205	0.58	9.4 to 9000
C_2H_6 ppbv	0.7–1.7(b)	1.903	1.09	1.8	1.9 to 2500
C_2H_4 ppbv	0.08–0.12(b)	0.932	0.674	0.73	19–2000

(a) from Marenco *et al.* (1989) – Free troposphere over Ivory Coast and Western Africa; (b) from Rudolph and Ehhalt (1981) and Rudolph and Johnen (1990) – Boundary layer, eastern Atlantic Ocean; (c) from Boissard (1992), results from TROPOZ II flight over Ivory Coast (January 1991).

Considering the whole set of samples, a first observation is that the average emission factors were very similar during the two experiments in 1989 and 1991. However, the values within each data set have a relatively large variability. The average $\Delta CO/\Delta CO_2$ was 11.04% (±4.4%) in 1989 and 11.44% (±8%) in 1991. Emission factors of CH_4 and total NMHC relative to CO_2 were respectively 0.54% (±0.24%) and 0.81% (±0.38%) in 1989 and 0.60% (±0.43%) and 1.08% (±0.7%) in 1991. Emission factors relative to CO were less variable, in particular CH_4/CO was 4.9% (±1.1%) in 1989 and 5.9% (±1.5%) in 1991. For the integrated samples collected far from the fire during the 1991 experiment, the emission factors relative to CO_2 were significantly lower than for the canister samples instantaneously collected close to the fire.

Due to this large variability of the emission factors, the collected samples were divided in two different series as discussed now.

It was shown by Crutzen and Andreae (1990) from laboratory studies, that substantial differences in the abundances of the combus tion products occurred between the flaming and the smoldering phases. Typical CO/CO_2 ratios during the flaming phase are lower than 10% and can increase up to 20–30% during the smoldering phase. For a given fuel, this ratio is driven by the combustion efficiency, depending on temperature and ventilation. In smoldering condition, incompletely oxidized compounds are produced (Lobert and Warnatz, 1992). However, a visual differentiation of the two stages of the combustion is somewhat difficult, a combustion efficiency determined as the percent of the total carbon released as CO_2 is generally adopted (Ward and Radke, 1992; Ward *et al.*, 1993; Hao and Ward, 1993). According to these authors, the CO/CO_2 ratio or $CO_2/(CO + CO_2)$ ratio is a quantitative criterion to parameterize the combustion efficiency and eventually to distinguish flaming and smoldering phases. It was clearly shown for example, that in forest fires, the CO/CO_2 ratio was 0–5% in flaming phase and 10–20% in the smoldering phase (Hao and Ward, 1993).

In our experiment, samples were first selected according to the observations on the field. Flaming samples were selected only for situations of intensive combustion, generally in heading fires. It was observed, as detailed below, that in these conditions, a CO/CO_2 ratio was always lower than 10% with typical values of the order of 6–8%.

Samples collected in the absence of visible flames were more difficult to select, since they can correspond either to intermediate samples between flaming and smoldering, or smoldering samples. Among these samples, only those with a CO/CO_2 ratio greater than 10% were considered. In these conditions it was assumed that low combustion efficiency processes were involved. Consequently, samples with a CO/CO_2 ratio greater than 10% were considered separately, and assumed to be mainly representative of low combustion efficiency processes and therefore strongly influenced by the smoldering conditions.

Results are summarized in Table II. The emission factors for CH_4, CO and NMHC relative to CO_2 and CH_4 and NMHC relative to CO are expressed in % of carbon. For the flaming conditions, we obtained for each experiment averaged (1989 and 1991): $\Delta CO/\Delta CO_2$ of 5.44 and 6.95%, $\Delta CH_4/\Delta CO_2$ of 0.37 and 0.42% and $\Sigma\Delta NMHC/\Delta CO_2$ of 0.62 and 0.69%. Despite the low number of samples in 1989 (4 flaming samples) the results of the two experiments are statistically comparable: the difference between the average values of the two sets of samples was not significant at 5% confidence level.

Samples collected in conditions of low combustion efficiency correspond to a typical $\Delta CO/\Delta CO_2$ of the order of 15%. The emission factors were also statistically compared to those obtained in flaming conditions. From high to low combustion efficiency, we observed a significant increase of the $\Delta CH_4/\Delta CO_2$ ratio up to 0.78%, whereas $\Delta CH_4/\Delta CO$ and $\Delta\Sigma NMHC/\Delta CO_2$ were not statistically different. The constant emission factors of CH_4 relative to CO, suggests that CH_4 and CO were predominantly emitted during the same stage of the combustion process. This close relationship between CH_4 and CO with a correlation coefficient of 0.96, and a linear slope of 0.050 is shown on Figure 2. An identical figure was also obtained by Helas (1993) from aircraft measurements.

We also observed that in low combustion efficiency processes, the $\Sigma NMHC/CO_2$ emission factor (0.77–1.08%) was very close to that of the flaming conditions, non statistically different for both series of samples and therefore independent of the efficiency of the combustion process. However, the emission factor of total NMHC relative to CO was different in the smoldering and the flaming phases. This observation suggests that the major hydrocarbons are not produced simultaneously with CO, and that the composition in hydrocarbons varies with the efficiency of the

TABLE II. Emission factors of CO, CO_2, CH_4, and NMHC in fire samples expressed in % of carbon standard deviation in parenthesis

	Number of samples	$\Delta CO/\Delta CO_2$	$\Delta CH_4/\Delta CO_2$	$\Delta NMHC/\Delta CO_2$	$\Delta CH_4/\Delta CO$	$\Delta NMHC/\Delta CO$
High combustion efficiency (flaming)						
Canisters	4	6.95	0.37	0.62	5.23	8.80
1989		(1.62)	(0.11)	(0.23)	(0.64)	(2.28)
Canisters	25	5.44	0.42	0.69	6.58	10.42
1991		(1.63)	(0.16)	(0.37)	(1.80)	(4.34)
Integrated						
samples	15	6.14	0.32	0.71	5.36	11.02
1991		(1.74)	(0.09)	(0.31)	(1.26)	(3.58)
Aircraft						
samples	3	4.8	0.46	0.57	9.8	13.7
1991		(1.91)	(0.12)	(0.41)	(1.93)	(2.62)
Low combustion efficiency						
Canisters	7	15.42	0.78	0.77	5.19	5.12
1989		(1.91)	(0.20)	(0.46)	(1.70)	(3.08)
Canisters	3	14.03	0.78	1.08	5.50	7.88
1991		(2.73)	(0.30)	(0.30)	(1.50)	(2.91)

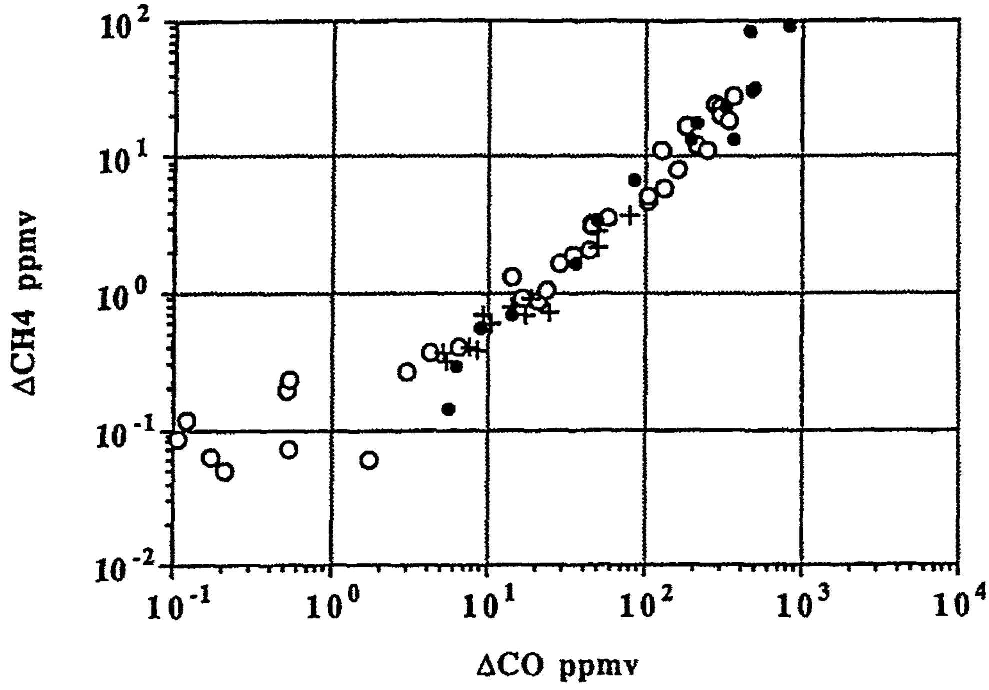

Fig. 2. Excess CH_4 versus excess CO in fire samples: open circles: flaming samples (canisters); closed circles: smoldering samples (canisters); crosses: integrated samples (Tedlar bags).

TABLE III. Composition of the fire emissions in NMHC's, expressed in % of total carbon standard deviation in parenthesis

	C_2H_4	C_2H_2	C_3H_6	C_2H_6	C_3H_8	iC_4H_{10}	nC_4H_{10}	iC_4H_8	$1C_4H_8$
High combustion efficiency (flaming)									
Canisters	52.66	18.74	10.49	7.60	1.46	0.10	0.30	0.99	0.10
1989	(1.71)	(0.82)	(0.74)	(0.71)	(0.24)	(0.03)	(0.09)	(0.16)	(0.03)
Canisters	51.59	24.34	10.68	7.00	1.38	0.14	0.23	1.25	2.24
1991	(6.74)	(5.56)	(3.34)	(2.41)	(0.68)	(0.24)	(0.17)	(1.12)	(0.99)
Integrated									
samples	46.55	21.08	8.08	6.58	1.62	0.26	1.41	1.54	2.02
1991	(7.82)	(4.75)	(2.32)	(0.65)	(0.79)	(0.21)	(0.67)	(0.86)	(1.13)
Aircraft									
samples	53.17	20.34	11.18	6.97	1.59	0.42	0.30	1.04	7.63
1991	(5.26)	(1.02)	(0.57)	(0.44)	(0.68)	(0.40)	(0.09)	(0.05)	(6.84)
Low combustion efficiency									
Canisters	35.28	10.75	13.58	15.08	4.77	0.63	1.48	2.42	0.63
1989	(8.56)	(4.73)	(3.52)	(4.94)	(2.26)	(0.45)	(0.68)	(0.89)	(0.45)
Canisters	42.48	14.62	17.14	14.87	3.82	0.22	1.24	2.10	3.50
1991	(6.27)	(9.28)	(2.47)	(7.52)	(2.77)	(0.17)	(0.41)	(0.98)	(0.49)

combustion. This point will be discussed further in the analysis of the individual NMHC contribution.

These emission factors for the 'integrated' samples collected at a distance from the fire plume were statistically nondifferent from those of the flaming samples. This suggests that the composition of the samples collected at a distance from the fire mainly reflects the composition of the flaming stage. The same observation is made for the samples collected by aircraft in the fire plume at 300 m height.

3.3. EMISSION PATTERN OF THE NMHC IN FIRE PLUME

The NMHC relative composition of the fire emissions (Table III), indicates a relatively low variability which denotes the existence of a typical signature. The composition being expressed as carbon, we observed that in the flaming samples, C_2H_4 represents the dominant hydrocarbon produced (52% in carbon of the whole NMHC's), acetylene is also produced in substantial amounts (19–24%), then C_3H_6, C_2H_6 and C_3H_8 represent 11, 7.5, and 1.4%, respectively, of the total amount of NMHC. The other saturated or monounsaturated NMHC contribute only on the order of 1% or less. This flaming composition signature was very similar in the 1989 and 1991 experiments with a low variability within the two data sets. The composition of the integrated samples as well as the aircraft samples was also very similar. Again, this confirms that at a distance from the fire, the composition of the emissions is close to that of the flaming stage of the biomass burning.

For low combustion efficiency (Table III) we observed that the contribution of ethene and acetylene was significantly reduced (35–42 and 11–15%, respectively) whereas the fraction of the other hydrocarbons, particularly alkanes (ethane, propane and butanes) was significantly increased. This observation indicates that the different species were not produced during the same phase of the combustion process.

Besides monounsaturated and saturated hydrocarbons we have also observed the occurrence of polyunsaturated NMHC's. Particularly propadiene, 1,3 butadiene and isoprene (Bonsang *et al.*, 1991) were identified in both series of samples (flaming and smoldering). In the canisters samples, close to the fire, the propadiene contribution was about 0.75% and that of 1,3 butadiene was found in significant amounts (3.9% of total NMHC) in the 1989 samples (Bonsang *et al.*, 1991). Unfortunately, due to analytical difficulties 1,3 butadiene was not completely separated from other hydrocarbons and thus was not systematically measured in the canister samples collected in 1991. In the integrated samples far from the plume, their contribution was significantly reduced: 0.5% for propadiene and 1.61% for 1,3 butadiene. This difference was probably due to the high reactivity of these compounds.

The importance of the hydrocarbons in the local photochemistry can be deduced from the composition considering the kinetic constant of oxidation by OH radicals. For a given hydrocarbon i, R_i being its contribution (in molecules) to the global NMHC production, $k_{i,\,\mathrm{OH}}$ its kientic constant of oxidation by OH, its contribution to the reaction frequency with OH is given by $R_i \times k_{i,\,\mathrm{OH}}/\Sigma R_i \times k_{i,\,\mathrm{OH}}$. C_2H_4 contributes therefore to about 50% of the reaction frequency with OH, this effect cumulated with those of C_3H_6 and butenes (ΣC_4H_8) reaches almost 90% of the reaction frequency with OH.

3.4. EVALUATION OF TRACE GAS EMISSIONS BY SAVANNA BURNING

Estimates of the total CO_2–C produced by total biomass burning in Africa have been evaluated by Crutzen (1989), Hao *et al.* (1990), and Delmas *et al.* (1991). For African savannas only these authors obtained a CO_2–C emission ranging from 940 to 993 Tg carbon per year. We will use an average value of 960 Tg/year. Using the data published by Crutzen and Andreae on the CO_2/CO emission variation during the combustion of grass, we derive that about 92% of the CO_2 is produced during the flaming period. Average emission factors are calculated for high combustion efficiency (flaming) and low combustion efficiency (smoldering) and used for budget calculations (Table IV).

Considering an average CH_4/CO_2 ratio of 0.41% during the flaming stage and 0.78% during the post flaming period, the global production of methane by savannas burning in Africa is estimated at $960 \times (0.41 \times 0.92 + 0.78 \times 0.08) \times 10^{-2} = 4.20$ Tg C as CH_4 per year a figure slightly larger than that of 3.10 Tg C as CH_4 per year, published by Delmas *et al.* (1991). The CO production by African savanna

TABLE IV. Averaged emission factors of CO, CO_2, CH_4 and NMHC in fire samples expressed in % of carbon used in the budget calculations

	Combustion efficiency		Weighted
	high	low	total
$CO_2/(CO + CO_2)$	0.95	0.87	
$CO_2/CO_{2\,total}$	92%	8%	100%
$\Delta CO/\Delta CO_2$	5.64%	15.0%	6.31%
$\Delta CH_4/\Delta CO_2$	0.41%	0.78%	0.44%
$\Delta\Sigma NMHC/\Delta CO_2$	0.68%	0.86%	0.69%
$\Delta C_2H_4/\Delta\Sigma NMHC$	51.73%	37.44%	50.68%
$\Delta C_2H_2/\Delta\Sigma NMHC$	23.56%	11.91%	22.63%
$\Delta C_3H_6/\Delta\Sigma NMHC$	10.65%	14.65%	10.97%
$\Delta C_2H_6/\Delta\Sigma NMHC$	7.08%	15.02%	7.71%
$\Delta C_3H_8/\Delta\Sigma NMHC$	1.39%	4.48%	1.63%

burnings can be estimated similarly at 65 Tg C as CO per year and the total NMHC production at 6.72 Tg C per year.

Based on the emission factors in Table IV, we then derive for the African savannas the emissions of individual NMHC: 3.42 Tg C_2H_4–C; 1.56 Tg C_2H_2–C; 0.71 Tg C_3H_6–C; 0.47 Tg C_2H_6–C and 0.09 Tg C_3H_8–C. These compounds represent 93% of the total carbon emission from all NMHC. It is interesting indeed to note that the C_2H_2–C/CO–C emission factor obtained in this way is 2.4% (i.e. 1.2% in vol/vol). The C_2H_2/CO relationship over tropical Africa obtained when gathering the data of DECAFE (Rudolph *et al.*, 1992), TROPOZ II (Boissard, 1992) and the data from this work is represented in Figure 3. The relationship obtained shows that even far from the regions of emission, (e.g. over the Congo), the C_2H_2/CO ratio is very similar to the ratio in the burning plume. Considering that C_2H_2 has a relatively long residence time (few weeks) in the atmosphere, it can be used as a good tracer for biomass burning even over long distances. Considering that biomass burning in African savannas represent about 50% of the biomass burnt in the tropics, the productions previously calculated can be roughly doubled in order to have an estimation of the contribution of the tropics to the global budget of these gases. This simple extrapolation does not take into account the differences in the emission factors of hydrocarbon which are higher in wood burning, particularly for CH_4/CO_2 (Delmas *et al.*, 1991) and for this reason must be considered as a lower estimate. This contribution appears to be nonnegligible for CH_4 (> 8 Tg C/year), and very significant for C_2H_2 (> 3 Tg C/year) whose global budget have been estimated at 10 Tg C/year (Boissard, 1992).

4. Summary and Conclusion

Fire samples were collected during the burning season in African savannas, and analysed for their content in CO, methane and hydrocarbons. Our emission ratios

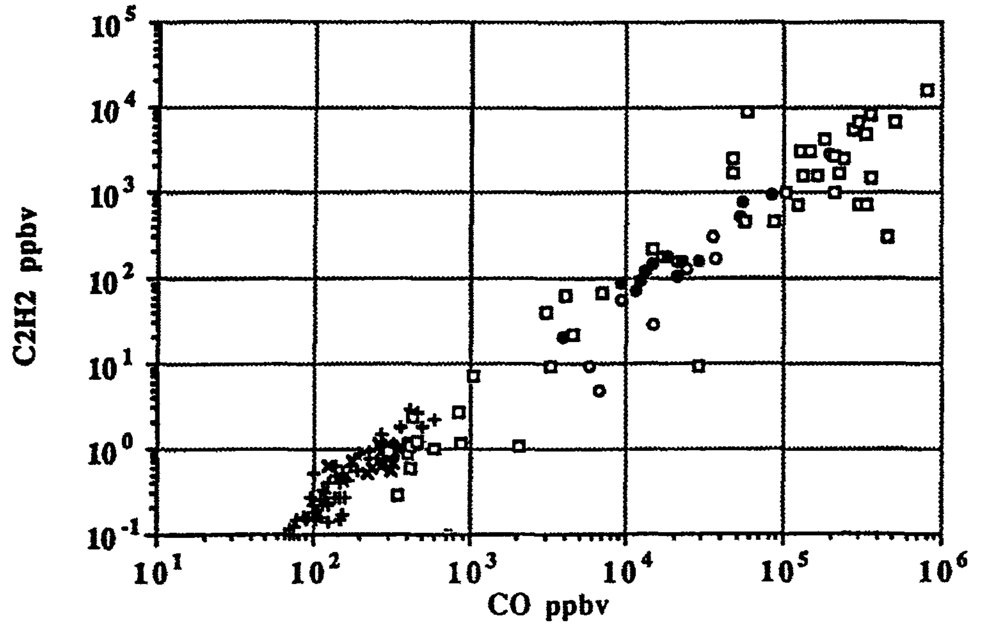

Fig. 3. C_2H_2 versus CO in FOS/DECAFE samples and for the background over Africa: open circles: 1989 FOS experiment: canisters; open squares: 1991 FOS experiment: canisters; closed circles: 1991 FOS experiment: integrated ground level samples; crosses: Aircraft measurements in and above the boundary layer: results from DECAFE experiment, TROPOZ I and TROPOZ II over tropical and equatorial Africa.

relative to CO_2 are slightly lower for CO and hydrocarbons than the figures already published for in situ experiments (Greenberg *et al.*, 1984; Crutzen *et al.*, 1985) and for laboratory experiments (Hao *et al.*, 1990). However, the variability of the emission ratios is substantial and the differences remain within the range of variation. Global emission factors of CO, CH_4 and NMHC relative to CO_2 show that the production of non methane hydrocarbons is roughly twice that of methane (of the order of 0.7% in carbon). If two phases of the combustion processes, based on the CO/CO_2 ratio, are distinguished (Ward and Hao, 1992), the variability of the emission factors is reduced and their average values are statistically different. In particular it is observed that light unsaturated C_2 hydrocarbons (C_2H_4, C_2H_2) are preferentially produced during the flaming stage with high combustion efficiency process, whereas other hydrocarbons, particularly alkanes, are preferentially emitted during low combustion efficiency processes (or higher reducing conditions).

We have also observed a good agreement between instantaneous samples collected very close to the fires, in flaming conditions, and time integrated samples or samples collected on board aircraft. A meaningful estimate of global emissions for savanna burnings in Africa were thus made on the basis of these in situ experiments. Using a figure of 960 × 10^6 tons of carbon per year released as CO_2 by the biomass burned in African savannas (Crutzen *et al.*, 1989), the global corresponding NMHC emission would reach a value of 7 × 10^6 tons of carbon per year, about twice the production of methane. The CO production by African savanna burning reaches a figure of 65×10^6 tons of carbon per year.

It is also very clear that C_2 unsaturated hydrocarbons are the major reactive NMHC produced during the combustion. The importance of these hydrocarbons in the local photochemistry can be deduced from the initial composition by considering the rate constant for the oxidation by OH radicals. It appears that the effect of NMHC produced by biomass burning on the tropospheric photochemistry concentrates on a few species, namely, C_2–C_4 alkenes.

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