

Field Study of the Emissions of Methyl Chloride and Other Halocarbons from Biomass Burning in Western Africa

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Abstract. A field study of trace gas emissions from biomass burning in Equatorial Africa gave methyl chloride emission ratios of $4.3 \times 10^{-5} \pm 0.8 \times 10^{-5}$ mol $\text{CH}_3\text{Cl}/\text{mol CO}_2$. Based on the global emission rates for CO_2 from biomass burning we estimate a range of $226 - 904 \times 10^9$ g/y as global emission rate with a best estimate of 515×10^9 g/y. This is somewhat lower than a previous estimate which has been based on laboratory studies. Nevertheless, our emission rate estimates correspond to 10–40% of the global turnover of methyl chloride and thus support the importance of biomass burning as methyl chloride source. The emission ratios for other halocarbons (CH_2Cl_2 , CHCl_3 , CCl_4 , CH_3CCl_3 , C_2HCl_3 , C_2Cl_4 , F-113) are lower. In general there seems to be a substantial decrease with increasing complexity of the compounds and number of halogen atoms. For dichloromethane biomass burning still contributes significantly to the total global budget and in the Southern Hemisphere biomass burning is probably the most important source for atmospheric dichloromethane. For the global budgets of other halocarbons biomass burning is of very limited relevance.

Key words: biomass burning, halocarbons, hydrocarbons, methylchloride, emission ratios.

1. Introduction

Biomass burning has been identified as one of the major sources for a variety of important atmospheric trace components (cf. Crutzen and Andreae, 1990). A substantial part of the biomass burning activities occur in tropical regions and thus may be the dominant trace gas source in these areas with otherwise only relatively small manmade emissions (Andreae, 1991). The most abundant organic trace gases emitted by biomass burning are carbon monoxide and a number of hydrocarbons (cf. Greenberg *et al.*, 1984; Crutzen *et al.*, 1985; Bonsang *et al.*, 1991). But also emissions of organic compounds containing hetero atoms, including halogens, have been reported (Crutzen *et al.*, 1979; Lobert *et al.*, 1991). It has been speculated that emissions from biomass burning contribute about 40% to the total global budget of methyl chloride (Crutzen and Andreae, 1990; Lobert *et al.*, 1991). The only other known major methyl chloride sources are emissions from the oceans,

but the exact magnitude of this source is still very uncertain (cf. Pearson, 1982; Fabian, 1986). Even in comparison with present day levels of manmade halocarbons methyl chloride is one of the most abundant halogen containing compounds in the atmosphere. It is the only relevant source gas for stratospheric chlorine which is not predominantly of industrial origin (cf. Penkett *et al.*, 1980). Thus the understanding of the contribution of biomass burning emissions to the atmospheric budget of methyl chloride is very important.

In spite of the potential importance of biomass burning as source for atmospheric chlorine containing trace gases there are only very few laboratory or field studies (cf. Lobert *et al.*, 1991; Rasmussen *et al.*, 1980; Crutzen *et al.*, 1979). No field investigations of emissions of methyl chloride or other halocarbons in tropical regions are known to us. In this paper we present estimates of emission rates for methyl chloride and some other C₁ and C₂ halocarbons derived from a field study in equatorial Africa during the biomass burning season.

2. Experiment

The study was made in the Lamto Reserve (5°02' W, 6°13' N) which is located in the centre of Ivory Coast. The area is a forest-savanna mosaic region with gallery forests along river beds. Details of the area and the various burning activities are given by Lacaux *et al.* (1991). The study was part of the FOS/DECAFE 91 (Fire Of Savannas/Dynamique Et Chimie de l'Atmosphère en Forêt Equatoriale) experiment which was conducted during February 1991 in Equatorial Africa. About 20 air samples were collected in the plumes of several savanna fires. In addition a few samples were collected before or after the fires.

The samples were collected in evacuated stainless steel canisters of 4 dm³ or 5 dm³ volume with metal bellows valves. All samples were collected at ground level between 9 and 18 February 1991. The samples were analyzed in the laboratory in Jülich for a broad range of hydrocarbons including methane, several halocarbons (CH₃Cl, CH₂Cl₂, CHCl₃, CCl₄, CH₃CCl₃, C₂HCl₃, C₂Cl₄, F-113), CO, and CO₂. For most of the samples the methyl chloride, hydrocarbon, CO, and CO₂ concentrations were far above the usual ambient levels and the concentrations covered several orders of magnitude. Our standard hydrocarbon and halocarbon measuring technique is designed for ambient background concentrations. Measurements of undiluted samples showed that the signal for the most abundant hydrocarbons and halocarbons was at the upper end or above the linear range of our instrument. In order to avoid linearity problems we diluted most of the samples with synthetic air by factors between 10 and 100, depending on the CO and CO₂ concentrations. This allowed us to analyse all samples with our standard measuring procedure.

The hydrocarbons and halocarbons were concentrated cryogenically at liquid nitrogen temperature in a 2 mm i.d. stainless steel tube of 30 cm length packed with porous glass beads. Sample volumes ranged from some ten to several hundred cm³. The hydrocarbons and halocarbons were separated on a combination of a

7 m micropacked Porapak QS column and a DB-5 60 m fused silica capillary column. As detector a combination of an electron capture detector (ECD) and flame ionization detector (FID) was used. The hydrocarbons were evaluated from the FID signal, the halocarbons from the ECD signal. Methyl chloride shows in both detectors a sufficiently strong signal for quantitative evaluation. However, in all the biomass burning samples we observed two FID peaks which overlapped with the methyl chloride signal (see Figure 1 for details). The interfering substances are tentatively identified as cyclopropane and propyne. No interference was observed for the ECD peak which therefore was used for the quantitative evaluation of methyl chloride.

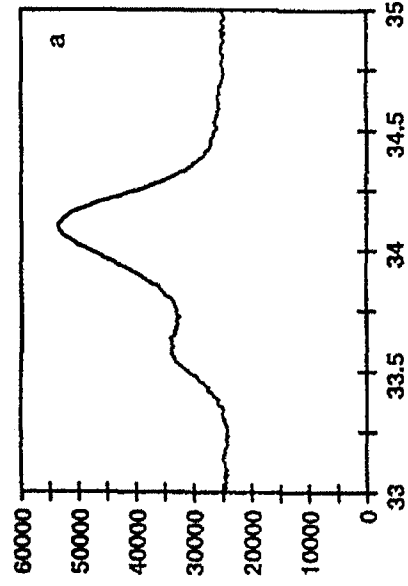
The reproducibility of the measurements is between 5% and 10% and the lower limit of detection for NMHC and CH_3Cl is 5–20 ppt, for the other halocarbons well below 1 ppt. Details of the analytical technique are given by Rudolph (1988) and Rudolph *et al.* (1986). The measurements were evaluated by comparison with a reference air of known composition. The reference air was calibrated with mixtures of the pure substances in synthetic air prepared by two or three step static dilution. We estimate that the accuracy of our calibration is better than 20%. For CHCl_3 , CCl_4 , CH_3CCl_3 and F-113 we had no own calibration and therefore compared our reference with a primary standard air purchased from the Oregon Graduate Center (OGC). This primary standard (tank #295) was prepared in July 1985 and adjusted to the ALE (Atmospheric Lifetime Experiment) calibration scale by R. A. Rasmussen. Our measurements of CHCl_3 , CCl_4 , CH_3CCl_3 and F-113 rely on the accuracy of this ALE-type standard. For CH_3Cl we compared our calibration with this primary standard and observed no difference within the uncertainty of the measurements (< 10%).

Methane, CO, and CO_2 were analyzed by a gaschromatographic method very similar to the one described by Heidt (1978). The detection limits are well below the tropospheric background concentrations of these substances. The reproducibilities of these measurements are 1% for methane, 3% for CO and 0.5% for CO_2 .

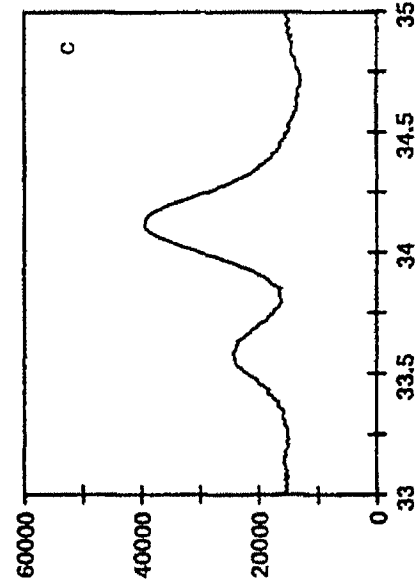
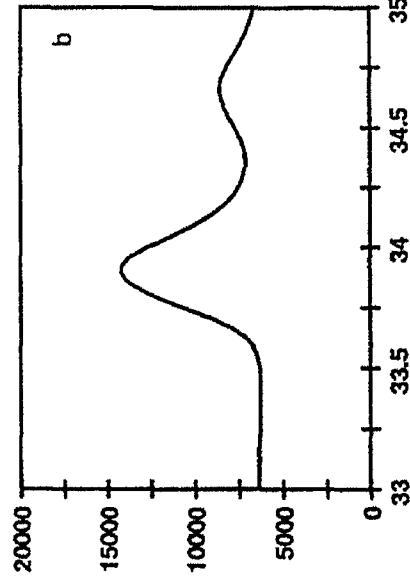
3. Results and Discussion

3.1. HALOCARBON AND HYDROCARBON EMISSION RATIOS

The relative molar emission ratios of the halocarbons and hydrocarbons were determined from linear regressions of the trace gas mixing ratios versus the CO_2 or CO mixing ratios. This procedure is very similar to the use of generally adopted $\Delta\text{X}/\Delta\text{CO}_2$ (or ΔCO) with ΔX being the difference between the concentrations in the plume and the background. However, the use of a linear regression avoids the problem to define a 'background' concentration which may add additional errors to the derived emission ratios. In our study even samples collected before or after the fire showed rather high CO mixing ratios of several hundred ppb to a few thousand ppb. This indicates that the impact of biomass burning on the atmosphere at Lamto is not restricted to the direct emissions from nearby fires.



Detector signal / arbitrary units



Retention time / minutes

Fig. 1. Methyl chloride peak and FID interferences in biomass burning samples (a) FID signal. (b) ECD signal, the retention time of methyl chloride is 33.9 minutes, the peak at 34.7 minutes is F-12. (c) Residual FID peaks after subtraction of the methyl chloride peak. The FID methyl chloride signal is determined from the ECD peak and the FID/ECD ratio of an interference free methyl chloride peak.

TABLE I. Emission ratios of several halocarbons and hydrocarbons

	Relative to CO ₂		Relative to CO			
	Emission ratio ^{a, d}	Relative error ^b %	Regression coefficient	Emission ratio ^{a, c}	Relative error ^b %	Regression coefficient
CH ₃ Cl	4.30E-05	22	0.7200	4.96E-04	7	0.9586
CH ₂ Cl ₂	3.45E-06	18	0.7778	2.48E-05	26	0.6461
CH ₃ CCl ₃	4.31E-07	45	0.6429	7.15E-06	63	0.5145
CCl ₄	8.00E-08	413	0.1201	-3.74E-06	253	-0.1941
CHCl ₃	7.74E-08	28	0.8736	6.85E-07	33	0.8353
C ₂ F ₃ Cl ₃	5.17E-08	51	0.4043	7.03E-07	53	0.3879
C ₂ Cl ₄	2.77E-09	632	0.0354	4.08E-08	371	0.0602
C ₂ HCl ₃	-3.83E-07	200	-0.1170	-2.70E-06	343	-0.3685
CH ₄	1.17E-02	31	0.5623	1.19E-01	9	0.9474
C ₂ H ₂	1.77E-03	25	0.6621	1.90E-02	16	0.8218
C ₂ H ₄	3.49E-03	24	0.6856	3.84E-02	13	0.8695
C ₂ H ₆	5.77E-04	35	0.5367	8.57E-03	10	0.9187
C ₃ H ₆	5.23E-04	25	0.6640	6.50E-03	7	0.9527
C ₃ LH ₈	1.17E-04	31	0.5827	1.05E-03	30	0.6018

^a Slope of the linear regression of compound X versus CO₂ or CO, respectively; ^b relative statistical error of the slope of the linear regression; ^c values are in mol per mol of CO; ^d values are in mol per mol of CO₂.

In Table I the emission ratios of the halocarbons and some hydrocarbons relative to CO₂ and CO are summarized. As an example for the linear correlations the plot of the methyl chloride versus the CO mixing ratios is shown in Figure 2.

The use of linear regressions or similar algorithms to determine emission ratios from field measurements is based on the assumption that the only relevant trace gas source for the investigated area is biomass burning. Although the Lamto Reserve is a continental site, it is a remote area without nearby cities or industrialized areas. We can compare the average of the trace gas mixing ratios observed during FOS/DECAPE 91 with the tropospheric background (Figure 3). For CO, CO₂, all hydrocarbons, and several of the halocarbons we observe average mixing ratios of some ten ppb or more, in most cases by factors of 2-30 higher than we would expect for the tropospheric background. In these cases we can be rather certain that biomass burning is the dominant trace gas source and that our observations reflect the impact of biomass burning.

However, for C₂F₃Cl₃, CCl₄, and CH₃CCl₃, our measurements are very close to the tropospheric background and we cannot completely rule out that sources other than biomass burning are the cause of such minor differences. Therefore for these substances our emission ratios can only be used to determine upper limits for the biomass burning emission rates. Also for those compounds listed in Table I where the regression coefficients are very poor and the uncertainties of the emission

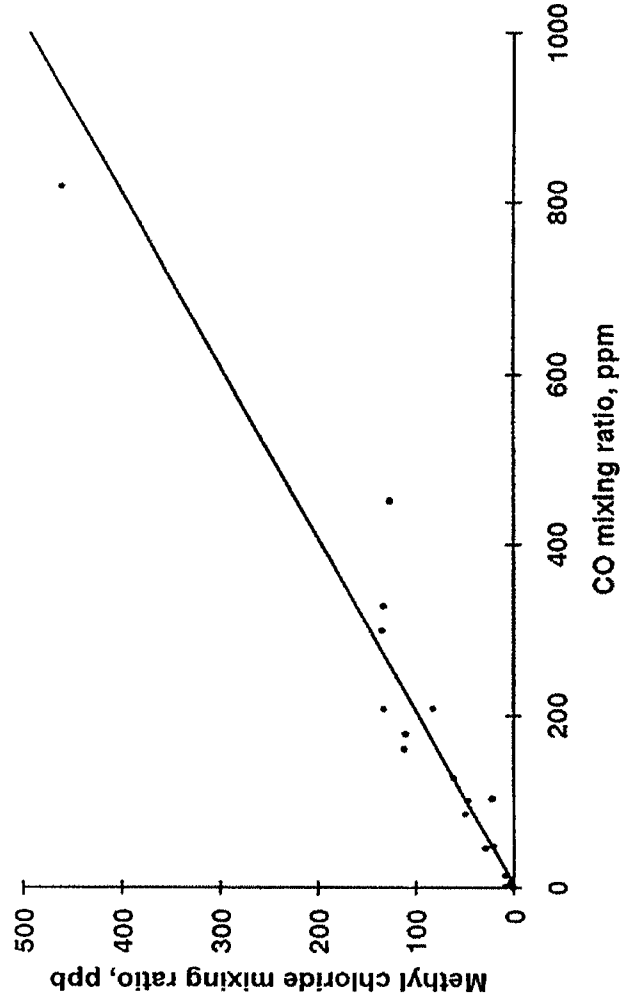


Fig. 2. Plot of methyl chloride versus CO mixing ratios. The solid line represents a linear least square fit.

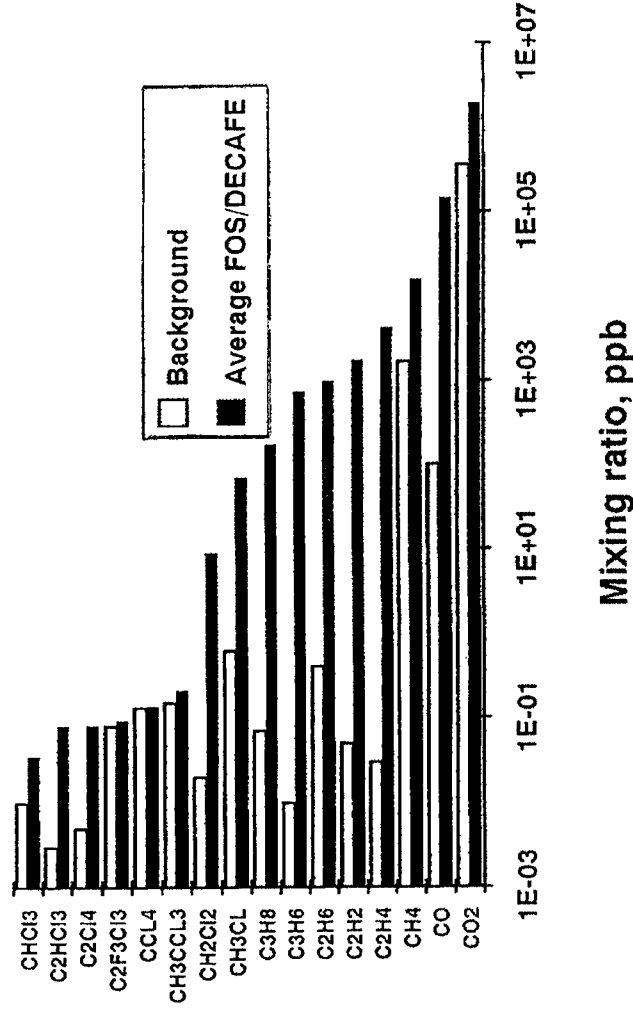


Fig. 3. Comparison of the average concentrations of hydrocarbons and halocarbon measured during FOS/DECAFE 91 with background concentrations. The background concentrations are taken from Koppmann *et al.* (1993), Fraser *et al.* (1991), Warneck (1988), and Rudolph (1988).

ratios large (CCl_4 , C_2Cl_4 , C_2HCl_3) we can use our results only to estimate upper limits.

3.2. COMPARISON WITH LITERATURE VALUES

There are a few published studies of methyl chloride emissions from biomass burning which give a substantial range for the methyl chloride emission ratios. Crutzen *et al.* (1979) report an average emission ratio of 2.3×10^{-5} mol $\text{CH}_3\text{Cl}/\text{mol CO}_2$ from 7 measurements made during a field study. Their data range from 0.44 to 5.7×10^{-5} mol $\text{CH}_3\text{Cl}/\text{mol CO}_2$. Rasmussen *et al.* (1980) made laboratory studies of the emissions of methyl chloride from the smouldering combustion of different types of biomass. They report emission ratios between 2.4×10^{-5} mol $\text{CH}_3\text{Cl}/\text{mol CO}_2$ and 30×10^{-5} mol $\text{CH}_3\text{Cl}/\text{mol CO}_2$ with an average of 10.4×10^{-5} mol $\text{CH}_3\text{Cl}/\text{mol CO}_2$. Similar values were obtained by Lobert *et al.* (1991) in a laboratory study. They report values between 1.8×10^{-4} mol $\text{CH}_3\text{Cl}/\text{mol CO}$ and 44×10^{-4} mol $\text{CH}_3\text{Cl}/\text{mol CO}$ and an average of 16×10^{-4} mol $\text{CH}_3\text{Cl}/\text{mol CO}$. Based on their average of 73×10^{-3} mol $\text{CO}/\text{mol CO}_2$ this corresponds to 1.3×10^{-5} mol $\text{CH}_3\text{Cl}/\text{mol CO}_2$ to 32×10^{-5} mol $\text{CH}_3\text{Cl}/\text{mol CO}_2$ with an average of 12×10^{-5} mol $\text{CH}_3\text{Cl}/\text{mol CO}_2$. With 4.3×10^{-5} mol $\text{CH}_3\text{Cl}/\text{mol CO}_2$ (Table I) our results are somewhat higher than the average of Crutzen *et al.* (1979), but at the lower end of the results reported by Lobert *et al.* (1991) and Rasmussen *et al.* (1980). In spite of the wide range of results, it is rather surprising, that the two laboratory studies (Rasmussen *et al.*, 1980; Lobert *et al.*, 1991) obtained substantially higher average emission ratios for CH_3Cl than our field study and the field study presented by Crutzen *et al.* (1979). This may be due to the specific limitations of laboratory studies. The study of Lobert *et al.* (1991) concentrated on different types of grass, hay, straw, etc. and included only one type of wood. They did not give individual emission rates for the different types of biomass but from the type of materials they investigated their results mainly represent the burning of grass, hay and similar materials.

Rasmussen *et al.* (1980) differentiated between various types of biomass. They observe the highest emission ratios between 8.5×10^{-5} mol $\text{CH}_3\text{Cl}/\text{mol CO}_2$ and 30×10^{-5} mol $\text{CH}_3\text{Cl}/\text{mol CO}_2$ for straw, cornstalk, and dead oak leaves. Their emission ratios for wood are much lower, between 2.4×10^{-5} mol $\text{CH}_3\text{Cl}/\text{mol CO}_2$ and 6×10^{-5} mol $\text{CH}_3\text{Cl}/\text{mol CO}_2$. The CH_3Cl emission ratios by Crutzen *et al.* (1979) were determined from a fire in a mature spruce and fir forest with dead woody material on the ground and little green vegetation. This may explain their relatively low emission ratios. The methyl chloride emission ratio we determined during FOS/DECAFE 91 is at the upper end of the values Rasmussen *et al.* (1980) report for wood burning, but they amount to only about one third of the emission ratios one would expect from the laboratory studies by Lobert *et al.* (1991) which mainly focussed on grass and similar materials. This cannot easily be reconciled with the

fact that 90% of the biomass in the area which was studied during FOS/DECAFE 91 consisted of perennial grasses (Lacaux *et al.*, 1991).

In addition to the type of biomass, there may be other factors which influence the emission ratios of methyl chloride, e.g. the chlorine content of the burnt material or the combustion conditions. Unfortunately none of the investigations give any information about the chlorine content of the biomass burnt. Lobert *et al.* (1991) report for several trace gases that the type of burning process (smouldering or flaming combustion) has a large impact on the trace gas emission ratios and they found that 72% of the CH₃Cl emissions occur during the smouldering stage. Rasmussen *et al.* (1980) give no results for the burning of grass, but they measured methyl chloride emission ratios for the ignition phase of straw and Red Alder fires and found approximately a factor of 3 higher emission rates compared to the average smoke composition. Our finding that CH₃Cl concentrations are better correlated with CO than with CO₂ points into the same direction because CO is primarily a product of smouldering combustion (Lobert *et al.*, 1991). Bonsang *et al.* (this issue) observed that the Lamto Reserve fires mainly represent flaming combustion. They suggest a CO/CO₂ emission ratio of more than 10% as criteria for smouldering combustion. Our mean CO/CO₂ emission ratio is 8.5% which indicates that our measurements on the average represent the conditions of flaming combustion. If we use the CO/CO₂ emission ratio of 10% as a criteria to differentiate between flaming and smouldering combustion for the individual samples, we find that 70% of our samples represent flaming combustion with CO/CO₂ emission ratios below 10%. For the samples from smouldering combustion (CO/CO₂ emission ratio > 10%) we find an emission ratio of $(8.9 \pm 1.4) \times 10^{-5}$ mol CH₃Cl/mol CO₂, about twice our average value. Although our set of samples from smouldering combustion is very limited, this supports the assumption that CH₃Cl is predominantly a product of smouldering combustion. The somewhat lower emission ratios for CH₃Cl observed in the Lamto Reserve fires may thus be due to a low fraction of smouldering combustion in these fires compared to the laboratory study by Lobert *et al.* However, if we use CO as an indicator for smouldering combustion and look at the CH₃Cl/CO emission ratio, we still find that our average value of 5×10^{-4} mol CH₃Cl/mol CO is a factor of three lower than the average value of 16×10^{-4} mol CH₃Cl/mol CO given by Lobert *et al.* (1991). For our subset of smouldering combustion samples we find an emission ratio of $(5.3 \pm 0.8) \times 10^{-4}$ mol CH₃Cl/mol CO. This is very similar to the emission ratio derived from the complete data set. Moreover, for this subset the relative error of the slope of the linear regression of CH₃Cl versus CO is only 15%, and the correlation coefficient is 0.9502. The comparison of these values with the corresponding values for the complete data set (Table I) indicates that the correlation of CO and CH₃Cl, and thus the emission ratio, is essentially independent of the type of burning process. Thus differences in the fraction of smouldering combustion can hardly explain the different CH₃Cl/CO emission ratios. Moreover, if we compare the CO and hydrocarbon emission ratios from our study with published literature values (Table II) there is no indication that the burning processes

TABLE II. Comparison of hydrocarbon emission ratios from biomass burning

	Emission ratios ^a						
	CO	CH ₄	C ₂ H ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈
Greenberg <i>et al.</i> , 1984 (Selva)	12	1.1	0.012	0.16	0.18	0.046	0.19
Greenberg <i>et al.</i> , 1984 (Cerrado)	11	0.60	0.11	0.11	0.15	0.045	0.046
Bonsang <i>et al.</i> , 1991	11	0.54	0.13	0.36	0.073	0.089	0.017
Lobert <i>et al.</i> , 1991	7.3	0.67	0.042	0.088	0.049	0.036	0.011
Hegg <i>et al.</i> , 1990	8.7	0.49	0.025	0.042	0.042	0.033	0.015
This work	8.5	0.83	0.18	0.35	0.058	0.058	0.012
Average	9.8	0.71	0.08	0.21	0.092	0.040	0.049
Standard deviation	1.7	0.23	0.07	0.13	0.058	0.009	0.071

^a Values are in % by volume relative to CO₂.

studied during FOS/DECAFE 91 are basically different from those investigated in other experiments. We have finally also to consider experimental uncertainties. As mentioned in the experimental section, for flame ionisation detection there is an overlap of the methyl chloride peak with two unknown peaks. Lobert *et al.* (1991) only used flame ionisation detection to determine methyl chloride. They give no details for their chromatographic separation but refer to the method described by Matusca *et al.*, 1986. Unfortunately the sample chromatograms shown by Matusca *et al.* contained none of the compounds we observed as interferences for methyl chloride. Matusca *et al.* used a nonpolar capillary column. We observed the interference for methyl chloride also on column of similar polarity and an interference similar to the one we observed for the FID signal is therefore possible for the column used by Matusca *et al.* (1986). This would result in a substantial overestimation of the methyl chloride concentrations.

The only study of biomass burning emissions of halocarbons other than methyl chloride which is known to us is the field study of Hegg *et al.* (1990). They report emission ratios for CF₂Cl₂. The average emission factor is 11 ± 7 mg/kg biomass burnt with a range of 0.4–45 mg/kg. From their emission factor of 1642 g of CO₂ per kg of biomass burnt we calculate an average emission ratio of 2.4×10^{-6} ($\pm 1.5 \times 10^{-6}$) mol CF₂Cl₂/mol CO₂ and a range of $9 \times 10^{-8} - 1 \times 10^{-5}$ mol CF₂Cl₂/mol CO₂. Our investigation did not include CF₂Cl₂. Nevertheless, the study of Hegg *et al.* (1990) supports our findings that biomass burning may be a source for halocarbons with several halogen atoms.

TABLE III. Global emission rates from biomass burning^a

	Average emission rate, 10 ⁹ g/y ^b	Range, 10 ⁹ g/y ^b
CH ₃ Cl	515	226-904
CH ₂ Cl ₂	70	32-118
CH ₃ CCl ₃	14	4-28
CCl ₄	3	0-22
CHCl ₃	2	0.9-4
C ₂ F ₃ Cl ₃	2	0.6-5
C ₂ Cl ₄	0.1	0-1
C ₂ HCl ₃	0	0-17

^a The emission rates are based on the CO₂ emission estimates by Crutzen and Andreae (1990) and our emission rates (Table I);

^b For calculated negative emission ratios zero is given as lower limit.

3.3. BIOMASS BURNING AS GLOBAL HALOCARBON SOURCE

The biomass in the investigated area represents only a small fraction of the total amount burnt annually on a global scale. However, the study of hydrocarbon emissions by Bonsang *et al.* (1995, this issue) indicates that the Lamto Reserve fires are reasonably representative for Savanna fires in general. Savanna fires contribute roughly 25% to the amount of biomass burnt globally and thus belongs to the most important biomass burning activities (Crutzen and Andreae, 1990). Nevertheless, all global extrapolations will have a very large uncertainty. However, we think that it is essential to put the biomass burning emissions of halocarbons into a global perspective in order to get an idea of the potential importance of this halocarbon source. We can calculate global emission rates from our emission ratios and the global emission rates of CO₂ or CO. We use the global CO₂ emission rates from biomass burning estimated by Crutzen and Andreae (1990). We decided to use CO₂ as reference because the uncertainty of the CO emission rates from biomass burning are much larger than for CO₂. If we used CO as reference, the average halocarbon emission rates would differ by roughly 10%. This is due to a difference in the CO to CO₂ emission ratios. We found an emission ratio of 0.085 mol CO/mol CO₂, whereas Crutzen and Andreae (1990) used a range of 5-10% which corresponds to an average of 0.075 mol CO/mol CO₂. However, the resulting small uncertainty is negligible compared to the total range of the emission rates. In order to estimate the plausible range of halocarbon emissions, we used the lower and upper limits of the biomass burning CO₂ source and also included the uncertainty of our emission ratios. The results are given in Table III.

By far the highest emission rates are found for methyl chloride. The dichloro- methane emissions are by a factor of roughly 5 lower and for trichloromethane

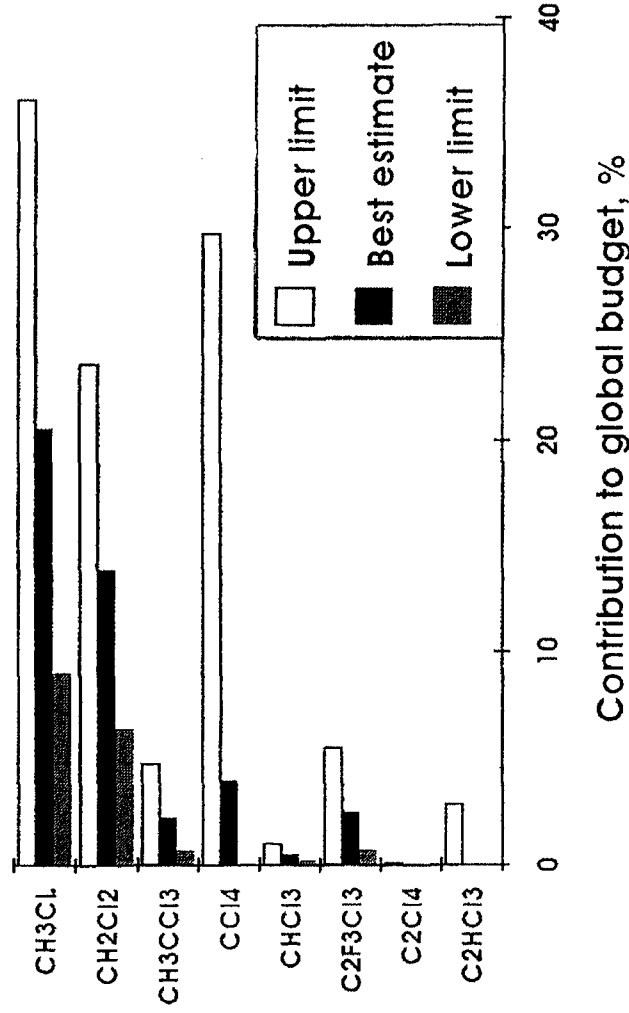


Fig. 4. Relative contribution of biomass burning emissions to the global budgets. The global budgets are taken from Fraser *et al.* (1991), Warneck (1988), Fabian (1986), Pearson (1982), and Penkett *et al.* (1980).

about a factor of 250. For these three compounds it is evident that the emission rates strongly decrease with increasing Cl atom number. The emission rate for the next compound in this series, tetrachloromethane, is very uncertain. Our results indicate a low emission rate comparable to that of trichloromethane, but the uncertainties are very high. However, the general trend of decreasing emission rates with increasing halogen atom number suggests that the tetrachloromethane emissions should be rather small. For tetrachloroethene and trichloroethene the emission rates are very low and not significantly different from zero. For $C_2F_3Cl_3$ and CH_3CCl_3 our emission rates are low, but statistically they are still different from zero on a 95% confidence level. However, as mentioned above, their average concentrations in our study were very close to the average background levels. Thus in these cases our emission rate estimates are only upper limits.

In Figure 4 the relative contributions of biomass burning emissions to the total global turnovers is shown. Only for methyl chloride and dichloromethane do we find that biomass burning is a relevant contribution to the global budgets. Our estimate indicates a 20% biomass burning contribution to the global methyl chloride budget. This is somewhat lower than previous estimates (Crutzen and Andreae, 1990). With a range of $226-904 \times 10^9$ g/y our methyl chloride emission rate is at the lower end of the range of $500-2000 \times 10^9$ g/y given by Crutzen and Andreae (1990). This is a consequence of the lower emission ratios we observed in our field study compared to the laboratory study of Lobert *et al.* (1991) which is the basis of the Crutzen and Andreae estimate.

The relative contribution to the global dichloromethane budget is slightly more than 10%. For the other substances the estimated emission rates contribute only 4% or less to the global budgets.

Moreover, for methylchloroform, trichloromethane, F-113, trichloroethene and tetrachloroethene the upper limit of our estimates is well below 10%. The uncertainty of the tetrachloromethane emission rates are rather large and would allow a biomass burning contribution to the global budget of up to 30%. On a hemispheric basis the picture is somewhat different. Except for methyl chloride, the halocarbons listed in Figure 4 are predominantly of urban and industrial origin. Only about 5% of the global trace gas emissions which are caused by the use of fossil fuels and similar industry or civilization related emissions occur in the Southern Hemisphere (cf. Isaksen *et al.*, 1985; Marland *et al.*, 1985). An exception is biomass burning with about 40% of the emissions occurring in the Southern Hemisphere (Crutzen and Andreae, 1990). For these halocarbons the biomass burning contributions are roughly an order of magnitude more important in the Southern Hemisphere compared to the global average which is given in Figure 4. Thus biomass burning is probably the most important Southern Hemispheric source of dichloromethane. On the other hand the contribution from biomass burning is only half of the values shown in Figure 4 for the Northern Hemisphere. Consequently for the Northern Hemisphere biomass burning emissions of halocarbons, with the exception of methyl chloride, play only a minor role.

4. Summary and Conclusions

Biomass burning is a source of a variety of halogen containing organic molecules. The largest emission rates are found for methyl chloride and they decrease with increasing halogen atom number and complexity of the compound. The emission ratios relative to CO₂ range from 4.3×10^{-5} mol/mol CO₂ for methyl chloride to less than 10^{-7} mol/mol CO₂ for more complex molecules such as F-113 or tetrachloroethene.

Our field study was limited to a small savanna region in Equatorial Africa and therefore all extrapolations to global scales should be made with some caution. Nevertheless, we think that our results given an estimate which is sufficient for a first overview of the global role of biomass burning as a halocarbon source. The largest contribution is found for methyl chloride. With an emission rate of roughly 500×10^9 g/y biomass burning contributes slightly more than 20% to the global methyl chloride budget. This estimate is somewhat lower than the estimate by Crutzen and Andreae (1990) which was based on laboratory studies. This shows that there still exist large uncertainties in the estimates of methyl chloride emissions from biomass burning. Nevertheless, our field study confirms the importance of biomass burning as a global methyl chloride source.

The only other halocarbon from our investigation which has a relevant biomass burning source is dichloromethane. Although the contribution of 12% to the global

budget is rather small, biomass burning is probably its most important Southern Hemisphere source. For trichloromethane the biomass burning emissions are very low and of no significance for its global or hemispheric budget. The methylchloroform, trichloroethane, trichloroethene, tetrachloroethene, F-113, and tetrachloromethane emission rates from biomass burning we derived in this study have rather large uncertainties. However, the upper limits we derived from our measurements show that, except for tetrachloromethane, they are only of minor importance for their global budgets. Only for very detailed budget interpretations such as for methylchloroform (cf. Prinn *et al.*, 1992) biomass burning may be of some relevance as a small disturbance due to the particular latitudinal distribution and seasonality of this source.

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