Methyl halide emissions from savanna fires in southern Africa

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Abstract. The methyl halides, methyl chloride (CH_3Cl), methyl bromide (CH_3Br), and methyl iodide (CH_3I), were measured in regional air samples and smoke from savanna fires in southern Africa during the Southern Africa Fire-Atmosphere Research Initiative-92 (SAFARI-92) experiment (August-October 1992). All three species were significantly enhanced in the smoke plumes relative to the regional background. Good correlations were found between the methyl halides and carbon monoxide, suggesting that emission was predominantly associated with the smoldering phase of the fires. About 90% of the halogen content of the fuel burned was released to the atmosphere, mostly as halide species, but a significant fraction (3-38%) was emitted in methylated form. On the basis of comparison with the composition of the regional background atmosphere, emission ratios to carbon dioxide and carbon monoxide were determined for the methyl halide species. The emission ratios decreased in the sequence $CH_3Cl > CH_3Br > CH_3I$. Extrapolation of these results in combination with data from other types of biomass burning, e.g. forest fires, suggests that vegetation fires make a significant contribution to the atmospheric budget of CH_3Cl and CH_3Br. For tropospheric CH_3I, on the other hand, fires appear to be a minor source. Our results suggest that pyrogenic emissions of CH_3Cl and CH_3Br need to be considered as significant contributors to stratospheric ozone destruction.

Introduction

Before the onset of the large-scale production and emission of halogenated substances, particularly the chlorofluorocarbons and halons, methyl chloride (CH_3Cl) and methyl bromide (CH_3Br) were the dominant sources of halogen compounds to the stratosphere. Even as late as 1950, the photodecomposition of CH_3Cl provided some 85% of stratospheric chlorine, and only around the year 1970 did industrially produced organochlorine compounds begin to overtake CH_3Cl as a source of stratospheric chlorine [*Weisenstein et al.*, 1992]. In spite of the obvious importance of CH_3Cl for the stratospheric ozone budget, its sources are not well quantified. Up to quite recently, the ocean was generally considered to be the dominant source of CH_3Cl [*Rasmussen et al.*, 1980; *Singh et al.*, 1983; *World Meteorological Organization (WMO)*, 1985, 1992]. However,

the emission of CH_3Cl from biomass burning had been noted already in the early 1970s, when this substance was first discovered in the atmosphere [*Lovelock*, 1975]. Since then, a number of authors measured CH_3Cl in smoke from biomass fires [*Palmer*, 1976; *Crutzen et al.*, 1979; *Rasmussen et al.*, 1980; *Tassios and Packham*, 1985; *Lobert et al.*, 1991; *Laursen et al.*, 1992]. On the basis of these results, and of estimates of the global amounts of biomass burned annually [*Crutzen and Andreae*, 1990; *Hao et al.*, 1990], the global annual CH_3Cl emission from biomass burning was estimated to be 1.8±0.9 Tg CH_3Cl yr^{-1} [*Andreae*, 1993]. From the mean atmospheric concentration of CH_3Cl (600 parts per trillion (ppt)) and its lifetime of 1.56 years [*Weisenstein et al.*, 1992], a total CH_3Cl source strength of 3.4 Tg yr^{-1} can be derived. Consequently, biomass burning may represent up to one half of the estimated global emission of this trace gas [*Andreae*, 1993; *Rudolph et al.*, 1995].

A similar situation applies in the case of CH_3Br, which was the only significant source of stratospheric bromine until the 1970s, when large amounts of the bromofluorocarbons (halons) began to be emitted. Today, CH_3Br still accounts for about one half of the bromine flux into the stratosphere [*Schauffler et al.*, 1993], a fraction which is likely to increase owing to the phase-out of the halons under the Montreal Protocol. The major sources of CH_3Br are ocean emissions, biomass burning, agricultural usage, and automobiles [*United Nations Environment Program (UNEP)*, 1992; *WMO/UNEP*, 1995]. Since CH_3Br can be formed during combustion in the same way as CH_3Cl (by reaction of halogen atoms with methyl radicals in the flame gases), its emission from biomass burning had been predicted, and was first observed experimentally by *Andreae et al.* [1993] and *Manø and Andreae* [1994]. On the basis of their results, they estimated that pyrogenic emission of CH_3Br accounts for about one third of its global source strength of

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~100 Gg yr^{-1}. In spite of the much lower emission flux and concentration of CH_3Br as compared to CH_3Cl, bromine compounds represent a significant sink for stratospheric ozone because of the much higher (by at least a factor of 50) efficiency of the catalytic cycles involving bromine. Because of the ongoing reduction in the emission of the synthetic chlorofluorocarbons and bromofluorocarbons, the relative importance of CH_3Br for stratospheric ozone loss is expected to increase. Furthermore, owing to the short atmospheric lifetime of CH_3Br (1.3-2.0 years [*WMO/UNEP*, 1995]), a significant reduction in its emission would have a relatively prompt effect on stratospheric bromine levels. The sources and atmospheric behavior of CH_3Br have therefore been the subject of considerable discussion in recent years [*UNEP*, 1992; *WMO/UNEP*, 1995], and it has been pointed out that improved estimates of the various source terms are urgently needed.

In this paper, we present data on the emission of the methyl halides, CH_3Cl, CH_3Br, and CH_3I, from savanna fires in southern Africa. These results were obtained during the IGAC/ BIBEX (International Global Atmospheric Chemistry/Biomass Burning Experiment) campaign SAFARI-92 (Southern Africa Fire-Atmosphere Research Initiative-92), which took place during the 1992 fire season (August to October). The results will be placed in the context of the total emission of these compounds from all types of biomass burning and from other sources in order to assess the role of savanna fires in the atmospheric methyl halide budget.

Methods

During SAFARI-92, four laboratories made measurements of methyl halides in ambient air and in smoke from savanna fires: the Max Planck Institute for Chemistry in field laboratories located at Kruger Park (MPIC-K) and in Pretoria (MPIC-P), the National Center for Atmospheric Research (NCAR), and the Forschungszentrum Jülich (KFA). The sampling and analysis procedures will be described only briefly in this paper; more details can be found in the papers by *Atlas et al.* [1993], E. Atlas et al. (manuscript in preparation, 1995), G. Helas et al. (manuscript in preparation, 1995), and R. Koppmann et al. (manuscript in preparation, 1995).

Sampling

Air samples were collected in stainless steel canisters. NCAR used cylindrical stainless steel canisters with a volume of 2.5 L, MPIC-P and KFA cylindrical canisters with a volume of 2.0 L, and MPIC-K spherical canisters with a volume of 1.0 L. All canisters are electron beam welded and electropolished inside and equipped with metal bellows valves and had been cleaned and tested for hydrocarbon and halocarbon measurements. Samples were collected at ground level (NCAR) by pressurizing the canisters with a metal bellows pump to about 3 bar in the smoke plume of the fires. On the research aircraft, a Cessna 310 (MPIC-K) and a DC-3 (MPIC-P, KFA), air was taken in using a continuously flushed stainless steel manifold and pumped into the canisters using metal bellows (DC-3) or Teflon membrane (Cessna) pumps. The sample collection took up to about 1 min. The canisters were filled to a pressure of about 2-3 bar. On the DC-3, the water content of the air was reduced by passing the sample air stream through a trap cooled with ice. No detectable losses of the methyl halides or CO_2 result from this drying procedure.

Methyl Halide, CO, and CO_2 Determinations

NCAR. Sample volumes of 0.1-1.0 L were preconcentrated on a glass bead trap at liquid argon temperature. The preconcentrated sample was transferred at ~85 °C to a 30 m x 0.25 mm x 1.0 μm DB-1 capillary column held at -65 °C. For separation, the column oven was held at -65 °C for 2 min and then ramped at 4 °C min^{-1} to 175 °C. A Hewlett-Packard 5971 mass selective detector in the selected ion mode was used for compound quantitation. Ions used for quantitation were as follows: CH_3Cl, 50; CH_3Br, 96; and CH_3I, 142. A primary standard mixture of methyl halides was prepared by Scott Specialty Gases, and the mixing ratios were confirmed by analyses at the National Institute of Standards and Technology (NIST). CO was measured by gas chromatography (GC) using a HgO reductive gas detector. CO_2 was determined on a separate aliquot of the samples using a gas chromatographic system which reduced CO_2 to CH_4 for quantitation by a flame ionization detector.

MPIC-K. Sample volumes of 60-600 mL air were preconcentrated by cryofocusing on a precolumn at -186 °C. Separation was on a 25 m GS-Q column (0.35 mm ID) using H_2 at 4 mL min^{-1} as carrier gas. A temperature program was used which consisted of 2 min at 30 °C, 10 °C min^{-1} to 150 °C, 35 °C min^{-1} to 220 °C, and 5 min isothermal at 220 °C. CH_3Cl was quantified using a flame ionization detector. The separation system was checked and optimized thoroughly with potentially coeluting substances to eliminate interferences. Calibration in the field was by secondary standards consisting of compressed air, which had been calibrated in the laboratory using gravimetrically prepared static dilution standards. CO was measured by gas chromatography using a HgO reductive gas detector, CO_2 by a non-dispersive infrared analyzer.

MPIC-P. Sample volumes of 0.1-0.3 L air were preconcentrated in a stainless steel tube filled with porous glass beads immersed in liquid argon. After preconcentration, the cold trap was immersed in boiling water and the samples were back-flushed from the trap to the GC column. The inlet of the column was held at liquid nitrogen temperature during the transfer to cryofocus the samples. The analytical column was a 50 m x 0.32 mm Cp-Sil-5 fused silica capillary (Chrompack) with 1.2 μm film thickness. The temperature program was as follows: -40 °C for 2 min, a 15 °C min^{-1} ramp to 40 °C, followed by a 10 °C min^{-1} ramp to 200 °C. The GC used was a Siemens Sicromat II equipped with a flame ionization detector. The chromatograms were integrated using ELAB® chromatography software. A compressed air sample which had been calibrated by KFA was used as field standard. CO and CO_2 were determined by KFA using the methods described below.

KFA. The samples were analyzed in the laboratory at Jülich using gas chromatography with flame ionization (FID) and electron capture (ECD) detectors. Hydrocarbons and halocarbons were preconcentrated cryogenically and separated on a combination of a 7-m micropacked Porapak QS column and a 105 m RTX-1 fused silica capillary column. CH_3Cl was evaluated from the ECD signal. Precision for this species is better than 10%, the detection limit about 5 ppt. In a number of chromatograms, the CH_3Cl peak overlapped with the water peak and could not be evaluated quantitatively. In some samples collected directly inside the smoke plumes, interferences with other peaks were observed (see also *Rudolph et al.* [1995]) which also precluded quantitative evaluation. CO and CO_2 were determined by a gas chromatographic method very similar to the one described by *Heidt* [1978]. The precision is 3% for CO and

0.5% for CO_2. Details of the analytical techniques are given by *Koppmann et al.* [1993] and *Rudolph et al.* [1995].

Halogen Element Determination in Fuels and Residues

The bulk (total) concentrations of the halogens in the savanna fuels and various fuel residues were determined by instrumental neutron activation analysis (INAA). Subsamples of 150 mg were packed in polyethylene vials for INAA. The analysis for the elements Cl and I involved a 5-min irradiation of each subsample separately at a thermal neutron flux of $2-3 \times 10^{12}$ neutrons $cm^{-2} s^{-1}$ in the Thetis reactor of the University of Gent, after which the sample was subjected to two consecutive gamma spectrometric measurements (one of 5 min and one of 30 min) with a high-resolution Ge detector. For the determination of Br we utilized a 7-hour neutron irradiation (up to six subsamples were irradiated simultaneously), and two measurements (of a few hours each) at 2 and 5 days after the irradiation. The net peak areas of selected γray lines of the product radionuclides ^{38}Cl, ^{82}Br, and ^{128}I were determined as described by *Schutyser et al.* [1978]. Concentration results were obtained from comparing these areas for the samples with those of multi-element standards. The standards had been prepared by pipetting solutions of the analyte elements onto Whatman filter paper.

Results and Discussion

Sampling Sites

During SAFARI-92, two types of samples were collected: smoke from experimental fires and from fires encountered during regional survey flights (Table 1), and ambient air from altitudes between 50 m (above ground level) and 4000 m (above sea level) over southern Africa (South Africa, Zimbabwe, Zambia, Botswana, Namibia, Angola, and Swaziland). The experimental fires were conducted in Kruger National Park (KNP), South Africa, and in sugarcane fields near Big Bend, Swaziland. All of the KNP fires were in sourveld savanna near Pretoriuskop, at the southern end of the park. This vegetation is relatively nutrient-poor, and had not been intensively grazed in spite of the intensive drought, which had prevailed in southern Africa for 2 years before the experiment. Additional information on the vegetation characteristics and fire behavior can be found

in the papers by *Trollope et al.* [this issue] and *Stocks et al.* [this issue]. Two of the KNP fires were conducted in small plots (Shabeni 5 and Kabeni "Extra") with an area of about 6 ha each; these were sampled from the ground only. The two fires on the large management blocks 55 and 56 (2043 and 2333 ha, respectively) were sampled from the ground and with the Cessna 310 and DC-3 aircraft. Fires of opportunity were sampled by the DC-3 aircraft in the Drakensberg Escarpment, where a mixture of native forest, shrub, and grass was burning, and over a savanna fire in Zambia. The sugarcane fires, which were sampled by the DC-3, represent burns which are typical of regional agricultural practices. They are set immediately before harvesting in order to facilitate the cutting and processing of the sugarcane. This practice results in substantial levels of air pollution in many sugar-growing areas. During SAFARI-92, emissions from fires on two sugarcane fields of 12 and 43.7 ha area were investigated. The fires burned very intensively with large flames and consumed about 25 tons of dry mass per hectare.

In the following discussion, we will make use of the concept of emission ratios. This is necessary because the absolute concentration of trace gases in smoke samples has little meaning, since it simply represents varying degrees of dilution of flame gases with ambient air, an effect that is particularly pronounced in aircraft sampling, where the transit time through the plume is comparable to the sampling time. We will therefore analyze our data in the form of emission ratios, e.g.:

$$ER_{CH_3Cl/CO} = \frac{\Delta CH_3Cl}{\Delta CO} = \frac{(CH_3Cl)_{Smoke} - (CH_3Cl)_{Ambient}}{(CO)_{Smoke} - (CO)_{Ambient}}$$

where CO (or CO_2) is used as reference species. The emission ratios are obtained by calculating the slope of the regression line between CH_3X and CO (or CH_3X and CO_2) for a given data set from a fire or plume. Note that emission ratios are different from emission factors, which are defined as the amount of trace gas emitted per amount of fuel burned.

The selection of CO or CO_2 as reference gas is determined by the final objective of the analysis. It has been shown previously [*Lovelock*, 1975; *Lobert et al.*, 1991; *Manø and Andreae*, 1994] that CH_3Cl is emitted preferentially in the smoldering stage of fires. CO is a suitable reference species for smoldering combustion, as it is also emitted predominantly

Table 1. Sampling Times and Locations for Smoke Samples Collected During SAFARI-92

| Site	Date (1992)	Number of Samples	Laboratory
Kruger Park			
Shabeni 5	15 Sept.	4	NCAR
Kabeni "Extra"	22 Sept.	3	NCAR
Large block 56	18 Sept.	25	NCAR, MPI-K, MPI-P
Large block 55	24 Sept.	38	NCAR, MPI-K, MPI-P
Sugarcane field 1	19 Sept.	5	MPIC-P, KFA
Sugarcane field 2	19 Sept.	3	MPIC-P, KFA
Drakensberg near Belfast	18 Sept.	2	MPIC-P, KFA
Drakensberg near Nelspruit	20 Sept.	12	MPIC-P, KFA
Zambia savanna (16°S, 23°E)	03 Oct.	2	MPIC-P, KFA
Ambient air	15 Sept. to 06 Oct.	113	MPIC-P, MPI-K, KFA, NCAR
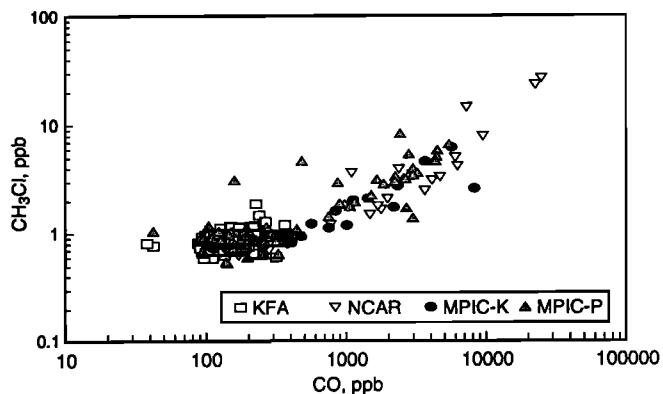
Figure 1. Methyl chloride concentrations in all samples collected during SAFARI-92 plotted against the corresponding CO concentrations.

during this stage [Lobert et al., 1991]. As a result, close correlations between smoldering-derived gases can usually be obtained, which allows accurate estimation of trace gas emissions from fires for which the CO emission is known. For smoldering-derived species, the emission ratio relative to CO is largely dependent on fuel characteristics, particularly the elemental composition (e.g., the halogen content) of the fuel. Correlations of these gases with CO_2, on the other hand, tend to be relatively poor, since the relative proportion of flaming versus smoldering combustion in different fires or even different parts of the same fire results in variable trace gas to CO_2 ratios. On the other hand, the emission ratio relative to CO_2 permits the estimation of trace gas emission from fires for which only the amount of biomass burned, but not the amount of CO emitted, is known. Therefore this ratio is more suitable for regional or global estimations.

Methyl Chloride

The CH_3Cl results from SAFARI-92 are shown in Figure 1 in the form of a scatterplot versus CO, with the measurements by the different laboratories identified by different symbols. This figure shows that there is no obvious analytical bias between the data from the different groups. The ambient air samples cluster in the lower left corner of the figure, representing the CH_3Cl and CO values typical of the lower 3 km of the atmosphere over southern Africa during SAFARI-92, about 0.6-1.1 ppb CH_3Cl and 100-300 ppb CO. In the smoke samples, CO concentrations up to 26 ppb CH_3Cl and 25 ppm CO were measured. This suggests that considerable dilution took place during sampling, since "pure" smoke from flaming and smoldering combustion contains hundreds to thousands of parts per million CO.

When the results from the various fires are analyzed separately, we find a surprising degree of consistency between fires in widely varying fuel types. The CH_3Cl values from the two small fire plots in KNP are plotted against CO in Figure 2a, those for the large plots 55 and 56 in Figures 2b and 2c, respectively. The regression slopes (Table 2) are not statistically different from one another, and we have therefore combined the data from all KNP fires in regression calculations done separately with the data from each of the three laboratories participating in the KNP measurements (Table 2). Again, the regression parameters are not significantly different, which shows that no significant interlaboratory biases are present. Furthermore,

the agreement between the NCAR data, which were obtained by GC/MS, and the MPIC measurements, which were made using electron capture and flame ionization detectors, demonstrates that no significant coelution problems interfered with the determination of CH_3Cl by the less selective detectors.

The results from the two Drakensberg fires and the sugarcane fires are shown in Figures 3a and 3b, respectively. Only two data points were available from the Drakensberg fire near Belfast, where grassland and native shrubland were burning. These two points suggest a substantially higher emission ratio $\Delta CH_3Cl/\Delta CO$ than measured in all other fires, about 4×10^{-3}, but
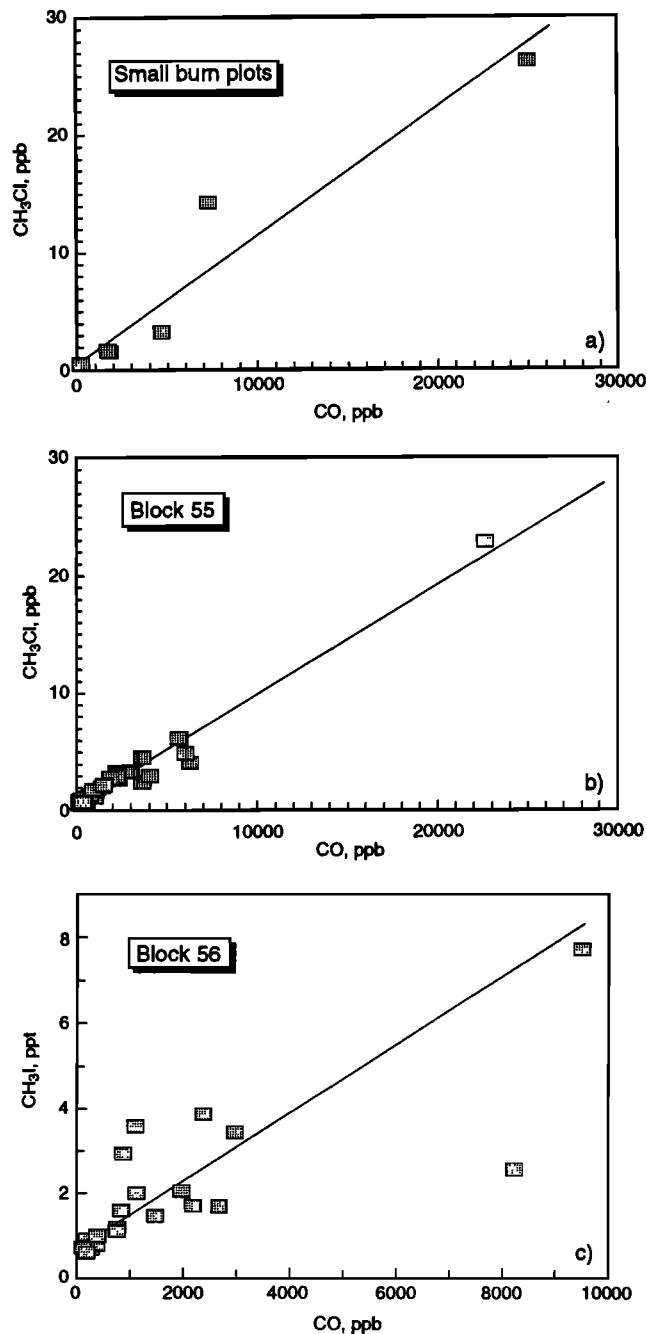

Figure 2. Methyl chloride concentrations in the samples collected from the smoke plumes of the Kruger Park experimental fires plotted against CO: (a) small plots; (b) large plot 55; (c) large plot 56.

Table 2. Methyl Chloride Emission Ratios From the Savanna Fires Sampled During SAFARI-92

Samples	$\Delta CO/\Delta CO_2$, x10^{-3}	$\Delta CH_3Cl/\Delta CO$, x10^{-3}	r^2	N	$\Delta CH_3Cl/\Delta CO_2$, x10^{-6}	r^2	N
KNP small plots	36±11	1.06±0.13	0.93	6	...	...	...
KNP large plot 56	33±3	0.74±0.18	0.82	22	32±8	0.53	17
KNP large plot 55	51±2	0.94±0.03	0.97	39	17±4	0.41	39
All Kruger Park fires							
MPIC-K data	40±20	0.98±0.04	0.96	25	21±2	0.81	23
MPIC-P data	48±3	1.04±0.13	0.83	14	53±3	0.96	14
NCAR data	27±9	1.01±0.06	0.93	23	14±8	0.19	14
Drakensberg (Nelspruit)	105±3	0.94±0.07	0.94	12	99±7	0.94	15
Sugarcane fires	18±2	1.05±0.14	0.92	7	19±3	0.77	10
Regional background	...	1.23±0.22	0.24	95	...	...	...
SAFARI-92, all data	53±21	0.95±0.01	0.95	176	20±2	0.42	173

the small sample number does not permit a statistically valid regression calculation. The measurements from the Drakensberg fire near Nelspruit yield a regression slope statistically indistinguishable from the KNP results (Table 2). The single measurement in a plume from a small savanna fire in northwestern Zambia also suggests a relatively high emission ratio (5.3x10^{-3}) if the samples taken before and after are used as ambient reference. Again, however, proper statistical analysis is not possible.

When the CH_3Cl concentrations from the samples taken outside of smoke plumes during the regional survey flights are plotted against CO, a more diffuse, but still highly significant correlation is observed (r^2=0.24, N=113, α<0.0005; Figure 4, Table 2). The regression slope is slightly higher than that measured in the plumes (1.23±0.22)x10^{-3}, but the difference is at the margin of statistical significance. These results are consistent, however, with the conclusion drawn from other trace gas and aerosol measurements taken during SAFARI-92, that the regional atmosphere over southern Africa was loaded with substantial amounts of biomass smoke [*Andreae et al.*, 1994; *Maenhaut et al.*, this issue; G. W. Harris et al., manuscript in preparation, 1995; R. Koppmann et al., manuscript in preparation, 1995]. The mean CH_3Cl concentration in the ambient samples was 886±180 ppt (mean and standard deviation; N=113), well above the global mean value of about 600 ppt [*Koppmann et al.*, 1993; *Rasmussen et al.*, 1980; *Singh et al.*, 1983]. Similarly, the mean CO concentration of 166±59 ppb was substantially greater than southern hemispheric "clean" air (about 50-80 ppb [*Novelli et al.*, 1994]). The regional distribution of these trace gases is discussed in companion papers [G. W. Harris, manuscript in preparation, 1995; G. Helas, manuscript in preparation, 1995; R. Koppmann, manuscript in preparation, 1995].
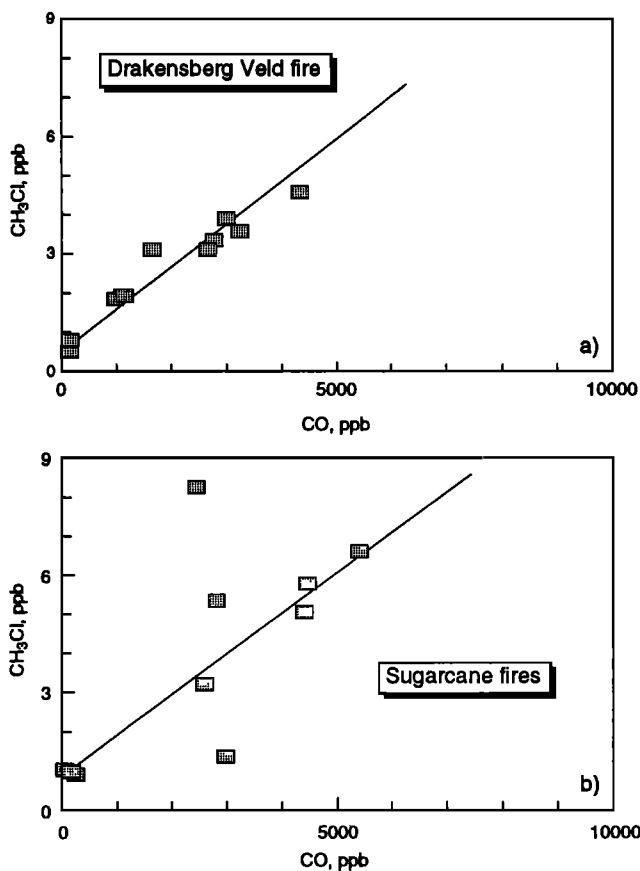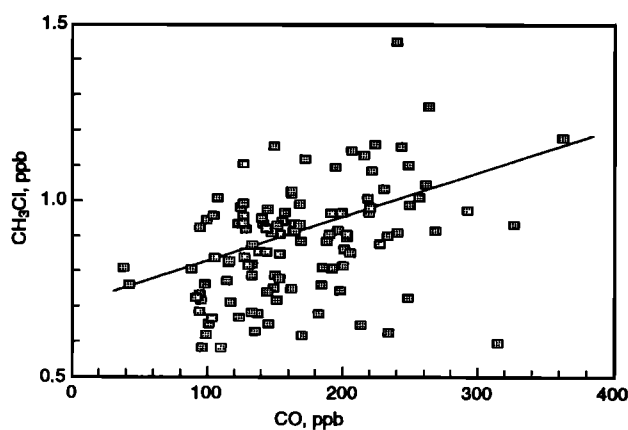

Figure 3. Methyl chloride concentrations in the samples collected from the smoke plumes of (a) the Drakensberg veld fire and (b) the sugarcane field fires plotted against CO.

Figure 4. Methyl chloride concentrations in the samples collected during the regional survey flights over southern Africa plotted against CO.

The correlations between CH_3Cl and CO_2 are much more variable than between CH_3Cl and CO (Table 2). When all data are used in the regression, a slope of $(33\pm3)\times10^{-6}$ is obtained with a relatively low r^2 of 0.26. Removing three obvious outliers (ground-based samples with extremely high CO concentration) reduces the emission ratio $\Delta CH_3Cl/\Delta CO_2$ to $(20\pm2)\times10^{-6}$, and improves r^2 to 0.42. The relatively weak overall correlation is due to significantly different emission ratios observed for the different fires. The most intensely flaming fires in the sugarcane fields and the KNP savanna had the lowest $\Delta CH_3Cl/\Delta CO_2$ ratios (Table 2), while the Drakensberg forest fires had a $\Delta CH_3Cl/\Delta CO_2$ ratio as high as $(99\pm7)\times10^{-6}$. These differences reflect mostly the different $\Delta CO/\Delta CO_2$ emission ratios of the fires, which also are lowest in the sugarcane and savanna fires, and highest in the forest fires. The higher CO emission ratios in the forest fires are due to the higher proportion of smoldering combustion typical of woody fuel. Surprisingly, however, the $\Delta CH_3Cl/\Delta CO_2$ and the $\Delta CO/\Delta CO_2$ emission ratios measured by the different groups for the KNP fires also differ from one another (Table 2), in spite of the good agreement between groups for the $\Delta CH_3Cl/\Delta CO$ ratio. This must be due to different parts of the fires having been sampled by the different groups, and argues strongly for the use of $\Delta CH_3Cl/\Delta CO$ emission ratios for making extrapolations from local measurements to regional and global CH_3Cl emissions.

Our $\Delta CH_3Cl/\Delta CO$ emission ratios (mean and range: $0.95(0.74-1.23)\times10^{-3}$) agree well with the results obtained from laboratory fires by *Lobert et al.* [1991], who give a mean $\Delta CH_3Cl/\Delta CO$ of 1.6×10^{-3} with a range of $(0.180-4.37)\times10^{-3}$ for a variety of fuels including savanna grass, hay, straw, and pine branches. Both our study and Lobert et al.'s gave $\Delta CH_3Cl/\Delta CO$ emission ratios well above those published by *Laursen et al.* [1992], who found a mean and range of $0.16(0.06-0.40)\times10^{-3}$ from forest fires in North America. Their highest values are from fires in California chaparral, their lowest emission ratios from fires in temperate conifer forests. Under constant combustion conditions, the amount of CH_3Cl emitted from fires is controlled by the amount of chloride present in the fuel [*Reinhardt*, 1987]. Since CH_3Cl is mainly produced during the smoldering phase, and CO is a specific tracer for this mode of combustion, it follows that $\Delta CH_3Cl/\Delta CO$ is predominantly a function of the fuel halogen content. The high values of $\Delta CH_3Cl/\Delta CO$ in smoke from savanna fires as compared to emissions from temperate forest fires are thus consistent with the high Cl content of savanna grasses relative to that of temperate forest biomass [*McKenzie et al.*, 1996].

On the other hand, our emission ratios relative to CO_2 $(20(14-99)\times10^{-6})$ agree well with Laursen et al.'s $(12(6-21)\times10^{-6})$, and also with the results from a Colorado forest fire $(23(4-57)\times10^{-6})$ published by *Crutzen et al.* [1979]. The emission ratios from southern Africa are somewhat lower than those of *Rudolph et al.* [1995], who obtained a mean $\Delta CH_3Cl/\Delta CO_2$ of 43×10^{-6} in smoke plumes from west African savanna fires. *Lobert et al.* [1991] did not give $\Delta CH_3Cl/\Delta CO_2$ ratios, but from their $\Delta CH_3Cl/\Delta CO$ and $\Delta CO/\Delta CO_2$ ratios a mean $\Delta CH_3Cl/\Delta CO_2$ of 120×10^{-6} can be estimated. This value and *Rasmussen et al.*'s [1980] value of 120×10^{-6} from laboratory burns of various fuels are well above our savanna ratio of about 20×10^{-6}. On the other hand, our measurements from the Drakensberg forest fire gave a ratio (99×10^{-6}) similar to *Rasmussen et al.*'s [1980]. This ratio is considerably higher than emission ratios from temperate forests [*Crutzen et al.*, 1979; *Laursen et al.*, 1992] and our own boreal forest measurements

(Siberia: 61×10^{-6}, Finland: 48×10^{-6}; M.O. Andreae, unpublished data, 1994). The highest mean $\Delta CH_3Cl/\Delta CO_2$ (290×10^{-6}) ratio was reported by *S. Tassios and D. R. Packham* [1985] from fires in eucalypt forests in Western Australia. It appears thus that tropical and subtropical forest fires emit more CH_3Cl per amount of CO_2 released (or biomass burned) than savanna fires, in spite of the higher Cl content of the savanna vegetation. This may be the result of the much larger fraction of smoldering combustion in forest fires compared to savanna fires.

Methyl Bromide

Methyl bromide and methyl iodide measurements are available only for the Kruger Park fires. The CH_3Br concentrations in the smoke samples from the small and the large fire plots are highly correlated with the corresponding CH_3Cl data, and when plotted together, all appear to be part of a common regression line (Figure 5a). The same applies to the relationship between CH_3Br and CO (Figure 5b). When regression calculations are performed separately for the different plots, some differences emerge (Table 3). The closest correlations are found for the samples from the large plot 55, where r^2 is 0.97 for CH_3Br versus CO and 0.99 for CH_3Br versus CH_3Cl and the regression slopes (emission ratios) are 9.5×10^{-3} and 9.6×10^{-3}, respectively. The data from the small fires give somewhat lower emission ratios, 8.1×10^{-3} and 7.7×10^{-3}, respectively. The difference in the emission ratios relative to CO is, however, not statistically significant. The measurements from the large plot 56 show the largest scatter and the lowest emission ratios. When all data points are used in the regression, the $\Delta CH_3Br/\Delta CO$ slope is only $(3.9\pm0.5)\times10^{-3}$; when the data point with the highest CO concentration is removed, the ratio increases to $(6.5\pm2.0)\times10^{-3}$, while r^2 decreases from 0.91 to 0.72. This sample came from a small heading fire separate from the main fire and may have had anomalous fuel composition or combustion conditions. Using the data from all SAFARI-92 fires, we obtain a $\Delta CH_3Br/\Delta CO$ ratio of $(8.3\pm0.4)\times10^{-3}$, which is in close agreement with the data by *Rowland et al.* [1994] who measured a ratio of 9×10^{-3} in smoke plumes from savanna and tropical forest fires in Brazil.

The scatterplot of CH_3Br versus CO_2 (Figure 5c) shows the same poor correlation as had already been observed for CH_3Cl versus CO_2. The three points with high very CO concentrations have been omitted from this plot and from the regression analysis. This is justified, since the kind of smoldering-dominated smoke represented by these samples contributes relatively little to the total CO_2 output of the fire. Therefore, their inclusion would result in an upward bias of the CO_2-based emission ratios. Analyzed for the individual fires, there is substantial apparent variation in the $\Delta CH_3Br/\Delta CO_2$ emission ratios, but in view of the large standard errors associated with the small sample numbers and low regression coefficients, these variations are not statistically significant. The $\Delta CH_3Br/\Delta CO_2$ emission ratios measured by *Manø* [1994] in smoke from a boreal forest fire also show great variability, depending on whether the samples were collected from flaming combustion (0.12×10^{-6}) or from smoldering combustion (up to 3.2×10^{-6}).

Methyl Iodide

The scatterplots for CH_3I versus CH_3Cl, CO, and CO_2 are shown in Figures 6abc. Again, good correlations are seen for CH_3I vs CH_3Cl and CO, and a much poorer correlation for CH_3I versus CO_2. The emission factor $\Delta CH_3I/\Delta CH_3Br$ is highly dependent on the inclusion of one point with very high CH_3I

trend line also in the scatterplots relative to CO and CO_2. As it is outside of the 95% confidence limits of the regression equation, it is rejected as an outlier, and the emission ratios in Table 4 are calculated after this value has been excluded.

Fuel Halogen Content and Halogen Species Volatilization

We determined the halogen element concentrations in fuel samples from the two large blocks and three of the small fire plots studied at KNP (Table 5). The average Cl and Br concentrations in the fuel, 1260±310 and 7.0±1.6 mg kg^{-1}, are somewhat higher than the values measured on miombo savanna vegetation from Zambia by *McKenzie et al.* [1996]. After weighting for the contributions of the different fuel components to the amount of fuel burned, their averages are 650 mg Cl kg^{-1} and 4.0 mg Br kg^{-1}. Some of this difference is due to the different fuel mixture at the two sites: At KNP, the grass fraction dominates and the fuel composition is essentially that of the grass component, whereas at the miombo site a large litter fraction with lower halogen content is present. The grass fraction at the miombo site (1000 mg Cl kg^{-1} and 4.8 mg Br kg^{-1} [*McKenzie et al.*, 1996]) is not significantly different from the KNP fuel. No iodine data are available in the literature for comparison.

The halogen concentrations in the savanna fuels are considerably higher than those in most forest fuels, especially in forest fuels from temperate regions [*McKenzie et al.*, 1996]. This helps to explain why the $\Delta CH_3Cl/\Delta CO$ values from savanna fires tend to be higher than those from forest fires. A generally high chloride content in savanna vegetation is also suggested by the very high levels of chloride in aerosols and precipitation influenced by biomass burning in both southern and west Africa [*Lacaux et al.*, 1991; *Lefeivre*, 1993; M. O. Andreae et al., manuscript in preparation, 1995].

The molar ratio Cl/Br in the KNP fuel is 406:1, somewhat higher than the ratio measured by *McKenzie et al.* [1996] in Zambia (366:1). At both savanna sites, the Cl/Br ratios are considerably higher than in forest vegetation from tropical and temperate regions, where *McKenzie et al.* [1996] found values near 100:1. This may explain the higher CH_3Cl/CH_3Br ratio in the savanna smoke (120:1) as compared to the smoke from boreal forest fires in Siberia (53:1) [*Manø and Andreae*, 1994] and Finland (21:1) (M.O. Andreae, unpublished data, 1994).

The amount of halogens released by the fires can be calculated from the halogen loadings in the fuel minus the halogens remaining in the unburned residue and ash. When this value is divided by the amount of halogen in the prefire fuel, the fraction emitted in the fire is obtained (fuel and residue loadings from *Kuhlbusch et al.* [this issue] were used for these calculations). This value is close to 80% for all three halogen elements analyzed (Table 6). The emission fraction relative to the fuel burned can be obtained from these numbers by dividing by 0.88, the fraction of the prefire fuel consumed in the fire. This
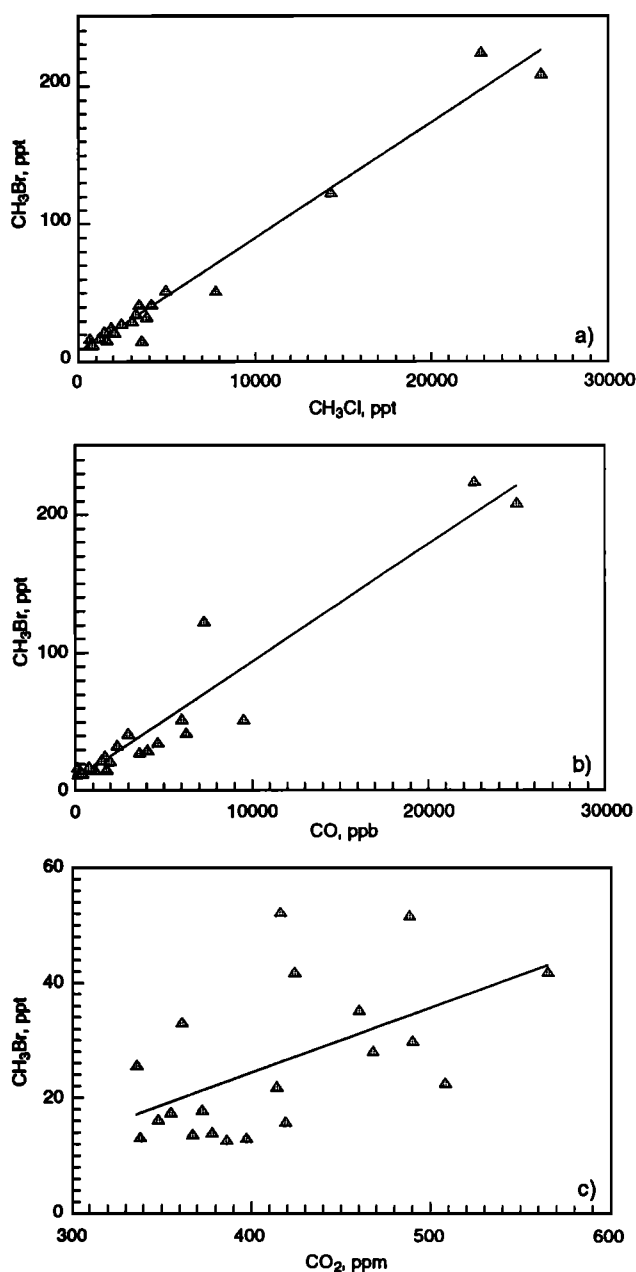

Figure 5. Methyl bromide concentrations in samples from the Kruger Park fires plotted against (a) methyl chloride, (b) CO, and (c) CO_2.

concentration: Upon removal of this point, the slope decreases from (4.5±0.6)x10^{-3} (r^2=0.71) to (2.6±0.2)x10^{-3} (r^2=0.83). This sample was collected on the ground and may represent unusual fuel composition or burning characteristics. It falls far from the

Table 3. Methyl Bromide Emission Ratios to CH_3Cl, CO, and CO_2 From the Kruger Park Savanna Fires

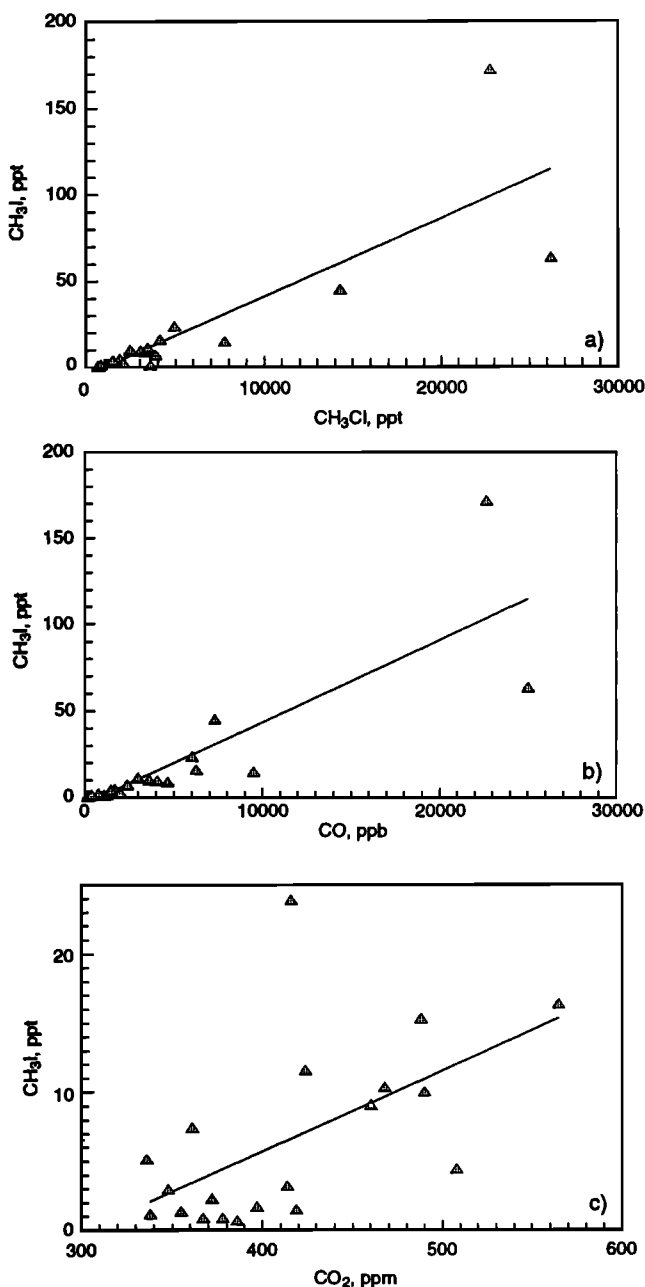| Samples	$\Delta CH_3Br/\Delta CH_3Cl$, x10^{-3}	r^2	$\Delta CH_3Br/\Delta CO$, x10^{-6}	r^2	$\Delta CH_3Br/\Delta CO_2$, x10^{-6}	r^2	N
Small plots	7.7±0.1	0.99	8.1±1.1	0.91	0.48±0.38	0.44	7
Large plot 56	5.2±0.3	0.99	3.9±0.5	0.91	0.20±0.11	0.46	6
Large plot 55	9.6±0.1	0.99	9.5±0.6	0.97	0.07±0.07	0.14	8
All KNP fires	8.3±0.3	0.97	8.3±0.4	0.95	0.11±0.04	0.30	23

Figure 6. Methyl iodide concentrations in samples from the Kruger Park fires plotted against (a) methyl chloride, (b) CO, and (c) CO_2.

shows that some 90% of the halogen elements present in the fuel burned were actually released to the atmosphere during combustion. The ratio of total halogen to CO_2 emitted by the fire (X_{total}/CO_2 in Table 6) as calculated from fuel and residue

analysis can be compared to the emission ratios of halogen and methyl halide species measured in the smoke. The emission ratios for the halide ions determined in the Kruger Park fires are in reasonable agreement with the ratios predicted from the fuel/residue budget. The chloride emission ratio $((1100\pm700)\times10^{-6})$ given in Table 6 is from *Andreae* [1996] and actually exceeds the amount of chlorine released by combustion; with the aerosol composition data of *Maenhaut et al.* [this issue] a chloride emission ratio of 510×10^{-6} and a fraction Cl_{inorg}/Cl_{total} of 56% would be obtained. These differences are probably mostly due to sampling variability, as the high standard deviation of *Andreae*'s [1996] value shows as well. These results suggest that most of the fuel halogen content is released either directly as halide particles or as hydrogen halides which rapidly combine with alkaline substances in the aerosol or with gaseous ammonia to give halide particles.

In Table 6 we also compare the methyl halide emission ratios with the total halogen element emission. For CH_3Cl, the methylated species accounts for $3.0\pm1.9\%$ of the total chlorine emitted. This fraction increases to $5.0\pm2.6\%$ for bromine and to $38\pm25\%$ for iodine. In the case of iodine, this fraction appears very large and may reflect measurement uncertainties and sampling variability. Nevertheless, our results suggest that a significant fraction of the fuel halogen content is methylated in the combustion process and that this fraction increases in the sequence $Cl < Br < I$.

Methyl Halide Emissions From Biomass Burning

In Table 7 we present the results of attempts to estimate the flux of the methyl halides from savanna fires and from all types of biomass burning worldwide. No formal assessment of the uncertainties involved in these calculations can be given, since the data required for an error analysis are not available. A rough estimate of uncertainty in the source estimates can be gained from the considerations that the pyrogenic emissions of CO and CO_2 (which are used in the extrapolation) are known to within about $\pm50\%$ and that uncertainties related to the emission ratios for the methyl halides are at least a factor of 2. The overall uncertainty is thus probably about a factor of 3, probably even larger in the case of CH_3Br and CH_3I.

For our calculations, we assume that the data from SAFARI-92 can be applied to savannas in general and use the estimate of 1660 Tg $C(CO_2)$ emitted annually from savanna fires proposed by *Andreae* [1993]. Using a mean $\Delta CO/\Delta CO_2$ of 0.063 for savanna fires [*Lacaux et al.*, 1995; *Ward et al.*, 1992; Andreae, 1995; G.W. Harris et al., manuscript in preparation, 1996] and the mean emission ratios from SAFARI-92, we obtain an annual emission of 420 Gg CH_3Cl, or about 10-15% of the global CH_3Cl source. When the calculation is based on CO_2, a much lower flux of 130 Gg yr^{-1} is obtained, but as we have argued above, the emission ratio relative to CO_2 is much less reliable than the CO-based one, which should be used

Table 4. Methyl Iodide Emission Ratios to CH_3Cl, CO, and CO_2 From the Kruger Park Savanna Fires

Samples	$\Delta CH_3I/\Delta CH_3Cl$, $\times10^{-3}$	r^2	$\Delta CH_3I/\Delta CO$, $\times10^{-6}$	r^2	$\Delta CH_3I/\Delta CO_2$, $\times10^{-6}$	r^2	N
KNP small plots	2.5 ± 0.2	0.98	2.6 ± 0.6	0.81	0.28 ± 0.20	0.40	6
Large plot 56	2.0 ± 0.4	0.85	1.5 ± 0.2	0.94	0.08 ± 0.04	0.49	8
Large plot 55	4.8 ± 0.4	0.96	3.1 ± 0.5	0.88	0.04 ± 0.04	0.12	6
All KNP fires	2.6 ± 0.2	0.93	2.6 ± 0.3	0.83	0.09 ± 0.05	0.14	23

Table 5. Halogen Element Content in the Savanna Fire Fuels and Residues From Kruger Park, and Fraction of Element Emitted to the Atmosphere During the Fires on the Large Blocks

	Chlorine	Bromine	Iodine
Concentration in Fuel, g kg^{-1}			
Plot Napi #3	1785 ± 70	9.8 ± 0.3	1.17 ± 0.19
Plot Shabeni #5	1530 ± 90	8.7 ± 0.4	1.13 ± 0.24
Plot Kabeni Extra	1160 ± 340	6.7 ± 0.5	1.10 ± 0.10
Large block 55	950 ± 120	6.0 ± 0.4	1.64 ± 0.16
Large block 56	1190 ± 130	5.4 ± 0.6	1.23 ± 0.30
Average	1260 ± 310	7.0 ± 1.6	1.28 ± 0.30
Block 55			
Prefire fuel halogen loading,g ha^{-1}	9530	60	16
Postfire halogen loading, g ha^{-1}	1180	6	4
Fraction emitted, %	88%	90%	76%
Block 56			
Prefire fuel halogen loading, g ha-1	6230	28	6
Postfire halogen loading, g ha-1	1350	8	ND
Fraction emitted, %	78%	71%	ND
Average, Blocks 55 and 56			
Fraction emitted, %	83%	81%	76%

ND denotes not determined.

preferentially. These emissions can be compared to the total worldwide CH_3Cl emissions from biomass burning, which include forest fires, agricultural burning, domestic biomass fuel use, etc. For this calculation, we use global pyrogenic CO and CO_2 emission estimates (13,200 Tg CO_2 yr^{-1} (3600 Tg $C(CO_2)$ yr^{-1}) and 680 Tg CO yr^{-1} (290 Tg $C(CO)$ yr^{-1}) [*Andreae*, 1993]) and the mean emission ratios calculated from the data in this study and from literature data cited above. With the CO- and the CO_2-based emission ratios, a global pyrogenic CH_3Cl emission of approximately 1100 or 1500 Gg yr^{-1}, respectively, is obtained, corresponding to about one third to one half of the total CH_3Cl source strength. This value is consistent with the range of emission estimates for CH_3Cl from biomass burning (650-2600 Gg yr^{-1}) proposed by *Andreae* [1993].

Methyl bromide emissions can be estimated based on CO, CO_2, or CH_3Cl as reference species. The same CO and CO_2 fluxes are used as for the CH_3Cl flux calculations, and for the estimate based on CH_3Cl, we use the pyrogenic CH_3Cl fluxes of 420 and 1300 Gg yr^{-1} derived in Table 7. For the estimates of CH_3Br emission from all biomass burning, we took the mean emission factors from *Mano and Andreae* [1994]. Again, the CO_2-based flux from the savanna fires comes out relatively low,

while the other estimates agree well with each other, suggesting an emission of about 7 Gg CH_3Br yr^{-1} from savanna fires and about 20 Gg yr^{-1} from all biomass burning. The latter value corresponds to about 20% of the total CH_3Br emission from all sources. The CH_3I emission estimates are obtained in the same way as those for CH_3Br, only that in the absence of literature data on pyrogenic CH_3I emission ratios from other types of fires we had to apply the SAFARI-92 values to all types of biomass burning. Clearly, the contribution of biomass burning to the tropospheric CH_3I budget (<10 Tg yr^{-1}) is trivial compared to the oceanic source of about 300 Tg yr^{-1} [*Singh et al.*, 1983].

Conclusions

We found that methyl chloride, bromide, and iodide were emitted from the savanna fires investigated during SA-FARI-92 in southern Africa. The concentrations of the methyl halides in smoke samples were highly correlated among each other; they were also strongly correlated with carbon monoxide concentrations. The correlation slopes (which are equivalent to emission ratios) are highly consistent between fires for most of the trace gas species pairs. The correlation between

Table 6. Fuel Elemental Composition, Volatilization Fraction, and Emission Ratios for Halogen Species

Element	Element Content in Fuel, mg kg^{-1}	Fraction Emitted, %	X_{total}/CO_2 Emitted μmol/mol	$\Delta X_{inorg}/\Delta CO_2$ in Smoke μmol/mol	X_{inorg}/X_{total} %	$\Delta CH_3X/\Delta CO_2$ in Smoke μmol/mol	CH_3X/X_{total} %
Carbon	$480,000 \pm 14,000$	88%	...	...		...	...
Chlorine	1260 ± 310	83%	910 ± 350	1100 ± 700	121%	27 ± 14	3.0%
Bromine	7.0 ± 1.6	81%	2.2 ± 0.8	1.7[b]	77%	0.11 ± 0.04	5.0%
Iodine	1.3 ± 0.3	76%	0.24 ± 0.09	0.17[b]	71%	0.09 ± 0.05	38%

[a] Mean $\Delta CH_3X/\Delta CO_2$ emission ratios for the KNP fires.
[b] Based on smoke aerosol composition data from *Maenhaut et al.* [this issue].

Table 7. Methyl Halide Emissions From Savanna Fires and All Types of Biomass Burning Worldwide

Species	SAFARI-92 Emission Ratio, $\times 10^{-6}$	Reference Species Flux, Tg yr^{-1}	All Savanna Fire Emissions, Gg yr^{-1}	Global Mean Emission Ratio[a], $\times 10^{-6}$	Reference Species Flux, Tg yr^{-1}	All Biomass Burning, Gg yr^{-1}
Methyl chloride						
$\Delta CH_3Cl/\Delta CO$	950	240	410	900	680	1100
$\Delta CH_3Cl/\Delta CO_2$	20	6090	140	100	13,200	1510
Methyl bromide						
$\Delta CH_3Br/\Delta CO$	8.3	240	6.8	8.3	680	19
$\Delta CH_3Br/\Delta CH_3Cl$	8300	0.41	6.4	8500	1.3	21
$\Delta CH_3Br/\Delta CO_2$	0.11	6090	1.4	0.85	13,200	24
Methyl iodide						
$\Delta CH_3I/\Delta CO$	2.6	240	2.8	2.6	680	8.0
$\Delta CH_3I/\Delta CH_3Cl$	2600	0.41	2.7	2600	1.3	8.5
$\Delta CH_3I/\Delta CO_2$	0.09	6090	1.6	0.09	13,200	3.4

[a] The mean emission ratios for all biomass burning are based on data from this study and on the papers by *Crutzen et al.* [1979], *Laursen et al.* [1992], *Lobert et al.* [1991], *Manø and Andreae* [1994], *Rasmussen et al.* [1980], *Rudolph et al.* [1994], and *Tassios and Packham* [1985].

the methyl halides and CO_2 in the smoke samples is much poorer and fluctuates over a wide range from one fire to another. This reflects the fact that the methyl halides and CO are emitted predominantly during smoldering combustion. Most of the halogen content of the fuel is released as halide species during combustion. But, especially in the smoldering stage, a significant fraction of the fuel halogen content is emitted in the form of methylated species. As a result, the overall methylhalide emission ratios are dependent both on the halide content of the fuel and on the proportion of flaming versus smoldering combustion in the fires.

The mean CH_3Cl emission ratio to CO_2 (19×10^{-6}) observed during SAFARI-92 is at the low end of the range of published values (($12-320)\times10^{-6}$), while the mean emission ratio to CO is close to the average value reported in the literature ($\sim900\times10^{-6}$). This can be explained by the high fraction of flaming versus smoldering combustion in the savanna fires, in conjunction with the high halogen content of the savanna vegetation. On the basis of these emission ratios, we estimate that the annual emission of CH_3Cl from savanna fires amounts to about 420 Gg yr^{-1}, about one third of the total pyrogenic emission of 1100-1500 Gg CH_3Cl yr^{-1}, and about 12% of the total source flux of 3400 Gg CH_3Cl yr^{-1}. This pyrogenic source estimate is subject to an uncertainty of at least a factor of 2-3; further studies, especially in tropical deforestation fires, are required to reduce this uncertainty.

The emission ratios for CH_3Br from savanna fires are also relatively low compared to forest fires, and savanna fires therefore make only a modest contribution (about 7 Gg yr^{-1}) to the global emissions of CH_3Br ($\sim$ 100 Gg yr^{-1}) and to the total pyrogenic flux of this species ($\sim$ 20-30 Gg yr^{-1}). Overall, however, we find that biomass burning contributes significantly to the budgets of stratospheric chlorine and bromine species. The importance of this contribution can be expected to increase as the emission reductions of industrially produced halocarbons take effect.

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