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Emission estimates of selected volatile organic compounds from tropical savanna burning in northern Australia

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[1] Here we present measurements of a range of carbon-based compounds: carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4), nonmethane hydrocarbons (NMHCs), methyl halides, and dimethyl sulfide (DMS) emitted by Australian savanna fires studied as part of the Biomass Burning and Lightning Experiment (BIBLE) phase B aircraft campaign, which took place during the local late dry season (28 August to 13 September 1999). Significant enhancements of short-lived NMHCs were observed in the boundary layer (BL) over the region of intensive fires and indicate recent emissions for which the mean transport time was estimated to be about 9 hours. Emission ratios relative to CO were determined for 20 NMHCs, 3 methyl halides, DMS, and CH_4 based on the BL enhancements in the source region. Tight correlations with CO were obtained for most of those compounds, indicating the homogeneity of the local savanna source. The emission ratios were in good agreement with some previous measurements of savanna fires for stable compounds but indicated the decay of emission ratios during transport for several reactive compounds. Based on the observed emission ratios, emission factors were derived and compared to previous studies. While emission factors (g species/kg dry mole) of CO_2 varied little according to the vegetation types, those of CO and NMHCs varied significantly. Higher combustion efficiency and a lower emission factor for methane in this study, compared to forest fires, agreed well with results for savanna fires in other tropical regions. The amount of biomass burned was estimated by modeling methods using available satellite data, and showed that 1999 was an above average year for savanna burning. The gross emissions of the trace gases from Australian savanna fires were estimated.   *INDEX TERMS:* 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 0322 Atmospheric Composition and Structure: Constituent sources and sinks

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1. Introduction

[2] Biomass burning is a globally significant source of important atmospheric trace gases such as CO, CO_2, CH_4, NMHCs, nitrogen oxides ($NO_x = NO + NO_2$), halogenated and oxygenated compounds, and aerosol particles, which together affect atmospheric chemistry and climate on regional and global scales [*Crutzen and Andreae*, 1990; *Granier et al.*, 1999; *Yokelson et al.*, 1999a].

[3] The photochemical oxidation of CO and volatile organic compounds (VOCs) in the presence of NO_x is a major source of tropospheric ozone (O_3). Tropospheric O_3 is an important greenhouse gas as well as a major precursor of the hydroxyl radical (OH) which plays a key role in tropospheric chemistry. Biomass burning is also a major source of the methyl halides; methyl chloride (CH_3Cl), methyl bromide (CH_3Br), and a minor source of methyl iodide (CH_3I). The methyl halides have come to the forefront in the last decade due to their potential for delivering ozone-depleting halogens

to the stratosphere [*Andreae et al.*, 1996; *Blake et al.*, 1996a; *World Meteorological Organization* (*WMO*), 1999].

[4] About 90% of global biomass burning occurs in the tropics and extensive field studies on the atmospheric effects of biomass burning have been conducted during the last decade [*Hao and Liu*, 1994; *Andreae et al.*, 1994; *Folkins et al.*, 1995; *Browell et al.*, 1996; *Connors et al.*, 1996; *Talbot et al.*, 1996; *Jonquières et al.*, 1998; *Blake et al.*, 1999; *Gregory et al.*, 1999; *Singh et al.*, 2000]. In northern Australia, biomass burning has occurred regularly in the dry season for many thousands of years. These fires called "bushfires" occur in a tropical eucalyptus savanna dominated by eucalyptus trees, small bushes and grasses [*Lacey et al.*, 1982] and are mainly anthropogenic in origin. Although biomass burning in Australia is a significant source of gases with regional and global influences on the troposphere, few studies have reported emissions from Australian savanna fires, as compared with Africa and tropical America [*Hurst et al.*, 1994a, 1994b]. In this paper, we estimate the annual gross emissions of several important atmospheric compounds (e.g., CO_2, CO, CH_4, NMHCs, methyl halides) from savanna burning in Australia, based on the trace gas measurements in smoke emitted from savanna burning in the late dry season.

2. Experiment

[5] Observations of atmospheric trace gases were made utilizing a Gulf stream-II (G-II) aircraft as part of BIBLE (Biomass Burning and Lightning Experiment) phase B sponsored by NASDA (National Space Development Agency of Japan) during the local late dry season (28 August to 13 September 1999). The campaign consisted of 1 test flight over Japan, 6 ferry flights between Japan and Australia, and 6 local flights over northern Australia to survey trace gas emissions from savanna burning. During the entire campaign, more than 600 whole air samples were collected aboard the G-II in 2-L stainless steel canisters. In situ measurements of O_3, CO, CO_2, NO, NO_y (= NO + NO_2 + NO_3 + N_2O_5 + PAN + HNO_2 + HNO_3 + HNO_4 + other nitrates), aerosols, condensation nuclei, soot particles, and UV flux were also made by other collaborating groups.

[6] The whole air samples were returned to a laboratory at the University of California, Irvine (UCI) and were analyzed by multicolumn gas chromatography. Two flame ionization detectors (FIDs) and two electron capture detectors (ECDs) in combination with four gas chromatographic (GC) columns were optimized for the determination of selected compounds. In addition, the system employed a bench-top quadrupole mass spectrometer (MS) to help positively identify unknown components. The FIDs were used to quantify C_2-C_8 nonmethane hydrocarbons (NMHCs) while the ECDs and MS detected halocarbons and alkyl nitrates. Most quantified gases were detected on more than one of the column/detector combinations, which provide an additional check on proper identification and quantification. Fifty-three compounds have been archived, including 24 halocarbons, 23 nonmethane hydrocarbons (NMHCs), 5 alkyl nitrates and dimethyl sulfide (DMS). The accuracy of the measurements ranges from 5–10%. The limit of detection for the NMHCs was 3 parts per trillion by volume (pptv) and the measurement precisions

range from 1–5%. The accuracy, precision and the limit of detection vary for each compound and are presented in the overview paper of the BIBLE campaign [*Kondo et al.*, 2002]. Further details about sampling procedures are given by *Blake et al.* [1992, 1994], and the experimental apparatus is described by *Blake et al.* [1996a], *Sive* [1998], and *Colman et al.* [2001]. CH_4 was analyzed by a separate GC/FID system with precision of 0.1%.

[7] During BIBLE-B, fast response in situ measurements of CO_2 and CO were made using a non-dispersive infrared analyzer (NDIR) and a resonance fluorescence technique, respectively. Details of the measurement techniques are described elsewhere [*Machida et al.*, 2002; *Takegawa et al.*, 2001]. Because measurement frequency of and sampling duration varied by species [*Kondo et al.*, 2002], the data were averaged over a common time interval before data analyses. The merged data used in this study were generated based on the sampling time of the whole air samples, which had the lowest sampling frequency of all the measurements reported in this paper.

3. Results and Discussion

[8] During the late dry season when BIBLE-B was conducted, active bushfires were a daily occurrence in northern Australia, as shown by hot spot distributions in NOAA/AVHRR satellite imagery [*Russell-Smith et al.*, 2003]. When the aircraft flew within the boundary layer (BL) below approximately 3 km over the source region north of the Northern Territory in Australia, it often passed through smoke plumes in which elevated mixing ratios of CO, CO_2, NO, and NO_y were observed. Typical CO values observed over the source region at altitudes <3 km were 160–200 ppbv while the values observed upwind of the source region were about 80 ppbv [*Takegawa*, 2003]. Figure 1 shows the time series of flight altitude and concentrations of selected trace gases observed during one of the local flights (flight 7 shown in *Kondo et al.*, this issue) over northeastern Australia ($10°$–$30°$S, $120°$–$150°$E). During the flight, CO values occasionally exceeded 1 ppmv and large enhancements of methyl halides were also observed in these plumes (data not shown). The mixing ratios of short-lived alkenes such as propene (C_3H_6) and butenes (1-C_4H_8, c-2-C_4H_8, and t-2-C_4H_8) observed in these plumes reached up to 2.8 ppbv, 390 pptv, 53 pptv, and 67 pptv, respectively, which indicate very rapid convection from active biomass fires [*Blake et al.*, 1996a].

[9] Figure 2 illustrates the correlations of selected trace gases versus CO for the BL subset of two intensive flights which deployed from Darwin. The data set consists of 92 samples collected over Arnhemland, which was strongly influenced by biomass burning emissions. Forty-three samples were collected at 1.7 km altitude during a flight conducted on 2 September, and 49 samples were collected during a flight conducted on 4 September, with 31 samples collected at 1.7 km and 18 samples at 3.0 km. The two flight paths are shown in Figure 3 together with the AVHRR hot spots observed close to the flight deployments at similar times.

[10] As shown in Figure 2, most of the trace gases such as CO_2, CO, CH_4, NMHCs, and methyl halides that are known to be produced in fires were highly correlated with each other ($r^2 > 0.9$). These tight correlations indicate the identical
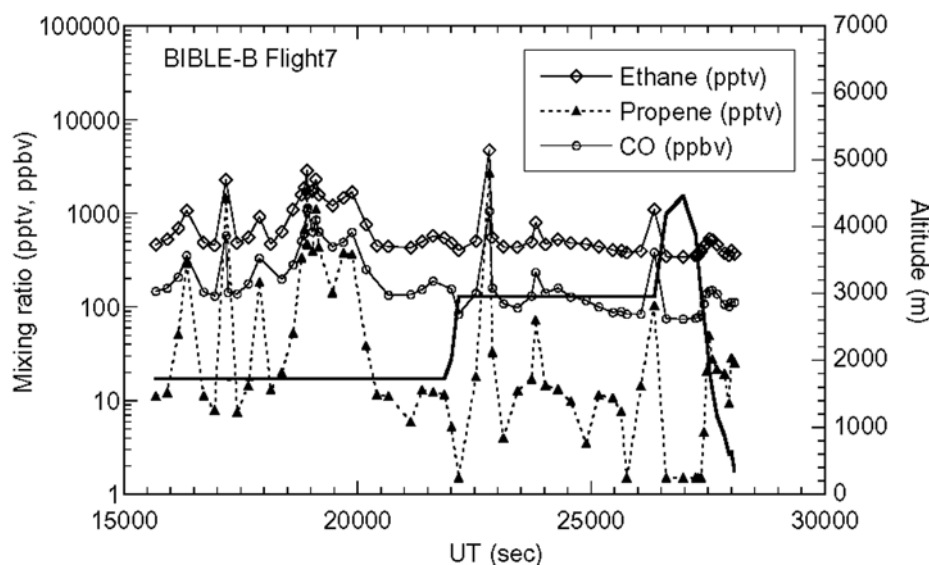
Figure 1. Time series of ethane, propene and carbon monoxide (CO) mixing ratios observed during local flight 7 over northern Australia on 4 September 1999. Thick solid line traces flight altitude.

source for those compounds, which apparently represents local savanna burning emissions. The urban tracer C_2Cl_4 showed no correlation with CO, indicating no contribution from urban sources (Figure 2). Aircraft measurements made in well-mixed downwind smoke made during this study should provide good integrated samples with which to evaluate the emissions of relatively stable compounds as indicated by the tight correlations shown in Figure 2.

[11] The possible contribution from oceanic sources to these samples was dismissed by the good correlations of the compounds that have both oceanic and biomass burning sources such as CH_3Cl, CH_3I, and DMS with CO. Observed DMS/CO was 0.006 pptv/ppbv (r^2 = 0.79). DMS is a precursor of sulfuric acid and particulate sulfate in the marine atmosphere, which affects the global radiation budget, rain acidity, etc [*Charlson et al.*, 1987; *Warneck*, 2000]. Although oceanic emissions greatly outweigh DMS emissions from fires on a global scale, the good DMS to CO correlation that was observed indicates that emission from fires form a considerable part of DMS emission to the atmosphere in the study region (S. Meinardi et al., Dimethyl disulfide and dimethyl sulfide emissions from biomass burning, submitted to *Science*, 2002, hereinafter referred to as Meinardi et al., submitted manuscript, 2002).

[12] Methyl halides are emitted from various sources, both natural and anthropogenic [*Butler*, 2000]. Along with high correlations with CO, significant correlations were observed for CH_3Cl versus CH_3Br (r^2 = 0.91), CH_3Cl versus CH_3I (r^2 = 0.91), and CH_3Br versus CH_3I (r^2 = 0.82). Assuming that each source has its unique emission ratio, the single regression line indicates a single dominant source, which is assumed to be local biomass burning in this case.

[13] To discriminate between various burning stages, we calculated the combustion efficiency of the fire using the modified combustion efficiency (MCE), indicator, defined as $\Delta CO_2/(\Delta CO_2 + \Delta CO)$ by [*Ward and Radke*, 1993]. We derived a mean MCE value of 0.92 for the aircraft samples

collected for this study. The observed aircraft MCE is within the range of typical values for savanna fires reported previously [*Bonsang et al.*, 1991; *Hurst et al.*, 1994a, 1994b; *Andreae et al.*, 1996; *Blake et al.*, 1996a]. The MCE value of 0.93 was observed for the ground samples collected during flaming stage of fires while much lower MCE (=0.81) values were observed for those collected during the smoldering stage of fires (Meinardi et al., submitted manuscript, 2002). The MCE for the aircraft samples was much closer to the MCE for the ground samples representing the flaming stage, suggesting a possible bias associated with aircraft samples that may better represent easily convected hot flaming emissions rather than cooler smoldering emissions [*Ferek et al.*, 1998].

4. Emission Ratios

[14] Biomass burning emissions are commonly characterized by determining the ratio of $\Delta Y/\Delta X$, where y is a compound either emitted by the fire or produced in the fire plume, x is a reference tracer; usually CO or CO_2; and Δ indicates the excess mixing ratio in the plume over the local background.

[15] CO_2 is often employed as the reference tracer for flaming products such as H_2O, NO, and SO_2, because the CO_2 emission rate is much higher in the flaming stage than in the smoldering stage. On the other hand, because CO is primarily emitted during smoldering, it is a good reference for other products of incomplete combustion, such as CH_4, NMHCs, and NH_3 [*Lobert et al.*, 1991; *Yokelson et al.*, 1996]. Because several compounds (including light unsaturated hydrocarbons) are found to be uncorrelated temporally with either CO or CO_2 [*Yokelson et al.*, 1996, 1997] in the process of combustion, we must note that the use of CO as a reference might underestimate calculated emission ratios for certain compounds. However, the very good correlation between CO_2 and CO (Figure 2) indicates that these aircraft samples represent well-mixed emissions of flaming and
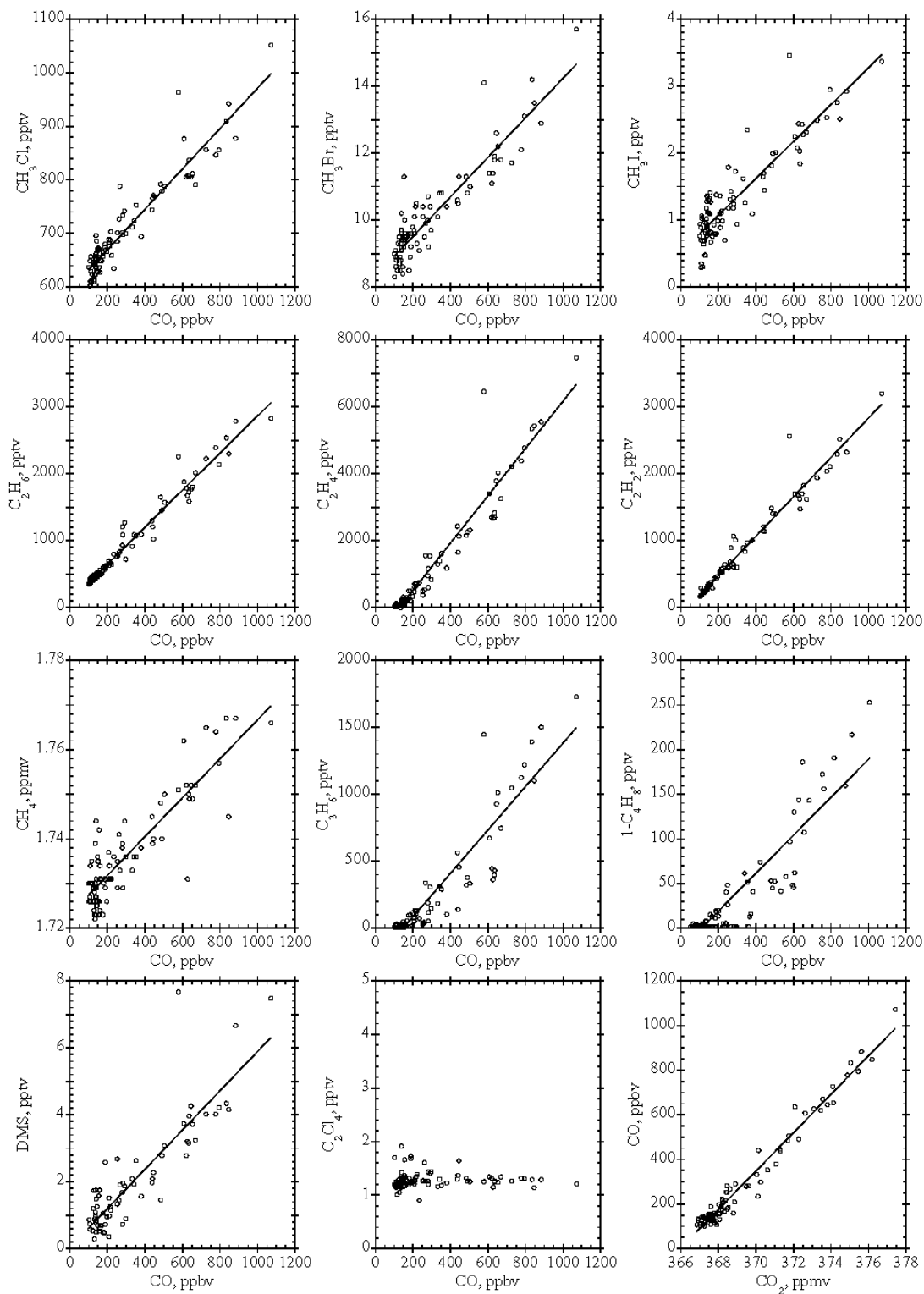
Figure 2. Correlation plots for savanna fire emissions observed during BIBLE-B.

smoldering combustion. A possible bias arising from using either CO or CO_2 as a reference gas is considered to be small.

[16]   The emission ratios relative to CO for selected trace gases determined in this airborne observation are presented in Table 1. The subset of 23 compounds listed were chosen from the larger set of compounds quantified with adequate precision and accuracy in this study, omitting the compounds that showed insignificant emission ratios. These emission ratios are the slopes of the correlation plots shown
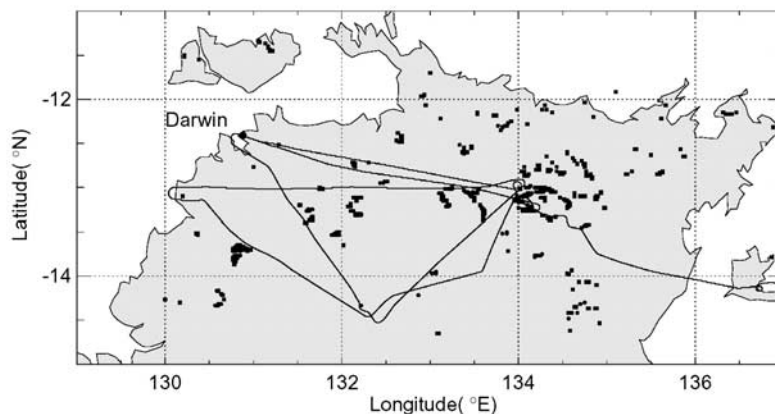
Figure 3. BIBLE-B flight paths on 2 and 4 September 1999. NOAA AVHRR hot spots are indicated by the circles and squares (solid circles: 2 September, 19:20 WST, 1999, and solid squares: 4 September, 18:37 WST, 1999). WST: Australian Western Standard Time; 8 hours ahead of GMT or UTC.

in Figure 2, thus avoiding the need to subtract "background" mixing ratios. Errors indicated in Table 1 are standard errors $= \sqrt{\left(\sum_{i=1}^{n} x_i^2 - n\bar{x}^2 \right)/n(n-1)}$.

[17] Emission ratios previously observed for African and Brazilian biomass burning are also presented in Table 1. These are the results from the Transport and Atmospheric Chemistry Near the Equator-Atlantic (TRACE-A) and the Brazil Fire Assessment (BFA) studies for which the experimental procedures were common with this study [*Blake et al.*, 1996b].

[18] Some general characteristics of emissions from Australian savanna fires are shown by the magnitude of the trace gas emission ratios (Table 1). For aliphatic compounds, emissions from savanna fires decrease with increasing carbon number. Among the series with the same carbon number, alkene emissions are higher than for alkanes or alkynes. Among aromatics, the emissions of benzene and toluene are prominent, and are comparable in magnitude to the emission of several C_3-C_4 aliphatic compounds. The highest emitted NMHC was C_2H_4, which accounts for 40% of the total NMHC emissions measured. The observed ratios agree fairly well with previous observations of African savanna fires for less reactive compounds which were little affected by decomposition during transport [*Bonsang et al.*, 1991; *Blake et al.*, 1996a; *Hao et al.*, 1996].

[19] The methyl halide emission ratios were well within the range of previous measurements (Table 1). Considering that these emissions are mainly controlled by halogen concentrations in fuels along with fire intensity and combustion efficiency [*Reinhardt and Ward*, 1995], the variations of emission ratios observed in different tropical regions were smaller than expected based on the large variations of halogen concentrations among fuels [*McKenzie et al.*, 1996]. As a result, it appears that the emissions of these compounds depend more on combustion efficiency than on halogen content in the fuels.

[20] When comparing emission ratios, the effects of photochemical processes and dilution must be taken into account. Emission ratios change during transport due to the different reactivity between the compound of interest and

the reference compound [*Mauzerall et al.*, 1998; *Goode et al.*, 2000]. This is apparent when the results of TRACE-A and BFA are compared (Table 1). While the emission ratios for relatively stable compounds such as alkanes vary little, those for very reactive alkenes vary considerably as a result of differences in transit times. Higher emission ratios for reactive compounds shown in the BFA results indicate shorter transport time compared to the TRACE-A observations [*Blake et al.*, 1996b].

[21] The factors that affect emission ratios were evaluated by comparing the emission ratios based on our aircraft observations with those based on ground samples collected at fires. Forty five whole air samples were collected on the ground at two different northern Australian savanna sites during the BIBLE-B experiment. These measurements are described in detail by Meinardi et al. (submitted manuscript, 2002). Both the magnitude and the variation of emission ratios for most of the observed trace gases were much higher for the ground samples than for aircraft samples. Compared to the background concentrations, the observed CO_2 enhancement was 100 times higher in ground samples and 1% higher in aircraft samples. For CO, the observed enhancement was 10,000 times higher in ground samples and 15 times higher in aircraft samples, compared to background levels.

[22] The variation of emission ratios observed for individual samples were greater for ground samples compared to aircraft samples. The larger variation among ground samples are because these samples were collected from a single fire over a relatively short sampling period (several minutes), and thus representing emissions from specific fuels at specific burning stages. By contrast, aircraft samples typically contain a mixture of emissions from multiple fires at various burning stages, thus representing emissions from many fires, or an average for the region. The emission ratios of each single fire deviate from the average according to fuel compositions and burning processes. However, for most of the ground samples taken during BIBLE-B, CO/CO_2 ratios were close to the aircraft CO/CO_2 value, except some samples that showed remarkably larger CO/CO_2 ratios. Those samples exhibiting extreme CO/CO_2 mixing

Table 1. Emission Ratios Relative to CO Observed for Tropical Biomass Burning (Based on Airborne Observation)

Name	Formula	Australia (BIBLE-B, 1999)		Brazil[a] (BFA, 1994)		Brazil[b] (TRACE-A, 1992)		Africa[b] (TRACE-A, 1992)	
		Ratio, pptv/ppbv	R^2	Ratio, pptv/ppbv	R^2	Ratio, pptv/ppbv	R^2	Ratio, pptv/ppbv	R^2
Methyl bromide	CH_3Br	5.9 ± 0.3 ($\times 10^{-3}$)	0.83	7.4 ± 0.9 ($\times 10^{-3}$)	0.49	10.6 ± 0.8 ($\times 10^{-3}$)	0.88	6.0 ± 0.5 ($\times 10^{-3}$)	0.78
Methyl chloride	CH_3Cl	0.38 ± 0.01	0.89	0.31 ± 0.03	0.90	0.85 ± 0.06	0.88	0.57 ± 0.03	0.92
Methyl iodide	CH_3I	2.8 ± 0.1 ($\times 10^{-3}$)	0.82	3.6 ± 0.3 ($\times 10^{-3}$)	0.60	1.2 ± 0.2 ($\times 10^{-3}$)	0.57	1.2 ± 0.2 ($\times 10^{-3}$)	0.70
Ethane	C_2H_6	2.8 ± 0.1	0.97	8.5 ± 0.4	0.84	8.3 ± 0.3	0.97	5.2 ± 0.2	0.96
Ethene	C_2H_4	7.1 ± 0.2	0.93	17.1 ± 0.4	0.95	6.1 ± 0.4	0.87	8.3 ± 0.6	0.78
Ethyne	C_2H_2	2.9 ± 0.1	0.96	4.6 ± 0.2	0.90	3.3 ± 0.1	0.97	4.5 ± 0.1	0.98
Propane	C_3H_8	0.58 ± 0.01	0.97	1.6 ± 0.1	0.79	1.6 ± 0.1	0.95	0.97 ± 0.04	0.94
Propene	C_3H_6	1.6 ± 0.1	0.86	4.9 ± 0.1	0.98	0.4 ± 0.1	0.62	1.0 ± 0.1	0.56
Isobutane	$i\text{-}C_4H_{10}$	0.048 ± 0.001	0.96	0.067 ± 0.004	0.78	0.055 ± 0.010	0.55	0.043 ± 0.004	0.77
Propadiene	C_3H_4	0.054 ± 0.002	0.91	0.56 ± 0.04	0.76	0.25 ± 0.02	0.93	0.29 ± 0.02	0.86
Normal-Butane	$n\text{-}C_4H_{10}$	0.11 ± 0.002	0.97	0.21 ± 0.02	0.70	0.21 ± 0.02	0.80	0.16 ± 0.01	0.88
Trans-2 Butene	$t\text{-}2\text{-}C_4H_8$	0.026 ± 0.003	0.52	0.26 ± 0.01	0.88	-	-	-	-
1-Butene	$1\text{-}C_4H_8$	0.23 ± 0.01	0.84	0.75 ± 0.02	0.75	0.06 ± 0.01	0.52	0.12 ± 0.04	0.54
Cis-2-Butene	$c\text{-}2\text{-}C_4H_8$	0.022 ± 0.002	0.60	0.20 ± 0.01	0.87	-	-	-	-
Iso-Pentane	$i\text{-}C_5H_{12}$	6.5 ± 0.5 ($\times 10^{-3}$)	0.69	0.020 ± 0.002	0.57	-	-	-	-
Normal-Pentane	$n\text{-}C_5H_{12}$	0.028 ± 0.001	0.97	0.043 ± 0.002	0.84	0.051 ± 0.005	0.80	0.053 ± 0.005	0.80
Hexane	C_6H_{14}	0.042 ± 0.002	0.89	-	-	-	-	-	-
Benzene	C_6H_6	0.86 ± 0.02	0.97	1.7 ± 0.03	0.97	1.29 ± 0.05	0.97	1.30 ± 0.04	0.96
Heptane	C_7H_{16}	0.017 ± 0.001	0.83	-	-	-	-	-	-
Toluene	C_7H_8	0.28 ± 0.01	0.93	0.72 ± 0.02	0.72	0.57 ± 0.03	0.93	0.49 ± 0.03	0.85
Meta-Xylene	$m\text{-}C_8H_{10}$	0.034 ± 0.002	0.85	-	-	0.042 ± 0.004	0.83	0.026 ± 0.007	0.52
Para-Xylene	$p\text{-}C_8H_{10}$	9.8 ± 0.5 ($\times 10^{-3}$)	0.81	-	-	0.023 ± 0.003	0.75	0.014 ± 0.004	0.59
Ortho-Xylene	$o\text{-}C_8H_{10}$	0.024 ± 0.001	0.90	-	-	0.027 ± 0.002	0.87	0.014 ± 0.004	0.53
Methane	CH_4	0.044 ± 0.003 v/v	0.78	0.107 ± 0.004 v/v	0.86	0.094 ± 0.013 v/v	0.70	0.078 ± 0.004 v/v	0.91
CO/CO2		0.086 ± 0.002 v/v	0.97	(0.035) v/v	0.44	0.037 ± 0.003 v/v	0.87	0.062 ± 0.002 v/v	0.96

[a]From *Blake et al.* [1996b].
[b]From *Blake et al.* [1996a].
v/v = ratio by volume.
These values are lower limits for reactive species; see text.

Table 2. Comparison of Emission Ratios Relative to CO in Aircraft Samples and Ground Samples[a]

Compounds	BIBLE Aircraft E. Ratio, pptv/ppbv	BIBLE Ground E. Ratio, pptv/ppbv	Grd/Air Ratio (ER/ER)
Lifetime Range in Months			
C_2H_6	2.8 ± 0.1	2.6 ± 0.5	0.93
Lifetime Range in Weeks			
C_2H_2	2.9 ± 0.1	3.0 ± 0.2	1.03
C_3H_8	0.58 ± 0.01	0.84 ± 0.12	1.45
C_6H_6	0.86 ± 0.02	0.75 ± 0.03	0.87
Lifetime Range in Days			
n-C_4H_{10}	0.11 ± 0.002	0.15 ± 0.02	1.36
i-C_4H_{10}	0.048 ± 0.001	0.051 ± 0.007	1.06
n-C_5H_{12}	0.028 ± 0.001	0.037 ± 0.006	1.32
C_6H_{14}	0.042 ± 0.002	0.024 ± 0.003	0.57
C_7H_8	0.28 ± 0.01	0.39 ± 0.04	1.39
Lifetime Range in Hours			
C_2H_4	7.1 ± 0.2	8.2 ± 0.3	1.15
C_3H_6	1.6 ± 0.1	2.3 ± 0.2	1.44
1-C_4H_8	0.24 ± 0.01	0.39 ± 0.02	1.63
c-2-C_4H_8	0.022 ± 0.002	0.084 ± 0.012	3.82
t-2-C_4H_8	0.026 ± 0.003	0.11 ± 0.02	4.23

[a]Several samples of extremely high CO/CO_2 ratios were excluded from the average (see text).

ratios were excluded from the comparison because they are biased to represent fires with extremely low combustion efficiency. Table 2 shows the emission ratios of selected NMHCs based on both aircraft samples and ground samples. Typical lifetimes for the conditions encountered during BIBLE-B for each compound are also shown in order to monitor the effect of destruction during transport, assuming the ground sample emission ratios represent initial values. Relative differences between ground and airborne ratios stay within ±60% for compounds with lifetimes longer than several hours, while up to 400% differences were observed for butene isomers with lifetimes of 2–3 hours (Table 2). In the following sections, only longer-lived compounds are taken into account when comparing emission ratios with previous studies.

[23] Using Y/CO (emission ratios of selected NMHCs) for ground samples and aircraft samples and the respective NMHC and CO lifetimes τ, the averaged air mass age from aircraft samples was calculated using ln r·τ, (r =

ER(ground)/ER(aircraft), τ = k(NMHC + OH)[OH]), assuming the lifetime of CO is greater than the transport time. Lifetimes were calculated based on OH oxidation as the dominant sink process with an estimated mean [OH] value of 2.7×10^6 molecules cm^{-3} for the altitude range 0–4 km [*Gregory et al.*, 1996]. It should be noted that a lower OH concentration is expected in the biomass burning plume, which is influenced by high levels of CO and hydrocarbons as well as low $J(O^1D)$ unless NO levels are high. However, in the plume we encountered during the BIBLE-B flights 6 and 7, when average NO levels were as high as 160 pptv (maximum 53 ppbv), it might well be that the reaction: HO_2 + NO –> OH + NO_2 worked as a buffer and OH concentrations did not drop significantly [*Ridley and Atlas*, 1999]. In this estimation, emission ratios for C_2H_6, C_2H_4, C_2H_2, C_3H_8, C_3H_6, n-C_4H_{10}, 1-C_4H_8, C_6H_6, and C_7H_8 were used. The 2-butene isomers were excluded to avoid overestimation of air mass age by ignoring O_3 oxidation as a sink. The reaction contributes comparably to OH reaction for those internal olefins that react rapidly with O_3.

[24] The mean transport time of sampled air was estimated to be 0.4 days (8 hours) as an average of ln(Y/CO)·τ calculated for the series of compounds listed in the Table 2. This estimate is consistent with the significant enhancements of short-lived alkenes whose lifetimes are less than 0.2 days at the low altitudes at which the plume was sampled. However, for a more precise estimation, the effects of dilution and entrainment on NMHC concentrations by mixing with circumambient air during transport must be considered for aircraft samples, which remains to be an issue in the future.

[25] In Table 3, previous emission ratios from Australian savanna biomass burning (derived from the ratios between excess mixing ratios $\Delta Y/\Delta X$), are shown with our airborne values converted into the same units. The previous experiments were conducted also during the late dry season over the same region, using a light aircraft flying at 50–700 m above the fires [*Hurst et al.*, 1994a, 1994b]. While *Hurst et al.* [1994a, 1994b] reported multiple measurements made using different instruments, the values presented in the Table are the results of flask sampling and GC analysis only, which was a similar technique to ours. For CO, and CH_4, the BIBLE-B emission ratios were in generally good agreement with the previous values for Australian savannas. This good

Table 3. Enhancement Ratios Relative to CO for Australian Savanna Fires (Based on Airborne Observation)[a]

	This Study		*Hurst* [1994a]		*Hurst* [1994b]	
	Ratio (pptv/ppbv)	R^2	Ratio (pptv/ppbv)	R^2	Ratio (pptv/ppbv)	R^2
CO/CO_2	0.089 ± 0.002 v/v	0.97	0.090 ± 0.026 v/v	0.86	0.058 ± 0.020 v/v	0.93
CH_4	0.043 ± 0.003 v/v	0.76	0.045 ± 0.009 v/v	0.95	0.068 ± 0.040 v/v	0.91
C_2H_2	3.0 ± 0.1	0.97	0.72 ± 0.37	0.74	2.5 ± 1.1	0.98
C_2H_4	7.5 ± 0.3	0.89	-	-	11 ± 5	0.97
C_2H_6	2.7 ± 0.1	0.97	-	-	4.8 ± 1.8	0.96
C_3H_6	1.6 ± 0.7	0.85	-	-	2.3 ± 1.0	0.98
C_3H_8	0.57 ± 0.01	0.97	-	-	0.77 ± 0.19	0.98
n-C_4H_{10}	0.11 ± 0.002	0.97	-	-	0.21 ± 0.04	0.99
i-C_5H_{12}	6.7 ± 0.3 ($\times 10^{-3}$)	0.80	-	-	0.25 ± 0.10	0.98
C_6H_6	0.85 ± 0.01	0.97	0.19 ± 0.15	0.68	0.42 ± 0.24	0.98

[a]These values are lower limits for reactive species. See text.

Table 4. Emission Factors Observed for Various Vegetation Types (g Species/kg dm)

	Australian Savanna			Brazilian Cerrado[b]	Global Savanna[c]	Australian Forest[d]	North American Deciduous Forest[e]	Alaskan Boreal Forest[f]
	This Study	*Hurst et al.* [1994a][a]	*Hurst et al.,* [1994b][a]					
CO_2	1613 ± 86	1595 ± 121	1646 ± 106	1722 ± 23	1640	1558	1671	1660
CO	88 ± 7	91	61	58	65	106	84.0	88.8
CH_4	2.22 ± 0.32	2.34	2.36	1.31	2.4	3.60	5.18	2.79
C_2H_6	0.53 ± 0.07	-	-				-	0.66
C_2H_2	0.24 ± 0.03	0.06	0.14				-	0.24
C_6H_6	0.21 ± 0.02	0.05	0.07				-	-

[a]Data originally presented in the different form [gC/gC DM (dry matter)] were converted into the common form [g species/kg DM].
[b]From *Ward et al.* [1992].
[c]From *Andreae et al.* [1996].
[d]From *Hurst et al.* [1996].
[e]From *Yokelson et al.* [1999a, 1999b].
[f]From *Goode et al.* [2000].

reproducibility indicates that both data sets represent Australian savanna fires in the late dry season.

5. Emission Factors

[26] Emission factors for trace gases were derived from trace gas measurements in fresh smoke from fires. Commonly, an emission factor (EF) is defined as the mass of species released per unit mass of fuel consumed (g species/ kg dry matter (DM)) [*Ward et al.*, 1992]. However, we start from a carbon mass balance method used by *Hurst et al.* [1994a, 1994b], which derives the fraction of the mass of carbon released to the atmosphere in the form of CO_2 relative to the dry mass of fuel carbon burned (g carbon/g carbon in dry matter (gC/gC DM)). The emission factor of CO_2 is calculated through the carbon balance equation shown below:

$$EF_{CO_2} = \frac{\Delta CO_2}{C_{fuel}} = \frac{\frac{\sum C_{emit}}{C_{fuel}}}{\frac{\Delta CO_2}{\Delta CO_2} + \frac{\Delta CO}{\Delta CO_2} + \frac{\Delta CH_4}{\Delta CO_2} + \frac{\Delta NMHC}{\Delta CO_2} + \frac{\Delta PC}{\Delta CO_2}}$$

where PC = particulate carbon, ΣC_{emit} = the mass of carbon released to the atmosphere, and C_{fuel} = the dry mass of fuel carbon burned.

[27] The fuel carbon content (46%), and the fraction of carbon emitted from the savanna fires to the atmosphere (96%) were taken from the weight and composition measurements of fuel and ash determined by *Hurst et al.* [1994a]. Fuels for the *Hurst et al.* [1994a] study were collected in the same northern Australian savanna in the late dry season as this study. A value of 0.088 ± 0.001 gC/gC DM was obtained for CO_2 and is in good agreement with the value of 0.087 ± 0.002 previously reported for Australian savanna fires by *Hurst et al.* [1994a, 1994b]. Emission factors of other compounds were determined using the same equation using the CO_2 fraction and emission ratios for the compounds of interest.

[28] Table 4 shows emission factors from this study converted to the common units of g species/kg DM [*Ward et al.*, 1992]. Comparing emission factors for different vegetation types, the variability for CO_2 was generally within the error range of different studies (Table 4). While the progress of the burning process for each ecosystem is largely characterized by its vegetation type, this result indicates that the emissions of CO_2 from a certain amounts

of biomass burned varies little according to the type of vegetation, after integration over the whole burning process for each ecosystem.

[29] By contrast, emission factors of CO and NMHCs vary significantly by ecosystem. This is closely related to the relationship between combustion efficiency and emission factors shown in Figure 4 (reproduced from *Ward et al.* [1992, Figure 8]. Strong linear correlations between combustion efficiency and emission factors of methane were shown based on combined data sets of previous field measurements which represent grassland (cerrado and savanna) and deforestation. Data from this study and *Hurst et al.* [1994a, 1994b] are plotted in Figure 4 as a solid triangle and a hollow triangle respectively, with the original two regression lines and the data points of *Ward et al.* [1992]. Our Australian data are reasonably distributed in the neighborhood of the model line for grassland ecosystems.

[30] These data show that more methane is emitted from forest fires than savanna fires of the same combustion efficiency. Higher methane emissions from forests are due to prolonged glowing combustion of logs, when alkanes and NH_3 are dominantly produced [*Yokelson et al.*, 1997]. The linear relationship between CO and other trace gases were presented in several other studies for both laboratory fires and the field fires [*Hao et al.*, 1996; *Yokelson et al.*, 1999a, 1999b]. Those results indicate that the variations of emission factors observed for different ecosystems can be explained by the different contribution ratios of each combustion process during which different gases are mainly produced. The proportion of each combustion process is mainly controlled by fuels and burning conditions of the ecosystems and emission factors of compounds mainly emitted during smoldering stage are expected to be greater for ecosystems with lower combustion efficiency. Because CO, CH_4, and most of the NMHCs are mainly emitted during the smoldering phase, the emission factors of those compounds were greater for forest fires than savanna fires (Table 4).

6. Estimation of Total Biomass Burned

[31] To estimate the gross emissions from biomass burning on a regional or global scale, we need to estimate the total biomass burned within the area of interest during the fire season. The estimation of total biomass burned is often accompanied by significant uncertainty, which can domi-
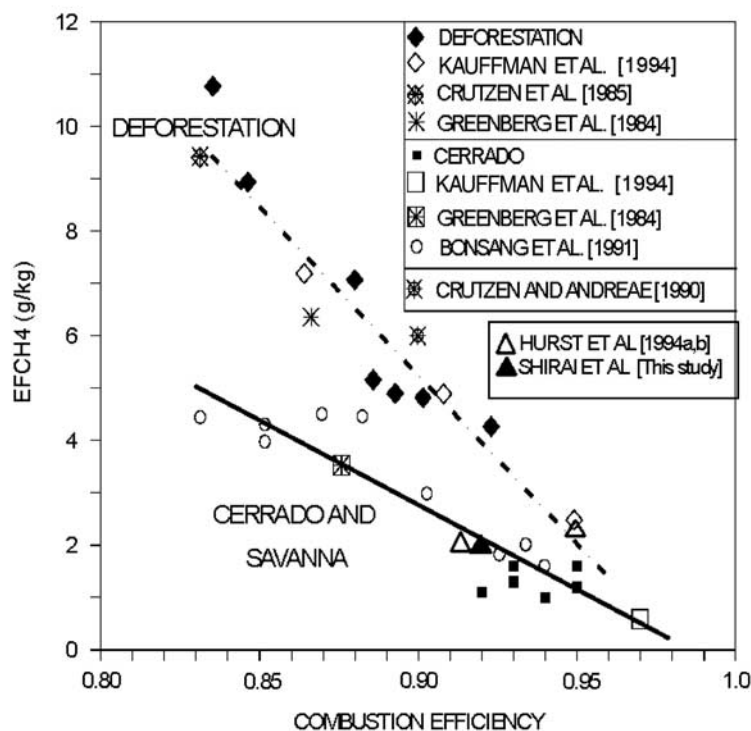
Figure 4. Methane production versus combustion efficiency shown for fires in grass-dominated and forested ecosystems (reproduced from *Ward et al.* [1992]).

nate the uncertainty of the gross emission estimates [*Seiler and Crutzen*, 1980; *Crutzen and Andreae*, 1990; *Hao and Liu*, 1994; *Scholes et al.*, 1996a, 1996b]. There have been two main methods (the "classification method" and the "modeling method") for calculating annual emissions from tropical savanna burning. The classification method classifies the region of interest by vegetation types and extrapolate mean fuel load and area burned to each class. The modeling method sums the emissions from each fire, taking into account the actual fuel load at the time of the burning using a model [*Scholes et al.*, 1996a]. When fuel loads are relatively constant throughout the year, emissions can be estimated from the total areas of savanna and grassland burned annually. However in tropical savannas, there are large changes in the amount of grass fuels as the grasses develop over the growing season. Hence, it is very important to accurately follow the large fluctuations of fuel loads and area burned with a sufficient time resolution.

[32] In this study, fuel loads were estimated by a version of the modeling method improved by the Northern Territory Bushfire Council (NTBC), an agency which has the responsibility for fire prevention and management in rural areas of the Northern Territory, Australia [*Russell-Smith et al.*, 2003]. The NTBC calculation was based on estimates of the extent of burning derived from interpretation of satellite imagery and the quantity of fine fuels (<6 mm diameter) burned using empirical regional fuel accumulation relationships associated with detailed vegetation mapping. NOAA-AVHRR satellite images (pixels around 1.1 km^2), were verified and calibrated by ground-verification studies and mapping of fire scars from fine-resolution LANDSAT TM

images (pixels 25 × 25 m). Derived values were 18.75 Mt DM yr^{-1} for the region north of 15°S in the Northern Territory during the BIBLE-B period (2 weeks), and 212.3 Mt dm yr^{-1} for the entire Australian savanna region in the year 1999. The confidence level of their fire extent mapping at larger regional scales was estimated to be 70–80%. The real amount of biomass burnt in 1999 cannot be less than the given estimates because heavier fuels (>6 mm diameter) were not accounted for in these estimates.

[33] A coarse estimation of the contribution of heavier fuels can be derived, however, from data presented by *Walker* [1981, Table 6]. Heavier fuel fractions (bark, shrubs, twigs) for Australian tropical savannas (Walker's region 3) are given as comprising typically 15% of total fuels (grass 65%, leaf litter 20%, bark 5%, shrubs 5%, and twigs 5%). Walker's tropical savanna region is, however, very extensive and most burning (including in 1999) occurred in higher rainfall regions of northern and northwestern Australia. Given evident relationships between both woody matter production and rainfall, and extent of late dry season (i.e., more intense) fires and consumption of woody fuels, it stands to reason that the proportion of heavier fuels consumed by fires in 1999 would be greater than the average 15% for the region as a whole. Conservatively, it is thus reasonable to assume that the heavier fuel component of savanna biomass burned in 1999 was at least 20% of all biomass burned in the tropical savanna region in 1999. Applying this qualification, we estimate that around 22 MT DM of biomass burned in the sample region during the 2 week period covering the BIBLE-B experiment, and around 255 MT DM was burned over the entire Australia savanna

Table 5. Source Strength Estimates for Australian Savanna Fires[a]

	Emission Factor, g/kg dm	Emission Estimates, Gg/year
CH_3Br	0.0018 ± 0.0003	0.45 ± 0.29
CH_3Cl	0.0605 ± 0.0072	15 ± 10
CH_3I	0.0013 ± 0.0002	0.32 ± 0.2
C_2H_6	0.13 ± 0.02	34 ± 21
C_2H_4	0.31 ± 0.04	80 ± 50
C_2H_2	0.12 ± 0.02	30 ± 19
C_3H_8	0.027 ± 0.003	6.9 ± 4.2
C_3H_6	0.071 ± 0.011	18 ± 12
$i\text{-}C_4H_{10}$	0.0022 ± 0.0003	0.6 ± 0.4
C_3H_4	0.0014 ± 0.0002	0.3 ± 0.2
$n\text{-}C_4H_{10}$	0.0051 ± 0.0006	1.3 ± 0.8
$t\text{-}2\text{-}C_4H_8$	0.0012 ± 0.0002	0.3 ± 0.2
$1\text{-}C_4H_8$	0.010 ± 0.001	2.6 ± 1.7
$c\text{-}2\text{-}C_4H_8$	0.00010 ± 0.0002	0.25 ± 0.17
$i\text{-}C_5H_{12}$	0.0003 ± 0.0001	0.08 ± 0.05
$n\text{-}C_5H_{12}$	0.0013 ± 0.0002	0.32 ± 0.20
C_6H_{14}	0.0019 ± 0.0003	0.48 ± 0.31
C_6H_6	0.035 ± 0.004	9.0 ± 5.6
C_7H_{16}	0.00077 ± 0.00012	0.20 ± 0.13
Toluene	0.012 ± 0.001	3.0 ± 1.9
m-Xylene	0.0014 ± 0.0002	0.36 ± 0.23
p-Xylene	0.0004 ± 0.0001	0.10 ± 0.07
o-Xylene	0.0010 ± 0.0001	0.25 ± 0.16
CH_4	2.2 ± 0.4	570 ± 380
CO	88 ± 8	23000 ± 13000
CO_2	1613 ± 111	410000 ± 230000
DMS	0.0011	0.3

[a]These values are lower limits for reactive species. See text.

region in 1999. These values are employed in the following emission estimates.

7. Emission Estimates

[34] Table 5 shows our estimates of trace gas gross emissions based on the derived emission factors and total biomass burned. This is the first emission inventory for Australian savanna fires for most gases except CO_2, CO, CH_4 and a few NMHCs that were measured by *Hurst et al.* [1994a, 1994b]. For compounds with lifetimes longer than several hours, the relative uncertainty of the emission estimates in this study is estimated to be about +50%, close to the uncertainty estimates of *Scholes et al.* [1996a]. The estimated uncertainty is dominated by the substantial uncertainty in estimating biomass burnt (+50%) [*Russell-Smith et al.*, 2003], rather than other components such as uncertainty in the emission factors (±5%). For highly reactive compounds, the uncertainty in the emission factor increases substantially and could be even larger than the error in the

Table 6. Estimates of Total Biomass Burned and Emissions of CO_2 and CH_4 for Australian Savanna Fires

	CO_2, Tg C/year	CH_4, Tg C/year	Biomass Burned, Tg/year	CH_4/CO_2
Current work	112 ± 64	0.42 ± 0.28	255 ± 128	0.0034
NGGIC [1998]	63	0.25	154	0.0042
Hurst et al. [1996]	69	0.28	173	0.0042
Hao et al. [1990]	174	-	425	-
Hao and Ward [1993]	-	0.30	290	0.0024
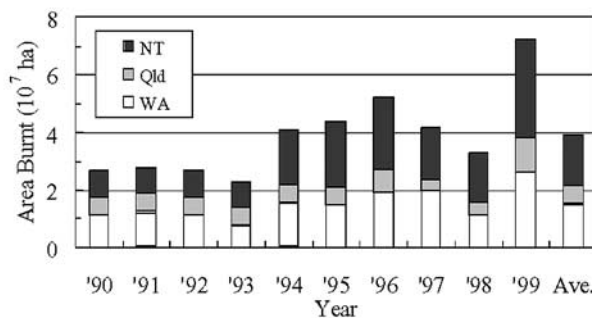
Figure 5. Area of land burned by prescribed burns of savanna and temperate grassland in Australia during 1990-1999 [*NGGIC*, 2000]. (NT: Northern Territory, Qld: Queensland, WA Western Australia).

estimation of biomass burned (i.e., ±75% for 1-butene). These errors were calculated using error propagation, considering each error associated with every parameter in the calculation (i.e., CO_2 gross emission: 410000 ± 230000 Gg $\doteq 1613 \pm 86$ g/kg DM $\times 255 \pm 128$ Tg DM).

[35] The latest report on Australia's greenhouse gas emissions was released by the Australian *National Greenhouse Gas Inventory* (*NGGI*) [2000]. Ten-year averages of the emission estimates of CH_4, N_2O, NO_x, CO, and nonmethane volatile organic compounds (NMVOC) from the prescribed burning of savanna and temperate grassland are given. The biomass burned was estimated by incorporating regional data for the biomass annually exposed to fire, the fraction of exposed biomass that burns, and the C content of the biomass. The average annual fuel loads and burning efficiencies (=0.72) were based on the review of *Tolhurst and Chatto* [1994], and the composition of the biomass and the emission factors were taken from *Hurst et al.* [1994a, 1994b].

[36] A tentative comparison of emission estimates from Australian savanna fires is shown in Table 6 [*Hao et al.*, 1990, 1996; *Hao and Ward*, 1993; *NGGI*, 2000; *Hurst et al.*, 1996; current study]. Our estimates of annual emission of CO_2 and CH_4 from savanna fires for 1999 are approximately 50% higher than the ten-year average presented by NGGIC. This difference is mainly due to higher fire activity in 1999 compared with the past ten years (Figure 5). This clearly suggests that our emission estimates are only for the specific year 1999 and cannot be applied for every year.

[37] Considering seasonal change of emission factors from biomass burning reported by *Hoffa et al.* [1999], emission factors are heavily affected by fuel moisture content and greater emission factors are expected in earlier dry season than later dry season for NMHCs. Thus the emission factors for NMHCs estimated in this study, based on the late dry season data might underestimate the emissions when applied to annual emission estimates. Accordingly, the effect of seasonal and annual variation of burning activity must be taken into account when using reported estimates of burning emissions.

8. Issues Involved in Emission Estimates

[38] To assess the contribution of biomass burning emissions to the global environment, a standardized data

set is of great importance. However, most of the emission estimates presented in previous studies were derived by various methods by various investigators [*Seiler and Crutzen*, 1980; *Hao et al.*, 1990; *Hao and Ward*, 1993; *Delmas et al.*, 1991]. In previous studies, *Scholes et al.* [1996a] pointed out that the amounts of biomass burned calculated by the "modeling method" were often substantially smaller than the amounts calculated by the "classification method". Estimates of biomass burned using the classification method [*Hao and Liu*, 1994] were a factor of five higher than estimates obtained by the modeling method [*Scholes et al.*, 1996a]. This great discrepancy indicates the importance of knowing the method on which biomass burning estimates are based when comparing data.

[39] For instance, significant differences between estimates of the amount of biomass burned are apparent among the different studies in Table 6. The amount of total biomass burned presented by *Hao et al.* [1990] was first calculated by the classification method based on the data from *Lacey et al.* [1982] and then updated by *Hao and Ward* [1993] based on data from *Galbally et al.* [1992]. These estimates by Hao et al. were presented as mean annual estimates for the region and not corresponding to any particular year, while the rest of the studies were presented as estimates based on a single year. Meanwhile, the updated estimate of 290 Mt DM/yr [*Hao and Ward*, 1993] is lower than their previous value by approximately 30%, and is much closer to our estimate of 255 Mt DM/yr for 1999. Values of 154 Mt DM/yr for 1998 [*NGGIC*, 2000] and 173 Mt DM/yr for 1990 [*Hurst et al.*, 1996] were also derived by the classification method, but the tendency toward overestimation by the classification method noted previously for southern African fires by *Scholes et al.* [1996a] is not apparent, indicating the recent improvement of the classification method to prevent overestimating bias.

[40] In Table 6, the emission estimates for CO_2 directly reflect the variation of the estimated values of total biomass burned, but those for CH_4 show the effect of different emission ratios. The CH_4 emission factor used by *Hao et al.* [1996] was derived from the linear regression relationships as shown in Figure 4, based on data from various tropical regions while emission factors used in other studies shown in Table 6 were based on the field observation specifically investigated Australian savanna fires. The smaller value of CH_4 emission factors shown by *Hao et al.* [1996] is the result of a canceling effect of the estimates of the amount of biomass burned and emission factors as shown in Table 6. This illustrates the importance of recognizing combined effects of various factors when comparing emission estimates.

9. Future Studies

[41] As shown in the previous section where the variations among the estimates of the amount of biomass burned (Table 6) were much smaller compared to the discrepancy reported by *Sholes et al.* [1996a], convergence of the estimates by various methods is suggested for recent studies. Possible factors which contribute to reducing this discrepancy include the upgrade of inventories, observational results, and remote sensing data. Such improvements

might be made possible given substantial progress in field observational studies and remote sensing.

[42] Detailed studies on combustion mechanisms have provided us much useful information about trace gas emission from fires. Available data indicate that there are multiple factors that affect emissions such as burning efficiency (oxygen supply), burning temperature, fuel compositions, and vegetation characteristics, and it is necessary to clarify the relative importance of each factor and establish the relationship between emission strength and each factor. For this investigation, well-designed laboratory work and field studies are required.

[43] More remote sensing data are becoming available with the development of algorithms to quantitatively derive burning areas and burned biomass, using infrared or visible bands in most cases [*Cahoon et al.*, 1994; *Menzel and Prins*, 1996; *Elvidge et al.*, 1996; *Setzer and Malingreau*, 1996; *Kendall et al.*, 1997; *Kauffman et al.*, 1998]. Remote sensing is an efficient tool not only to obtain a precise estimate for certain areas and periods but to derive mean value of required parameters and to consider the magnitude of temporal variations once data are accumulated for enough long periods. As more efforts are made to improve algorithms and plans to launch sensors for fire detection unfold in the near future, utilization of remote sensing data will be one of the key factors to improve emission estimates.

[44] Tropospheric chemistry transport models (CTMs) are very efficient for considering the effect of trace gas emissions on the chemical composition and the oxidizing power of the global troposphere [*Poisson et al.*, 2000]. However, inventories provided for those models are not sufficient due to large uncertainties in emissions because some data are either not reported in national statistics and not reflecting fluctuations and trends during recent years [*Olivier et al.*, 1996]. For instance, *Granier et al.* [1999] found 25–50% differences in the amount of biomass burnt and CO_2 emitted when comparing results from their 3-D CTM and estimates by *Andreae* [1991]. These large discrepancies were considered to be mainly due to the scarcity of information on the amount of biomass burned in a given year and the large year-to-year variations in the amount of biomass burned. Data sets with higher spatial and temporal resolution are greatly needed as input for models.

[45] Finally, to build a reliable data set, available data must be standardized and integrated. The approaches for this integration are getting started recently [*Andreae and Merlet*, 2001]. The reasonable assessment of the effect of biomass burning emission to the global environment will be possible when all the above listed progress were achieved in the near future.

10. Conclusions

[46] Selected atmospheric trace gases emitted by Australian savanna fires were measured in the local late dry season. Emission ratios and emission factors were determined for various trace gases based on BL enhancements in the source region. The emission ratios obtained for Australian savanna fires agreed well with previous measurements for Brazil and Africa for stable compounds such as CH_4 and alkanes, while lower ratios were observed for

highly reactive compounds such as alkenes affected by oxidation during transport. The emission factors depended heavily on burning conditions such as combustion efficiency. Emission factors of CO, CH_4 and NMHCs varied significantly among different vegetation types, while those of CO_2 varied little.

[47] The annual trace gas emissions of Australian savanna fires were deduced from the emission factors and estimates of burned fuel using a modeling method appropriate for 1999. Emission parameters such as emission ratios and emission factors were based on an excellent data set obtained by aircraft observations and appropriately interpreted remote sensing data. As a result, uncertainty in estimates of Australian savanna fire emissions was considerably reduced compared to previous studies. While significant uncertainty still remains in estimates of the total biomass burned, mainly due to the difficulty of taking spatial and temporal variation into account, diminishing discrepancies among different studies indicate a general improvement in methods and databases. As shown in this study, the use of remote sensing data has a great potential to provide databases with sufficient spatial/temporal resolution. Approaches for integrating component data sets are now being developed which, in future years, will facilitate more reliable estimates of emissions from biomass burning.

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