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# Emissions of organic trace gases from savanna fires in southern Africa during the 1992 Southern African Fire Atmosphere Research Initiative and their impact on the formation of tropospheric ozone

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**Abstract.** CO, $CH_4$, and organic trace gases were measured in air samples collected during several flights with a DC-3 aircraft through the plumes from savanna fires and agricultural fires during the SAFARI 92 campaign in southern Africa in September and October 1992. In all samples a variety of higher molecular weight organic compounds was found, most of which are very reactive. More than 70 of the roughly 140 major components present could be identified. Typically, mixing ratios of several hundred parts per billion carbon of organic compounds were measured inside the plumes, corresponding to an emission ratio of total organic carbon relative to $CO_2$ of up to 1%. About 50% of these emissions were in the form of oxygenated and unsaturated compounds. The contributions of still unknown compounds to the total emission of organic compounds add up to another 20–30%. The observed emission ratios relative to $CO_2$ show a considerable variation depending on the fuel type and the burning stages of the fire. The lowest value of the emission ratio of the sum of all identified organic compounds relative to $CO_2$ was found for a sugar cane fire with $(1.7 \pm 0.7) \times 10^{-3}$ (ppb C/ppb $CO_2$). For a large savanna fire in Kruger National Park the ratio was $(7.4 \pm 1.6) \times 10^{-3}$ (ppb C/ppb $CO_2$). The highest value was $(13.7 \pm 0.9) \times 10^{-3}$ (ppb C/ppb $CO_2$) for an uncontrolled fire of mainly wood and shrub in the Drakensberg region. Results of model calculations show that in biomass-burning plumes, reactive organic compounds contribute significantly to the formation of ozone, especially during the initial phase of photochemical processing.

## Introduction

Emissions from biomass burning are known to be a considerable source of atmospheric hydrocarbons, especially in tropical and subtropical regions [*Greenberg et al.*, 1984; *Greenberg and Zimmerman*, 1984; *Crutzen et al.*, 1985; *Zimmerman et al.*, 1988; *Rasmussen and Khalil*, 1988; *Bonsang et al.*, 1991; *Rudolph et al.*, 1992, 1995]. Owing to transport, these emissions have also a significant impact on the budget of organic trace gases in the tropical marine atmosphere [*Koppmann et al.*, 1992; *Swap et al.*, 1996]. Moreover, owing to their impact on photochemical ozone formation, organic trace gases influence the budget of tropospheric ozone [*Chatfield and Delany*, 1990; *Fishman et al.*, 1990; *Helas et al.*, 1995; *Thompson et al.*, 1996]. The biomass burned annually on a global scale is estimated to be about $8.6 \times 10^{15}$ g of dry material, 45% of which is savanna grassland [*Levine*, 1991]. Savanna fires are thus the largest single source of biomass-burning emissions.

In recent years a growing number of studies were published that deal with field measurements of emissions from biomass burning in Africa, which contains about two thirds of the world's savanna regions [*Delmas*, 1982; *Bonsang et al.*, 1991; *Rudolph et al.*, 1995; *Lacaux et al.*, 1995]. These data were obtained from both ground-based and airborne measurements in the vicinity of and over large fires. The results showed that during the biomass-burning season the concentrations of CO and organic trace gases in the planetary boundary layer were considerably enhanced over those in the wet season [*Rudolph et al.*, 1992]. Meanwhile, laboratory experiments have supplied more information about the parameters that determine the emission factors, such as different burning stages, meteorological conditions, and fuel types [*Lobert et al.*, 1991; *Manø*, 1997; *Czapiewski*, 1995]. It has been shown that the burning of organic material in oxygen-deficient fires leads to the emission of methane, nonmethane hydrocarbons (NMHC), and a variety of partially oxidized organic compounds. In some cases the emissions of medium- and higher-molecular-weight organic compounds exceed those of light NMHC. Thus these emissions contribute significantly to the local budgets of organic trace gases in the regions of biomass burning and may have a considerable impact on the formation of ozone in these areas. Very recent studies showed the significant abundance of higher-molecular-weight volatile organic compounds (VOC) in biomass-burning plumes. However, only the sum over all organic compounds on a parts per billion (ppb) carbon basis were given without specifying the contributions of individual compounds [*Hurst et al.*, 1994]. The aim of the present paper is to study the variety of VOC that are emitted by biomass burning. The data



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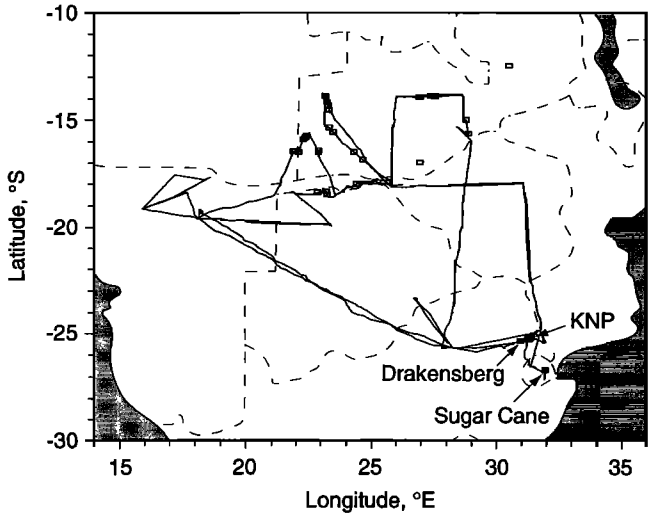


**Figure 1.** Flight tracks of the SAFARI project. The sampling locations for this study are indicated.

were obtained during the airborne measurements of the Southern African Fire-Atmosphere Research Initiative (SAFARI) campaign in southern Africa, which was conducted under the International Geosphere-Biosphere Program (IGBP) core project International Global Atmospheric Chemistry (IGAC). The objectives and a summary of the main results are given by *Andreae et al.* [1994] and *Fishman et al.* [1996]. Flask samples were collected from different types of fire in order to investigate the composition of biomass-burning emissions. Parts of these measurements are used to estimate the impact of VOC on the photochemical ozone formation. Special emphasis is placed on VOC with five or more carbon atoms since ozone formation in biomass-burning plumes during the initial phase of the photochemical processing cannot be explained with the oxidation of $CH_4$, CO, and light NMHC alone. Although the existing data on the organic composition of biomass-burning plumes are limited, it can be expected that many of the higher-molecular-weight VOC are very reactive and thus contribute significantly to the photochemistry in the plumes.

## Experiment

During SAFARI 92, prescribed savanna fires in the Kruger National Park (South Africa) and sugar cane fires as well as uncontrolled fires were investigated. Before the prescribed fires were ignited, the fuel load, fuel type, and spatial distribution were measured within the burning areas [*Stocks et al.*, 1996]. During the fires a large set of trace compounds and aerosols were measured from ground-based and airborne platforms [*Andreae et al.*, 1996; *Le Canut et al.*, 1996]. The fire stages and burning conditions were controlled and monitored during the campaign. After the fires, the type and amount of the remaining biomass as well as the ash were analyzed.

The measurements discussed here are based on samples collected on three flight legs. During flight SAF04 on September 19, 1992, the plumes of two prescribed sugar cane fires on the Ubombo Ranches plantation near Big Bend, Swaziland, were probed. It is standard regional agricultural practice to set such fires before harvesting to facilitate the cutting and processing of the sugar cane. The two fields had an area of 12 and 43.7 ha, respectively. A controlled burn on block 55 (2333 ha) in the Pretoriuskop section of the Kruger National Park was investigated during flight SAF06 on September 24, 1992. Details on fuel and fire behavior are given by *Stocks et al.* [1996], and details on particle emissions are given by *Le Canut et al.* [1996]. During flight SAF05 on September 20, 1992, an uncontrolled "fire of opportunity" in the Drakensberg region was encountered. The burned biomass was a mixture of forest, shrub, and grass.

Sampling was done aboard a DC-3 aircraft operating between 100 m and 4000 m altitude. Figure 1 gives an overview of the flight tracks of the SAFARI project and the sampling locations for this study.

### Sampling

About 120 whole air samples were collected in evacuated stainless steel canisters of 2-L volume. Figure 2 shows a schematic drawing of the air-sampling system. The air intake was a stainless steel tube (6-mm ID) mounted on the top the aircraft extending beyond the boundary layer of the DC-3. The exhaust line was mounted in the back of the aircraft. Once the DC-3 was airborne, the inlet line was continuously flushed with ambient air. The air samples were pressurized with a metal bellows pump to a pressure of about 300 kPa. Typical sampling times were between 1 and 2 min depending on the altitude of the aircraft. This time is comparable to the transit time through the plumes. The dates, times, locations, and altitudes of the plume samples are given in Table 1.

### Analysis

The samples were analyzed in the laboratory in Jülich, Germany, by gas chromatography for CO, $CO_2$, $CH_4$, and nonmethane hydrocarbons. CO, $CO_2$, and $CH_4$ were determined by a gas chromatographic method very similar to the one described by *Heidt* [1978]. The precision is 3% for CO, 0.5% for $CO_2$ and 1% for $CH_4$. The higher-molecular-weight VOC were analyzed using gas chromatography with flame ionization (FID) and electron capture (ECD) detectors. The hydrocarbons were preconcentrated cryogenically from volumes between several hundred milliliters and about 2 L depending on the expected concentrations in the plume samples and background samples and separated on a combination of a 7-m micropacked Porapack QS column and a 105-m RTX-1 fused silica capillary column. The detection limits were between 10 ppt (parts per trillion) for the measurements on the packed column ($C_2$–$C_4$ hydrocarbons) and below 1 ppt for the mea-

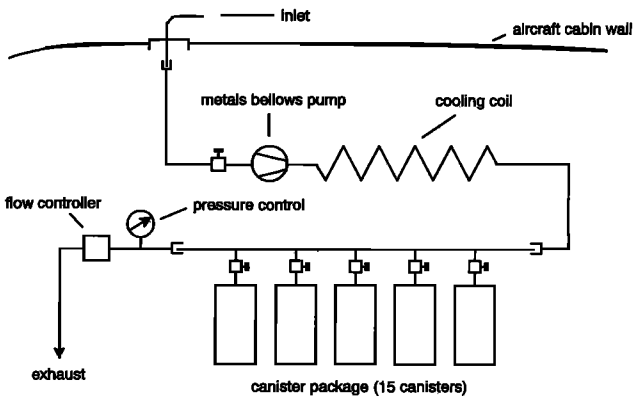


**Figure 2.** Schematic drawing of the sampling system installed on board the DC-3.

**Table 1a.** Plume Samples From the Sugar Cane Fire During Flight SAF04 on September 19, 1992

| Sample | Sampling Time, UT | Latitude, °S | Longitude, °E | Altitude, m | Passage | $CH_4$, ppb | CO, ppb | $CO_2$, ppm |
|---|---|---|---|---|---|---|---|---|
| | | | *Sugar Cane Field 1 Plume* | | | | | |
| 3583 | 0703 | 26.73 | 32.00 | 489 | 1 | 1938 | 2586 | 392 |
| 3584 | 0706 | 26.74 | 32.01 | | 2 | 1874 | 2444 | 396 |
| 3585 | 0711 | 26.71 | 32.00 | 327 | 4 | 1866 | 4469 | 549 |
| 3586 | 0714 | 26.72 | 32.00 | 313 | 5 | 1832 | 4403 | 534 |
| | | | *Sugar Cane Field 2 Plume* | | | | | |
| 3588 | 0745 | 26.72 | 31.94 | 778 | 10 | 1797 | 2814 | 463 |
| 3589 | 0748 | 26.71 | 31.94 | 363 | 11 | 1837 | 5407 | 644 |
| 3590 | 0810 | 26.78 | 31.94 | 291 | 18 | 2036 | 2980 | 485 |
| Mean | | | | | | 1883 | 3587 | 495 |
| s.d. | | | | | | 80 | 1157 | 89 |

Plume crossings are identified by broad maxima in the continuous CO and $CO_2$ measurements. The time for one plume passage was between 1 and 2 min, and the sampling time was about 1 min.

surements on the capillary column ($C_5$–$C_{10}$ organic trace gases). The reproducibility ranged between 10 and 30% depending on the compound. Details of the analytical techniques are given by *Koppmann et al.* [1992, 1993] and *Rudolph et al.* [1986, 1995].

For a number of plume samples the medium-molecular-weight organic trace gases ($C_5$–$C_{10}$) were additionally analyzed with a mass spectrometer (Fisons, MD 800). For this purpose the effluent of the capillary column was split with a ratio of 3:1 between the FID detector and the mass spectrometer (MS). The FID was used for quantification of the compounds in the sample, and the MS was used for identification purposes. With this technique is was possible to record mass spectra even of compounds with mixing ratios as low as a few parts per trillion. It should be noted that this technique, including the sampling in stainless steel canisters, is not an adequate method for all organic compounds that can be observed in the samples. It is well known that reactive and highly polar compounds are not stable in canisters or in stainless steel lines and that others cannot be preconcentrated and desorbed quantitatively [*Rudolph et al.*, 1990]. For these types of compounds the mixing ratios and emission ratios given here should therefore be considered as lower limits. Significant losses in the canisters and in our preconcentration system due to reactions with ozone can be excluded owing to the fast decay of ozone on stainless steel surfaces [*Greenberg et al.*, 1992; *Koppmann et al.*, 1995].

## Results and Discussion

### Organic Composition of Biomass-Burning Emissions

Vegetation material is made up of cellulose, hemicelluloses, lignin, proteins, nucleic acids, amino acids, and volatile substances [*Franke*, 1989]. During the first phase of a fire the volatile compounds such as aldehydes, alcohols, and terpenes are released. In the following phase, thermal cracking of the fuel molecules occurs. Higher-molecular-weight compounds are decomposed into a variety of volatile organic compounds [*Lobert and Warnatz*, 1993]. In addition to the light hydrocarbons, which were the only organic compounds investigated in previous field studies, a large number of higher-molecular-weight organic trace gases is expected in the emissions from biomass burning. They include alcohols, aldehydes, ketones, carboxylic acids, esters, ethers, furanes, etc. These partly oxidized compounds are predominantly emitted during the smoldering phase of fires [*Czapiewski*, 1995]. Figure 3 shows a capillary column chromatogram of $\geq C_5$ VOC of an air sample collected inside the plume of the Drakensberg fire during flight SAF05 (sample 3602). The mixing ratios of $CO_2$ and CO in this sample were 399.5 ppm and 4420 ppb, respectively. The average $\Delta(CO)/\Delta(CO_2)$ ratio (calculated from samples collected during all passages through the plume) was 9.36 ± 1.30%. This indicates a mix of flaming and smoldering combustion at the

**Table 1b.** Plume Samples From the Drakensberg Fire During Flight SAF05 on September 20, 1992

| Sample | Sampling Time, UT | Latitude, °S | Longitude, °E | Altitude, m | Passage | $CH_4$, ppb | CO, ppb | $CO_2$, ppm |
|---|---|---|---|---|---|---|---|---|
| 3593 | 1106 | 25.30 | 31.09 | 1039 | 1 | 2022 | 2907 | 384 |
| 3592 | 1110 | 25.28 | 31.07 | 1160 | 2 | 1831 | 1100 | 368 |
| 3594 | 1114 | 25.29 | 31.09 | 1110 | 3 | 2039 | 3100 | 383 |
| 3595 | 1117 | 25.28 | 31.11 | 1069 | 4 | 1986 | 2764 | 382 |
| 3596 | 1120 | 25.28 | 31.10 | 1013 | 5 | 1902 | 1719 | 374 |
| 3598 | 1130 | 25.47 | 30.69 | 1656 | 6 | 1825 | 975 | 369 |
| 3599 | 1133 | 25.45 | 30.72 | 1701 | 7 | 1833 | 1150 | 372 |
| 3601 | 1142 | 25.44 | 30.70 | 1303 | 8 | 2103 | 3413 | 389 |
| 3602 | 1145 | 25.45 | 30.70 | 1463 | 9 | 2236 | 4417 | 400 |
| Mean | | | | | | 1976 | 2394 | 380 |
| s.d. | | | | | | 141 | 1210 | 10 |

Nine passages through this plume were flown during flight SAF05. Plume crossings are identified by broad maxima in the continuous CO and $CO_2$ measurements. The time for one plume passage was about 2 min, and the sampling time was about 1 min.

**Table 1c.** Plume Samples from the Kruger National Park Fire 2 (Block 55) During Flight SAF06 on September 24, 1992

| Sample | Sampling Time, UT | Latitude, °S | Longitude, °E | Altitude, m | Passage | $CH_4$, ppb | CO, ppb | $CO_2$, ppm |
|---|---|---|---|---|---|---|---|---|
| 3610 | 1041 | 25.27 | 31.32 | 1423 | 3 | 1868 | 2243 | 398 |
| 3611 | 1043 | 25.20 | 31.32 | 1359 | 4 | 1883 | 3007 | 410 |
| 3613 | 1047 | 25.29 | 31.35 | 1442 | 5 | 1791 | 1061 | 374 |
| 3614 | 1053 | 25.25 | 31.33 | | 7 | 1861 | 2226 | 393 |
| 3616 | 1057 | 25.29 | 31.29 | 1756 | 8 | 1747 | 442 | 365 |
| 3617 | 1059 | 25.21 | 31.32 | 1760 | 9* | 1833 | 1860 | 398 |
| 3618 | 1101 | 25.26 | 31.32 | 1730 | 9* | 1779 | 899 | 370 |
| 3620 | 1105 | 25.28 | 31.31 | 1754 | 10 | 1812 | 1508 | 384 |
| Mean | | | | | | 1822 | 1656 | 386 |
| s.d. | | | | | | 48 | 842 | 16 |

Eight samples were taken during a total of 22 passages through this plume during flight SAF06. Plume crossings are identified by broad maxima in the continuous CO and $CO_2$ measurements. Typical times for one plume passage were between 1.5 and 2 min; the sampling time in all cases was about 1 min.

*Two samples were taken in the same plume. The time for passage 9 was 3.5 min.

time of the plume passages. The sum over the mixing ratios of $C_2$ and $C_3$ hydrocarbons was 364 ppb C. For the analysis of this sample the mass spectrometer was used in parallel to the FID and ECD. More than 140 major peaks are found in this chromatogram, about 70 of which could be identified. Table 2 gives the retention times of the peaks and the identification of the compounds. In a first step these compounds were identified by comparing the mass spectra with MS data from the U.S. National Institute of Standards and Technology (NIST) library. In some cases two or more compounds overlapped into one peak. These compounds are included only if an identification of at least one compound (agreement better than 90%) was possible. This was then verified by comparing the relative retention times and the known boiling point of the compounds. The quantitative analysis of the organic compounds was based on the FID response. The response of the FID is proportional to the molar mass of the compounds; i.e., within one group of organic trace gases the response increases linearly with the mass of the molecule. The response, however, is slightly different for groups of compounds with hetero atoms such as oxygen, nitrogen, and sulfur or for compounds with different functional groups. Generally, in these cases the response is lower than for "pure" hydrocarbons. Because for this analysis we treated all compounds as "pure" hydrocarbons and because of the aforementioned problems of a quantitative determination of some of these compounds, our emission ratios can be seen as lower limits; i.e., the "real" emission ratios may be higher than the values given here.

As a result of this analysis a large number of organic trace gases could be identified that were previously not known to be emitted by biomass burning. In general, the mixing ratios of the different members of the various compound groups decrease with increasing number of carbon atoms. This is in good agreement with laboratory studies carried out with tropical wood which showed very similar emission patterns [*Czapiewski*, 1995]. From these data, emission ratios are calculated on a ppb carbon basis, and the contribution of these compounds to the total emission of organic trace gases and relative to CO and $CO_2$ can be derived.

### Emission Ratios of Organic Trace Gases

$CO_2$ is the dominant carbon species emitted from fires, followed by CO. The emission ratio of CO relative to $CO_2$, $\Delta CO/\Delta CO_2$, is used to characterize the different burning stages. During the flaming phase this ratio is relatively low, in general, 5–10%. During the smoldering phase of a fire, more CO is

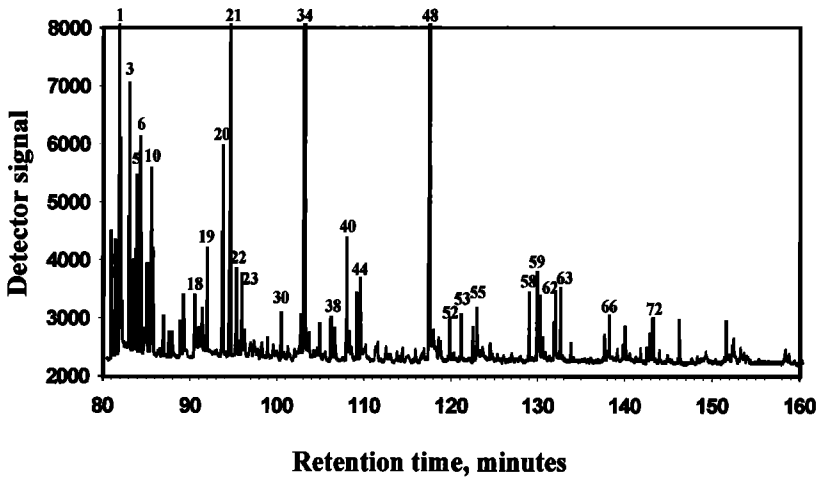


**Figure 3.** Chromatogram of sample 3602. The major peaks are identified by numbers. The numbers in the chromatogram correspond to the numbers given in Table 2.

emitted owing to low oxygen supply, and the ratio of $\Delta CO/\Delta CO_2$ increases. Typical values observed during this phase vary between 10 and 15%. Also, the emissions of organic compounds vary as a function of the burning stages. The correlation of an organic trace gas with $CO_2$ the emission ratios of that trace gas to be estimated as a function of type of fire and the different burning processes and the burning stages.

Table 3 summarizes the emission ratios of the two sugar cane fires, the Kruger National Park fire, and the Drakensberg fire for CO, $CH_4$, the sum of $C_2$–$C_4$ hydrocarbons, and the sum of organic trace gases with five or more carbon atoms. The total amount of organic trace gases with five or more carbon atoms is based on all FID-responsive compounds found in the chromatograms. Table 4 gives the individual emission ratios for the most abundant organic compounds identified. In all cases the highest emission ratios were observed for the Drakensberg fire, while the sugar cane fires showed the lowest emission ratios. As was mentioned above, the emission ratio of CO relative to $CO_2$ allows the burning conditions of the different fires to be characterized. For the fire at Drakensberg, smoldering is likely to be the dominant burning process, while the sugar cane fires were largely flaming fires. The fire of block 55 in the Kruger National Park seemed to be a mixture of both. The flaming phase of the fire was followed by a brief smoldering phase. Since this fire covered a large savanna area, emissions from both phases of the fire converge in the smoke plumes, leading to the observed emission ratios. It can be seen that the emissions of the sum of the light NMHC are comparable or even larger than the emission ratio of methane. This has already been observed during previous field studies of large savanna fires with similar $\Delta CO/\Delta CO_2$ ratios in Africa and Australia [*Bonsang et al.*, 1991; *Rudolph et al.*, 1992; *Hurst et al.*, 1994]. Our results show further that the emission ratio of organic compounds with carbon number of 5 or more add up to at least half of the contribution of light NMHC.

The emission ratios of the total measured organic compounds relative to $CO_2$ were $(13.7 \pm 0.9) \times 10^{-3}$ (ppb C/ppb $CO_2$) for the Drakensberg fire, $(7.4 \pm 1.6) \times 10^{-3}$ (ppb C/ppb $CO_2$) for the Kruger National Park fire, and $(3.9 \pm 2.9) \times 10^{-3}$ and $(1.7 \pm 0.7) \times 10^{-3}$ (ppb C/ppb $CO_2$) for sugar cane fires 1 and 2, respectively. These values compare well with measurements of fires under laboratory conditions as reported by *Manø* [1997] and *Czapiewski* [1995], who give an average emission ratio of the sum of organic compounds for their experiments of $8.4 \times 10^{-3}$ and $3 \times 10^{-3}$, respectively. *Lobert et al.* [1991] report an average of $11.9 \times 10^{-3}$ based on 10 different experiments. The ratio found for the Kruger National Park fire is in good agreement with the laboratory measurements, while the ratio found for the Drakensberg fire exceeds the laboratory values. The emission ratios of the predominantly flaming sugar cane fires are considerably lower than the results of the laboratory studies. This may be due to the fact that large flaming combustion can not be simulated realistically in confined fires, which are controlled by their artificial boundaries. Especially the response of fires to wind and the access to oxygen for combustion, which affects mainly the flaming phases, differs significantly between free and confined fires [*Albini*, 1993].

## Impact of Volatile Organic Compounds

### Ozone Formation

In order to estimate the impact of VOC on the formation of ozone in biomass-burning plumes we conducted a simple

**Table 2.** Compounds Positively Identified in Sample 3602

| Peak | Retention Time, min | Identification |
|---|---|---|
| 1 | 81.61 | acetone |
| 2 | 81.81 | *i*-pentane |
| 3 | 82.82 | 1-pentene |
| 4 | 83.30 | 2-methyl-1-butene |
| 5 | 83.66 | n-pentane |
| 6 | 84.08 | isoprene |
| 7 | 84.21 | (E) 2-pentene |
| 8 | 84.60 | 2-methyl-2-propanol |
| 9 | 84.89 | methylacetate |
| 10 | 85.34 | 2-methyl-2-butene |
| 11 | 85.57 | (E) 1,3-pentadiene |
| 12 | 85.91 | 1,2-pentadiene |
| 13 | 86.36 | $CS_2$ + ? |
| 14 | 86.74 | (Z) 1,3-pentadiene |
| 15 | 87.77 | propanenitrile |
| 16 | 88.68 | tetrahydrofuran |
| 17 | 89.08 | cyclopentane |
| 18 | 90.33 | methylvinylketone + 2-methyl-1-pentane |
| 19 | 91.75 | butanal |
| 20 | 93.60 | 1-hexene |
| 21 | 94.42 | 2-methylfuran |
| 22 | 95.04 | ethylacetate |
| 23 | 95.21 | *n*-hexane |
| 24 | 95.81 | 3-methylfurane |
| 25 | 96.15 | 4-methyl-2-pentene |
| 26 | 97.26 | 2-methyl-1-propanol + ?? |
| 27 | 98.13 | 4-methyl-2-pentene |
| 28 | 98.77 | 2,3-dihydrofuran |
| 29 | 99.47 | methylcyclopentane |
| 30 | 100.37 | 3-methylbutanal |
| 31 | 101.15 | 3-methylbutanon |
| 32 | 101.91 | 1-butanol |
| 33 | 102.59 | 2,4-hexadiene |
| 34 | 102.95 | benzene |
| 35 | 103.59 | thiophene |
| 36 | 104.51 | 1-penten-3-one |
| 37 | 104.82 | 2-pentanone |
| 38 | 106.09 | cyclopentanal |
| 39 | 106.57 | cyclohexane |
| 40 | 107.94 | 1,2-dimethylcyclopentane |
| 41 | 108.27 | trichlorethene |
| 42 | 108.50 | 2-ethylfuran |
| 43 | 109.07 | 2,4-dimethylfuran + 3-hexen-1-ol-acetate |
| 44 | 109.51 | *n*-heptane |
| 45 | 111.26 | phenol |
| 46 | 112.47 | 2-hexanone + ?? |
| 47 | 113.74 | dimethylsulfide |
| 48 | 117.41 | toluene |
| 49 | 117.96 | 2-methylheptane |
| 50 | 118.20 | 2.2-dimethylpentanal |
| 51 | 118.56 | dimethylcyclohexane |
| 52 | 119.82 | hexanal |
| 53 | 121.05 | 1-octene |
| 54 | 122.45 | acetic acid 2-methylpropylester |
| 55 | 122.91 | n-octane |
| 56 | 123.38 | 2-octene |
| 57 | 123.62 | 2-furaldehyde |
| 58 | 128.98 | ethylbenzene |
| 59 | 129.89 | *p*,*m*-xylene + 3-heptanone |
| 60 | 130.55 | 2-heptanone |
| 61 | 131.81 | styrene |
| 62 | 132.00 | 7-methyl-1-octene |
| 63 | 132.61 | *o*-xylene |
| 64 | 133.81 | *n*-nonane |
| 65 | 137.68 | 6-methyl-2-heptanone |
| 66 | 138.24 | benzaldehyde |
| 67 | 139.18 | propylbenzene |
| 68 | 139.84 | 1-ethyl-3-methylbenzene |
| 69 | 140.01 | benzonitrile + ?? |
| 70 | 140.62 | 1,2,4-trimethylbenzene |
| 71 | 141.85 | 1-ethyl-4-methylbenzene |
| 72 | 143.28 | benzofuran |

**Table 3.** Emission Ratios of Methane, Carbon Monoxide, Light NMHC and Higher-Molecular-Weight Organic Trace Compounds Calculated From the Plume Samples

| Passage | $\Delta(CO)/\Delta(CO_2)$, % | $\Delta(CH_4)/\Delta(CO_2)$, % | $\Delta(\Sigma\ C_2\text{–}C_4)/\Delta(CO_2)$, % | $\Delta(\Sigma\ C_5\text{–}C_9)/\Delta(CO_2)$, % |
|---|---|---|---|---|
| | | *Flight SAF04, Sugar Cane Field 1* | | |
| 1 | 6.97 | 0.57 | 0.22 | 0.16 |
| 2 | 5.90 | 0.35 | 0.59 | 0.27 |
| 4 | 2.25 | 0.07 | 0.13 | 0.06 |
| 5 | 2.41 | 0.05 | 0.10 | 0.04 |
| Mean | 4.38 | 0.26 | 0.26 | 0.13 |
| s.d. | 2.09 | 0.22 | 0.20 | 0.09 |
| | | *Flight SAF04, Sugar Cane Field 2* | | |
| 10 | 2.52 | 0.05 | 0.11 | 0.05 |
| 11 | 1.83 | 0.03 | 0.07 | 0.02 |
| 18 | 2.21 | 0.23 | 0.18 | 0.08 |
| Mean | 2.19 | 0.11 | 0.12 | 0.05 |
| s.d. | 0.28 | 0.09 | 0.05 | 0.02 |
| | | *Flight SAF05, Drakensberg* | | |
| 1 | 9.81 | 1.04 | 0.40 | 0.41 |
| 2 | 8.77 | 0.93 | 1.92 | 0.54 |
| 3 | 11.53 | 1.27 | 0.99 | 0.48 |
| 4 | 10.46 | 1.05 | 0.87 | 0.43 |
| 5 | 9.22 | 1.07 | 0.77 | 0.40 |
| 6 | 7.32 | 0.78 | 0.68 | 0.37 |
| 7 | 7.36 | 0.72 | 0.72 | 0.38 |
| 8 | 9.86 | 1.17 | 1.00 | 0.49 |
| 9 | 9.86 | 1.20 | 1.02 | 0.48 |
| Mean | 9.36 | 1.03 | 0.93 | 0.44 |
| s.d. | 1.30 | 0.17 | 0.40 | 0.05 |
| | | *Flight SAF06, Kruger National Park Fire 2* | | |
| 3 | 5.23 | 0.32 | 0.48 | 0.21 |
| 4 | 5.51 | 0.28 | 0.45 | 0.21 |
| 5 | 5.68 | 0.32 | 0.51 | 0.48 |
| 7 | 5.86 | 0.35 | 0.50 | 0.20 |
| 8 | 4.15 | 0.10 | 0.38 | 0.38 |
| 9 | 4.27 | 0.23 | 0.35 | 0.16 |
| 9 | 6.37 | 0.34 | 0.54 | 0.35 |
| 10 | 5.26 | 0.28 | 0.44 | 0.23 |
| Mean | 5.29 | 0.28 | 0.46 | 0.28 |
| s.d. | 0.71 | 0.07 | 0.06 | 0.10 |

model calculation using the regional acid deposition model (RADM2) published by *Stockwell et al.* [1990]. We are aware of the fact that RADM2 was not originally designed for a VOC mix as observed in biomass-burning plumes, and not all measured organic compounds are accounted for individually. They are lumped according to their reactivity with regard to OH radicals. The substantial contributions from the light hydrocarbons are taken explicitly into account. Nevertheless, we used this model as a simplified approximation to simulate the formation of ozone in the plumes and get information about the contribution of VOC to this process.

The calculations were initialized with measured mixing ratios from the sugar cane fires, which showed the lowest VOC emission ratios, and the Drakensberg fire, which had the highest observed VOC emission ratios. The $NO_2$ mixing ratio was derived from the $NO_2/CO_2$ ratio given by *Andreae et al.* [1996] and our $CO_2$ measurements. The initial mixing ratios for short-lived trace gases that were not measured (OH, $HO_2$, NO, etc.) were derived from a steady state approximation. The solar zenith angle was fixed to 24°.

Under realistic conditions, ozone formation is substantially influenced by transport processes causing a dilution of the trace gases within the plume [e.g., *Lelieveld et al.*, 1997]. In order to account for this, we included dilution with surrounding air in our simulation. Initially, the plume is enclosed in a volume $V(0)$ that increases with time to the volume $V(t)$ thereby mixing in background air with fixed mixing ratios of $[CO]^0$ = 100 ppb, $[CH_4]^0$ = 1.7 ppm, $[O_3]^0$ = 50 ppb, and $[VOC]^0$ = 5 ppb C. The time dependence of $V(t)$ was parameterized by

$$V(t) = V(t_e) + (1 - V(t_e)) \exp(-t/\tau)$$

where $\tau$ is the time constant for dilution and $V(t_e)$ is the final size of the plume at the end of the integration at time $t_e$, assuming ($\tau \ll t_e$). The dilution factor is given by $D = V(t_e)/V(0)$. Measurements of air samples collected outside the plumes gave $CO_2$ mixing ratios that were on average 10 ppm above the global background. The dilution was treated in a way that the $CO_2$ mixing ratios measured in the plumes was finally reduced to the $CO_2$ mixing ratio observed in the air outside of the plumes.

In the case of the Drakenberg fire the final dilution was $D$ = 2, and the dilution time constant was assumed to be $\tau$ = 2 hours. Ozone mixing ratios (initialized with a background value of 50 ppb) in the plume are shown in Figure 4. If only $CH_4$ and CO as oxidizable carbon compounds are taken into account, ozone reaches a maximum mixing ratio of 134 ppb after 30 sunlit hours. The VOC were included in two steps, first

**Table 4.** Mean and Standard Deviation of Emission Ratios of the Most Abundant Organic Trace Gases of Intermediate Molecular Weight Relative to Excess $CO_2$ (in ppb carbon) for the Different Types of Fires

| Compound | Emission Ratio, ppb C | | |
|---|---|---|---|
| | Drakensberg Fire | KNP Fire 2 | Sugar Cane Fires |
| 1-pentene | $(1.1 \pm 0.3) \times 10^{-4}$ | $(5.8 \pm 1.3) \times 10^{-5}$ | $(1.7 \pm 2.5) \times 10^{-5}$ |
| 2-methyl-1-butene | $(5.9 \pm 1.9) \times 10^{-5}$ | $(0.5 \pm 1.0) \times 10^{-5}$ | $(0.7 \pm 1.2) \times 10^{-5}$ |
| 2-methyl-2-butene | $(8.7 \pm 2.0) \times 10^{-5}$ | $(1.8 \pm 1.2) \times 10^{-5}$ | $(5.7 \pm 9.2) \times 10^{-6}$ |
| 4-methyl-1-pentene | $(7.9 \pm 3.5) \times 10^{-5}$ | $(7.8 \pm 5.2) \times 10^{-5}$ | $(2.7 \pm 3.5) \times 10^{-5}$ |
| 1-hexene | $(1.3 \pm 0.3) \times 10^{-4}$ | $(8.4 \pm 1.1) \times 10^{-5}$ | $(2.6 \pm 4.0) \times 10^{-5}$ |
| 1-octene | $(2.2 \pm 0.8) \times 10^{-5}$ | $(1.6 \pm 0.8) \times 10^{-5}$ | $(0.7 \pm 1.2) \times 10^{-5}$ |
| 2-octene | $(2.0 \pm 1.8) \times 10^{-6}$ | — | $(2.8 \pm 3.1) \times 10^{-7}$ |
| 2-methyl-2-propanol | $(6.7 \pm 6.9) \times 10^{-6}$ | $(6.1 \pm 7.0) \times 10^{-6}$ | $(1.4 \pm 1.0) \times 10^{-5}$ |
| 1-butanol | $(6.0 \pm 1.8) \times 10^{-6}$ | $(5.9 \pm 4.6) \times 10^{-6}$ | $(3.8 \pm 5.7) \times 10^{-6}$ |
| Cyclopentanol | $(5.0 \pm 2.5) \times 10^{-5}$ | $(5.1 \pm 3.8) \times 10^{-5}$ | $(2.8 \pm 3.0) \times 10^{-5}$ |
| 2-methyl-propanal | $(1.8 \pm 0.8) \times 10^{-5}$ | $(1.3 \pm 0.9) \times 10^{-5}$ | $(3.1 \pm 2.3) \times 10^{-6}$ |
| Butanal | $(8.4 \pm 1.9) \times 10^{-5}$ | $(6.7 \pm 6.1) \times 10^{-5}$ | $(2.9 \pm 3.5) \times 10^{-5}$ |
| 3-Methylbutanal | $(2.4 \pm 0.7) \times 10^{-5}$ | $(1.6 \pm 1.5) \times 10^{-5}$ | $(7.4 \pm 9.3) \times 10^{-6}$ |
| 2,2-Dimethylpetanal | $(5.7 \pm 4.5) \times 10^{-6}$ | $(1.2 \pm 2.5) \times 10^{-6}$ | $(1.4 \pm 2.1) \times 10^{-6}$ |
| Hexanal | $(4.9 \pm 2.8) \times 10^{-5}$ | $(3.9 \pm 2.2) \times 10^{-5}$ | $(1.9 \pm 1.3) \times 10^{-5}$ |
| Benzaldehyde | $(4.2 \pm 1.9) \times 10^{-5}$ | $(4.5 \pm 3.0) \times 10^{-5}$ | $(1.4 \pm 1.3) \times 10^{-5}$ |
| Acetic acid-2-methylpropylester | $(1.5 \pm 0.5) \times 10^{-5}$ | $(8.2 \pm 0.5) \times 10^{-5}$ | $(1.7 \pm 2.4) \times 10^{-6}$ |
| 3-methylbutanone | $(8.2 \pm 1.2) \times 10^{-6}$ | $(7.5 \pm 5.2) \times 10^{-6}$ | $(2.5 \pm 3.1) \times 10^{-6}$ |
| 1-penten-3-one | $(6.6 \pm 2.7) \times 10^{-6}$ | $(4.4 \pm 2.5) \times 10^{-6}$ | $(2.1 \pm 3.0) \times 10^{-6}$ |
| 2-pentanone | $(3.7 \pm 1.8) \times 10^{-5}$ | $(2.5 \pm 1.8) \times 10^{-5}$ | $(0.9 \pm 1.1) \times 10^{-5}$ |
| 2-heptanone | $(2.9 \pm 1.9) \times 10^{-6}$ | $(9.5 \pm 7.6) \times 10^{-6}$ | $(3.9 \pm 2.2) \times 10^{-6}$ |
| 6-methyl-2-heptanone | $(3.3 \pm 1.6) \times 10^{-5}$ | $(2.5 \pm 1.8) \times 10^{-5}$ | $(1.3 \pm 0.6) \times 10^{-7}$ |
| 2-methylfuran | $(2.9 \pm 0.8) \times 10^{-4}$ | $(8.0 \pm 3.4) \times 10^{-5}$ | $(2.0 \pm 3.3) \times 10^{-5}$ |
| 3-methylfuran | $(5.0 \pm 1.0) \times 10^{-5}$ | $(1.8 \pm 0.2) \times 10^{-5}$ | $(5.2 \pm 8.0) \times 10^{-6}$ |
| Tetrahydrofuran | $(2.5 \pm 0.6) \times 10^{-5}$ | $(2.4 \pm 1.7) \times 10^{-5}$ | $(0.9 \pm 1.1) \times 10^{-5}$ |
| 2,3-dihydrofuran | $(2.1 \pm 0.7) \times 10^{-5}$ | $(1.9 \pm 1.1) \times 10^{-5}$ | $(0.8 \pm 1.0) \times 10^{-5}$ |
| 2-ethylfuran | $(6.0 \pm 3.5) \times 10^{-6}$ | $(2.1 \pm 2.5) \times 10^{-6}$ | $(0.9 \pm 1.3) \times 10^{-6}$ |
| 2,4-dimethyalfuran | $(4.1 \pm 1.1) \times 10^{-5}$ | $(1.4 \pm 0.3) \times 10^{-5}$ | $(4.2 \pm 6.5) \times 10^{-6}$ |
| Benzofuran | $(2.9 \pm 1.2) \times 10^{-5}$ | $(2.5 \pm 1.5) \times 10^{-5}$ | $(7.8 \pm 9.2) \times 10^{-6}$ |
| 1-ethyl-2-methylbenzene | $(5.2 \pm 2.5) \times 10^{-6}$ | $(3.8 \pm 2.9) \times 10^{-6}$ | $(1.3 \pm 1.2) \times 10^{-6}$ |
| 1,2,4-trimethylbenzene | $(3.2 \pm 2.7) \times 10^{-6}$ | $(0.9 \pm 1.3) \times 10^{-6}$ | $(1.3 \pm 1.5) \times 10^{-6}$ |
| 1-ethyl-3-methylbenzene | $(7.8 \pm 1.1) \times 10^{-6}$ | $(4.9 \pm 2.0) \times 10^{-6}$ | $(2.6 \pm 3.7) \times 10^{-7}$ |
| Propylbenzene | $(3.2 \pm 2.7) \times 10^{-6}$ | $(2.1 \pm 2.1) \times 10^{-6}$ | $(7.0 \pm 6.7) \times 10^{-7}$ |
| *o*-xylene | $(2.9 \pm 0.8) \times 10^{-5}$ | $(1.7 \pm 1.0) \times 10^{-5}$ | $(6.8 \pm 9.4) \times 10^{-6}$ |
| Ethylbenzene | $(2.8 \pm 1.1) \times 10^{-5}$ | $(1.8 \pm 1.0) \times 10^{-5}$ | $(6.6 \pm 1.1) \times 10^{-5}$ |
| Toluene | $(4.6 \pm 2.3) \times 10^{-4}$ | $(2.2 \pm 0.6) \times 10^{-4}$ | $(5.7 \pm 8.7) \times 10^{-5}$ |
| Benzene | $(8.8 \pm 1.3) \times 10^{-4}$ | $(4.9 \pm 0.7) \times 10^{-4}$ | $(3.1 \pm 1.8) \times 10^{-4}$ |
| Phenol | $(1.0 \pm 0.6) \times 10^{-5}$ | $(5.2 \pm 2.4) \times 10^{-6}$ | $(1.8 \pm 2.8) \times 10^{-6}$ |

KNP, Kruger National Park.

the light hydrocarbons up to $C_4$ (figures in parentheses) and then all VOC. Taking into account the measured VOC the ozone mixing ratio increases steeper and earlier, because the ozone formation is now driven by the degradation of the hydrocarbons that react faster with OH than CO and $CH_4$. Ozone mixing ratios increase rapidly to values around 90 ppb within the first 2 hours after the emissions, followed by a further slower increase to about (175 ppb) 195 ppb. Thus the mixing ratio of ozone in the plume is about (30%) 45% larger if the impact of VOC is included with the peak mixing ratio reached about 30 hours after the emission. The initial $NO_2$ mixing ratio of 30 ppb was taken from the average of the measured data, which varied between 6 ppb and 60 ppb for different plume passages. The amount of ozone produced depends strongly on the $NO_2$ mixing ratio (Figure 5). Clearly, better temporally and spatially resolved $NO_x$ data are necessary to further assess the impact of biomass burning to the global ozone budget.

To assess the total amount of ozone being produced, we have also calculated the excess ozone averaged over the final volume $V(t_e)$ denoted by $\langle \Delta O_3 \rangle$. The maximum $\langle \Delta O_3 \rangle$ was 150 ppb with VOC and 85 ppb without VOC.

The temporal behavior of the ozone mixing ratio in the plume of the sugar cane fire is similar to that of the Drakensberg fire, although the sugar cane combustion is different from that at Drakensberg. For the sugar cane fire the dilution factor was $D = 13$ and the time constant was again $\tau = 2$ hours. The most striking difference is the much larger initial $NO_2$ burden of 200 ppb inferred from the average of the measured data. The larger initial $NO_2$ and CO mixing ratios compared with the Drakensberg case causes the substantially smaller difference between the cases with and without VOC. The maximum $\langle \Delta O_3 \rangle$ for the sugar cane fire plume was 68 ppb including all measured VOC and 62 ppb without VOC. The results of this simple simulation show that in these cases, about 10 to 50% of the ozone formed in the plumes is due to the impact of VOC.

### Global VOC Emissions

The analysis of NOAA AVHRR data indicates that in 1992 the burning season in southern Africa occurred between July

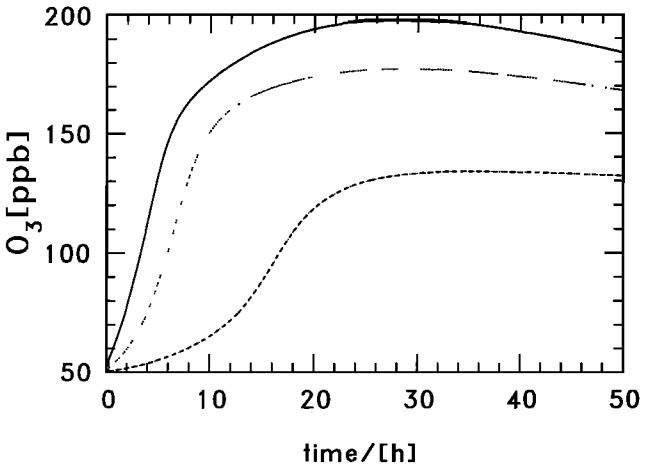


**Figure 4.** Model results for the time dependence of the ozone mixing ratio. The initial mixing ratios were taken from the Drakensberg fire. The dashed line shows results for the calculation without VOC, the dotted line shows the calculation with light NMHC up to $C_4$, and the solid line shows the calculation with all measured VOC.

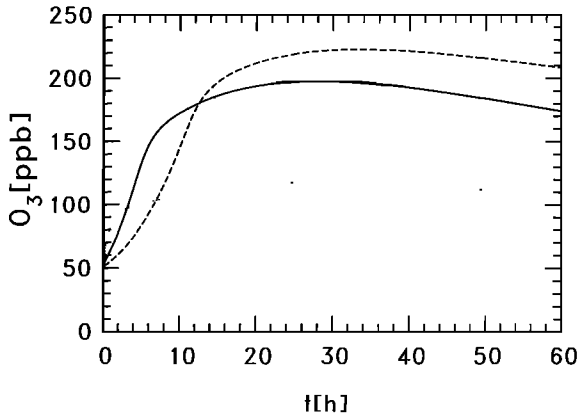


**Figure 5.** Model results for the time dependence of the ozone mixing ratio. The initial mixing ratios were taken from the Drakensberg fire. The curves refer to different initial $NO_2$ mixing ratios. The dashed line shows initial $NO_2$ = 60 ppb, the solid line shows initial $NO_2$ = 30 ppb, and the dotted line shows initial $NO_2$ = 6 ppb.

and September with the SAFARI campaign covering the end of the burning season. Furthermore, in 1992 there was about 50% less burning than in 1989 [*Justice et al.*, 1996]. It should be added that the samples are not likely to be representative for biomass burning on a global scale, since they represent only a very limited fraction of the areas burned globally each year. Therefore any extrapolations of our emission ratios to global scales are highly uncertain. In order to get an idea about the impact of biomass burning emissions to atmospheric chemistry, it is nevertheless worthwhile to compare the emissions of organic trace gases with global budgets. Table 5 summarizes the emission of total carbon species and CO from the various types of biomass burning based on a compilation of literature data [*Andreae*, 1991, 1993; *Hao and Liu*, 1994; *Andreae et al.*, 1996; and references therein]. Since the emissions of VOC are better correlated with CO than with $CO_2$, we base our extrapolation on VOC/CO emission ratios. If we use the emission ratios from the sugar cane fire 2 as a lower limit (mean $\Delta(VOC)/\Delta(CO)$ = 0.08%) and those from the Drakensberg fire as an upper limit (mean $\Delta(VOC)/\Delta(CO)$ = 0.15%), the estimated total carbon released in the form of VOC ($CH_4$ not included) ranges between 25 $\times$ $10^{12}$ g C/yr and 48 $\times$ $10^{12}$ g C/yr.

The higher molecular VOC contribute up to 50% to that value. This coarse estimate of the source strength of organic compounds based on our measurements is a factor of 2 higher than the results of previous estimates by *Bonsang et al.* [1991], who give 12 $\times$ $10^{12}$ g/yr derived from measurements over large savanna fires during the Dynamique et Chimie de l'Atmosphère en Forêt Equatoriale (DECAFE) project in the Ivory Coast. This number is below the lower limit of the emission range based on our estimates because *Bonsang et al.* [1991] based their estimates on measurements of light NMHC only. From laboratory studies, *Lobert et al.* [1991] calculate 42 $\times$ $10^{12}$ g/yr, a value at the upper end of our estimation range. These results indicate that the emissions from biomass burning contribute significantly to the local and regional budget of organic compounds in the troposphere.

## Summary and Conclusions

In all samples collected in the plumes of the savanna and agricultural fires during SAFARI, a large variety of organic trace gases was found. They include alcohols, aldehydes, ketones, carboxylic acids, esters, ethers, furanes, and others. The observed emission ratios show a considerable variation depending on the fuel type and the burning conditions and stages of the fires. The emission ratio of the sum of light VOC was in the same order of magnitude as or even higher than that of methane. Our results show that higher-molecular-weight and oxygenated compounds, most of which are highly reactive, contribute significantly to the load of volatile organic compounds in biomass-burning emissions. Presently, roughly 70 of

**Table 5.** Emissions of Total Carbon Species and CO From the Various Types of Biomass Burning

| Source | Biomass Burned (Dry Matter), Tg/yr | Carbon Released, Tg/yr | CO Emission Ratio, % | CO Emission, Tg C/yr |
|---|---|---|---|---|
| Tropical forest | 1260 | 567 | 10.9 | 62 |
| Extratropical forest | 1150 | 518 | 11.2 | 58 |
| Savanna | 3690 | 1661 | 6.2 | 103 |
| Biomass fuel | 1940 | 873 | 8.3 | 73 |
| Charcoal | 21 | 42 | 20.0 | 8 |
| Agricultural waste in fields | 850 | 383 | 7.2 | 28 |
| Total | 8911 | 4043 | 8.2 | 331 |

some 140 major compounds could be identified in the samples, a number of which were previously not known to be emitted by biomass burning and thus were not included in estimates of the influence on the regional atmospheric chemistry. The uncontrolled fire in the Drakensberg forest showed emission ratios of the sum of organic compounds relative to $CO_2$ of $(13.7 \pm 0.9) \times 10^{-3}$ (ppb C/ppb $CO_2$) which are the highest values found during this campaign.

Simple model calculations were carried out in order to investigate the temporal development of the chemical ozone formation and the contribution of the individual ozone precursors. The simulation for the Drakensberg fire shows a maximum excess ozone with and without taking into account the impact of VOC of 150 ppb and 85 ppb, respectively, leading to 65 ppb of additional ozone in the plume due to the impact of VOC. For the sugar cane fire the simulation yields a maximum excess ozone of 68 ppb with VOC and 62 ppb without VOC, leading to 6 ppb of additional ozone due to the impact of VOC. Thus in the first case the impact of VOC is responsible for about 40% of additional ozone formed in the plumes, and in the second case it is responsible for <10%.

Our results show that higher-molecular-weight organic trace gases are a significant part of these emissions and play an important role for the photochemistry in biomass burning plumes. Their impact on the formation of tropospheric ozone is significant, especially during the initial phase of photochemical processing of biomass-burning emissions.

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