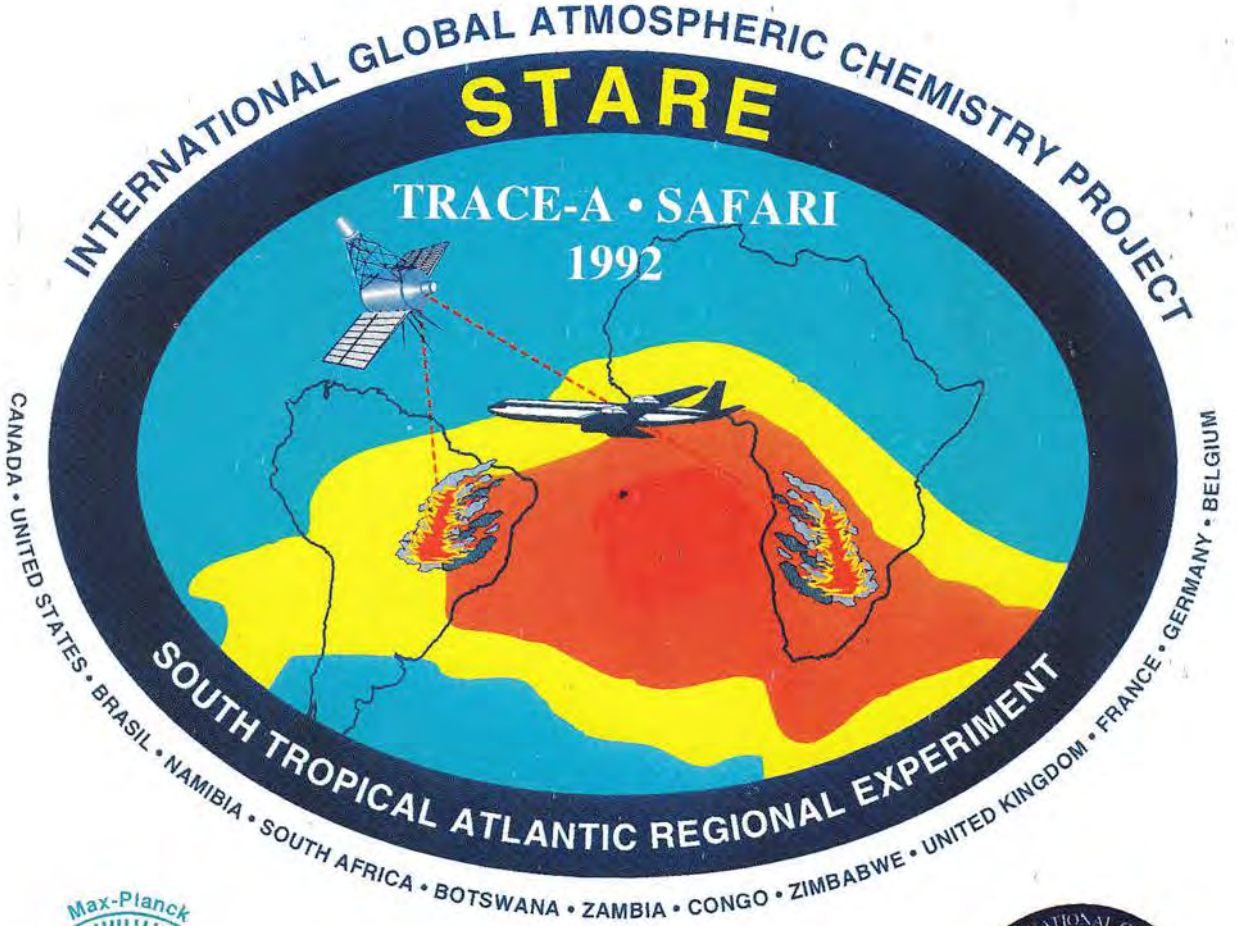
TRACE A and SAFARI Special Issue



Reprinted from the Journal of Geophysical Research

Published by American Geophysical Union

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 101, NO. D19, PAGES 23,651–23,665, OCTOBER 30, 1996

Black carbon formation by savanna fires: Measurements and implications for the global carbon cycle

T. A. J. Kuhlbusch,[1,2] M. O. Andreae,[3] H. Cachier,[4] J. G. Goldammer,[3]
J.-P. Lacaux,[5] R. Shea,[6] and P. J. Crutzen[1]

Abstract. During a field study in southern Africa (Southern African Fire-Atmosphere Research Initiative (SAFARI-92)), black carbon formation was quantified in the residues of savanna fires. The volatilization ratios of C, H, N, and S were determined by measuring their contents in the fuel and residue loads on six experimental sites. The volatilization of sulfur (86±8%) was significantly higher than previously reported. Volatilization of H, N, and S was significantly correlated with that of carbon, enabling us to estimate their volatilization during savanna fires by extrapolation from those of carbon. By partitioning the residues in various fractions (unburned, partially burned, and ash), a strong correlation between the H/C ratio in the residue and the formation of black carbon was obtained. The ratio of carbon contained in ash to carbon contained in the unburned and partially burned fraction is introduced as an indicator of the degree of charring. As nitrogen was enriched in the residue, especially in the ash fraction of > 0.63 mm, this indicator may be useful for an assessment of nutrient cycling. We show that the formation of black carbon is dependent on the volatilization of carbon as well as the degree of charring. The ratio of black carbon produced to the carbon exposed to the fire in this field study (0.6-1.5%) was somewhat lower than in experimental fires under laboratory conditions (1.0-1.8%) which may be due to less complete combustion. The average ratio of black carbon in the residue to carbon emitted as CO_2 ranged from 0.7 to 2.0%. Using these ratios together with various estimates of carbon exposed or emitted by savanna fires, the worldwide black carbon formation was estimated to be 10-26 Tg C yr^{-1} with more than 90% of the black carbon remaining on the ground. The formation of this black carbon is a net sink of biospheric carbon and thus of atmospheric CO_2 as well as a source of O_2.

1. Introduction

The formation of black carbon (BC, defined here as a highly polyaromatic to elemental or graphitic carbon fraction in the particulate material) in the smoke and residues of vegetation fires and its importance for the global carbon cycle were first discussed by *Seiler and Crutzen* [1980] and subsequently in various publications [*Houghton*, 1991; *Crutzen and Andreae*, 1990; *Mack*, 1994]. BC in combustion residues and primary carbonaceous aerosols is formed by charring of the organic fuel during combustion. The processes involved in the pyrolysis are well described by *Edwards* [1974, pp. 61-68]. The main factors influencing the pyrolysis and thus BC formation are the oxygen supply and fuel composition. Oxygen supply and hence the amount of energy liberated are very much dependent on the state of aggregation of the solid fuels which "may range from finely divided particles to objects as large as a building" [*Edwards*, 1974, p. 149]. Using wood burning as an example, oxygen must first diffuse into the surface to further oxidize the carbon enriched, charred, nonvolatile, and dehydrated material. Further oxidation of nonvolatile matter in, e.g., savanna grass may be easier compared to wood because the fuel is not so condensed. Thus oxygen and heat may reach the nonvolatiles from any direction. Thermal conduction, which in most solid fuels is relatively slow, is less important for savanna grass burning than for, e.g., wood burning.

The formation of primary aerosols is described by *Edwards* [1974, p. 152] as follows: "High surface temperatures are achieved during combustion. Cracks and fissures of the surface material result. Particulate matter, in fact particles of rather large dimensions may be dislodged in the process." This process is taking place during the combustion, but some charred material may become airborne by wind erosion long after the fire extinguished and thus may be significantly contributing to atmospheric background concentrations of black and organic carbon rich aerosols. Visual observations of a burned savanna site by one of the authors (T.K.) showed that a large proportion of the black-colored residue was transported off site in the absence of rain within three to four weeks. *Suman et al.* [1996] estimated a flux of 10 Tg BC yr^{-1} to marine sediments, mainly to those of the continental shelves, representing 4-20% of the total black carbon produced by vegetation fires annually.

[1]Luftchemie, Max-Planck-Institut für Chemie, Mainz, Germany.
[2]Now National Research Council Associate at the National Exposure Research Laboratory, U.S. Environmental Protection Agency, Athens Georgia.
[3]Biogeochemie, Max-Planck-Institut für Chemie, Mainz, Germany.
[4]Commissariat à l'Energie Atomique, Centre National de la Recherche Scientifique, Gif-sur-Yvette, France.
[5]Laboratoire d'Aerologie, Université Paul Sabatier, Centre National de la Recherche Scientifique, Toulouse, France.
[6]Department of Rangeland Resources, Oregon State University, Corvallis.

Paper number 95JD02199.
0148-0227/96/95JD-02199$09.00

Once formed by any combustion processes, black carbon, in the residues on the ground and in atmospheric emissions, represents a sink of atmospheric CO_2 (and a source of O_2) as it is no longer available for uptake by plants or microbial breakdown. The long residence time of black carbon can be deduced from its presence in soils, ice, and sediments [*Herring*, 1977; *Clark and Robinson*, 1993; *Sternberg*, 1968; *Chyleck et al.*, 1987]. The oldest charcoal record in a carbonaceous matrix reported in a review by *Cope and Chaloner* [1980] was found in Pennsylvanian coal seams that formed approximately 350 million years ago. Thus carbon is sequestered by the formation of black carbon from the short-term biospheric cycle to the long -term geological cycle. This effect on the global carbon cycle is a significant factor in the understanding of past and prediction of future atmospheric CO_2 levels.

Crutzen and Andreae [1990] estimated the annual formation rate of black carbon to be in the range of 0.2-0.6 Pg (10^{15}g) C, but pointed to a high uncertainty due to a deficiency of measurements. Emissions of BC as a constituent of carbonaceous aerosols have been thoroughly investigated [*Chang et al.*, 1982; *Ogren and Charlson*, 1982; *Penner et al.*, 1993] because of their radiative and catalytic properties. On the other hand, measurements of charcoal formation in postfire residues have only been conducted for Amazonian deforestation fires by *Fearnside* [1991] and *Comery et al.* [1981] for a prescribed fire on a longleaf pine site in Florida. No field data on the formation of black carbon in residues for agricultural waste, firewood, and savanna fires have yet been published. Residues from the combustion of different vegetation types in a burning apparatus were analyzed for the first time for BC by *Kuhlbusch and Crutzen* [1995]. They were able to show a negative correlation between black carbon as a fraction of the total residual carbon (BC/TRC) and the molar CO/CO_2 ratio in the gases emitted, indicating that flaming rather than smoldering combustion is the main source of BC. For nonwoody fuel, about 1.5% (1.0-1.8%) of the fire-exposed carbon (CE) was converted to BC while 90% of the exposed carbon was volatilized.

During the Southern African Fire-Atmosphere Research Initiative (SAFARI-92), six experimental sites were burned for joint multidisciplinary research activities in the Kruger National Park, South Africa. At these study sites, several international research groups conducted measurements on the impact of savanna fires on the savanna ecosystem and the role of fire in the regional and global atmosphere and in the global carbon cycle. We quantified the exposed, residual and black carbon on three plots of each experimental site. Elemental contents and volatilization ratios of hydrogen, sulfur, and nitrogen were also determined. Studies of the formation of black carbon and its relation to gaseous emissions and fuel and residue characteristics were conducted. The present study focuses on black carbon in savanna fires to obtain a better estimate of the sequestering of carbon from the short-term to the long-term carbon cycle.

2. Experimental Techniques

2.1. Sampling

The experimental sites in Kruger National Park can be characterized as a deciduous, open-tree savanna parkland. More detailed information about the vegetation composition is given by *Shea et al.* [this issue] and *Trollope et al.* [this issue]. To quantify the carbon load before and after the fire, we chose three or four sampling plots on each of the six experimental sites. Each sampling plot consisted of approximately 100 m^2 with above average vegetation density (by vegetation height and patchiness) to ensure that the area was burned during the fire, since the vegetation was patchy owing to 2 years of drought conditions. Thus the determined vegetation densities do not represent the average vegetation density of the experimental sites. Each sampling plot consisted of three squares (each 0.25 m^2) with low, medium, and high vegetation density. Vegetation was manually sampled and divided into grass, litter, and herbs. Herbs included all standing vegetation which was neither grass nor woody vegetation, litter included all vegetation laying on the soil, mainly dead grass, and grass included standing dead and living grass. Only about 5-10% of the standing grass could be considered as living, "green" grass. The residues were sampled from squares just beside the ones where we sampled prior to the fire, normally within 10 min. to 2 hours after the fire past the sampling plots. This ensured that the postfire residues we sampled were derived from vegetation types and fuel load similar to those sampled prior to the fire. The residues were partitioned into unburned (UB), partially burned (PB) (both manually collected), and ash (collected with a handheld vacuum cleaner) (Figure 1). The vacuum cleaner technique was preferred to trays, as by *Sharrow and Wright* [1977], *Shea et al.* [this issue], and *Kauffman et al.* [1995], for several reasons. Trays would have had to be placed below the litter, a major fuel component, to ensure full recovery of the ash, which would have meant a disturbance of the fuel, arbitrarily influencing the density and combustion process. Nevertheless, we tested metal ash collection trays in several areas to compare the two techniques and found a poor recovery. The turbulence during the fire had blown almost all of the ash out of the metal trays. To ensure that vacuum cleaning did not lead to a significant contamination for the black carbon determination, we looked carefully at the soil prior to the fire for any black carbon particles from previous fires, but could find only very few. Second, we vacuum cleaned five plots, after sampling the biomass to determine the vegetation density prior to the fire, and analyzed those samples for black carbon. From these analyses we derived

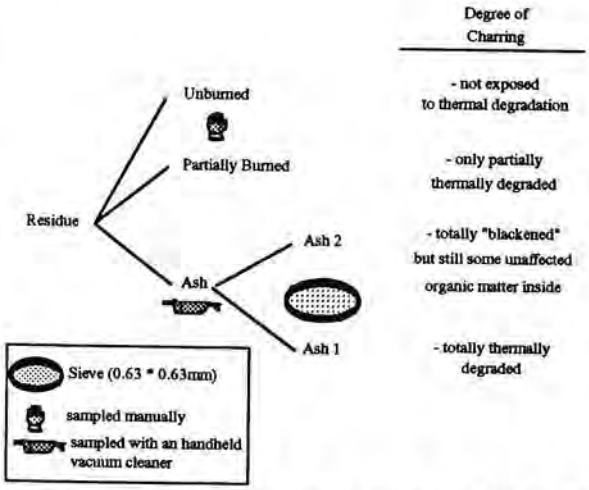


Figure 1. The different residue fractions and the degree of charring concerning their structure. The unburned and partly burned fractions were manually sampled, whereas ash was sampled with a handheld vacuum cleaner. Ash was then divided into ash 2 and ash 1 by sieving (0.63 x 0.63 mm).

a maximum contamination of black carbon from previous fires of 9% of the black carbon determined in ash 1 (ranging from 0.3% on KP/3 to 8.9% on KPE/1), and hence a maximum contamination of 6% of the total quantified black carbon. Trace elemental analyses by W. Maenhaut (personal communication, 1994) showed that soil contamination was not significant in the ash 1 and ash 2 fractions.

Prior to the determination of the elemental composition we separated the ash fraction by sieving (0.63 x 0.63 mm) into ash 1 (A1) and ash 2 (A2) (Figure 1). The fraction left in the sieve (A2) was found to have a different composition than A1. A1 consisted of particles smaller than 0.63 mm diameter and was composed of burned and thermally totally degraded matter. The A2 fraction was totally blackened from outside but still had the original cell structure of the vegetation and did contain some less pyrolyzed organic matter inside. In comparison, partially burned material showed the original structure and color as well as pyrolyzed parts. Then all samples were oven-dried at 80°C for 24 hours to determine the dry weight. They were milled to an average particle size of 40 μm and analyzed for carbon (TC), hydrogen (TH), sulfur, and nitrogen. To avoid any influence by moisture deposition on the dried samples on the H/C ratio, samples were redried at 100°C for 3 min. directly prior to the elemental analysis. Using the fuel loads and the corresponding measured carbon contents, we calculated the carbon exposed to the fire (CE), total carbon in the residue (TRC), and thus the volatilized carbon (VC). The same calculations were conducted for hydrogen, sulfur, and nitrogen. Other abbreviations used are summarized in Table 1.

2.2. Black Carbon Measurements

Black carbon was measured in the different residue fractions by a two-step method developed by *Kuhlbusch* [1995] here briefly explained. During the first step the samples were treated with a series of aqueous solvents (70% HNO_3, 1% HCl, 1 *M* NaOH, H_2O) to remove all inorganic carbon (IC) and as much organic carbon (OC1) as possible. For several residue samples (12 are shown in Table 2) an elemental analysis after this first step (TC1 and TH1, Table 2) was performed. Thus the IC and OC1 removed by the solvent extraction were obtained by subtraction of TC1 from TC. Similar calculations were conducted for hydrogen. In the second step all remaining organic carbon (OC2) was removed by a thermal treatment at 340°C for 2 hours in pure oxygen. Afterwards, black carbon as well as the corresponding "black hydrogen" (BH) was measured by an elemental analysis. OC2 and OH2 were calculated by subtraction of BC and BH from TC1 and TH1, respectively. To quantify the inorganic carbon content in the residues, a separate fraction (approximately 1 g) of the sample was treated with 25% HCl for 24 hours to evolve the carbonates as CO_2. Subsequently the samples were oven-dried at 80°C for 24 hours, reweighed after 12 hours acclimatization in a desiccator, and analyzed for carbon (TC2). By subtracting this time TC2 from TC we calculated the IC content of the samples and thus the OC1 fraction as well. Results for four different plots are listed in Table 2 and will be discussed in section 3.1.2. A general carbon balance of a fire visualizing the carbon partitioning by the fire and in the residue by the analytical method is shown in Figure 2.

Table 1. Explanations of the Abbreviations

Abbreviation	Explanation
	Elemental Fractions
TC + TH	Total carbon and hydrogen content of a sample
TC1 + TH1	Carbon and hydrogen content of a sample after solvent extraction
BC + BH	Black carbon and hydrogen: carbon and hydrogen content of a sample after solvent extraction and thermal treatment at 340°C in pure oxygen for 2 hours
OC1 + OH1	Organic carbon and hydrogen 1: carbon and hydrogen removed by the solvent extraction; calculated by subtraction of TC1 from TC (TH-TH1)
OC2 + OH2	Organic carbon and hydrogen 2: carbon and hydrogen removed by the thermal treatment; calculated by subtraction of BC from TC1 (TH-BH)
TC2	Carbon content of a sample after acid treatment
IC	Inorganic carbon, carbonates: removed by acid treatment (TC-TC2)
VC, VH, VN, VS	Volatilized carbon, hydrogen, nitrogen, and sulfur by the fire; expressed in percent of the element being exposed to the fire
CE	Carbon exposed to the fire: sum of the carbon being quantified in the different vegetation fractions
TRC	Total carbon in the residue: sum of the carbon being quantified in the different residue fractions
removed mass	Mass being removed by the solvent extraction
%-d.m.	Mass of the element or specific elemental fraction expressed in percent of the dry mass of the original sample; e.g., BC 3.5 [%-d.m.] means that 3.5 % of the total dry mass of the residue was black carbon
	Residue Fractions
UB	Unburned: residue fraction which did not show any visual alteration due to the fire
PB	Partially burned: residue fraction which showed the original structure and color as well as some pyrolysed parts
A	Ash; all residue material smaller than 2 cm collected with a handheld vacuum cleaner: totally blackened from outside but some material still showed the structure of the grass
A2	Ash 2: ash fraction with a particle size bigger than 0.63 mm diameter: blackened from outside but still some unaffected matter inside
A1	Ash 1: fine ash, ash fraction with a particle size smaller than 0.63 mm diameter: totally thermally degraded

Table 2. Results of the Elemental Analyses to Determine the Different Carbon Fractions and Their H/C Ratios

Plot	TC %-d.m.	TH %-d.m.	TC1 %-d.m.	TH1 %-d.m.	IC %-d.m.	OC1 %-d.m.	OC2 %-d.m.	BC %-d.m.	BH[a] %-d.m.	OC1 H/C mol	OC2 H/C mol	BC[b] H/C mol
KPE/2 PB	27.1	2.70	7.62	0.61	0.38 1.4%[c]	19.14 70.5%[c]	6.74 24.9%[c]	0.88 3.2%[c]	0.03	1.30	1.02	0.11
KPE/2 A2	44.6	3.28	18.71	0.84	0.88 2.0%[c]	24.98 56.0%[c]	13.17 29.5%[c]	5.54 12.4%[c]	0.09	1.16	0.68	0.15
KPE/2 A1	18.2	1.13	10.35	0.39	0.64 3.5%[c]	7.23 39.7%[c]	7.55 41.4%[c]	2.80 15.4%[c]	0.07	1.22	0.50	0.22
56/1 PB	27.5	2.61	5.81	0.48	0.14 0.5%[c]	21.50 78.3%[c]	5.07 18.4%[c]	0.74 2.7%[c]	0.02	1.18	1.07	0.02
56/1 A2	42.9	3.09	17.13	0.69	1.11 2.6%[c]	24.68 57.5%[c]	11.51 26.8%[c]	5.62 13.1%[c]	0.09	1.16	0.62	0.15
56/1 A1	12.6	0.86	8.41	0.24	2.11 16.7%[c]	2.12 16.8%[c]	6.14 48.6%[c]	2.27 18.0%[c]	0.06	3.48	0.35	0.18
KPE/1 PB	34.0	3.54	6.05	0.58	1.23 3.6%[c]	26.72 78.6%[c]	5.37 15.8%[c]	0.68 1.8%[c]	0.02	1.32	1.21	0.02
KPE/1 A2	44.8	3.46	15.11	0.71	0.58 1.3%[c]	29.15 65.0%[c]	10.35 23.1%[c]	4.76 10.6%[c]	0.08	1.12	0.73	0.14
KPE/1 A1	13.5	1.03	7.33	0.21	0.15 1.1%[c]	6.02 44.6%[c]	5.64 41.8%[c]	1.69 12.5%[c]	0.05	1.62	0.34	0.22
KP3/2 PB	35.4	3.90	8.89	0.94	2.44 6.9%[c]	24.08 68.0%[c]	8.13 23.0%[c]	0.76 2.1%[c]	0.03	1.46	1.34	0.06
KP3/2 A2	45.2	3.44	17.35	0.63	0.64 1.4%[c]	27.24 60.2%[c]	8.74 19.3%[c]	8.61 19.0%[c]	0.12	1.23	0.69	0.14
KP3/2 A1	14.4	0.96	9.42	0.33	0.48 3.3%[c]	4.54 31.4%[c]	6.27 43.4%[c]	3.15 21.8%[c]	0.07	1.65	0.49	0.19

Abbreviations are as follows: %-d.m., % of the dry mass of the sampled fraction; sample abbreviations: exp./j x; exp., the experimental site; j, the number of the plot; x, the sampled residue fraction; exp. = SP5, Shambeni 5; KPE, Kambeni extra; FP4, Faai 4; 56, block 56; 55, block 55; other abbreviations see Table 1.

[a]not corrected.

[b]corrected for the hydrogen not bonded to carbon, on average 0.022 %-d.m., see section 3.1.3.

[c]Percent of TC.

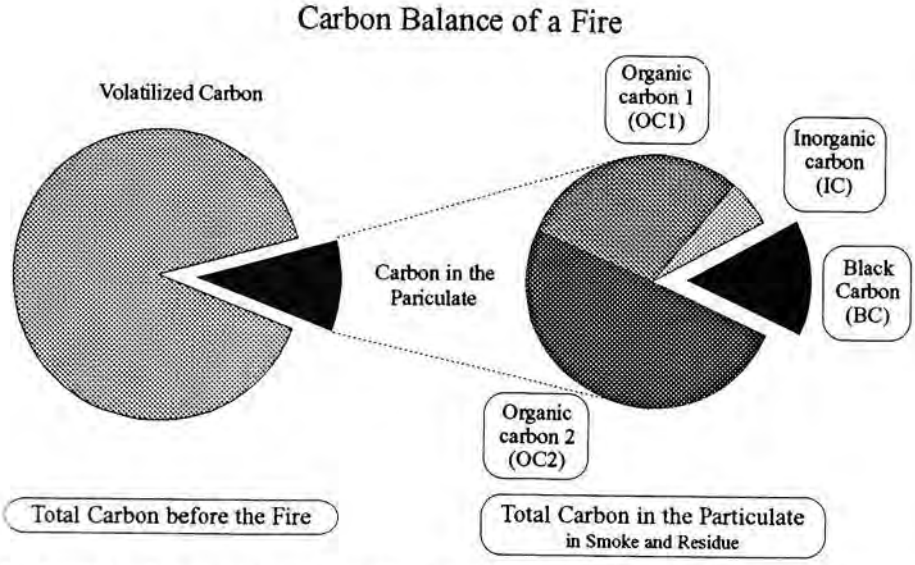


Figure 2. General carbon partitioning caused by savanna fire. (left) Partitioning of the carbon exposed to fire into volatilized and residual carbon. (right) The different carbon fractions in the residue as determined by the analytical method.

Table 3. Elemental Content of the Different Fuel and Residue Fractions

	C[a,b] %-d.m.	H[a,b] %-d.m.	N[a,b] %-d.m.	S[a,b] %-d.m.	H/C molar
Fuel	43.9±1.4	5.7±0.1	0.57±0.14	0.21±0.04	1.55±0.02
Grass	44.0±1.3	5.9±0.2	0.53±0.21	0.20±0.05	1.61±0.03
Litter	43.6±3.4	5.4±0.3	0.63±0.16	0.22±0.05	1.49±0.07
herbs	44.1±4.7	5.6±0.8	1.12±0.34	0.21±0.05	1.51±0.08
Residue	26.4±6.0	2.3±0.7	0.75±0.09	0.15±0.05	1.01±0.10
Unburned	44.1±2.6	5.3±0.7	0.83±0.18	0.18±0.04	1.42±0.12
Partially burned	35.9±8.3	3.6±0.9	0.67±0.13	0.15±0.06	1.22±0.09
Ash	21.9±5.3	1.5±0.5	0.80±0.16	0.17±0.08	0.83±0.08
Ash 2 (>0.63 mm)	44.3±2.7	3.2±0.6	1.13±0.19	0.20±0.09	0.86±0.14
Ash 1 (<0.63 mm)	14.8±3.2	1.0±0.2	0.69±0.16	0.17±0.08	0.81±0.06
Data for comparison					
African savanna[c]					
Fuel	42.1		0.30		
Residue	35.0		0.25		
Austral. savanna[d]					
Fuel	46		0.48	0.04	
Residue	20		0.61	0.09	
Rice straw[e]					
Fuel	40.4±0.1	5.4±0.1	0.6±0.1	0.07±0.02	1.61±0.05
Residue	13.2±2.0	0.5±0.1	0.3±0.1	0.07±0.02	0.47±0.06
Charcoal[f]	74.5	2.5	0.53		0.40
Wood (Beech)[g]	48.3±0.1	6.7±0.2	0.23±0.02		1.66±0.05

[a]Here %-d.m. denotes percent of dry matter of the sample.
[b]Average and standard deviation of 20 sampling plots for the fuel and 18 plots for the residue.
[c]*Lacaux et. al.* [1994b].
[d]*Hurst et al.* [1994], *Cook* [1994].
[e]*Jenkins et al.* [1991].
[f]*Lacaux et. al.* [1994a].
[g]*Lobert* [1989].

3. Results and Discussion

3.1. Biomass Fuel and Residue Characteristics

3.1.1. Elemental content of C, H, S, and N and volatilization ratios. Table 3 lists the average elemental composition (C, H, N, S) for the different fractions of biomass and the residue after the fire (Figure 1). The average mass ratio of grass/litter/herbs for all experimental sites was 1/0.75/0.03, indicating that herbs do not represent a significant fraction of the average total dry vegetation mass of 6133±2235 kg/ha. The average mass ratio after the fire for ash/PB/UB for all experimental sites was 1/0.71/0.05 with unburned as a minor fraction. This ratio was significantly different for site FP4 (1/1.14/0.32), showing that for this site the PB and UB fractions represent the major fractions and hence explaining the low BC/TRC ratios for these sites in Table 6. The site FP4 had by far the lowest vegetation density (Table 6), the greatest patchiness of the vegetation and thus the lowest volatilization ratio for carbon. The average total dry mass of the residue for the six sites was 1055±247 kg/ha. In all cases, the ash was dominated by the fine fraction. The average mass ratio of A1/A2 was 1/0.2, meaning that only about 17% of the total mass of ash had a particle size larger than 0.63 mm. The last ratio is in good agreement with results for Australian savanna fires obtained by *Cook* [1994] who found that 10-30% of the total mass of ash had a particle size > 1 mm. The main residue fraction with a particle size < 0.63 mm is especially accessible for wind erosion and is readily transported off site. Details about the vegetation types and fire behavior for the different experimental sites are given by *Shea et al.* [this issue] and *Trollope et al.* [this issue].

The average C and N contents in the biomass and residues are comparable to those of prescribed fires in the tropical Australian savanna [*Hurst et al.*, 1994]. Like these authors, we observed an increase of the N content in ash compared to the fuel. Especially interesting is the increase of nitrogen in the unburned and A2 fraction. In the case of the unburned matter the increase is quite surprising and indicates that in spite of the absence of any visual evidence some alteration due to the fire had taken place. A2 as explained above was totally blackened on the surface but still contained some less pyrolyzed matter inside. Therefore the doubling of the nitrogen content in A2 (with respect to fuel N) is possibly due to drying and elimination processes with the organic compounds containing nitrogen being far less volatile than other organic compounds. *Cook* [1994] made a similar observation in residues of Australian savanna fires. He measured nitrogen contents of 0.4 %-d.m. for ash < 1 mm and 1.1 %-d.m. for ash > 1 mm. Along with the

Table 4: Carbon, Hydrogen, Nitrogen, and Sulfur Volatilization in Percent of the Element Exposed to the Fire

Plot	VC[a]	VH[a]	VN[a]	VS[a]
SP5/1	96.8±0.9	97.9±0.6	94.5±1.8	95.9±1.3
SP5/2	91.9±2.3	94.9±1.1	89.9±3.3	98.0±2.1
SP5/3	87.5±6.5	91.8±4.4	73.0±12.0	91.3±4.1
KPE/1	85.4±8.8	89.2±5.8	76.5±14.2	85.2±7.4
KPE/2	84.2±2.2	89.7±2.5	54.8±2.8	82.5±1.4
KPE/3	84.0±2.2	89.8±1.6	60.8±3.7	81.8±1.0
KP3/1	88.1±6.7	93.6±3.8	57.3±25.5	93.5±4.0
KP3/2	91.0±1.4	94.3±1.4	70.2±3.1	89.0±0.9
KP3/3	95.5±1.8	97.2±1.3	80.1±6.0	94.3±2.8
FP4/1	78.2±3.8	83.7±3.7	74.9±5.2	77.1±2.2
FP4/2	72.0±1.0	80.3±1.3	68.0±1.8	70.4±6.0
FP4/3	87.8±1.6	91.1±1.0	85.0±2.1	74.0±3.3
56/1	89.8±1.7	93.0±1.4	78.1±4.4	87.2±2.9
56/2	88.3±0.7	92.5±0.8	65.7±7.8	82.6±4.0
56/4	92.6±2.2	96.1±0.8	61.2±17.5	92.8±2.5
55/1	94.6±1.6	96.7±1.1	85.6±1.1	84.9±3.7
55/2	89.5±2.7	94.0±1.6	68.6±3.3	81.8±3.8
55/3	94.0±1.8	96.0±1.3	84.8±5.1	90.7±1.6
Average	88±6	92±5	74±11	86±8
Data for comparison				
Austr. Savanna[b]	96±2		89±5	85.0
Afr. Savanna[c]	97-98		93-95	35-67
Afr. Savanna[d]	80.4		79.6	
Rice Straw[e]	94±1	98±0	92±1	80±8

[a]VC: volatilized carbon; VH: hydrogen; VN: nitrogen; VS: sulfur: standard deviation of the three squares per plot.
[b]*Hurst et al.* [1994], Cook [1994].
[c]*Delmas* [1982].
[d]*Lacaux et. al.* [1994b].
[e]*Jenkins et al.* [1991].

doubling of the nitrogen content in A2 we note a carbon content that is similar to that of the fuel and is on average higher than in PB.

For sulfur, no significant change between the fuel and residue content was observed, which is in agreement with results with rice straw by *Jenkins et al.* [1991]. The absolute sulfur content in the biomass (0.2%-d.m., dry matter) is at the low end of the range given by *De Kok* [1990] for sulfur contents of plants (0.1-1.5%-d.m.) and a factor 2 higher than the average value given by *Menaut et al.* [1991] of 0.1%-d.m. for savanna grass.

The molar H/C ratios for the different fuel and residue fractions are given in the right-hand column of Table 3. The molar H/C ratio was fairly constant (1.6±0.1) for the different fuels (grass, litter, herbs, wood, rice straw). The decrease of the H/C ratio of the unburned fraction (1.4±0.1 mol) is another indicator of some chemical changes in this fraction. In Figure 1 we show the different residue fractions together with the degree of charring which increases from unburned to A1. Comparing the H/C ratios, a decrease of the ratio with an increase of the degree of charring was observed. Despite the fact that the carbon contents of A1 and A2 differ by a factor of 3, the H/C ratios are quite similar. This indicates that A2 already underwent the initial drying/distilling process of pyrolysis, during which most of the elimination reactions take place as well. That this initial process of pyrolysis may even lead to an enrichment of carbon can be seen by looking at charcoals or forest fires residues with carbon contents of up to 80 %-d.m.; this explains the carbon content of A2. Further pyrolytic reactions are mainly temperature-caused cracking of the fuel molecules and partial oxidization. That the latter process did not influence the general composition is indicated by the similarity of the H/C ratios for A1 and A2 and stressed by similar BC to TC ratios determined in A1 and A2 of 17.0±5.2% and 14.6±8.0% respectively.

Table 4 gives the amount of carbon, hydrogen, nitrogen, and sulfur released (in percent of element exposed to the fire) for each plot. Comparing the volatilization ratios of the different elements, we see an increase of the release ratios in the following order: N, S, C, H. The overall volatilization ratios for the elements are fairly similar to those in the literature (Table 4). *Jenkins et al.* [1991] found a higher volatilization rate for nitrogen relative to sulfur. The volatilization ratio for sulfur according to *Delmas* [1982] is in the range of 30 to 60%, whereas we found a volatilization ratio of 70 to 98% with an average around 80%. This may be due to the form in which sulfur is stored in the biomass. Detailed investigations conducted by *Sanborn and Ballard* [1991] show that increasing concentrations and proportions of sulfate in Douglas fir foliage significantly reduce the percentage of total S lost during combustion according to the thermal stability of the main salts of sulfate (e.g., K_2SO_4, Na_2SO_4, $CaSO_4$). A more detailed discussion on the nitrogen and sulfur balance as well as their emissions during SAFARI-92 is given by *Lacaux et al.* [this issue].

Correlation studies of the volatilization ratios of carbon to the other determined elements (VH, VN, VS) for the different plots gave good linear regressions for VH and VN and a fairly good correlation to VS (Table 5). Two plots (FP4/1 and FP4/2) were not used in this correlation study because of the high amount of unburned matter in the residue (see low VC in Table 6). The linear regression parameters for the different elements are given in Table 5 which might be useful to estimate the released S, N, and H.

In Table 6, the carbon load before and after the fire, the type of fire, the black carbon content, the ratio of grass carbon to litter carbon, and the ratio of ash carbon to partially burned plus unburned carbon (DoC) for the different plots are summarized. The average relative standard deviations for the carbon load before and after the fire were 40% and 50%, respectively, describing the range of the vegetation density in that area. In general, our grass loads are a factor 1.8±0.4 higher than the average data given by *Shea et al.* [this issue] for the whole experimental sites. This is due to the fact that we chose our plots

Table 5. Correlation of VH, VN, and VS to VC

	Linear Regression Parameters			
	r^2	Constant	Slope	Confidence Interval (t Test)
VH	0.95	0.32±0.01	0.69±0.01	>99%
VN	0.42	-1.05±0.10	1.99±0.62	99%
VS	0.33	0.04±0.05	0.93±0.36	>98%
Data for comparison				
Delmas et al. [1994][a]	0.60	-0.90±0.09	1.91±1.12	<95%
Lobert [1989][a]	0.89	-0.80±0.03	1.78±0.10	>99%

Without FP4/1 and FP4/2.
[a] VN, from experimental fires in the laboratory.

Table 6. Carbon Contents and Densities of the Fuel and Residue, and the Ratio of Black Carbon to the Fire-Exposed Carbon, Carbon in the Residue, and CO_2 Emitted by the Fire

Plot	Carbon Exposed, kg/ha	Carbon Exposed, %-d.m.	Carbon in Residue, kg/ha	Carbon in Residue, %-d.m.	VC, % of CE	Type of Fire	BC, %-d.m.	BC of TRC, %	BC of CE, %	BC/CO_2,[a] mol	CO/CO_2,[b] mol	DoC,[c] C-ratio	Grass to litter, C Ratio
SP5/1	3157	43.6	105.3	21.1	96.8	B	2.11	10.01	0.33	0.33	4.80	2.19	1.67
SP5/2	2833	43.9	292.8	33.6	91.9	H	2.10	6.25	0.63	0.76	5.83	2.01	1.66
SP5/3	2241	43.9	279.5	22.7	87.5	H	2.03	8.93	1.11	1.41	5.83	2.18	1.66
KPE/1	2158	44.1	315.9	32.3	85.4	H	1.39	4.30	0.63	0.82	n.d.	0.34	0.82
KPE/2	2418	46.2	382.3	26.1	84.2	B	2.02	7.75	1.22	1.62	4.58	0.71	1.54
KPE/3	3567	43.9	570.5	30.5	84.0	B	3.53	11.56	1.85	2.45	4.58	0.88	0.97
KP3/1	3661	45.5	437.2	25.0	88.1	B	3.53	14.09	1.68	2.12	4.80	2.53	1.31
KP3/2	1796	44.2	161.7	21.9	91.0	H	3.26	14.86	1.34	1.63	5.73	2.10	1.24
KP3/3	2627	42.6	117.0	16.1	95.5	H	2.83	17.57	0.78	0.91	5.73	2.97	1.82
FP4/1	1601	46.0	348.8	38.8	78.2	B	1.03	2.65	0.58	0.82	6.91	0.41	1.06
FP4/2	1211	44.6	338.4	35.5	72.0	B	1.21	3.41	0.95	1.47	6.91	0.46	1.45
FP4/3	1444	46.2	176.2	37.2	87.8	B	1.26	3.39	0.41	0.52	6.91	0.49	0.90
56/1	2617	44.7	268.0	23.9	89.8	B	1.53	6.40	0.66	0.81	3.41	0.39	1.16
56/2	1840	41.6	204.3	18.5	88.3	B	1.84	10.49	1.16	1.45	3.41	1.79	2.07
56/3[d]	1796	44.6											
56/4	2923	43.9	215.0	21.6	92.6	B	2.59	11.99	0.88	1.06	3.41	3.03	1.85
55/1	6000	43.8	320.3	21.0	94.6	H	3.19	15.46	0.82	0.97	n.d.	0.83	1.54
55/2	2990	40.0	312.9	22.0	89.5	H	3.62	16.45	1.72	2.14	n.d.	1.00	1.80
55/3	2231	43.6	133.8	26.3	94.0	B	2.60	9.90	0.59	0.70	n.d.	1.08	1.99
55/4[e]	5377	39.1											1.54
Heading fire (7)	2949	44.5	257.2	24.3	90.8		2.63	11.97	1.00	1.23	5.41	1.63	1.44
Backing fire (11)	2424	43.2	298.1	27.7	86.9		2.11	8.33	0.94	1.22	5.48	1.27	1.45

Abbreviations are as follows:

n.d., not determined; H, heading fire, fire spreading with the wind; B, backing fire, fire spreading against the wind; SP5, Shambeni 5; KPE, Kambeni extra; KP3, Kambeni 3; FP4, Faai 4; 56, block 56; 55, block 55, followed by the number of the sample site; for other abbreviations see Table 1.

[a]See section 3.2, calculated with a molar ratio of 4.00 for backing fires and 6.00 for heading fires if CO/CO_2 was not determined.

[b]Measured by *Lacaux et al.* [this issue].

[c]Degree of charring for the whole residue, see section 3.3.

[d]Area did not burn.

[e]Site was not sampled.

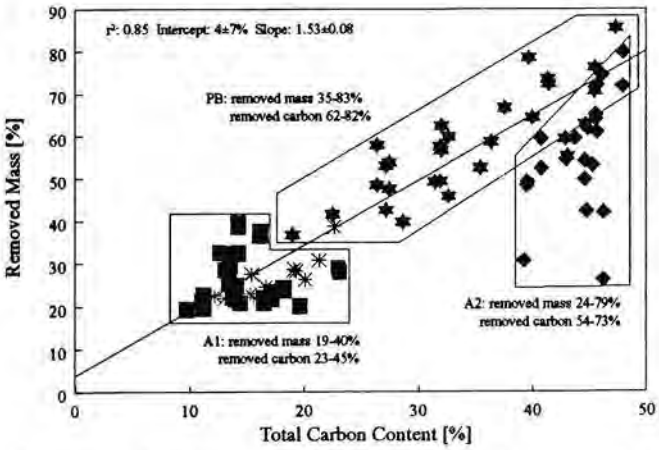


Figure 3. The mass removed by the solvent extraction as a function of the carbon content of that residue fraction. Solid squares represent A1; solid diamonds, A2; solid stars, PB; and asterisks ash sampled by *Shea et al.* [this issue].

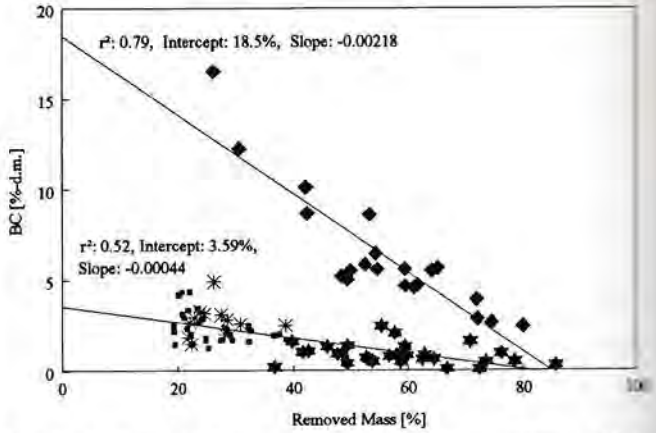


Figure 5. Black carbon as a function of the mass removed by the solvent extraction, showing that the higher the BC content the less mass is removed. Solid squares represent A1; solid diamonds, A2; solid stars, PB; and asterisks ash sampled by *Shea et al.* [this issue].

in areas with an above average fuel load to ensure that this area got burned.

3.1.2. Results of the residue analysis. Plotting the mass removed from the residue samples by the solvent extraction versus their carbon contents (TC), a positive correlation (r^2=0.85, Figure 3) was obtained. The A2 fraction, however, was not included. The slope of the linear regression line indicates that the mass removed by solvent extraction depends on the initial carbon content. Besides this correlation, we are able to distinguish the three groups A1, A2, and PB which were initially divided because of different color and structure. The high variability of the mass removed by the solvent extraction for A2 represents the high variability of the degree of charring of this fraction (the higher the degree of charring, the less mass is removed).

When black carbon is shown as a function of the total carbon content (both in %-d.m.), the same variability in A2 was observed as in the mass removed by the solvent extraction (Figure 4). Again, the three kinds of residues (A1, A2, PB) can be differentiated. If BC was produced by the pretreatment steps, a correlation should be seen, at least within a residue fraction. As no correlation was found and because of blank measurements [*Kuhlbusch*, 1995], it was concluded that charring (formation of BC by the analytical technique) is negligible and that the measured black carbon was produced by the combustion and not by the analytical method.

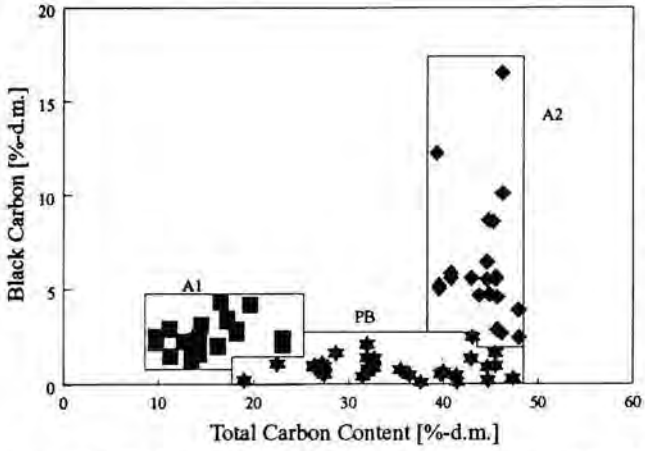


Figure 4. Black carbon as a function of the carbon content of that residue fraction. The three different residue fractions can be differentiated by the BC content. Solid squares represent A1; solid diamonds, A2; and solid stars, PB.

For comparable carbon contents more mass was removed from partially burned samples (PB) than from A2 (Figure 3) because PB samples were less exposed to thermal degradation. The high variability of A2 (Figures 3 and 4) and its degree of charring indicate the dependence of especially this fraction on fire characteristics like heat transfer, oxygen availability, and fire type (smoldering versus flaming), as reflected by the molar CO/CO_2 ratio.

Figure 5 also shows that A2 was different from the other residue fractions; it also had double the amount of nitrogen (see section 3.1.1). In Figure 5, BC (%-d.m.) is plotted against the mass removed by the solvent extraction. The linear regressions obtained for the A2 fraction and the A1 + PB fractions show that the removed mass displays how much the organic matter was exposed to thermal degradation. The less black carbon was produced, the more mass could be removed by the solvent extraction. The slope of the linear regression for A2 is steeper by a factor of 5. These differences in A2 may be associated with the charred surface protecting the inner area and with the fact that dehydration and elimination processes were predominant to oxidation. A2 represented on average about 11% of the total mass after the fire but contained about 35% of the total amount of black carbon produced.

3.1.3. The different carbon fractions and the corresponding H/C ratios. In Table 2 the results of the different carbon fractions (IC, OC1, OC2, and BC) for the different kinds of residues on four exemplary plots are shown. For all plots a clear dependence of OC1, OC2, and BC on the degree of charring was evident. The structure and the H/C ratio of the remaining material were considered as indicators of the degree of charring (Figure 1 and Table 3). BC as a fraction of TC (Table 2) clearly increases with the degree of charring (A1 > A2 > partially burned) and decreases with increasing H/C ratios (Table 3). As

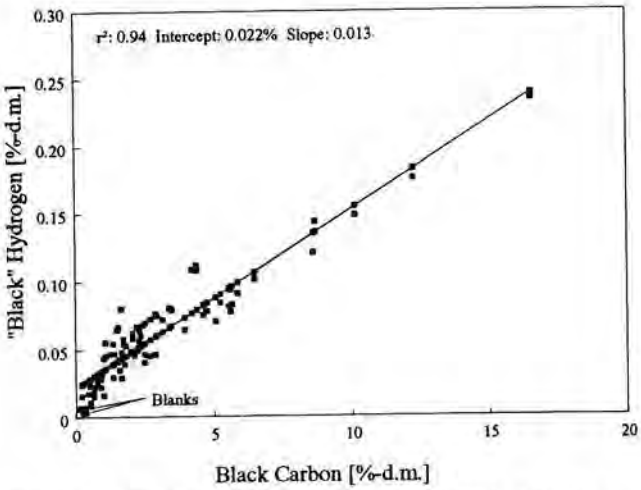


Figure 6. Black hydrogen as a function of black carbon to determine the H/C ratio of black carbon.

for BC in Table 2 the same relationship for OC2 but a negative one for OC1 was observed, indicating that BC and at least part of OC2 were produced in the field fires. We emphasize again, as treated in detail by *Kuhlbusch and Crutzen* [1995], that some of the OC2 carbon may, like black carbon, decompose only very slowly by microbial action. The actual carbon partitioning differs widely depending on the burning conditions; BC can range from 3-18% of the average 270±110 kg TRC/ha as can be seen in Table 6. Factors determining the burning conditions are, e.g., wind speed, humidity, fuel moisture, fuel density, fuel composition, and heat release. Since OC1, OC2, and IC were not quantified for all plots, we give the ranges obtained from the plots listed in Table 2 which are 62±10%, 26±6%, and 3±1% of TRC, respectively. BC in Table 2 comprises 8.7±4.4% of the total residual carbon. The amount of inorganic carbon is not dependent on the degree of charring. It was in the range of 0.5-6.9% of total carbon (the exception 56/1 A1, 16.7%, may be due to woody characteristics of the material). This inorganic carbon does not represent an important mass fraction but is partly responsible for the alkaline character of ash and aerosols. CO_2 may be produced following the deposition of acid rain or its mixing with acid material.

Before discussing the molar H/C ratios for the different carbon fractions, corrections are required for the H/C ratio for BC, since some measured hydrogen is bonded to elements other than carbon as shown by *Kuhlbusch* [1995]. Therefore "black" hydrogen was plotted versus black carbon in Figure 6 (both in %-d.m., dry matter). BC measurements of savanna grass sampled prior to the fire are given as "blanks" in Figure 6. The mass ratio of 0.013 derived from the regression slope (Figure 6) was used to calculate the correct H/C ratio for black carbon. An average molar H/C ratio for BC of 0.16 was obtained, which is slightly higher than that derived from experimental fires (0.11 [*Kuhlbusch and Crutzen*, 1995]). This H/C ratio is a good indicator of higher polyaromtic or elemental carbon derived from combustion processes. The intercept of 0.022±0.014% (Figure 6) represents the amount of hydrogen bonded to elements other than carbon, most probably silicate. Additionally, we show with a correlation coefficient (r^2) of 0.94 that the BC fraction can be defined by the H/C ratio.

It is possible to differentiate the three carbon fractions (OC1, OC2, and BC) in Table 2 when comparing the molar H/C ratios. OC1 with an average ratio of 1.2 is close to that of unburned residues (1.4), whereas OC2 (0.77±0.34) and BC (0.13±0.07 corrected for hydrogen not bonded to carbon, Table 2) have much lower ratios. It is interesting to note the dependence of the molar H/C ratio of OC2 material on the degree of charring (PB > A2 > A1). This may indicate that OC2 consists of two carbon fractions with different H/C ratios and that the carbon fraction with the high ratio was consumed in A2 and A1 by the fire. As discussed by *Kuhlbusch and Crutzen* [1995] this molar H/C ratio is an indicator for the degree of aromaticity and may be useful as a first approximation to predict the resistance of this carbon to microbial and chemical degradation. A decrease in the H/C ratios expresses a higher degree of aromaticity leading up to elemental or graphitic carbon. An overview of the H/C ratios for the different residues and carbon fractions is given in Figure 7.

3.1.4. Backing/heading fires carbon volatilization and BC production. Table 6 contains some indicators of the type of fire and the residues produced. In general, backing fires (spreading against the wind) have higher volatilization ratios for carbon compared to heading fires (spreading with the wind). The latter spread much faster and burn bigger areas in the same time as backing fires, albeit they are less efficient in burning vegetation. If we compare the type of fire with our measured VC values (90.8±3.7% heading fires; 86.9±7.1% backing fires) no significant differences are observed. This may be due to the inhomogeneity of the vegetation on the experimental sites and the high variability in heading fires. The ratio between carbon in the ash residue to carbon in the partially burned and unburned residue (DoC) did not show any relationship to VC or to the type of fire.

Laboratory experiments [*Kuhlbusch and Crutzen*, 1995] showed for similar vegetation higher ratios of black carbon as a fraction of the total carbon in the residue (BC/TRC) for backing compared to heading fire. *Cachier et al.* [1994] stated that heading and backing fires cannot generally be distinguished just by the BC/TC ratio in the aerosols but "samples collected under backing fire conditions during well established burning regimes from larger fires, seem to produce aerosols significantly enriched in black carbon" thus indicating similar formation laws of BC in aerosols and combustion derived residues. During SAFARI-92, residues of heading as well as backing fires on four experimental sites were collected. Two sites showed higher BC/TRC ratios for backing and two for heading fire. We measured average BC/TRC ratios of 12.0±5.0% and 8.3±3.7% for seven heading and 11 backing plots, respectively, thus

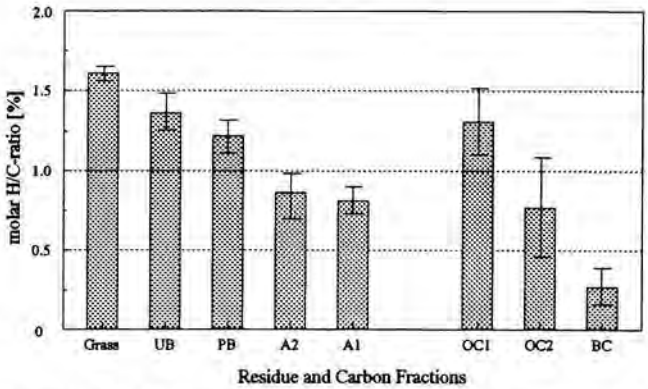


Figure 7. The molar H/C ratio for the different residue and carbon fractions. For abbreviations see Table 1.

giving no significant indication of the dependence on the type of fire. Similarly, no dependence of the conversion ratio BC/CE on the type of fire (heading 1.00±0.38%; backing 0.94±0.48%) was observed. Thus no dependence of the type of fire and the production of BC was observed under field conditions. We believe that this is due to the high variability of the fire regimes, the few measurements, and especially the patchiness of the vegetation on the plots.

3.2. Relationship Between BC Formation and the Molar CO/CO_2 Emission Ratio

In residues derived from various experimental fires under laboratory conditions [*Lobert et al.*, 1991] a negative correlation between the formation of BC and the emission ratio of CO/CO_2 as an indicator of the burning conditions was obtained [*Kuhlbusch and Crutzen*, 1995]. This indicates that flaming rather than smoldering combustion is the main source of BC. To compare this finding with the field data, the BC/TC ratio of the ash fraction was used, which eliminated any differences caused by the amount of thermally unaffected matter. Table 7 summarizes the BC/TC ratios of the ash fractions and the corresponding CO/CO_2 ratios measured by *Lacaux et al.* [this issue] and *Ward et al.* [this issue]. *Lacaux et al.* [this issue] determined the CO/CO_2 ratios with power-autonomous mobile pumping units, a NDIR-CO-CO_2 spectrometer, and emissions sampled via a pole held in the plumes. *Ward et al.* [this issue] used fixed-upright poles standing in the field, sampling the smoke in canisters when the fire burned through. The CO/CO_2 emission ratios determined by *Lacaux et al.* [this issue] were measured near the sampling plots and were used for ashes sampled by us. The ratios determined by *Ward et al.* [this issue] were used for ashes sampled by *Shea et al.* [this issue] around the fixed poles.

Table 7: Black Carbon and CO/CO_2 Emission Ratio

Plot	BC/TC for ash, %	CO/CO_2, mol-%	Type of Fire
SP5/1	12.99	4.80	B
SP5/2	10.33	5.83	H
SP5/3	12.92	5.83	H
KPE/1	11.91		H
KPE/2	15.02	4.58	B
KPE/3	20.92	4.58	B
KPE/I[a]	12.21	7.10[b]	H
KPE/II[a]	10.56	5.30[b]	H
KPE/III[a]	11.09		H
KP3/1	16.44	4.80	B
KP3/2	21.45	5.73	H
KP3/3	25.57	5.73	H
KP3/I[a]	24.51	6.20[b]	H
KP3/II[a]	18.94	8.60[b]	H
KP3/III[a]	20.11	7.20[b]	H
FP4/1	11.94	6.91	B
FP4/2	10.14	6.91	B
FP4/3	9.79	6.91	B
56/1	17.11	3.41	B
56/2	16.65	3.41	B
56/4	16.47	3.41	B
56/I[a]	14.80	7.00[b]	H
56/II[a]	17.26	8.00[b]	H
56/III[a]	14.41	7.50[b]	H
55/1	25.12		H
55/2	27.12		H
55/3	19.01		B
55/I[a]	12.30	6.50[b]	H
55/II[a]	19.30	8.10[b]	H
55/III[a]	19.50		H

CO/CO_2: measured by *Lacaux et al.* [1996].
Abbreviations are as follows: H, heading fire, fire spreading with the wind; B, backing fire, fire spreading against the wind.
[a]Sampled by Shea *et al.* [this issue].
[b]Measured by Ward *et al.* [this issue].

For the following correlation study it is important to note the variability of the CO/CO_2 ratio even within one experimental site and combustion phase. The lack of oxygen and thermal quenching especially during heading fires may cause dramatic changes in the combustion conditions expressed by CO/CO_2 ratios of up to 20% as observed by one of the authors (H.C.). Thus measuring the CO/CO_2 ratio not exactly for the sampled residue may lead to high errors and explain the lack of any relationship between the BC/TC ratio and the CO/CO_2 ratio for mixed type of fires. The combustion process is not subject to such dramatic changes during backing fire conditions, resulting in a negative regression when only backing fire samples were considered (r^2: 0.62; intercept: 24.2%; slope: -1.89; eight degrees of freedom). To improve this relationship, additional measurements and integrative sampling of residues and the corresponding emissions in the field would be required.

By using the measured CO/CO_2 ratios and assuming that CO + CO_2 accounted for 95% of the quantified volatilized carbon (CE (kilograms per hectar)-TRC (kilograms per hectar)), it was possible to compute the emitted CO_2. This enabled us to calculate the BC/CO_2 ratios (in grams C-BC/grams C-CO_2) for each plot as shown in Table 6. These data have to be looked at as a first approximation. On average the ratio of BC to CO_2 is 1.3±0.6%. This ratio is at the low end of the range of those obtained from laboratory studies (BC/CO_2 1.2-2.6% [*Kuhlbusch and Crutzen*, 1995]).

3.3. Relations Between Black Carbon Formation, Carbon Volatilization, and Degree of Charring

In this section we will discuss the mechanisms and quantitative aspects of BC formation in the residues. Figure 8a shows BC as a fraction of the total carbon in the residue (BC/TRC) plotted against VC. The positive correlation in Figure 8a indicates that the BC fraction of TRC becomes more important with an increasing volatilization ratio of carbon. This is in good agreement with results found for the different residue fractions (A1, A2, partially burned, see above) and to a laboratory study [*Kuhlbusch and Crutzen*, 1995]. In this laboratory study an equation was derived with the assumptions that the residues are homogeneous and that low VC values are accompanied by less thermal degradation of the fuel, thus forming less BC. The following equation was used:

$$BC/TRC = \frac{BC/TRC_{max}}{A^{(VC_{1/2} - VC)} + 1} \quad (1)$$

A is a constant term, BC/TRC_{max} represents the maximum BC/TRC ratio, VC is the total volatilized carbon, and $VC_{1/2}$ is

the VC value at which BC/TRC is half of BC/TRC_{max}. With BC/TRC_{max}=16.3%, $VC_{1/2}$=85.3%, and A=1.15, we calculated a correlation coefficient (r^2) of 0.38. This correlation lies within a confidence interval of 99% (t test, 16 degrees of freedom)[*Miller and Miller*, 1986]. The BC/TRC_{max} obtained from the laboratory data is about 10% lower, whereas $VC_{1/2}$ is of similar magnitude (laboratory value 88.4%). The comparatively low value of BC/TRC_{max} during this field study can be explained by the fact that laboratory fire residues had hardly any unburned or partially burned fraction.

Figure 8b shows the conversion ratio BC/CE plotted against volatilized carbon (VC), showing good agreement with the laboratory data [*Kuhlbusch and Crutzen*, 1995]. By multiplying equation (1) (see above) with TRC/CE (CE=100%) we derive equation (2) (Figure 8b):

$$BC/CE = \frac{BC/TRC_{max}}{A^{(VC_{1/2} - VC)} + 1} \times \frac{100 - VC}{100} \qquad (2)$$

With a correlation coefficient (r^2) of 0.24 the data are within a confidence interval of 95% (t test, 16 degrees of freedom)[*Miller and Miller*, 1986]. The fit is not a good one, reflecting the uncertainty in the values of CE and TRC (section 3.1.1).

The wide scatter of the data in Figure 8 compared to those of the laboratory study is due to several factors. In part it can be explained by the large standard deviation of TRC and CE (50% and 40%, respectively) from which VC was calculated. The error in BC/TRC was also higher in the field study than in the laboratory study [*Kuhlbusch and Crutzen*, 1995]. During the laboratory studies the mass burned was measured continuously during the whole experiment and only one integrative residue sample had to be analyzed. In comparison, three different fractions had to be sampled, weighed, and analyzed during this field study to calculate the BC/TRC ratio.

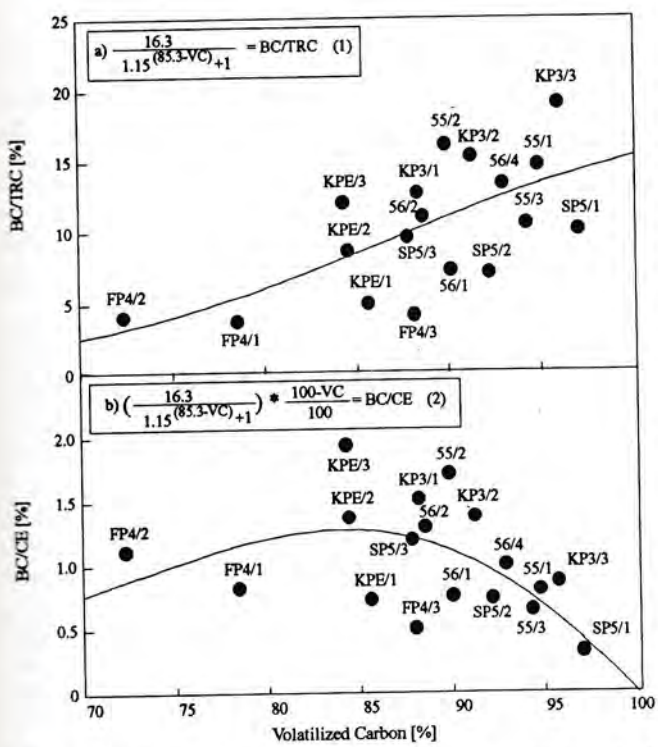


Figure 8. Black carbon in percent of the total residual and of the fire-exposed carbon as a function of the total volatilized carbon. The curves were obtained by fitting equations (1) and (2) to the determined data.

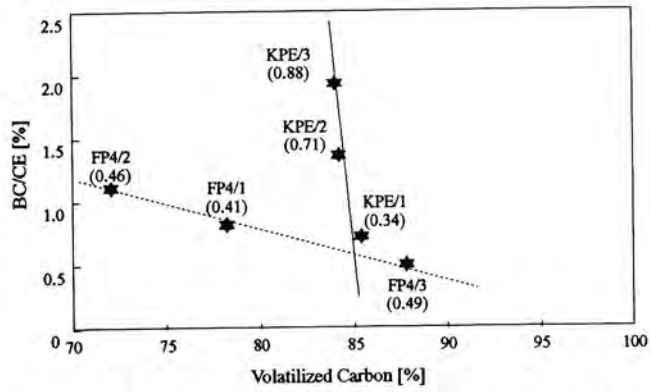


Figure 9. The conversion factor as a function of VC. The two lines indicate the dependence of the conversion factor of VC (site FP4) and on DoC (site KPE), with DoC values in parentheses.

Another reason for the above mentioned wide scatter in the field data compared to the laboratory study could be the inhomogeneity of the residues collected in this field campaign. Comparing the residues of the experimental fires [*Kuhlbusch and Crutzen*, 1995] to those sampled during SAFARI-92 there were hardly any partially burned and unburned fractions in the laboratory experiments. Therefore an indicator of the degree of charring (DoC) was defined by calculating the ratio of ash carbon to partially burned and unburned carbon (Table 6):

$$\frac{C_{(ash)}}{C_{(unburned + partially\ burned)}} = DoC \quad \text{(of the whole residue)} \qquad (3)$$

This ratio should be calculated excluding carbonates (IC); otherwise, potash (mainly K_2CO_3, residues from wood burning) would have an infinite DoC, VC < 100%, and a BC/TRC ratio of zero. But for this investigation DoC was calculated without excluding carbonates, which produced no significant error because of generally low IC contents.

On average we find a DoC ratio of 1.4, ranging from 0.3 to 3.0 (Table 6). As already mentioned for the laboratory study we hardly had any partially burned or unburned matter, giving an infinite but constant DoC ratio. Thus it is not surprising to find relatively good correlations with equations (1) and (2) for the laboratory residues with uniform charring. This difference in the residues of the laboratory and field study may be significant for the use of experimental laboratory fires, e.g., concerning nutrient cycling. One reason for the comparable high amount of UB and PB, besides the high variability of the combustion process in the field, is that especially the aboveground biomass near the soil surface remains unburned or partially burned.

To investigate the dependence of the conversion ratio BC/CE on VC and DoC in more detail, data from two experimental sites, FP4 and KPE were plotted in Figure 9. Figure 9 shows that plots on FP4 have nearly constant DoC values while the conversion ratio decreases with increasing VC. In contrast, VC values for KPE are nearly constant, and the conversion ratio increases with the degree of charring. However, it is not as

straightforward to show the combined effect of VC and DoC on the formation of BC. Further investigation to get more detailed information on the formation of BC in residues is necessary.

Another parameter which might influence the formation of BC is whether the burned matter was grass or litter. For all plots the carbon ratios of grass to litter are shown in Table 6, and it seems that no significant dependence of the formation of BC between grass and litter exists. Still such an interpretation must be considered cautiously since most of the litter was dead grass which was not very different from the yellow standing grass. Only about 5-10% of the standing grass was living, "green" grass.

3.4. Thermograms

In Figure 10, thermograms taken of PB, A2, and A1 residue samples collected on plot KPE/1 are shown. The different carbon fractions for each residue fraction of KPE/1 are given in Table 2. The heating rate for these thermograms was 108°C/min. with a gas flow of 20 vol.% O_2 in N_2 (for details see *Kuhlbusch* [1995]). The data for hydrogen and carbon in Figure 10 are plotted on the same scale so that equivalent heights express a molar H/C ratio of 1.

In Figure 1 we expressed the degree of charring by the color and structure of the sampled fraction and saw an increase from PB to A2 and then to A1. The same order of the degree of charring can be seen in the thermograms (Figure 10). Whereas the low temperature carbon peak (~500°C) in the PB sample is of similar height to the high temperature carbon peak (~600°C), it nearly completely vanishes in the A1 sample (Figure 10). The same results can be seen for hydrogen. The thermogram obtained from the A1 sample shows the same peaks and has nearly the same shape as one obtained from ash of pine needle litter [*Kuhlbusch*, 1995].

In section 3.3 we defined an indicator for the degree of charring by the amount of carbon contained in the different residue fractions. The thermograms and the observations presented in Figure 1 indicate that each residue fraction has a different degree of charring. In section 3.1.3 we saw that BC and to some extend OC2 were combustion derived. Thus we defined the following ratio as an indicator for the degree of charring within a residue fraction.

$$\frac{OC2+BC}{OC1} = DoC \quad \text{(within a residue fraction)} \qquad (4)$$

With the data given in Table 2 we calculated an average degree of charring for PB of 0.32±0.08, for A2 of 0.65±0.1, and for A1 of 2.2±1.3. The two indicators for the degree of charring (equation (3) + (4)) are not directly comparable but increase the more the organic matter was thermally affected. Since the degree of charring is constant within a residue fraction, the degree of charring for the whole residue is determined by the mass share of each residue fraction.

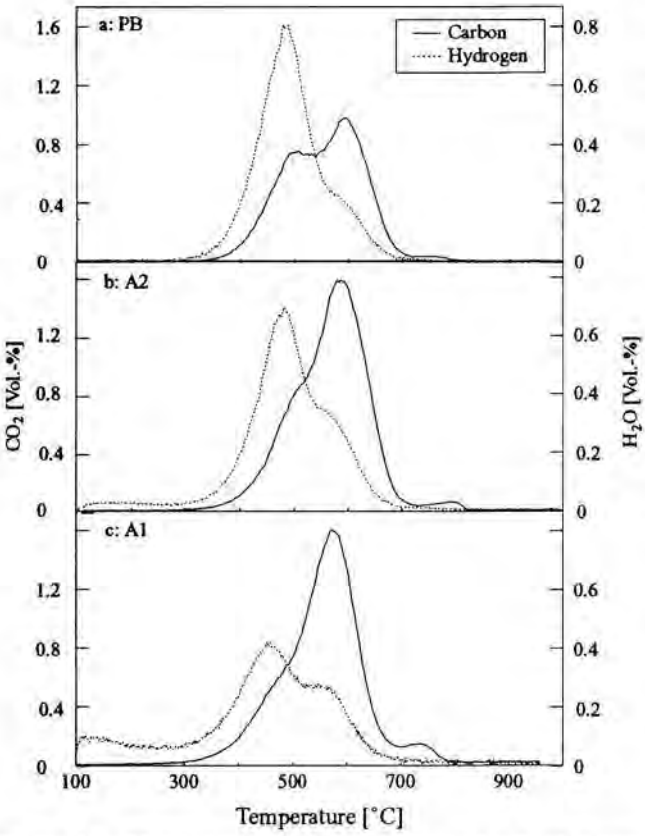


Figure 10. Thermograms of the different residue fractions on plot KPE/1. Equivalent heights for carbon and hydrogen express a molar H/C ratio of 1. The peak at temperatures above 700°C is mainly due to inorganic carbon, e.g., calcium carbonate.

4. Estimation of Black Carbon production by Savanna Fires

The global BC formation in the residues of savanna fires is estimated in three different ways: (1) by the BC/CO_2 ratio (1.3%, see section 3.2); (2) by the BC/CE-conversion ratio; and (3) by the BC/TRC ratio. The range for the BC/CE-conversion ratio derived from Figure 8b for an average volatilization ratio of carbon of approximately 90% (89% for the six experimental fires during SAFARI-92) was between 0.5 and 2%. To estimate the formation of BC by savanna fires in Table 8 by using the exposed carbon weighting an average conversion ratio of 1% was used. The average BC/TRC ratio derived from Table 6 is 9.8±4.6%. Thus a ratio of 10% was used in Table 8 when using the amount of residue left on the ground.

A comparison of the BC/CO_2 ratio of 1.3% for the black carbon formation in the residue to the one for BC in the carbonaceous aerosol fraction (0.11% [*Cachier et al.*, 1994]) indicates that more than 90% of the BC produced by a fire remains on site in the residues. A BC/CO_2 ratio of 0.11% was used in Table 8 to calculate the amount of BC emitted in the smoke.

In Table 8 we summarize regional and worldwide estimates of vegetation affected by savanna fires. With these estimates and the above mentioned factors we calculated the production rate of BC. In the second column from the right we averaged the different estimates of BC in the residues and added the BC emitted in the smoke. About 70% of all BC formed by savanna fires is produced in Africa. On average, 18 Tg BC (10-26 Tg BC) is annually produced by savanna fires. This formation rate is 4-52% of the total amount of BC produced annually by vegetation fires worldwide (50-270 Tg BC [*Kuhlbusch and Crutzen*, 1995]).

The BC formed by savanna fires represents a net O_2 source of 27-69 Tg yr^{-1} and a CO_2 sink of 10-26 Tg C yr^{-1}. The carbon

Table 8: Estimates of BC Formation by Savanna Fires in Different Regions of the World

Region	Vegetation Exposed to Fire, dm yr^{-1}	Vegetation Burned, dm yr^{-1}	Residual Mass, dm yr^{-1}	Carbon Exposed to Fire,[a] C yr^{-1}	Carbon in the Residue,[b] C yr^{-1}	Carbon Emitted,[c] C yr^{-1}	CO_2 Emitted,[d] C yr^{-1}	BC in the Smoke,[e] C yr^{-1}	BC in the Residue,[f] C yr^{-1} by BC/CO_2	BC in the Residue,[g] C yr^{-1} by BC/CE	BC in the Residue,[h] C yr^{-1} by BC/TRC	BC Total Average, C yr^{-1}	Source
America	924[i]	767[i]	157[i]	345	31	314	282	0.34	3.67	3.45	3.14	3.76	*Hao et al.* [1990]
Africa	2925[i]	2428[i]	497[i]	1093	99	993	894	1.07	11.62	10.93	9.94	11.90	*Hao et al.* [1990]
	3132[i]	2520[i]	612[i]	1134	122	1012	910	1.09	11.84	11.34	12.24	12.90	*Delmas et al.* [1991]
	1566	1300[i]	266	900	53	532	479	0.57	6.22	5.85	5.33	6.37	*Lacaux et al.* [1993]
West Africa							119.5[i]	0.14	1.55			1.70	*Menaut et al.* [1991]
Australia	512[i]	425[i]	87[i]	191	17	174	156	0.19	2.03	1.91	1.74	2.08	*Hao et al.* [1990]
	292[i]	242[i]	50	131	20	111[i]	100	0.12	1.30	1.32	2.00	1.66	*Hurst et al.* [1994]
						48[i]	43	0.05	0.56			0.61	*Cheney et*
						190[i]	171	0.21	2.22			2.43	*al.* [1980]
Asia	86[i]	71[i]	15[i]	32	3	29	26	0.03	0.34	0.32	0.30	0.35	*Hao et al.* [1990]
World	3953	3254	699	1475	145	1319	1187	1.42	15.43	14.75	14.48	16.20	this table
World	4447[i]	3691[i]	756[i]	1661	151	1510	1359	1.63	17.66	16.61	15.12	18.10	*Hao et al.* [1990]
				400[i]	100	300[i]	270	0.32	3.51	4.00	10.00	6.16	*Crutzen and Andreae*
				2000[i]	400	1600[i]	1440	1.73	18.72	20.00	40.00	27.97	[1990]

All values are in teragrams (10^{12}g) dry mass (dm) or carbon per year.
[a]Forty-five percent carbon content in exposed vegetation [this work; *Hurst et al.*, 1994; *Menaut et al.*, 1991].
[b]Twenty percent carbon content in residue [this work; *Hurst et al.*, 1994; *Jenkins et al.*, 1991].
[c]Carbon exposed minus carbon in residue.
[d]Ninety-five percent of emitted carbon as CO_2 [*Crutzen and Andreae*, 1990; *Lobert et al.*, 1991].
[e]Equal to 0.11% of carbon emitted [*Cachier et al.*, 1994; *Patterson et al.*, 1986].
[f]BC/CO_2 is 1.3% [this work].
[g]BC/CE is 1.0% [this work].
[h]BC/TC is 10% [this work].
[i]Data from the indicated sources.

fixed prior to the fire in the vegetation was part of the biospheric carbon cycle. By conversion to BC it is sequestered from the short-term to the long-term (geological) carbon cycle. Black carbon produced in savanna fires represents a net carbon sink considering that periodic savanna fires do not represent a net source of atmospheric CO_2 because of the regrowth during the growing season.

5. Summary and Conclusions

In this field study the C, H, S, and N loadings in the biomass before and after the fires were determined, and average volatilization ratios for these elements of 88±6%, 92±5%, 86±8%, and 74±11%, respectively, on the six experimental sites obtained. By partitioning the residue in unburned, partially burned, A2 (> 0.63 mm), and A1 (< 0.63 mm) fractions, a correlation between the degree of charring of a residue fraction and the corresponding molar H/C ratio was established. A2, comprising approximately 11% of the residual mass, was chemically different from the other residue fractions. A2 was significantly enriched in nitrogen and carbon, and had a molar H/C ratio (0.86±0.14) of that of A1. Black carbon was quantified in the different residue fractions. Various correlation studies were conducted to derive detailed information on formation mechanisms and quantities of black carbon. Comparing the results obtained from this field study to those from experimental fires under laboratory conditions, it was found that the field residues were much more inhomogeneous and of different structure. Thus, besides the dependence of the formation of black carbon on the volatilized carbon a second factor was identified, the degree of charring. This latter factor might affect nutrients in the vegetation fire residues as well. Based on these results and various estimates of carbon exposed or released by savanna fires we estimate the worldwide black carbon deposition in the residue of savannas to be 9-24 Tg C yr^{-1}. Adding the 1-2 Tg BC yr^{-1} in the smoke of savanna fires, 10-26 Tg black carbon are produced annually. Since this black carbon will not be broken down over geological timescales it represents a net sink of atmospheric CO_2 and a source of 27-69 Tg O_2 yr^{-1}.

Acknowledgments. The authors would like to thank the staff of the Kruger National Park, A. Potgieter, and L. Trollope for enabling and organizing SAFARI-92 in the Kruger Park. We also wish to thank K. Weiß, R. Wirz, H. Abberger, and U. Petersen for their collection of vegetation and residue samples, and W. Dindorf for the elemental analyses for S and N. Thanks are extended to M. Berges, R. Cox, and the reviewers N. Cheney and P. Khanna for reviewing and certainly improving the manuscript. It was a great pleasure to work with all the people involved in SAFARI-92.

References

Cachier, H., C. Liousse, P. Buat-Ménard, and A. Gaudichet, Particulate content of savanna fire emissions, *J. Atmos. Chem.*, in press, 1994.

Chang, S. G., R. Brodzinsky, L. A. Gundel, and T. Novakov, Chemical and catalytic properties of elemental carbon, in *Particulate Carbon: Atmospheric Lifecycle*, edited by G. T. Wolff and R. L. Klimisch, pp. 159-181, Plenum, New York, 1982.

Cheney, N. P., R. J. Raison, and P. K. Khanna, Release of carbon to the atmosphere in Australian vegetation fires, in *Carbon Dioxide and Climate: Australian Research*, edited by G. I. Pearman, pp. 153-158, Aust. Acad. of Sci., Canberra, 1980.

Chylek, P., V. Srivastava, L. Cahenzli, R. G. Pinnick, R. L. Dod, T. Novakov, T. L. Cook, and B. D. Hinds, Aerosol and graphitic carbon content of snow, *J. Geophys. Res.*, *92*, 9801-9809, 1987.

Clark, J. S., and J. Robinson, Paleoecology of fire, in *Dahlem Workshop Reports: Fire in the Environment: The Ecological, Atmospheric, and Climatic Importance of Vegetation Fires*, edited by P. J. Crutzen and J. G. Goldammer, pp. 193-213, Dahlem Workshop, John Wiley, New York, 1993.

Comery, J. A., G. R. Fahnestock, and S. G. Pickford, Elemental carbon deposition and flux from prescribed burning on a longleaf pine site in Florida, in *final report to the National Center for Atmospheric Research*, College of Forest Resources, University of Washington, Seattle, WA, 1981.

Cook, G. D. The fate of nutrients during fires in a tropical savanna, *Aust. J. Ecol.*, *19*, 359-365, 1994.

Cope, M. J., and W. G. Chaloner, Fossil charcoal evidence of past atmospheric composition, *Nature*, *283*, 647-649, 1980.

Crutzen, P. J., and M. O. Andreae, Biomass burning in the tropics: Impact on atmospheric chemistry and biogeochemical cycles, *Science*, *250*, 1669-1678, 1990.

De Kok, L. J., Sulfur metabolism in plants exposed to atmospheric sulfur, in *Sulfur Nutrition and Sulfur Assimilation in Higher Plants*, edited by H. Rennenberg, C. Brunold, L. J. De Kok, and I. Stulen, pp. 111-130, SPB Acad., The Hague, Netherlands, 1990.

Delmas, R. A., On the emission of carbon, nitrogen, and sulfur in the atmosphere during bushfires in intertropical savannah zones, *Geophys. Res. Lett.*, *9*, 761-764, 1982.

Delmas, R. A., P. Loudjani, A. Podaire, and J.-C. Menaut, Biomass burning in Africa: Assessment of annually burned biomass, in *Global Biomass Burning*, edited by J. S. Levine, pp. 126-131, MIT Press, Cambridge, Mass., 1991.

Delmas, R., J.-P. Lacaux, J. C. Menaut, L. Abbadie, X. Le Roux, G. Helas, and J. M. Lobert, Nitrogen compound emission from biomass burning in tropical African Savanna FOS/DECAFE 91 Experiment (Lamto, Ivory Coast), *J. Atmos. Chem.*, in press, 1994.

Edwards, J. B., *Combustion: Formation and Emission of Trace Species*, Technomic, Lancaster, Pa., 1974.

Fearnside, P. M., Greenhouse gas contributions from deforestation in Brazilian Amazonia, in *Global Biomass Burning*, edited by J. S. Levine, pp. 92-105, MIT Press, Cambridge, Mass., 1991.

Hao, W. M., M.-H. Liu, and P. J. Crutzen, Estimates of annual and regional releases of CO_2 and other trace gases to the atmosphere from fires in the tropics, based on the FAO statistics for the period 1975-1980, in *Fire in the Tropical Biota*, edited by J. G. Goldammer, pp. 440-462, Springer, New York, 1990.

Herring, J. R., Charcoal fluxes into Cenozoic sediments of the North Pacific, Ph.D. thesis, Scripps Inst. of Oceanogr., Univ. of Calif., San Diego, La Jolla, 1977.

Houghton, R. A., Tropical deforestation and atmospheric carbon dioxide, *Clim. Change*, *19*, 99-118, 1991.

Hurst, D. F., D. W. T. Griffith, and G. C. Cook, Trace gas emissions from biomass burning in tropical Australian savannas, *J. Geophys. Res.*, *99*, 16441-16456, 1994.

Jenkins, B. M., S. Q. Turn, R. B. Williams, D. P. Y. Chang, O. G. Raabe, J. Paskind, and S. Teague, Quantitative assessment of gaseous and condensed phase emissions from open burning of biomass in a combustion wind tunnel, in *Global Biomass Burning*, edited by J. S. Levine, pp. 305-317, MIT Press, Cambridge, Mass., 1991.

Kauffman, J. B., D. L. Cunnings, D. E. Ward, and R. Babbitt, Fire in the Brazilian Amazon: Biomass, nutrient pools, and losses in slashed primary forests, *Oecologia*, in press, 1995.

Kuhlbusch, T. A. J., Method determining black carbon in residues of vegetation fires, *Environ. Sci. & Techn.*, *29*, 2695-2702, 1995.

Kuhlbusch, T. A. J., and P. J. Crutzen, Toward a global estimate of black carbon in residues of vegetation fires representing a sink of atmospheric CO_2 and source of O_2, *Global Biogeochem. Cycles*, *9*, 491-501, 1995.

Lacaux, J.-P., H. Cachier, and R. Delmas, Biomass burning in Africa: An overview of its impact on atmospheric chemistry, in *Dahlem Workshop Reports: Fire in the Environment: The Ecological, Atmospheric, and Climatic Importance of Vegetation Fires*, edited by P. J. Crutzen and J. G. Goldammer, pp. 159-188, John Wiley, New York, 1993.

Lacaux, J.-P., D. Brocard, C. Lacaux, R. Delmas, A. Brou, V. Yoboué, and M. Koffi, Traditional charcoal making: An important source of atmospheric pollution in the African tropics, *Atmos. Res.*, *35*, 71-76, 1994a.

Lacaux, J.-P., J. M. Brustet, R. Delmas, J. C. Menaut, L. Abbadie, B. Bonsang, H. Cachier, J. Baudet, M. O. Andreae, and G. Helas, Biomass burning in the tropical savannas of Ivory Coast: An overview of the field experiment Fire of Savannas (FOS/DECAFE 91), *J. Atmos. Chem.*, in press, 1994b.

Lacaux, J. P., R. Delmas, C. Jambert and T. A. J. Kuhlbusch, NO_x emissions from African savanna fires, *J. Geophys. Res.*, this issue.

Lobert, J. M., Verbrennung pflanzlicher Biomasse als Quelle atmosphärischer Spurengase: Cyanoverbindungen, CO, CO_2, und NO_x, Ph.D. thesis, Johannes Gutenberg-Univ. Mainz, Germany, 1989.

Lobert, J. M., D. H. Scharffe, W. Hao, T. A. J. Kuhlbusch, R. Seuwen, P. Warneck, and P. J. Crutzen, Experimental evaluation of biomass burning emissions: Nitrogen and carbon containing compounds, in *Global Biomass Burning*, edited by J. S. Levine, pp. 289-304, MIT Press, Cambridge, Mass., 1991.

Mack, F., The influence of vegetation fires on the global carbon cycle, Ph.D. thesis, Inst. for Plant Ecol., Justus-Liebig-Univ., Gießen, Germany, 1994.

Menaut, J.-C., L. Abbadie, F. Lavenu, P. Loudjani, and A. Podaire, Biomass burning in west African savannas, in *Global Biomass Burning*, edited by J. S. Levine, pp. 133-142, MIT Press, Cambridge, Mass., 1991.

Miller, J. C., and J. N. Miller, *Statistics for analytical chemistry*, pp. 89-91, Ellis Horwood, Chichester, England, 1986.

Ogren, J. A. and R. J. Charlson, Elemental carbon in the atmosphere: Cycle and lifetime, *Tellus*, *35*, 241-254, 1982.

Patterson, E. M., C. K. McMahon, and D. E. Ward, Absorption properties and graphitic carbon emission factors of forest fire aerosols, *Geophys. Res. Let.*, *13*, 129-132, 1986.

Penner, J. E., H. Eddleman and T. Novakov, Towards the development of a global inventory for black carbon emissions, *Atmos. Environ.*, *27A*, 1277-1295, 1993.

Sanborn, P. T., and T. M. Ballard, Combustion losses of sulphur from conifer foliage: Implications of chemical form and soil nitrogen status, *Biogeochemistry*, *12*, 129-134, 1991.

Seiler, W., and P. J. Crutzen, Estimates of gross and net fluxes of carbon between the biosphere and the atmosphere from biomass burning, *Clim. Change*, *2*, 207-247, 1980.

Sharrow, S. and H. A. Wright, Effects of fire, ash, and litter on soil nitrate, temperature, moisture and to Tobosagrass production in the rolling planes, *J. Range Manage.*, *30*, 260-270, 1977.

Shea, R. W., B. W. Shea, J. B. Kauffman, D. E. Ward, C. I. Haskins, M. C. Scholes, Fuel biomass and combustion factors associated with fires in savanna ecosystems of South Africa and Zambia, *J. Geophys. Res.*, this issue.

Sternberg, H. O., Man and environmental change in South America, in *Biogeography and Ecology in South America*, edited by E. J. Fittkau, T. S. Elias, H. Klinge, C. H. Schwabe, and H. Sioli, pp. 413-445, SPB Acad., The Hague, Netherlands, 1968.

Suman, D. O., T. A. J. Kuhlbusch, and B. Lim, Marine sediments: A reservoir for black carbon and their use as spatial and temporal records of combustion, in *Sediment records of biomass burning and global change*, edited by J. S. Clark, H. Cachier, J. G. Goldammer, and B. J. Stocks, Springer, in press, 1996.

Trollope, W. S. W., A. L. F. Potgieter, N. Zambatis, and L. A. Trollope, SAFARI-92: Characterization of biomass and fire behavior in controlled burns in the Kruger National Park, *J. Geophys. Res.*, this issue.

Ward, D. E., W. M. Hao, R. A. Susott, R. A. Babbitt, R. W. Shea, J. B. Kauffman, and C. O. Justice, Effect of fuel composition on combustion efficiency and emission factors for African savanna ecosystems, *J. Geophys. Res.*, this issue.

M. O. Andreae and J. G. Goldammer, Biogeochemie, Max-Planck-Institut für Chemie, Postfach 3060, 55020 Mainz, Germany. (e-mail: moa@cco.caltech.edu; jggold@ruf.uni-freiburg.de)

H. Cachier, Centre des Faibles Radiactivites, Laboratoire mixte CNRS-CEA, avenue de la Terrasse, 91198 - GIF sur Yvette CEDEX, France. (e-mail: Helene.Cachier@cfr.cnrs-gif.fr)

P. J. Crutzen, Luftchemie, Max-Planck-Institut für Chemie, Postfach 3060, 55020 Mainz, Germany.

T. A. J. Kuhlbusch, NERL, U.S. Environmental Protection Agency, 960 College Station Rd., Athens, GA 30605. (e-mail: Kuhlbusch.Thomas@epamail.epa.gov)

J.-P. Lacaux, Laboratoire d'Aérologie, CNRS-UPS, 14 avenue Eduard Belin, 31400 Toulouse, France. (e-mail: lacjp@aero.obs-mip.fr)

R. Shea, 2855 NW Johnson Avenue, Corvallis, OR 97330.

(Received July 20, 1994; revised July 8, 1995;
accepted July 8, 1995.)