

## Airborne measurements of carbonaceous aerosols in southern Africa during the dry biomass burning season

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[1] Particulate matter collected aboard the University of Washington's (UW) Convair-580 research aircraft over southern Africa during the dry biomass burning season was analyzed for total carbon (TC), organic carbon (OC), and black carbon (BC) contents using thermal and optical methods. Samples were collected in smoke plumes of burning savanna and in regional haze. A known artifact, produced by the adsorption of organic gases on the quartz filter substrates used to collect the particulate matter samples, comprised a significant portion of the TC collected. Consequently, conclusions derived from the data are greatly dependent on whether or not OC concentrations are corrected for this artifact. For example, the estimated aerosol coalbedo ( $1 - \text{single scattering albedo (SSA)}$ ), which is a measure of aerosol absorption, of the biomass smoke samples is 60% larger using corrected OC concentrations. Thus, the corrected data imply that the biomass smoke is 60% more absorbing than do the uncorrected data. The BC to (corrected) OC mass ratio (BC/OC) of smoke plume samples ( $0.18 \pm 0.06$ ) is lower than that of samples collected in the regional haze ( $0.25 \pm 0.08$ ). The difference may be due to mixing of biomass smoke with background air characterized by a higher BC/OC ratio. A simple source apportionment indicates that biomass smoke contributes about three quarters of the aerosol burden in the regional haze, while other sources (e.g., fossil fuel burning) contribute the remainder. *INDEX TERMS*: 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 9305 Information Related to Geographic Region: Africa; *KEYWORDS*: organic carbon, black carbon, SAFARI, positive sampling artifact, evolved gas analysis, light absorption

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### 1. Introduction

[2] Biomass burning is a major source of aerosol particles. Biomass-derived aerosols impact regional, and likely global, atmospheric radiation budgets by perturbing light extinction and cloud microphysical processes [Andreae, 1997]. Savanna fires, including those in tropical Africa, comprise the largest fraction of biomass emissions worldwide [Hao and Liu, 1994].

[3] Carbonaceous material, composed mainly of light-scattering organic carbon (OC) and light-absorbing black carbon (BC), comprises a large fraction of biomass smoke particle mass [Cachier *et al.*, 1995; Andreae *et al.*, 1998]. It is therefore important to accurately measure the concentrations and optical properties of this carbonaceous material to properly assess the radiative effects of biomass smoke.

[4] In this paper, we discuss airborne measurements of carbonaceous aerosols during the South African Regional Science Initiative (SAFARI 2000). The aerosol sampling was

performed from the University of Washington's (UW) Convair-580 research aircraft in August and September 2000. A description of all of the measurements made aboard the Convair-580 aircraft, and the flight paths during SAFARI 2000, are given by P. V. Hobbs [Sinha *et al.*, 2003, Appendix]. A description of the fires encountered, including locations and vegetation types, is given by Sinha *et al.* [2003].

[5] The focus of this paper is the sampling and analytical procedures relevant to the determination of carbonaceous aerosol concentrations. Particular emphasis is placed on an artifact that can introduce an uncertainty in the measurement of carbonaceous aerosol concentrations [Turpin *et al.*, 2000]. We discuss the magnitude of this artifact, and demonstrate its impact on derived concentrations and inferred optical properties of the carbonaceous aerosols.

### 2. Experimental

#### 2.1. Sample Collection

[6] Particulate matter in smoke plumes was collected using a custom built sampling apparatus. It was constructed to facilitate point sampling and filled a 2.5 m<sup>3</sup> bag made of

velostat (carbon-doped, electrically conducting polyethylene; 3M Worldwide) within a few seconds. This is particularly useful for sampling smoke plumes because the aircraft flies through plumes too quickly for many analytical systems to sample adequate volume. After filling, air from the bag was drawn through quartz filters supported in stainless steel holders, typically over a period of 5–15 min, to collect samples of particulate matter for subsequent analyses. The bag sampler was not used to collect samples when the aircraft was outside of the direct influence of smoke plumes (hereafter referred to as haze samples). In this case, the air was drawn from the stainless steel sample line at a point prior to the bag inlet. In both cases, the aerosol intake system had an effective particle size cutoff of about 4  $\mu\text{m}$  in diameter [Hobbs *et al.*, 2003].

[7] Two quartz filters were placed in tandem (front and backup) in the filter holder during sample collection. We used this filter configuration to correct the loading of OC for an artifact that results from the adsorption of organic gases [e.g., Turpin *et al.*, 1994; Kirchstetter *et al.*, 2001]. Organic gases adsorb on the quartz fiber filter during sampling and may lead to overestimation of particulate carbon concentration; this is referred to as the positive artifact. The backup filter can be used to estimate the contribution of adsorbed organic gases to the carbon content of the front quartz filter provided the amount of adsorption is the same on both filters. Correcting for this artifact significantly influences the derived total carbon (TC = OC + BC) and OC concentrations, as shown below.

[8] Forty-seven millimeter quartz filters (Pallflex 2500 QAT-UP) were precleaned of residual carbonaceous material by baking them in a furnace at 800°C in air for about 6 hours. The filters were stored in clean glass jars with Teflon-lined caps until needed for sample collection. Samples collected on Teflon filters for subsequent gravimetric mass, ion and individual organic compound analyses are discussed by Gao *et al.* [2003]. Filters that were loaded into filter holders and flown aboard the aircraft but not used for sample collection were used as field blanks. Field blanks were momentarily exposed to cabin air as they were connected to the sampling system, thereby mimicking the handling of the filters used to collect samples.

## 2.2. Analytical Methods

[9] The evolved gas analysis (EGA) method was used to analyze the carbonaceous material collected on the quartz filter samples. The EGA method [Novakov, 1981, 1982] and recent applications [Kirchstetter *et al.*, 2000, 2001] have been described previously. In EGA, a portion of the sample, typically one or more 1.1  $\text{cm}^2$  circular punches, is heated from room temperature to an endpoint temperature at a linear rate of increase in a pure oxygen atmosphere. The heating rate was 40°C  $\text{min}^{-1}$  for this study. In general, all noncarbonate carbon completely evolves from the filter by 650°C. The carbon containing gases, evolving from the sample as a result of evaporation, decomposition, and combustion, pass over a bed of  $\text{MnO}_2$  catalyst maintained at approximately 800°C to ensure their complete oxidation to  $\text{CO}_2$ . A nondispersive infrared analyzer (Beckman Model 870) is used to measure the concentration of  $\text{CO}_2$  throughout the process.

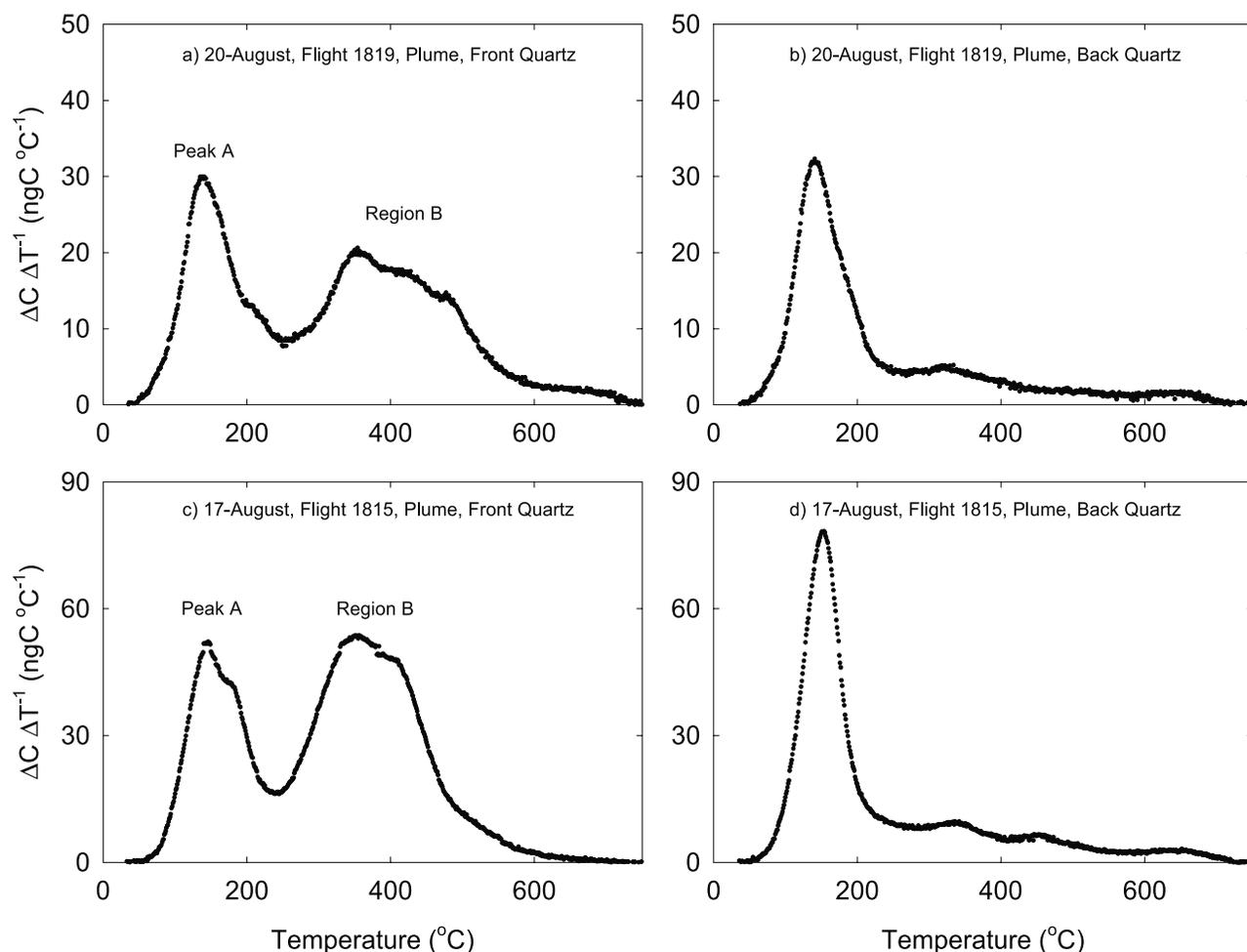
[10] The output of the analysis is a thermogram: a plot of  $\text{CO}_2$  concentration (more properly the rate of evolution of

carbon,  $\Delta C/\Delta T$ ) versus sample temperature. A thermogram is qualitatively similar to a chromatogram except that the thermogram peaks are generally broad and not the result of a single compound, but many compounds. The temperature at which a compound will evolve depends on its volatility and its interaction with the filter substrate and other material contained in the sample. The area under the thermogram curve is proportional to the TC content of the analyzed sample. OC evolves at lower temperatures than the more refractory BC. However, it is not always clear at what temperature the evolution of OC ends and the evolution of BC begins. Coevolution of OC and BC due to catalytically induced combustion of BC (e.g., by potassium or calcium contained in the sample [Novakov and Corrigan, 1995]), or the presence of highly refractory OC, results in a thermogram that does not have a distinct BC peak.

[11] Since biomass smoke may exhibit both of the aforementioned traits, we measured the BC content of samples using a light transmission method similar to that described by Rosen and Novakov [1983]. BC is the principal absorbing aerosol component and its surface concentration on the filter is proportional to the attenuation of light (ATN) transmitted through the particle deposit [Gundel *et al.*, 1984].  $\text{ATN} = 100 \times \ln(I_0/I)$ , where  $I_0$  and  $I$  are the transmitted light intensities through the clean and particle-laden filter, respectively. The BC surface concentration is related to ATN according to the following equation:  $\text{BC} (\mu\text{g cm}^{-2}) = \text{ATN}/\sigma$ , where  $\sigma$  ( $\text{m}^2 \text{g}^{-1}$ ) is the specific attenuation coefficient. We used a value of  $\sigma = 20 \text{ m}^2 \text{g}^{-1}$  for the reasons discussed below.

[12] The spectral response of our light transmission device is governed by the light source, which is an incandescent bulb, and the silicon photodiode detector. The energy emitted from incandescent bulbs and the spectral response of silicon photodiodes is greatest in the infrared region (approximately 750–1000 nm) of the electromagnetic spectrum. We determined the effective spectral response of our light transmission device by measuring light absorption by various particulate matter samples ( $n = 25$ ) on quartz filters with the transmission device and a light spectrometer. Absorption measurements of the light transmission device were equal to those of the light spectrometer at  $890 \pm 65 \text{ nm}$ . Our use of  $\sigma = 20 \text{ m}^2 \text{g}^{-1}$  at 890 nm is consistent with the empirical value of  $\sigma = 25 \text{ m}^2 \text{g}^{-1}$  that Gundel *et al.* [1984] derived by comparing BC concentrations measured using the EGA method and light absorption measurements made with the light transmission device equipped with a 633 nm He-Ne laser (rather than an incandescent bulb), and a  $\lambda^{-1}$  spectral dependence of absorption by BC [Bergstrom *et al.*, 2002]. More recently, we confirmed the empirical value of  $\sigma = 20 \text{ m}^2 \text{g}^{-1}$  using the light transmission device equipped with an incandescent bulb and the experimental method of Gundel *et al.* [1984]. Finally, we note that our use  $\sigma = 20 \text{ m}^2 \text{g}^{-1}$  is consistent the calibration factor of the commercial aethalometer, which is a very similar optical transmission technique [Bodhaine, 1995].

[13] The precision of the EGA instrument, based on replicate analyses of standards (potassium phthalate and glucose solutions applied to filters) and samples, is 5% for TC. A greater source of uncertainty is the result of sampling artifacts: the positive artifact referred to above and a



**Figure 1.** Thermograms of front and back quartz filters for two biomass smoke plume samples: 20 August, UW flight 1819 (a) front quartz and (b) back quartz and 17 August, UW flight 1815 (c) front quartz and (d) back quartz.

negative artifact due to evaporation of organic particles during sample collection [e.g., Cui *et al.*, 1998]. These artifacts can introduce errors that are much greater in magnitude than those of the analytical method. We consider the magnitude of the positive artifact in this paper. Eatough *et al.* [2003] discuss the negative artifact. The uncertainty in BC concentrations is related to the value of the specific attenuation coefficient [e.g., Lioussse *et al.*, 1993; Petzold *et al.*, 1997].

### 3. Results and Discussion

#### 3.1. Determination of Carbon Loading on the Filters

[14] Since there is not a standard methodology for dealing with the sampling artifacts, we describe how the EGA method provides a means to correct for the positive sampling artifact. The approach is a refinement of that used by Novakov *et al.* [1997].

[15] Carbon thermograms of the front and backup filters of one biomass smoke plume sample are shown in Figures 1a and 1b. Determination of the TC loading of this sample is straightforward. The most volatile organic material in the sample (peak A) evolved first during analysis, and a nearly

equal amount of this material was collected on both the front and backup filters. Less volatile material (region B, which is several coevolving peaks) was collected predominantly on the front filter. This material consisted of both OC and BC, as evidenced by the darkness of the filter deposit (as well as the measurement of light absorption by the deposit).

[16] In view of the high particle filtration efficiency of quartz filters, we can safely assume that the carbonaceous material on the backup filter is the result of adsorption of organic gases. Given the similarity in evolution temperature, shape, and area of peak A in the thermograms of the front and back filters, and knowing that an adsorbed organic gas will produce similar front and back filter thermograms [Kirchstetter *et al.*, 2001], we conclude that the front and back filters collected the same gas-phase organic compounds. Therefore, the TC content of the front filter is an overestimate of the amount of particulate carbon in the air that was filtered. In this case, subtraction of the OC loading on the backup filter from that on the front filter is a valid way to correct for the positive absorption artifact.

[17] Thermograms features of some samples, exemplified by those shown in Figures 1c and 1d, differ from those

described above. For these samples, the correction for the absorption artifact is not straightforward because the peak attributed to the adsorption of organic gases (peak A) is greater in area in the thermogram of the backup filter. While it is plausible that the front filter may absorb a greater mass of gas-phase organic compounds than the back filter (because the front filter may diminish the concentration of the gas-phase organics in the air prior to passage through the back filter), it is not expected that adsorption on the back filter will be in excess of that on the front filter. Nonetheless, our interpretation of Figures 1c and 1d, which are representative of many of our samples, is that the mass of organic gases adsorbed on the back filter is greater than that on the front filter.

[18] If our interpretation of Figures 1c and 1d is correct, then it is not appropriate to subtract the total mass of organics on the back filter from that on the front filter. This would overcorrect TC and OC concentrations for the positive artifact. Therefore, when estimating TC and OC concentrations for these cases, we attributed all of the carbonaceous material evolving below  $\sim 180^\circ\text{C}$  to the adsorption of organic gases and limited the integration of the thermograms to the regions above the evolution of peak A. Likewise, *Novakov et al.* [1997] concluded that the carbonaceous material that evolved from quartz filters below  $180^\circ\text{C}$  was due entirely to the positive adsorption artifact and, therefore, limited integration of thermograms to temperatures above this cutoff.

[19] At present we do not have enough information to explain why many back filters adsorbed a greater mass of organic gases than their corresponding front filters. *Kirchstetter et al.* [2001] reported that variability in the adsorption capacity of quartz filters could result in such a disparity. The variable adsorption capacity was observed with front and back filters that were cut from different manufacture lots of filter material. In this study, however, we cut all the filters from the same lot of filter material.

[20] Our observation challenges the validity of the tandem filter method commonly employed to correct for the positive sampling artifact because the tandem filter method is valid only if the back filter adsorbs the same amount of organic gases as the front filter. Despite the fact that our observation (of excess adsorption on the back filter) has not been discussed previously in the literature, it is possible that the tandem filter method may often be inappropriately used unintentionally. Widely used methods for analyzing quartz filters for carbon content may not thermally resolve the carbonaceous material finely enough to distinguish between adsorbed gases and collected particles. The two-step methods [e.g., *Lavanchy et al.*, 1999; *Cachier et al.*, 1989] do not thermally resolve the OC in the sample. The thermal-optical analytical methods [e.g., *Birch and Cary*, 1996; *Chow et al.*, 1993] resolve the OC into several fractions (e.g., OC1, OC2, OC3, and OC4) through a stepwise ramping of the sample temperature. The resolution of these methods may be fine enough to assess the validity of the tandem filter method as we have done here, but any such attempt is not known to us.

[21] It is possible that the velostat bag used for “grab” samples within smoke plumes may have emitted organic vapors and contributed to the positive quartz filter artifact.

However, the magnitude of this artifact was larger for haze samples (not collected with velostat bag) than for smoke samples, and the plume and haze samples collected with quartz filters using an independent sampler aboard the Convair-580 aircraft were similarly afflicted by the positive sampling artifact [*Eatough et al.*, 2003]. These observations are a strong indication that the artifact was not solely a result of the velostat bag.

[22] Last, we do not expect that a negative sampling artifact, which may result if particulate material evaporates after it is collected on the front filter, interfered with the tandem filter method we employed to correct for the positive artifact (i.e., back filter carbon subtracted from front filter carbon). If particulate matter evaporates after collection, it may adsorb to some extent onto the filters, or it may fully pass through the filters. *Eatough et al.* [2003] used a diffusion denuder sampler to collect particulate matter samples aboard the Convair-580 aircraft and found that quartz filters did not appreciably collect evaporated carbonaceous material. *Turpin et al.* [2000] also reported that quartz filters do not efficiently adsorb organic material that evaporates from collected particles.

### 3.2. Carbonaceous Aerosol Concentrations

[23] The average TC loading ( $\mu\text{g cm}^{-2}$ ) of biomass smoke and haze samples (14.7 and 12.2, respectively) was an order of magnitude larger than that of the field blanks ( $1.1 \pm 0.3$ ,  $n = 8$ ). Similarly, the average BC content ( $\mu\text{g cm}^{-2}$ ) of the blanks was small ( $0.00 \pm 0.05$ ,  $n = 8$ ) compared to that of biomass smoke and haze samples (0.64 and 0.60, respectively). Since the samples were loaded well above blank levels, and the correction for the positive sampling artifact inherently adjusts for filter contamination (i.e., (front filter – blank) – (back filter – blank) = front filter – back filter), no blank corrections were made.

[24] TC and BC concentrations ( $\mu\text{g m}^{-3}$ ) were calculated from the measured filter mass loadings ( $\mu\text{g}$ ), adjusted as discussed above for the positive adsorption artifact, and corresponding sample volumes ( $\text{m}^3$ ). OC was calculated as the difference between TC and BC. These concentrations are listed in Table 1. Also included in Table 1 is the magnitude of the positive adsorption artifact, which is calculated as the ratio of the carbon content of the backup filter to that of front filter. This ratio averaged 41% and 57% for biomass smoke and haze samples, respectively.

[25] Table 2 shows a subset of the data (the samples collected in smoke plumes) to demonstrate the significance of the positive sampling artifact. Uncorrected TC and OC concentrations are, on average, about 1.5 times the corrected values, and uncorrected BC/TC and BC/OC ratios are 0.6 times the corrected values. The uncertainties caused by the sampling artifact are large and, therefore, affect the comparison of present data with uncorrected literature values. Furthermore, the closure between in situ chemical data and, for example, apportionment of column optical depth to aerosol species will depend on whether or not carbonaceous aerosol concentrations are corrected for this artifact. These points are illustrated below.

[26] The average BC/TC ratio ( $0.15 \pm 0.04$ ) obtained in this study (of fires that were predominantly in the flaming combustion phase [*Sinha et al.*, 2003]) is greater than the ratios of  $0.12 \pm 0.03$  and  $0.05 \pm 0.02$  for flaming and

**Table 1.** Concentrations (in  $\mu\text{g m}^{-3}$ ) of Carbonaceous Particulate Matter Collected Aboard the UW Convair-580 Aircraft During SAFARI 2000

Date <sup>a</sup>	UW Flight Number	Time <sup>b</sup>	Sample Type	TC <sup>c</sup>	OC <sup>c</sup>	BC	TC, B/F <sup>d</sup>
10 August	1810	1157	haze	2.6	n/a <sup>e</sup>	n/a	0.91
10 August	1810	1335	haze	4.7	n/a	n/a	0.84
14 August	1812	1309	haze	4.9	n/a	n/a	0.62
15 August	1814	847	haze	5.3	4.5	0.7	0.69
17 August	1815	829	haze	3.2	2.6	0.6	0.72
17 August	1815	1000	plume	47.4	42.1	5.3	0.53
17 August	1815	1110	plume	251.2	224.4	26.7	0.24
18 August	1816	857	haze	3.5	n/a	n/a	0.80
18 August	1816	915	plume	137.3	113.2	24.0	0.31
18 August	1816	1137	haze	5.4	4.7	0.7	0.77
18 August	1816	1227	plume	206.1	176.8	29.3	0.26
20 August	1819	1157	haze	5.2	n/a	n/a	0.66
20 August	1819	1251	plume	35.9	29.5	6.4	0.51
20 August	1819	1356	plume	250.0	210.1	39.9	0.28
20 August	1819	1411	haze	4.5	n/a	n/a	0.77
22 August	1820	715	haze	3.7	2.7	1.1	0.75
22 August	1820	810	haze	4.5	3.4	1.0	0.60
22 August	1820	935	haze	4.1	3.6	0.5	0.76
24 August	1822	657	haze	5.0	4.0	1.0	0.65
24 August	1822	813	haze	2.3	1.6	0.7	0.73
29 August	1823	848	haze	6.8	5.5	1.3	0.62
29 August	1823	1004	haze	6.6	5.3	1.3	0.73
29 August	1824	1421	plume	60.3	50.7	9.6	0.54
31 August	1825	944	haze	9.4	8.0	1.4	0.54
31 August	1825	1121	plume	70.7	61.7	9.1	0.43
31 August	1825	1201	plume	43.6	39.8	3.9	0.42
1 September	1826	559	haze	5.1	4.4	0.6	0.53
1 September	1826	802	haze	14.3	10.7	3.6	0.57
1 September	1826	903	plume	68.9	58.0	10.9	0.41
1 September	1826	948	plume	32.5	27.0	5.5	0.59
1 September	1828	1403	haze	4.4	3.8	0.6	0.54
2 September	1829	758	haze	7.8	6.1	1.7	0.50
2 September	1829	954	haze	12.5	10.0	2.5	0.41
2 September	1829	1145	haze	11.0	9.0	2.0	0.39
3 September	1830	720	haze	14.8	12.0	2.8	0.39
3 September	1830	834	haze	23.7	19.2	4.5	0.42
3 September	1830	1055	haze	20.4	16.2	4.2	0.35
5 September	1831	903	haze	17.1	13.7	3.4	0.40
5 September	1831	1159	plume	49.1	36.5	12.7	0.50
6 September	1832	728	haze	26.9	20.6	6.2	0.35
6 September	1832	758	haze	32.3	25.6	6.7	0.41
6 September	1832	934	haze	27.9	22.6	5.2	0.39
6 September	1833	1229	haze	21.1	16.8	4.3	0.28
7 September	1834	844	plume	240.9	205.9	35.0	0.20
7 September	1834	925	plume	64.4	56.7	7.7	0.37
7 September	1834	1016	plume	40.8	34.1	6.7	0.51
10 September	1835	620	haze	9.1	7.5	1.5	0.43
10 September	1835	620	haze	20.1	16.5	3.5	0.33
13 September	1837	1131	haze	14.5	12.5	2.1	0.36
16 September	1839	1036	haze	4.4	3.3	1.0	0.62

<sup>a</sup>All samples were collected in the year 2000.<sup>b</sup>Sample collection start time (UTC).<sup>c</sup>Concentrations of TC and OC have been corrected for the positive sampling artifact produced by the adsorption of organic gases on the quartz filters (see text).<sup>d</sup>Magnitude of the positive sampling artifact (see text), expressed as TC content of the back quartz filter (B) divided by TC content of the front quartz filter (F).<sup>e</sup>Not available.

smoldering savanna fires, respectively, reported by Cachier *et al.* [1995] using single filter sampling. The difference may due to the fact that our TC data are corrected for the positive artifact. (BC concentrations were measured optically and were not affected by this artifact.) Our uncorrected BC/TC ratio is  $0.09 \pm 0.03$ , which is consistent with the

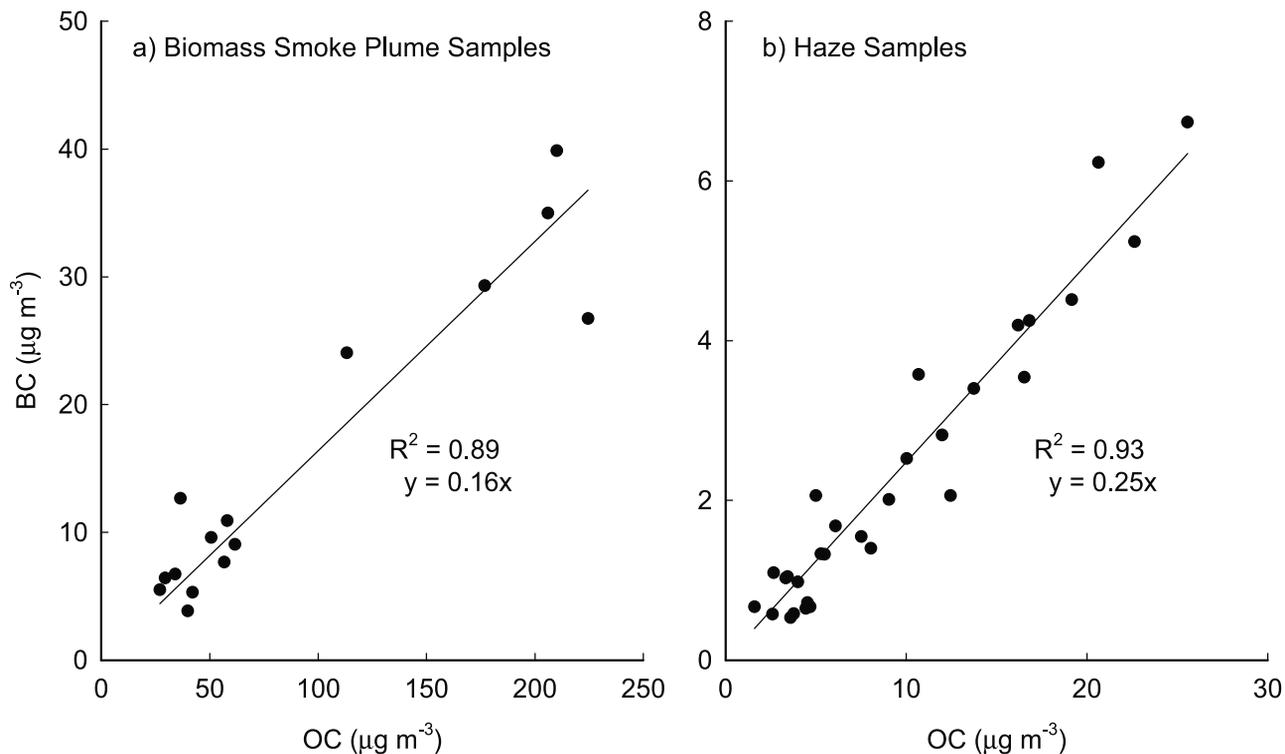
ratios of Cachier *et al.* for predominantly flaming savanna fires.

[27] More importantly, artifact-corrected data suggest that the biomass plume particles are considerably more absorbing than inferred from uncorrected values. Table 2 shows the estimated single scattering albedo (SSA) of the carbonaceous fraction of the biomass smoke plumes. Assuming the values of 4 and  $6 \text{ m}^2 \text{ g}^{-1}$  for the mass scattering coefficients of BC and organic matter (OM, equal to  $1.5 \times \text{OC}$ ), respectively, and  $10 \text{ m}^2 \text{ g}^{-1}$  for the mass absorption coefficient of BC [Ramanathan *et al.*, 2001, see supplemental text for that paper], we obtain an average  $\text{SSA} = 0.78$  if OC concentrations are corrected for the positive artifact, and an average  $\text{SSA} = 0.86$  if OC concentrations are not corrected for the positive artifact. Similarly, aerosol absorption (given by the coalbedo,  $1 - \text{SSA}$ ) is 60% larger if OC concentrations are corrected for the positive artifact. These differences are substantial and should be considered in calculating the column radiative properties from in situ composition data. These findings, in addition to those of Novakov *et al.* [1997], clearly indicate the need to correct carbonaceous aerosol measurements for the positive sampling artifact.

**Table 2.** Impact of the Positive Sampling Artifact on Biomass Smoke Plume Samples

Date <sup>a</sup>	UW Flight Number	Time <sup>b</sup>	Concentration ( $\mu\text{g m}^{-3}$ )					SSA <sup>c</sup>
			TC	OC	BC	BC/TC	BC/OC	
<i>Corrected for positive artifact</i>								
17 August	1815	1000	47	42	5	0.11	0.13	0.84
17 August	1815	1110	251	224	27	0.11	0.12	0.84
18 August	1816	915	137	113	24	0.18	0.21	0.75
18 August	1816	1227	206	177	29	0.14	0.17	0.79
20 August	1819	1251	36	29	6	0.18	0.22	0.75
20 August	1819	1356	250	210	40	0.16	0.19	0.77
29 August	1824	1421	60	51	10	0.16	0.19	0.77
31 August	1825	1121	71	62	9	0.13	0.15	0.81
31 August	1825	1201	44	40	4	0.09	0.10	0.87
1 September	1826	903	69	58	11	0.16	0.19	0.77
1 September	1826	948	33	27	5	0.17	0.20	0.76
5 September	1831	1159	49	36	13	0.26	0.35	0.65
7 September	1834	844	241	206	35	0.15	0.17	0.79
7 September	1834	925	64	57	8	0.12	0.13	0.83
7 September	1834	1016	41	34	7	0.16	0.20	0.77
		averages	107	91	16	0.15	0.18	0.78
<i>Not corrected for positive artifact</i>								
17 August	1815	1000	86	81	5	0.06	0.07	0.91
17 August	1815	1110	329	302	27	0.08	0.09	0.88
18 August	1816	915	187	163	24	0.13	0.15	0.81
18 August	1816	1227	260	230	29	0.11	0.13	0.83
20 August	1819	1251	74	67	6	0.09	0.10	0.87
20 August	1819	1356	322	282	40	0.12	0.14	0.82
29 August	1824	1421	103	93	10	0.09	0.10	0.86
31 August	1825	1121	114	105	9	0.08	0.09	0.88
31 August	1825	1201	75	71	4	0.05	0.05	0.92
1 September	1826	903	106	95	11	0.10	0.11	0.85
1 September	1826	948	80	75	5	0.07	0.07	0.90
5 September	1831	1159	92	79	13	0.14	0.16	0.80
7 September	1834	844	300	265	35	0.12	0.13	0.83
7 September	1834	925	100	92	8	0.08	0.08	0.89
		averages	154	138	16	0.09	0.10	0.86

<sup>a</sup>All samples were collected in the year 2000.<sup>b</sup>Sample collection start time (UTC).<sup>c</sup>Aerosol SSA, based only on carbonaceous species (see text).



**Figure 2.** BC versus OC concentrations of (a) biomass smoke plume and (b) haze samples. Least squares linear regression statistics (slope and  $R^2$ ) are shown for trend lines forced through the origin of each graph.

[28] Thirty-five samples were collected while flying in the haze over the study region, and 15 were collected in the plumes from individual biomass fires (Table 1). The highest carbonaceous aerosol concentrations measured were in the smoke plumes. The BC/OC mass ratio is plotted in Figure 2 for each sample, and separately for the haze and plume samples. BC and (corrected) OC are well correlated in both cases, as indicated by the linear correlation coefficient ( $R^2$ ). The average BC/OC ratio of samples collected in the smoke plumes from the burning of savanna ( $0.18 \pm 0.06$ ) was lower than that of samples collected in the regional hazes ( $0.25 \pm 0.08$ ). The relatively higher BC/OC ratio in the regional hazes could be the result of other (e.g., industrial) sources.

[29] Mixing of the biomass smoke with air that is influenced by combustion sources that have a characteristic BC/OC ratio higher than that measured in the biomass smoke plumes is a distinct possibility. A simple source apportionment equation:

$$0.18f + \alpha(1 - f) = 0.25$$

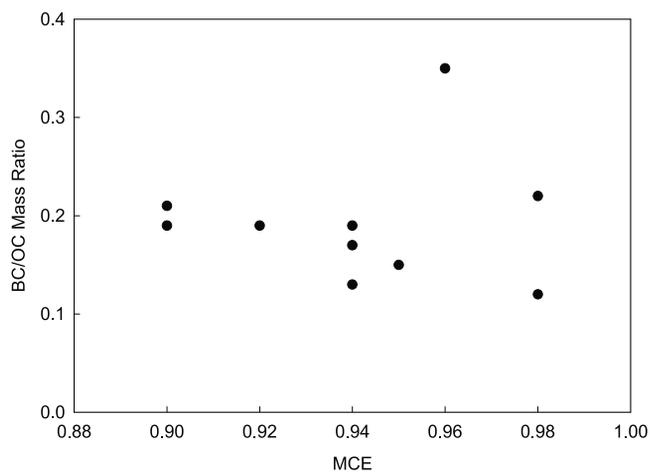
where  $f$  is the fraction of carbonaceous aerosol of biomass smoke origin and  $\alpha$  the BC/OC ratio typical of nonbiomass sources, can be used to estimate the contribution of biomass smoke to the aerosol loading in the regional hazes. If we assume  $\alpha = 0.50$  (e.g., fossil fuel burning), then it follows that biomass smoke contributed 78% of the carbonaceous aerosols, and the contribution from other sources was 22%. While this estimate is based on significant oversimplification, it suggests that, even in the high fire season in southern

Africa, other sources may contribute nonnegligibly to the regional aerosol burden. The present data are insufficient to identify the nonbiomass sources of OC and BC. To resolve this question, regional emission inventories of these species and measurements in source regions are needed. We note that *Maenhaut et al.* [1996] found that biomass burning (pyrogenic emissions) contributed 40%, and fossil fuel burning and industrial activity contributed about 30% of the fine ( $<2 \mu\text{m}$  diameter) particulate matter in southern Africa during the dry biomass burning season in 1992.

[30] Several researchers [e.g., *Cachier et al.*, 1995, and references therein] have reported higher values of BC/OC in smoke from flaming fires than from smoldering fires. *Ward and Hardy* [1991] reported that higher combustion efficiencies indicate that a fire is generally in the flaming phase, while lower efficiencies indicate a greater predominance of smoldering combustion. However, this trend is not evident in our data, as illustrated (in Figure 3) by the comparison of BC/OC ratio and modified combustion efficiency (MCE). (*Sinha et al.* [2003] note that MCE is a valid surrogate for combustion efficiency.) In fact, if the data point with the highest BC/OC ratio in Figure 3 is ignored, the opposite trend is evident, though the linear correlation coefficient is not high. Hence, our data suggest that in southern Africa MCE is not a good predictor of BC/OC ratio in smoke plumes.

#### 4. Summary

[31] Quartz filter samples collected in southern Africa aboard the UW Convair-580 aircraft during SAFARI 2000



**Figure 3.** BC/OC mass ratio versus MCE. The MCE values are from the study of *Sinha et al.* [2003].

were analyzed for carbonaceous aerosol content using the EGA technique. The positive sampling artifact, due to the absorption of organic gases, was found to be significant. Therefore, estimates of TC and OC loadings on the filters needed to be corrected for this artifact. The tandem (dual filter) sampling method was not appropriate in all cases for correcting for the artifact, so we modified this correction method. Uncorrected TC and OC concentrations were 1.5 times larger than corrected concentrations. The derived aerosol radiative properties, for example SSA, are sensitive to whether or not data are corrected for this sampling artifact.

[32] The BC/OC ratio measured in individual smoke plumes from savanna fires ( $0.18 \pm 0.06$ ) was lower than that in the regional hazes ( $0.25 \pm 0.08$ ). A simplified source apportionment indicated that biomass smoke contributed about three quarters of the aerosol burden in the regional hazes, while other sources, for example fossil fuel burning, contributed the remainder. Modified combustion efficiencies, which are an indication of flaming versus smoldering fire conditions, were not well correlated with measured BC/OC ratios.

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