Inorganic and carbonaceous aerosols during the Southern African Regional Science Initiative (SAFARI 2000) experiment: Chemical characteristics, physical properties, and emission data for smoke from African biomass burning

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[1] We collected filter samples of the atmospheric aerosol during the Southern African Regional Science Initiative (SAFARI 2000) experiment onboard the UK Met Office C-130 aircraft. The main operational area was the Atlantic Ocean offshore of Namibia and Angola, where biomass-smoke haze at least 1–2 days old was widespread. The size-fractionated aerosol samples were analyzed for the major inorganic ions, carbonaceous material (elemental and organic carbon), and elements with atomic numbers between 11 (Na) and 82 (Pb). The regional haze aerosol was composed mostly of carbonaceous aerosols (on the average, 81% of the submicron mass), with secondary inorganic aerosols (sulfate, ammonium, and nitrate) accounting for another 14%. K+ and Cl−, typical pyrogenic species, constituted only 2% of the mass. The aerosol chemical data were used to estimate mass emission fluxes for various aerosol components. For African savanna/grassland burning, the estimated emission flux of carbonaceous particles (particulate organic matter plus elemental carbon) is 14 ± 1 Tg yr−1, and that of the nitrogen species (nitrate and ammonium) is 2 ± 2 Tg yr−1. For the flight segments in regional haze, the mean particle scattering coefficient at 550 nm was σs = 101 ± 56 Mm−1 and the mean particle absorption coefficient σa at 565 nm averaged 8 ± 5 Mm−1 (mean single scattering albedo of 0.93 ± 0.06 at 550 nm). The dry mass scattering efficiency σs, calculated from the linear regression of the mean scattering versus the estimated submicron mass, is estimated to be between 4.2 ± 4.6 ± 0.6 m2 g−1, depending on the assumptions made in calculating the aerosol mass. The dependence of the scattering enhancement ratios Δσs/ΔCO on the distance from the burning regions suggests that the evolution of particle size with time influences the light scattering efficiency. Fresh smoke was sampled during a dedicated flight in the proximity and within the plume of an active biomass burning fire. Here the enhancement ratio with respect to CO of particles in the Aitken-size range (5–100 nm diameter) was ΔNAitken/ΔCO ~25 cm−3 (STP) ppb−1. These particles were removed rapidly after emission, and they were not detectable in the regional haze. The enhancement ratio for accumulation mode particles (0.1–1 μm diameter) ΔNAcc/ΔCO was ~26–30 cm−3 (STP) ppb−1 in young smoke, and 16 ± 3 cm−3 (STP) ppb−1 in aged haze, suggesting that the number concentration of accumulation mode particles was reduced by about 41% during aging. INDEX TERMS: 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0335 Atmospheric Composition and Structure: Ion chemistry of the atmosphere (2419, 2427); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 9305 Information Related to Geographic Region: Africa; KEYWORDS: chemical composition, biomass burning, airborne, SAFARI 2000


1. Introduction

[2] The last decade has seen an increasing interest in the role of aerosol particles in altering the Earth’s climate. This has resulted in a series of dedicated experimental programs, mainly, but not exclusively, under the umbrella of the International Geosphere Biosphere Program/International Global Atmospheric Chemistry (IGBP/IGAC). Description
and findings of some of the major international field campaigns are reported in a series of publications [e.g., Andreae et al., 1996, 2002; Bates et al., 1998; Kaufman et al., 1998; Russell et al., 1999; Raes et al., 2000; Ramathan et al., 2001].

[1] This research has revealed the complexity of the climate effects of atmospheric aerosols. Aerosols scatter light, increasing the amount of solar radiation backscattered into space; but can also absorb solar radiation, thereby decreasing the amount of backscattered radiation at the top of the atmosphere. Both scattering and absorption processes decrease the amount of solar radiation reaching the Earth’s surface [Intergovernmental Panel on Climate Change (IPCC), 2001]. Aerosols potentially modify cloud size, lifetime, brightness, and precipitation [IPCC, 2001], and the concentrations of trace gases [Deutener et al., 1996]. All these radiative, physical, and chemical effects depend in complicated ways on the aerosol composition and size, which makes it difficult to determine their effect on the Earth’s radiation budget and biogeochemical cycles [Ramanathan et al., 2001; IPCC, 2001; Andreae et al., 2002].

[4] A notable example is that of pyrogenic (biomass burning) aerosols. Burning of biomass in natural and man-induced fires is one of the most intense sources of aerosol particles. Andreae and Merlet [2001] have estimated that about 82 Tg (1 Tg = 10^{12} g) of total particulate matter (TPM) are emitted globally per year by biomass burning fires, of which 58 Tg are particles smaller than 2.5 \mu m diameter. These values have uncertainties of at least +50% [Andreae and Merlet, 2001]. Pyrogenic aerosols consist mainly of carbonaceous material, as elemental and organic carbon, in proportions dependent on the fuel type, oxygen availability, and the burning phase of the fire (flaming or smoldering) [Andreae and Merlet, 2001]. Although their response to the ambient relative humidity is modest as far as the scattering properties are concerned [Kotchenuather and Hobbs, 1998], the significant water-soluble fraction of organic carbon aerosols in fire smoke [Mayol-Bracero et al., 2002a], could respond to atmospheric relative humidity and change their light absorption efficiency [Redemann et al., 2001]. Furthermore, the availability of water-soluble material ultimately determines the cloud condensation nuclei activity of biomass burning aerosols [Roberts et al., 2002].

[5] In this paper, we present the results of the aerosol sampling that was conducted between 5 and 16 September 2000 on board the UK Met Office C-130 aircraft operating from Windhoek, Namibia, during the Southern African Regional Science Initiative (SAFARI 2000) experiment. SAFARI 2000 aimed to “identify and understand the relationships between the physical, chemical, biological, and anthropogenic processes that underlie the biogeochemical and biogeochemical systems of southern Africa” (see http://safari.gecp.virginia.edu/pdfs/planfinal1.pdf). With reference to one of the scientific questions of the SAFARI 2000 science plan “What are the chemical properties of the emitted aerosols?” (see http://safari.gecp.virginia.edu/pdfs/planfinal1.pdf), we measured water-soluble inorganic ions, carbonaceous (organic and elemental carbon) material, and the total elemental concentration of selected aerosol species within aged haze layers offshore Namibia and Angola, in the outflow region of the southern African anticyclone [Garstang et al., 1996].

[6] Data are discussed in terms of their relevance to the optical efficiency and emission inventories of biomass burning aerosols. As a term of reference for discussing our results, three antecedent field experiments on biomass burning are chosen: the Experiment for Regional Sources and Sinks of Oxidants (EXPRESSO); the Smoke, Clouds, and Radiation-Brazil (SCAR-B), and the Southern Africa Fire-Atmosphere Research Initiative 1992 (SAFARI-92) [Ruellan et al., 1999; Ferek et al., 1998; Reid et al., 1998; Le Canut et al., 1996; Andreae et al., 1998].

2. Methods

[7] Instruments were operated on board the Meteorological Research Flight (MRF) Hercules C-130 of the UK Met Office. The aircraft has a maximum endurance of 12 h (with fuel tank reserves). The minimum operational flight altitude is 17 m over water and 35 m over land, and the maximum operational flight altitude is \sim 11,000 m.

2.1. Sampling

2.1.1. Aerosol Particle Chemical Composition

[8] The aerosol sampling system used onboard the C-130 is described in detail by Andreae et al. [2000]. The aerosol inlet consists of a thin-walled inlet nozzle with a curved leading edge; the design was based on criteria for aircraft engine intakes at low Mach numbers [Andreae et al., 1988a]. This design reduces distortion of the pressure field at the nozzle tip and the resulting problems associated with flow separation and turbulence. The sampling system operated at flow rates that averaged 120 L min^{-1} (at ambient pressure and temperature); the flow was adjusted to maintain slightly subsisokinetic sampling conditions. The aerosol intake system was designed so that rain and large cloud water droplets would be removed from the sampled air stream by inertial separation. A careful but empirical characterization of the intake system of the aircraft conducted during the second Aerosol Characterization Experiment (ACE-2) showed that the inlet passes about 35% of the sea-salt mode and that no losses were detectable for the accumulation mode [Andreae et al., 2000]. Based on this comparison, and using the mean sea salt mass size distribution of Seinfeld and Pandis [1998], an approximate 50% cut-off diameter is calculated at around 3 \mu m aerodynamic diameter (for a particle density of 1.2 at 70% relative humidity). It is evident that this cut-off value is only very indicative, as a precise estimate would require a careful characterization of the inlet performances in a wind tunnel. However, the precise estimation of the inlet cut-off in the supermicron fraction is rather unimportant for the rest of the discussion, which will focus on submicron aerosols.

[9] Aerosol particles were sampled by filtration onto two stacked-filter units (SFUs) mounted in parallel. Each SFU can hold a maximum of three sequential 47-mm diameter polyethylene supports, but only two stages were used during SAFARI 2000. Samples were collected only during horizontal flight legs lasting not less than 20–30 min in order to guarantee sufficient loading of the filter samples. The first stage of each SFU consisted of a Nuclepore filter (nominal pore size 8.0 \mu m). The 50% cut-off diameter of the 8-\mu m
Nuclepore filter is about 0.9–1 µm for particles with a density of 1.35 g cm$^{-3}$ at a face velocity of about 70 cm s$^{-1}$ [John et al., 1983].

[16] One SFU was used to collect samples for the determination of water-soluble ions. Here the second stage consisted of a PTFE Teflon filter (nominal pore size 1.0 µm; 99.99% collection efficiency for submicron aerosols). Blank samples were collected on every flight by placing filters in the sampling line as if they were actual samples, and exposing them to the air stream for few seconds. The idea is to reproduce the actual conditions (contamination from the inlet, and from the aircraft environment during handling and loading) experienced by the actual samples. Immediately after each flight, loaded and blank filters were stored in precleaned 30 mL HDPE bottles, and kept in a refrigerator until extraction.

[11] The second SFU was used for collecting samples to measure carbonaceous aerosols. In this case the second stage consisted of two Pallflex quartz filters arranged in a tandem configuration. This allows estimating the positive artifacts in the particulate organic carbon determination due to adsorption of gaseous organic compounds by the filters [Novakov et al., 1997]. The assumption is that the “front” quartz filter collects aerosol particles with 100% efficiency, while carbon collected on the “back” filter indicates the amount of gaseous organics absorbed on the quartz filters, which contribute a positive artifact to the organic aerosol fraction. The limits of this assumption are discussed by Huebert and Charlson [2000]. All the quartz filters used during SAFARI-2000 were prebaked at 800°C for approximately 12 hours to eliminate organic impurities. Samples and blanks (collected in the same way as for the other SFU) were unloaded immediately after each flight and stored in a freezer in precleaned glass vials.

2.1.2. Aerosol Particle Size Distribution, Total Number Concentration, and Scattering and Absorption Coefficients

[12] Aerosol particle size distributions were measured onboard the C-130 with a Passive Cavity Aerosol Spectrometer Probe (PCASP-100X, PMS Inc., Boulder, Colorado). The PCASP’s measurement principle is based on the fact that the light scattering by a particle depends on its size. In this way the PCASP classifies the particles into 15 size channels in the diameter range between 0.1 and 3 µm (nominal). However, light scattering also depends on the refractive index, the humidity state, and the shape of the aerosols [Collins et al., 2000]. The effect of these uncertainties on the particle size distribution measured onboard the C-130 is discussed by Haywood et al. [2003a].

[13] The total particle number concentration, CN, for particles larger than 3 nm was measured by a condensation particle counter (CPC3025, TSI Inc., St. Paul, MN). The upper cut-off of the probe was ~1 µm. The actual calibration shows that the CPC3025 counts particles of 5 nm diameter at 50% efficiency, increasing to 80–85% at sizes > 10 nm, but lower than 50% at sizes less than 5 nm. This is slightly less efficient than the manufacturer’s claim of 50% efficiency at the lower limit of 3 nm. The data reported in this paper have been corrected for the estimated counting efficiency. The total number of particles in the Aitken size range ($N_{\text{Aitken}}$, particle diameter range 5–100 nm) was obtained as the difference between CN and the total accumulation mode particle number ($N_{\text{acc}}$) calculated by integrating the PCASP size distributions in the range 100 nm to 1 µm. The absolute error on the aerosol number is calculated according to Poisson counting statistics as the square root of the measured counts, i.e., the relative accuracy increases as the number concentration increases.

[14] The particle volume scattering coefficient $\sigma_v$ (dry state) at 450, 550, and 700 nm was measured using a three-wavelength integrating nephelometer (TSI 3563, TSI Inc., St. Paul, Minnesota). A Particle Soot Absorption Photometer (PSAP, Radiance Research, Seattle, Washington) measured the aerosol particle absorption coefficient $\sigma_a$ at 565 nm. The scattering and backscattering data were corrected for angular truncation and Lambertian nonidealities according to Anderson and Ogren [1998], while the correction procedure for the absorption coefficients followed the suggestions of Bond et al. [1999]. Corrections and uncertainties are described by Haywood and Osborne [2000, available from Met Office, Bracknell, UK]. The precision of the aerosol scattering coefficient measurements is estimated to be within 10%, while the overall uncertainty on the absorption coefficients is estimated to be around 20–30%.

The particle scattering and the absorption coefficients are used to estimate the aerosol single scattering albedo $\omega_s$ at 550 nm as $\omega_s = \sigma_v / (\sigma_v + \sigma_a)$. The wavelength-dependence of $\sigma_v$ was assumed to be 1/λ [Haywood et al., 2003a; Bergstrom et al., 2002].

[15] In the following, the particle number concentrations, and the scattering, absorption, and extinction coefficients are converted to standard temperature and pressure (STP) using T = 273 K and p = 1013.25 hPa.

2.1.3. Trace Gases

[16] The CO measurements were made with a fast-response vacuum–UV resonance fluorescence instrument built for the C-130 at the Institut für Chemie und Dynamik der Geosphäre, Forschungszentrum Jülich, Germany. It has a one-second-time resolution, a detection limit of 3 ppb and a precision of ±1.5 ppb at an atmospheric mixing ratio of 100 ppb. Calibrations are carried out in-flight at least every half hour using a British Oxygen Company (BOC) alpha standard (see Gerbig et al. [1999] for more information).

2.2. Analysis

2.2.1. Water-Extractable Ions and Total Elemental Concentration

[17] The filter samples were cut in halves to be analyzed for water-extractable ions and total elemental concentration, respectively. As a check, the Nuclepore filters were weighed with a microanalytical balance (absolute accuracy ±1 µg) before and after being cut. The original weight was reproduced within 1% by the sum of the weights of the two halves.

[18] Water-extractable ions ($Cl^-$, $NO_3^-$, $SO_4^{2-}$, $Ox^{2-}$, $NH_4^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$) were determined using isocratic suppressed ion chromatography (IC) and conductivity detection, using the procedure described by Andreae et al. [2000]. For the separation of weak and strong acid anions, a combination of two columns of different capacity (AS9-HC and AS4A-SC; DIONEX, Sunnyvale, CA) was used. For determination of the major cations a CS14 column (DIONEX, Sunnyvale, CA) was employed. Nuclepore filters were extracted in 5 mL of distilled water in 30 mL vials (50 µL of chloroform were
added). The Teflon filters were extracted with 1 mL of methanol and 4 mL of distilled water in the 30 mL vials; no chloroform was added. In the following discussion, concentrations are expressed as molar mixing ratios in air \((\text{ppt} = \text{pmol mol}^{-1})\) or as mass concentrations \((\mu g \, m^{-3})\) at STP. Also, because extraction in water is possible only for compounds that are water-soluble, we will refer to extractable ions as water-soluble ions, as it is more common in the literature. The repeated analysis of water samples and standard solutions indicated accuracy within 4%, and reproducibility within 3%. Blank mixing ratios, obtained from filters exposed a few seconds to the airflow (section 2.1.1), were within 0.4 \(\mu g \, L^{-1}\) (\(\sim 13\) ppt at the average flow rate of SAFARI 2000), less than 15% of the measured mixing ratios of the major ions \((\text{NO}^3_2, \text{SO}_4^2-, \text{NH}_4^+, \text{K}^+, \text{Ca}^{2+}, \text{Mg}^{2+}, \text{Mn}, \text{Fe}, \text{Cu}, \text{Zn}, \text{and I})\). The Teflon filters (fine fraction) were only analyzed by INAA for Na, Mg, Al, Cl, Ca, Ti, V, Cr, Mn, Fe, Cu, Zn, and I. The Teflon filters are an oxidizing atmosphere is soot-like or nearly elemental. A property of the carbon, which is interpreted on the assumption that the carbon that volatilizes at higher temperatures in an oxidizing atmosphere is soot-like or nearly elemental. A property of the carbon, which is interpreted on the assumption that the carbon that volatilizes at higher temperatures in an oxidizing atmosphere is soot-like or nearly elemental. 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3. Results

3.1. Atmospheric Conditions in the Study Area

[26] The Met Office C-130 performed seven research flights from Windhoek (22.5°S, 17.5°E), Namibia, during the period 5–16 September 2000. September is at the end of the dry burning season in southern Africa [Scholes and Andreae, 2000]. The aircraft operated mainly over the ocean off the coast of Namibia and Angola (see Haywood et al. [2003a, Figure 1] for a picture of the flight patterns), in the outflow region of the Southern African anti-cyclone, a persistent circulation pattern responsible for the transport of air masses over scales of thousands of kilometers in two absolute stable layers, the first at 700 hPa (~3 km asl, i.e., about 1.5 km above the mean ground level of the South African plateau) and the second at 500 hPa (~6 km asl) [Garstang et al., 1996]. The atmospheric stratification favors the large-scale transport of pollutants at high altitudes (for the case of industrial emissions, see, e.g., S. J. Piketh et al., Chemical evidence of long-range atmospheric transport over southern Africa, Journal of Geophysical Research, submitted, 2002). This was observed also by the C-130 (see, e.g., the vertical profiles of carbon monoxide and the total particle number between 0.1 and 3 μm diameter [Haywood et al., 2003a, Figures 10 and 11]).

[27] The aerosol samples discussed in this paper were collected mainly over the Atlantic Ocean in the region between 16°–24°S and 11°–18°E, in elevated layers between 2 and 6 km asl. Between 5 and 10 September 2000, air masses traveled easterly from the Atlantic Ocean toward the sampling region. From 11 September on, however, the airflow direction changed, and air masses were transported in a large anti-cyclone from South Africa, Zimbabwe, and Zambia (Figure 1). The elevation of the smoke-laden air masses remained almost constant with time, and always above the 700-hPa level, during the last five days prior to sampling. Active fires, located using the active fire maps of the ATSR World Fire Atlas (http://shark1.esrin.esa.it/iona/FIRE/AF/ATSR/), were mostly concentrated between 10°S and 20°S, but extending also south of 20°S, on the eastern part of South Africa. Among the various ecosystems distinguishable in the corridor between 10°S and 20°S (moist and arid woodlands and savannas, and fertile/infertile grasslands), arid, fertile savanna are the most common [Scholes et al., 1996].

[28] The back trajectories indicate that the C-130 generally flew within a regional haze that was a few days old at the time of sampling. The exception was flight A790 (13 September 2000), when a fresh plume from an active arid savanna fire in northern Namibia was sampled. Indications on the age and type of emissions sampled can be derived from the enhancement ratios, ER, of various gaseous and particulate tracers. The ER of a tracer X with respect to CO is defined as [Andreae and Merlet, 2001]

\[
ER = \frac{X_B - X_h}{CO_B - CO_h}
\]  

Figure 1. Five-day back trajectories initialized at the midpoint of the exposure time of the filter sampling leg. The horizontal transport is shown in the upper panel, the vertical motion in the lower panel. Solid thick lines correspond to trajectories ending prior 11 September 2000, dotted lines after 11 September 2000. The solid squares represent (not in scale) the 1 × 1 km² active fire pixels of the ATSR World Fire Atlas.

The suffix “h” indicates concentrations measured inside the haze layers, while “b” refers to the background concentrations measured outside the haze layers. The ER thus represents the enhancement of X due to the contribution of a specific source, normalized to the enhancement of a reference compound; in this case CO. CO is a good indicator of biomass burning [Andreae and Merlet, 2001], because it is emitted from biomass fires at a much higher CO/CO₂ ratio than is typical of fossil fuel emissions [Holloway et al., 2000]. The underlying assumption of the ER is that compounds in the individual sources can be fingerprinted by unique ratios to their reference tracer. ER values were calculated for trace gases and aerosol particles for the time periods corresponding to the filter sampling legs. As the variability of each of these components over the sampling leg duration was generally very low, the arithmetical mean and standard deviation were used to derive ER values. The same does not apply to the sampling legs within fresh smoke plumes during flight A790, for which the particle counts in the Aitken and accumulation legs within fresh smoke plumes during flight A790, for which the particle counts in the Aitken and accumulation sizes ranges changed rapidly from ambient concentrations of about 5,000 cm⁻³ to peaks above 100,000 cm⁻³. Order-of-magnitude changes within minutes were observed also in the nephelometer readings of the scattering coefficient σₚ, from σₚ ≈ 150 Mm⁻¹ to peaks up to 1,000 Mm⁻¹.

[29] At count rates above approx. 20,000 cm⁻³, saturation due to coincidence artifacts can occur in the particle counters [Le Canut et al., 1996]. Saturation was observed also in the measurement of the absorption coefficient, σₐ, by
the PSAP. The PSAP reading topped at 27 Mm\(^{-1}\) during passes in the fire plumes. Abrupt decreases toward zero absorption were observed in correspondence of the sharp transition of the scattering coefficient. To avoid biases, when calculating the regional ER values for the particle numbers for these flight segments, we removed from the particle and the CO data the sharp peaks corresponding to the passage through plumes, and only looked at the “background” values. The fresh plumes were characterized separately, as discussed below.

[30] The ER values for the trace gases measured during SAFARI 2000 (O\(_3\), NO\(_x\), methanol, acetonitrile, acetone, and SO\(_2\)) in the haze are consistent with the predominance of biomass burning emissions [Jost et al., 2003]. A closer look at the SO\(_2\) time series suggests that anthropogenic activities other than biomass burning (e.g., mining in the Zambian Copperbelt region) also had an influence [Jost et al., 2003]. The ER for O\(_3\) relative to CO was 0.26 ± 0.03 in the regional haze, which indicates that significant photochemical production of ozone had occurred when air masses were sampled offshore Namibia.

[31] The linear correlation between \(\Delta N_{\text{Acc}}\) and \(\Delta \text{CO}\) is shown in Figure 2, separately for the aged haze data and flight A790. \(\Delta N_{\text{Acc}}/\Delta \text{CO}\) was 16 ± 3 cm\(^{-3}\) (STP) ppb\(^{-1}\) \((r^2 = 0.76)\) for aged aerosols, and 10 ± 6 cm\(^{-3}\) (STP) ppb\(^{-1}\) \((r^2 = 0.74)\) on the three flight segments of flight A790 prior encountering the fresh plumes. The two values are not statistically different within one standard deviation, which indicates that the legs during flight A790 were upwind the active fires and thus unaffected by the fresh smoke. The ER values for \(N_{\text{Acc}}\) are in the range indicated by Le Canut et al. [1996] and Anderson et al. [1996], and three times higher than the lower limit value of 5 ± 3 cm\(^{-3}\) (STP) ppb\(^{-1}\) reported by Andreea et al. [1994] and Mauzerall et al. [1998] for 2–6 days old haze layers that had gone through clouds.

[32] Values of \(\Delta N_{\text{Acc}}/\Delta \text{CO}\) for fresh smoke were calculated instead by integration of \(N_{\text{Acc}}\) and \(\text{CO}\) over the times of transit in some of the minor smoke plumes encountered during flight A790. The choice of minor plumes was dictated by the necessity of avoiding saturation artifacts. The background values just before or after the occurrence of these plumes were 3,000 cm\(^{-3}\) (STP) for \(N_{\text{Acc}}\) and 260 ppb for \(\text{CO}\), respectively. These values are rather high (actually of comparable magnitude than those measured during the first three legs during flight A790), reflecting the haziness of the atmosphere on a regional scale. The impossibility of estimating truly pollution-free values is likely to lower the ER values for the fresh plumes. Bearing this in mind, the \(\Delta N_{\text{Acc}}/\Delta \text{CO}\) calculated on these minor plumes was ~26–30 cm\(^{-3}\) (STP) ppb\(^{-1}\), still within the range provided by previous findings for young smoke [Andreea et al., 1994; Le Canut et al., 1996; Anderson et al., 1996; Mauzerall et al., 1998]. The reduced ER for \(N_{\text{Acc}}\) in the regional haze suggests that the number concentration of accumulation mode particles in the aged smoke has decreased by at least about 40% with respect to the young smoke. The ER value is independent of dilution, and changes reflect an actual decrease in the number of particles [Le Canut et al., 1996]. Immediately after emission, particles will undergo rapid condensational growth and coagulation. Slow coagulation of accumulation mode particles continues once the smoke has diluted and becomes the dominant process when concentrations are around 5,000 cm\(^{-3}\) [Reid et al., 1998]. However, at ambient concentrations (\(N_{\text{Acc}}\sim 5,000\) cm\(^{-3}\)), coagulation would decrease only slightly the total accumulation mode particle number.

[33] The shift in the modal diameters in the submicron mode (0.1–1 \(\mu\)m diameter) observed in the particle number size distributions within aged smoke offshore the African coast (and down to Ascension Island, 2,500 km off the Namibian Coast) with respect to fresh aerosol [Haywood et al., 2003a], can be explained as growth by particle coagulation. Integrating these normalized lognormal number size distributions shows that the aerosol mass for the particles below 1 \(\mu\)m diameter increased by a factor of 1.7 during the evolution from young to aged smoke. For particles below 3.5 \(\mu\)m, the total mass increases by a factor of 1.9. Similar growth rates for evolving smoke plumes have been found by Reid et al. [1998] over a period of 1–3 days.

[34] The ratio \(\text{CN}/N_{\text{Acc}}\) (ratio of particles in the range 0.005–1 \(\mu\)m to those in the range 0.1–1 \(\mu\)m), estimated as the slope of the linear regression \(\text{CN} \text{ versus } N_{\text{Acc}}\), was 1.1 ± 0.1 \((r^2 = 0.83)\) on all flights but A790. This indicates that, at the time of sampling, the aerosols had stayed in the atmosphere long enough for most particles in the range <0.1 \(\mu\)m have grown into the accumulation mode. The Aitken-size particle fraction was evident on flight A790. Immediately after emission, these particles provide the surface for gas condensation, and grow to larger sizes by condensation and coagulation. As the smoke becomes diluted and the partial pressure of condensable vapors decreases, coagulation becomes more significant. Bursts

**Figure 2.** Linear regression of \(\Delta N_{\text{Acc}}\) versus \(\Delta \text{CO}\). \(\Delta N_{\text{Acc}}\) represents the enhancement of the total accumulation particle number \(N_{\text{Acc}}\) (particles smaller than 1 \(\mu\)m diameter) with respect to background conditions, while \(\Delta \text{CO}\) represents the enhancement of \(\text{CO}\). Circles are data acquired during passes on fresh smoke (flight A790). Squares are data collected in aged haze. Crossed circles are data also acquired during flight A790, but not included in the linear regression in order to avoid artifacts due to saturation of the PCASP probe.
of particles in the Aitken-size range (CN-to-N_{Ac} ~ 18 – 30), anti-correlated to CO, were observed on two runs at 100 m asl over the ocean on flights A785 and A792 (5 and 16 September 2000), but these were unrelated to the processing of biomass aerosol.

The ratio ΔN_{Aitken}/ΔC0 was around 25 cm^{-3} (STP) ppb^{-1} in the minor smoke plumes during flight A790. There are no data in the literature on the ER for Aitken-size particles in fresh smoke. In aged plumes (2 – 6 days old), ΔN_{Aitken}/ΔC0 is in the range 8 – 18 cm^{-3} (STP) ppb^{-1} [Andreae et al., 2001]. The disappearance of the Aitken-size particles observed in the aged smoke is more consistent with the lower limit of this range.

### 3.2. Chemical Composition

From the combination of TOT, IC, PIXE, and INAA, we were able to determine OC, EC_{av}, Cl, SO_{4}^{2-}, NO_{3}^{-}, Ox, NH_{4}^{+}, K^{+}, Ca^{2+}, Mg^{2+}, Al, Mn, Br, and I (the last five only in a few samples), were detected. The availability of the PIXE/INAA and the IC measurements for Cl, S/SO_{4}^{2-}, K, Mg, and Ca in the coarse fraction, allows cross-checking of the measurements and determining the water-soluble fraction of those elements. The square of the regression coefficient, r^{2}, of the linear correlation between water-soluble and total components was always better than 0.9. The water-soluble-to-total ratios for Cl, K, and Ca were equal to one within 10%, indicating that these elements are predominantly water-soluble. In particular, the water-soluble fraction of K was 93 ± 5%, in agreement with the measurements of Yamase et al. [2000] for cerrado biomass burning. The water-soluble fraction of Ca in mineral dust aerosols has been found of the order of 80% (P. Formenti et al., The chemical composition of mineral dust aerosol during the SHADE airborne campaign in the Cape Verde region, September 2000, manuscript in preparation, 2002, hereinafter F2002). The coarse Ca fraction has also a biogenic component from vegetation debris [Artaxo et al., 1988; Andreae et al., 1998]. The water-soluble fraction of Mg, an element also present in vegetation debris, was allowed to vary between 1 and 2. A value of 2 was the 5–95% percentile range for the fine fraction. Low Cl^{-} concentrations have been observed previously in samples taken within 150 km from prescribed savanna fires [Liu et al., 2000]. Particulate Cl^{-} is not a conservative tracer, as it tends to evaporate to the gas phase once in the atmosphere, due to SO_{2}-acidification of NaCl particles in the coarse fraction, and of KCl in the fine. Evaporation from filter media might also cause sampling artifacts [Maenhaut et al., 1996]. In contrast, sulfur- and nitrogen-containing particles are formed in the atmosphere by SO_{2} and NO_{x} oxidation and cloud processing [Seinfeld and Pandis, 1998].

#### Table 1. Arithmetic Mean and Standard Deviations of the Species Concentrations Measured During SAFARI 2000 in the Fine (<1 μm Diameter) and Coarse (>1 μm Diameter) Fractions

<table>
<thead>
<tr>
<th>Element</th>
<th>Fine fraction</th>
<th>Coarse fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Aged smoke</td>
<td>Fresh smoke</td>
</tr>
<tr>
<td>EC_{av}</td>
<td>1030 ± 38</td>
<td>2025 ± 1349</td>
</tr>
<tr>
<td>OC</td>
<td>6150 ± 3628</td>
<td>20421 ± 18025</td>
</tr>
<tr>
<td>NO_{2}^{-}</td>
<td>1019 ± 825</td>
<td>1415 ± 1760</td>
</tr>
<tr>
<td>SO_{4}^{2-}</td>
<td>1984 ± 1509</td>
<td>1935 ± 1472</td>
</tr>
<tr>
<td>Ox</td>
<td>790 ± 187</td>
<td>755 ± 440</td>
</tr>
<tr>
<td>NH_{4}^{+}</td>
<td>910 ± 758</td>
<td>1591 ± 2415</td>
</tr>
<tr>
<td>K</td>
<td>406 ± 420</td>
<td>4460 ± 8118</td>
</tr>
<tr>
<td>Mg^{2+}</td>
<td>13 ± 6</td>
<td>–</td>
</tr>
<tr>
<td>Ca^{2+}</td>
<td>51 ± 33</td>
<td>104 ± 20</td>
</tr>
<tr>
<td>Na</td>
<td>190 ± 33b</td>
<td>–</td>
</tr>
<tr>
<td>Mg</td>
<td>660 ± 135</td>
<td>–</td>
</tr>
<tr>
<td>Al</td>
<td>264 ± 149</td>
<td>–</td>
</tr>
<tr>
<td>Si</td>
<td>–</td>
<td>823 ± 854</td>
</tr>
<tr>
<td>P</td>
<td>–</td>
<td>92 ± 63</td>
</tr>
<tr>
<td>S</td>
<td>–</td>
<td>720 ± 482</td>
</tr>
<tr>
<td>Cl</td>
<td>–</td>
<td>102 ± 41</td>
</tr>
<tr>
<td>K</td>
<td>–</td>
<td>450 ± 502</td>
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<td>Ca</td>
<td>–</td>
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<tr>
<td>Ti</td>
<td>–</td>
<td>28 ± 19</td>
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<tr>
<td>Fe</td>
<td>–</td>
<td>0.9 ± 0.6</td>
</tr>
<tr>
<td>Mn</td>
<td>6 ± 2</td>
<td>11 ± 14</td>
</tr>
<tr>
<td>Cu</td>
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<td>7 ± 4</td>
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<tr>
<td>Zn</td>
<td>–</td>
<td>10 ± 7</td>
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<tr>
<td>Br</td>
<td>15 ± 8</td>
<td>28 ± 16</td>
</tr>
<tr>
<td>Sr</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>I</td>
<td>3 ± 2</td>
<td>3 ± 1</td>
</tr>
</tbody>
</table>

*Data refer to samples measured in regional haze, far from active fires. Concentrations measured during flight A790, in the proximity of an active fire, are also shown. Concentrations are expressed in ng m^{-3} (STP). A dash indicates that values are not available.

Above detection limit only on three over eighteen samples.
the order of 10% otherwise. Therefore, NH$_4^+$ is considered as the superimposition of NH$_2$NO$_3$ on (NH$_4$)$_2$SO$_4$. The high correlation of NH$_4^+$ with K$^+$ is typical of biomass burning [Andreæ et al., 1998]. NH$_4$Cl particles have been found in smoke as a condensation product [Andreæ et al., 1998; Liu et al., 2000], however, in our samples Cl$^-$ only could account for 1% of the measured NH$_4^+$.

[40] For all the flights, the SO$_4^{2-}$ mass concentrations (sum of the coarse and the fine fraction) were in the range 0.6–5.8 μg m$^{-3}$. The lowest value, measured in clean air during flight A791, agrees extremely well with the background sulfate concentrations above the Namibian desert reported by Annegarn et al. [1983]. Hence, the value 0.6 μg m$^{-3}$ was used as an estimate for the unperturbed sulfate concentrations, and the excess SO$_4^{2-}$ due to the haze layers was calculated by subtracting this value from the measured SO$_4^{2-}$ concentrations. Samples taken over the ocean generally had SO$_4^{2-}$ concentrations on the order of 2–3 μg m$^{-3}$. Now, the question is whether enough SO$_2$ was emitted by the vegetation fires to explain the measured SO$_4^{2-}$ ambient concentrations. We will not consider the possible concurrent contribution of industrial sources (particularly, the copper mining in Zambia). Because SO$_2$ was not measured during flight A790, SO$_2$ mass concentrations from fires are calculated from the above-background CO mass concentrations measured during that flight, and weighted by the SO$_2$-to-CO mass emission ratios for savanna/grassland burning (equal to 0.00534) from Andreaæ and Merlet [2001]. Incidentally, this coincides with the ER value obtained using the measured SO$_2$ on the two flights where SO$_2$ data are available. The SO$_2$ concentration near the source is about 2.5–3 μg m$^{-3}$. Once in the atmosphere, SO$_2$ will undergo dry and wet deposition, and OH-oxidation to form sulfuric acid (H$_2$SO$_4$). Neglecting for the moment the effect of wet deposition, the lifetime of SO$_2$ for dry deposition is about 40 hours for a dry deposition velocity of 1 cm s$^{-1}$ and a mixed layer thickness of 1.5 km. In this time, at an oxidation rate of 1–3% per hour (daytime average) [Seinfeld and Pandis, 1998], 40–100% of SO$_2$ is converted into sulfate aerosols, which means that between 1 and 3 μg m$^{-3}$ SO$_4^{2-}$ are produced. This is fully consistent with the observed excess-SO$_4^{2-}$ concentrations. The lower limit of the oxidation rate leaves room for sulfate production by in-cloud processes. Layers of stratocumulus clouds were frequently observed above the Ocean; however, the top of the cloud layer was generally around 950 hPa, and clearly separated by a “clean air slot” from the bottom of the aerosol layer aloft [Haywood et al., 2003a]. Therefore, apart from the passage of the plume through convective cloud above and downwind of the fires, interactions between aerosols and clouds at lower altitudes might not be significant for the data discussed here, which were taken in the elevated haze layers.

[41] Excess fine potassium, K$_f$, is a tracer for primary pyrogenic emissions [Andreæ, 1983]. Sea salt and mineral aerosols are additional sources of K, but affect almost exclusively the coarse fraction and are corrected for in the calculation of excess K. During SAFARI 2000, the mean K$_f$ concentrations in the fine fraction were 606 ng m$^{-3}$ in regional haze, and 4460 ng m$^{-3}$ during flight A790. The minimum total K$^+$ concentration (116 ng m$^{-3}$, sum of fine and coarse masses) measured during flight A791, agrees with the background value of 94 ng m$^{-3}$ of Annegarn et al. [1983]. The fine K$^+$ concentration of 77 ng m$^{-3}$ corresponding to the minimum K$^+$ concentration measured during flight A791 was used to estimate the enhancement of fine K$^+$ due to the haze.

[42] In the fine fraction, the mass ratio K$^+$/SO$_4^{2-}$ was 0.3 ($r^2 = 0.91$; molar ratios of 0.7). Assuming that 100% of the fine sulfur is present as SO$_4^{2-}$, the corresponding K/S ratio is 0.9. This is on the lower side of the values found in the literature for smoke haze [Gaudichet et al., 1995; Maenhaut et al., 1996; Andreæ et al., 1998; Ruellan et al., 1999; Liu et al., 2000; Yamasoe et al., 2000]. Note that the airborne measurements of Andreæ et al. [1998] over prescribed savanna and subtropical forest fires gave K/S around 2. The difference might be due to the enhancement of SO$_4^{2-}$ due to further secondary production during plume aging.

[43] In contrast to previous observations [Andreæ et al., 1998], NO$_3$ was one of the major aerosol components in the fine fraction, with a mean concentration of 1.0 ± 0.8 μg m$^{-3}$ in the regional haze (1.4 ± 1.8 μg m$^{-3}$ during flight A790). In the coarse fraction, NO$_3$ was also abundant (1.2 ± 1.2 μg m$^{-3}$ and 4.2 ± 0.7 μg m$^{-3}$ in regional haze and young smoke, respectively). Nitrate is a secondary aerosol product formed in the atmosphere by deposition of nitric acid on sea salt (to form NaNO$_3$ or mineral particles, but also through neutralization of nitric acid by ammonia to form ammonium nitrate (NH$_4$NO$_3$) [Seinfeld and Pandis, 1998].

[44] We already mentioned that NO$_3$ in the fine fraction correlated with NH$_4^+$ and SO$_4^{2-}$. In the coarse fraction, NO$_3$ correlated with NH$_4^+$, Na, Ca$^{2+}$, and also with SO$_4^{2-}$. The correlation with Na ($r^2 = 0.67$) was observed only during flight A790, inland. Na was otherwise detected only at very low concentrations. Samples were always collected in the aerosol layers well above the mixing layer and therefore sea salt is expected to be only a minor component, even in the coarse fraction. Coarse Cl and Na were modestly correlated ($r^2 = 0.60$), and the Cl/Na ratio was 0.8, about two times lower than in sea salt. Chlorine depletion in sea salt particles can occur because of heterogeneous reaction with nitric acid (HNO$_3$), to cause degassing of HCl and formation of NaNO$_3$ particles [Seinfeld and Pandis, 1998]. It seems more likely, however, that the low Cl/Na ratio was due to the contribution of soil material to Na. The coarse Na correlated well with Al ($r^2 = 0.92$).

[45] The measured NO$_3$ and NH$_4^+$ concentrations are attributed to atmospheric conversion of their gaseous precursors, NH$_3$ and NO$_x$, since only a very minor fraction of the nitrogen contained in the biomass is released in the particulate form during burning [Andreæ et al., 1998]. A mean concentration of 15 ppb of NO$_x$ was measured in the plumes during flight A790, and around 1 ppb in the regional haze. The lifetime of NO$_x$ against reactions with the OH radical is about 1–2 days. Using a mean HNO$_3$/NO$_x$ ratio of 3, as found in regional haze over the Amazon basin by Andreæ et al. [1988a, 1998b], aged smoke should contain about 3 ppb HNO$_3$. In analogy, from the emission ratios for savanna burning [Andreæ and Merlet, 2001], we estimate that ~14 ppb NH$_3$ could be expected in the plume of a fire like the one sampled during flight A790. With NH$_3$ and HNO$_3$ concentrations at these levels, particle formation is possible [Seinfeld and Pandis, 1998].
The soil signature was traced using the Al concentrations. Al in the fine fraction was detected in few samples at significant concentrations (~200 ng m^{-3}). In the coarse fraction, Al averaged ~260 ng m^{-3} in the regional haze, and ~1350 ng m^{-3} during flight A790. Coarse Si, Fe, Ti, V correlated with Al (r^2 > 0.98), and were not enriched with respect to the crustal composition of Mason [1966]. Coarse Na, P, S, K, Ca, Mn, and Zn also correlated, but were enriched. These elements are found in plants, and are released to some extent during biomass burning [Artaxo et al., 1988; Gaudichet et al., 1995; Maenhaut et al., 1996].

### 3.2.2. Carbonaceous Aerosols

Fine organic carbon (OC) and apparent elemental carbon (ECa) were highly correlated (r^2 = 0.81, Figure 3). The slope of the linear correlation varied depending on the age of the aerosols. For flight A790, ECa/OC was 0.062 ± 0.004 (r^2 = 0.99), and 0.08 on the sample with highest carbon content. Conversely, excluding flight A790, the aged smoke had ECa/OC equal to 0.11 ± 0.02 (r^2 = 0.72). ECa accounted for 6–8% of the total fine carbon (TC) in fresh smoke, and for 11% in the regional haze. Some of the organic carbon component might evaporate or be oxidized to CO or CO2 during aging, therefore increasing the relative fraction of ECa [Lioussse et al., 1995; Cachier et al., 1995; Gaudichet et al., 1995; Ferek et al., 1998; Andreae et al., 1998; Ruellan et al., 1999]. Haywood et al. [2003a] validated these observations with the values of single scattering albedo calculated from the scattering and absorption coefficients measured by the nephelometer and the PSAP instruments.

### 3.2.3. Estimate of the Particulate Organic Matter in the Fine Fraction

Based on the previous discussion, the aerosol mass for particles smaller than 1 μm diameter was reconstructed from the contributions of ammonium nitrate (NH4NO3), ammonium sulfate/bisulfate ((NH4)2SO4), pyrogenic inorganic species (potassium and chlorine), soil mass as calcium carbonate (CaCO3), elemental carbon (ECa), and particulate organic matter (POM). Estimating the POM from the measured OC implies the a priori knowledge of the fraction of oxygen, hydrogen, and nitrogen associated with the carbon in the organic matter [Seinfeld and Pandis, 1998]. Values of the POM/OC ratio vary between 1.3 and 3, depending on the age and source of the aerosol [Turpin et al., 2000].

An approximate estimate of the POM/OC ratio was done by comparing the total submicron mass obtained from the PCASP number size distributions averaged over the filter sampling times (particle density of 1.35 ± 0.15 g cm^{-3} [Haywood et al., 2003a]), to that estimated from the filters. The POM/OC ratio is left as free parameter. Implicitly, we are assuming that all of the unmeasured components present in the aerosol mass are due to POM. This is not strictly the case. For example, sea salt is an unquantified minor component that is likely being miscounted as POM. Na (major sea salt tracer) was below detection limit (~180 ng m^{-3}) in most but two samples. Multiply the Na detection limit with the typical Na/sea salt ratio (0.308 [Riley and Chester, 1971]) gives an upper limit for the sea salt mass of 760 ng m^{-3}. The soil mass could also be underestimated, as, from our data set, we are only able to estimate calcium carbonate from the water-soluble Ca fraction. However, calcium measured by IC should represent essentially the entire calcium concentration (water-soluble and insoluble), as suggested in the supermicron fraction by the identity (within 10%) of the IC and PIXE measurements. Also, the soil mass as aluminum silicate is left unquantified, as Al was detected only on a few samples. For the mean concentration obtained on those, and using the typical Al/dust mass ratio (0.0813 [Mason, 1966]), the dust concentration could be of the order of 2.5 μg m^{-3}.

For the chosen density value, the filter aerodynamic upper diameter of 0.9–1 μm corresponds to the PCASP geometric particle diameter of 0.77–0.86 μm. Because submicron biomass aerosols are mostly near-spherical and only moderately hygroscopic, the error in the PCASP size distributions is predominantly due to the shift in the PCASP bin diameters caused by the difference in the relative index between the actual particle and the latex calibration particles [Haywood et al., 2003a]. For particles below 0.154 μm diameter, the correction is 12–20% of the diameter that would be obtained if particles were non-absorbing latex spheres [Haywood et al., 2003a]. Particles in this size range, however, account for only 15% of the submicron aerosol mass of aged smoke encountered during SAFARI 2000. Corrections are within 9% for larger particles below 0.77 μm. The PCASP showed that, on the average, 90% of the accumulation mode mass was below 0.35 μm (aerodynamic diameter), and 98% below 0.7 μm. The Aitken size range, which is not accounted for in this calculation, is negligible in terms of aerosol mass. Assuming an average sizing error of 10% in the accumulation mode would correspond to an underestimation of particle volume and mass by 33%.

The linear regression between the filter and the PCASP submicron fine mass is shown in Figure 4 for fixed (upper panel) and for variable (lower panel) POM/OC ratios. It is clear that the POM/OC conversion factor estimated this way is uncertain due to the numerous assumptions in reconstructing the submicron mass both from the filter samples and the PCASP number size distribution. Error bars shown in Figure 4 are constrained by the upper limit blank concentrations (section 2.2.1) in the
case of the measured filter mass, and by the percent diameter shift and the estimated particle density in the case of the PCASP number size distributions. Random measurement errors and the uncertainty relating to the particle density are within ±20%, whereas the refractive index correction may result in systematic error of ~33%. When this correction is ignored, the fixed POM/OC ratio that provides the best agreement between the two estimates of the submicron aerosol mass is 2.6, consistent with the hypothesis of burning of organic material (slope of the linear regression 1.0 ± 0.2, $r^2 = 0.62$). Applying the refractive index correction would decrease the POM/OC ratio to 2.0. The scattering around the regression line is eliminated by varying point by point the slope of organic material ($r^2 = 1.0 ± 0.2$, $r^2 = 0.62$). Applying the refractive index correction would decrease the POM/OC ratio to 2.0. The scattering around the regression line is eliminated by varying point by point the slope of organic material ($r^2 = 1.0 ± 0.2$, $r^2 = 0.62$). Applying the refractive index correction would decrease the POM/OC ratio to 2.0. The scattering around the regression line is eliminated by varying point by point the slope of organic material ($r^2 = 1.0 ± 0.2$, $r^2 = 0.62$).

### 3.3. Enhancement Ratios and Emission Factors

In section 3.1, enhancement ratios ER with respect to CO for the total particle number in the Aitken and accumulation modes have been calculated. Now, we look at the ER values of OC, K$^+$, SO$_4^{2-}$, NH$_4^+$, NO$_3^-$, and the estimated submicron mass (ESM) with respect to CO in regional haze samples. All compounds have been corrected for their background components. The values for various types of vegetation burning reviewed by Andreae and Merlet [2001], as well as the observational data from EXPRESSO, SCAR-B, and SAFARI-92 [Ruehl et al., 1999; Ferek et al., 1998; Le Canut et al., 1996; Andreae et al., 1998] are used as terms of comparison. The results of Mayol-Bracero et al. [2002b] during the Indian Ocean Experiment (INDOEX) are taken as representative of a hybrid situation of an aerosol load dominated by fossil fuel emissions (for about two thirds), and a significant contribution by biomass burning (about one third), mainly from biofuel burning.

Results are reported in Table 2. There is a clear difference between the INDOEX values of Mayol-Bracero et al. [2002b], and those found in this study. In particular, note the higher EC$_a$/OC and SO$_4^{2-}$/CO ratios in the INDOEX aerosol. Our EC$_a$/OC ratio is closer to the experimental data from SCAR-B, which was conducted in the Amazon Basin, and to the value for savanna haze estimated during EXPRESSO. The EXPRESSO EC$_a$/OC ratio for savanna flaming fires is higher (0.22), as high temperatures during flaming conditions favor the production of elemental carbon [Andreae et al., 1998]. The proportion between elemental and organic carbon is substantially identical for very different ecosystems, such as savanna/grassland (prevailing in the area that was sampled during SAFARI 2000) and tropical forest [Andreae and Merlet, 2001]. The EC$_a$/OC analysis for SCAR-B and EXPRESSO were conducted by the same laboratory as in this analysis. Artificial differences due to the analytical protocols should be minimal, and the higher value would reflect a different type of burning. Central Africa, were EXPRESSO was conducted, is densely populated, and burning of biofuel might mix with the savanna emissions.

The mass enhancement ratio of the estimated submicron mass (ESM) to CO is 0.08 ± 0.02 (ESM either calculated from the filters for a variable POM/OC ratio, or from the PCASP). To allow comparison with the literature values, which are generally for the PM$_{2.5}$–PM$_{3.0}$ mass fraction (PM$_{y}$ = particle mass below $y$ μm diameter), we integrated the PCASP distribution over the full size range. The PM$_{2.5}$/CO ratio was 0.09 ± 0.02. These values are consistent with the results of Le Canut et al. [1996] for SAFARI 92. For a particle density of 1 g cm$^{-3}$, the SAFARI 2000 Δ(ESM)/ΔCO ratio becomes 0.08 ± 0.02 and Δ(PM$_{2.5}$)/ΔCO = 0.09 ± 0.04.

Next, we will derive estimates for the emission factors of the aerosol species of interest. The emission factor (EF$_X$) for an aerosol species X is calculated from the ER$_{X/CO}$ values in Table 2 as

$$\text{EF}_X = \text{ER}_{X/CO} \times \text{ER}_{CO/CO_2} \times \text{EF}_{CO_2}$$  \hspace{1cm} (2)$$

where ER$_{CO/CO_2}$ is the emission ratio of CO with respect to CO$_2$ and EF$_{CO_2}$ is the emission factor of CO$_2$.

Because EF$_{CO_2}$ does not change very much from one type of fire to another we can adopt a mean value of 1600 grams of CO$_2$ per kilogram dry mass (g(CO$_2$) kg$^{-1}$ dm) in equation (2) with good accuracy [Andreae et al., 1998]. Since we have no measurement of ER$_{CO/CO_2}$, we attempt to

### Figure 4. Linear regression of the submicron aerosol mass estimated from the filter samples and that obtained from the PCASP number size distributions averaged over the filter sampling times. The aerosol density is set to 1.35 g cm$^{-3}$. In the upper panel the filter mass is obtained using a POM/OC ratio of 2.6 (POM = particulate organic matter), in the lower panel the POM/OC ratio is varied between 2 and 3.
The value, normalized for the same particle density, is 104 ± 19 ng m⁻³ (STP) ppb⁻¹, and 93 ± 19 ng m⁻³ (STP) ppb⁻¹ from the filter measurements.

From the PCASP mass distribution (density = 1.35 g cm⁻³), ESM/CO = 0.02 ± 0.02.

Ratio EC a/OC and Mass Enhancement Ratios (ER X) of savanna/grassland, biofuel, and agricultural residues are better approached by our data, and there are also plausible source types in our study region. Since we do not know the contributions from each potential source type, we took the ER X values of Andreae and Merlet [2001] for these three ecosystems to estimate the species EF X “as if” we had detected the haze from the burning of only one of those ecosystems. The agreement is of course obtained for the savanna/grassland EF EC, but will depend on the many parameters (such as the reaction time, the aerosol conversion efficiency) ruling the gas-to-particle conversion. “Aerosol yield” might be a better definition in this case. The comparison with values of SCAR-B [Ferek et al., 1998] and SAFARI 92 [Andreae et al., 1998] is overall reasonable. Our EF X have large variability due to the variability of the ER X. The best agreement is of course obtained for the savanna/grassland emission factors, which was the prevailing vegetation type investigated both by Ferek et al. [1998] and Andreae et al. [1998]. The largest differences are for the sulfate and nitrogen species, which have higher enhancement factors

Table 2. Ratio EC/OC and Mass Enhancement Ratios (ER X) Measured in Aged Haze During SAFARI 2000

<table>
<thead>
<tr>
<th></th>
<th>EC/OC</th>
<th>ER EC/OC</th>
<th>ER SO₂⁻/CO</th>
<th>ER NO₃⁻/CO</th>
<th>ER NH₄⁺/CO</th>
<th>ER K⁺/CO</th>
<th>ER ESM</th>
<th>CO, Arithmetic Mean and Standard Deviation) for Various Aerosol Species X Measured in Aged Haze During SAFARI 2000</th>
</tr>
</thead>
<tbody>
<tr>
<td>This study</td>
<td>0.11 ± 0.02</td>
<td>0.007 ± 0.001</td>
<td>0.04 ± 0.01</td>
<td>0.013 ± 0.019</td>
<td>0.007 ± 0.011</td>
<td>0.007 ± 0.012</td>
<td>0.0008 ± 0.0053</td>
<td>0.08 ± 0.02²</td>
</tr>
<tr>
<td>Savanna/grassland</td>
<td>0.14</td>
<td>0.0073</td>
<td>0.0515</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.0053</td>
<td>0.078²</td>
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<tr>
<td>Tropical forest</td>
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<td>0.0063</td>
<td>0.0504</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.0028</td>
<td>0.086²</td>
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<tr>
<td>Extratropical forest</td>
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<td>Biofuel</td>
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<td>–</td>
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<td>INDOEX</td>
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<td>–</td>
<td>0.022 ± 0.013</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.042²</td>
</tr>
<tr>
<td>EXPRESSO</td>
<td>0.08 –0.22</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>SCAR-B³</td>
<td>0.12 ± 0.03</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>36 (± 6.5) – 83 (± 45)</td>
</tr>
</tbody>
</table>

Table 3. Aerosol Yields Equivalent to Mass Emission Factors (EF X, Mean and Standard Deviation) for Various Aerosol Species X Measured in Aged Haze During SAFARI 2000

<table>
<thead>
<tr>
<th></th>
<th>EF EC, Mean and Standard Deviation) for Various Aerosol Species X Measured in Aged Haze During SAFARI 2000</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EF EC</td>
</tr>
<tr>
<td>Savanna/grassland</td>
<td>0.45 ± 0.06</td>
</tr>
<tr>
<td>Biofuel</td>
<td>0.56 ± 0.08</td>
</tr>
<tr>
<td>Agricultural residues</td>
<td>0.68 ± 0.10</td>
</tr>
<tr>
<td>SCAR-B³</td>
<td>0.32 ± 0.03</td>
</tr>
<tr>
<td>SAFARI-92²</td>
<td>0.59²</td>
</tr>
<tr>
<td>This study</td>
<td>0.007 ± 0.001</td>
</tr>
</tbody>
</table>

1Data are expressed in gram species per kilogram dry mass (g (X) kg⁻¹ dm⁻¹). The mass enhancement ratio ER X for each species is also shown in the last row.
2Ferek et al. [1998]. The original EF values expressed in grams of species per kilogram of carbon have been converted to grams of species per kilogram of dry mass assuming an average carbon content in dry mass of 45% [Andreae and Merlet, 2001]. The upper value is for cerrado burning, and the lower value is for grass burning.
3Andreae et al. [1998].
4Values for tropical savanna and grassland.
5Values for PM3.0 (particulate matter < 3 µm diameter).
6ESM = estimated submicron mass (aerodynamic D₉₀ < 1 µm). The value in the table has been estimated from the filter measurements for a variable POM/OC ratio between 2 and 3. From the PCASP mass distribution (density = 1.35 g cm⁻³), ESM/CO = 0.02 ± 0.02.
in our and the SAFARI 92 estimates than in SCAR-B. This difference could be due to different age of the sampled air masses.

3.4. Optical Properties

[59] The relationship between the aerosol chemical and optical properties is investigated by looking at the linear regressions of the dry particle scattering and absorption coefficients ($\sigma_s$ at 550 nm and $\sigma_a$ at 565 nm, respectively), averaged over the filter sampling times, against the estimated submicron mass (ESM) and EC$_a$, respectively. If correlated, the slopes of the regression lines yield the mass scattering and absorption efficiencies, respectively $\alpha_s$ and $\alpha_a$ in units of m$^2$ g$^{-1}$. These are essential parameters in estimating the aerosol direct climate forcing, given the total atmospheric aerosol burden and its hydration state [Charlson et al., 1999]. There is substantial uncertainty in this type of calculation, which depends crucially on the ability of reproducing the total aerosol mass based on the relative concentration of its individual components, and their degree of mixing, as well as in the correct measurement of the aerosol scattering and absorption [Charlson et al., 1999]. Because the ambient relative humidity was always well below 50% during the campaign, relating the filter measurements at ambient conditions to the scattering and absorption, measured at controlled low RH, is not an issue.

[60] While all the submicron aerosols (organic and inorganic) scatter light, elemental carbon is considered the major light-absorbing component [Seinfeld and Pandis, 1998]. Assuming that aerosols are externally mixed, $\alpha_s$ can be calculated from the linear regression of $\sigma_s$ versus the total submicron mass, and $\alpha_a$ from that of $\sigma_a$ versus the EC$_a$ mass. This, however, might not be fully rigorous for biomass burning aerosols, which after a certain time from emission tend to become internally mixed, as elemental carbon particles might get coated with organic material [Martins et al., 1998]. The opposite process may also occur, as our data for the elemental versus organic carbon ratio suggest that organic carbon might have evaporated while in the atmosphere. Furthermore, in pyrogenic aerosols there may be additional absorption due to colored organic compounds (“brown carbon”) [Mukai and Ambe, 1986].

[61] The mean particle scattering coefficient at 550 nm for the flight segments considered in this paper was $\sigma_s = 101 \pm 56$ Mm$^{-1}$ in regional haze and $154 \pm 26$ Mm$^{-1}$ for the legs during flight A790, excluding direct passes in the plumes, when values up to 1,000 Mm$^{-1}$ were measured. We recall that “regional haze” refers to the few-day-old aerosol layers that were sampled offshore Namibia and Angola, while fresh smoke was encountered during the over flight of an active agricultural fire in Namibia (see section 3.1). For regional haze, the mass scattering efficiency $\alpha_s$ was $4.2 \pm 0.8$ m$^2$ g$^{-1}$ ($r^2 = 0.71$) assuming a fixed POM/OC ratio, and $\alpha_a = 4.6 \pm 0.6$ m$^2$ g$^{-1}$ ($r^2 = 0.79$) when varying the POM/OC ratio between 2 and 3 (Figure 5).

[62] The mean particle absorption coefficient $\sigma_a$ at 565 nm averaged $8 \pm 5$ Mm$^{-1}$ in regional haze. We commented in section 3.1 about some of the difficulties in measuring the absorption coefficient within the fresh smoke, when excluding the sharp peaks corresponding to the direct transit in the plumes, the absorption coefficient was of the order of 20 Mm$^{-1}$. For samples taken at low concentrations, the reading of the PSAP was often below 1 Mm$^{-1}$, and many values had to be discarded. As a result, the linear correlations of the absorption coefficient with the scattering coefficient and with CO were only modest over the sampling legs considered ($r^2 \sim 0.4$, not shown). The linear correlation of $\sigma_a$ with EC$_a$ (taken as representative of the light-absorbing mass) yielded $\alpha_a = 4.0 \pm 0.8$ m$^2$ g$^{-1}$ excluding flight A790 ($r^2 = 0.64$). This value is below the lower limit $\alpha_a \sim 5$ m$^2$ g$^{-1}$ of the range of values reported for pure elemental (black) carbon by Martins et al. [1998]. Recent research in the Amazon basin has shown that a fraction of the organic matter in the biomass-burning aerosol might absorb light (P. Guyon and M. O. Andreae, personal communication, 2002). In this case, the EC$_a$ obtained by chemical methods based on the carbon refractory properties (as the TOT) would underestimate the mass of light absorbing carbon. As a result of underestimating the mass concentration of light-absorbing matter, $\alpha_a$ would therefore be actually overestimated, which does not seem the present case. The slope of the regression line of $\sigma_a$ against the total estimated submicron mass is around $0.1 \pm 0.1$ m$^2$ g$^{-1}$ ($r^2 = 0.36$), much lower than predicted by Ross et al. [1998] for aerosols with an average EC$_a$ content of 4%.

[63] The dominance of scattering over absorption for the regional haze yields a mean single scattering albedo $\omega_s$ of $0.93 \pm 0.06$ at 550 nm. The standard deviation is calculated from the sample-to-sample variability of the measured scattering and the absorption coefficients, and not on their experimental errors. This mean value obtained by averaging over the filter sampling times is somewhat higher than the flight averages reported by Haywood et al. [2003a], as expected by flight-to-flight variability as well as by the inherent aerosol variability during each flight. Also, Haywood et al. [2003a, 2003b] have shown that the airborne
are very persistent on timescales of weeks. Results have shown that haze layers over Southern Africa are compatible within one standard deviation with the values retrieved by ground-based remote sensing for biomass burning plumes (the cluster of three points $\Delta \sigma_s$ with $>150$ Mm$^{-1}$ in Figure 6) are included in the linear regression for fresh smoke. Within these limits, the increase of the ratio of light scattering to CO should be between 14% and 65% due to aging. This is consistent with the calculations of Haywood et al. [2003a] of the mass extinction efficiency, obtained by Mie theory from the lognormal fits of the measured PCASP number size distributions, and the refractive indexes from the filter samples. These authors indicate that the mass extinction efficiency would increase by about 64% during aging. It should be noted that the method of Haywood et al. [2003a] is significantly different as it assumes internally mixed aerosols, and the calculated mass extinction efficiency is dependent upon the assumed density and refractive index.

Finally, in Figure 7 the variation of the enhancement ratio $ER$ of $\sigma_a$ and $\sigma_s$ (corrected for background values) is plotted as a function of longitude. Given the transport pathways of the air masses shown in Figure 1, the longitude can be taken as a measure of the distance from the smoke sources, at least for samples taken after 11 September. The Namibian coastline is approximately at 13–14°E, therefore longitude east of ~14°E represents sampling over land, and longitude west of ~14°E sampling over the ocean. The enhancement ratio for the scattering coefficient $\Delta \sigma_a/\Delta CO$ (upper panel) decreased linearly ($r^2 = 0.92$) over land at a rate of $0.14 \pm 0.02$ Mm$^{-1}$ ppb$^{-1}$ degree$^{-1}$, that is, by about 58% from 17.5°E (where the young smoke samples were collected, see the three rightmost points in Figure 7) to 14°E. This distance, in average, was covered by the air masses in less than 1 day (Figure 1). Figure 7 also shows that over water $\Delta \sigma_a/\Delta CO$ actually increased with longitude.

Figure 6. Linear regression of $\Delta \sigma_s$ versus $\Delta CO$. $\Delta \sigma_s$ represents the enhancement of the particle scattering coefficient at 550 nm with respect to background conditions, while $\Delta CO$ represents the enhancement of CO. Squares indicate data acquired in the regional haze, open circles data taken during flight A790, close to an active fire. The dotted and dashed regression lines refer to the young smoke data. The dotted line is the regression line when the three points with highest $\Delta \sigma_s$ are excluded, the dashed line when the three points are included.

Single scattering albedo values are generally higher than values retrieved by ground-based remote sensing in Zambia and Brazil; however, they are compatible within one standard deviation with the ground-based retrievals made using measurements over Namibia during SAFARI 2000. As the flow rate of the PSAP is low, it is also possible that the airborne measurements of the particle absorption coefficient suffered from possible aging effects. We do the same by plotting $\Delta \sigma_a$, the enhancement of the scattering coefficient in the haze with respect to background values, as a function of $\Delta CO$, separately for regional haze and fresh smoke (Figure 6). On the timescales involved, CO is essentially conserved. The decrease of $\Delta \sigma_a$ versus $\Delta CO$ for each individual curve is related to aging processes, such as coagulation and condensation, but also to dilution. Dilution should be efficient only immediately after emission, as previous results have shown that haze layers over Southern Africa are very persistent on timescales of weeks [Garstang et al., 1996]. However, comparing the ratios of light scattering to CO (i.e., the slopes of each individual regression line) is independent of dilution. Figure 6 shows that the slope of the linear regression line is higher for aged than for young air masses, meaning that aged aerosol haze will contribute more to light scattering than a younger air mass with a comparable amount of CO. The magnitude of this increase, estimated as the ratio of the slopes for aged and young smoke, depends on whether the samples in the A790 active fires plumes (the cluster of three points $\Delta \sigma_a$ with $>150$ Mm$^{-1}$ in Figure 6) are included in the linear regression for fresh smoke. Within these limits, the increase of the ratio of light scattering to CO should be between 14% and 65% due to aging. This is consistent with the calculations of Haywood et al. [2003a] of the mass extinction efficiency, obtained by Mie theory from the lognormal fits of the measured PCASP number size distributions, and the refractive indexes from the filter samples. These authors indicate that the mass extinction efficiency would increase by about 64% during aging. It should be noted that the method of Haywood et al. [2003a] is significantly different as it assumes internally mixed aerosols, and the calculated mass extinction efficiency is dependent upon the assumed density and refractive index.

Figure 7. Linear regressions of $\Delta \sigma_a/\Delta CO$ (upper panel), $\Delta \sigma_s/\Delta CO$ (middle panel), and $\Delta \omega_a/\Delta CO$ (lower panel) as a function of longitude.
The behavior of the $\Delta \sigma_a/\Delta \text{CO}$ ratio is interpreted by saying that in the first day after emission, light scattering efficiency decreases as the particle size distributions undergo rapid modification due to coagulation and condensation, for example, the transfer of the Aitken-size particle to the accumulation mode. Once these processes are completed, the light scattering efficiency stabilizes and then increases as the accumulation modal diameter shifts to larger sizes, more efficient in scattering. An alternative explanation would be that, over the Ocean, we detected the additional contribution of sea salt particles. The thermodynamic structure of the atmosphere, with the substantial decoupling between the surface and the haze layer, argues against this.

Conversely, the enhancement ratio for the absorption coefficient $\Delta \sigma_a/\Delta \text{CO}$ decreased steadily with decreasing longitude ($r^2 = 0.5$). The decrease is of the order of 50%, and might not be significant when compared to the experimental error of the measurement of $\sigma_a$ ($\sim 22\%$), which doubles when calculating background-corrected values, as well as considering the uncertainties in measuring $\sigma_a$. A decrease in the absorption coefficient might be due either to a decrease in the mass absorption efficiency, or to the absorbing aerosol mass (i.e., $\text{EC}_i$). The latter was not observed appreciably. From Mie theory, the mass absorption efficiency for the chemical composition and particle size distribution observed for aged haze during SAFARI 2000 (fixed aerosol refractive index of $n = 1.54 - 0.018 i$; see Haywood et al. [2003a] for details), is fairly independent of particle size in the 0.1–1 μm diameter range. Our data are therefore not conclusive in this respect.

The single scattering albedo calculated from scattering and absorption corrected for background (Figure 7, lowest panel), increased with longitude, which is consistent with growth by coagulation [Reid et al., 1998]. The different behavior of scattering and absorption over water suggests as well that particles are externally mixed.

4. Summary and Conclusions

The chemical composition of aerosol samples obtained onboard the C-130 aircraft during SAFARI 2000 is overall in fair agreement with previous findings for biomass burning aerosols [Gaudichet et al., 1995; Cachier et al., 1995; Maenhaut et al., 1996; Le Canut et al., 1996; Andreae et al., 1998; Ferek et al., 1998; Reid et al., 1998]. The observed agreement must be considered in the context of the variability of the environmental conditions (differing ecosystems, burned fuels, types of combustion), and the biases due to the differing sampling and analytical protocols of the various experiments.

Our data suggest that the haze layers sampled in the outflow region of the South African anticyclone offshore Namibia and Angola had undergone significant modification while in the atmosphere, due to coagulation and condensation within 1–2 days from emission. This was evident in the nearly twofold increase of the particle mass in the accumulation mode (0.1–1 μm diameter, section 3.1), and in the elevated concentrations of secondary species such as $\text{SO}_3^-$, $\text{NH}_4^+$, and $\text{NO}_3^-$. Aitken-size particles (smaller than 0.1 μm) were detected only close to active fires, but rapidly disappeared due to particle coagulation. This is commonly observed in the time evolution of the smoke plume [Radke et al., 1995]. The depletion rate of the accumulation mode particle number in the evolution from young to aged smoke is estimated at about 40%. The persistence of particles with large-surface area in the elevated smoke layers can inhibit new particle formation over a region that extends geographically over thousands of kilometers. Bursts of Aitken particles over the Atlantic Ocean were in fact occasionally observed only below the haze layers, close to the sea surface, but no connected with biomass haze.

[70] The carbonaceous (organic and elemental) fraction of the estimated submicron mass was of the order of 80% in the aged haze layers, while sulfate and nitrogen species accounted for about 15%. This might have important implications for the direct and indirect aerosol radiative effect, and for the transfer of nutrients to the Ocean. The “aerosol yield” calculated in section 3.4 show that biomass-burning haze in Africa is able to mobilize a significant quantity of nitrogen. For the average amount of dry biomass burned per annum in Africa savannas (2000 Tg dm yr$^{-1}$) [Scholes and Andreae, 2000], the flux of carbonaceous particles (particulate organic matter plus elemental carbon) for African savanna/grassland burning is estimated at 14 ± 1 Tg yr$^{-1}$, and that of nitrogen species (nitrate and ammonium) at 2 ± 2 Tg yr$^{-1}$.

[71] The aerosol optical properties for the regional haze were dominated by scattering over absorption, yielding a mean single scattering albedo of 0.93 ± 0.06 at 550 nm. The absorption coefficients on the flight segments considered in this paper were rather low, often dropping below 1 Mm$^{-1}$, and uncorrelated to the scattering coefficient or to CO. The mean mass absorption efficiency $\alpha_m$, calculated as the slope of the regression line between the absorption coefficients and the chemical EC mass concentrations, is lower than expected for elemental (black) carbon in biomass burning according to the results of Martins et al. [1998].

[72] The mass scattering efficiency $\alpha_s$, estimated as the slope of the regression line of the scattering coefficient versus the estimated submicron mass (ESM) is of the order of 4.6 m$^2$ g$^{-1}$. This is entirely consistent with the current estimates for aerosols with a prevalent organic carbon fraction [e.g., Reid et al., 1998; Haywood et al., 2003a]. Changes in the aerosol optical properties were observed and attributed to aging processes.

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References


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