

Atmospheric tar balls: Particles from biomass and biofuel burning

Mihály Pósfai,¹ András Gelencsér,² Renáta Simonics,¹ Krisztina Arató,¹
Jia Li,³ Peter V. Hobbs,⁴ and Peter R. Buseck^{3,5}

Received 17 September 2003; revised 6 January 2004; accepted 14 January 2004; published 27 March 2004.

[1] “Tar balls” are amorphous, carbonaceous spherules that occur in the tropospheric aerosol as a result of biomass and biofuel burning. They form a distinct group of particles with diameters typically between 30 and 500 nm and readily identifiable with electron microscopy. Their lack of a turbostratic microstructure distinguishes them from soot, and their morphology and composition (~90 mol % carbon) renders them distinct from other carbonaceous particles. Tar balls are particularly abundant in slightly aged (minutes to hours old) biomass smoke, indicating that they likely form by gas-to-particle conversion within smoke plumes. The material of tar balls is initially hygroscopic; however, the particles become largely insoluble as a result of free radical polymerization of their organic molecules. Consequently, tar balls are primarily externally mixed with other particle types, and they do not appreciably increase in size during aging. When tar balls coagulate with water-bearing particles, their material may partly dissolve and no longer be recognizable as distinct particles. Tar balls may contain organic compounds that absorb sunlight. They are an important, previously unrecognized type of carbonaceous (organic) atmospheric particle.

INDEX TERMS: 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; **KEYWORDS:** tar ball, aerosol, biomass burning

Citation: Pósfai, M., A. Gelencsér, R. Simonics, K. Arató, J. Li, P. V. Hobbs, and P. R. Buseck (2004), Atmospheric tar balls: Particles from biomass and biofuel burning, *J. Geophys. Res.*, 109, D06213, doi:10.1029/2003JD004169.

1. Introduction

[2] Carbonaceous particles constitute an important fraction of tropospheric aerosol particles because of their abundance and climate effects [Liou *et al.*, 1996; Houghton *et al.*, 2001; Chung and Seinfeld, 2002]. Carbon-bearing particles have a variety of natural and anthropogenic sources, both biogenic and pyrogenic. Primary and secondary particles are produced that form an extremely heterogeneous part of the atmospheric aerosol, and many unresolved questions remain about these materials. Soot is the main absorber of shortwave radiation in the atmosphere [Haywood and Ramaswamy, 1998; Jacobson, 2001]. Except for the study of Jacobson [2002b], atmospheric models of the climate effects of carbonaceous aerosols assume that no light-absorbing particles are pro-

duced in the air by secondary mechanisms. The main optical effect of organic carbon (OC) particles is thought to be scattering of sunlight [Chung and Seinfeld, 2002]. In addition, such particles are important agents of cloud nucleation [Novakov and Penner, 1993; Hitzenberger *et al.*, 1999]. Determination of the atmospheric roles and climate effects of carbonaceous particles is made even more difficult by the internal mixing of soot and OC particles of various origins with other components of the aerosol. It is therefore of great importance to identify distinct carbonaceous particle types and study their properties and atmospheric effects.

[3] Several types of carbonaceous particles can be distinguished by transmission electron microscope (TEM) studies. Distinguishing features include morphology, composition, structure, mixing, and behavior in the electron beam [Buseck and Pósfai, 1999; Buseck *et al.*, 2002; Pósfai *et al.*, 2003; Li *et al.*, 2003]. Figure 1 shows examples of the main types of carbon-bearing particles from various locations. Since the observable properties differ, individual particle characterization does not necessarily result in the identification of the same groups as with other methods such as mass spectrometry [Murphy *et al.*, 1998]. Some particles are dehydrated and may be modified by the vacuum of the electron microscope. Nevertheless, when distinct types of particles can be identified that consistently show the same properties in the TEM, we assume that such particles share a common origin and likely have the same atmospheric effects.

¹Department of Earth and Environmental Sciences, University of Veszprém, Veszprém, Hungary.

²Air Chemistry Group, Hungarian Academy of Sciences, Veszprém, Hungary.

³Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona, USA.

⁴Department of Atmospheric Sciences, University of Washington, Seattle, Washington, USA.

⁵Department of Geological Sciences, Arizona State University, Tempe, Arizona, USA.

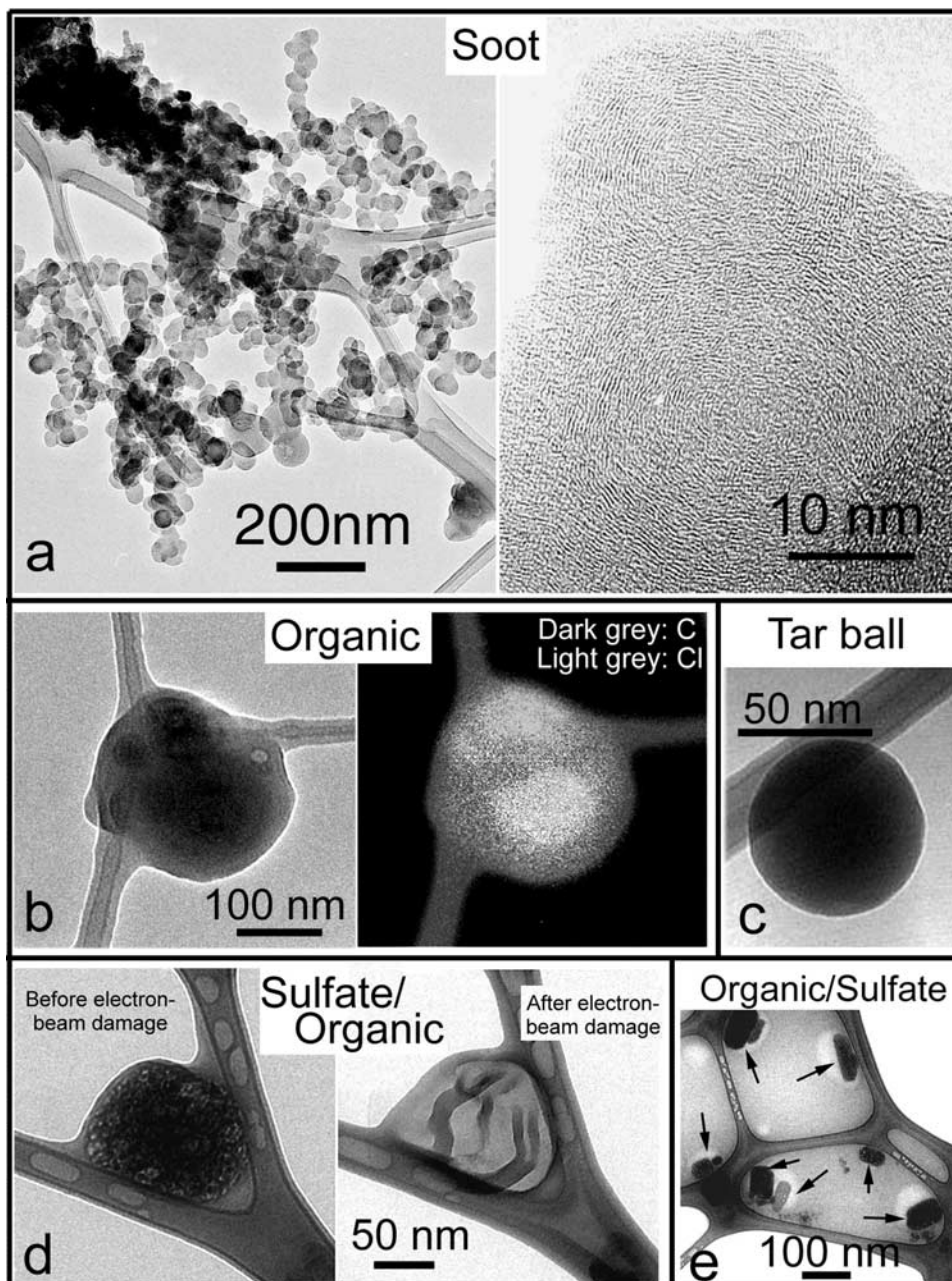


Figure 1. Various types of carbon-bearing particles in the troposphere identified using transmission electron microscopy. (a) Soot; the left panel shows the organization of individual spherules into large, irregular or chain-like aggregates. The right panel is a high-resolution image of two merged spherules showing wavy, concentric layers that form the typical subgraphitic microstructure of soot. (Particles from biomass smoke, Timbavati Game Reserve (left panel) and Kruger National Park (right panel), South Africa.) (b) Bright-field image (left panel) and a composite of electron energy-loss images (center panel) of an organic particle with KCl inclusions from biomass smoke (west of Beira, Mozambique). The irregular shape of the particle indicates that it likely was hydrated when collected. (c) Tar ball from central Europe, in winter (K-pusztá, Hungary). (d) Sulfate particle coated by an organic film (K-pusztá, Hungary); under the irradiation by the electron beam, ammonium sulfate sublimates and only the carbonaceous coating remains (center panel). (e) Organic particles, presumably of natural origin, containing minor ammonium sulfate (shown with arrows) (clean summer sample, K-pusztá, Hungary). The particle(s) spread and filled the holes of the lacey support film, indicating that they were liquid and presumably hydrated at the time of collection.

[4] Biomass burning emits vast quantities of gases and aerosol particles with highly variable properties that depend on fire and fuel characteristics [Crutzen and Andreae, 1990; Cachier et al., 1991; Hobbs et al., 1997; Andreae et al., 1998; Andreae and Merlet, 2001; Sinha et al., 2003]. It is important to characterize the particle types in biomass smoke, since the regional and global climate effects of aerosols from biomass burning depend strongly on particle properties [Martins et al., 1998a; Roberts et al., 2003]. It is especially challenging to account for the absorbing component of biomass smoke from smoldering fires under conditions when soot formation is suppressed [Ward et al., 1992].

[5] In this study we describe and characterize a distinct group of carbonaceous particles that is common in the smoke of biomass and biofuel combustion. We call them “tar balls” because of their carbon-dominated elemental composition and typical spherical morphology. Although spherical particles that may be identical to tar balls have been observed [Cachier et al., 1991; Gaudichet et al., 1995; Martins et al., 1998a, 1998b; Alfaro et al., 2003], they have not been recognized as a distinct particle type; instead, they have been considered to be a variety of soot (or BC) particles. Here we show that tar balls are distinct from soot and represent an intermediate stage in the aging of organic particles emitted by biomass and biofuel burning. We outline a possible secondary formation mechanism for tar balls during smoke aging and discuss their potential effects on climate.

2. Experiment

[6] We analyzed two sets of samples, one was collected during the Southern African Regional Science Initiative (SAFARI) 2000 campaign [Sinha et al., 2003, Appendix A by P. V. Hobbs] and the other at a regional air pollution monitoring station (K-puszt) in Hungary [Mészáros et al., 1997; Molnár et al., 1999; Gelencsér et al., 2000; Krivácsy et al., 2001]. The SAFARI samples were obtained from fresh and aged biomass smoke as well as from regional hazes over southern Africa during the dry, biomass-burning season. The samples were obtained from the University of Washington’s Convair-580 research aircraft, using a three-stage impactor (model MPS-3, California Measurements, Inc.) with nominal cuts at 2 and 0.3 μm (first stage: $d > 2$; second stage: $2 > d > 0.3$; third stage: $d < 0.3 \mu\text{m}$); we studied mainly the second- and third-stage samples. Sampling details are given by Pósfai et al. [2003]. The K-puszt samples were obtained using a two-stage impactor; data in this paper are given for particles on the stage with a nominal cut at 1 μm diameter. Particles were collected on copper TEM grids that were covered with a lacey Formvar supporting film.

[7] Transmission electron microscopy was performed using a Philips CM20 TEM operated at 200 kV accelerating voltage and equipped with an ultra-thin-window Noran Voyager energy-dispersive X-ray detector. Electron energy-loss images were obtained using a 125-kV Hitachi 7100 TEM with an attached Gatan Imaging Filter that acts as both an electron energy-loss spectrometer and an imaging device.

[8] Quantitative chemical analyses were obtained from energy-dispersive X-ray spectrometry (EDS) using the CM20 TEM. We analyzed standards to obtain sensitivity factors (“k-factors”) [Cliff and Lorimer, 1975; Pósfai et al., 1995] for thin-film analyses of C, O, Na, Mg, Si, S, Cl, K,

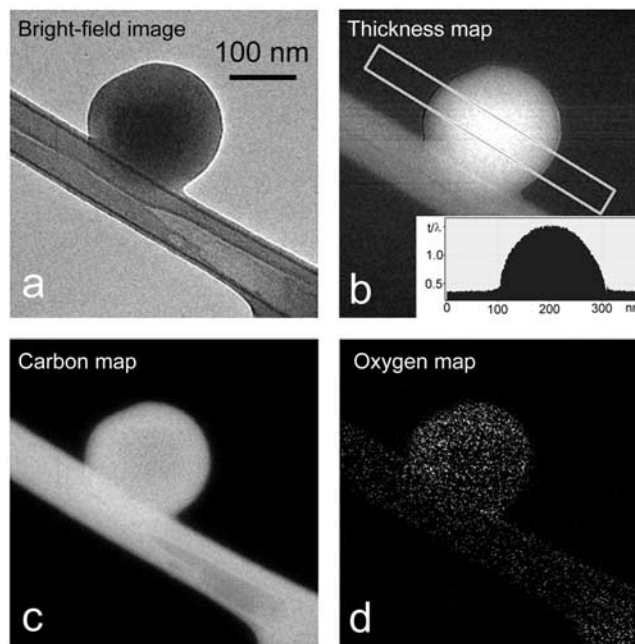


Figure 2. Electron energy-loss images of a tar ball from biomass smoke (west of Beira, Mozambique) attached to a ribbon of the lacey Formvar support film. (a) Bright-field image. (b) Map of the relative particle thickness, with an inserted profile along the indicated section (t , thickness along the electron beam; λ , mean free path of the electrons as they travel through the material; $t/\lambda = 1$ is equivalent to a thickness of ~ 125 nm). (c) Carbon map. (d) Oxygen map.

and Ca. Spectra were acquired for 60 s, with the diameter of the electron beam adjusted to include the entire particle. Data for light elements such as C and O are semi-quantitative because most particles cannot be analyzed without at least some contribution from the Formvar film (which also contains C and O). We used a low-intensity electron beam to avoid particle decomposition during spectrum acquisition.

[9] Energy-filtered imaging based on electron energy-loss spectroscopy (EELS) was used for obtaining compositional maps; these are made using electrons that lose a specific amount of their energy in inelastic interactions with the atoms in the specimen. We selected the energy range to produce element-specific images in which the brighter areas correspond to larger concentrations of the selected element. By using certain parts of an EELS spectrum, it is also possible to obtain an image in which the thickness of a particle is proportional to pixel brightness [Egerton, 1986]. The two-dimensional projection provided by the bright-field image is then complemented by information about the third dimension of the particle. Selected-area electron diffraction (SAED) patterns were obtained from particles to determine whether they are crystalline.

3. Properties of Tar Balls

3.1. Shape

[10] Tar balls can be recognized in TEM (and SEM) images by their shapes (Figures 1c and 2a); thickness maps confirm the spherical morphologies (Figure 2b), which can

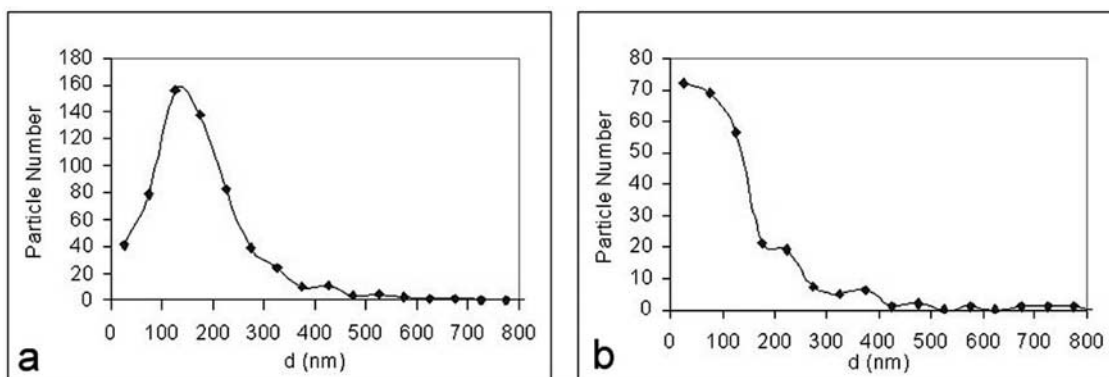


Figure 3. Size distributions of tar balls from (a) southern African biomass smoke and (b) polluted winter air in Hungary. The particle diameters were measured on electron micrographs. The data points represent 50-nm size ranges and are plotted at the centerpoints of the corresponding ranges.

also be inferred from their circular projections in bright-field images. In contrast to other widespread and spherical aerosol particle types, such as sulfates, tar balls are stable and do not change visibly under the electron beam. Fly-ash particles can also be spherical, but most are significantly larger than tar balls and consist of silica or metal oxides.

3.2. Structure

[11] Tar balls are amorphous; electron diffraction patterns do not show reflections or even continuous rings. Soot particles are aggregates of spherules that consist of concentrically wrapped graphitic layers, observable in HRTEM images (Figure 1a, right panel), but tar balls neither possess a semi-ordered microstructure, nor do they form aggregates. The lack of any microstructure clearly means that tar balls are a distinct particle type rather than just individual soot spherules.

3.3. Composition

[12] EDS and EELS spectra indicate that tar balls mainly consist of C. All contain minor O, and some contain variable but minor amounts of S, K, Cl, and Si. EDS data [Pósfai *et al.*, 2003] show that tar balls are compositionally distinct from other carbonaceous (organic) particles in biomass smoke (Figure 1b), as well as from organic/sulfate mixed particles that contain significant sulfate (Figures 1d and 1e). Since the particles were analyzed in the vacuum of the TEM, the data may not represent original compositions; volatile species would have been lost when the specimens were inserted into the TEM. Nevertheless, tar balls have distinct and fairly uniform compositions. Energy-filtered maps indicate that carbon and oxygen are homogeneously distributed within the particles (Figures 2c and 2d), and tar balls lack cores or shells.

3.4. Size Distributions

[13] Size distributions of tar balls were obtained by measuring their diameters on digitized TEM images. Since essentially the same curves resulted for various SAFARI samples, all distributions are combined in Figure 3a. For the SAFARI samples, the lower ends of the distributions may have been affected by poor collection efficiency of <300 nm particles on the TEM grids [Pósfai *et al.*, 2003]; thus the symmetrical shape of the peak in Figure 3a is likely an

artifact. Size distributions from the K-pusztas samples do not suffer from such artifacts. However, because of the low concentration of tar balls in clean air samples (see below), data are again combined for six samples (Figure 3b). Both size distributions are narrow, have a single peak, and few particles are larger than 400 nm. The SAFARI samples were obtained from fresh and aged (~ 1 hour old) biomass smoke as well as from regional hazes; the size distributions of tar balls are essentially the same in every sample, suggesting no particle growth [Pósfai *et al.*, 2003].

3.5. Mixing With Other Particles

[14] In contrast to other carbonaceous particles that seem to readily form internal mixtures with sulfate [Pósfai *et al.*, 1999, 2003], tar balls are typically externally mixed with other particles. Even in air masses that contained aged aerosol, such as the regional hazes in southern Africa, few tar balls were aggregated with other particles.

3.6. Occurrence

[15] Tar balls occur in a variety of atmospheric environments that are affected by human activities, including polluted layers over both land and oceans. They are primarily associated with and are among the products of biomass burning, as indicated by their high relative concentration in biomass smoke. Samples obtained from fresh and ~ 1 -hour-old biomass smoke from the same fire in Mozambique (Figure 4a) revealed significant changes in relative particle concentrations. During aging of the smoke tar balls became the dominant particle type [Pósfai *et al.*, 2003]. However, with further aging the relative concentration of tar balls decreased, as seen from their low numbers in the regional hazes (Figure 4a). At the K-pusztas site, tar balls occurred in fall and winter samples (Figure 4b); their high relative abundances in the November and January samples were not obviously related to a particular air mass origin, nor were they associated with high concentrations of industrial emissions such as fly ash. The tar balls were likely produced by household wood combustion.

[16] Spherical, carbonaceous particles that look identical to tar balls have been described in several studies. Martins *et al.* [1998a, 1998b] distinguished spherical and nonspherical (chain- and cluster-like) smoke particles in plumes from biomass burning in Brazil; after about one hour aging, the

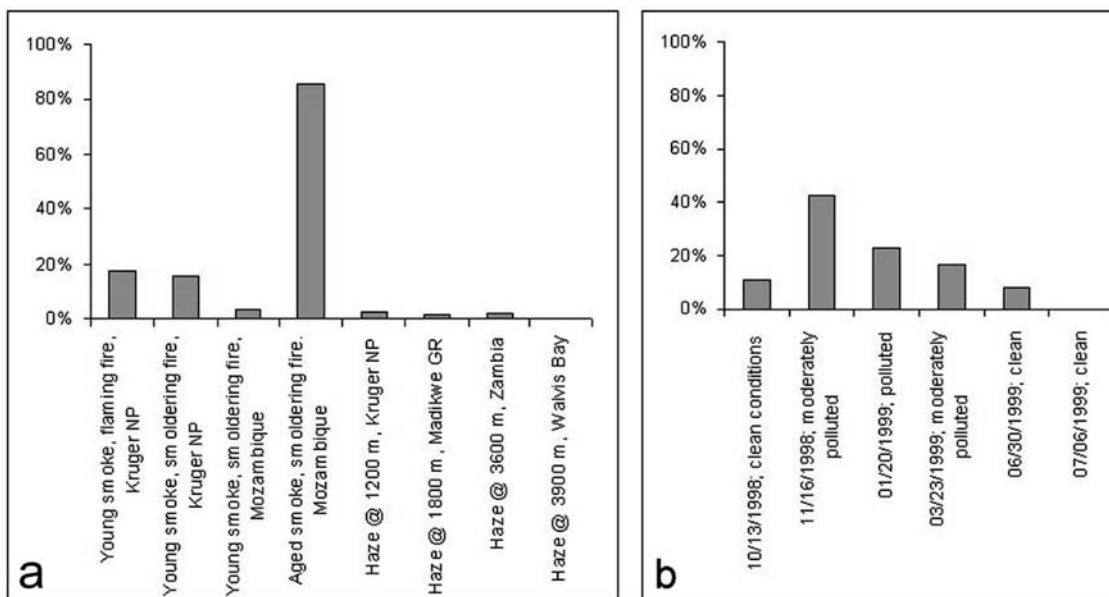


Figure 4. Relative number concentrations of tar balls (a) in biomass smoke and regional haze samples from southern Africa [see Pósfai *et al.*, 2003] and (b) from the continental air in Hungary, collected in all four seasons and under both polluted and clean conditions.

particles were mostly spherical. Similar spherical, carbonaceous particles with minor K, Cl, and S contents are characteristic products in aged biomass or biofuel smoke in India [Alfaro *et al.*, 2003]. In both studies, the spherical particles were interpreted as “soot cores coated with non-absorbing organic matter” [Martins *et al.*, 1998b; Alfaro *et al.*, 2003]. However, in light of the results reported here, we believe that these authors observed tar balls that are distinct from soot in both their formation mechanism and, presumably, optical properties.

4. Discussion

4.1. Proposed Mechanism for Tar Ball Formation

[17] Vast quantities of low-volatility organic compounds (LVOC), such as lignin pyrolysis products, are released in biomass burning [Rogge *et al.*, 1998; Sinha *et al.*, 2003]. These oxygenated polar compounds bear the signature of the vegetation taxa and may be used as tracers for biomass smoke aerosol [Simoneit *et al.*, 1993; Sinha *et al.*, 2003; Yokelson *et al.*, 2003]. Because of their low volatility, these species rapidly revert to the aerosol phase and account for a significant part of new particles in the smoke [Gao *et al.*, 2003; Eatough *et al.*, 2003]. The concentration of condensation nuclei decreases rapidly during the first ~10 min of aging, probably because of coagulation [Hobbs *et al.*, 2003]. The particles also grow by condensation of other semi-volatile organic species [Pankow, 1994]. Owing to their polar and hydrophilic nature many organic compounds from biomass burning readily dissolve in water [Corrigan and Novakov, 1999; Ruellan *et al.*, 1999; Mayol-Bracero *et al.*, 2002; Gao *et al.*, 2003], and pure organic particles become hydrated [Novakov and Corrigan, 1996]. However, laboratory experiments show that phenolic acids originating from biomass burning readily undergo polymerization with OH radicals in droplets to yield larger molecular weight and

less water-soluble species [Gelencsér *et al.*, 2003]. These changes lead to a reduction of the equilibrium size of the droplet because of the lowered Raoult effect, adding to the size reduction that results from the decrease in relative humidity upon dilution of a plume by ambient air. As the droplet size decreases, the solution will be more concentrated and the rate of polymerization enhanced, provided that it is not limited by the supply of OH radicals from the gas phase. Ultimately, the organic polymer becomes largely insoluble in water; when the water evaporates, only the tar ball will remain.

4.2. Properties of the Resulting Particles

4.2.1. Shape and Size

[18] Assuming that tar balls form by bimolecular homogeneous nucleation with water vapor, grow by coagulation and condensation, and transform in solutions of hydrated smoke particles, their shapes remain spherical. Growth by condensation and coagulation can result in the observed maximum of the size distribution at about 100 nm. The subsequent gradual shrinking of the hydrated particles through polymerization, and the resulting increase in the concentration of the solution, prevents the uptake of trace gases. We assume the organic polymer material of tar balls is mostly insoluble in water, and therefore particle sizes are not altered by cloud processing. Consequently, the number size distribution of tar balls does not shift significantly even during long-range transport.

4.2.2. Composition

[19] The compositions of tar balls reflect the molecular composition of their precursors, modified by the stoichiometry of the envisaged free-radical polymerization reaction. On the basis of the composition of potential precursors [Rogge *et al.*, 1998] and the mechanism of polymerization [Gelencsér *et al.*, 2003] we estimate that the particles should consist primarily of C and O with an average molar ratio of

about 6. Our semi-quantitative EDS data show a higher average C/O ratio (~ 10) in tar balls from biomass smoke, a difference that could result from the loss of O-rich functional groups (decarboxylation) in the vacuum of the electron microscope.

[20] The organic polymer is produced in the well-mixed aqueous solution of the hydrated smoke particle, resulting in a uniform composition throughout the particle (except perhaps on the surface). Since polymerization under atmospheric conditions yields high-molecular-weight refractory organic matter [Gelencsér *et al.*, 2003], the tar balls are not lost under the high vacuum of the TEM and do not volatilize upon irradiation.

4.2.3. Occurrence in the Atmosphere

[21] LVOC precursors are primarily emitted from smoldering fires. For example, Gao *et al.* [2003] identified a much higher content of water-soluble organic species ($\sim 14\%$) in smoke from smoldering fires than in particles from primarily flaming fires ($\sim 3\%$). Consequently, more tar balls presumably occur in plumes of smoldering fires than of flaming fires; Martins *et al.* [1998b] noted that smoldering combustion produced more spherical particles than flaming combustion. Tar balls occur exclusively in biomass and biofuel smoke, since fossil fuel burning releases mostly apolar compounds that do not tend to polymerize under atmospheric conditions. To our knowledge, individual-particle studies of coal and oil burning emissions and of urban aerosols do not indicate the presence of tar balls [Ramsden and Shibaoka, 1982; Rietmeijer and Janeczek, 1997; Parungo *et al.*, 1992; Katrinak *et al.*, 1992].

4.3. Relationship to Other Particulate Products of Biomass Burning, and Evolution of Individual Particles in Biomass Smoke Plumes

[22] On the basis of properties observable with the TEM, we distinguished three main particle types in the smoke of southern African savanna fires: organic particles with inorganic inclusions (Figure 1b), tar balls, and soot [Pósfai *et al.*, 2003; Li *et al.*, 2003]. The differences among these three particle types are important in terms of their formation mechanisms and evolution with the aging of smoke.

[23] The first particulate products of biomass fires are probably soot and inorganic salts such as KCl and K_2SO_4 . Soot is produced in flames, where unsaturated hydrocarbons condense at high temperatures ($>1000^\circ\text{C}$; Wagner [1981]) and form typical subgraphitic, layered structures [Lahaye and Prado, 1981]. The 10- to 50-nm spherules aggregate at the source. Since most of the emitted K^+ and Cl^- partition into particles even in the youngest biomass smoke [Hobbs *et al.*, 2003; Sinha *et al.*, 2003], we assume that K-salts are also among the first particles to form. Low-volatility, polar organic compounds condense onto existing surfaces (preferentially onto the hygroscopic K-salt particles instead of soot) and also form new particles through gas-to-particle conversion, as outlined above. Within the first few minutes after the smoke is emitted, pure organic particles consist of water-soluble polar species and thus are probably hydrated; the collected organic particles will spread on the TEM grids, and few spherical tar balls, if any, will occur (Figure 5a).

[24] Unless they contain a sizeable component of salt that holds the water in the particles, the organic particles become tar balls during aging of the smoke (Figure 5b). In TEM

samples collected at this stage (when the age of smoke is between a few minutes and several hours), dry and refractory tar balls are clearly distinct from other organic particles that contain inorganic inclusions and are still hydrated at the time of collection.

[25] Coagulation among the accumulation-mode particles continues when biomass smoke plumes mix with and are diluted by ambient aerosol [Reid and Hobbs, 1998; Formenti *et al.*, 2003]. Numerical analyses [Jacobson, 2002a] show that coagulation, condensation, dissolution, hydration, and chemical reaction mix most particles within half a day under even moderately polluted conditions (in the absence of a continuous source of new particles). Therefore, with sufficient time (hours to days), most tar balls probably become internally mixed with sulfates or the organic particles with inorganic inclusions, both of which are hydrated. Once the tar balls are again in contact with an aqueous droplet or within a mixed particle that contains water, they may partly dissolve and their spherical shape will disappear within the internally mixed particle. The material of tar balls will then no longer be uniquely recognizable in the TEM (Figure 5c). This proposed dissolution process is consistent with our observation that tar balls are internally mixed with soot (which is also hydrophobic) but not with sulfates or organic particles with inorganic inclusions. The coagulation of tar balls with hydrated particles also explains why the number of tar balls is small in regional hazes (Figure 4a) relative to the number of organic/sulfate particles that typically dominate in hazes affected by biomass burning [Okada *et al.*, 2001; Pósfai *et al.*, 2003].

[26] The particle types in the K-puszta winter samples in Hungary differed from those in southern African biomass smoke: tar balls were present, but the organic particles with inorganic salt inclusions, typical of the southern African savanna emissions, did not occur. Most were internally mixed ammonium sulfate/organic particles. We hypothesize that tar balls formed from the emissions of wood combustion, used for household heating. Firewood burning does not emit as much K and Cl as do shrubs and grasses [Turn *et al.*, 1997], the main fuels of the African savanna fires; therefore KCl and K_2SO_4 particles are unlikely to form from domestic fires. The organic compounds emitted by wood combustion either formed pure organic particles that became tar balls during aging, or combined with the abundant sulfate particles to form sulfate/organic internal mixtures. Any combustion emissions that we sampled at the K-puszta site could be regarded as aged (at least tens of minutes old) aerosol.

4.4. Potential Atmospheric Effects

[27] Indirect evidence indicates that tar balls may be only slightly light absorbing. Martins *et al.* [1998b] found that the mass absorption efficiency of smoke particles is related to their shape, with samples dominated by the spherical particles being less absorbing than those containing primarily chain aggregates (soot). Smaller and more absorbing particles occurred in south African biomass smoke that was only a few minutes old than in the aged regional haze [Haywood *et al.*, 2003]. On the other hand, the chemical nature of some of the organic matter in biomass smoke aerosol [Mayol-Bracero *et al.*, 2002; Gao *et al.*, 2003] suggests that these substances are colored (“brown carbon”) and thus absorbing [Gelencsér

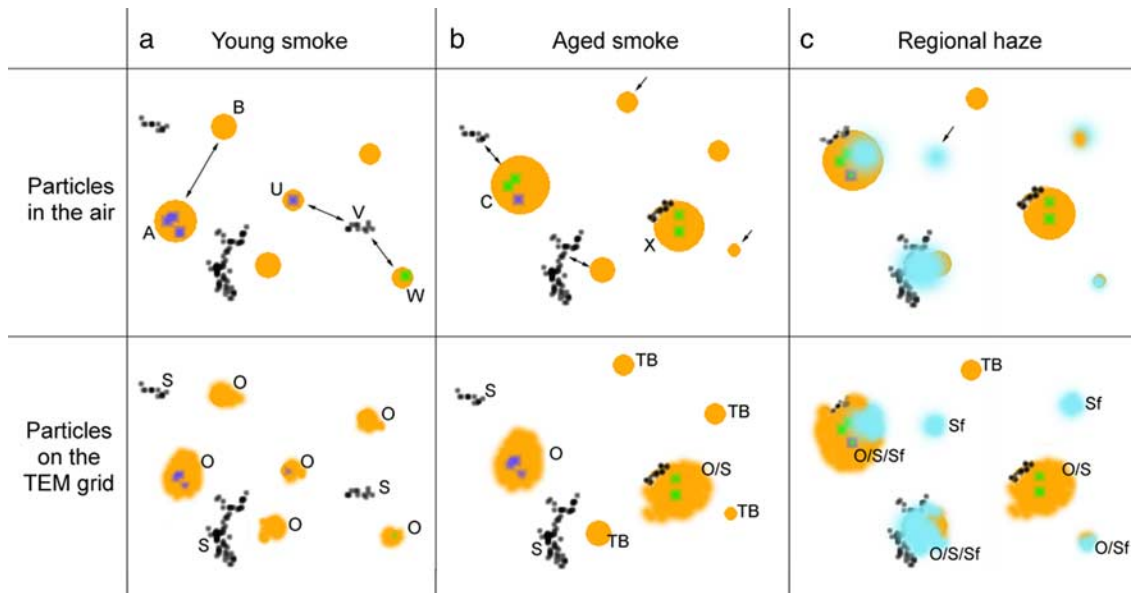


Figure 5. Presumed evolution of individual aerosol particles, in air and as observed in the TEM, during the aging of biomass smoke. Orange, organic particles (including tar balls); black, soot; light blue, sulfate; dark blue and green squares within orange particles, crystalline KCl and K_2SO_4 inclusions, respectively (KCl reacts to form K_2SO_4 as the smoke ages). Double arrows mark particles that later coagulate (A and B in young smoke form C in aged smoke; U, V, and W in young smoke form X in aged smoke); single arrows mark newly formed particles in aged smoke and in the regional haze. O, S, Sf, and TB mark organic, soot, sulfate, and tar ball particles, respectively, as identified in the TEM. All orange particles are spherical in the air in young smoke, but they have irregular shapes on the TEM grid as a result of their being hydrated during collection. In TEM samples from aged smoke, tar balls are spherical, and organic particles with inorganic salt inclusions have irregular shapes, reflecting the difference between the hydration states of the two particle types.

et al., 2003]. We assume that the polymerized organic material within tar balls may be slightly absorbing in the visible range of the spectrum.

[28] The optical properties of the particles may change during aging [Lioussse *et al.*, 1995; Reid and Hobbs, 1998]. Kirchstetter *et al.* [2003] observed that the BC/OC mass ratio of southern African smoke-plume samples is lower than that of samples from the regional haze. They suggested the difference was a result of mixing of biomass smoke with background air with a higher BC/OC ratio. However, we propose an alternative explanation. Since the mass absorption efficiency of internal mixtures of soot/sulfate is enhanced relative to that of externally mixed soot [Chylek *et al.*, 1995; Fuller *et al.*, 1999; Jacobson, 2001], an apparent increase of the BC/OC ratio (measured using optical methods) can result from the internal mixing of soot with ambient sulfates (as also noted by Lioussse *et al.* [1993]). Tar balls and other organic particles may play a minor, but as yet undetermined, role in the change of the mass absorption efficiency of biomass smoke as it ages.

[29] Indirect information exists about the hygroscopic behavior and cloud condensation nuclei (CCN) activity of tar balls. The lack of hygroscopic growth is apparent since the particle size distribution curves are essentially the same for tar balls from fresh and aged smoke as well as from the regional haze [Pósfai *et al.*, 2003]. Both southern African [Magi and Hobbs, 2003] and Brazilian [Kotchenruther and Hobbs, 1998] biomass smoke aerosols exhibit hygroscopic growth, with the aerosol total light scattering coefficient

increasing with RH without a marked discontinuity (i.e., no deliquescence). However, the sizes of particles in biomass smoke depend less on RH than that of the ambient aerosol; in general, biomass smoke particles can be regarded as moderately hygroscopic. We attribute the CCN activity of biomass smoke particles to the organic particles that contain inorganic sulfate, chloride, or nitrate inclusions [Li *et al.*, 2003]; the size distributions of this particle type show signs of growth with aging [Pósfai *et al.*, 2003]. The remaining particles in the smoke (soot and tar balls) seem unlikely to be effective as CCN as long as they are externally mixed with the more hygroscopic particle types.

5. Conclusions

[30] Our interpretation of the properties and formation mechanism of tar balls provides a framework for understanding the evolution of organic substances in biomass smoke. First, low-volatility organic gases are emitted that convert into aerosol particles and form water-soluble compounds; these then polymerize in hydrated smoke particles and, by becoming less soluble, they likely lose water. When such particles are captured on TEM grids, they are either tar balls (if they do not contain inorganic salt inclusions) or irregularly shaped organic particles with salt inclusions. Further processing of tar balls is possible if they coagulate with hydrated sulfates or the abundant organic particles in biomass smoke that contain strongly hygroscopic inorganic inclusions. This sequence of events can explain changes in

the optical and hygroscopic behavior of biomass smoke as it ages. Tar balls are important both as indicators of aged biomass smoke and as an abundant particle type, the radiative effects of which deserve further study.

[31] **Acknowledgments.** We thank Thomas Kirchstetter and Kristy Ross for their help with sampling in southern Africa and Ágnes Molnár for sampling in Hungary and discussions. This research was supported by NASA grants NAG5-9838, NAG5-9022, and NAG5-7675, NSF grant ATM-990162, and Hungarian Science Foundation grant T035012.

References

- Alfaro, S. C., A. Gaudichet, J. L. Rajot, L. Gomes, M. Maillé, and H. Cachier (2003), Variability of aerosol size-resolved composition at an Indian coastal site during the Indian Ocean Experiment (INDOEX) intensive field phase, *J. Geophys. Res.*, *108*(D8), 4235, doi:10.1029/2002JD002645.
- Andreae, M. O., and P. Merlet (2001), Emissions of trace gases and aerosols from biomass burning, *Global Biogeochem. Cycles*, *15*, 955–966.
- Andreae, M. O., T. W. Andreae, H. Annegarn, J. Beer, H. Cachier, P. le Canut, W. Elbert, W. Maenhaut, I. Salma, F. G. Wienhold, and T. Zenker (1998), Airborne studies of aerosol emissions from savanna fires in southern Africa: 2. Aerosol chemical composition, *J. Geophys. Res.*, *103*, 32,119–32,128.
- Buseck, P. R., and M. Pósfai (1999), Airborne minerals and related aerosol particles: Effects on climate and the environment, *Proc. Natl. Acad. Sci. U. S. A.*, *96*, 3372–3379.
- Buseck, P. R., D. Jacob, M. Pósfai, J. Li, and J. R. Anderson (2002), Minerals in the air: An environmental perspective, in *Frontiers in Geochemistry: Global Inorganic Chemistry, Konrad Krauskopf*, vol. 1, *Geol. Soc. Am. Int. Book Ser.*, vol. 5, edited by W. G. Ernst, pp. 106–122, Bellwether, Columbia, Md.
- Cachier, H., J. Ducret, M.-P. Brémond, V. Yoboué, J.-P. Lacaux, A. Gaudichet, and J. Baudet (1991), Biomass burning aerosols in a savanna region of the Ivory Coast, in *Global Biomass Burning*, edited by J. S. Levine, pp. 174–184, MIT Press, Cambridge, Mass.
- Chung, S. H., and J. H. Seinfeld (2002), Global distribution and climate forcing of carbonaceous aerosols, *J. Geophys. Res.*, *107*(D19), 4407, doi:10.1029/2001JD001397.
- Chylek, P., G. Videen, D. Ngo, R. G. Pinnick, and J. D. Klett (1995), Effect of black carbon on the optical properties and climate forcing of sulfate aerosols, *J. Geophys. Res.*, *100*, 16,325–16,332.
- Cliff, J., and G. W. Lorimer (1975), The quantitative analysis of thin specimens, *J. Microsc.*, *102*, 203–207.
- Corrigan, C. E., and T. Novakov (1999), Cloud condensation nucleus activity of the organic component of biomass smoke particles, *Atmos. Environ.*, *33*, 2661–2668.
- Crutzen, P. J., and M. O. Andreae (1990), Biomass burning in the tropics: Impact on atmospheric chemistry and biogeochemical cycles, *Science*, *250*, 1669–1678.
- Eatough D. J., N. L. Eatough, Y. Pang, S. Sizemore, T. W. Kirchstetter, T. Novakov, and P. V. Hobbs (2003), Semivolatile particulate organic material in southern Africa during SAFARI 2000, *J. Geophys. Res.*, *108*(D13), 8479, doi:10.1029/2002JD002296.
- Egerton, R. F. (1986), *Electron Energy-Loss Spectroscopy in the Electron Microscope*, 410 pp., Plenum, New York.
- Formenti, P., W. Elbert, W. Maenhaut, J. Haywood, S. Osborne, and M. O. Andreae (2003), 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, *J. Geophys. Res.*, *108*(D13), 8488, doi:10.1029/2002JD002408.
- Fuller, K. A., W. C. Malm, and S. M. Kreidenweis (1999), Effects of mixing on extinction by carbonaceous particles, *J. Geophys. Res.*, *104*, 15,941–15,954.
- Gao, S., D. A. Hegg, P. V. Hobbs, T. W. Kirchstetter, B. Magi, and M. Sadilek (2003), Water-soluble organic components in aerosols associated with savanna fires in southern Africa: Identification, evolution and distribution, *J. Geophys. Res.*, *108*(D13), 8491, doi:10.1029/2002JD002324.
- Gaudichet, A., F. Echalar, B. Chatenet, J. P. Quisefit, G. Malingre, H. Cachier, P. Buat-Menard, P. Artaxo, and W. Maenhaut (1995), Trace elements in tropical African savanna biomass burning aerosols, *J. Atmos. Chem.*, *22*, 19–39.
- Gelencsér, A., A. Hoffer, Á. Molnár, Z. Krivácsy, G. Kiss, and E. Mészáros (2000), Thermal behaviour of carbonaceous aerosol from a continental background site, *Atmos. Environ.*, *34*, 823–831.
- Gelencsér, A., A. Hoffer, G. Kiss, E. Tombácz, R. Kurdi, and L. Bencze (2003), In-situ formation of light-absorbing organic matter in cloud water, *J. Atmos. Chem.*, *45*, 25–33.
- Haywood, J. M., and V. Ramaswamy (1998), Global sensitivity studies of the direct radiative forcing effect due to anthropogenic sulfate and black carbon aerosols, *J. Geophys. Res.*, *103*, 6043–6058.
- Haywood, J. M., S. R. Osborne, P. N. Francis, A. Keil, P. Formenti, M. O. Andreae, and P. H. Kaye (2003), The mean physical and optical properties of regional haze dominated by biomass burning aerosol measured from the C-130 aircraft during SAFARI 2000, *J. Geophys. Res.*, *108*(D13), 8473, doi:10.1029/2002JD002226.
- Hitzenberger, R., A. Berner, H. Giebl, R. Kromp, S. M. Larson, A. Rouc, A. Koch, S. Marischka, and H. Puxbaum (1999), Contribution of carbonaceous material to cloud condensation nuclei concentrations in European background (Mt. Sonnblick) and urban (Vienna) aerosols, *Atmos. Environ.*, *33*, 2647–2659.
- Hobbs, P. V., J. S. Reid, R. A. Kotchenruther, R. J. Ferek, and R. Weiss (1997), Direct radiative forcing by smoke from biomass burning, *Science*, *275*, 1776–1778.
- Hobbs, P. V., P. Sinha, R. J. Yokelson, I. T. Bertschi, D. R. Blake, S. Gao, T. W. Kirchstetter, T. Novakov, and P. Pilewskie (2003), Evolution of gases and particles from a savanna fire in South Africa, *J. Geophys. Res.*, *108*(D13), 8485, doi:10.1029/2002JD002352.
- Houghton, J. T., et al. (Eds.) (2001), *Climate Change 2001, the Scientific Basis: Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change*, Cambridge Univ. Press, New York.
- Jacobson, M. Z. (2001), Strong radiative heating due to the mixing state of black carbon in atmospheric aerosols, *Nature*, *409*, 695–697.
- Jacobson, M. Z. (2002a), Analysis of aerosol interactions with numerical techniques for solving coagulation, nucleation, condensation, dissolution, and reversible chemistry among multiple size distributions, *J. Geophys. Res.*, *107*(D19), 4366, doi:10.1029/2001JD002044.
- Jacobson, M. Z. (2002b), Control of fossil-fuel particulate black carbon and organic matter, possibly the most effective method of slowing global warming, *J. Geophys. Res.*, *107*(D19), 4410, doi:10.1029/2001JD001376.
- Katrinak, K. A., P. Rez, and P. R. Buseck (1992), Structural variations in individual carbonaceous particles from an urban aerosol, *Environ. Sci. Technol.*, *26*, 1967–1976.
- Kirchstetter, T. W., T. Novakov, P. V. Hobbs, and B. Magi (2003), Airborne measurements of carbonaceous aerosols in southern Africa during the dry biomass burning season, *J. Geophys. Res.*, *108*(D13), 8476, doi:10.1029/2002JD002171.
- Kotchenruther, R. A., and P. V. Hobbs (1998), Humidification factors of aerosol from biomass burning in Brazil, *J. Geophys. Res.*, *103*, 32,081–32,089.
- Krivácsy, Z., A. Hoffer, Z. Sárvári, D. Temesi, U. Baltensperger, S. Nyéki, E. Weingartner, S. Kleefeld, and S. G. Jennings (2001), Role of organic and black carbon in the chemical composition of atmospheric aerosol at European background sites, *Atmos. Environ.*, *35*, 6231–6244.
- Lahaye, J., and G. Prado (1981), Morphology and internal structure of soot and carbon blacks, in *Particulate Carbon: Formation During Combustion*, edited by D. C. Siegla and G. W. Smith, pp. 33–55, Plenum, New York.
- Li, J., M. Pósfai, P. V. Hobbs, and P. R. Buseck (2003), Individual aerosol particles from biomass burning in southern Africa: 2. Compositions and aging of inorganic particles, *J. Geophys. Res.*, *108*(D13), 8484, doi:10.1029/2002JD002310.
- Lioussé, C., C. Cachier, and S. G. Jennings (1993), Optical and thermal measurements of black carbon aerosol content in different environments: Variation of the specific attenuation cross-section, sigma (σ), *Atmos. Environ., Part A*, *27*, 1203–1211.
- Lioussé, C., C. Devaux, F. Dulac, and H. Cachier (1995), Aging of savanna biomass burning aerosols: Consequences on their optical properties, *J. Atmos. Chem.*, *22*, 1–17.
- Lioussé, C., J. E. Penner, C. Chuang, J. J. Walton, H. Eddleman, and H. Cachier (1996), A global three-dimensional model study of carbonaceous aerosols, *J. Geophys. Res.*, *101*, 19,411–19,432.
- Magi, B. I., and P. V. Hobbs (2003), Effects of humidity on aerosols in southern Africa during the biomass burning season, *J. Geophys. Res.*, *108*(D13), 8495, doi:10.1029/2002JD002144.
- Martins, J. V., P. Artaxo, C. Lioussé, J. S. Reid, P. V. Hobbs, and Y. J. Kaufman (1998a), Effects of black carbon content, particle size, and mixing on light absorption by aerosols from biomass burning in Brazil, *J. Geophys. Res.*, *103*, 32,041–32,050.
- Martins, J. V., P. V. Hobbs, R. E. Weiss, and P. Artaxo (1998b), Sphericity and morphology of smoke particles from biomass burning in Brazil, *J. Geophys. Res.*, *103*, 32,051–32,057.
- Mayol-Bracero, O. L., P. Guyon, B. Graham, G. Roberts, M. O. Andreae, S. Decesari, M. C. Facchini, S. Fuzzi, and P. Artaxo (2002), Water-

- soluble organic compounds in biomass burning aerosols over Amazonia: 2. Apportionment of the chemical composition and importance of the polyacidic fraction, *J. Geophys. Res.*, *107*(D20), 8091, doi:10.1029/2001JD000522.
- Mészáros, E., T. Barcza, A. Gelencsér, J. Hlavay, G. Kiss, Z. Krivácsy, A. Molnár, and K. Polyák (1997), Size distributions of inorganic and organic species in the atmospheric aerosol in Hungary, *J. Aerosol Sci.*, *28*, 1163–1175.
- Molnár, A., E. Mészáros, H. C. Hansson, H. Karlsson, A. Gelencsér, G. Kiss, and Z. Krivácsy (1999), The importance of organic and elemental carbon in the fine atmospheric aerosol particles, *Atmos. Environ.*, *33*, 2745–2750.
- Murphy, D. M., D. S. Thomson, and M. J. Mahoney (1998), In situ measurements of organics, meteoritic material, mercury, and other elements in aerosols at 5 to 19 kilometers, *Science*, *282*, 1664–1669.
- Novakov, T., and C. E. Corrigan (1996), Cloud condensation nucleus activity of the organic component of biomass smoke particles, *Geophys. Res. Lett.*, *23*, 2141–2144.
- Novakov, T., and J. E. Penner (1993), Large contribution of organic aerosols to cloud-condensation-nuclei concentrations, *Nature*, *365*, 823–826.
- Okada, K., M. Ikegami, Y. Zaizen, Y. Makino, J. B. Jensen, and J. L. Gras (2001), The mixture state of individual aerosol particles in the 1997 Indonesian haze episode, *J. Aerosol Sci.*, *32*, 1269–1279.
- Pankow, J. F. (1994), An absorption-model of the gas aerosol partitioning involved in the formation of secondary organic aerosol, *Atmos. Environ.*, *28*, 189–193.
- Parungo, F., B. Kopcewicz, C. Nagamoto, R. Schnell, P. Sheridan, C. Zhu, and J. Harris (1992), Aerosol particles in the Kuwait oil fire plumes: Their morphology, size distribution, chemical composition, transport, and potential effect on climate, *J. Geophys. Res.*, *97*, 15,867–15,882.
- Pósfai, M., J. R. Anderson, P. R. Buseck, and H. Sievering (1995), Compositional variations of sea-salt-mode aerosol particles from the North Atlantic, *J. Geophys. Res.*, *100*, 23,063–23,074.
- Pósfai, M., J. R. Anderson, P. R. Buseck, and H. Sievering (1999), Soot and sulfate aerosol particles in the remote marine troposphere, *J. Geophys. Res.*, *104*, 21,685–21,693.
- Pósfai, M., R. Simonics, J. Li, P. V. Hobbs, and P. R. Buseck (2003), Individual aerosol particles from biomass burning in southern Africa: 1. Compositions and size distributions of carbonaceous particles, *J. Geophys. Res.*, *108*(D13), 8483, doi:10.1029/2002JD002291.
- Ramsden, A. R., and M. Shibaoka (1982), Characterization and analysis of individual fly-ash particles from coal-fired power stations by a combination of optical microscopy, electron microscopy and quantitative electron microprobe analysis, *Atmos. Environ.*, *16*, 2191–2206.
- Reid, J. S., and P. V. Hobbs (1998), Physical and optical properties of young smoke from individual biomass fires in Brazil, *J. Geophys. Res.*, *103*, 32,013–32,030.
- Rietmeijer, F. J. M., and J. Janeczek (1997), An analytical electron microscope study of airborne industrial particles in Sosnowiec, Poland, *Atmos. Environ.*, *31*, 1941–1951.
- Roberts, G. C., A. Nenes, J. H. Seinfeld, and M. O. Andreae (2003), Impact of biomass burning on cloud properties in the Amazon Basin, *J. Geophys. Res.*, *108*(D2), 4062, doi:10.1029/2001JD000985.
- Rogge, W. F., L. M. Hildemann, M. A. Mazurek, G. R. Cass, and B. R. T. Simoneit (1998), Sources of fine organic aerosol: 9. Pine, oak, and synthetic log combustion in residential fireplaces, *Environ. Sci. Technol.*, *32*, 13–22.
- Ruellan, S., H. Cachier, A. Gaudichet, P. Masclet, and J. P. Lacaux (1999), Airborne aerosols over central Africa during the Experiment for Regional Sources and Sinks of Oxidants (EXPRESSO), *J. Geophys. Res.*, *104*, 30,673–30,690.
- Simoneit, B. R. T., W. F. Rogge, M. A. Mazurek, L. J. Standley, L. M. Hildemann, and G. R. Cass (1993), Lignin pyrolysis products, lignans, and resin acids as specific tracers of plant classes in emissions from biomass combustion, *Environ. Sci. Technol.*, *27*, 2533–2540.
- Sinha, P., P. V. Hobbs, R. J. Yokelson, I. T. Bertschi, D. R. Blake, I. J. Simpson, S. Gao, T. W. Kirchstetter, and T. Novakov (2003), Emissions of trace gases and particles from savanna fires in southern Africa, *J. Geophys. Res.*, *108*(D13), 8487, doi:10.1029/2002JD002325.
- Turn, S. Q., B. M. Jenkins, J. C. Chow, L. C. Pritchett, D. Campbell, T. Cahill, and S. A. Whalen (1997), Elemental characterization of particulate matter emitted from biomass burning: Wind tunnel derived source profiles for herbaceous and wood fuels, *J. Geophys. Res.*, *102*, 3683–3699.
- Wagner, H. G. (1981), Soot formation: An overview, in *Particulate Carbon: Formation During Combustion*, edited by D. C. Siegla and G. W. Smith, pp. 1–29, Plenum, New York.
- Ward, D. E., R. A. Susott, J. B. Kaufman, R. E. Babbitt, D. L. Cummings, B. Dias, B. N. Holben, Y. J. Kaufman, R. A. Rasmussen, and A. W. Setzer (1992), Smoke and fire characteristics for cerrado and deforestation burns in Brazil: Base-B experiment, *J. Geophys. Res.*, *97*, 14,601–14,619.
- Yokelson, R. J., I. T. Bertschi, T. J. Christian, P. V. Hobbs, D. E. Ward, and W.-M. Hao (2003), Trace gas measurements in nascent, aged, and cloud-processed smoke from African savanna fires by airborne Fourier transform infrared spectroscopy (AFTIR), *J. Geophys. Res.*, *108*(D13), 8478, doi:10.1029/2002JD002322.

K. Arató, M. Pósfai, and R. Simonics, Department of Earth and Environmental Sciences, University of Veszprém, POB 158, Veszprém, H-8200 Hungary. (posfaim@almos.vein.hu)

P. R. Buseck and J. Li, Departments of Chemistry/Biochemistry and Geological Sciences, Arizona State University, Tempe, AZ 85287-1404, USA.

A. Gelencsér, Air Chemistry Group, Hungarian Academy of Sciences, Veszprém, POB 158, H-8200 Hungary.

P. V. Hobbs, Department of Atmospheric Sciences, University of Washington, Seattle, WA 98195, USA.