

## A large organic aerosol source in the free troposphere missing from current models

Colette L. Heald,<sup>1</sup> Daniel J. Jacob,<sup>1</sup> Rokjin J. Park,<sup>1</sup> Lynn M. Russell,<sup>2</sup> Barry J. Huebert,<sup>3</sup> John H. Seinfeld,<sup>4</sup> Hong Liao,<sup>4</sup> and Rodney J. Weber<sup>5</sup>

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[1] Aircraft measurements of organic carbon (OC) aerosol by two independent methods over the NW Pacific during the ACE-Asia campaign reveal unexpectedly high concentrations in the free troposphere (FT). Concentrations average  $4 \mu\text{g sm}^{-3}$  in the 2–6.5 km column with little vertical gradient. These values are 10–100 times higher than computed with a global chemical transport model (CTM) including a standard 2-product simulation of secondary organic aerosol (SOA) formation based on empirical fits to smog chamber data. The same CTM reproduces the observed vertical profiles of sulfate and elemental carbon aerosols, which indicate sharp decreases from the boundary layer to the FT due to wet scavenging. Our results suggest a large, sustained source of SOA in the FT from oxidation of long-lived volatile organic compounds. We find that this SOA is the dominant component of aerosol mass in the FT, with implications for intercontinental pollution transport and radiative forcing of climate. **Citation:** Heald, C. L., D. J. Jacob, R. J. Park, L. M. Russell, B. J. Huebert, J. H. Seinfeld, H. Liao, and R. J. Weber (2005), A large organic aerosol source in the free troposphere missing from current models, *Geophys. Res. Lett.*, 32, L18809, doi:10.1029/2005GL023831.

[2] Organic carbon (OC) is a major component of the atmospheric aerosol [Turpin *et al.*, 2000]. Better understanding of its concentrations, composition, and sources is critical for environmental issues ranging from air quality to climate change. Early aircraft measurements identified a high-altitude source [Novakov *et al.*, 1997; Murphy *et al.*, 1998]. The ACE-Asia aircraft mission over the NW Pacific in April–May 2001 [Huebert *et al.*, 2003a] provided the first quantitative measurements of OC aerosol mass concentrations in the free troposphere (FT), obtained by three research groups using two independent methods [Maria *et al.*, 2003; Huebert *et al.*, 2004; Mader *et al.*, 2002]. We show here that the FT observations are 10–100 times higher than expected from a standard OC aerosol model, with potential implications for interconti-

ental transport of pollution and for the radiative forcing of climate.

[3] The ACE-Asia campaign involved a C-130 aircraft with ceiling of 6.5 km, and a Twin Otter aircraft with ceiling of 3.7 km, flying from Iwakuni, Japan. Its focus was to characterize the radiative properties of Asian aerosols transported over the NW Pacific. Aerosol measurements on both aircraft included OC, elemental carbon (EC), and inorganic ions. The OC measurements were made by thermal optical analysis aboard both aircraft [Huebert *et al.*, 2004; Mader *et al.*, 2002], and also aboard the C-130 by Fourier transform infrared transmission spectroscopy [Maria *et al.*, 2003]. Intercomparison between the two methods found excellent agreement ( $R^2 = 0.93$  and slope of 0.91) [Maria *et al.*, 2003]. Sample collection times varied from 15 to 290 minutes. All measurements were above the detection limits.

[4] Figure 1 shows the measured vertical profiles of OC aerosol concentrations. Also shown are the mean profiles from the GEOS-Chem global 3-D chemical transport model (CTM) [Park *et al.*, 2003, 2004] sampled along the flight tracks. Anthropogenic OC aerosol emissions in the model are from Cooke *et al.* [1999]. Formation of secondary organic aerosol (SOA) follows the scheme of Chung and Seinfeld [2002] based on empirical fits to smog chamber data [Griffin *et al.*, 1999]. The scheme involves oxidation of biogenic terpenes and other reactive volatile organic compounds (VOCs) to produce semivolatile secondary organic gases (SOG) that partition into the aerosol phase as a function of temperature and available OC volume. Aerosol scavenging in GEOS-Chem follows the scheme of Liu *et al.* [2001]. Sulfate aerosol is assumed 100% water-soluble. Emitted carbonaceous aerosol includes a hydrophobic fraction (50% for OC, 80% for EC) that becomes hydrophilic (and hence susceptible to scavenging) on a 1.2-day e-folding time scale. The scavenging efficiency of SOA is assumed 80% [Chung and Seinfeld, 2002]. The GEOS-Chem CTM has been applied to analysis of observations from the TRACE-P campaign [Jacob *et al.*, 2003], conducted in the same region as ACE-Asia one month earlier. TRACE-P included a broader range of chemical measurements than ACE-Asia but no OC aerosol. Park *et al.* [2005] showed that the model gives a good simulation of mean TRACE-P vertical profiles of sulfur oxides ( $\text{SO}_x \equiv \text{SO}_2 + \text{sulfate}$ ), nitrate, and EC aerosol, implying a successful description of wet scavenging processes during lifting to the FT.

[5] The ACE-Asia observations reveal remarkably high OC aerosol concentrations in the FT, averaging  $4 \mu\text{g sm}^{-3}$  up to 6.5 km altitude (“ $\text{sm}^{-3}$ ” refers to a cubic meter at standard conditions of temperature and pressure). In con-

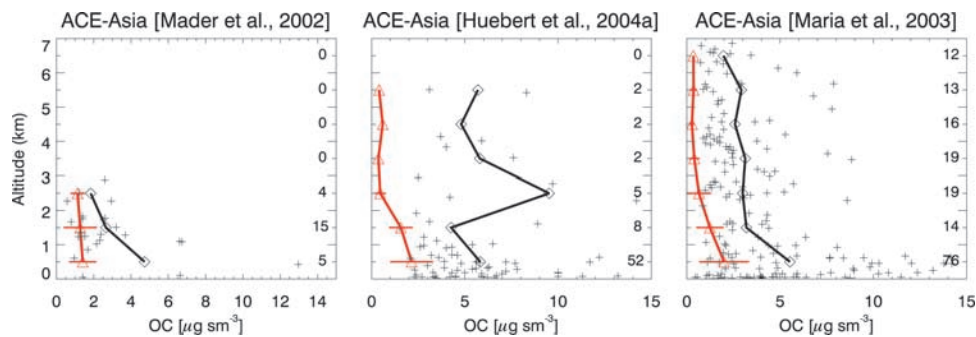
<sup>1</sup>Department of Earth and Planetary Sciences, Harvard University, Cambridge, Massachusetts, USA.

<sup>2</sup>Scripps Institution of Oceanography, University of California, La Jolla, California, USA.

<sup>3</sup>Department of Oceanography, University of Hawaii at Manoa, Honolulu, Hawaii, USA.

<sup>4</sup>Department of Chemical Engineering, California Institute of Technology, Pasadena, California, USA.

<sup>5</sup>School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, Georgia, USA.



**Figure 1.** Mean vertical profiles of organic carbon (OC) aerosol concentrations from the ACE-Asia aircraft mission off the coast of Japan. Observations are shown in black, with individual measurements as crosses. Results from the GEOS-Chem model are shown in red with standard deviations for each altitude interval. The number of observations in each averaging interval is shown at the right of each panel. Model values are sampled along the flight tracks.

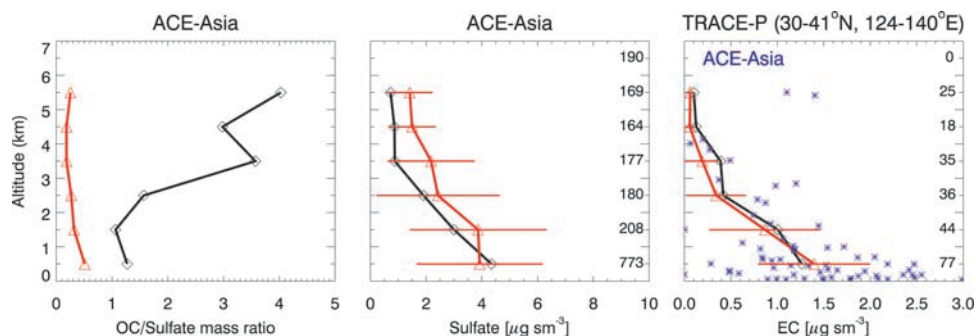
trast, observed sulfate concentrations drop rapidly with altitude (Figure 2), as was found also in TRACE-P [Park *et al.*, 2005]. EC aerosol concentrations measured in TRACE-P [Clarke *et al.*, 2004] also show a rapid decline with altitude due to scavenging (Figure 2), as discussed by Park *et al.* [2005]. Only a few EC aerosol measurements were made in the FT in ACE-Asia [Huebert *et al.*, 2004] and are shown as symbols in Figure 2; concentrations were generally low, consistent with TRACE-P, although there are two high outliers which are not correlated with CO or sulfate and for which we have no explanation.

[6] The GEOS-Chem model reproduces the observed decreases of sulfate and EC concentrations with altitude, as shown in Figure 2. For sulfate the model is too high by about 50%; there is a similar overestimate in the TRACE-P data, which is corrected when comparison is done for SO<sub>x</sub> instead [Park *et al.*, 2005], implying that the model error is in the rate of SO<sub>2</sub> oxidation. By contrast to sulfate and EC, there is considerable discrepancy between model and observations for OC aerosol. The model is 50% too low in the boundary layer, which could reflect a factor of 2 underestimate in Asian emissions. It is a factor of 10–100 too low in the FT, which cannot be simply explained by such a correction to emissions. Observations of CO in TRACE-P showed a strong biomass burning influence from SE Asia in air masses sampled in the FT south of 30°N but not at the

higher latitudes where ACE-Asia took place [Liu *et al.*, 2003]. ACE-Asia was also conducted later in the season, when biomass burning had abated [Heald *et al.*, 2003]. Maria *et al.* [2003] did not find an association of elevated OC aerosol in ACE-Asia with air masses originating from SE Asia. Satellite fire maps show no Siberian fires during that period. We find no correlation of OC aerosol with potassium, a tracer of biomass burning [Ma *et al.*, 2003].

[7] Maria *et al.* [2003] showed that OC aerosol concentrations in ACE-Asia were correlated with CO, a product of inefficient combustion and more generally a tracer of Asian outflow. However, we find that this correlation is weak when only data in the FT are considered. Although the highest free tropospheric OC aerosol observations in ACE-Asia are associated with elevated CO, there is a free tropospheric background of 1–3 μg sm<sup>-3</sup> that is not correlated with CO or sulfate.

[8] Reconciling model results with the observed OC aerosol concentrations in the FT is not easily achieved. Most of the free tropospheric OC aerosol in the model is primary and of Asian origin. Simulated SOA concentrations in the FT do not exceed 0.03 μg sm<sup>-3</sup>, and the mean SOG/SOA mass concentration ratio is 4. We could increase SOA concentrations in the model by assuming that SOA condensation takes place on all aerosols (not just preexisting OC) or by otherwise increasing the



**Figure 2.** Mean vertical profiles of OC/sulfate mass ratio (left) and sulfate concentrations (center) from the ACE-Asia campaign, and elemental carbon (EC) aerosol concentrations from the TRACE-P campaign (right). Observations are shown in black. GEOS-Chem model results are shown in red, with standard deviations of concentrations for each altitude interval. Individual EC observations from the ACE-Asia campaign are shown as blue symbols. The number of observations in each averaging interval is shown at the right of each panel. Model values are sampled along the flight tracks.

partitioning to the aerosol phase, but this allows only a factor of 2–4 increase. The *Maria et al.* [2003] observations indicate that a substantial fraction of the OC aerosol mass was water-soluble. It seems unlikely that OC aerosol would be less water-soluble than EC, which shows a strong decrease of concentrations with altitude that is captured by the model (Figure 2). A sensitivity simulation with decreased conversion efficiency of carbonaceous aerosols from hydrophobic to hydrophilic (e-folding time of 10 days) demonstrated only small increases in OC aerosol concentrations in the FT.

[9] Simple adjustments to the model sources of SOA are not satisfactory either. SOA in the *Chung and Seinfeld* [2002] mechanism is solely biogenic but this is consistent with current understanding of SOA formation outside urban areas [*Tsigaridis and Kanakidou*, 2003]. Aromatic compounds are thought to provide the main anthropogenic source of SOA [*Kanakidou et al.*, 2005], but the corresponding emissions in the *Streets et al.* [2003] inventory are 7 times lower (by carbon mass) than the biogenic SOA precursor emissions [*Guenther et al.*, 1995] in East Asia. A GEOS-Chem simulation of aromatic hydrocarbon observations in TRACE-P does not indicate an underestimate of regional sources in the *Streets et al.* [2003] inventory (M. Fu, personal communication, 2005). SOA formation can be enhanced in the presence of acid catalysts [*Jang et al.*, 2002], but this effect is at most 40% [*Gao et al.*, 2004].

[10] The most likely explanation for the free tropospheric OC concentrations observed in ACE-Asia is the sustained formation of SOA following the venting of insoluble VOCs to the FT. SOA formation in the *Chung and Seinfeld* [2002] mechanism occurs in the first stage of oxidation of the emitted hydrocarbons (within hours of emission for terpenes). As pointed out by *Aumont et al.* [2000], *Derwent et al.* [2003], and *Bonn et al.* [2004], successive generations of oxidation products would add to the condensable pool. Product yields could also be different at the cold temperatures of the FT; for example, oxy radicals RO could add O<sub>2</sub> instead of thermolyze [*Johnson et al.*, 2004], promoting subsequent OC aerosol formation. SOA yields at ambient low nitrogen oxides concentrations may also be underestimated by smog chamber data [*Song et al.*, 2005].

[11] Previous field studies offer evidence for sustained SOA formation in aging air masses. Ship observations by *de Gouw et al.* [2005] off New England show continued SOA formation in North American air masses after aging times of 2–3 days. *Kawamura et al.* [2005] find rapid halogen-mediated SOA formation in the Arctic at sunrise, implying the presence of long-lived SOA precursors. *Crahan et al.* [2004] and *Maria et al.* [2004] report enhanced SOA formation under cloudy conditions. SOA particles produced in the FT can be transported over long distances because precipitation is infrequent. Assuming a 2-week lifetime for aerosols in the FT [*Balkanski et al.*, 1993], a uniform 1 μg sm<sup>-3</sup> global background of organic carbon aerosol in the 2–7 km column would require a steady state source of 105 TgC yr<sup>-1</sup>. Annual VOC emissions are estimated to be ~500–1000 TgC yr<sup>-1</sup> [*Intergovernmental Panel for Climate Change (IPCC)*, 2001]. Global source estimates for acetone and methanol, known to be important gas-phase OC species in the FT, are by comparison, 30 and

90 TgC yr<sup>-1</sup> respectively [*IPCC*, 2001; *Jacob et al.*, 2005]. Measurements by *Wiley et al.* [2000] indicate a global dissolved organic carbon flux in rainwater of 400 TgC yr<sup>-1</sup>. Despite uncertainties in the OC lifetime, the FT OC aerosol background suggested by the ACE-Asia observations is therefore not inconsistent with independent estimates of the global organic carbon balance.

[12] An anthropogenic source for this OC in the FT would have significant implications for intercontinental pollution transport and for radiative forcing of climate. Previous GEOS-Chem analyses of transpacific transport of anthropogenic Asian aerosols to North America found it to be dominated by sulfate because of efficient scavenging of OC aerosol from Asian outflow [*Park et al.*, 2003, 2004]. However, recent observations by *Jaffe et al.* [2005] at a western U.S. mountain site indicate that air masses of Asian and marine origins have twice as much OC aerosol (0.53 μg m<sup>-3</sup>) as sulfate (0.24 μg m<sup>-3</sup>). The ACE-Asia observations have an OC/sulfate mass ratio of 3 in the FT (Figure 2), consistent with the *Jaffe et al.* [2005] data. A uniform OC aerosol concentration of 4 μg sm<sup>-3</sup> in the 2–7 km column, based on the ACE-Asia data (Figure 1), would have an optical depth of 0.057 at 550 nm and 50% relative humidity according to the Global Aerosol Data Set [*Köpke et al.*, 1997], with a top-of-atmosphere radiative forcing of -1.2 W m<sup>-2</sup> [*Haywood and Shine*, 1995]. Ground and ship-based measurements of aerosol optical depth (AOD) during ACE-Asia were typically in the range 0.3–0.8 [*Quinn et al.*, 2004; *Eck et al.*, 2005].

[13] Further work to understand the large free tropospheric source of SOA revealed by the ACE-Asia observations is needed. Field measurements in other regions should be conducted. Laboratory studies should probe SOA formation over aging periods of several days and at cold temperatures and low pressures. Improved model mechanisms should be developed to match the constraints from the field observations and assess the environmental implications of this previously unrecognized SOA burden.

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C. L. Heald, D. J. Jacob, and R. J. Park, Department of Earth and Planetary Sciences, Harvard University, 29 Oxford Street, Cambridge, MA 02138, USA. (heald@fas.harvard.edu)

B. J. Huebert, Department of Oceanography, University of Hawaii at Manoa, 1000 Pope Road, MSB 205, Honolulu, HI 96822, USA.

H. Liao and J. H. Seinfeld, Department of Chemical Engineering, California Institute of Technology, 1200 E. California Blvd., Mail Code 210-41, Pasadena, CA 91125, USA.

L. M. Russell, Scripps Institution of Oceanography, University of California-San Diego, 9500 Gilman Drive, Mail Code 0221, La Jolla, CA 92093-0221, USA.

R. J. Weber, School of Earth and Atmospheric Sciences, Georgia Institute of Technology, 311 Ferst Dr. NW, Atlanta, GA 30332, USA.