

Organic and Elemental Carbon Measurements during ACE-Asia Suggest a Longer Atmospheric Lifetime for Elemental Carbon

H. -J. LIM,[†] B. J. TURPIN,^{*,†}
L. M. RUSSELL,[‡] AND T. S. BATES[§]

Department of Environmental Sciences ENSR,
Rutgers University, P.O. Box 231, 14 College Farm Road,
New Brunswick, New Jersey 08901-8551, Princeton University,
Princeton, New Jersey 08544, and NOAA Pacific Marine
Environmental Laboratory, Seattle, Washington 98115

During the ACE-Asia intensive field campaign (March 14–April 20, 2001), PM_{1.0} organic (OC) and elemental carbon (EC) concentrations were measured onboard the NOAA R/V *Ronald H. Brown* over the Northwest Pacific Ocean using a semi-continuous automated carbon analyzer downstream of a carbon-impregnated filter denuder. This OC and EC measurement achieved a mean time resolution of about 200 min over the Pacific Ocean, substantially lower than that achieved previously (24 h). The semi-continuous measurements, in which the adsorption artifact was substantially reduced using the denuder, showed good agreement with integrated artifact-corrected measurements made without a denuder. Mean particulate OC and EC concentrations were 0.21 and 0.09, 0.70 and 0.29, 1.00 and 0.27, and 2.43 and 0.66 μg of C m⁻³ over the background Pacific Ocean, Asian-influenced Pacific Ocean, offshore of Japan, and Sea of Japan, respectively. On April 11, 90-min average OC and EC concentrations peaked at 4.0 and 1.3 μg of C m⁻³, respectively, offshore of Korea over the Sea of Japan. The OC/EC ratio of 3.7 over the Sea of Japan and offshore of Japan was substantially higher than that of 2.5 over the Asian-influenced Pacific Ocean, even though backward air mass trajectories put the “Asian-influenced Pacific Ocean” sample downwind. The OC/EC ratio decreased with increasing time since the air mass encountered the source regions of China, Japan, and Korea. This suggests a longer atmospheric residence time for EC than for OC.

Introduction

The direct and indirect effects of atmospheric particulate carbon introduce large uncertainties in estimates of climate change (1). Atmospheric particulate carbon is mainly comprised of organic (OC) and elemental (or black) carbon (EC or BC). OC contributes to scattering, whereas EC contributes to absorption of solar radiation. Although sulfate is a major contributor to global radiative forcing, both OC and EC play important roles in global climate change directly and by

influencing the properties and nucleating ability of cloud condensation nuclei (CCN).

Novakov and Penner (2) reported that in the coastal atmosphere of Puerto Rico 67% of particles in the CCN size range were organic matter and 33% were sulfate particles. Organic particles comprise a substantial fraction of CCN-sized particles in European background and urban aerosols (3). Water-soluble organic compounds are likely contributors to CCN. Laboratory experiments have demonstrated that both primary organic aerosols emitted from biomass burning (4) and secondary organic compounds formed in the atmosphere (5) can act as CCN. Matsumoto et al. (6) concluded that water-soluble organic compounds contribute to CCN formation on the basis of a significant correlation between the mass concentration of water-soluble particulate OC and the CCN concentration over an island in the Northwest Pacific Ocean. A variety of water-soluble organic compounds have been measured or are predicted to be present in atmospheric aerosols (7).

The International Global Atmospheric Chemistry Program (IGAC) established the Asian Aerosol Characterization Experiment (ACE-Asia) to understand the impact of natural and anthropogenic emissions in the east Asian region on global climate change (8). In the spring of 2001, an international team of ACE-Asia scientists conducted a variety of atmospheric and oceanographic measurements during a 36-d cruise from Hawaii to the Sea of Japan, across the Pacific Ocean along 33° N, and around the Sea of Japan and the East China Sea onboard the National Oceanic and Atmospheric Administration (NOAA) R/V *Ronald H. Brown*. As part of this effort, Rutgers University conducted short-duration automated measurements of particulate OC and EC using an in-situ thermal–optical carbon analyzer.

Anthropogenic primary particles and particle precursors are emitted in large quantities from northeastern Asia, where about one-third of the world's population lives. For example, about 1×10^{12} g yr⁻¹ of fossil fuel EC is emitted into the atmosphere from China (9, 10). Transport of anthropogenic pollutants over the North Pacific Ocean is likely since naturally generated Asian dust is transported across the North Pacific Ocean (11–14). Although some measurements of carbonaceous aerosol over the North Pacific Ocean have been made previously (15, 16), little is known about the spatial distribution, emission sources, and transformations of particulate carbon in this region.

The objective of this research was to investigate the performance of a newly developed denuder and semi-continuous carbon analyzer system in a marine environment and to present particulate OC and EC concentrations over the Northwest Pacific Ocean. Particulate OC and EC concentrations measured during the cruise are then used to provide insights into atmospheric processing.

Experimental Section

Sampling and Analysis. Particulate OC and EC concentrations were measured using an automated thermal–optical transmittance (TOT) carbon analyzer (Sunset Laboratory, Forest Grove, OR) on R/V *Ronald H. Brown* during the ACE-Asia intensive field campaign from March 14 to April 20, 2001. This commercially available instrument is based on the in-situ carbon analyzer developed by Turpin et al. (17). Versions of this instrument have been used to better understand atmospheric chemistry in Los Angeles, CA (18), and Atlanta, GA (19). The carbon analyzer was located in a

* Corresponding author phone: (732)932-9540; fax: (732)932-8644; e-mail: turpin@aesop.rutgers.edu.

[†] Rutgers University.

[‡] Princeton University.

[§] NOAA Pacific Marine Environmental Laboratory.

NOAA container in the forward section of the ship. Air was drawn at $1 \text{ m}^3 \text{ min}^{-1}$ through a 5 cm diameter common sampling inlet nozzle 18 m above the sea surface, maintained at 55% RH. A total of 10 L min^{-1} of this flow was pulled through a 1.91 cm diameter stainless steel tube, a $1 \mu\text{m}$ diameter cutpoint impactor at 55% RH (20), and about 4 m of 1.27 cm diameter copper tubing into a plenum. In the plenum, the flow was split between the semi-continuous carbon analyzer and two auxiliary filter holders. The measurement system was connected to the NOAA-PMEL pump control system, which closed a valve to prevent sampling when the sampling manifold was impacted by the ship-stack emissions.

Sample air for semi-continuous OC and EC measurement was drawn through a parallel-plate diffusion denuder placed before the carbon analyzer to substantially reduce the adsorption of vapor-phase organics on the semi-continuous carbon analyzer quartz fiber sampling filter. Without reduction of this artifact or correction for this artifact, particle-phase OC concentrations would be substantially overestimated (21). The denuder contains 15 strips ($L \times W$: $20.3 \text{ cm} \times 3.15 \text{ cm}$) of carbon-impregnated filter (CIF; Schleicher Schuell, Keene, NH) spaced at 2-mm intervals inside an aluminum housing. The residence time of the sample air in the denuder was 0.19 s at the sampling flow rate of 7.8 L min^{-1} . Particles in the sample air were then collected downstream on a quartz fiber filter (1.5 cm^2) at a face velocity of 73 cm s^{-1} inside the carbon analyzer and analyzed automatically by TOT immediately after collection. This filter was changed about every 7 d, before the buildup of refractory materials had any noticeable influence on the transmittance through the filter.

Integrated filter samples were collected concurrently in two ports. One port contained a 47-mm quartz fiber filter (QAT-UP, PallGelman, Ann Arbor, MI). The other contained a 47-mm Teflon filter (Teflo $2 \mu\text{m}$, PallGelman) followed by a 47-mm quartz fiber filter (QAT-UP, PallGelman). Quartz fiber filters used for integrated measurements were cleaned in a muffle furnace at $550 \text{ }^\circ\text{C}$ for more than 2 h before the cruise. This two-port system is a typical approach to the measurement of 24-h average particulate carbon concentrations (21). The backup quartz fiber filter behind the Teflon filter samples particle-free ambient air and provides an estimate of OC adsorbed on the front quartz fiber filter. While only a small fraction of the total organic vapor adsorbs on the filter, the quantity of adsorbed vapor is often 30–60% of the collected OC (ref 21 and references therein). Particulate OC and EC were reported by subtracting the backup filter values from the concurrently collected quartz fiber front filter values and dividing by the sample air volume. These auxiliary parallel measurements were made for quality assurance purposes.

The semicontinuous OC/EC sample collection time was varied between 1 and 8 h to account for the large variations in atmospheric concentrations and downtime to avoid ship-stack emissions. Auxiliary sample filters were changed every 24 h, with some exceptions to accommodate the ship sampling schedule and changing ambient conditions. Sampling flow rates were maintained at 7.8, 11.1, and 11.1 L min^{-1} for the carbon analyzer, auxiliary quartz filter, and auxiliary Teflon quartz filter ports, respectively. All integrated filter samples were stored frozen during the cruise, hand-carried on the flight from Japan to New Jersey in an insulated bag with blue-ice packs, and stored in a freezer at Rutgers University until analysis. OC and EC analyses of integrated filter samples were performed with a laboratory version of the Sunset Laboratory TOT carbon analyzer.

Both semi-continuous and laboratory carbon analyzers were operated using the analytical procedures adopted by the ACE-Asia science team for all study carbon analyses (22).

TABLE 1. Number of OC and EC Measurements (Total), Number and Percent of Measurements above Method Detection Limit (>MDL), and Sample Collection Time at Various Locations for Semi-continuous Measurements Onboard *Ronald H. Brown* during ACE-Asia

| location | OC | | EC | | Sampling min ^b |
|--|-------|-------------------|-------|-------------------|---------------------------|
| | total | >MDL ^a | total | >MDL ^a | |
| Sea of Japan ^c | 54 | 54 (100) | 54 | 54 (100) | 83 (0.87) |
| offshore of Japan ^d | 73 | 68 (93.2) | 73 | 44 (60.3) | 119 (0.84) |
| Asia-influenced Pacific Ocean ^e | 15 | 10 (66.7) | 15 | 8 (53.3) | 197 (0.65) |
| background Pacific Ocean ^f | 29 | 3 (10.3) | 29 | 4 (13.8) | 201 (0.80) |
| Yokosuka Port ^g | 44 | 31 (70.5) | 44 | 36 (81.8) | 35 (1.00) |

^a Number in parentheses is in percent. ^b Number in parentheses represents the ratio of actual to set sample collection times. ^c Represents DOY 97–103. ^d Represents DOY 90–96 and 104–109. ^e Represents DOY 85–89. ^f Represents DOY 75–84. ^g Represents DOY 110–112.

This protocol was selected to match that used for U.S. EPA compliance samples and inspired by the NIOSH method (23). The major difference is that, for the semi-continuous instrument, samples are collected in the analyzer, the air is purged, and analysis begins without sample handling. In contrast, an aliquot of each previously collected sample is physically introduced into the laboratory carbon analyzer for integrated filter analysis. On-line sampling and analysis dramatically reduces instrument detection limits and thus enables short duration sampling.

On average, the sampling pump of the in-situ carbon analyzer was turned on about 82% of the set sampling time during the cruise. (The pump was turned off when contamination of sample air by ship exhaust was suspected.) Actual sampling duration was in the range of 80–200 min over the marine environment of the cruise (see Table 1). Although the air over the background Pacific Ocean was extremely clean, samples were successfully collected with a mean time resolution of about 200 min using the semi-continuous carbon analyzer.

Briefly, air is purged from the analyzer (He; 100 mL/min ; 8 min ; $20\text{--}25 \text{ }^\circ\text{C}$) after sample collection ($20\text{--}25 \text{ }^\circ\text{C}$) on the quartz fiber filter mounted in the semi-continuous analyzer or after a 1.45-cm^2 punch of sampled filter is loaded in the laboratory analyzer. The quartz fiber filter is then heated in a He environment stepwise to $870 \text{ }^\circ\text{C}$ to volatilize OC. The quartz filter is cooled to $550 \text{ }^\circ\text{C}$, and EC is eluted by combustion in 2% O_2 in He, heating stepwise to $880 \text{ }^\circ\text{C}$. A calibration gas with a known amount of methane (1.63 mL) is automatically injected in the last step of the analysis for quantitation. The transmittance of light through the quartz fiber filter is monitored using a diode laser and a photodetector to correct for pyrolysis of OC to EC during analysis. During heating in an oxygen-free environment, some OC pyrolyzes, reducing the transmittance through the filter. The amount of OC that has been pyrolytically converted to EC is considered to be the amount of EC that must be removed to return the transmittance to its prepyrolysis value. Thus, all carbon removed before the transmittance returns to its prepyrolysis level (i.e., the OC-EC split-point) is considered to be OC and afterwards is EC. (Additional analytical details and quality control procedures are provided in Supporting Information.)

Submicron carbonate carbon was not separately determined. It is a small contributor to continental submicron carbon (24–26). ACE-Asia Ca^{2+} and Mg^{2+} concentrations suggest that it averaged 3% of submicron OC on the R/V *Ronald H. Brown*. Carbonate carbon is expected to evolve in a sharp peak in the $870 \text{ }^\circ\text{C}$ temperature step in He (23). While we did observe such a feature in some ACE-Asia coarse

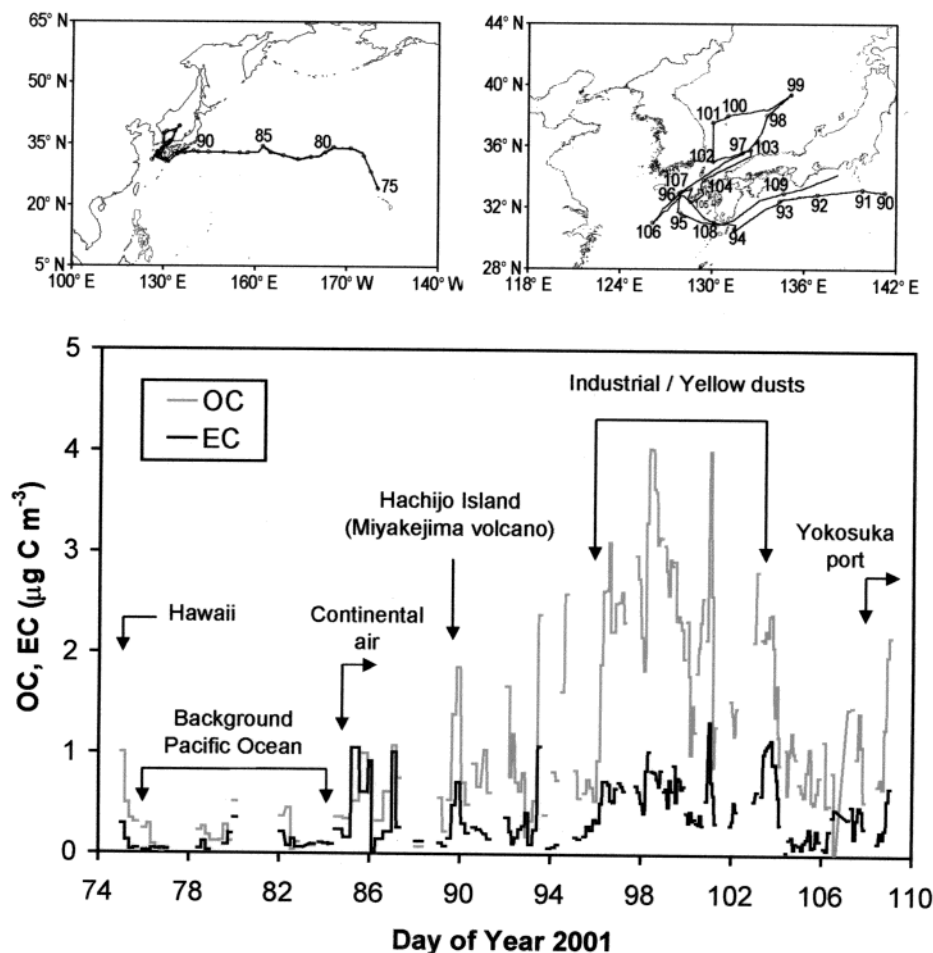


FIGURE 1. Particulate organic (OC) and elemental carbon (EC) concentrations during the *Ronald H. Brown* cruise of ACE-Asia. March 16 corresponds to day of year (DOY) 75.

particle analyses, such a sharp peak was not discernible in these submicron ACE-Asia samples. Any carbonate carbon present will be reported as OC.

Additional measurements made aboard the ship and used in this analysis include concentrations of SO_2 and total particle number (27), O_3 (28), CO (29), and radon (30). Three-dimensional air mass back-trajectories were calculated at three altitudes using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPPLIT) 4 model (31), which is based on the NCEP-FNL wind fields. All references to time are reported here in Coordinated Universal Time (UTC).

Measurement Validation. A comprehensive evaluation of instrument performance, including quality control measures and an assessment of positive and negative sampling artifacts, was conducted and is reported in detail in text and figures in Supporting Information. The number of samples above detection limits is also provided in Table 1. The denuder substantially reduced the amount of adsorbed vapor on the sampling filter; however, correction for adsorption was still significant at low loadings (see Figure S2, Supporting Information). Good agreement was found between the undenuded integrated 2-port filter sampler and the denuded semi-continuous carbon analyzer (see Figure S3, Supporting Information).

Results and Discussion

Particulate Carbon Concentrations. Figure 1 shows the time series of particulate OC and EC concentrations measured during the ACE-Asia cruise. The high concentrations on March 15 were made offshore of Hawaii. (March 15 corresponds to DOY 74). After leaving Hawaii, OC and EC

concentrations were no more than a few tenths of one microgram of carbon per cubic meter and generally increased with decreasing distance from the East Asian continent. On March 26 (DOY 85), 8-h average OC and EC concentrations increased to 1.00 and 0.61 $\mu\text{g of C m}^{-3}$, respectively. The corresponding air mass had been over Asia 3 d earlier. Figure 2 shows that concentrations of O_3 , CO, SO_2 , and radon and number concentrations of particles larger than 13 nm in diameter ($D_p > 13 \text{ nm}$) concurrently increased with OC and EC. Seven-day backward air mass trajectories with a starting pressure of 950 mbar arriving at the ship between DOY 83.5 and 85.5 show that air arriving at the ship after March 26 was influenced by long-range transport from the Asian continent (see Figure 3).

R/V *Ronald H. Brown* reached offshore of Hachijo Island, Japan, on March 30 (DOY 89). On March 30, intercomparison measurements were conducted with the ground measurement site at Hachijo Island. An active volcano on Miyakejima ($34^{\circ}04'43''\text{N}$, $139^{\circ}31'46''\text{E}$) near Hachijo Island continues to emit gases. Interestingly, elevated carbonaceous aerosol concentrations (1.86 and 0.71 $\mu\text{g of C m}^{-3}$ for 4-h average OC and EC, respectively) were observed at the location, following high SO_2 concentrations from Miyakejima (Figure 2). Daily average OC and EC concentrations were 0.66–0.91 and 0.08–0.23 $\mu\text{g of C m}^{-3}$, respectively, while R/V *Ronald H. Brown* cruised around Japan to the Sea of Japan. R/V *Ronald H. Brown* cruised through the Sea of Japan during April 7–13, where the most elevated OC and EC concentrations were observed. On April 8 (DOY 98), 2-h averaged OC and EC concentrations on the Sea of Japan increased to 4.03 and 1.03 $\mu\text{g of C m}^{-3}$, respectively. On April 11 (DOY 101), 90-min

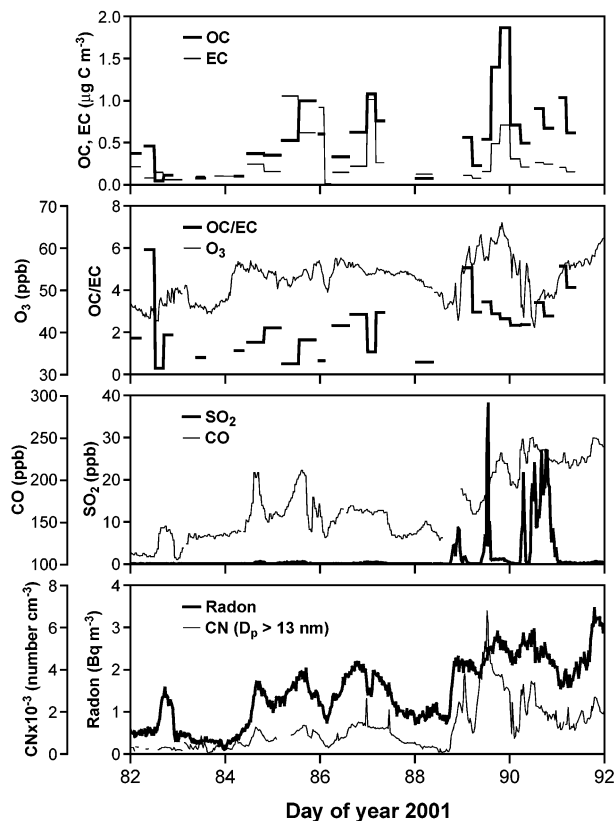


FIGURE 2. Particulate organic (OC) and elemental carbon (EC) and OC/EC ratio with ozone, carbon monoxide, sulfur dioxide, radon, and particle ($D_p > 13$ nm) number concentrations between day of year (DOY) 82 and 92.

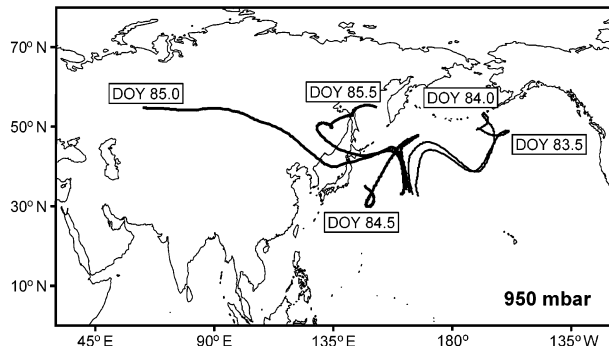


FIGURE 3. Seven-day backward trajectories of air masses arriving at *Ronald H. Brown* with the starting pressure of 950 mbar at day of year (DOY) 83.5, 84.0, 84.5, 85.0, and 85.5.

averaged OC and EC concentrations peaked at 4.00 and 1.32 $\mu\text{g of C m}^{-3}$, respectively, offshore of Korea over the Sea of Japan. During April 15–16 (DOY 105–106), OC and EC concentrations over the East China Sea were 0.6 and 0.2 $\mu\text{g of C m}^{-3}$, respectively. The *R/V Ronald H. Brown* cruised around the coast of Japan April 17 and arrived at the Port of Yokosuka, Japan, on April 20 (DOY 110) after the 35-d cruise (Figure 1).

Pollution Episodes. Figure 4 shows OC and EC concentrations and OC/EC ratio with O_3 , CO, SO_2 , and radon concentrations for the very polluted air mass between DOY 95.5 and DOY 104.5. Several concurrent ozone and OC peaks were observed during the episode. The additional OC that does not co-vary with EC and CO is likely to be secondary OC. High CO concentrations suggest the influence of combustion during the episode. On DOY 101, a sharp spike in CO and EC were observed. This was also observed on DOY

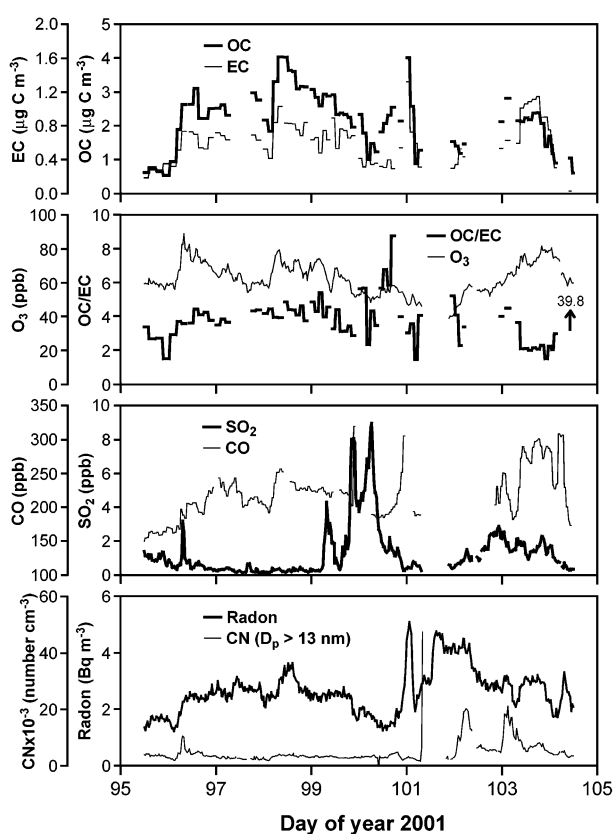


FIGURE 4. Particulate organic (OC) and elemental carbon (EC) and OC/EC ratio with ozone, carbon monoxide, sulfur dioxide, radon, and particle ($D_p > 13$ nm) number concentrations between day of year (DOY) 95 and 105.

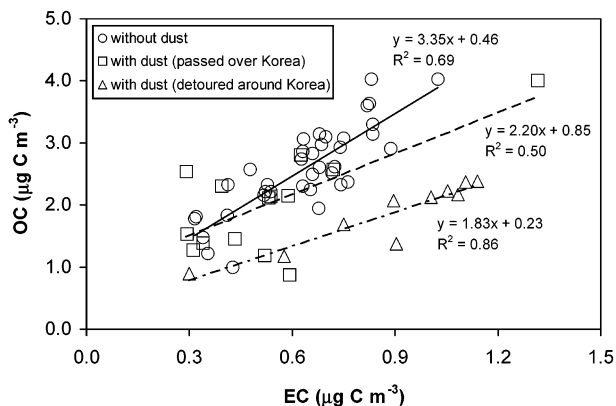


FIGURE 5. Particulate organic (OC) and elemental carbon (EC) concentrations for the pollution episode between day of year (DOY) 96.5 and 105.5. Circle, square, and triangle represent polluted air without dust, mixed with dust that passed over Korea, and mixed with dust that detoured around Korea, respectively.

104. The corresponding peak in OC is probably of combustion origin. The increased concentrations of radon, an indicator of soil, on DOY 101–104 suggests the strong influence of dust during the later half of the pollution episode. This period was classified by NOAA scientists as a polluted dust event (8) on the basis of extensive measurements, including CO, SO_2 , particle number concentrations, light scattering and absorption, and air backward trajectories. Backward air trajectories of very polluted air between DOY 96.5 and DOY 100.5 and very polluted air mixed with dust between DOY 100.5 and DOY 104 show that the polluted air without dust was transported over Japan and Korea. The polluted air mass

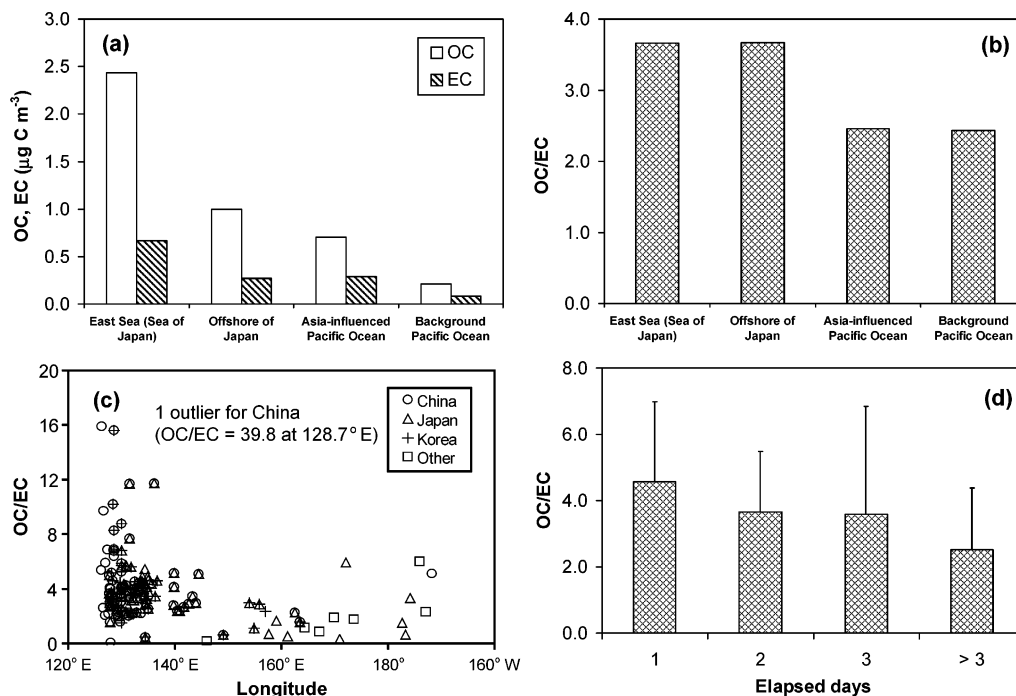


FIGURE 6. Particulate organic (OC) and elemental carbon (EC) concentrations and OC/EC ratio for the *Ronald H. Brown* cruise of ACE-Asia. (a) OC and EC concentrations and (b) OC/EC ratio over background Pacific Ocean: March 16–25, 2001; Asian-influenced Pacific Ocean: March 26–30, 2001; Sea of Japan: April 7–13, 2001; Offshore of Japan: March 31–April 6 and April 14–18, 2001. (c) OC/EC ratio as a function of longitude for air that passed over China, Japan, Korea, and other regions over the previous 7 d. (d) OC/EC ratio as a function of time since the air mass passed over land (including China, Japan, and Korea). Uncertainties represent 1 standard deviation of mean values.

mixed with dust was transported over the Gobi Desert and industrialized regions of China and Korea (see Figure S4 of Supporting Information) The dust episode can be classified into two groups based on the corresponding backward trajectories: (i) air that passed over Korea and (ii) air that detoured around Korea over urban/industrial China. Figure 5 shows that substantially higher OC/EC ratios were observed before and during the dust event when air was transported over Korea in comparison to times when the air detoured around Korea over urban/industrial China. This suggests that the characteristics of carbonaceous aerosol downwind of the northeast Asian continent vary with source region and with atmospheric residence time.

In the clean marine environment of the Pacific Ocean, mean OC and EC concentrations were 0.25 and 0.06 μg of C m^{-3} , respectively (March 15–20). OC and EC concentrations averaged 2.43 and 0.66 μg of C m^{-3} , respectively, over the Sea of Japan (April 7–13). The carbonaceous aerosol measurements continued during April 20–22, after the arrival of *R/V Ronald H. Brown* at the Port of Yokosuka. OC and EC concentrations at the port were 2.46 and 6.56 μg of C m^{-3} , respectively. The extremely high EC concentration suggests that emissions from ships in the port strongly influence carbonaceous aerosol concentrations in the area (see Figure S5 of Supporting Information)

Atmospheric Lifetime of OC and EC. Figure 6 shows OC and EC concentrations over the study area categorized into the background Pacific Ocean, Asian-influenced Pacific Ocean, offshore of Japan, and Sea of Japan. The ship was under the influence of polluted air from the Hawaiian Islands during the first 2 d of the cruise (March 14–15). Backward air mass trajectory analyses show that enhanced OC and EC concentrations after March 26 were impacted by air from the East Asian continent. Therefore, measurements made during March 16–25 are classified as the background Pacific Ocean. Since the ship arrived around Hachijo Island of Japan

on March 30, measurements conducted during March 26–30 represent the Asian-influenced Pacific Ocean. OC and EC concentrations measured during April 7–13 represent the Sea of Japan. OC and EC concentrations measured during other periods of the study are categorized as offshore of Japan. Particulate OC and EC concentrations were 0.21 and 0.09, 0.70 and 0.29, 1.00 and 0.27, and 2.43 and 0.66 μg of C m^{-3} over the background Pacific Ocean, Asian-influenced Pacific Ocean, offshore of Japan, and Sea of Japan, respectively. Note that values for the background Pacific Ocean are likely quite uncertain since the fraction of reported OC and EC data above MDL is only 10% and 14% for OC and EC, respectively (see Table 1).

Figure 6 also presents the OC/EC ratios over the four research areas. Interestingly, the OC/EC ratio ($\text{OC}/\text{EC} = 3.7$) over the Sea of Japan and offshore of Japan was substantially higher than that over the Pacific Ocean ($\text{OC}/\text{EC} = 2.5$). Secondary organic aerosol (SOA) formation, the source region influencing the air mass, and the atmospheric lifetime of OC and EC can affect the OC/EC ratio of atmospheric particles. SOA formation would result in an increase in the OC/EC ratio with increasing residence time in the atmosphere (i.e., increasing distance from the source region). The effects of source region and time since the air mass passed over the source region were examined using 7-d air mass backward trajectories. Figure 6c shows OC/EC ratio as a function of longitude. The data were grouped into four different source regions: China, Japan, Korea, and other based on the corresponding backward trajectories. Generally, carbonaceous aerosols transported from China, Japan, and Korea all show decreasing OC and EC concentrations and OC/EC ratios with distance (and time) from the source region. Figure 6d shows that the mean OC/EC ratio was 4.6 and 2.5 for the elapsed time of 1 d and greater than 3 d, respectively. These findings suggest a longer residence time in the marine atmosphere for EC than for OC.

A difference in OC and EC residence times might occur because of differences in OC and EC volatility and scavenging rates. EC is a nonvolatile and thermally very stable species, whereas particulate OC contains many semi-volatile species that partition between gas and particle phases. As air from the source regions is transported and diluted with clean air, some particulate organic compounds are likely to evaporate to regain gas-particle equilibrium. Additionally, in-cloud scavenging could explain a shorter atmospheric lifetime for OC than EC. Wet deposition is a main removal process of particles in the atmosphere. A substantial fraction of atmospheric particulate matter is comprised of water-soluble organic compounds, and a substantial amount of OC has been observed in fog water and rainwater (32, 33). Some water-soluble particulate organics such as oxalic acid have wet-scavenging efficiencies comparable to sulfate (34). However, clouds and fogs ineffectively scavenge hydrophobic EC in the atmosphere (35–37). A field study in the Po Valley of Italy showed that EC was preferentially enriched in interstitial particles relative to fog droplets and that the fraction of EC scavenged to fog droplets was 6%, considerably lower than 18% of sulfate (35, 36). Chýlek et al. (37) found that over 90% of EC was in interstitial particles in clouds over southern Nova Scotia, Canada. The preferential scavenging of OC over EC is also consistent with semi-continuous measurements in Atlanta, GA, which show decreased OC/EC ratios during rain events (38). It should be noted that nonhygroscopic particles (e.g., EC-containing combustion particles) become more hygroscopic through surface oxidation reactions and condensation/sorption of oxidation products during transport (39, 40). This is consistent with the observation of increased EC wet-scavenging efficiencies in a remote area (41) and points out the importance of including data both close and distant from source regions in the estimation of EC lifetimes.

Precipitating clouds were a common occurrence in the Asian-influenced Pacific Ocean, as observed by the ship's rain records and regional satellite rainfall images. Rainfall occurred on 19% of the ship's 30-min average rain records and on 70% of the 36 cruise days between DOY 74 and DOY 109. As long as OC and EC are not completely internally mixed, it is quite likely that OC is preferentially scavenged, resulting in a shorter atmospheric lifetime for OC.

Previous advanced climate modeling studies (ref 40 and references therein) assume a longer lifetime for EC (4–10 d) than for OC (4–5 d). The measurements reported herein provide important direct observations to support this assumption. A decrease in the OC/EC ratio from 4.6 to 2.5 over 4–5 d of transit time is consistent with an OC lifetime of 4 d and an EC lifetime of 8–10 d.

Acknowledgments

This work was funded by the National Science Foundation (ATM-0003936-01). The authors thank David Smith and Robert Cary (Sunset Laboratory, Inc.) for their technical assistance in semi-continuous carbon analysis measurements for the *Ronald H. Brown* cruise of ACE-Asia. The authors are grateful to Drew Hamilton, Derek Coffman, James Johnson, Theresa Miller, and Patricia Quinn (NOAA-PMEL) for their assistance and advice in the installation and operation of the semi-continuous carbon analyzer for the cruise measurements. This research is a contribution to the International Global Atmospheric Chemistry (IGAC) Core Project of the International Geosphere Biosphere Program (IGBP) and is part of the IGAC Aerosol Characterization Experiments (ACE).

Supporting Information Available

A comprehensive evaluation of the semi-continuous carbon analyzer performance, denuder performance, quality control

measures, and supporting figures as noted in the text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Literature Cited

- (1) Intergovernmental Panel on Climate Change (IPCC). *Climate Change 2001: Radiative Forcing of Climate*; Cambridge University Press: New York, 2001.
- (2) Novakov, T.; Penner, J. E. *Nature* **1993**, *365*, 823–826.
- (3) Hitztenberger, R.; Berner, A.; Giebel, H.; Kromp, R.; Larson, S. M.; Rouc, A.; Koch, A.; Marischka, S.; Puxbaum, H. *Atmos. Environ.* **1999**, *33*, 2647–2659.
- (4) Novakov, T.; Corrigan, C. E. *Geophys. Res. Lett.* **1996**, *23*, 2141–2144.
- (5) Cruz, C. N.; Pandis, S. N. *Atmos. Environ.* **1997**, *31*, 2205–2214.
- (6) Masumoto, K.; Tanaka, H.; Nagao, I.; Ishizaka, Y. *Geophys. Res. Lett.* **1997**, *24*, 655–658.
- (7) Saxena, P.; Hildemann, L. M. *J. Atmos. Chem.* **1996**, *24*, 57–109.
- (8) Pacific Marine Environmental Laboratory (PMEL). ACE-Asia; <http://saga.pmel.noaa.gov/aceasia/> (accessed May 2002).
- (9) Parungo, F.; Nagamoto, C.; Zhou, M.-Y.; Hansen, A. D. A.; Harris, J. *Atmos. Environ.* **1994**, *28*, 3251–3260.
- (10) Cooke, W. F.; Wilson, J. J. N. *J. Geophys. Res.* **1996**, *101*, 19395–19409.
- (11) Duce, R. A.; Unni, C. K.; Ray, B. J.; Prospero, J. M.; Merrill, J. T. *Science* **1980**, *209*, 1522–1524.
- (12) Parrington, J. R.; Zoller, W. H.; Aras, N. K. *Science* **1983**, *220*, 195–197.
- (13) Merrill, J. T.; Uematsu, M.; Bleck, R. *J. Geophys. Res.* **1989**, *94*, 8584–8598.
- (14) Husar, R. B.; Prospero, J. M.; Stowe, L. L. *J. Geophys. Res.* **1997**, *102*, 16889–16909.
- (15) Rau, J. A.; Khalil, M. A. K. *Atmos. Environ.* **1993**, *27A*, 1297–1307.
- (16) Kim, Y. P.; Moon, K.-C.; Shim, S.-G.; Lee, J. H.; Kim, J. Y.; Fung, K.; Carmichael, G. R.; Song, C. H.; Kang, C. H.; Kim, H.-K.; Lee, C. B. *Atmos. Environ.* **2000**, *34*, 5053–5060.
- (17) Turpin, B. J.; Cary, R. A.; Huntzicker, J. J. *Aerosol Sci. Technol.* **1990**, *12*, 161–171.
- (18) Turpin, B. J.; Huntzicker, J. J. *Atmos. Environ.* **1995**, *29*, 3527–3544.
- (19) Lim, H.-J.; Turpin, B. J. *Environ. Sci. Technol.* **2002**, *36*, 4489–4496.
- (20) Berner, A.; Lurzer, C.; Pohl, F.; Preining, O.; Wagner, P. *Sci. Total Environ.* **1979**, *13*, 245–261.
- (21) Turpin, B. J.; Saxena, P.; Andrews, E. *Atmos. Environ.* **2000**, *34*, 2983–3013.
- (22) Schauer, J. J.; Mader, B. T.; Deminter, J. T.; Heidemann, G.; Bae, M. S.; Seinfeld, J. H.; Flagan, R. C.; Cary, R. A.; Smith, D.; Huebert, B. J.; Bertram, T.; Howell, S.; Quinn, P.; Bates, T.; Turpin, B.; Lim, H. J.; Yu, J.; Yang, C. H. ACE-Asia Intercomparison of a Thermal-Optical Method for the Determination of Particle-Phase Organic and Elemental Carbon. *J. Geophys. Res.* **2003**, *37*, 993–1001.
- (23) Birch, M. E.; Cary, R. A. *Aerosol Sci. Technol.* **1996**, *25*, 221–241.
- (24) Mueller, P. K.; Mosler, R. W.; Pierce, L. B. *J. Colloid Interface Sci.* **1972**, *39*, 235–239.
- (25) Nunes, T. V.; Pio, C. A. *Atmos. Environ.* **1993**, *27A*, 1339–1346.
- (26) Ohta, S.; Hori, M.; Yamagata, S.; Muraio, N. *Atmos. Environ.* **1998**, *32*, 1021–1025.
- (27) Bates, T. S.; Quinn, P. K.; Covert, D. S.; Coffman, D. J.; Johnson, J. E.; Wiedensohler, A. *Tellus* **2000**, *52*, 258–272.
- (28) Johnson, J. E.; Gammon, R. H.; Larsen, J.; Bates, T. S.; Oltmans, S. J.; Farmer, J. C. *J. Geophys. Res.* **1990**, *95*, 11,847–11,856.
- (29) Johnson, J. E.; Bates, T. S. *Global Biogeochem. Cycles* **1996**, *10*, 347–359.
- (30) Whittlestone, S.; Zahorowski, W. *J. Geophys. Res.* **1998**, *103*, 16743–16752.
- (31) Draxler, R. R. *Hybrid Single-Particle Lagrangian Integrated Trajectories (HYSPLIT): Version 3.0, User's Guide and Model Description*; Technical Report ERL ARL-195; National Oceanic and Atmospheric Administration: Silver Spring, MD, 1992.
- (32) Decesari, S.; Facchini, M. C.; Matta, E.; Lettini, F.; Mircea, M.; Fuzzi, S.; Tagliavini, E.; Putaud, J.-P. *Atmos. Environ.* **2001**, *35*, 3691–3699.
- (33) Blando, J. D.; Turpin, B. J. *Atmos. Environ.* **2000**, *34*, 1623–1632.
- (34) Limbeck, A.; Puxbaum, H. *J. Geophys. Res.* **2000**, *105*, 19857–19867.
- (35) Noone, K. J.; Orgen, J. A.; Hallberg, A.; Hansson, H.-C.; Wiedensohler, A.; Swietlicki, E. *Tellus* **1992**, *44B*, 581–592.

- (36) Hallberg, A.; Ogren, J. A.; Noone, K. J.; Heintzenberg, J.; Berner, A.; Krusiz, S. C.; Reischl, G.; Fuzzi, S.; Facchini, M. C.; Hansson, H.-C.; Wiedensohler, A.; Svenningsson, I. B. *Tellus* **1992**, *44B*, 545–555.
- (37) Chylek, P.; Banic, C. M.; Johnson, B.; Damiano, P. A.; Isaac, G. A.; Leitch, W. R.; Liu, P. S. K.; Boudala, F. S.; Winter, B.; Ngo, D. *J. Geophys. Res.* **1996**, *22*, 29105–29110.
- (38) Lim, H.-J.; Turpin, B. J. *Environ. Sci. Technol.* **2002**, *36*, 4489–4496.
- (39) Lioussé, C.; Penner, J. E.; Chuang, C.; Walton, J. J.; Eddleman, H.; Cachier, H. *J. Geophys. Res.* **1996**, *101*, 19411–19432.
- (40) Chung, S.; Seinfeld, J. H. *J. Geophys. Res.* **2002**, *107* (D19), 4407, DOI: 10.1029/2001JD001397.
- (41) Hitzenberger, R.; Berner, A.; Kromp, R.; Kasper-Giebl, A.; Limbeck, A.; Tschewenka, W.; Puxbaum, H. *Atmos. Environ.* **2001**, *35*, 5135–5141.

Received for review October 15, 2002. Revised manuscript received April 24, 2003. Accepted May 1, 2003.

ES020988S