

Photochemistry, ozone production, and dilution during long-range transport episodes from Eurasia to the northwest United States

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[1] On the basis of observations from the 1997–2002 Photochemical Ozone Budget of the Northeast Pacific (PHOBEA) experiments, we have identified 11 transpacific long-range transport (LRT) episodes, which contain significantly elevated levels of CO, O₃, and aerosol scattering. The LRT episodes were determined from aircraft and ground-based observations of CO, O₃, aerosol scattering coefficient, and 281 whole air samples analyzed for nonmethane hydrocarbons (NMHC). The ratio of excess O₃ to excess CO ($\Delta O_3/\Delta CO$) for the 11 LRT episodes ranged from -0.06 to 1.52 . Lower $\Delta O_3/\Delta CO$ ratios (<0.10) are characteristic of LRT episodes transported in the boundary layer or in the presence of substantial mineral dust. These events lack O₃ enhancements, even though O₃ precursors (CO, NMHCs) are elevated. Ratios of $\Delta O_3/\Delta CO$ of 0.2 – 0.5 are characteristic of LRT episodes of industrial and/or biomass burning where excess CO is coincident with expected excesses in O₃. High $\Delta O_3/\Delta CO$ ratios (>0.50) are found in LRT episodes transported higher in the free troposphere and are probably due to a mixing of LRT pollution plumes with ozone-rich upper tropospheric air. Using PHOBEA observations, backward trajectories, and data from other experiments in the North Pacific (TRACE-P, ACE-Asia, PEM-West B) we calculate OH concentrations using two different methods. For the LRT episodes we obtain mean OH concentrations between 1.9×10^5 and 1.3×10^6 molecules cm⁻³. We also present a method using dispersion models and observations to calculate the rate of dilution, k_{dil} , with background air during LRT. A low k_{dil} indicates less mixing with background air during transport, while a high value represents more entrainment with background air. For the April 2001 LRT episode we calculate a mean k_{dil} of 0.010 ± 0.004 hr⁻¹ and an OH radical concentration of 2×10^5 molecules cm⁻³. On the basis of these calculations we find that the large mineral dust transport episode, which took place in April 2001, was associated with the lowest OH concentration of the 11 episodes considered, implicating a strong role for heterogeneous chemistry during LRT. **INDEX TERMS:** 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0340 Atmospheric Composition and Structure: Middle atmosphere—composition and chemistry; 0341 Atmospheric Composition and Structure: Middle atmosphere—constituent transport and chemistry (3334); 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; **KEYWORDS:** long-range transport, photochemistry, Pacific

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1. Introduction

[2] In recent years, growth in emissions from transportation and industrial sources throughout East Asia has occurred due to economic and industrial development [Akimoto and Narita, 1994; Streets and Waldhoff, 2000]. Such pollutants emitted on the Eurasian continent can be exported to the North Pacific by midlatitude westerly transport, where they impact trace gas concentrations and photochemistry along the West Coast of the United States [Andreae et al., 1988; Parrish et al., 1992; Jaffe et al., 1999, 2001; Bailey et al., 2000]. For instance, during the 1997–2002 PHOBEA airborne and ground-based experiments, episodes of enhanced aerosols and trace gases, such

as ozone (O_3), nonmethane hydrocarbons (NMHCs) and carbon monoxide (CO) were observed and attributed to LRT from Eurasian sources 6–10 days back [Kotchenruther *et al.*, 2001; Price *et al.*, 2003; Jaffe *et al.*, 2003a, 2003b; Bertschi *et al.*, 2004].

[3] Westerly flow brings CO, PAN, aerosols, and NMHCs to the West Coast of the United States. This coupled with springtime increases in UV flux, enhances the production and transport of secondary pollutants, such as O_3 , which together have important implications for U.S. air quality. Recent observations and modeling studies suggest that Eurasia is an important source for CO and O_3 transported into the United States [Jacob *et al.*, 1999; Jaeglé *et al.*, 2003; Jaffe *et al.*, 2003a; Forster *et al.*, 2004; Liang *et al.*, 2004]. According to Liang *et al.* [2004], Asian sources contribute 44 ppbv (30%) to the surface CO levels at Cheeka Peak Observatory. Another modeling study by Jaeglé *et al.* [2003] captures well the vertical distributions of CO in the northeast Pacific when compared to aircraft observations. A study of West Coast observations by Jaffe *et al.* [2003c] shows a 10 ppbv (30%) increase in O_3 since the mid-1980s and attributes the trend to increased NO_x emissions in Asia. However, using models to predict O_3 , a secondary pollutant with complicated chemistry and source apportionment is difficult. This challenge makes it important to use a variety of methods and observations to clarify the impact of Eurasian emissions on U.S. air quality and impacts on O_3 . One important consideration is the effect of photochemistry on O_3 during specific LRT episodes.

[4] In an analysis of six LRT episodes, Jaffe *et al.* [2003a] found wide variations in the degree of apparent O_3 production. High O_3 production was observed for most LRT episodes transported in the free troposphere, while low or no O_3 production was found in cases where transport took place in the boundary layer and during the large mineral dust event of April 2001. For the April 2001 episode, this was attributed to heterogeneous chemistry, where O_3 or its precursors were lost on mineral dust particles during transport. Global models and laboratory studies suggest that the production of O_3 and other oxidants such as OH is reduced by heterogeneous chemistry [Dentener *et al.*, 1996; Dickerson *et al.*, 1997; He and Carmichael, 1999; Martin *et al.*, 2003].

[5] Information about photochemistry during LRT episodes can be gleaned from the relationships between O_3 and pollutants such as CO, aerosol scattering at 550 nm (σ_{sg}), and NMHCs. The ratio of O_3 and CO is useful because, with a tropospheric lifetime of ~ 2 months, CO is a long-lived tracer of anthropogenic sources and therefore helps differentiate between O_3 sources. For instance, Parrish *et al.* [1998] used O_3 and CO ratios to estimate the amount of O_3 exported to the North Atlantic troposphere from North America. The relationship between O_3 and σ_{sg} gives us information about the impact of heterogeneous chemistry of aerosols and O_3 . Ozone photochemistry is also closely linked with NMHCs, which are oxidized in bimolecular reactions with OH during LRT. Because of varying reaction rates, NMHCs can act as a photochemical “clock” providing necessary information about air mass age, source region, and/or OH concentration.

[6] Although notable gains have been made in measuring OH [Eisele and Tanner, 1991; Eisele *et al.*, 1994; Stevens *et*

al., 1994; Brune *et al.*, 1998; Ehhalt *et al.*, 1998; Mauldin *et al.*, 2003], direct observations are still difficult to make, particularly from small aircraft platforms with limited weight and space requirements such as the one we used for the PHOBEA experiments. This makes it important to explore other methods for estimating OH concentrations for specific air masses [Parrish *et al.*, 1992; Blake *et al.*, 1993; McKeen *et al.*, 1996; Dillon *et al.*, 2002]. Parrish *et al.* [1992] and Blake *et al.* [1993] used the rate of decay of two hydrocarbons with different photochemical lifetimes to study the photochemical age of air masses reaching the California coast and for an urban plume in Athens, Greece, respectively. The method does not use an explicit dilution rate, but by using a ratio of two hydrocarbons with different lifetimes, dilution is assumed to be common to both species. Taking this method a step further, Dillon *et al.* [2002] added an explicit factor for dilution and determined both the dilution rate and OH concentration for an urban plume in the Sacramento Valley.

[7] Although there is always some level of Asian pollution coming across the Pacific as part of the background [Jaeglé *et al.*, 2003; Liang *et al.*, 2004], in this paper we focus on 11 episodes of rapid transport of pollution from the Eurasian continent observed during the springtime PHOBEA experiments in 1997, 1999, 2001 and 2002. We explore the O_3 sources by examining the $\Delta O_3/\Delta CO$ and O_3/σ_{sg} ratios, and present two methods for characterizing photochemical oxidation and dilution for a number of LRT episodes across the North Pacific. One method uses the ratios of NMHCs, while the other uses individual NMHCs and includes an explicit dilution factor calculated from both observations and meteorological models.

2. Methods

2.1. Data

[8] The primary data source were our observations in the northeast Pacific during the PHOBEA I and II experiments [Jaffe *et al.*, 2001; Kotchenruther *et al.*, 2001; Price *et al.*, 2003]. Identification of the springtime transpacific LRT episodes are based on NMHCs, σ_{sg} , O_3 and CO data from the PHOBEA experiments between 1997–2002 at the Cheeka Peak Observatory (CPO) and from airborne observations off the coast of Washington State [Jaffe *et al.*, 2001; Kotchenruther *et al.*, 2001; Price *et al.*, 2003; Bertschi *et al.*, 2004].

[9] During these experiments, whole air samples were collected in stainless steel canisters and analyzed for NMHCs using gas chromatographic systems with flame ionization detectors as detailed by Doskey and Bialk [2001] and Price *et al.* [2003]. Aerosol scattering was measured using a 3-wavelength integrating nephelometer (TSI 3563; Shoreview, Minnesota) on the Duchess in 2001 and 2002 and King Air in 1999. In this analysis we used only data from the green channel (550 nm). Ozone was measured at CPO and on the King Air, using a Dasibi UV instrument and on the Duchess aircraft using a miniature ultraviolet instrument (2B Technologies Ozone Monitor; Golden, Colorado) [Bognar and Birks, 1996]. Several methods were used to measure CO. For the 1999 and 2001 airborne observations we used reduction gas

Table 1. Observational Data and OH Calculation Results From Equation (2), for LRT Episodes Observed During the 1997–2002 PHOBEA Experiments^a

Date	Transit Time	PHOBEA Altitude	Transit Altitude	σ_{sg} , Mm^{-1}		Ozone, ppbv		CO, ppbv		$\Delta\text{O}_3/\Delta\text{CO}$	Type	OH
				Mean	Δ	Mean	Δ	Mean	Δ			
29 March 1997	6.0	0.5	0.7	19	10	45	1	173	22	0.05	III	5.5E + 05
9 April 1999	7.5	2.9	3.0	21	19	67	9	171	39	0.24	II	5.7E + 05
29 March 2001	6.5	2.2	3.5	20	17	72	27	167	18	1.52	I	5.6E + 05
14 April 2001	5.8	4.9	4.2	25	22	44	-2	184	56	-0.04	III	1.9E + 05
6 May 2001	8.0	2.9	3.3	12	11	58	11	153	15	0.69	I	8.8E + 05
27 March 2002	5.0	0.5	0.4	4	8	47	2	187	36	0.06	III	5.0E + 05
15 April 2002	5.5	4.9	5.0	18	17	75	14	233	97	0.14	II	1.0E + 06
20 April 2002	8.0	0.5	2.3	10	2	43	-2	183	32	-0.06	III	8.1E + 05
14 May 2002	9.5	4.4	2.3	21	19	75	17	180	29	0.58	I	8.7E + 05
17 May 2002	10.0	4.0	2.1	31	29	77	19	194	43	0.44	II	6.3E + 05
23 May 2002	8.0	4.2	6.8	29	27	79	21	188	37	0.55	I	1.3E + 06
Median	7.5	2.9	3.0	20	17	67	11	183	36	0.24	NA	6.3E + 05

^aOH calculation results are in radical cm^{-3} . Delta (Δ) refers to the enhancement from spring background. PHOBEA altitude is the height, in kilometers, of observation during the PHOBEA experiments. Transit altitude is the mean height, in kilometers, of transpacific transport, and transit time, in days, are both determined from the NOAA HYSPLIT Ready backward trajectory for each LRT episode. Aerosol scattering coefficients, σ_{sg} , are STP corrected.

analysis (Trace Analytical, Inc. Model TA3000) on the canister samples. For the 2002 airborne observations we also used a continuous ultraviolet resonance-fluorescence CO analyzer (Aerolaser, Inc., Model 5002). At CPO a commercial nondispersive infrared instrument was used (API-300, Advance Pollution Instruments, San Diego, California). Specific details on the instruments, calibrations, and collection techniques used during each experiment are given by *Jaffe et al.* [2001], *Kotchenruther et al.* [2001], *Price et al.* [2003], and *Bertschi et al.* [2004].

[10] In addition, we used data from a number of other sources, including the 1994 PEM-West B [*Talbot et al.*, 1997], 2001 Transport and Chemical Evolution over the Pacific (TRACE-P) [*Jacob et al.*, 2003] and the 2001 Asian Pacific Regional Aerosol Characterization Experiment (ACE-Asia) [*Huebert et al.*, 2003]. We also used Asian emissions estimates for Trace-P [*Streets et al.*, 2003], and dispersion and trajectory models including the FABtraj trajectory model from the NOAA Aeronomy Laboratory [*Cooper et al.*, 2004a] and the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model from the NOAA Air Resources Laboratory [*Draxler and Hess*, 1997].

[11] The FABtraj trajectory model [*Cooper et al.*, 2004a] calculates three-dimensional forward and backward trajectories using the u , v and w wind fields from the National Weather Service's National Centers for Environmental Prediction (NCEP) Final Analyses (FNL). The FNL analyses were downloaded from the National Center for Atmospheric Research data archive, available every 6 hours with a horizontal grid spacing of $1^\circ \times 1^\circ$, and 22 vertical levels between the surface and 100 hPa. The three-dimensional trajectories were calculated using a linear interpolation scheme in space and time.

[12] The HYSPLIT model is a hybrid between a Lagrangian approach for transport calculations and a Eulerian approach for dispersion calculations (<http://www.arl.noaa.gov/ready/hysplit4.html>). Trajectories and dispersion reflect flow using FNL meteorology from NCEP. During the PHOBEA experiment, trajectories were calculated online (<http://www.arl.noaa.gov/ready/hysplit4.html>) using assimilated FNL data and dispersion calcu-

lations were run by Roland Draxler at NOAA Air Resources Laboratory.

2.2. LRT Characterization

[13] Transpacific LRT episodes were identified by the levels of trace gases or aerosols measured in the NE Pacific, compared to the median level determined from observations taken during the same season and year. For a particular air mass to be considered part of a long-range transport episode, the mixing ratio for at least two species must be more than one standard deviation above the median value for that altitude and during that year's observations.

[14] From the PHOBEA observations during the springs of 1997–2002, we have selected 11 transpacific LRT episodes for analyses. Eight of the eleven LRT episodes were observed from the aircraft from a total of 39 research flights made during 1999, 2001 and 2002, with the other three LRT episodes observed at CPO during 1997 and 2002. In all LRT episodes, backward trajectory calculations indicated transport from Asia. While there have been more than 11 LRT episodes from Asia observed from the aircraft and at CPO, according to PHOBEA observations, we've selected these particular episodes because they include NMHC observations necessary for analysis. A summary of these LRT episodes is shown in Table 1. The delta values (Δ) represent the difference from the median spring backgrounds during the same year as the LRT episode. Because of the small sample sizes, and to mitigate the effects of outliers and variability in observations, we followed a more conservative approach and used medians of the spring backgrounds rather than means.

[15] The LRT episodes we've selected for analyses have enhancements in CO ranging from 15 to 97 ppbv with a mean enhancement of $39 \pm 23(1\sigma)$ ppbv. Enhancements for O_3 and σ_{sg} in the LRT episodes range from -2 to 27 ppbv and 4 to 31 Mm^{-1} with means of $11 \pm 10(1\sigma)$ ppbv and $19 \pm 8(1\sigma)$ Mm^{-1} , respectively. The mean transit altitude calculated from HYSPLIT backward trajectories is $3.1 \pm 1.8(1\sigma)$ km above sea level (ASL) and the mean altitude for the LRT episode observations during PHOBEA is $2.9 \pm 1.8(1\sigma)$ km. The LRT episode transit times, also calculated from the HYSPLIT back-

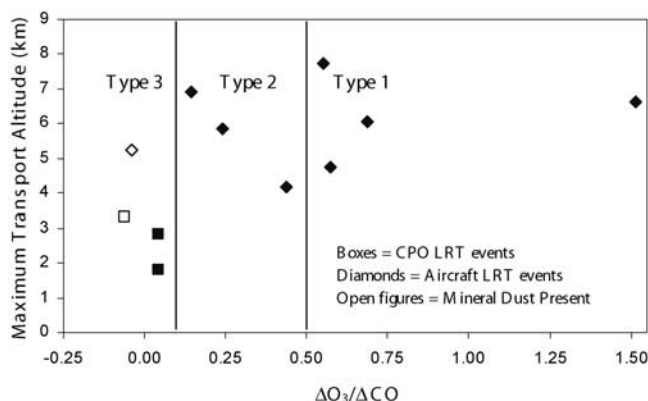


Figure 1. $\Delta\text{O}_3/\Delta\text{CO}$ versus maximum altitude for all LRT episodes. Types I, II, and III are described in the text.

ward trajectories, range from 5–10 days with a mean of $7.3 \pm 1.6(1\sigma)$ days.

3. Results and Discussion

3.1. Relationships Between CO , O_3 , and σ_{sg} During LRT Episodes

[16] Table 1 shows the mean and Δ values for σ_{sg} , O_3 , CO , and ratio of excess O_3 to excess CO ($\Delta\text{O}_3/\Delta\text{CO}$) for the 11 LRT episodes. The mean $\Delta\text{O}_3/\Delta\text{CO}$ ratio is 0.38 ± 0.46 and ranges from -0.06 to 1.52 . Figure 1 shows the $\Delta\text{O}_3/\Delta\text{CO}$ versus the maximum transport altitude, as calculated from the HYSPLIT backward trajectory model. The correlation coefficient is $R = 0.52$. However, a slightly lower correlation results when average transit altitude is used ($R = 0.39$).

[17] From the $\Delta\text{O}_3/\Delta\text{CO}$ ratios we define three LRT episode types, which reflect the degree of O_3 enhancement. While the distinction between these is somewhat arbitrary, the following analyses show that this nomenclature is useful.

[18] Type I episodes have $\Delta\text{O}_3/\Delta\text{CO}$ ratios ranging from 0.5 – 2.0 and are characterized by high O_3 enhancement relative to CO enhancement, with a mean transit altitude of 4.0 ± 1.9 km. Since typical urban and/or biomass burning sources result in excess O_3/CO ratios of 0.2 – 0.5 , type I is characterized by enhanced O_3 . This enhancement is likely due to mixing of pollutants with stratospheric intrusions bringing lower stratospheric/upper tropospheric O_3 -rich and low CO air into the mid-troposphere [Jaeglé et al., 2003]. For example, the LRT event observed on 29 March 2001 ($\Delta\text{O}_3/\Delta\text{CO} = 1.52$) had elevated O_3 and σ_{sg} , with ΔO_3 of 27 ppbv and $\Delta\sigma_{\text{sg}}$ of 17 Mm^{-1} . The NMHCs and CO were also elevated but within one standard deviation of median background levels. The excess ozone present in this event is attributed to the mixing of Eurasian industrial and/or biomass burning pollution with upper tropospheric air during transport [Jaffé et al., 2003a; Price et al., 2003]. The mixing of ozone rich air from the UT with anthropogenic emissions from the surface has been reported in other studies of LRT in the North Pacific and North Atlantic regions [Carmichael et al., 1998; Cooper et al., 2002, 2004b]. For instance, Carmichael et al. [1998] suggests that O_3 -rich air in the middle troposphere can mix with O_3 and precursors flowing

from anthropogenic sources in East Asia. Evidence of this was detected by Cooper et al. [2004b], where trajectory ensembles and observations show the mixing of polluted air originating in Asia with stratospheric air from tropopause folding during the ITCT experiment in May 2002. Similar results were also found for the outflow of a North American pollution plume to the North Atlantic region during April 1996 [Prados et al., 1999], which was observed at 3.5 – 5.5 km, and contained elevated CO and O_3 and a $\Delta\text{O}_3/\Delta\text{CO} = 0.58$. Prados et al. [1999] claims that the high level of O_3 present was more than can be reasonably produced by in situ chemistry and was most likely due to downward transport of O_3 from the UT, which subsequently mixed with a North American pollution plume. In addition to these UT episodes, data from the 1999 PHOBEA measurements identified two episodes with an even stronger UT/stratospheric signal. In those cases O_3 levels reached 311 ppbv and 1320 ppbv [Kotchenruther et al., 2001]. Since O_3 was the only enhanced species in those cases, they were not considered in the present study.

[19] Next, type II episodes have $\Delta\text{O}_3/\Delta\text{CO}$ ratios of 0.1 – 0.5 and a lower mean transit altitude compared to type I, at 3.4 ± 1.5 km. These are attributed to episodes of LRT of plumes from combustion sources, such as industrial and/or biomass burning. The 15 April 2002 LRT episode which contained a mixture of industrial and possible Siberian and tropical biomass-burning emissions is an example of a type II episode [Bertschi et al., 2004]. The $\Delta\text{O}_3/\Delta\text{CO}$ ratio was 0.18 , and the episode contained elevated O_3 accompanied by elevated precursor ($\Delta\text{CO} = 97$ ppbv) and NMHCs ($\Delta\text{ethane} = 0.8$ ppbv). Observations of biomass-burning plumes during the 1990 Arctic Boundary Layer Expedition (ABLE 3B) at 3 – 5 km over eastern Canada show similar $\Delta\text{O}_3/\Delta\text{CO}$ ratios ranging from 0.1 – 0.2 [Goode et al., 2000]. The industrial LRT episode observed on 9 April 1999 at 2.9 km is another example of a type II, with a $\Delta\text{O}_3/\Delta\text{CO}$ ratio of 0.24 .

[20] Finally, type III LRT episodes have $\Delta\text{O}_3/\Delta\text{CO}$ ratios less than ~ 0.1 . These episodes have elevated O_3 precursors such as CO and NMHCs, but O_3 is not significantly elevated. To date we have only seen cases of type III episodes transported in the marine boundary layer or in the presence of substantial mineral dust. Out of the four type III episodes seen, three were observed in the BL at CPO. The mean transit altitude for these four events is 1.9 ± 1.7 km, with the three surface observed LRT events averaging 1.1 ± 1.0 km and the April 2001 mineral dust LRT event at 4.1 ± 0.9 km.

[21] The type III episodes observed on 20 April 2002 and 14 April 2001 included substantial mineral dust. On the basis of observations of CO , σ_{sg} , and filter measurements of Si, Al, and Ca, the episode observed in the BL on 20 April 2002 ($\Delta\text{O}_3/\Delta\text{CO} = -0.06$) is attributed to a mix of mineral dust and industrial and/or biomass burning pollution. The 14 April 2001 LRT episode, with a $\Delta\text{O}_3/\Delta\text{CO}$ ratio of -0.04 , also contained substantial mineral dust mixed with anthropogenic pollution [Price et al., 2003; Jaffé et al., 2003b]. This was also the only type III episode observed above the BL at 4 – 6 km.

[22] A number of factors may have contributed to the lack of O_3 enhancement in these events. Heterogeneous reactions may destroy O_3 or NO_x species on mineral dust aerosols

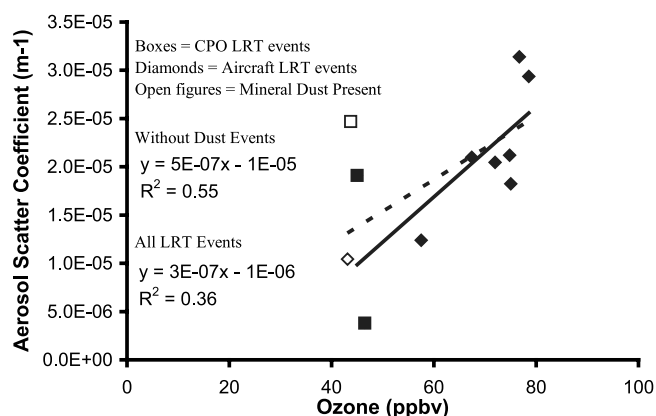


Figure 2. Ozone versus aerosol scattering coefficient (σ_{sg}) for LRT aircraft and ground episodes observed during the 1997 through 2002 springtime PHOBEA experiments. Each LRT event is represented by the flight leg with the highest pollution levels observed within the event. A flight leg represents 5–20 min of observations where the aircraft remained at a relatively steady altitude.

during transport, reduced UV in the source region due to substantial mineral dust, or the presence of CO but low NO_x in the source region could result in under-production of O_3 . For the episodes observed at CPO, another possibility may result from either a shorter O_3 lifetime due to transport in the BL and/or to loss on sea salt aerosols, which may have contributed to the lack of O_3 enhancement. One proposed mechanism for loss in the BL is suggested by *Vogt et al.* [1996] and *Aranda et al.* [1997], where O_3 may be lost in the BL through reaction with bromine species originating from sea salt aerosols.

[23] The relationship between O_3 and σ_{sg} for the 11 LRT episodes is shown in Figure 2. Episodes observed from the aircraft are shown as solid diamonds, while ground observations are shown as squares. The presence of mineral dust is shown with open diamonds or squares. In Figure 2, the LRT episodes cluster depending on type, with those observed at the surface and the 14 April 2001 event (substantial mineral dust), showing lower O_3 levels compared to all other events observed from the aircraft. The lack of O_3 in these LRT events supports our previous results [*Price et al.*, 2003] and indicates that the presence of mineral dust aerosols and/or boundary layer transport are likely contributing factors for the lack of enhanced O_3 for these LRT events.

3.2. Estimating OH

[24] To calculate OH for the 11 LRT events we used two methods: (1) a photochemical method detailed by *Parrish et al.* [1992] and used by *Blake et al.* [1993], which uses a ratio of two NMHCs with different lifetimes and (2) an extension of the model used by *Dillon et al.* [2002], which includes a dilution factor determined from observations or meteorological models.

[25] The first method accounts for dilution by using a ratio of two hydrocarbons with different lifetimes relative to reaction with OH. This method assumes that both hydrocarbons have negligible background levels, that the longer-

lived hydrocarbon is less reduced by OH over the transit time, and that OH is the only significant loss process, neglecting losses such as reactions with halogens and/or scavenging. Thus assuming a constant OH value, the decay of hydrocarbons A and B are first order.

$$A = A_o e^{-(k_A[\text{OH}]t)} \quad B = B_o e^{-(k_B[\text{OH}]t)} \quad (1)$$

Dividing A by B and simplifying, results in

$$\ln(A/B) = \ln(A_o/B_o) - (k_A - k_B)[\text{OH}]t \quad (2)$$

where A/B and A_o/B_o are the final and initial hydrocarbon concentration ratios and k_A and k_B are the rate constants for reaction of A and B with OH, respectively. *Blake et al.* [1993] used this method to estimate the OH concentration for a pollution plume in Athens, Greece, using acetylene in the denominator. Because equation (2) assumes that species A and B have negligible background concentrations, we will use the ratio of n -butane to propane to estimate the OH radical concentration.

[26] The second method we used to calculate OH is an extension of one used previously by *Dillon et al.* [2002], which includes two terms; one term for the entrainment of background air and a second term for photochemical loss to describe the change in species X over time.

$$dX/dt = -\text{entrainment of background air} - \text{photochemical loss} \quad (3)$$

$$dX/dt = -k_{\text{dil}}(X(t) - X_b) - k[\text{OH}]X(t) \quad (4)$$

[27] This method includes a first order dilution rate, k_{dil} , which we determine from various meteorological models and observations, described further in section 3.4. Integrating equation (4) with respect to time and simplifying results in equation (5)

$$X(t) = \frac{k_{\text{dil}}X_b}{k_{\text{dil}} + k_x[\text{OH}]} + \left(X_o - \frac{k_{\text{dil}}X_b}{k_{\text{dil}} + k_x[\text{OH}]} \right) e^{-(k_{\text{dil}} + k_x[\text{OH}])t} \quad (5)$$

where $X(t)$ is the mixing ratio for the species of interest in the LRT plume at time t , k_{dil} is the dilution rate, k_x is the OH rate constant for X , and X_b is the concentration of species X in entrained background air. Background air is considered to have NMHC mixing ratios as defined by the median mixing ratio for a given species at the altitude of interest and during the same year as the LRT episode being considered. In using equation (5), we assume no new emissions and no deposition for the hydrocarbons of interest along the transit path.

[28] In determining OH with these methods, potential sources of error include injection of fresh emissions into the air mass during transport, dilution of the air parcel by background air with a different mixing ratio than our median values, and measurement errors. Injection of fresh hydrocarbons partially resets the clock so the calculated OH concentrations are too small. Conversely, dilution by air with aged air masses containing hydrocarbons below the assumed background makes the clock run fast so the

Table 2. Initial *n*-Butane Versus Propane Ratios Used to Calculate OH in Equation (2)

Data Source	<i>n</i> -Butane/Propane Ratio
PEM-West B (spring 1994)	0.37 ± 0.08
ACE-Asia (11 April 2001)	0.35 ± 0.03
ACE-Asia (8 April 2001)	0.34 ± 0.03
2001 Trace-P (Jilin emissions)	0.37
Mean	0.36

calculated OH concentrations are too large. Additionally, as photochemical aging occurs, the most reactive hydrocarbon will be the first to approach its detection limit. Thus if blank problems occur in the GC measurement, the more reactive NMHC will be systematically high, causing the calculated photochemical age to be too short or OH concentration too low.

3.3. Calculating OH Using Equation (2)

[29] To calculate OH using equation (2), we use initial *n*-butane versus propane ratios from the source region. Table 2 gives various observations of this value. Ratios from PEM-West B are the maximum observations of Asian outflow taken above 20°N and above the boundary layer at 2–7 km during spring 1994 [Talbot *et al.*, 1997]. Emissions ratios are taken from the Trace-P emissions data files representing 2000 emission estimates [Streets *et al.* 2003], where the emissions of *n*-butanes are estimated as half of the total butane emissions. Ratios from ACE-Asia are from observations of Asian outflow taken on 11 April (33°N, 124°E) and 8 April (34°N, 132°E) above and in the boundary layer, respectively (T. Chen, personal communications, 2003). Table 2 shows good agreement between these ratios. An average of all these ratios was used to calculate OH using equation (2).

[30] Table 1 lists the resulting OH concentrations for the 11 LRT episodes. The mean OH concentration for the 11 LRT episodes is $7.1 \times 10^5 \pm 3.0 \times 10^5 (1\sigma)$ molecules cm^{-3} . The values range from $1.9 \times 10^5 - 1.3 \times 10^6$ with the 14 April 2001 episode having the lowest value. Although factors such as the very short lifetime (0.5 s) for OH and differences in precursors (O_3 , H_2O , and UV flux) make comparisons difficult, our results are comparable to OH observational and modeling results from the TRACE P experiment [Davis *et al.*, 2003; Mauldin *et al.*, 2003]. Davis *et al.* [2003] used a model to estimate the 24 hour average OH level during TRACE P at 25°–40°N and 0–7 km, ranging from 5 to 9×10^5 molecules cm^{-3} . Measurements of OH made by Mauldin *et al.* [2003] aboard the NASA P-3B showed a typical range of OH levels from $2-6 \times 10^6$ molecules cm^{-3} during the day and $<5 \times 10^5$ molecules cm^{-3} at night. These values are not dissimilar from our results, given that a typical midday OH level of 3×10^6 molecules cm^{-3} translates to $\sim 1 \times 10^6$ molecules cm^{-3} when averaged over a 24 hour period.

[31] Figure 3 shows a scatterplot of calculated OH versus O_3 . The lowest OH values calculated using equation (2) tends to correspond to LRT events with lower O_3 levels (Figure 3). The linear correlation coefficient for the calculated OH versus O_3 is $R = 0.57$. Although there is a relationship between O_3 and OH chemistry, there are many

other factors such as relative humidity, sunlight, and/or temperature that may also affect this relationship.

3.4. Determining Dilution Rates

[32] In the following sections (3.4 and 3.5) and calculations, we focus on the 14 April 2001 LRT event, which has been extensively studied and contains a large amount of data for use in a case study [Thulasiraman *et al.*, 2002; Price *et al.*, 2003; Jaffé *et al.*, 2003c; Gong *et al.*, 2003]. Price *et al.* [2003] describes the σ_{sg} and trace gases present in this episode as it reached the U.S. West Coast, while Jaffé *et al.* [2003b] focused on the evolution of the mineral dust plume, including its transport and impact on continental U.S. air quality. Though this episode is not characteristic of a typical LRT episode observed during PHOBEA, a similar LRT mineral dust episode was observed in 1998 [Tratt *et al.*, 2001].

[33] A key aspect of this episode, which sets it apart from typical anthropogenic LRT episodes, is the entrainment of a large amount of mineral dust originating in the Gobi desert region, with anthropogenic emissions from northeastern Asia. Illustrating this, Figure 4 shows the SeaWiFS image from 8 April 2001. Between 6 and 9 April, two midlatitude cyclones initiated the lofting of mineral dust from a presumably clean source region, the Gobi desert. During eastward transport the dust plume was entrained with pollution as it moved east over the industrial regions of northeast Asia and on to North America [Price *et al.*, 2003; Jaeglé *et al.*, 2003].

[34] To calculate OH using equation (5), an estimate of the first order dilution rate, k_{dil} is required for the species of interest in the LRT plume. Thus for the April 2001 LRT episode, we calculate k_{dil} using multiple methods; meteorological models, chemical observations, and aerosol observations. The meteorological method uses trajectory and dispersion models based on assimilated and gridded wind fields to estimate dilution of these plumes during LRT, while the chemical method uses observations of a long-lived pollutant. The meteorological tools used to calculate dilution include the FABtraj trajectory model from the NOAA Aeronomy Laboratory [Cooper *et al.*, 2004a] and the HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model from the NOAA Air Resources Laboratory [Draxler and Hess, 1997].

[35] Forward trajectory ensembles using the FABtraj model were initialized at 10×10 km horizontal spacing and 25-hPa vertical spacing. For the April 2001 case, we

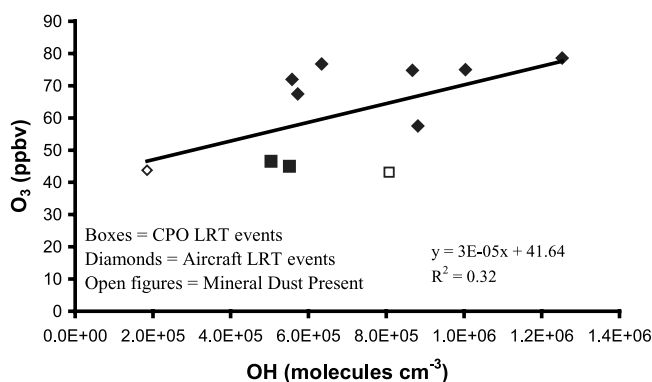


Figure 3. Calculated OH versus O_3 for LRT episodes observed during the 1997–2002 PHOBEA experiments.

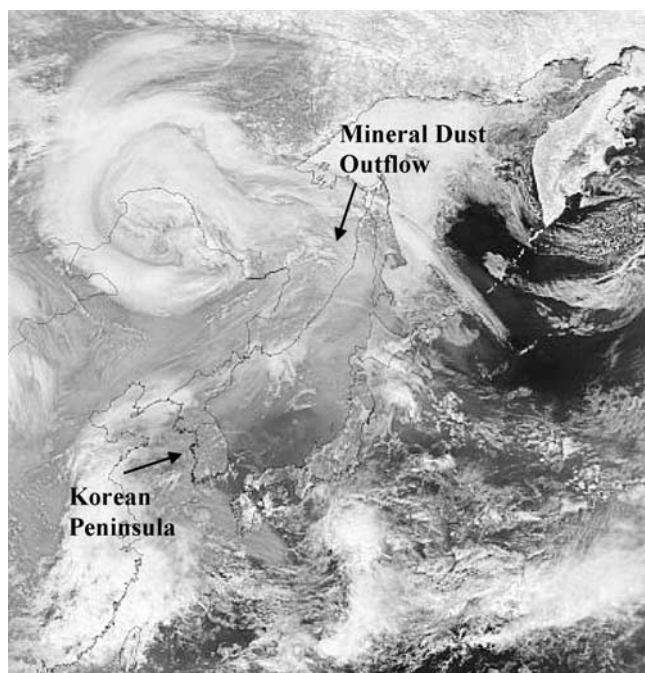


Figure 4. SeaWiFS image of mineral dust outflow from Asia on 8 April 2001. Image provided by the SeaWiFS Project, NASA Goddard Space Flight Center, and ORBIMAGE. See color version of this figure at back of this issue.

“released” 43,771 forward trajectory particles from the source region 3–5 km over Asia.

[36] Owing to the meteorological complexity and difficulty in determining the dilution of a plume during transport from the surface and out of the boundary layer, we focus on the zonal transport after the plume has already been trans-

ported out of the boundary layer. Thus we are using the 3–5 km region for the initial source parameter rather than running the trajectories from the surface.

[37] Figure 5 shows a comparison of FABtraj particle trajectory distributions on 8 April 2001 at 3–5 km region above sea level and between 42° – 50° N and 133° – 142° E at 0000 UTC with particle distributions reaching a 2×2 degree box at 4–6 km above Cheeka Peak on 14 April 2001. These locations, shown by boxes in Figure 5, match the locations for the initial source and for the PHOBEA observations, and are used to estimate the rate of dilution for the LRT episode. Because each trajectory represents an equal mass of air we can calculate the concentration of Asian air in the source and receptor boxes and determine the air mass dilution and the dilution rate from 8 April through 14 April 2001.

[38] The HYSPLIT model is a hybrid of Eulerian and Lagrangian approaches, where concentrations are calculated on a fixed (Eulerian) grid and advection and diffusion calculations are made using a Lagrangian framework. The transport and dispersion of a pollutant is calculated using either a single puff or from the dispersal of a cluster of particles. In the case of a single puff release, the puff will expand until it exceeds the meteorological grid cell space and then divide into several separate puffs. For a complete description of the model, readers are referred to *Draxler and Hess* [1997]. Changes to the model, to integrate the necessary dust algorithm into the model’s emission module, are described by *Draxler et al.* [2001]. To calculate k_{dil} using the HYSPLIT model, we compared the concentration of particles in the 3–6 km bin released over the source region on 8 April 2001, 1600 UTC at 47.0° N, 142.7° E, to those reaching the 3–6 km bin on 14 April 2001 at 0100 UTC at 48.31° N, 124.7° W.

[39] For the chemical methods, we use observations of CO, ethane, and/or aerosols, which are long-lived with

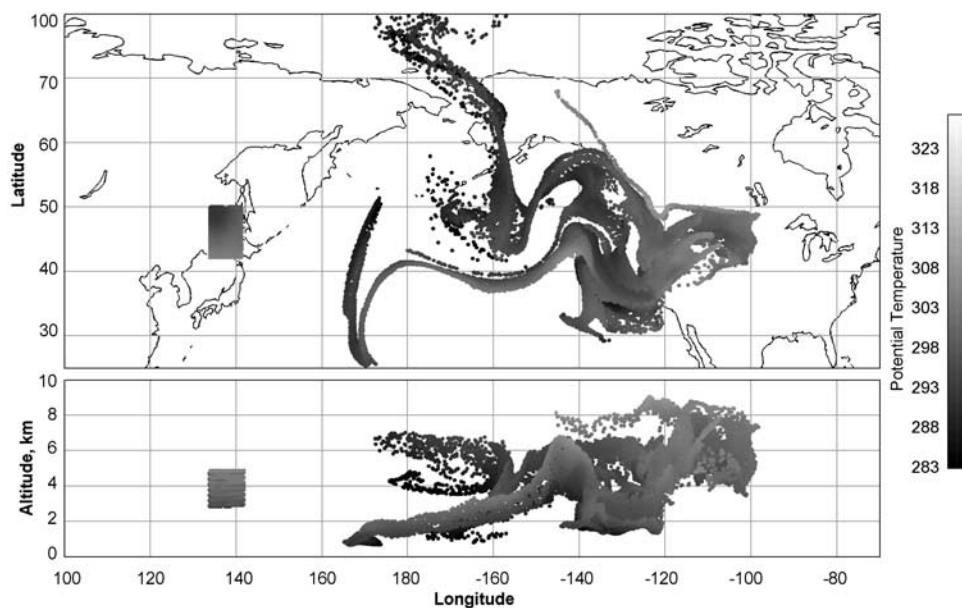


Figure 5. Initial and final FABtraj model results for particle forward trajectories during the April 2001 dust and pollution LRT episode. The box over northwest Japan represents the initial particle release on 8 April. See color version of this figure at back of this issue.

Table 3. Dilution Factors Determined From NMHC, CO, Aerosol, and Meteorological Tools^a

Species	X_i	X	X_b	Dilution Factor k_{dil} , hr ⁻¹
Ethane ^b	2801	1613	1220	0.0097
Ethane ^c	3771	1613	1220	0.0130
CO ^c	300	177	131	0.0090
TOMS-AI	4.2	2.0	0.0	0.0052
HYSPLIT	9.6e-10	4.84e-10	0.0	0.0048
FABtraj ^d	1000	20.0	0.0	0.0112
FABtraj ^e	1000	12.5	0.0	0.0144
Mean				0.010 ± 0.004

^a X is the mixing ratio measured in the LRT episode during PHOBEA, X_i is the initial mixing ratio for species X above the boundary layer in the source region near the coast of Asia and X_b is the background mixing ratio from PHOBEA observations at 3.5–6 km.

^bData from ACE-Asia on 11 April 2001.

^cData from Talbot *et al.* [1997] PEM-West B.

^dFor trajectories beginning at 0000 UTC on 8 April 2001.

^eFor trajectories beginning at 1200 UTC on 8 April 2001.

respect to OH oxidation and transpacific transport time, and where wet deposition appears to be unimportant. Removing from equation (4) the photochemical loss term, and integrating with respect to time gives

$$k_{dil} = \frac{1}{t} \ln \left(\frac{X_i - X_b}{X(t) - X_b} \right) \quad (6)$$

where X_i is the initial mixing ratio for species X at the source, $X(t)$ is the mixing ratio at time t and X_b is the background mixing ratio. For our application, we calculate the mean k_{dil} for the rapid free troposphere transpacific LRT of these air masses. Thus X_i is the mixing ratio of species X in the polluted free tropospheric air mass near the coast of Asia, and $X(t)$ is the mixing ratio near the U.S. West Coast. For the background mixing, X_b , we used the median springtime values measured during the PHOBEA experiments in the NE Pacific troposphere. For X_i we use observations from the ACE-Asia experiment on 11 April 2001 at 124.5°E longitude, 33.1°N latitude and an altitude of 1.4 km and for $X(t)$, PHOBEA observations of this LRT episode taken on 14 April 2001 at 124.7°W longitude, 48.3°N longitude and an altitude of 4–6 km are used.

[40] Table 3 lists the calculated k_{dil} for the 14 April 2001 LRT episode. These values are based on observations of long-lived ethane and CO above the boundary layer, aerosol index from TOMS, and the NOAA meteorological models, described previously. Observations from ACE-Asia of a long-lived hydrocarbon (ethane) during the dust/pollution event taken on 11 April, (33°N, 124°E, and 1.4 km) gives a k_{dil} of 0.0097 hr⁻¹. Using aerosol index data from the Total Ozone Mapping Spectrometer instrument on the Earth Probe satellite, $k_{dil} = 0.0052$ hr⁻¹. Using TOMS AI will tend to underestimate dilution since data are given as a vertical column. Similar results were found using the HYSPLIT dispersion model, $k_{dil} = 0.0048$ hr⁻¹. The dilution rates from the FABtraj model are 0.011 hr⁻¹ and 0.014 hr⁻¹ for model runs starting at 0000 and 1200 GMT, respectively. Given uncertainties in each method, the dilution rates for all of these give reasonable agreement. Therefore in the following section we use the overall mean k_{dil} value (0.010 ± 0.004) to calculate OH using equation (5).

[41] Our mean dilution rate (0.010) is smaller than that calculated by Dillon *et al.* [2002] ($k_{dil} = 0.2$ hr⁻¹). This is not

surprising, as Dillon *et al.* [2002] considered the dilution rate for a plume transported from the Sacramento urban area into nearby hills under summertime boundary layer flow conditions, while transport for our April 2001 case took place in the free troposphere, where horizontal advective transport dominated over vertical and turbulent mixing.

3.5. Calculation of OH Using Equation (5)

[42] Using equation (5), the OH radical concentration for the 14 April 2001 LRT event (Table 4) was calculated to be 2×10^5 molecules cm⁻³. To calculate this, the overall k_{dil} of 0.010 hr⁻¹ and initial NMHC values (X_i) from ACE-Asia observations of propane and ethyne during outflow conditions to the free troposphere over Asia were used. In comparison, the previous method (equation (2)) gave an OH radical concentration of $1.9 \times 10^5 \pm 0.8 \times 10^5$ molecules cm⁻³.

[43] The two methods used to calculate OH concentration for the 14 April 2001 LRT episode show good agreement. However, there is significant uncertainty in these values. Uncertainty in the calculated OH values stem from a number of variables. These include uncertainties in calculating NMHC rate constants (±15%) [Atkinson, 1997], k_{dil} , NMHC measurements (±10%), transit times determined from backward trajectories and assumptions made in choosing the initial NMHC concentrations. We estimate the uncertainty in timing the transit time from the HYSPLIT backward trajectories to be on the order of half a day, or roughly ±10%. The greatest uncertainty comes from uncertainty in the k_{dil} and assumptions made in choosing initial NMHC concentrations, leading to an estimated total uncertainty of approximately 100 percent. However, since many of these uncertainties impact the calculated OH concentrations equally, the relative uncertainty between the values in Table 1 should be much less.

[44] As shown in Table 1, the 14 April 2001 episode had the lowest OH concentration of all events considered. Combined with the $\Delta O_3/\Delta CO$ and O_3/σ_{sg} ratios, this suggests that heterogeneous chemistry was an important driver of chemical processing during the 14 April 2001 event. The lack of ozone and low OH in this LRT episode is likely due to heterogeneous reactions resulting in the loss of O₃ or precursors on the mineral dust aerosols. This is supported by previous models and field observations showing an anticorrelation between aerosols and O₃ concentrations, which suggests that O₃ loss can occur on aerosols or low O₃ production may occur in the source region due to the presence of mineral aerosols [Dentener *et al.*, 1996; de Reus *et al.*, 2000; Tang *et al.*, 2003; Usher *et al.*, 2003]. For instance, from observations of O₃ and mineral dust aerosols, de Reus *et al.* [2000] used a model to calculate 40 percent depletion of O₃ during a 3-day Saharan mineral dust episode

Table 4. OH Calculated for 14 April 2001 Transport Episode Using a Dilution Factor of 0.01 hr⁻¹ and Initial (X_i) Observations of Asian Outflow From the ACE-Asia 2001 Experiment on 11 April 2001

Species	X	X_i	X_b	[OH]
Propane	462	1190	270	3×10^5
Ethyne	427	1048	232	1×10^5
Mean				2×10^5

in July of 1997. The model's main pathway for O₃ depletion was evenly divided between direct removal of O₃ on dust aerosols and heterogeneous removal of precursor nitrogen species [de Reus *et al.*, 2000]. In contrast, Tang *et al.* [2003] also found aerosols can lead to increases in O₃ precursors such as NO_x and NMHCs, as a result of decreased J-values reducing photochemical loss. Tang *et al.* [2003] used a regional chemical transport model to study the influence of aerosols on photolysis rates (J-values) for the TRACE P experiment. Tang *et al.* [2003] also found that because they are co-emitted with other pollutants, aerosols can reduce photolysis rates, leading to overall reductions in photochemical products such as O₃. Thus for the 14 April 2001 episode, a combination of heterogeneous chemistry (through direct uptake of O₃, OH) and reduced photolysis rates due to the presence of substantial mineral dust are the most likely drivers for the lack of enhanced O₃ and low OH.

4. Summary and Conclusion

[45] In this paper, we described the photochemistry, dilution, and ozone production of 11 transpacific LRT episodes observed during the springtime PHOBEA experiments from 1997–2002. We explored the relationships between O₃, CO, and aerosol scattering in the 11 LRT episodes. We found that the episodes transported in the boundary layer or in the presence of mineral dust lack significant O₃ enhancements, even though O₃ precursors (CO, NMHCs) were elevated. The LRT episodes transported with substantial mineral dust (14 April 2001 and 20 April 2002) have ΔO₃/ΔCO ratios of −0.04 and −0.06, respectively, while the mean ratio of ΔO₃/ΔCO for the 11 LRT episodes shows considerable variability (0.38 ± 0.46) and ranges from −0.06 to 1.52. The relationship between O₃ and aerosol scattering further supports this. Episodes observed with substantial mineral dust (14 April 2001 and 20 April 2002) or at the surface with elevated σ_{sg} from industrial pollutants (27 March 1997) were also elevated in O₃ precursors, CO and NMHCs, but these lacked O₃ enhancements. We also found that a third of the LRT episodes analyzed had O₃ enhancements greater than can be attributed to photochemical production alone. The 6 May 2001 with a ΔO₃/ΔCO ratio of 0.69 is an example of this, where the O₃ enhancement at 1.5–3 km is attributed to a mix of Eurasian-anthropogenic and upper tropospheric O₃ sources.

[46] Using observations of hydrocarbons taken during these and other experiments conducted in the North Pacific, including the 1994 PEM-West B, 2001 Trace P, and the 2001 ACE-Asia experiments, we estimated an average OH concentration of $7.1 \times 10^5 \pm 3.0 \times 10^5$ molecules cm^{−3} for the 11 LRT episodes. Focusing on the April 2001 LRT episode, we described two methods for determining dilution rates, k_{dil} . One method used observations of long-lived tracers, such as CO, ethane, or aerosols under dry transport conditions ($k_{dil} = 0.011 \pm 0.002$ hr^{−1}), and the other used NOAA meteorological models ($k_{dil} = 0.010 \pm 0.005$ hr^{−1}). Using the overall average $k_{dil} = 0.010 \pm 0.004$ hr^{−1}, we estimate an OH concentration of 2×10^5 molecules·cm^{−3} for the April 2001 LRT episode. This compares to OH calculated using equation (2), which gives $1.9 \times 10^5 \pm 0.8 \times 10^5$ molecules cm^{−3}.

[47] The 14 April 2001 mineral dust and pollution event had the lowest calculated OH concentration of the 11 LRT events analyzed. The results of the calculated OH concentrations and the ΔO₃/ΔCO and O₃/σ_{sg} ratios suggest that heterogeneous chemistry was an important driver in the lack of O₃ enhancement in this LRT event. The OH concentration calculated using equation (2) is the lowest OH value of all the LRT events. Additionally, the O₃/CO and O₃/σ_{sg} ratios for this event show a lack of O₃ enhancement compared to the other events that contained biomass burning and/or industrial pollution.

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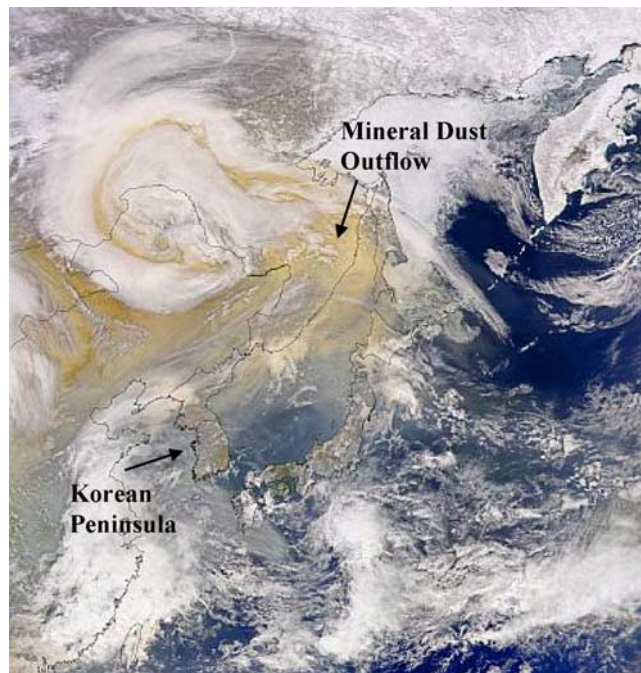


Figure 4. SeaWiFS image of mineral dust outflow from Asia on 8 April 2001. Image provided by the SeaWiFS Project, NASA Goddard Space Flight Center, and ORBIMAGE.

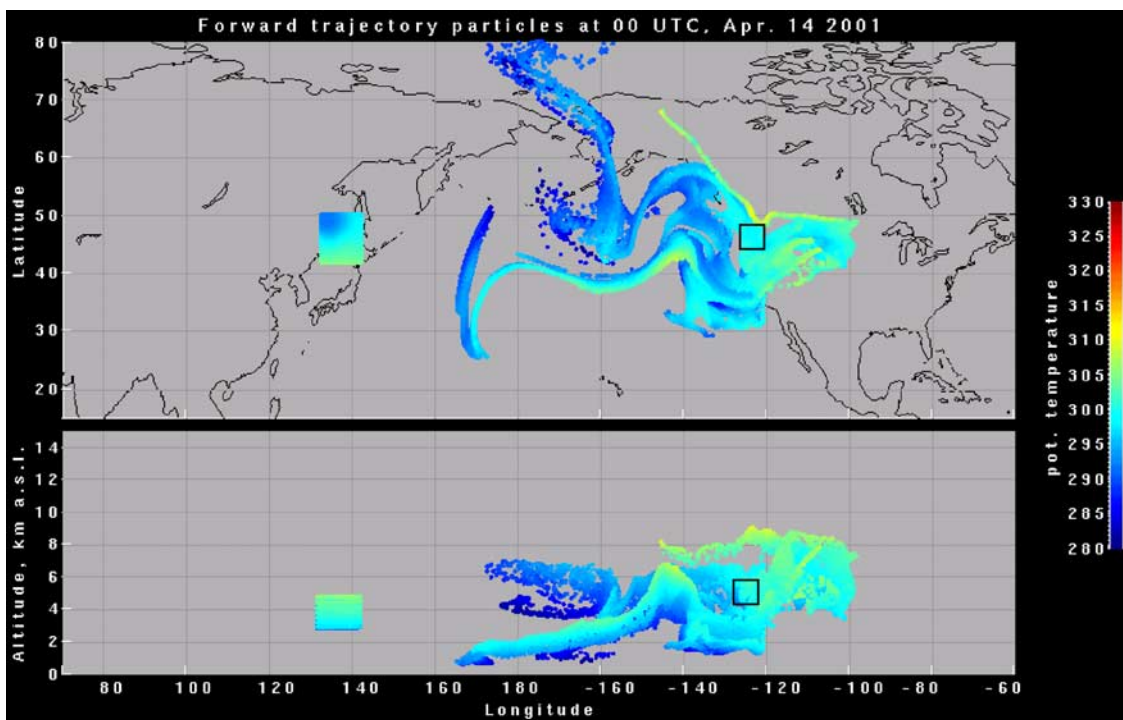


Figure 5. Initial and final FABtraj model results for particle forward trajectories during the April 2001 dust and pollution LRT episode. The box over northwest Japan represents the initial particle release on 8 April.