

Observations of ozone and related species in the northeast Pacific during the PHOBEA campaigns

1. Ground-based observations at Cheeka Peak

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Abstract. As part of the Photochemical Ozone Budget of the Eastern North Pacific Atmosphere (PHOBEA) project, we made observations of CO, O₃, NO_x, peroxyacetyl nitrate (PAN), nonmethane hydrocarbons (NMHC), Rn, aerosol scattering, aerosol absorption, and aerosol number density during the springs of 1997 and 1998 at the Cheeka Peak Observatory (CPO) on the western tip of Washington State. The data have been segregated to quantify the mixing ratio of these species in the Pacific marine atmosphere. However, even in these marine air masses, there are occasionally substantial enhancements of NO_x and aerosols, but not CO, which we attribute to diesel exhaust from ship traffic to and from major ports in the region. The marine air masses were further classified into four categories based on 10-day back isentropic trajectories; high, mid, and low latitude and those which had crossed over the Asian industrial region. Mean marine mixing ratios in 1998 were significantly higher than the 1997 values for CO (1997 mean equal to 151, 1998 mean equal to 170 ppbv), ethane (1771, 1968 parts per trillion by volume (pptv)), and ethyne (306, 452 pptv). Also, segregation of the 1998 data by air mass origin produced smaller differences in the mixing ratios for most species when comparing different source regions. We attribute both of these results to elevated emissions associated with unusually large areas of biomass burning which took place in Indonesia and Siberia during late 1997 and 1998. The relative enhancements of CO, ethane, ethyne, and propane we observed at CPO are consistent with enhanced biomass burning and industrial sources in the spring of 1998, relative to the spring of 1997.

1. Introduction

Ozone plays a key role in tropospheric chemistry. It is the primary source for the OH radical which is the most important oxidant in the troposphere. It is also a greenhouse gas and has toxic and phytotoxic effects at levels not far above ambient. Tropospheric ozone has two major sources: stratospheric intrusions and photochemical production [Crutzen, 1988]. The relative contributions of these two sources remains an open question. Photochemical ozone production in the troposphere requires nitrogen oxides, hydrocarbons, and light. In most regions of the troposphere the limiting precursor for ozone production is NO_x (NO + NO₂). As a result of anthropogenic emissions of NO_x, tropospheric ozone has substantially increased over preindustrial

values [Volz and Kley, 1988]. Ozone mixing ratios are continuing to increase in some regions of the world, most notably East Asia [Logan, 1994; Lee *et al.*, 1998], due to the continued rapid increase of NO_x emissions (~4%/yr) from East Asia [Akimoto and Narita, 1994; Streets and Waldhoff, 2000].

In situ ozone production requires NO mixing ratios of at least 10-20 parts per trillion by volume (pptv) [Fehsenfeld and Liu, 1993]. The short lifetime of NO_x (of the order of 1 day or less) means that most O₃ production will take place relatively close to NO_x sources. Over the remote oceans the lack of direct sources results in ozone production rates that are nearly in balance between sources and sinks, or negative (sinks larger than sources) [e.g., Ridley *et al.*, 1992].

Because both peroxyacetyl nitrate (PAN) and tropospheric O₃ are known to have a spring maximum at

clean Northern Hemisphere (NH) sites [Oltmans and Levy, 1994], Penkett and Brice [1986] have suggested that PAN plays a key role in explaining the spring O_3 maximum. Moxim *et al.* [1996] summarize a mechanism in which the thermally unstable PAN can provide a source for NO_x following air mass warming due to subsidence. In this mechanism, NO_x forms PAN at the source regions [Singh and Hanst, 1981] and is then transported to the free troposphere where it is relatively stable. When an air mass containing enhanced PAN warms, as during subsidence, the PAN decomposes and releases NO_x . According to the modeling results of Moxim *et al.* this is the primary source of NO_x in the lower troposphere over the remote oceans. However, several researchers have recently suggested that direct NO_x emissions from ships may be a substantial NO_x source to the global marine boundary layer [Lawrence and Crutzen, 1999; Corbett *et al.*, 1999].

At remote sites, spring is also the season when the highest mixing ratios are observed for a number of other species including CO and nonmethane hydrocarbons (NMHC) [Blake and Rowland, 1986; Novelli *et al.*, 1992; Jaffe *et al.*, 1997]. This results from reduced CO loss by reaction with OH in the winter, but is also due, in part, to more rapid transport from source regions [e.g., Duce *et al.*, 1980; Merrill *et al.*, 1989; Prospero and Savoie, 1989; Jaffe *et al.*, 1999].

In the western North Pacific region the NASA Pacific Exploratory Mission-West (PEM-West) campaigns have made comprehensive observations of O_3 and related species. The PEM-West campaigns took place during the fall of 1991 and the early spring of 1994 [Hoell *et al.*, 1997] in the region immediately to the east of the Asian continent. During spring, substantial outflow of anthropogenic emissions was observed [e.g., Talbot *et al.*, 1997].

Previously, we have shown that anthropogenic emissions from East Asia can be transported to Washington State during spring in as little as 5 days [Jaffe *et al.*, 1999]. This conclusion was based on our measurements of CO, PAN, NMHCs, aerosol scattering, and aerosol absorption during the spring of 1997 at Cheeka Peak, a coastal site on the northwest tip of Washington State. The impact from Asian emissions on the O_3 mixing ratio in air arriving to North America has also been considered in two recent modeling studies [Berntsen *et al.*, 1999; Jacob *et al.*, 1999].

In this paper we examine the Cheeka Peak data from the springs of both of 1997 and 1998 to identify the sources, patterns, and relationships among the measured species. In a separate paper we present the aircraft data taken in the same region during the spring of 1999 [Kotchenruther *et al.*, this issue], and in a future paper we will present the results of an analysis of the NO_x and O_3 photochemistry for the northeastern Pacific.

2. Experiment

We conducted measurements in two successive spring campaigns, March-April 1997 and 1998, at the Cheeka Peak Observatory (CPO) in Washington State (48.3°N, 124.6°W, 480 m above sea level (asl)). This site is located on the northwestern tip of the Olympic

Peninsula immediately adjacent to the Pacific Ocean (see Figure 1). During westerly flow the air masses that arrive at the site are generally unaffected by recent North American emissions and are characteristic of the North Pacific atmosphere [Anderson *et al.*, 1999]. Easterly winds bring air from the more polluted continental boundary layer. The CPO site has been used for atmospheric chemistry and aerosol research for approximately 15 years [Anderson *et al.*, 1999, and references therein]. During these two campaigns we measured O_3 , NO_x , PAN, CO, $J(NO_2)$, NMHCs, radon, aerosol number density, aerosol absorption, and aerosol light scattering, along with meteorological parameters.

Back isentropic trajectories [Harris *et al.*, 1992] were calculated twice each day (0000 and 1200 UTC) for the period of the two campaigns, using data from the European Centre for Medium-Range Weather Forecasts (ECMWF). While our previous work with isentropic trajectories has given us much useful information regarding transport to CPO [e.g., Jaffe *et al.*, 1999] it should be kept in mind that there are a number of possible sources of error associated with isentropic trajectories, including low-resolution meteorological data, nonisentropic transport, and/or subgrid-scale vertical motions. Possible trajectory errors have been discussed in several recent publications [e.g., Kahl, 1996; Stohl, 1998].

For the NO_x measurements we used a Teflon (PFA) inlet line (approximately 10-m length, 3.1 mm ID). A separate line was used for each of the NO chemiluminescence detectors (see below). A third sampling inlet line was shared for the CO, O_3 , and PAN measurements. The lines were affixed to the top of a 10-m sampling tower. While the station height (480 m) does reduce sea-salt concentrations considerably, there is still a significant sea-salt component to the aerosol [Anderson *et al.*, 1999]. To minimize the admission of sea-salt into the instruments for CO, O_3 , PAN, and NO_x instruments, we added a 2 μ m Teflon filter to each inlet, effectively eliminating all particles down to sub-micron sizes.

For NO_x we used a high-sensitivity chemiluminescence instrument built in our laboratory and previously described by Beine *et al.* [1997]. NO was detected directly. NO_2 was detected as NO following UV photolysis. One instrument cycled between NO and NO_2 modes. In addition, during the 1997 campaign we used a second high-sensitivity NO instrument. This allowed us to conduct an informal intercomparison of our NO results.

Because our NO_x measurement techniques have been described previously [Beine *et al.*, 1997], only an overview is given here. The flow through the reaction chamber was set to 1 standard liter per minute (sLpm). The NO chemiluminescence detector was automatically calibrated once every 3 hours, except for the first part of the 1997 campaign (March 9 to March 21), when it was calibrated once every 6 hours. For calibration we used a flow of 5 $cm^3 min^{-1}$ STP of 3.00 ppmv NO in N_2 (Scott-Marrin, Inc. 3.00 ± 0.06 ppmv NO) as a standard addition to the ambient flow. After the campaign, the calibration gas was cross-calibrated against a National Institute of Standards and Technology (NIST) standard (NO in N_2 , 4.73 ± 0.07 ppmv), which led to a correction

of the Scott-Marrin standard mixing ratio to 3.21 ± 0.09 ppmv NO. The median NO sensitivities for the 1997 and 1998 campaigns were 4.23 and 3.84 counts per second (cps)/pptv NO, respectively. The 3σ detection limits for NO for the 1-minute averages for 1997 and 1998 were 5.37 pptv and 6.09 pptv, respectively, and 1.79 pptv and 2.03 pptv in the hourly averages (9 one-minute measurements of NO and NO₂ per hour). The median NO₂ sensitivity for the whole campaign was 1.21 cps/pptv NO₂ and 1.19 cps/pptv NO₂ for 1997 and 1998, respectively. The 3σ NO₂ detection limits for the one-minute averages were 18.76 pptv NO₂ and 19.49 pptv for 1997 and 1998, respectively, and 6.25 pptv and 6.50 pptv for the hourly averages in 1997 and 1998, respectively. The overall uncertainties for NO and NO₂ were 10% and 25%, respectively, at levels well above their detection limits.

During the 1997 campaign a second NO instrument (called "NO-II") was used to provide NO_y calibrations for the PAN instrument and to provide an additional quality control and intercomparison with the primary NO_x instrument. This NO instrument was very similar to the primary NO chemiluminescence detector and shared calibration gas with the primary instrument. The second instrument spent most of its time measuring ambient NO; it was switched manually to NO_y mode only for calibrations. Thus, for most of the 1997 campaign, we have duplicate NO measurements. We compared the hourly averaged NO mixing ratios at all times where each instrument reported data and found a slope of 0.983 (for NO-II response divided by the primary NO response) with an *R*-squared value of 0.978, *N*=1032 for the full data set. Because each instrument ran on separate measure-zero cycles, which were not synchronized, there are some differences at high levels when there was more ambient variability. Comparing only the data below 75 pptv, we get a mean, median, and root mean square difference (NO primary minus NO-II) of -4, -4, and 6 pptv, with a *R*² for the regression of 0.91. The difference at low levels is mostly due to a positive offset in the NO-II instrument, which is apparent from the nighttime NO data. The data used in this paper are from the primary NO instrument which exhibited no nighttime offset.

CO was measured with a commercial nondispersive infrared absorbance instrument (API-300, Advanced Pollution Instruments, San Diego, California) modified to reduce water vapor interference and improve detection limits [Jaffe *et al.*, 1998]. Water vapor was removed from the sample stream with a nafion gas dryer in reflux mode. In this configuration the 3σ CO detection limit was 42 ppbv for a 20 minute average. The overall uncertainty in the hourly averages is 6% at a mixing ratio of 150 ppbv. Previously CO measurements made with this instrument were intercompared against observations by the NOAA-CMDL group at a remote site [Jaffe *et al.*, 1998]. The two measurements had a mean absolute difference of 3.1%. Ozone was recorded with a commercial ultraviolet absorption instrument (Dasibi 1008 RS). The instrument was calibrated before and after the campaign using a standard ozone calibrator (Columbia Scientific Inc.), and the total uncertainty is approximately 2%.

PAN measurements were made using a gas chromatograph with electron capture detector (GC-ECD, Hewlett-Packard 5890). The 30 m (0.53 mm ID) megabore capillary column (J&W DB-210) was kept at 35°C, and the ECD was kept at 50°C. The carrier and makeup gas were 5% CH₄ in Ar flowing at 15 mL/min through the column and 35 mL/min through the ECD. Samples (1 mL) were injected every 15 min. Calibrations were performed approximately every other week using a PAN standard which was generated by dynamic dilution using a diffusion tube containing PAN in tridecane [Gaffney *et al.*, 1984]. In the 1997 campaign the dynamic PAN standard was quantified as NO following reduction by CO in a 350°C catalytic gold converter [Bollinger *et al.*, 1983]. Thus the PAN measurements were referenced to the same NIST traceable standard as was used for the NO measurements. During the 1998 campaign the PAN calibrations were made with a commercial PAN calibrator. The commercial calibrator (Meteorologie Consult GmbH, Glashütten, Germany) generates known mixing ratios of PAN from the photolysis of acetone in the presence of NO and O₂. Since the conversion is nearly quantitative, the PAN mixing ratio can be directly related to the NO mixing ratio. For this test the NO calibration gas was the same as that used for the NO instrument, and a PAN conversion efficiency of 100% was assumed for the commercial calibrator. The PAN detection limit was 6 pptv, and the uncertainty of the measurements was 18%.

The photolysis rate of NO₂ was measured using a spherically integrating radiometer (Meteorologie Consult GmbH, Glashütten, Germany) based on the design of Junkermann *et al.* [1989]. The sensor measures the actinic flux (4π) in the 300-400 nm band using two filtered radiometers, one for downwelling and one for upwelling radiation. The instrument is calibrated by the manufacturer annually with a chemical actinometer at the Forschungszentrum-Jülich, Germany. The sensor was installed at the top of a 12 m tower to minimize shadow effects. This is the same instrument that was used in our previous studies [e.g., Beine *et al.*, 1997]. The uncertainty is given by the manufacturer as 8%, considering both cloud and zenith angle effects [Volz-Thomas *et al.*, 1996; Beine *et al.*, 1999].

The aerosol instrumentation is described in detail by Anderson *et al.* [1999], so only a brief summary is given here. The aerosol instruments sampled the air through a vertical duct 40 cm in diameter from the top of the 10 m tower. The nature of the aerosol inlet results in a size cut that varies with wind speed. At wind speeds up to 10 m/s, encompassing 90% of our observations, the aerosol inlet collects particles with diameters of at least 5 μ m. A condensation particle counter (CPC) was used to measure particle number density for particles with a diameter greater than 10 nm. We used an integrating nephelometer (model 3563, TSI Inc., St. Paul, Minnesota) to measure total light scatter and backscatter at three wavelengths. Light absorption was measured using absorption photometers (model PSAP, Radiance Research, Seattle, Washington) that are calibrated to a wavelength of 550 nm [Bond *et al.*, 1999]. For both the nephelometer and the PSAP instruments a valve switched sequentially between coarse ($d < 10 \mu$ m) and

fine ($d < 1 \mu\text{m}$) mode aerosol. In this paper we will use only the fine mode data for total scattering (σ_{sp}) and absorption (σ_{ap}), both at 550 nm. During both the 1997 and 1998 campaigns, three different PSAP instruments were compared. The agreement between the three instruments was within 4%, averaged over the entire campaign. The total uncertainty for σ_{sp} and σ_{ap} depends on the air mass. In marine air the uncertainty averaged 14% and 56%, respectively, but the relative precision is much better at 7% and 33% [Anderson *et al.*, 1999]. Note that since we are only interested in relative changes, the aerosol scattering and absorption coefficients reported in this paper have not been corrected for a number of instrumental effects as described by Anderson *et al.* [1999].

Whole air samples were collected in stainless steel canisters for GC-flame ionization detection analysis of nonmethane hydrocarbons (NMHCs) [Blake *et al.*, 1994, 1999]. Radon gas (Rn), which is a useful continental tracer owing to its 3.8 day half-life and exclusively continental sources, was monitored by detection of radon daughter products captured on a filter [Whittlestone *et al.*, 1996].

3. Results

Measurements were made from March 9 to April 29, 1997 (day of year (DOY) 68-119), and March 1 to April 30, 1998 (DOY 60-120). Table 1 shows results for the two campaigns.

A plot of these data versus wind direction (not shown) indicates that the highest values for nearly all parameters arrive at the site with easterly winds. This comes as no surprise given the high density of emissions from the busy Vancouver-Seattle-Tacoma corridor. Because the focus of this work is on the atmospheric chemistry of the North Pacific environment, we segregated the data conservatively to consider only periods when we were fairly certain that recent emissions from North America had not impacted our observations. In this paper we will use the term “marine” to refer to air masses which have not crossed over or been influenced by North American emissions within at least the past 3 days, and “continental” to refer to the portion of the data for which a North American influence is likely. Note that marine air masses can still contain continental and/or anthropogenically emitted compounds resulting from long-range transport [e.g., Jaffe *et al.*, 1999].

To separate marine and continental air masses, we used the wind direction, the wind speed, and the 10-day back trajectories. We classified as marine, periods with (1) wind directions between 150° and 300° , (2) wind speeds greater than 2 m/s, and (3) trajectories which had no land contact for at least 3 days prior to reaching the station. For 1997, 814 out of 1451 hours were classified as marine (56%), and for 1998, 566 out of 1432 hours were classified as marine (40%). Table 2 shows the data for periods classified as marine. NMHC mixing ratios for marine flow (as defined above) are given in Tables 3a and 3b. Figure 2a shows a time series of the 1998 marine data for CO, O₃, and PAN, and Figure 2b shows the marine data for C₂H₆, C₂H₂, C₃H₈, and n-C₄H₁₀.

For most species the marine classification generates a data set which is comparable to other marine Northern Hemispheric sites and consistent with the observed latitude gradients in the Pacific. For example, springtime CO values at Mauna Loa average 100-120 ppbv, whereas at high-latitude sites, such as Shemya and Barrow, Alaska spring mixing ratios typically average 180-200 ppbv [Novelli *et al.*, 1992; Jaffe *et al.*, 1997]. Compared to these values, the CPO spring averages of 151 ppbv from 1997 and 170 ppbv for 1998 seem reasonable.

However, for NO_x our values seem somewhat high, compared to other remote sites. For example, the median NO_x mixing ratio in continental outflow from Asia was 120 pptv, as observed during the PEM-West campaigns in the spring of 1994 [Kondo *et al.*, 1997]. Thus the CPO median of 108 pptv for the 1997 observations seems somewhat high, considering that our marine data set should not have been influenced by continental sources for at least 3 days.

Examining a histogram of the NO_x data (not shown), it is clear that the high average NO_x mixing ratio is caused by a relatively small number of points. To explore the cause for these high values, we segregated the marine data into high and low NO_x periods, as shown in Table 4. When NO_x mixing ratios are high, other species, especially CPC, σ_{ap} , and σ_{sp} , are also elevated. Mixing ratios for O₃, CO, and PAN (at least in 1997) are nearly unaffected during these high-NO_x periods.

An example of a 10-day period with several spikes in NO_x and CPC during marine periods is shown in Figure 3. It is important to reiterate that these data have already been selected for “marine” classification based on wind direction, speed, and back trajectories. During the periods with high NO_x mixing ratios the average wind direction remains nearly due west, in the middle of the marine sector (150° - 300°). For the elevated periods in 1997 at DOY 81.9, 82.9, and 85.4 (shown in Figure 3), winds were steadily from the west or southwest in each case.

The average NO_x mixing ratios during the 1997 measurement period were significantly larger than those measured during the 1998 campaign. This is mostly because there were 46 hours with NO_x mixing ratios greater than 500 pptv during the 1997 measurements, but only 17 during the 1998 campaign. However, these 17 hours brought much higher particle counts and aerosol absorption, as compared to the high-NO_x periods in 1997. Presumably, this reflects differences in the sources being sampled at these times.

There are several possible explanations for these relatively high NO_x and CPC values. First, it is possible that complex meteorological patterns could bring air masses back to the station from North America. However, based on our screening criteria, these would have had to have been transported over the Pacific for at least 3 days, and this seems an unlikely explanation given the short lifetime for NO_x and particle number density.

That these elevated periods are not due to recirculated North American emissions is shown by the absence of a CO enhancement in these air masses. For example, we can calculate the CO enhancement

expected if these periods were due to recirculated regional sources. This can be done using the CO/NO_x relationship in the full CPO data set which has a CO/NO_x slope of 19 ($R^2=0.49$). The relationship is dominated by high-pollution events when winds are blowing from the Puget Sound region to CPO. Presumably, this reflects the average ratio of anthropogenic emissions in the region, modified by processing enroute to Cheeka Peak. Using this ratio, we would expect that a 1 ppbv enhancement in NO_x would generate a 19 ppbv enhancement in CO, which would be readily detectable. That there is essentially no enhancement in CO during the elevated NO_x periods argues that the source characteristics have a much higher NO_x/CO ratio than typical urban pollution as seen at Cheeka Peak.

A second possibility is that we are seeing the effect of local emissions. While Cheeka Peak Observatory is located in one of the most remote parts of the continental United States, there are a small number of nearby sources in the marine wind sector. These include a very small number of houses (fewer than five) and a dirt road to the west, which provides access to Shishi beach. While these sources are very nearly at sea level, and the station is at 480 m, it is nonetheless possible that these small sources could occasionally contribute to our elevated mixing ratios. However, looking at Figure 3, we see that these periods with elevated NO_x typically last for several hours and show the characteristics of medium-range transport (tens of kilometers), rather than local sources, which tend to be much spikier.

A third possibility is that emissions from ships in the near shore region account for the elevated NO_x and aerosols. This seems a strong possibility given the high density of ship traffic in the region, which is traveling to and from the numerous major ports in the Vancouver, British Columbia/Seattle region and the fact that ships are a substantial source of NO_x [Lawrence and Crutzen, 1999; Corbett *et al.*, 1999]. The Washington State Department of Ecology collects data on cargo, large passenger, and tanker traffic in the region. On the basis of the 1999 data (Washington Department of Ecology, unpublished report, 1999) there were 4992 one-way transits of large vessels through the Strait of Juan de Fuca (see Figure 1). This includes cargo ships and passenger vessels of 300 tons gross weight or larger, and tankers of any size. Transits for 1997 and 1998 were within 10% of the 1999 numbers. Presumably, most of these ships would have also departed via the Strait of Juan de Fuca, so the total number of transits through the Strait is approximately double this number. Once a ship reaches the western end of the Strait of Juan de Fuca, it arrives at the open ocean and will change course for its final destination. Many of these ships will pass directly west of CPO (see Figure 1).

While this explanation seems plausible, we must ask why other gaseous species do not show enhancements from ship emissions. The answer to this is a result of several factors: (1) the high concentration of NO_x and particles in diesel exhaust; and (2) the short lifetime for both NO_x and particles, which gives rise to very low background concentrations. To examine this hypothesis, we can estimate the impact on CO and NO_x

from a diesel plume emitted off the Pacific coast, a few kilometers from the station. To do this, we use a molar emissions ratio for NO_x/CO of 1.8, as reported by the U.S. Environmental Protection Agency (EPA) for marine vessels in U.S. waters [U.S. EPA, 1996]. These emissions are dominated by diesel exhaust. Then, assuming a ship plume reaches CPO with 1 ppbv of NO_x, this plume would enhance CO by 0.56 ppbv. While the NO_x enhancement from this plume would be huge compared to a background value in the 50-100 pptv range, the CO enhancement would be insignificant compared to its background value of 150 ppbv. It is possible that NMHC observations would also show a signature of ship exhaust, but in searching through our data of discrete canister samples, we do not find any that coincide with periods of high NO_x and CPC.

Thus we believe that ship exhaust is the most likely cause for most of these periods based on the following: (1) the steady westerly winds during these high NO_x periods; (2) the absence of other significant nearby sources in the marine wind sector; (3) the substantial amount of ship traffic traveling through the Strait of Juan de Fuca to and from the Puget Sound; and (4) the presence of elevated NO_x and aerosols, but not CO, during these periods which is consistent with emissions from diesel exhaust and inconsistent with the CO/NO_x ratio from urban emissions.

It is important to recognize that the existence of nearby emissions from ship traffic does not change our previous conclusions on the role of long-range transport from Asia on air masses arriving at CPO [Jaffe *et al.*, 1999]. This is because ship emissions have a significant influence on only NO_x and CPC at CPO, whereas long-range transport from Asia was identified based on the levels of CO, PAN, Rn, aerosol absorption, aerosol scattering, and numerous NMHCs [Jaffe *et al.*, 1999]. None of the air masses we previously identified as coming from Asia had elevated NO_x or CPC. However, this does point out the complexity of identifying local versus distant sources and the importance of having both short-lived species (e.g., NO_x and CPC) as well as longer-lived tracers.

However, in the 1998 data, there is one period of marine air (DOY 111.0) with elevated NO_x, CO, O₃, PAN, Rn, CPC, σ_{sp} , and σ_{ap} (12 hour means of 500 pptv, 192 ppbv, 47 ppbv, 278 pptv, 1088 mbq/m³, 5563 cm⁻³, 7.0 Mm⁻¹, and 1.5 Mm⁻¹, respectively). This one event explains why these species were elevated in the 1998 "high NO_x" cases shown in Table 4. This period had back trajectories which originated from the Sea of Okhotsk and northeastern Asia, very near to regions where significant biomass burning was occurring at the time (see discussion below). However, it is difficult to reconcile the trajectories, which take at least 5-7 days to cross the Pacific, with elevated NO_x and CPC, unless the emissions were extremely high. Unfortunately, we do not have NMHC data for this event, so it is difficult to be more specific on the nature of the source or sources for this event.

3.1. Comparison With Other Observations in the Northeastern Pacific

In a companion paper, Kotchenruther *et al.* [this issue] describe the vertical profiles made in the spring of

1999 off the coast of Washington State using the Wyoming King Air. Because flights were only conducted during strong westerly flow conditions, very little evidence of North American pollution was observed. Thus it is reasonable to compare the aircraft data from the 0-2 km layer with the Cheeka Peak marine data, keeping in mind that these data were collected during different years. These data are shown in Table 5. To make the comparison more meaningful, the NO data from CPO are shown for the hours of 1800-2400 UTC (1000-1600 PST), which is when the bulk of the aircraft data were collected.

From this comparison a few points can be made. First, the King Air data in the 0-2 km column during spring show reasonable agreement with the 1997 CPO data for CO, ethane, and propane, as well as other NMHCs not shown. A few differences should be noted. O₃ is higher for the 0-2 km layer than at CPO (480 m asl) which likely reflects that some of the 0-2 km layer data includes air from above the marine boundary layer. NO and σ_{sp} are higher at CPO. The higher NO probably reflects a greater influence of ship emissions at CPO, and higher σ_{sp} probably results from higher concentrations of sea salt and ship emissions.

3.2. Segregation by Trajectory Source Region

To help identify the role that latitudinal gradients and transport play at CPO, the marine data set was segregated based on the 10 day back isentropic trajectories. Our goal was to quantify the mixing ratio of each species segregated by trajectory type. Four trajectory classifications were used, those arriving from (1) midlatitudes; (2) high latitudes; (3) lowlatitudes, or (4) the Asian continent. In our previous work [Jaffe *et al.*, 1999], only two classifications were used; Asian trajectories and non-Asian trajectories.

To categorize each trajectory, we first considered whether the 10 day transport crossed over the Asian continent (defined by the box from 0°-50°N and 100°-150°E). Those trajectories which crossed over the Asian industrial region were classified as "Asian." Following this step, we classified each trajectory based on whether the point 5 days backward in time was located in the low-, mid, or high-latitude region, defined by the latitude lines at 35°N and 55°N. It should be apparent that both the midlatitude and Asian trajectories are arriving from the same direction, the only difference is the overall speed.

Trajectories were available for 0000 and 1200 UTC each day. We generated a 12 hour average from the hourly marine data centered on the trajectory time (+/-6 hours), provided there were at least three valid points in the average. Each 12 hour average was then paired with a trajectory type. Using the 12 hour averages has the added advantage of eliminating autocorrelation in the data and thus simplifies the statistical analysis, compared to using the hourly data. Results of this analysis are presented in Table 6 for the 1997 and 1998 data. Note that we have omitted the NMHCs in Table 6 because there are too few samples.

Interpretation of the 1997 results is fairly straightforward. The trajectory segregation shows the impact of long-range transport from Asia and the latitudinal gradients for several species, for example,

PAN and CO. For PAN the lower mixing ratios in lower-latitude air masses is particularly apparent, a result of the higher temperatures all along the transport path. Low-latitude trajectories arrive at CPO about 2°C warmer, on average, than the midlatitude trajectories. Comparing the periods of midlatitude trajectories with periods of Asian trajectories, we find that there are statistically significant differences ($P > 95\%$) for CO, PAN, Rn, aerosol scattering, and aerosol absorption. These results are essentially the same as we have previously reported [Jaffe *et al.*, 1999]. Comparing the periods with low-latitude versus midlatitude trajectories, we find statistically significant differences ($P > 95\%$) for Rn, O₃, PAN, aerosol scattering, and absorption. For CO the low-latitude cases are significantly different from the mid-latitude cases at the 86% confidence level. For the high-latitude cases, aerosol scattering and absorption are significantly lower than the midlatitude cases, but at somewhat lower confidence levels $P = 94$ and 89%, respectively. Our interpretation of these results is that, in general, lower latitudes bring lower mixing ratios of most continentally emitted species, compared to the midlatitude trajectories. The high-latitude trajectories arrive with generally lower amounts of aerosol scattering and absorption and similar amounts of CO, Rn, and PAN. Although, the Asian trajectories have the highest concentrations of all species (except O₃), the impact of Asian sources is certainly seen in the "midlatitude" trajectories as well.

For 1998 a somewhat different pattern emerges. Only PAN shows a statistically different mixing ratio during the period with Asian trajectories (higher PAN) and low-latitude trajectories (lower PAN), compared to the midlatitude cases. However, the statistical significance is lower, 89% in both cases. This observation seems to indicate that during the spring of 1998, the latitudinal gradients were substantially reduced or eliminated. Also during 1998, O₃ was elevated in the Asian and low-latitude cases, compared to the midlatitude cases ($P = 82$ and 86%, respectively). These observations, along with the fact that several species were significantly elevated compared to 1997, suggests that the spring of 1998 was significantly different from the spring of 1997.

3.3. Interspecies Correlations

Correlations between measured species can give information on the similarity of sources and/or sinks. Table 7a shows the correlation coefficient R , using the hourly averages for those relationships with an R value greater than 0.35. For the relationships shown, there are between 300-700 hourly data pairs. Considering the autocorrelation in the hourly averages, significant up to a time lag of approximately 10 hours, this results in 30-70 degrees of freedom for each correlation. Thus an R value equal or greater than 0.35 corresponds to a significant correlation at a probability of 95% or higher. Table 7b shows the correlation coefficients for NMHC species and CO. For the NMHC comparison we used a 3 hour average CO concentration to reduce instrumental noise in the hourly CO data. Because there are insufficient samples from 1997, the NMHC correlations are only calculated from the 1998 marine data set.

There are a number of patterns which are brought out by this analysis. In general, a number of these species including PAN, CO, Rn, σ_{sp} , and σ_{ap} were significantly correlated in both the 1997 and 1998 data. O_3 was weakly correlated with CO in the 1997 data set ($R=0.28$), although this is significant with a confidence of 98%; however, CO and O_3 were uncorrelated in the 1997 data set. Most likely this reflects the multitude of sources responsible for tropospheric O_3 . In contrast, at sites in the northeastern corner of North America, downwind, and much closer to large continental sources, Parrish *et al.* [1993, 1998] have observed a strong correlation between CO and O_3 during summer outflow. Under these conditions the bulk of the observed O_3 is probably due to photochemical production associated with North American NO_x emissions. At more remote sites a CO- O_3 relationship is not generally found [e.g., Jaffe *et al.*, 1998]. That the CO-PAN correlation was significant in both years and that PAN is generally correlated with aerosols implies that industrial emissions are the dominant source for both species.

3.4. Comparison Between the 1997 and 1998 Observations

For a remote observation site such as CPO we expect that a variety of natural and anthropogenic sources contribute to the observed mixing ratios. However, these sources, and the transport are not necessarily constant from year to year. To examine these variations, we conducted a statistical comparison of the 1997 and 1998 data sets. In doing this comparison it is necessary to consider that the hourly averaged data has a significant autocorrelation associated with it. While there are several ways to take this into account, the most straightforward method is to use the 12 hour averaged data set, described above, which has no autocorrelation. Species with significant differences are shown in Table 8.

Robust differences are seen for CO, ethane, and acetylene. For O_3 the difference between the 2 years, approximately 2%, is nearly the same as our total uncertainty in the measurements; thus this difference should be treated with more caution. For the NMHC species the differences are large enough to be greater than the measurement uncertainty; however, some care should be taken in interpreting these since there were not a large number of samples taken during 1997 and the samples were not uniformly spaced through the 2 month period.

3.5. Impacts of Biomass Burning on the North Pacific Atmosphere?

The fall-winter of 1997-1998 brought significant drought conditions to large parts of Southeast, eastern and northern Asia, associated with one of the strongest El Niño events on record. While this El Niño does not seem to have had a significant impact on temperatures or trajectories types at CPO, weather patterns in many parts of the world were impacted. Associated with this El Niño was substantial biomass burning in Southeast Asia that took place in 1997 and 1998 [World Meteorological Organization (WMO), 1998; Tsutsumi *et al.*, 1999; Matsueda *et al.*, 1999; Levine *et al.*, 1998; Levine, 1999]. The burning took place mainly during

two time periods, September through November 1997 and again in February and March 1998, with a total burned area of approximately 45,000 km². Data given by Levine *et al.* [1998] indicate that about 1/3 of the total area burned in Indonesia and Sumatra during this period was burned in February and March 1998. Levine [1999] estimates the CO emissions at 16-49 million tons of carbon for the fires that burned in Kalimantan and Sumatra, Indonesia, with a best guess value of 32 million metric tons of carbon. This can be compared with global emissions from all sources of about 1000 million metric tons per year (as C) [Khalil *et al.*, 1999]. Assuming that 1/3 of the Kalimantan and Sumatra CO was emitted during February and March 1998, then these fires emitted about 6% of the global CO emissions during these months. Levine *et al.* [1998] state that these emissions should be considered lower limits because fires in other parts of Southeast Asia were not included. Substantially elevated mixing ratios of many species have been reported both within Southeast Asia [e.g., Tsutsumi *et al.*, 1999; Matsueda *et al.*, 1999; Burrows *et al.*, 1999; Hauglustaine *et al.*, 1999] and at Mauna Loa [Rinsland *et al.*, 1999].

During March 1998, large fires also began in the area near northern Vietnam. These fires produced large amounts of CO and other trace species and are believed to have had a widespread influence on trace species throughout the North Pacific (G. Carmichael, personal communications, March 2000). Although an emission inventory for these fires is not yet available, the CO output from the northern Indochina fires may be at least as large as the Indonesian fires.

Additionally, between April and September 1998, substantial biomass burning also occurred in Mongolia and far eastern Russia. The fires started in the region surrounding Lake Baikal (approximately centered on 110°E x 55°N) during April and May and subsequently moved eastward, so that in the period July-October they were concentrated in far eastern Siberia, adjacent to Sakhalin island (approximately 140°E x 55°N). These fires were probably larger than any other event since 1971, including the famous 1987 Siberian event [Nilsson and Shvidenko, 1998]. A preliminary estimate of the total area burned during April-October 1998 is 111,000 km², with August exhibiting the largest area burned. The area burned in April was roughly 8600 km². These estimates are determined from analysis of advanced very high resolution radiometer (AVHRR) infrared satellite observations made by the Institute of Solar-Terrestrial Physics at Irkutsk. Because of the extensive smoldering that occurs in forest fires, particularly in the peat deposits that underlay a significant portion of the forests in both Indonesia and Siberia, oxidation of the carbon in the wood and peat to CO₂ is far from complete. Levine [1999] estimates that 8.5% of the carbon in the wood and 18.15% of the carbon in the peat are oxidized to CO.

During April 1998, the fires were located in areas of Mongolia and central Siberia surrounding Lake Baikal, in primarily grassland and mixed deciduous/coniferous forest vegetation. No significant peat combustion occurred in this month. Most of the CO emissions in April 1998 were generated by superficial on-ground burning of coniferous forest litter. For these reasons CO

emissions in April were significantly smaller than in the subsequent summer months, when full-scale burning of forests and underlying peat deposits occurred. Nevertheless, our estimate of CO emitted from the Siberian forest fires in April 1998 is 400 Gg CO, or 173 Gg C [Y. Kajii et al., manuscript in preparation, 2000]. For comparison, emissions for the entire 7-month period from April-October were 50 Tg CO, or 21 Tg C. These estimates are subject to an uncertainty of about +/- 20%, mainly due to difficulties in accurately characterizing the mass of material combusted and hence the amount of total carbon released.

Isentropic trajectories show that air arriving to CPO has frequently come from eastern and northeastern Asia within the past 10 days. Thus, we expect that biomass burning sources in these regions are an important source for many trace species at CPO. For example, as mentioned above we saw one case of elevated CO, O₃, PAN, aerosols, and other species which appears to be associated with rapid transport from northern Asia during a period when substantial biomass burning was occurring (DOY 111, 1998).

Direct transport from Southeast Asia to CPO is quite rare. Nonetheless, the Southeast Asian emissions could still be important for the CPO observations by contributing to a global or hemispheric accumulation of CO. While the lifetime of CO is relatively short in the tropical boundary layer (a few weeks), it is significantly longer during mid and high-latitude winter and outside of the boundary layer, due to much lower OH levels. Thus emissions from the Southeast Asian fires during the fall and winter of 1997-1998 could have contributed to a global enhancement during the winter and spring of 1998. This enhancement could occur if emissions from the Indonesian region were lifted out of the boundary layer and transported to higher latitudes, as in the Hadley cell circulation. Observations of outflow from the Indonesian fires were reported by *Matsueda et al.* [1999], who found substantially elevated mixing ratios of CO, CO₂, and CH₄ in the 8-13 km region. Thus some of the CO emitted in Southeast Asia must have been transported long distances in the upper troposphere. To the extent that this CO was transported to higher latitudes, where lifetimes during winter will be much longer, this would enhance the global CO burden. We believe this mechanism is plausible to explain some of the 1998 CPO data, even when trajectories are not coming directly from Asia.

While many studies have identified a biomass burning "signature" based on observations of CO and NMHCs in relatively fresh plumes [e.g., *Blake et al.*, 1994, 1996], these emissions will change dramatically over time as a result of mixing and chemical processing during transport. However, for longer-lived species, such as CO, ethane, ethyne, and propane, we might expect to see the ratios of these species preserved over longer times and transport distances. *Rinsland et al.* [1999] reported enhanced column CO and ethane at Mauna Loa for the November 1997 to January 1998 period, relative to earlier years, which they attributed to biomass burning in Asia. Using their Mauna Loa Observatory (MLO) observations for November 1997, the molar ratio of the CO to ethane enhancement has a value of 130. *Blake et al.* [1996] and *Blake et al.* [1994]

have summarized biomass burning emission factors from a number of studies and report molar ratios between 120-330, 178-495, and 504-2006 for the ratio of CO to ethane, ethyne, and propane, respectively. By comparison, we found molar enhancements ($\Delta\text{CO}/\Delta\text{NMHC}$) of 33, 65, and 46 for ethane, ethyne, and propane, relative to CO, for Asian industrial emissions [*Jaffe et al.*, 1999]. The mean molar enhancements ($\Delta\text{CO}/\Delta\text{NMHC}$) we observed at CPO in 1998, relative to 1997, were 93, 130, and 154 for ethane, ethyne, and propane, respectively. In all cases the enhancements we observed at CPO in 1998 are intermediate between the biomass burning and industrial values. Thus it would seem that both enhanced biomass burning and enhanced transport of industrial emissions is needed to explain the higher mixing ratios we observed at CPO during 1998.

3.6. Summary and Future Work

In this paper we have described the observations of CO, O₃, NO_x, PAN, NMHCs, Rn, aerosol scattering, aerosol absorption, and aerosol number density at the Cheeka Peak Observatory during the PHOBEA measurement campaigns during the spring of 1997 and 1998. From these data we examine how the mixing ratios of these species in the eastern Pacific are controlled by long-range transport, ships, and latitudinal gradients. There are a number of significant differences between the 1997 and 1998 observations in terms of the relationships to source regions and the mean mixing ratios. We attribute these differences to the strong El Niño present in late 1997 and 1998 and the much larger biomass burning emissions in late 1997 and early 1998. In addition to the CPO observations, vertical profiles of a nearly identical set of chemical compounds were made in this region during the spring of 1999 using the Wyoming King Air and are described by *Kotchenruther et al.* [this issue]. Taken together, the PHOBEA ground and aircraft data are currently the most comprehensive database of tropospheric chemistry in the northeastern Pacific during spring. Future work using this database will focus on an analysis of the tropospheric O₃ budget in this region and developing a better understanding of the factors that control long-range transport from distant source regions.

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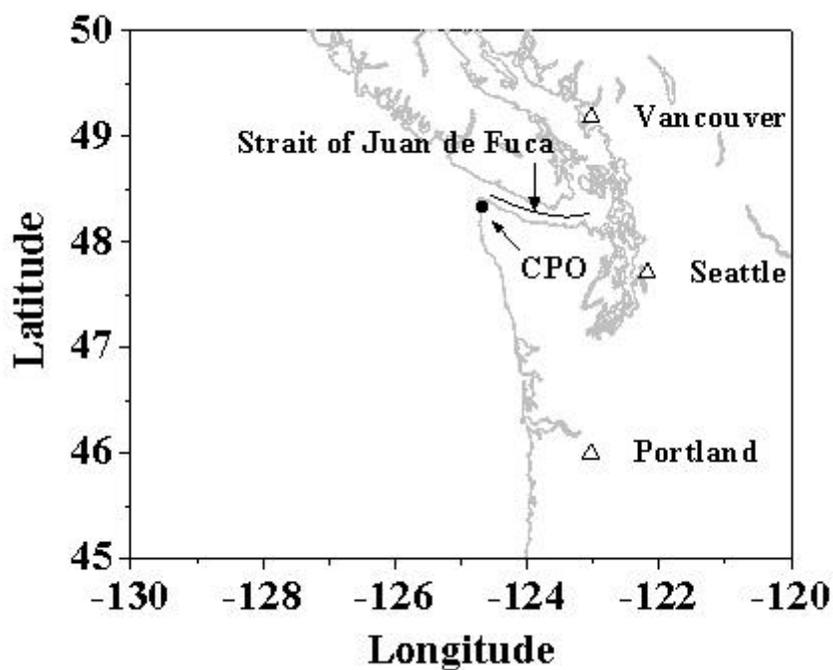


Figure 1. Map showing the location of the Cheeka Peak Observatory and the Strait of Juan de Fuca, which separates Washington State from British Columbia, Canada.

Figure 2a: 1998 CPO Marine Observations

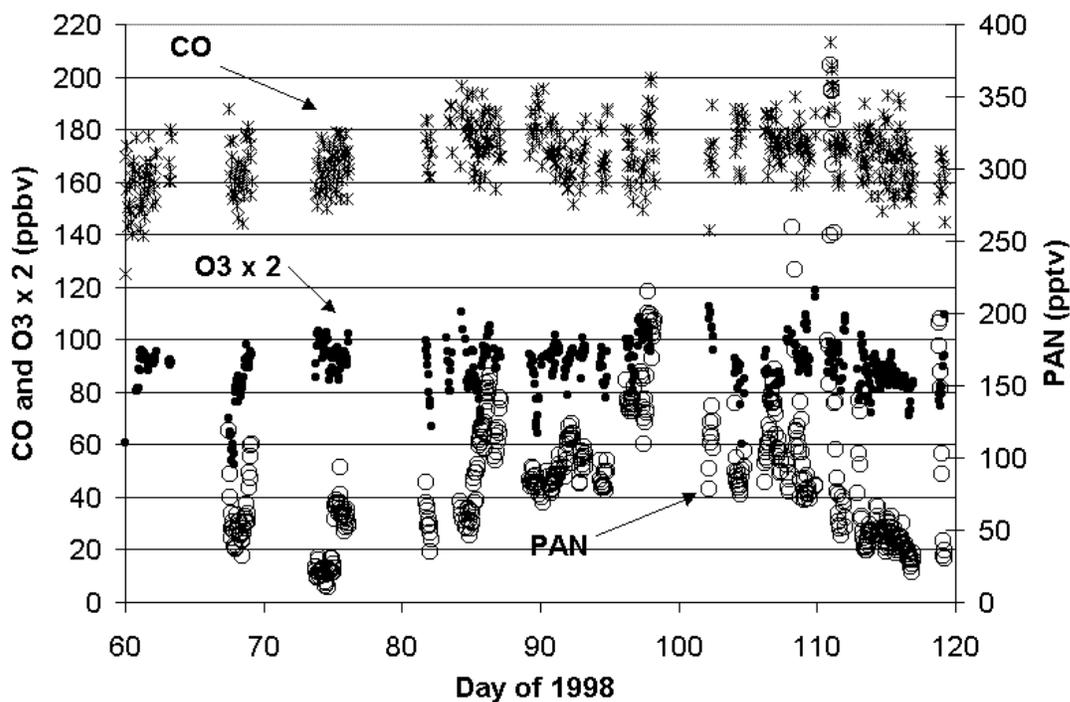


Figure 2a. Time series of the 1998 marine data for CO and O₃. Note that the continental data are omitted from this plot.

Figure 2b: 1998 CPO Marine Observations

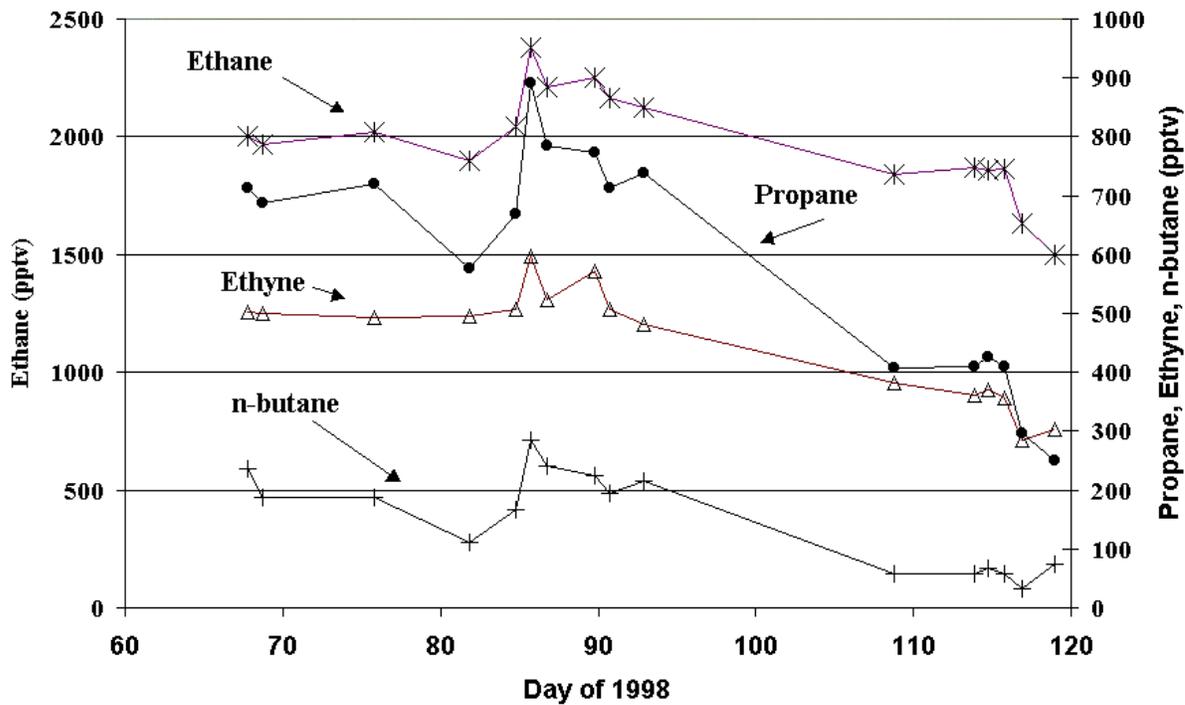
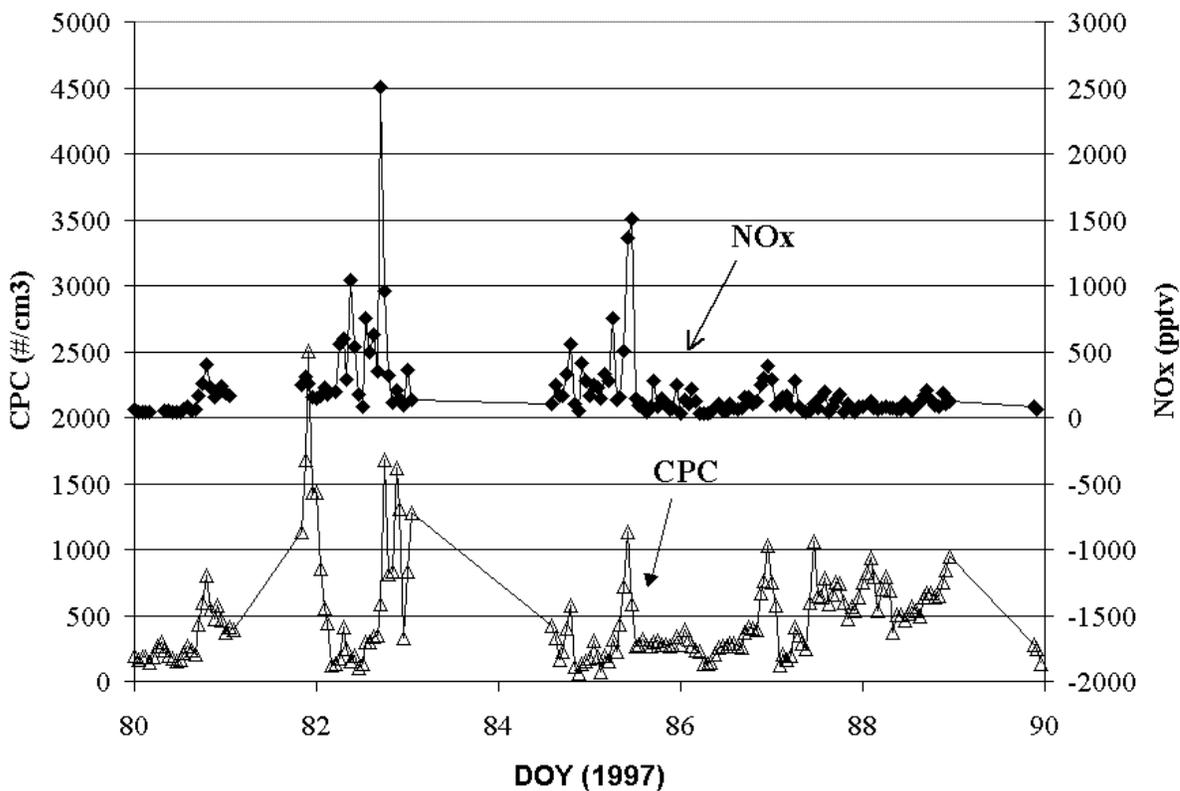
Figure 2b. Time series of the 1998 marine data for C_2H_6 , C_2H_2 , C_3H_8 , and $n-C_4H_{10}$.Figure 3. Hourly data for NO_x and CPC between DOY 80-90, 1997. Only data for marine periods are shown.

Table 1. Complete Data Set for 1997 and 1998 CPO Observations, Hourly Averages

	Mean (1997)	Median (1997)	s.d. (1997)	N, Hours (1997)	5 th Percentile (1997)	95 th Percentile (1997)	Mean (1998)	Median (1998)	s.d. (1997)	N, Hours (1998)	5 th Percentile (1998)	95 th Percentile (1998)
CO, ppbv	160	156	22	1319	132	201	178	174	22	1388	154	220
O ₃ , ppbv	43	44	5	1327	34	50	44	45	6	1407	34	54
NO _x ^a , pptv	95	25	185	534	3	411	67	11	169	406	16	316
NO _x , pptv	538	188	836	1100	38	2541	402	120	795	1345	16	1594
$J(\text{NO}_2)$, ^a 10 ⁻³ s ⁻¹	4.50	3.7	3.18	562	0.76	10.5	4.61	3.83	3.15	407	0.78	11.0
PAN, pptv	140	103	129	1234	11	395	134	101	102	1291	31	363
Rn, mBq/m ³	861	685	542	1451	357	1968	925	690	619	1432	441	2508
CPC, cm ⁻³	1177	564	1425	1384	99	4109	1438	943	1399	775	214	3866
σ_{sp} , Mm ⁻¹	5.55	4.20	4.95	847	0.2	16.8	5.25	3.40	4.89	775	0.80	15.30
σ_{ap} , Mm ⁻¹	0.83	0.30	1.04	838	0	2.9	0.89	0.30	1.16	775	0.00	3.40

^aDaytime only, defined by $J(\text{NO}_2) > 0.0005 \text{ s}^{-1}$.

Table 2. The 1997 and 1998 CPO Marine Data

	Mean (1997)	Median (1997)	s.d. (1997)	N (1997)	5 th Percentile (1997)	95 th Percentile (1997)	Mean (1998)	Median (1998)	s.d. (1997)	N (1998)	5 th Percentile (1998)	95 th Percentile (1998)
CO, ppbv	131	151	14	743	128	176	170	171	11	565	152	188
O ₃ , ppbv	44	44	4	746	36	50	45	46	5	556	38	52
NO _x ^a , pptv	29	14	54	308	2	96	9	6	10	150	1	27
NO _x , pptv	189	108	251	626	33	574	115	59	174	525	12	395
PAN, pptv	79	66	59	697	7	191	87	80	52	510	24	177
Rn, mBq/m ³	602	513	300	814	338	1198	621	574	196	566	422	971
CPC, cm ⁻³	480	342	436	784	75	1324	818	540	971	363	195	1953
σ_{sp} , Mm ⁻¹	4.1	3.3	3.8	425	0.1	12.4	3.17	2.6	2.15	363	0.7	7.79
σ_{ap} , Mm ⁻¹	0.34	0.2	0.6	421	0	1.6	0.33	0.2	0.43	363	0	1.3

^aDaytime only, defined by $J(\text{NO}_2) > 0.0005 \text{ s}^{-1}$.

Table 3a. NMHC Observations for Marine Periods, 1997 Data^a

	Mean	Median	s.d.	N
Ethane	1771	1669	276	11
Ethene	139	142	86	11
Ethyne	306	316	189	8
Propane	468	353	263	11
Propene	80	81	53	11
i-Butane	76	46	60	11
n-Butane	118	95	85	11
i-Pentane	59	55	43	11
n-Pentane	46	29	38	11
Benzene	148	140	66	11
Toluene	178	81	270	11
CH ₃ Cl	541	550	20	10
MeBr	12	11	1	10
CCl ₄	106	106	1	10
C ₂ Cl ₄	13	13	2	11

^aUnits are in pptv.

Table 3b. NMHC Observations for Marine Periods, 1998 Data^a

	Mean	Median	s.d.	N
Ethane	1977	1983	225	16
Ethene	50	53	11	16
Ethyne	452	494	95	16
Propane	592	678	196	16
i-Butane	75	85	44	16
n-Butane	150	176	83	16
i-Pentane	49	47	54	16
n-Pentane	29	17	32	16
Benzene	99	87	35	16
Toluene	11	14	10	16
C ₂ Cl ₄	9	9	1	16

^aUnits are in pptv.**Table 4.** Average Gas and Aerosol Parameters During Selected Periods

	Hours with No _x data	No _x , pptv	CPC, cm ⁻³	S _{ap} , Mm ⁻¹	S _{sp} , Mm ⁻¹	Wind Speed, m/s	Wind Direction	Rn, mbq/m ³	CO, ppbv	O ₃ , ppbv	PAN, pptv
1997 data											
All marine	626	189	480	0.3	4.1	7.0	228	602	151	44	79
NO _x >1000	10	1512	1315	0.9	6.2	4.3	263	676	145	42	97
NO _x >500	42	876	900	0.5	5.0	4.6	255	630	145	43	81
NO _x <500	584	134	456	0.3	4.0	7.2	227	601	152	44	79
1998 data											
All marine	525	115	818	0.3	3.2	4.6	241	620	170	45	87
NO _x >1000	6	1195	4561	1.4	6.9	4.2	250	811	188	48	213
NO _x >500	17	879	3819	1.2	6.4	4.3	252	860	184	46	204
NO _x <500	508	89	698	0.3	3.0	4.6	241	614	170	45	83

Table 5. Comparison of CPO Marine Data With King Air Data, Median Values

	CO, ppbv	O ₃ , ppbv	NO _x , pptv	NO _x ^a , pptv	PAN, pptv	CPC, cm ⁻³	s _{sp} , Mm ⁻¹	C ₂ H ₆ , pptv	C ₃ H ₈ , pptv
CPO 1997	151	44	108	17	66	342	3.3	1669	353
CPO 1998	171	46	59	14	80	540	2.6	1983	678
King Air 1999 ^b (0-2 km average)	146	49	30	10	72	360	1.9	1686	313

^aFrom 1800-2400 UT.^bFrom Kotchenruther et al.**Table 6.** Marine Data (12 Hour Averages) Segregated by Trajectory Classification

	Midlatitude			High Latitude			Low Latitude			Asian		
	Mean	s.d.	N	Mean	s.d.	N	Mean	s.d.	N	Mean	s.d.	N
1997 Observations												
CO, ppbv	150.7	11.1	39	150.2	6.8	12	146.3	9.6	17	165.7	10.0	9
O ₃ , ppbv	44.1	3.2	39	43.2	3.2	12	44.5	5.2	17	44.1	2.7	9
PAN, pptv	77	50	37	85	24	11	42	22	16	157	63	9
σ _{sp} , Mm ⁻¹	4.0	2.4	33	2.7	1.5	10	1.6	1.5	9	10.2	6.3	7
σ _{ap} , Mm ⁻¹	0.28	0.39	33	0.16	0.10	10	0.09	0.12	9	1.27	1.11	7
Rn, mbq/m ³	586	253	44	653	301	13	470	190	18	859	240	9
1998 Observations												
CO, ppbv	171.4	8.1	26	172.5	4.3	13	166.7	10.3	9	170.9	9.1	11
O ₃ , ppbv	44.6	4.3	27	44.2	3.0	13	46.8	2.6	8	46.7	3.5	10
PAN, pptv	85	55	24	90	31	13	44	22	5	108	23	9
σ _{sp} , Mm ⁻¹	3.4	2.6	21	3.7	1.6	12	2.9	1.0	5	2.5	1.1	10
σ _{ap} , Mm ⁻¹	0.37	0.50	21	0.41	0.30	12	0.14	0.11	5	0.21	0.18	10
Rn, mbq/m ³	655	224	26	598	94	13	509	48	9	687	134	11

Table 7a. Correlation Coefficient R Using Hourly Averaged Marine Data Sets ^a

Relationship	R (1997 Data)	R (1998 Data)
CO-PAN	0.50	0.40
CO- σ_{sp}	0.37	ns
CO- σ_{ap}	0.37	ns
CO-Rn	0.36	ns
PAN- σ_{sp}	0.70	0.51
PAN- σ_{ap}	0.71	0.62
PAN-CPC	0.38	0.61
PAN-Rn	0.63	0.44
σ_{sp} - σ_{ap}	0.89	0.92
σ_{sp} -CPC	0.43	0.45
σ_{sp} -Rn	0.54	0.46
σ_{ap} -CPC	0.39	0.59
σ_{ap} -Rn	0.59	0.57
CPC-Rn	0.42	0.47

^aOnly those relationships with an R value >0.35 are shown (statistically significant at a 95% confidence or greater). Here ns, not significant.

Table 7b. Correlation Coefficient R for NMHC Species and CO Measured During the 1998 Campaign^a

	CO	Ethane	Ethyne	Propane	n-Butane	i-Butane
Ethane	0.69					
Ethyne	0.73	0.92				
Propane	0.61	0.94	0.97			
n-Butane	ns	0.86	0.92	0.96		
i-Butane	0.60	0.90	0.94	0.97	0.99	
C ₂ Cl ₄	ns	0.77	0.85	0.85	0.88	0.90

^aFor this analysis we used the marine data set and a 3 hour running average for CO. All correlations are significant at better than 95% except for CO-ethane (94%), CO-propane (76%), and CO-i-butane (72%). Here ns, not significant.

Table 8. Statistical Comparison of 1997 and 1998 Marine Data (12 Hour Averages)[†]

	CO, ppbv	O ₃ , ppbv	Ethane, pptv	Propane, pptv	Ethyne, pptv
1997 average	151.4	44.1	1771	468	306
1998 average	170.7	45.2	1977	592	452
P value	>0.99	0.91	0.95	0.80	0.93

[†]The P value gives the probability that the two species were significantly different in the 1997 and 1998 data sets.