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

1. Ground-based observations at Cheeka Peak

Dan Jaffe, 1,2 Theodore Anderson, 2 Dave Covert, 2 Barbara Trost, 3 Jen Danielson, 3 William Simpson, 3 Donald Blake, 4 Joyce Harris, 5 David Streets 6

Abstract. As part of the Photochemical Ozone Budget of the Eastern North Pacific Atmosphere (PHOBEA) project, we have made observations of CO, O3, NOx, 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 NOx 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, ethene, 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 remain open. Photothermal 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 (NO + NO2). As a result of anthropogenic emissions of NOx, 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 NOx 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 NOx (of the order of 1 day or less) means that most NOx production will take place relatively close to NOx 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 O3 maximum. Moxim et al. [1996] summarize a mechanism in which the thermally unstable PAN can provide a source for NOx following air mass warming due to subsidence. In this mechanism, NOx 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 NOx. According to the modeling results of Moxim et al. this is the primary source of NOx in the lower troposphere over the remote oceans. However, several researchers have recently
suggested that direct NOx emissions from ships may be a sub-
stantial NOx source to the global marine boundary layer [Law-
rence 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 in-
cluding 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., Duve et al., 1980; Merrill et al., 1989;
Prospero and Savoie, 1989; Jaffe et al., 1999].

In the western North Pacific region the NASA Pacific Ex-
ploratory Mission-West (PEM-West) campaigns have made
comprehensive observations of O3 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 im-
mEDIATELY 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 conclu-
sion 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
O3 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, pa-
terns, 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 is-
 sue], and in a future paper we will present the results of an
analysis of the NOx and O3 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 adja-
cent to the Pacific Ocean (see Figure 1). During westerly
flow the air masses that arrive at the site are generally una-
fected by recent North American emissions and are charac-
teristic of the North Pacific atmosphere [Anderson et al.,
1999]. Easterly winds bring air from the more polluted con-
tinental boundary layer. The CPO site has been used for at-
mospheric chemistry and aerosol research for approximately
15 years [Anderson et al., 1999, and references therein].
During these two campaigns we measured O3, NOx, PAN,
CO, J(NO2), NMHCs, radon, aerosol number density, aerosol
absorption, and aerosol light scattering, along with meteorol-
ogical parameters.

Back isentropic trajectories [Harris et al., 1992] were cal-
culated 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 trajec-
tories, including low-resolution meteorological data, nonisen-
trropic transport, and/or subgrid-scale vertical motions. Pos-
sible trajectory errors have been discussed in several recent
publications [e.g., Kahl, 1996; Stohl, 1998].

For the NOx 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, O3, 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, O3, PAN, and NOx instru-
ments, we added a 2 mm Teflon filter to each inlet, effectively
eliminating all particles down to sub-micron sizes.

For NOx we used a high-sensitivity chemiluminescence in-
strument built in our laboratory and previously described by
Beine et al. [1997]. NO was detected directly. NO2 was de-
tected as NO following UV photolysis. One instrument cy-
cled between NO and NO2 modes. In addition, during the
1997 campaign we used a second high-sensitivity NO instru-
ment. This allowed us to conduct an informal intercompari-
on of our NO results.

Because our NOx measurement techniques have been de-
scribed 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 chemilumin-
escence 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 cm3 min-1 STP of 3.00 ppmv
NO in N2 (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
N2, 4.73 ± 0.07 ppmv), which led to a correction of the Scott-

![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.](image-url)
Median NO sensitivities for the 1997 and 1998 campaigns were 4.23 and 3.84 counts per second (cps)/pptv NO, respectively. The 3 σ 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 3 σ 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 calibrations for the PAN instrument and to provide an additional quality control and intercomparison with the primary NO instrument. This NO instrument was very similar to the primary NO chemiluminescence detector and shared the same gas with the primary instrument. The second instrument spent most of its time measuring ambient NO; it was switched manually to NOv measurements 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, Glasthitten, Germany) generates known mixing ratios of PAN from the photoysis of acetone in the presence of NO and O3. 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, Glasthitten, 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 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].
cient pro's 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 Hemisphere 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 NOₓ our values seem somewhat high, compared to other remote sites. For example, the median NOₓ 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...
Table 3a. NMHC Observations for Marine Periods, 1997

<table>
<thead>
<tr>
<th>Data</th>
<th>Mean</th>
<th>Median</th>
<th>s.d.</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane</td>
<td>1771</td>
<td>1669</td>
<td>276</td>
<td>11</td>
</tr>
<tr>
<td>Ethene</td>
<td>139</td>
<td>142</td>
<td>80</td>
<td>11</td>
</tr>
<tr>
<td>Ethyne</td>
<td>306</td>
<td>316</td>
<td>189</td>
<td>8</td>
</tr>
<tr>
<td>Propane</td>
<td>468</td>
<td>353</td>
<td>263</td>
<td>11</td>
</tr>
<tr>
<td>Propene</td>
<td>80</td>
<td>81</td>
<td>53</td>
<td>11</td>
</tr>
<tr>
<td>i-Butane</td>
<td>76</td>
<td>46</td>
<td>60</td>
<td>11</td>
</tr>
<tr>
<td>n-Butane</td>
<td>118</td>
<td>95</td>
<td>85</td>
<td>11</td>
</tr>
<tr>
<td>i-Pentane</td>
<td>59</td>
<td>55</td>
<td>43</td>
<td>11</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>46</td>
<td>29</td>
<td>38</td>
<td>11</td>
</tr>
<tr>
<td>Benzene</td>
<td>148</td>
<td>140</td>
<td>66</td>
<td>11</td>
</tr>
<tr>
<td>Toluene</td>
<td>178</td>
<td>81</td>
<td>270</td>
<td>11</td>
</tr>
<tr>
<td>CHCl3</td>
<td>541</td>
<td>550</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td>MeBr</td>
<td>12</td>
<td>11</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>C2C14</td>
<td>13</td>
<td>13</td>
<td>2</td>
<td>11</td>
</tr>
</tbody>
</table>

*Units are in pptv.

Table 3b. NMHC Observations for Marine Periods, 1998

<table>
<thead>
<tr>
<th>Data</th>
<th>Mean</th>
<th>Median</th>
<th>s.d.</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane</td>
<td>1977</td>
<td>1983</td>
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<td>16</td>
</tr>
<tr>
<td>Ethene</td>
<td>50</td>
<td>53</td>
<td>11</td>
<td>16</td>
</tr>
<tr>
<td>Ethyne</td>
<td>452</td>
<td>494</td>
<td>95</td>
<td>16</td>
</tr>
<tr>
<td>Propane</td>
<td>592</td>
<td>678</td>
<td>196</td>
<td>16</td>
</tr>
<tr>
<td>i-Butane</td>
<td>75</td>
<td>85</td>
<td>44</td>
<td>16</td>
</tr>
<tr>
<td>n-Butane</td>
<td>150</td>
<td>176</td>
<td>83</td>
<td>16</td>
</tr>
<tr>
<td>i-Pentane</td>
<td>49</td>
<td>47</td>
<td>54</td>
<td>16</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>29</td>
<td>17</td>
<td>32</td>
<td>16</td>
</tr>
<tr>
<td>Benzene</td>
<td>99</td>
<td>87</td>
<td>35</td>
<td>16</td>
</tr>
<tr>
<td>Toluene</td>
<td>11</td>
<td>14</td>
<td>10</td>
<td>16</td>
</tr>
<tr>
<td>C2C14</td>
<td>9</td>
<td>9</td>
<td>1</td>
<td>16</td>
</tr>
</tbody>
</table>

*Units are in pptv.

that our marine data set should not have been influenced by continental sources for at least 3 days.

Examining a histogram of the NOx data (not shown), it is clear that the high average NOx 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 NOx periods, as shown in Table 4. When NOx mixing ratios are high, other species, especially CPC, σap, and σsp, are also elevated. Mixing ratios for O₃, CO, and PAN (at least in 1997) are nearly unaffected during these high-NOx periods.

An example of a 10-day period with several spikes in NOx 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 NOx 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 NOx 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 NOx 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-NOx
periods in 1997. Presumably, this reflects differences in the sources being sampled at these times.

There are several possible explanations for these relatively high NOx 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 NOx 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/NOx relationship in the full CPO data set which has a CO/NOx 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

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**Figure 2a.** Time series of the 1998 marine data for CO, O3, and PAN. Note that the continental data are omitted from this plot and that O3 mixing ratios have been doubled for clarity.

**Figure 2b.** Time series of the 1998 marine data for C2H6, C2H2, C3H8, and n-C4H10.
by processing enroute to Cheeka Peak. Using this ratio, we would expect that a 1 ppbv enhancement in NO\textsubscript{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\textsubscript{x} periods argues that the source characteristics have a much higher NO/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\textsubscript{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\textsubscript{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\textsubscript{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\textsubscript{x} and particles in diesel exhaust; and (2) the short lifetime for both NO\textsubscript{x} and particles, which gives rise to very low background concentrations. To examine this hypothesis, we can estimate the impact on CO

![Figure 3. Hourly data for NO\textsubscript{x} and CPC between DOY 80-90, 1997. Only data for marine periods are shown.](image-url)
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. Thus, 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, O$_3$, PAN, Rn, CPC, $\sigma_{mp}$, and $\sigma_{pp}$ (12 hour means of 500 pptv, 192 ppbv, 47 ppbv, 278 ppbv, 1088 mbq/m$^3$, 5563 cm$^{-3}$, 7.0 M$_m^{-1}$, and 1.5 M$_m^{-1}$, 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. O$_3$ is higher for the 0-2 km layer then 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 $\sigma_{pp}$ are higher at CPO. The higher NO probably reflects a greater influence of ship emissions at CPO, and higher $\sigma_{pp}$ 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) low latitudes, 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

| Table 5. Comparison of CPO Marine Data With King Air Data, Median Values |
|------------------------|----------------|-----------------|---------------|---------------|---------------|---------------|---------------|---------------|
|                        | CO, ppbv | O$_3$, ppbv | NO$_x$, pptv | NO$_x$' pptv | PAN, pptv | CPC, cm$^{-3}$ | $\sigma_{mp}$, M$_m^{-1}$ | C$_2$H$_6$, pptv | C$_3$H$_8$, pptv |
| CPO 1997               | 151      | 44           | 108          | 17           | 66          | 342           | 3.3           | 1609          | 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           |

$^a$From 1800-2400 UT.
$^b$From Kotchenruther et al. [this issue].
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, O\(_3\), PAN, aerosol scattering, and absorption. For CO the low-latitude cases are significantly different from the midlatitude 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 O\(_3\)), 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-latitudes 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, \( O_3 \) 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 then 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 with an 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.

### Table 6: Marine Data (12 Hour Averages) Segregated by Trajectory Classification

<table>
<thead>
<tr>
<th></th>
<th>Mean</th>
<th>s.d.</th>
<th>N</th>
<th>Mean</th>
<th>s.d.</th>
<th>N</th>
<th>Mean</th>
<th>s.d.</th>
<th>N</th>
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<td></td>
<td>CO, ppbv</td>
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<td>197.5</td>
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<td>( O_3 ), ppbv</td>
<td>41.1</td>
<td>9.2</td>
<td>37.0</td>
<td>8.5</td>
<td>35.7</td>
<td>7.0</td>
<td>44.3</td>
<td>6.2</td>
</tr>
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<td></td>
<td>( N_2O ), ppmv</td>
<td>67.6</td>
<td>13.4</td>
<td>63.7</td>
<td>15.0</td>
<td>58.8</td>
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<td>70.1</td>
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<td>0.04</td>
<td>0.28</td>
<td>0.04</td>
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<td>0.04</td>
<td>0.28</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>1998 Observations</td>
<td>586.0</td>
<td>253.4</td>
<td>44.1</td>
<td>57.3</td>
<td>17.1</td>
<td>42.0</td>
<td>4.1</td>
<td>171.4</td>
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<tr>
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<td>38.8</td>
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<td>60.6</td>
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<td>0.04</td>
<td>1.28</td>
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<td>252.4</td>
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<tr>
<td></td>
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<td>0.04</td>
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Table 7a. Correlation Coefficient R Using Hourly Averaged Marine Data Sets

<table>
<thead>
<tr>
<th>Relationship</th>
<th>R (1997 Data)</th>
<th>R (1998 Data)</th>
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<tr>
<td>CO-PAN</td>
<td>0.50</td>
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<td>CO-Csp</td>
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<td>ns</td>
</tr>
<tr>
<td>CO-Rn</td>
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<td>ns</td>
</tr>
<tr>
<td>PAN-Csp</td>
<td>0.70</td>
<td>0.51</td>
</tr>
<tr>
<td>PAN-Rn</td>
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</tr>
<tr>
<td>PAN-CPC</td>
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<td>0.61</td>
</tr>
<tr>
<td>PAN-Gap</td>
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<td>0.44</td>
</tr>
<tr>
<td>σgP-Csp</td>
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<td>0.92</td>
</tr>
<tr>
<td>σgP-CPC</td>
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</tr>
<tr>
<td>σgP-Rn</td>
<td>0.54</td>
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<tr>
<td>σeCPC</td>
<td>0.39</td>
<td>0.59</td>
</tr>
<tr>
<td>σeP-Rn</td>
<td>0.59</td>
<td>0.57</td>
</tr>
<tr>
<td>CPC-Rn</td>
<td>0.42</td>
<td>0.47</td>
</tr>
</tbody>
</table>

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

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, σgP, and σeP were significantly correlated in both the 1997 and 1998 data. O3 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 O3 were uncorrelated in the 1997 data set. Most likely this reflects the multitude of sources responsible for tropospheric O3. 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 O3 during summer outflow. Under these conditions the bulk of the observed O3 is probably due to photochemical production associated with North American NOx emissions. At more remote sites a CO-O3 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 O3, 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 Nino events on record. While this El Nino 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 Nino 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 [Nils-son 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 derived 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 been transported long distances in the upper troposphere. "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 emissions 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 (ΔCO/ΔNMHC) 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 (ΔCO/ΔNMHC) 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, NOₓ, 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 O$_3$ 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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References

Akimoto, H., and H. Narita, Distribution of SO$_2$, NO$_x$, and CO$_2$ emissions from fuel combustion and industrial activities in Asia with 1x1° resolution, Atmos. Environ., 28, 213-225, 1994.


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