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A comparison of aircraft and ground-based measurements at Mauna Loa Observatory, Hawaii, during GTE PEM-West and MLOPEX 2

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Abstract. During October 19-20, 1991, one flight of the NASA Global Tropospheric Experiment (GTE) Pacific Exploratory Mission (PEM-West A) mission was conducted near Hawaii as an intercomparison with ground-based measurements of the Mauna Loa Observatory Photochemistry Experiment (MLOPEX 2) and the NOAA Climate Modeling and Diagnostics Laboratory (CMDL). Ozone, reactive nitrogen species, peroxides, hydrocarbons, and halogenated hydrocarbons were measured by investigators aboard the DC-8 aircraft and at the ground site. Lidar cross sections of ozone revealed a complex air mass structure near the island of Hawaii which was evidenced by large variation in some trace gas mixing ratios. This variation limited the time and spatial scales for direct measurement intercomparisons. Where differences occurred between measurements in the same air masses, the intercomparison suggested that biases for some trace gases was due to different calibration scales or, in some cases, instrumental or sampling biases. Relatively large uncertainties were associated with those trace gases present in the low parts per trillion by volume range. Trace gas correlations were used to expand the scope of the intercomparison to identify consistent trends between the different data sets.

Introduction

To undertake a comprehensive study of atmospheric photochemistry, a wide range of rather complex chemical measurements must be carried out simultaneously within one or several coordinated experimental programs. Uncertainties

related to the individual measurements must be specified to allow meaningful interpretation and to compare with model calculations which rely on the entire suite of chemical measurements. Errors and uncertainties in any of the measurements may have profound implications on the overall data interpretation [e.g., *Liu et al.*, 1992].

A number of different instrument intercomparison exercises have been carried out in recent years to examine the reliability of current measurement techniques. These include aircraft-based programs such as the Global Tropospheric Experiment (GTE) Chemical Instrumentation Test and Evaluation (CITE) series and a number of ground-based studies which address specific measurement issues [e.g, *Fehsenfeld et al.*, 1987; *Hoell et al.*, 1990, 1993; *Kleindienst et al.*, 1988]. These intensive intercomparisons provide valuable information on biases or offsets between techniques in a given experimental setting, but they do not necessarily reflect the "routine" application of the different measurement techniques; in addition, not all chemical species normally measured in a single comprehensive campaign have been intercompared.

As chemical models become more sophisticated, a combination of chemical measurements obtained from different field programs and from different investigators will be required to test model predictions. However, there have been few instances during which different measurement programs can be directly intercompared. The Pacific Exploratory Mission-West (PEM-West) and Mauna Loa Observatory Photochemistry Experiment 2 (MLOPEX 2), both studying aspects of the photochemistry of the troposphere over the Pacific Ocean, were performing many of the same measurements. Thus, colocation of the two programs for one of the PEM-West flights offered the opportunity for an intercomparison under conditions which were "normal" for each measurement program.

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The intercomparison which could be conducted near the Mauna Loa Observatory (MLO) site provides an optimum situation to examine data intercomparibility between different investigations.

This report summarizes and compares chemical measurements from the DC-8 aircraft and the ground based MLO site during flight 20 of the PEM-West mission. Not all measurements were performed at both sites, and a description of these data are not included here. More detailed descriptions and interpretations based on the entire data sets are presented in a series of papers elsewhere [see Hoell et al., 1996 (PEM-West A Special Issue]. This report includes comparisons of ozone and a variety of trace gases used to assess oxidant budgets in the remote troposphere. These species include tracer species (halogenated hydrocarbons, nonmethane hydrocarbons), radical reservoirs (peroxides), odd-nitrogen species (NO_y, NO_x, PAN, nitric acid), and reactive hydrocarbons (alkenes).

Measurements and Techniques

The different measurements which will be compared are given in Table 1. A brief description of the individual techniques and estimated errors are presented here, but details of the instrumentation and methodology are given in references by the individual investigators.

Ozone

For the ground-based measurements, instrumentation is based on UV absorption measurement. The MLOPEX instrument was a pressure and temperature compensated Thermo Environmental Instruments (TECO) Model 49 calibrated with a TECO Model 49-PS calibrator. Data are reported as 1 min averages. The PEM-West instrument is based on ozone-ethylene chemiluminescence which is calibrated with NO-O_3 gas phase titration traceable to National Institute of Standards and Technology (NIST) NO standards [Gregory et al., 1983, 1992]. Each of the ozone instruments is reported to have a precision of at least ±2 ppbv [Walega et al., 1992; Gregory et al., 1983]. An ozone instrument was also in operation at the CMDL, but that instrument reports hourly averages and the data are not included in this comparison. We note that throughout the MLOPEX intensives, there was good agreement between the CMDL and MLOPEX ozone data. For example, during the free tropospheric flow periods of the first intensive, the mean difference between the two instruments was only 1.1 (±1.8) ppbv (MLOPEX >CMDL), which indicates agreement within the estimated precision of the techniques.

Total Reactive Oxidized Nitrogen (NO_y)

NO_y was measured in two airborne systems and from a 10-m tower at the MLO site. All instruments rely on the gold-catalyzed reduction of reactive nitrogen to NO [Bollinger et al., 1983] which is detected using either laser induced fluorescence (LIF) [Bradshaw et al., 1985; Sandholm et al., 1990] or chemiluminescence (CL) detection [Hübler et al., 1992a,b; Kondo et al., 1996]. The airborne instrumentation included one LIF and one CL system; the ground-based instrument was a CL system. Data are reported as 1-min averages for the chemiluminescence-based systems and 90-s averages for the LIF system. Estimated uncertainty of each is 10 - 20 %.

Nitric Acid and Aerosol Nitrate

Nitric acid was measured using three different techniques at the MLO site, and a fourth technique was used aboard the DC-8. One ground system was based on collection of aerosol nitrate and nitric acid on a Teflon/nylon filter pair [Norton et al., 1992]. The second system used an aqueous-based

Table 1. Summary of Measurements for Intercomparison During PEM-West Flight 20 and MLOPEX 2, October 20, 1991

| Measurement | PEM-West | | MLOPEX | |
	Investigator	Technique	Investigator	Technique
Ozone	G. Gregory	Chemiluminescence	B. Ridley/J. Walega	UV absorption
			S. Oltmans*	UV absorption
NO_y	J. Bradshaw	LIF	G. Hübler	Chemiluminescence
	Y. Kondo	Chemiluminescence		
HNO_3	R. Talbot	Mist Chamber/IC	R. Norton	Nylon filter
			J. Lind	Denuder/IC
NO	Y. Kondo	Chemiluminescence	B. Ridley	Chemiluminescence
	J. Bradshaw	LIF		
NO_2	J. Bradshaw	LIF	B. Ridley	Chemiluminescence
PAN	H. Singh	GC/ECD	B. Ridley	GC/ECD
HOOH/ROOH	B. Heikes	HPLC/ Fluorescence	G. Kok	Dual Enzyme/Fluor.
	B. Heikes	Fluorescence	G. Kok	HPLC/ Fluorescence
			G. Mackay	TDLAS
NMHC	D. Blake	GC/FID	J. Greenberg	GC/FID (in situ)
Methane	G. Sachse	TDL	E. Dlugokencky*	GC/FID (in situ)
CO	G. Sachse	TDL	S. Schauffler	GC/HgO (in situ)
C_2Cl_4	D. Blake	GC/ECD	E. Atlas	GC/ECD (in situ)
	H. Singh	GC/ECD (in situ)		
Halocarbons	D. Blake	GC/ECD	J. Elkins*	GC/ECD (in situ)
Nitrous Oxide	G. Sachse	TDL	J. Elkins*	GC/ECD (in situ)
SO_2	A. Bandy	GC/MS	G. Hübler	Pulse Fluorescence

*Measurements as part of NOAA's Climate Monitoring and Diagnostic Laboratory program.

diffusion denuder to separate nitric acid from aerosol nitrate. A packed coil downstream of the denuder continuously collected aerosol nitrate [*J.A. Lind et al.*, unpublished manuscript, 1992]. The third system was based on the difference between two NO_y measurements. One NO_y channel samples air passed through a nylon wool filter to remove nitric acid and at least some aerosol nitrate; the second channel sampled unfiltered air. Since aerosol nitrate was a small relative to nitric acid during this intercomparison, an upper limit estimate of nitric acid is the difference between the two channels [*Hübler et al.*, 1992a]. The airborne system used a mist chamber to collect nitric acid [*Talbot et al.*, 1990; *Dibb et al.*, 1996]; an upstream filter removed aerosol nitrate prior to collection in the mist chamber. A separate filter system was used for quantitative measurement of aerosol nitrate aboard the aircraft. Except for the NO_y difference technique, all systems used ion chromatography for analysis of the aqueous extracts. Sample integration times for the different techniques were as follows: 12.5 min for the diffusion denuder, 2 hours for the Teflon/nylon filter pair, 1 min for the NO_y difference, and 15-50 min for the mist chamber. Estimated uncertainties for these methods are in the range of 15-25%.

NO and NO_2

NO was measured using a NO/O_3 chemiluminescence technique at both the ground site [*Carroll et al.*, 1992; *Ridley et al.*, 1994] and aboard the DC-8 [*Kondo*, 1996]. The second airborne system was based on the LIF technique [*Bradshaw*, 1995]. NO_2 measurements were obtained only with the ground-based system and the airborne LIF instrument. Both instruments measured NO_2 by photolytic conversion of NO_2 to NO, and the ground-based system cooled the photolysis cell to 0°C. Detection limits for both airborne instruments were better than 2 pptv for NO and 4 pptv for NO_2. The ground-based system quotes the uncertainties for mixing ratios <100 pptv as NO, ±(0.9 + 4% reading) pptv; NO_2 (night), ±(2.5 + 4% reading) pptv. Overall uncertainties estimated in these systems were on the order of 15 - 20%.

Peroxyacetyl Nitrate (PAN)

PAN measurements in the ground and aircraft systems were based on gas chromatography with electron capture detection. Both the MLOPEX instrument and the airborne instrument cryogenically preconcentrated air for analysis [*Walega et al.*, 1992; *Singh et al.*, 1992, 1994]. Limits of detection were <1 and 4 pptv in the ground-based and airborne instruments, respectively. Uncertainties in the measurement are estimated to be in the range of 8 - 15%.

Hydrogen Peroxide/Organic Hydroperoxides

Several different systems were used to measure hydrogen and organic peroxides. At the MLO site, hydrogen peroxides were measured by three systems. A continuous dual-enzyme hydroperoxide analytical system provided the highest-frequency data [*Lazrus et al.*, 1986]. A second system using cryogenic collection and high-performance liquid chromatography (HPLC) supplemented the coil data, but provided only hourly integrated data [*Kok et al.*, 1995]. These systems measured both hydrogen and organic peroxides. A tunable diode laser instrument (TDLAS) was the third technique to measure hydrogen peroxide, and half hourly

integrated data were reported [*Mackay et al.*, this issue]. A detailed comparison of these measurements is presented by *Staffelbach et al.* [this issue].

Aboard the aircraft, an aqueous coil system similar to the ground-based instrument was used to measure hydrogen and organic peroxides [*Heikes et al.*, 1996]. A second airborne system used high-pressure liquid chromatography to analyze hydrogen and organic peroxides, and this system was used as a basis of standardization of the continuous coil instrument. Instrument detection limits were on the order of 30 pptv for hydrogen peroxide in the fluorescence based instruments and near 100 pptv in the TDLAS instrument. Organic hydroperoxide detection limits were near 50 pptv. Uncertainties in the peroxide instruments are estimated to be on the order of 15%.

Non-methane Hydrocarbons (NMHC)

Aboard the aircraft, whole air samples were collected in stainless steel canisters, and the NMHC were analyzed using gas chromatography with flame ionization detection [*Blake et al.*, 1994]. The system was calibrated with a secondary whole air standard referenced to NIST scales. The calibration mixture was analyzed between every four sample canisters. Detection limits reported for the aircraft system were between 3 and 5 pptv, depending on the specific compound. NMHC analyses at the MLO site were performed using an automated in situ GC/FID system [*Greenberg et al.*, 1994]. In this system, standardization was based on dilutions of NBS standard hydrocarbon mixtures. Detection limits for the MLO in situ system were from 0.2 to 2 pptv.

Tetrachloroethylene (C_2Cl_4)

Tetrachloroethylene was measured in two systems aboard the DC-8 and in one ground-based instrument. One measurement aboard the aircraft is performed along with the PAN measurement [*Singh et al.*, 1992], and is based on in situ GC/ECD. The second airborne measurement is from the stainless steel canisters described for NMHC analyses. For these samples, a portion of the air sample is directed through an electron capture detector for the analyses of halocarbons [*Blake et al.*, 1994]. The ground-based instrument used solid adsorbent collection in an in situ instrument which was based on capillary gas chromatography with electron capture detection [*Atlas et al.*, 1992a, and unpublished report, 1993]. Detection limit in the measurements from the aircraft and the ground-based system are < 0.1 pptv.

Methane/Carbon Monoxide

Methane and carbon monoxide were measured onboard the DC-8 with a tunable diode laser system [Sachse et al., 1991]. The system provided measurement precisions (2σ) of 2% for CO and 0.2% for methane with the accuracy tied to calibration standards obtained from NOAA/CMDL. Ground based methane was measured as part of NOAA's CMDL long-term monitoring program [*Dlugokencky et al.*, 1994; *Harris et al.*, 1992]. Instrument precision is estimated at 0.2% (3 ppb), with an overall uncertainty of 1.5%. Carbon monoxide was measured at the MLO site using an in situ gas chromatography with a reductive gas (HgO) detector. Instrument problems of the ground-based instrument during the measurement period increased the uncertainty of the CO measurement to

approximately 15 ppbv (S. Schauffler et al., unpublished report, 1993).

Sulfur Dioxide (SO$_2$)

Sulfur dioxide was measured on the DC-8 as part of an isotope dilution GC/MS system for sulfur species [*Thornton et al.*, 1996]. Integrated samples (40 s) were analyzed every 5 min in this system. Detection limits are estimated at <4 pptv with an overall uncertainty of better than 10%. The ground-based system was a modified TECO pulsed fluorescence instrument. Detection limits from 1-min averaged data were estimated at ±66 pptv, with an overall uncertainty of 20% (G. Hübler, personal communication, 1992). The purpose of the ground-based instrument was to detect local volcanic emissions at the site rather than to measure background levels of SO$_2$.

Long-lived Halocarbons and N$_2$O

Several long-lived species including CFC-12, CFC-11, methyl chloroform, carbon tetrachloride, and N$_2$O were measured. The airborne measurements for the halocarbon compounds were included as part of the analyses of whole air from stainless steel canisters [*Blake et al.*, 1994]. Precision of the halocarbon analyses range from 1 to 5%, with an estimated accuracy of between 2 and 10%. We note that the canister data used in this comparison are modified from the original archive to correct for a calculation/transcription error in the data file. Airborne N$_2$O was measured by a TDLAS instrument with a nominal precision of ±0.2% (2σ) and an accuracy of ±1% based on standards obtained from NOAA/CMDL. Nominal precision is ±.05 ppbv and accuracy is within ±1%. The ground-based instrument uses an in situ GC/ECD, and these measurements are part of the CMDL program [*Elkins et al.*, 1993; *Montzka et al.*, 1992]. Precisions are determined by the reproducibility of the analysis of the two calibration standards during the period of the experiment. Estimated precisions (±1 s.d.) for N$_2$O, CFC-12, CFC-11, methyl chloroform, and carbon tetrachloride are ±0.26, 0.40, 0.22, 0.83, and 0.66%, respectively. The absolute scale is based on independent gravimetric standards made at CMDL, and the related uncertainty is based on the ability to reproduce the standards. Estimated accuracies for N$_2$O, CFC-12, CFC-11, methyl chloroform, and carbon tetrachloride are ±0.3%, 1%, 1%, 5%, 2%, respectively [see *Elkins et al.*, 1993]. The total uncertainty in the mixing ratio is the square root of the sum of the squares of the individual uncertainties. The resulting total uncertainty for N$_2$O, CFC-12, CFC-11, methyl chloroform, and carbon tetrachloride are ±0.4, 1.08, 1.02, 5.07, and 2.11%.

Site description and meteorological conditions. During the last four decades, the Mauna Loa Observatory has been the site for an extended series of chemical and meteorological measurements. The site, located at 3.4 km altitude on the upper north slope of the Mauna Loa volcano on the island of Hawaii, is operated by NOAA's Climate Monitoring and Diagnostic Laboratory. The observatory was also the site of the first MLOPEX study in spring of 1988 [*Ridley and Robinson*, 1992]. Meteorological conditions at the site have been well described and show the site to be strongly influenced by a diurnal upslope/downslope flow regime. For some period during most nights, the downslope flow allows air representative of the free troposphere (FT) near 3.4 km to be sampled. For this reason, the PEM flight was scheduled to be

in the vicinity of the site and near the island during a portion of the "normal" downslope flow period (often from 2200 to 1000 HST).

Atmospheric conditions near the island of Hawaii are routinely monitored with twice daily soundings. The sounding from Hilo at 0200 on the night of the flyby shows that MLO (680 mbar) was located above the trade wind inversion (720-750 mbar); winds from 900 to 550 mbar were from the east to east-southeast at 5 - 10 knots; dew point decreased from -10°C at 700 mbar to -24°C at 500 mbar (Figure 1). At the MLO site, local winds shifted from northerly to southerly starting near 2100 on October 19 and the local wind remained southerly at 5 - 7 m/sec until ≈0730 the following morning. Steady winds from the south are the result of the switch to downslope flow at the site. Other measurements at the site indicated that the downslope flow period should be representative of free tropospheric air during the flyby. Along with the shift to southerly winds, condensation nuclei dropped from a midafternoon high of 600 - 700 cm^{-3} to 140 - 200 cm^{-3} during the downslope period. Dew point reached a minimum of -30°C during a brief period near 2230 HST on October 19, and increased to -15°C by 0100 (October 20) where it remained for the rest of the downslope period. This early dew point minimum was also associated with an ozone maximum which will be discussed later. SO$_2$, an indicator of local volcanic emissions, was below the limit of detection at the beginning of the downslope period, but levels slowly increased during the night and early morning to an average value of 140 pptv. Occasional spikes of SO$_2$ reached as high as 600 pptv. An increase of about 1 ppmv of CO$_2$ was also observed during the period of increased SO$_2$. The observed increases in SO$_2$ and CO$_2$ suggests that air sampled at MLO was likely affected by emissions from small vents on the upper slopes of Mauna Loa. These emissions should not have an impact on the other chemical species considered here, with the possible exception of hydrogen peroxide. A summary of the transition to downslope flow and conditions during the flight mission are shown in Figure 2. On the basis of the observed winds, dew point, etc., conditions at the MLO site (except for CO$_2$ and SO$_2$) during the PEM-West flyby can be considered as representative of the free troposphere near Hawaii.

Mission 20 flight track. The flight left Honolulu on October 20, 1991, at 0338 HST. The first flight segment was a west-east transect near 6.0 km over the center of the island of Hawaii (leg 1). This leg was followed by a chevron pattern at about 400 m altitude off the eastern edge of the island (0500 - 0534 HST); the leg ended off the southern shore of the island (leg 2). The plane then ascended to 3.3 km (near the altitude of the MLO site) and proceeded in a counter-clockwise circle of the island (0548 - 0652 HST) (leg 3). The island circle was followed by a second chevron at about 4.8 km (leg 4) stacked above the first chevron leg (0700 - 0732 HST). After this leg, the plane headed on a north-south transect near 3.6 km which passed within 20 km of the MLO site at approximately 7:50 HST (7:34 - 8:00 HST) (Leg 5). A low-altitude chevron was repeated after the MLO site overflight (leg 6) and before the plane returned to Honolulu. This flight track is illustrated in Figure 3.

The rationale for the flight track allowed for examination of trace gas composition in the marine boundary layer (MBL) as well as a comparison between airborne and ground-based measurements in free tropospheric air, though we consider
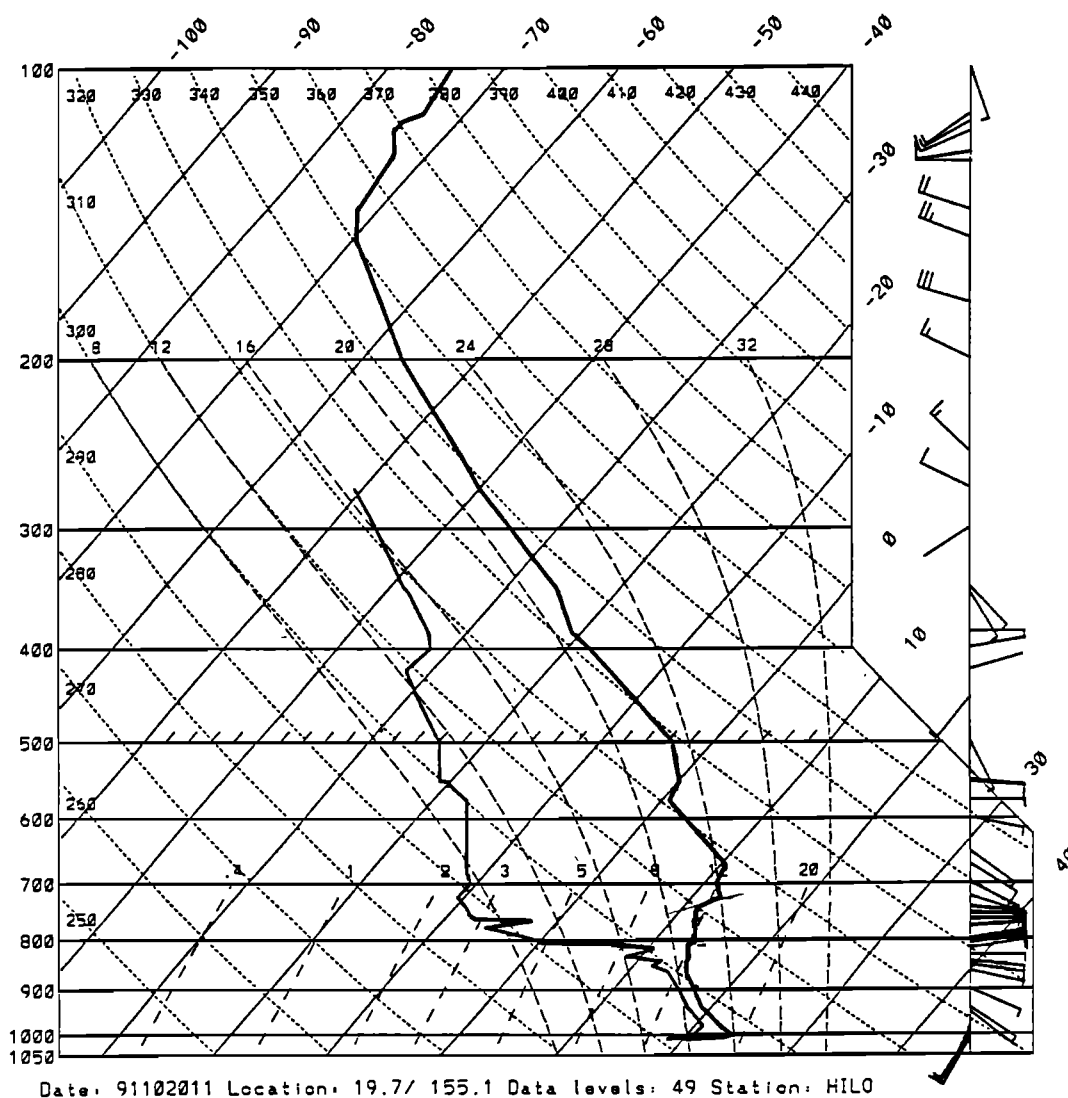
Date: 91102011 Location: 19.7/ 155.1 Data levels: 49 Station: HILO

Figure 1. Atmospheric sounding from Hilo, Hawaii, at 0100 (HST), October 20, 1991. The pressure at Mauna Loa Observatory is near 680 mbar.

only aspects related to the intercomparison in this manuscript. The first high-altitude overpass of Hawaii was to obtain lidar cross sections of ozone and aerosol abundance. The initial low-altitude chevron examined chemical composition of the nighttime marine boundary layer. The island circle was the primary flight leg to allow the most detailed intercomparison of free tropospheric air at the altitude of MLO, but away from the ground. The circle provided both upwind and downwind sectors for comparison. The second high-altitude chevron provided a comparison of chemistry higher in the FT for comparison to the MBL chevrons. A pass over the island and nearby the MLO site gave the most direct comparison between airborne and ground-based measurements. The final chevron gave a comparison between chemistry in the sunlit versus the nighttime MBL .

Results

The basis for comparing measurements from the aircraft and from the ground site is not as straightforward as it was planned, even for a site in the remote midtroposphere. On a scale that is required for detailed intercomparisons, there were

significant variations of many of the chemical species considered here. At the altitude of MLO, measurable changes occur in certain chemical species over timescales of several hours and over space scales of several hundred meters. The variability around Hawaii on the morning of the intercomparison is perhaps best illustrated in the vertical section of ozone obtained during the first high-altitude pass over the island (Figure 4). A broad ozone maximum is located between 2.5 and 4 km altitude, with maximum ozone mixing ratios over 40 ppbv observed in a lens centered near 3.3 km altitude just west of the island. Interleaving of air parcels with different ozone concentration also is noticeable to the east of the island between 2 and 3 km altitude. It is clear that there were different air masses in the vicinity of Hawaii during the night of the intercomparison. Considering only the altitude of MLO, there is nearly a factor of 2 variation in ozone concentration (Plate 1).

The problem is to choose the most appropriate data for intercomparison in this reasonably complex meteorological situation. Even given the observed winds, there is not sufficient information to be certain that the same air parcel sampled on the ground was also sampled by the aircraft. The
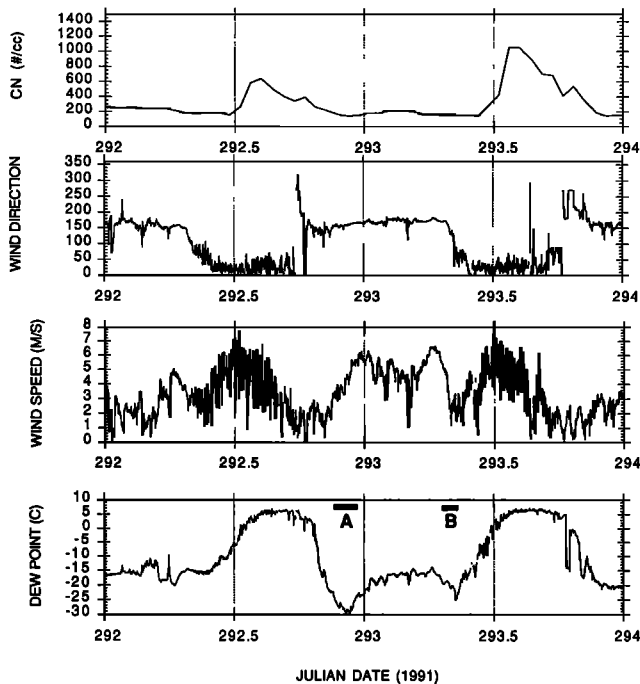
Figure 2. Local conditions of condensation nuclei (cubic centimeters), wind direction, wind speed (meters per second), and dew point at Mauna Loa Observatory near the time of the flyby mission. Heavy horizontal bars A and B indicate the time periods from used for comparison to the aircraft measurements. "A" indicates the ozone maximum period (see Table 2) and "B" is the overflight (see Table 3).

most direct, but most limited, comparison is during the MLO overflight. Here the aircraft came nearest in time and space to MLO. Along with the close proximity of the measurements, the observation that dew point measured aboard the aircraft (-22° ±1.7°C) was near that measured at the ground site (-19.5 ± 1.0°C) is a reasonable indicator that the same air mass was being sampled during the overflight. A second, reasonably direct comparison between the measurements is available for an air mass which intersected the MLO site between 2130 and 2400, just prior to the PEM-West flight operations. As noted, during this period there was a pronounced decrease in dew point and an increase in ozone mixing ratio. Wind direction and speed are consistent with the assumption that the same air mass (or a portion of it) was encountered by the aircraft during the western segment of the island circle leg (0600-0615 HST). Ozone shows a marked increase of ≈10 ppbv during that time; dew point, however, is not uniformly low, but shows a spike of more moist air during this segment. The ozone maximum observed in situ during the island circle appears to be related to the layer observed earlier in the lidar section. A summary of the ground-based and aircraft measurements for the two periods of most direct comparison are given in Tables 2 and 3.

The data presented in Tables 2 and 3 indicate the level of agreement between the ground-based and airborne measurements. It should be emphasized that these limited time periods represent a brief snapshot or subsample of the entire data sets. Because of the individual measurement imprecisions and the relatively little data available for comparison, it is difficult from these data alone to ascertain possible systematic, calibration, offset, or sampling biases contained in the different
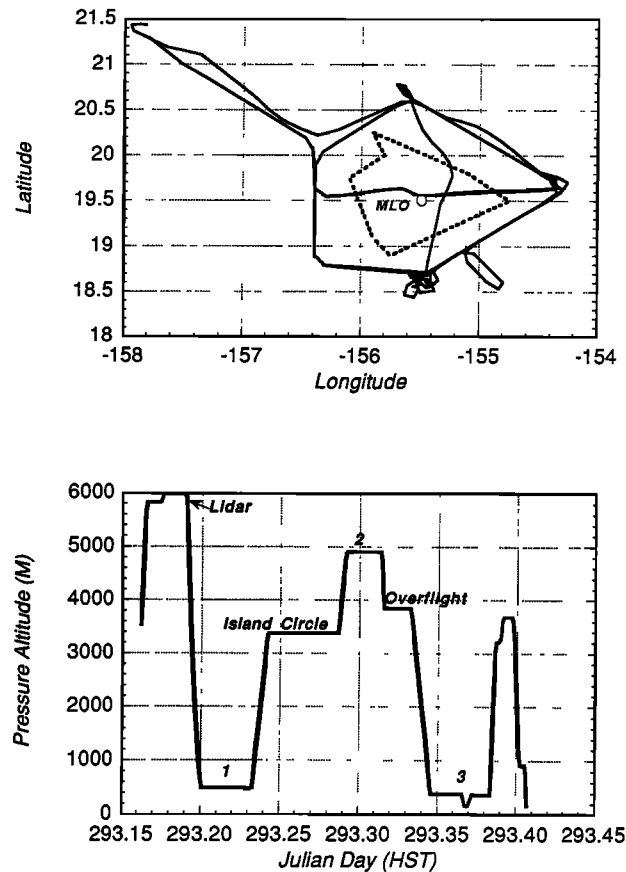

Figure 3. Flight track and altitude profile of Flight 20. Numerals 1 - 3 indicate chevron patterns east of Hawaii. These correspond to legs 2, 4, and 6, respectively, described in the text.

measurement sets. It is useful to be able to extend the comparison using a larger data set. One way to obtain additional information for evaluating measurement comparability is by examining tracer-tracer correlations from both ground-based and aircraft data. We examine correlations between selected trace gas measurements for one to several
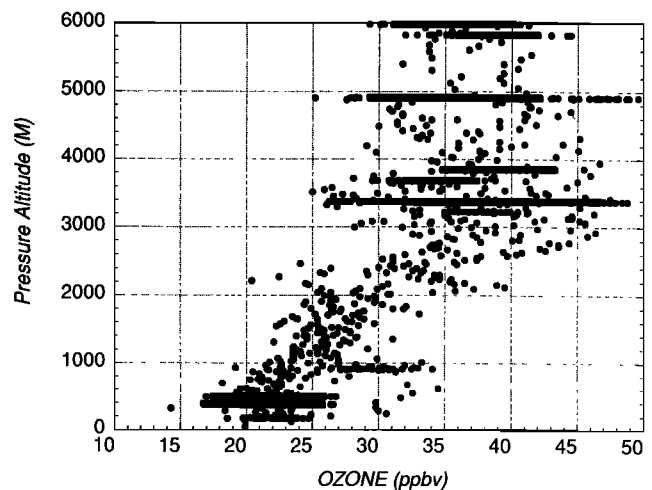

Figure 4. Lidar cross section of ozone mixing ratio (parts per billion by volume) during the first high-altitude overflight of Hawaii.

MAUNA LOA FLY BY
PEM WEST A   FLIGHT 20   10-20-91
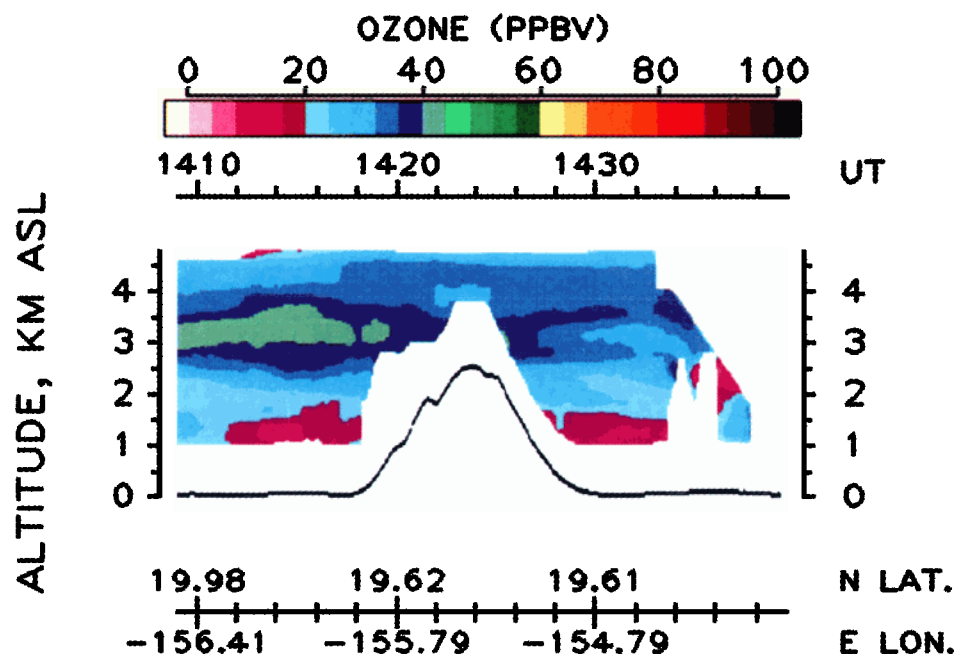## OZONE DISTRIBUTION

Plate 1. Vertical profile of ozone mixing ratio from the in situ aircraft measurements. These data are a compilation of all ozone measurements during the flight near Hawaii.

Table 2. Intercomparison of Measurements From the Nearest Flyby to MLO

Measurement	PEM - WEST A					MLOPEX					Ratio
	N	Minimum	Maximum	Mean	S.d.	N	Minimum	Maximum	Mean	S.d.	
Ozone, ppbv	142	36	43	40	2	18	34.5	37.2	35.9	0.7	1.11
CFC 12, pptv	17	491	513	500	5.2	2	496	497	496	0.5	1.01
CFC 11, pptv	17	260	271	266	2.5	2	269	270	270	1.3	0.98
CH_3CCl_3, pptv	17	125	156	144	6	2	138	141	140	1.9	1.03
CCl_4, pptv	17	104	113	109	2.1	2	104	105	105	0.3	1.04
N_2O, ppbv	164	309.0	309.5	309.3	.09	2	308.3	308.9	308.6	0.4	1.00
C_2Cl_4 (IS)*, pptv	6	3.4	5.7	4.3	0.8	2	2.2	2.5	2.3	0.2	1.87
C_2Cl_4 (SS)*, pptv	17	2.3	3.2	2.8	0.3						1.21
Methane, ppbv	178	1711	1718	1714	2	1			1718		1.00
Ethane, pptv	17	471	502	485	11	2	477	519	499	30	0.97
Ethene, pptv	17	11	25	16	3.7	2	0.6	1.1	0.9	0.4	17.8
Propan, pptv	17	15	25	19	2.6	2	20.5	28.8	24.7	5.9	0.76
Propene, pptv	2	12	14	13	1.4	0					-
n-Butane, pptv	2	6	7	6.5	1.4	1			0.3		21.7
Ethyne, pptv	17	35	43	38	2.4	2	52.1	63	57.6	7.7	0.66
Benzene, pptv	8	6	16	9	3.7	1			10.2		0.88
CO, ppbv	178	71.2	74.9	72.6	0.9	3	84	92	88	4	0.83
NO (LIF)*, pptv	11	4.1	10.7	6.9	2.2	19	5	6.7	5.7	0.5	1.21
NO (CL)*, pptv	13	4.8	10.8	7.6	1.6						1.33
NO_2, pptv	11	12.2	21.5	14.1	2.7	17	15	18	16.7	0.9	0.84
HNO_3 (Den)*, pptv	1			21		2	62	71	66	6.2	0.32
HNO_3 (Ny)*, pptv						2	52	60	56	5.8	0.38
D NOy, pptv									70		0.30
NO_3-, pptv	0					1			4.9		-
PAN, pptv	6	8	18	14	4.5	2	6.3	7.1	6.7	0.6	2.1
NOy (LIF)*, pptv	11	105	167	132	18	7	125	146	135	9.4	0.98
NOy (CL)*, pptv	10	89	120	109	10						0.81
H_2O_2, pptv	59	657	823	737	37	23	450	570	500	30	1.47
H_2O_2 (TDL)*, pptv						1			535	88	1.38
ROOH, pptv	59	260	328	288	15	13	220	300	260	20	1.11
SO_2, pptv	4	39	41	40	1.2	23	-113	120	24	61	1.67

Ground and airborne measurements are taken from 0734 to 0800 HST (see text).
* IS, in situ; SS, stainless canisters; LIF, laser induced fluorescence; CL, chemiluminescence; TDL, tunable diode laser; Den, Denuder; Ny, Nylon.

Table 3. Intercomparison of Measurements From the Ozone Maximum Period

Measurement	PEM - WEST A					MLOPEX					
	N	Minimum	Maximum	Mean	S.d.	N	Minimum	Maximum	Mean	S.d	Ratio
Ozone, ppbv	90	40	49	44	2	129	39	47	44	2	1.0
CF-12, pptv	4	495	506	501	5.6	2	484	496	490	8.4	1.02
CF-11, pptv	4	263	268	265	2.5	2	270	269	270	0.6	0.98
CH_3CCl_3, pptv	4	149	157	154	4	2	140	140	140	0.4	1.10
CCl_4, pptv	4	109	131	110	1.5	2	104	105	105	0.2	1.05
N_2O, ppbv	119	308.8	309.2	309.1	.08	2	307.9	308.1	308.0	0.1	1.00
C_2Cl_4 (IS)*, pptv	3	3.0	3.8	3.4	0.4	1			2.4	-	1.42
C_2Cl_4 (SS)*, pptv	4	3.2	5.2	4.0	0.9						1.67
Methane, ppbv	142	1720	1728	1725	1.9	4	1736	1741	1738	2.7	0.99
Ethane, pptv	4	516	547	531	14	1			502		1.06
Ethene, pptv	4	11	22	15	5	1			9.6		1.56
Propane, pptv	4	22	26	24	1.7	1			23.7		1.01
Propene, pptv	2	5	12	8.5	4.9	1			5.6		1.85
n-Butane, pptv	0					1			1.8		-
Ethyne, pptv	4	49	53	52	1.9	1			62.5		0.83
Benzene, pptv	4	7	18	11	5.2	1			12.1		0.91
CO, ppbv	142	77.4	80.6	79.5	.8	8	85	93	89	2	0.89
NO (LIF)*, pptv	9	1.4	1.5	1.4	.05	92	-1.3	.97	-0.2	0.45	-
NO (CL)*, pptv	8	-2.5	1.5	-0.9	1.2						
NO_2, pptv	9	9 5	19.1	13	3.2	80	21.3	30.4	25.8	1.7	0.50
HNO_3 (Den)*, pptv	1			22		0			-	-	-
HNO_3 (Ny)*, pptv						1			57.2		0.38
D NOy, pptv									120		0.18
NO_3^-, pptv	1			11		1			6		1.83
PAN,pptv	3	4.3	14	9.7	4.9	6	6.7	7.6	7.2	0.4	1.34
NO_y (LIF)*, pptv	9	123	149	135	11	32	167	228	201	18	0.67
NO_y (CL)*, pptv	8	66	94	74	9.6						0.37
H_2O_2, pptv	57	605	721	655	29	125	390	550	460	36	1.42
H_2O_2 (TDL)*, pptv						5	382	586	478	80	1.36
ROOH, pptv	59	227	343	287	31	59	170	260	210	20	1.37
SO_2, pptv	2	42	47	44.5	3.5	117	-106	118	3	52	14.8

Airborne measurements are from 0600 to 0615 (Oct. 20) and ground-based measurements are from 2130 to 2400 (Oct. 19) (see text).

*IS, in situ; SS, stainless canisters; LIF, laser induced fluorescence; CL, chemiluminescence; TDL, tunable diode laser; Ny, Nylon filter; Den, Denuder.

days at the ground site and over an appropriate altitude range for the aircraft. This type of correlation can extend the comparison to a larger data set based on extended timescales for the ground-based site and over larger space scales for the aircraft measurements. Over a time period near the flyby experiment, the MLO site samples air masses and mixtures characteristic of the midtroposphere of the central Pacific. During the flyby period, the aircraft should subsample these same air masses seen at the ground site. Even if the air masses are not sampled coincidently, there should be a consistent tracer-tracer correlation observed in the ground-based and aircraft data sets if the measurements are comparable. We will use this approach for several of the trace gases examined here.

Discussion

Ozone

The ozone concentrations measured aboard the aircraft and at the MLO site are in excellent agreement. During both the overflight and the "ozone maximum" period, the measurements agree within ±1 standard deviation of the variation observed over each time period, and also within the stated precision of the instruments (±2 ppbv). Because of the good agreement between these data sets, ozone will be one of the gases used in subsequent analyses when examining trace gas correlations for the ground-based and aircraft data sets.

Long-lived Halocarbons and N_2O

The agreement between canister sampling (PEM) and in situ analysis for the fluorocarbons CFC-12 (CCl_2F_2)and CFC-11 (CCl_3F) (NOAA/CMDL) is excellent (within 2%) for both compounds. Average differences are higher (7 and 5%) for methyl chloroform and carbon tetrachloride. For both of these molecules, the canister results are higher than in situ data. Typically, reports of sample artifacts for methyl chloroform and carbon tetrachloride in canisters indicate losses within the canister rather than positive artifacts. Thus, the observed bias suggested a difference in calibration scales for methyl chloroform and carbon tetrachloride used by the individual laboratories. The canister results are consistent with those of the University of California, Irvine (UCI) latitudinal monitoring project, and the CMDL data are consistent with their long-term monitoring network data. These calibration differences between the CMDL and UCI concentration estimates are not significant when dealing with individual data sets. Within each data set, relative changes in the concentration of these tracer species can provide information about source regions and transport effects. However, consistency in absolute calibration is required to properly combine data sets and for use in evaluating global budgets and trends of these trace gases. The utility of intercomparisons is clearly shown in this case where calibration offsets can be identified and addressed.

Measurements of N_2O show excellent agreement, well within the stated uncertainty limits. In addition to the direct intercomparisons shown in Tables 2 and 3, the entire data sets were used to provide better statistical significance to the comparison. During the full autumn 1991 intensive there was no measurable trend in N_2O mixing ratio. Similarly, there was no measurable difference in N_2O at different locations and altitudes of the aircraft. Measurements from the autumn 1991 intensive and the full N_2O data set from Flight 20 yield an average (±2 standard error) N_2O mixing ratio of 307.9±.04 (MLO) and 309.25±.01 (PEM) ppbv.

Tetrachloroethylene

This compound is more reactive than the halocarbon species just mentioned, and its mixing ratio is nearly 2 orders of magnitude lower. This molecule has been used as a tracer of urban source emissions in the remote atmosphere [*Atlas et al.*, 1992a; *Singh et al.*, 1994; *Blake et al.*, 1994]. During the comparison periods, the two sets of aircraft measurements agreed to within 1.5 pptv. Evaluation of the time series of data through the flight show no consistent bias between the two sets of measurements, but no significant correlation either (Figure 5). For the entire flight, both aircraft data sets had a mean mixing ratio of 4 pptv with a standard deviation of 1.3 pptv (in situ) and 0.9 pptv (canister). The ground measurement was significantly lower at 2.4 pptv. The difference could be the result of a variable residual signal or blank level in the analytical systems or from differences in the standards used. The range of mixing ratios seen here is small, and data are insufficient to separate these effects. On the basis of these data we can approximate an uncertainty of ±1 pptv for the measurement of tetrachloroethylene.

Methane and Non-methane Hydrocarbons (NMHC)

There were only a few measurements of hydrocarbons available for direct comparison, but there seemed to be some consistent relationships between the sets of measurements. For methane, excellent agreement between the airborne TDL
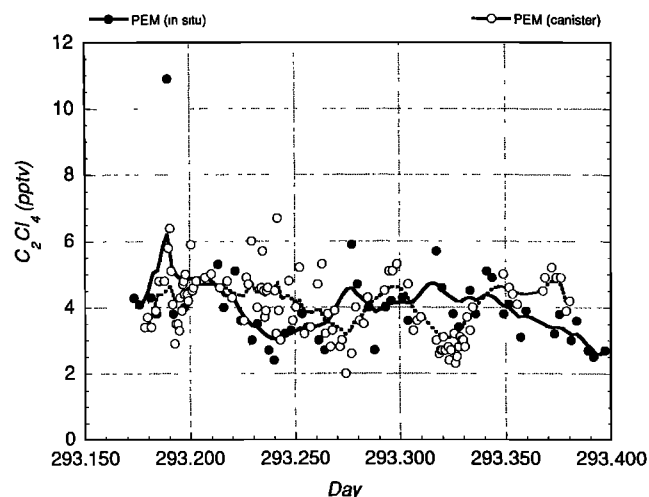

Figure 5. Time series of tetrachloroethylene (C_2Cl_4) mixing ratios from the airborne in situ GC measurements (solid circle and line) and from canister analyses (open circles, dotted line)

system and the ground-based GC measurement was obtained. During the overflight, these measurements differed by only 4 ppbv, and for the ozone maximum period, the difference was 13 ppbv (<0.8%). For the NMHC, agreement between the measurement sets depended on the individual species (See Tables 2 and 3). Ethane, propane, and benzene appear to be in very good agreement considering the associated analytical uncertainties. Ethyne and the alkenes do not agree well during the comparison periods. Mixing ratios of butane are too near the detection limit for meaningful intercomparison here.

The data comparison can be extended by examining correlations between different hydrocarbon compounds. A correlation plot of ethane versus propane shows a consistent relationship from the two data sets (Figure 6a). For days 290-296, the MLO data are described by the relationship: ethane=435+2.41*propane; the PEM-West data the relationship is: ethane=458+2.55*propane. Ethyne appears to be consistently higher in the ground-based measurements, and a correlation plot of ethane versus ethyne confirms the consistent bias between the two data sets (Figure 6b). The data indicate an approximate 20 - 30% difference in calibration for ethyne or a consistent bias of about 20 pptv higher mixing ratios in the ground-based measurements. For the C_2 and C_3 alkenes, measurements are higher in the canister samples than from the in situ ground-based measurements. During the comparison periods, differences are in the range of a few to 15 pptv. Correlation plots from the two data sets indicate the same relative slope between ethene and propene; however, the ground-based data extend to lower mixing ratios of ethene and propene compared to the aircraft data. Difference in the minimum levels are about 10 pptv of ethene and 3 pptv of propene (Figure 6c). Certainly, these differences could be due to the limited sampling of the aircraft during this period and uncertainties at the limit of detection, or possibly to small biases between in situ and canister-based sampling.

Greenberg et al. [this issue] describe a comparison of their own in situ and canister-based NMHC measurements taken during MLOPEX 2. Interestingly, their data point to the same biases or offsets as described here. The differences they observed for ethyne could be ascribed either to calibration differences between different instruments used to analyze canister and in situ samples or to losses of ethyne in canisters. No cause could be ascribed to the positive bias they observed for alkenes in canisters (ethene, 14 pptv; propene; 8 pptv), but it is interesting to note the same level of difference that is reported here between the in situ and aircraft samples. No ground-based canisters were collected during the flyby for comparison of canister-based collections.

In the remote atmosphere, where the reactive hydrocarbon levels are extremely low, levels of reactive alkenes of even a few parts per trillion by volume may be significant to local photochemical processes. Thus it is important to identify the source of a small bias for ethene and propene mixing ratios. The low levels of alkanes and ethyne do not contribute significantly to local photochemistry, but the ratios of these hydrocarbons are often used to infer photochemical "ages" of air masses or to suggest potential emission sources. Biases and uncertainties associated with these ratios can limit their usefulness, but on-going intercalibration efforts [e.g., *Apel et al.*, 1994] should lead to improved data comparability for NMHC.
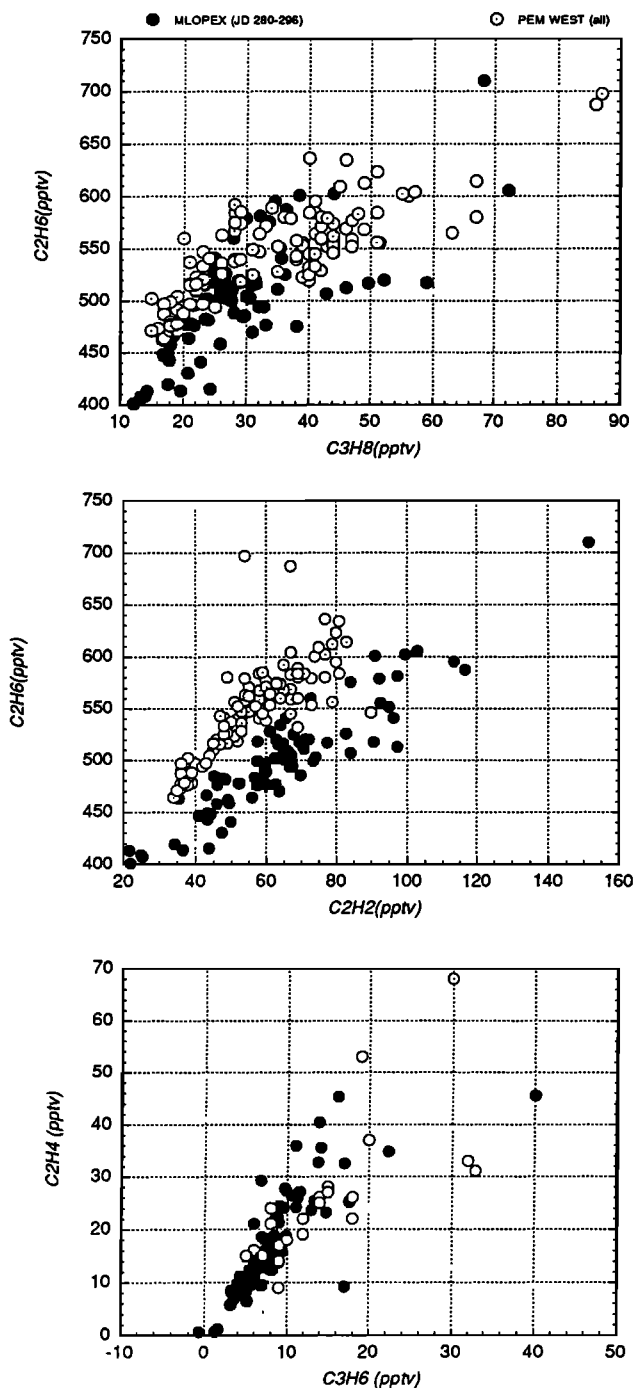
Figure 6. (top) Correlation of ethane and propane from MLOPEX (Julian date 280 - 296) (solid circles) and from PEM-West (all data, Flight 20) (open circles). (middle) Correlation of ethane and ethyne from MLOPEX (Julian date 280 - 296) (solid circles) and from PEM-West (all data, Mission 20) (open circles). (bottom) Correlation of ethene and propene from MLOPEX (Julian date 280 - 296) (solid circles) and from PEM-West (all data, Flight 20) (open circles).

Carbon Monoxide

Carbon monoxide measurements at the ground site were 11 - 18% higher than observed aboard the aircraft. Comparison of the CO/ethane correlations from both data sets suggests that there is a consistent bias between the airborne and ground-

based measurements. An estimated uncertainty of ±15% was assigned to the ground-based data for this intensive, because of instrumental problems during the MLOPEX 2 autumn intensive. With the combined uncertainties, the data sets become comparable, but the reason for the average bias is undetermined. Subsequent CO measurements with a reconfigured instrument during later MLOPEX intensives showed increased precision and excellent agreement with an independent CO instrument operated by CMDL during the summer 1992 intensive [*Greenberg et al.*, this issue].

NO + NO₂

The comparison during the O_3 maximum was in the nighttime for both the ground-based and airborne data sets. During the dark, NO is expected to be zero, and all systems were in good agreement to within about 1 pptv for this period. One airborne system (LIF) reported data as limit of detection (S/N=2/1; 1.4 - 1.5 pptv), while the other (CL) system showed a 1.2 pptv standard deviation around an average of -0.9 pptv. The ground based system averaged -0.2 pptv (±0.5 pptv). During the early morning flyby period, the sun had risen and NO had increased several parts per trillion by volume. At this time, all systems were comparable at 6.7 ± 1 pptv. These data are well within the specified uncertainties of the NO instrumentation.

The agreement between the NO_2 measurements was inconsistent for the two comparison periods. NO_2 measurements from both instruments were comparable during the overflight period within the observed variation. A difference of 2.6 pptv during this period was within the standard deviation of the measurements. Measurement of NO_2 in the ozone maximum, however, was quite different. A factor of 2 difference (=13 pptv) is found between the airborne and ground-based measurement, and this is near the limit expected from the combined instrumental uncertainties. At this time, we have no suggestions to account for this apparent discrepancy.

HNO₃ and NO₃⁻

Nitric acid and particulate nitrate data are difficult to evaluate because of the relatively long sample integration times, and, consequently, few data are available for comparison. During the overflight, three sets of ground-based measurements of nitric acid (using different techniques) averaged ≈64 pptv with a ±10% standard deviation. The single integrated measurement from the aircraft was 21 pptv. During the ozone maximum period, not all ground-based instruments were operating, and there is a discrepancy between the two available measurements. Because of the long integration time of the filter technique and the variable conditions during the ozone maximum period, the filter data may not be appropriate for comparison here. The NO_y difference technique measured nitric acid at ≈120 pptv during the ozone maximum comparison period. The denuder measurement came on line shortly after the ozone maximum had past MLO site, and it showed comparable mixing ratios and temporal trend compared to the NO_y difference technique. The aircraft nitric acid measurement was 22 pptv, still a factor of 2.5 to 5 times less than that observed on the ground. Only one comparison of particulate nitrate was made. Both measurements showed low values of aerosol NO_3^-, with the aircraft measuring 5 pptv higher than the ground site.

The large difference in nitric acid levels observed in the two data sets can have important implications on the reservoirs and cycling of NO_x in the troposphere. Earlier side-by-side tests of mist chamber with the denuder system and with the filter pack (E. Atlas, unpublished data, 1991) showed agreement within about ±25% or better. This suggests that there were some instrumental problems during the flyby which influenced the results in this case. On the basis of the comparisons to NO_y, reasonable agreement between ground based measurements and known problems with nitric acid transmission through inlet systems suggests nitric acid was underestimated in the aircraft measurements during this flyby intercomparison. One possibility is inlet contamination by seasalt during low-altitude flight legs, but other reasons for the discrepancy cannot be excluded. Subsequent tests of the same inlet system on later flights showed a nitric acid passing efficiency of 76±7% [B. Talbot et al., submitted in August 1995 for special J. Geophys. Res. issue on PEM-West B].

Peroxyacetyl Nitrate (PAN)

During both comparison periods, the airborne instrument measured a higher mixing ratio of PAN compared to the ground site. The differences were from 3 to 7 pptv, and mean values were only twice these deviations. Visual inspection of the data using a correlation of PAN with ozone suggests a possible constant bias of ≈5 pptv PAN between the data sets (aircraft data higher than the ground-based data), but this is near the combined uncertainties of the two instruments. This level of agreement is better than that suggested in a previous intercomparison between these same laboratories during the GTE - CITE 2 campaign [Gregory et al., 1990]. The earlier comparison, which encountered a larger range of PAN mixing ratios, suggested an average bias of 17 pptv for PAN mixing ratios less than 100 pptv (also with NASA > NCAR).

Total Reactive Oxidized Nitrogen (NO_y)

Two instruments were measuring NO_y aboard the aircraft. During the overflight, both sets of aircraft measurements were in reasonable agreement with the ground-based measurement, with the mean value from the airborne CL instrument slightly lower than the others. The three sets of measurements (±1 s.d.) were PEM: LIF = 132±18; CL=109±10: MLO: 135±9 pptv. However, there were significant differences between measurements for the earlier ozone maximum period. There was a maximum difference of nearly a factor of 3 between the mean mixing ratios from the different instruments, and both airborne instruments measured a lower NO_y mixing ratio compared to the ground-based instrument. The mean and standard deviations were PEM: LIF = 135±11; CL = 74±10; MLO: 201±18 pptv.

A useful way to evaluate these data sets is with the correlation between ozone and NO_y, since a close correlation of ozone with NO_y is often observed in the atmosphere [Hübler et al., 1992a,b; Murphy et al., 1993]. A comparison of the NO_y/ozone correlation from the three data sets shows quite different relationships (Figure 7). The ground-based data show the best correlation. The slope of NO_y/O_3 = 5.4, which is within the range of ratios reported for the remote troposphere and is characteristic of much of the September/October data at MLO. Approximately two thirds of the airborne LIF measurements of NO_y fall within the spread of
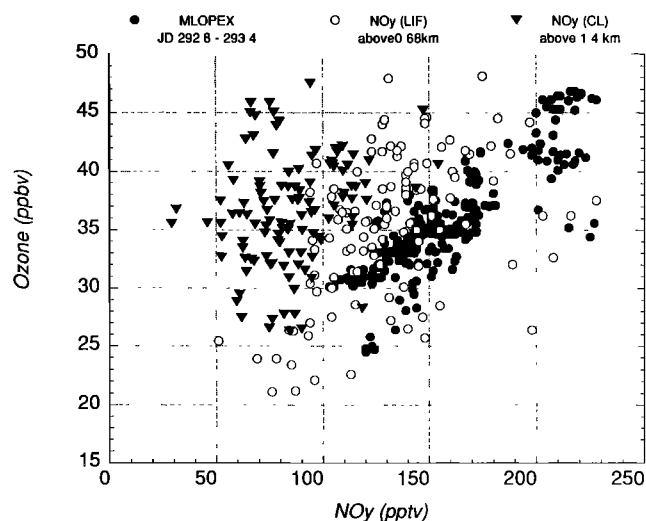

Figure 7. Correlation of NO_y with ozone from MLOPEX data (Julian date: 292.6 - 293.4)(solid dots) and from airborne measurement above 600 m. Open circles: PEM LIF measurement; inverted triangles: PEM CL measurement.

the ground-based correlation, with a tendency for those falling outside the correlation envelope to have lower NO_y at a given ozone mixing ratio. The NO_y/ozone correlation from the airborne CL instrument is nearly independent of ozone. Compared to the ground-based correlation envelope, most data from the airborne CL instrument have a lower NO_y mixing ratio at a given ozone level. This trend suggests inlet losses of NO_y compounds, perhaps nitric acid [Crosley, 1996]. It should be emphasized, though, that the correlation shown in Figure 7 does not necessarily represent the behavior of the NO_y instruments during other flights of the PEM-West A mission. A more complete description of the full NO_y data sets from PEM-West A can be found in work by Kondo et al. [1996] and Singh et al. [1996].

Hydrogen peroxide/organic peroxides

Hydrogen peroxide from the dual enzyme, aqueous coil data is consistently lower in the ground-based measurements by 42 - 47% compared to the aircraft data. The absolute difference in mixing ratio is near 0.2 ppbv. Organic hydroperoxides, which were found to be exclusively methyl hydroperoxide, are also lower in the ground-based measurement by 11 - 37%. This is an absolute difference is 0.02 - 0.08 ppbv, which is near the uncertainty of the measurement.

During this same time, hydrogen peroxide was also measured at MLO by the TDLAS system. During the two short intercomparison periods, the TDLAS system was in good agreement with the ground-based dual enzyme technique. The remainder of the night the TDLAS data were lower than the coil data by an average of 0.14 ppbv. A ground-based comparison of the same instrumentation was conducted during the MLOPEX winter intensive (1992) and is discussed in detail by Staffelbach et al. [this issue]. They found good agreement for hydrogen peroxide in dry air masses, and also reasonable agreement for organic hydroperoxides at mixing ratios near 0.2 - 0.3 ppbv. Thus the differences observed during the present comparison for hydrogen
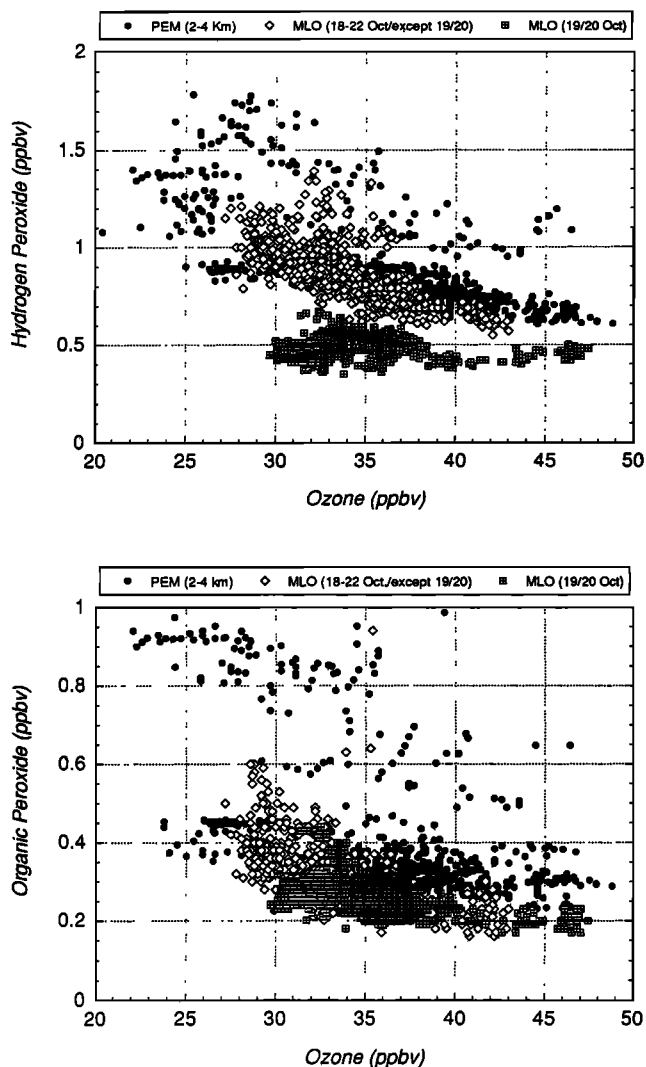
Figure 8. (top) Correlation of hydrogen peroxide and ozone from MLOPEX data (nights of 291/292, 293/294, and 294/295)(crosses) and from flyby period (night of 292/293) (squares); PEM Data from 1200 to 4300 m are shown as open circles. (middle) Correlation of organic peroxides and ozone from MLOPEX data (nights of 291/292, 293/294, and 294/295)(crosses) and from flyby period (night of 292/293) (squares); PEM data from 1200 to 4300 m are shown as open circles.

peroxide are outside the range generally observed in the subsequent comparison.

Ozone/peroxide correlation plots for the time period on either side of the flyby indicate that the actual period of the flyby had low hydrogen peroxide mixing ratios measured at MLO (Figure 8a). Organic peroxides, though, appeared to be consistent during the flyby compared to adjacent days (Figure 8b).

There are several possible reasons for the observed lower hydrogen peroxide during the night of October 19-20, though none are fully consistent with other chemical observations at the time. First, the lowered hydrogen peroxide relative to methyl hydroperoxide at MLO suggests preferential removal of hydrogen peroxide by aqueous processing, since hydrogen peroxide is more soluble than methyl hydroperoxide. However, other soluble species do not seem to be affected. For

example, the nitric acid/NO_y ratio remains uniform in the FT over the same time period that H_2O_2 is changing. Another possible influence on H_2O_2 is heterogeneous oxidation of SO_2 to sulfate. Thus we examined possible influence of SO_2 from vocanic emission, but no trends or episodes of SO_2 emission from the volcano could be correlated with the lower hydrogen peroxide levels. For example, there was no measurable increase in SO_2 during the ozone maximum period of the flyby, and hydrogen peroxide levels at the ground remained consistently low compared to the aircraft measurements. This suggests that lower levels of hydrogen peroxide also observed during the overflight period are not influenced by the small SO_2 emissions from nearby vents. It appears that unspecified factors, including meteorology, influenced the ground-based hydrogen peroxide measurements during the night of the October 19-20. In their examination of the full peroxide data set, Staffelbach et al. [this issue] comment on the pattern of days of consistent comparison interspersed with periods of poor data comparability. The night of the flyby may be one of the periods of relatively poor correlation.

SO₂

Though sulfur dioxide was measured at the ground site, the instrumentation was not designed for accurate measurement of background levels of SO_2. Rather, the main use of the instrument was to identify periods at the MLO site which were influenced by volcanic emission. Episodes could be larger than several parts per billion by volume of SO_2, but smaller scale emissions, such as that observed during the flyby, could be detected (G. Hübler, personal communication, 1992). Background levels of SO_2 measured aboard the aircraft were near 40 pptv, and indicate little influence of volcanic emission on the atmosphere near Hawaii during this flyby experiment. Whether other measurements are influenced by the low-level SO_2 emissions cannot be determined by this data intercomparison.

Summary

Most of the instrumental protocols used in the study described here are designed to cover a very wide range of chemical conditions in the atmosphere. Thus, instruments are designed to encounter air masses with a large range of mixing ratios for individual species. In the very broad sense, chemical measurements from MLOPEX and from the PEM-West Flyby indicate a "clean" maritime atmosphere relative to near-source chemical signatures. Under these challenging conditions, instruments are being pushed to perform near the lower limits of detection, and uncertainties can be large. The limited intercomparison reported here illustrates the uncertainties associated with obtaining and interpreting chemical measurements from the remote atmosphere. The data comparison shown here is not from novice experimenters, but represent the efforts of experimenters who are experienced in the use of their instrumentation in challenging environments.

For the most part, the measurements showed good comparability between the data sets, especially considering the low mixing ratios of most species, but there were enough inconsistencies to limit the use of the combined data to understand the chemistry of the mid-Pacific troposphere. One straightforward aspect to consider with respect to the MLO

site is the extent to which measurements at the ground-site are "representative" of the free troposphere near the altitude of the Mauna Loa Observatory. If ground-based measurements are biased by gases interacting with the lava surface, gases which can deposit readily would be expected to be lower at the ground site. Measurements most sensitive to this test would be NO_y, nitric acid, and hydrogen peroxide. During the flyby, NO_y (which is about 50% nitric acid at MLO [*Atlas et al.*, 1992b]) and nitric acid mixing ratios are consistently higher in the ground based measurements, but hydrogen peroxide is lower than expected at the groundsite. These sets of measurements provide an inconsistent answer to this question and indicate that there are potential instrumental biases or unexpected air mass processing which contribute to the discrepancy. A second example to consider is the partitioning of NO_y in the marine troposphere. It is clear from the differences in the NO_y measurements and in all the individual NO_y species that the data can show a strikingly different picture of the levels and partitioning of reactive odd nitrogen depending on the combination of data which is used. Whether the observed differences are related to any (or all) individual measurements cannot be fully resolved from this limited intercomparison. Other differences in calibration or measurement can provide conflicting interpretations to other data. The partitioning of peroxides between hydrogen peroxide and organic peroxides appears different between the ground and the aircraft for one of two cases. Differences in the partitioning may be interpreted on the basis of different removal rates for hydrogen and organic peroxides, but instrumental biases or calibration shifts may contribute to the uncertainty. Similarly, differences of only a few parts per trillion by volume in hydrocarbon mixing ratios may lead to different conclusions about source characteristics, photochemical processing, or the availability of reactive hydrocarbons in the free troposphere.

The data from this intercomparison show the level of uncertainty associated with particular measurements, though it should be emphasized that this intercomparison is a small snapshot of instrumental performance from a much larger data set. Special problems may have occurred in this time period which are not indicative of the overall instrument performance. Still, as chemical measurements improve, we begin to see that there are chemical and dynamical features in the remote atmosphere which can only be probed with increasingly more sensitive measurements with smaller uncertainties than exist at present for many chemical species. The data comparison here underscores the necessity of comprehensive measurement programs which can provide sufficient checks on data consistency and interpretations. This becomes especially important when examining subtle effects which may be typical of the chemistry of the remote troposphere.

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