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Measurement of O_3 and related compounds over southern Nova Scotia
1. Vertical distributions

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Abstract. As part of the North Atlantic Regional Experiment, the National Research Council of Canada Twin Otter aircraft was used to measure the concentration of O_3 and related compounds in the atmosphere over southern Nova Scotia. Forty-eight flights were conducted, primarily over the surface sampling site in Chebogue Point, Nova Scotia, or over the adjoining Atlantic Ocean. A typical flight included one or more vertical profiles from 30 m above the surface to an altitude of 3 or 5 km. We present here O_3 measurements and supporting chemical and meteorological data including NO_y, CO, accumulation mode aerosol particles, winds, temperature, and dew point. Data are presented in a format which illustrates day-to-day variability and vertical structure. We find that Nova Scotia is impacted by a wide variety of air masses with varying chemical content depending on flow conditions relative to the locations of upwind emission regions. As an aid to understanding the chemical composition of the air, we characterize four types of events: (1) moist continental boundary layer air with high concentrations of O_3 and other anthropogenic pollutants which is advected to Nova Scotia in relatively thin vertical layers, usually with a base altitude of several hundred meters; (2) "background" air with concentrations of anthropogenic ingredients much lower than experienced in continental pollution episodes but higher than observed in more remote regions of Canada, suggesting a dilute anthropogenic or biomass burning influence; (3) near-surface air which because of a strong temperature inversion over the Atlantic Ocean, is decoupled from air aloft, with the consequence that near-surface measurements do not give a representative view of the eastward transport of the North American plume; and (4) dry air masses with high O_3 concentration in which we have to distinguish between boundary layer and upper atmosphere source regions.

1. Introduction

Eastern North America is a major source region for many pollutants including sulfur and nitrogen compounds, CO, hydrocarbons, aerosol particles, and O_3. Prevailing winds transport these pollutants eastward where they affect air quality over the North Atlantic Ocean and eventually contribute to an increase in "background" levels over still larger spatial scales. There is concern that the chemical composition and oxidizing capacity of the northern hemisphere are being perturbed as a result of anthropogenic inputs. The observational basis for this concern is reviewed by *Fehsenfeld et al.* [this issue (a)].

Nova Scotia is located several hundred kilometers to the east-northeast of major industrial and population centers. Previous field measurement campaigns have indicated very high concentrations of O_3 and other pollutants when the wind flow places Nova Scotia in the North American plume [*Parrish et al.*, 1993; *Berkowitz et al.*, 1995]. Much lower concentrations are recorded when the wind flow is from the north, east, or south, placing Nova Scotia downwind of less populated Canadian areas or the Atlantic Ocean. A description of synoptic meteorology in the North Atlantic Regional Experiment (NARE) region and its effect on transport is given by *Berkowitz et al.* [this issue] and *Merrill and Moody* [this issue].

Ozonesonde measurements at Cape Race, Newfoundland, from the summer of 1991 show that concentrations at 1–2 km altitude can be a factor of 2 greater than occur near the surface [*Fehsenfeld et al.*, this issue (a)]. Aircraft measurements made during the summer of 1992 revealed that the transport of O_3 and other pollutants from North America was occurring in well-defined layers located several hundred meters above the ocean surface [*Berkowitz et al.*, 1995]. These studies indicated the importance of aircraft sampling in defining the chemical climatology of the North American pollutant plume.

As part of the NARE effort to investigate the North Amer-

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ican continental plume, the Atmospheric Environment Service of Canada (AES), Brookhaven National Laboratory (BNL), and the National Research Council of Canada (NRC) collaborated on aircraft measurements over the southern tip of Nova Scotia. A DHC-6 Twin Otter aircraft from the NRC Institute of Aerospace Research (IAR) served as the instrument platform. In addition to the instrumentation provided by AES, BNL, and IAR, hydrocarbon samples were analyzed at York University.

Our strategy was to make measurements at a fixed location and observe the characteristics of different air masses and meteorological systems as they impacted the area. This sampling strategy dictated frequent flights covering a restricted geographic domain. The Twin Otter conducted 48 flights between August 6 and September 8, 1993. Most flights were confined to a relatively limited area which included the surface site at Chebogue Point near the southern tip of Nova Scotia and also adjoining portions of the Atlantic Ocean. Flights usually included one or more vertical profiles from near the surface to either 3 or 5 km altitude.

The primary objective of this article is to present the O_3 measurements made by the Twin Otter and provide supporting meteorological and chemical data for interpreting these measurements. Data are presented in a format which illustrates the day-to-day and altitude variations in chemical composition. A discussion of winds and back trajectories relevant to understanding the recent history of the air masses sampled in Nova Scotia is included. We concentrate on several features of the data set:

1. Characteristics of air masses with high concentrations of O_3 and other anthropogenic pollutants are examined. As has been reported by others [*Berkowitz et al.* 1995; *Daum et al.*, this issue], we find many instances in which the North American pollutant plume has been advected eastward several hundred kilometers, maintaining high concentrations of multiple pollutants within a relatively thin vertical layer.
2. The composition of "background" air is compared with measurements in other remote locations and plumes. Trace gas concentrations are much lower than plume values when air flow is not from industrialized continental regions.
3. Chemical composition near the surface is compared with observations at higher altitude. We address the question of the representativeness of surface measurements in describing conditions in the continental plume.
4. Characteristics of dry air masses having high concentrations of O_3 are examined. We present measurements bearing on the question as to whether O_3 in these air masses has a primary origin in the lower troposphere or in the upper troposphere or stratosphere.

Part 2 of this study [*Kleinman et al.*, this issue] continues our examination of the distribution of O_3 and other trace substances as measured during the 1993 NARE intensive from the Twin Otter. Whereas the emphasis in part 1 is to provide an overview of the data set, the emphasis in part 2 is to discuss several flights in detail, give photochemical age estimates based on the concentration ratios of light hydrocarbons, and show how vertical lifting can modify the concentrations of soluble constituents. Measurements of winds [*Angevine and MacPherson*, 1995], peroxides (J. Weinstein-Lloyd, manuscript in preparation, 1996), horizontal transport of ozone and sulphur [*Banic et al.*, this issue], carbonyl compounds [*Lee et al.*, this issue], aerosol composition [*Chylek et al.*, this issue; *Li et al.*, this issue], and cloud chemical and microphysical properties [*Leaitch et al.*, this issue] are described elsewhere.

2. Experiment

Instrumentation

The NRC Twin Otter uses a noseboom-mounted Rosemount 858 five-hole probe and a Litton 90-100 Inertial Reference System to measure the three orthogonal components of atmospheric motion and the resulting wind speed and direction over a frequency range of 0–5 Hz [*MacPherson*, 1990]. A comparison of the aircraft-measured winds with those from a wind profiler during NARE concluded that any bias in mean winds was less than 0.1 m s^{-1} and that the random error in either system was less than 1 m s^{-1} [*Angevine and MacPherson*, 1995]. Geographical position was measured by an ARNAV R-40-AVA-100 Loran-C system. Total (dynamic) pressure was sensed by a Rosemount 102DJICG heated fast-response probe and corrected to static air temperature using total and static pressures measured on the nose-mounted gust boom. Dew point temperature was recorded from an EG&G, Inc., model 137-S10 chilled mirror sensor.

Table 1 lists the chemical, cloud microphysics, and radiometric instruments that were onboard the Twin Otter during the 1993 NARE intensive. Analysis of observations from many of these instruments, including a description of experimental techniques, are the subjects of separate studies, as indicated in the preceding section. Here we briefly describe the instruments used in the present study, which focuses on O_3; other anthropogenically generated trace gases (NO_y and CO); accumulation mode aerosol particles (PCASP); and the meteorological parameters, wind speed and direction, temperature, and dew point.

A three-channel NO_y chemiluminescence detector built at BNL was used for the first time during the 1993 NARE intensive. The three-channel design permits simultaneous measurement of NO (channel 1), NO + NO_2 (channel 2), and NO_y (channel 3). Dry ice is used to cool the three $1\frac{1}{8}$-inch-diameter photomultiplier tubes (Hamamatsu R-2228). A 300-W photolysis lamp converts NO_2 into NO for detection in channel 2. Conversion efficiency is 25% under the conditions of 200 torr and a residence time of ~3 s. Total NO_y is converted to NO in channel 3 in a heated molybdenum converter operating at 350°C. Conversion efficiency for NO_2 in this converter has been measured at 98 ± 2% during ground-based tests. Oxygen is supplied from an internal cylinder to a silent discharge ozone source. This source provides 100 sccm of ~1.5% ozone to each of the three channels. Zeroes were taken in flight by mixing the ozone with the sample stream upstream of the reaction chambers. The instrument occupies 89 vertical cm in a standard instrument rack and weighs ~90 kg (exclusive of the pump). Power consumption is ~550 VA (exclusive of the pump). A single stage pump weighing 26 kg with a 15-A, 24-V dc motor was used in this program. With this pump the reaction chamber pressure was limited to 20 torr with a 1 standard liter per minute (slpm) flow rate in each chamber. Under these conditions the absolute sensitivity of the instrument was ~350 c/s/ppbv. Instrument baseline (continuously monitored) varied from <100 to ~2000 c/s due to varying humidity (see below). The estimated statistical precision based on these figures for a 30-s integration time is <20–50 parts per trillion (ppt). Uncertainties in the overall system calibration add a factor of about ±15%.

Table 1. Twin Otter Instrumentation

Measurement	Instrument/Technique
Dry accumulation mode aerosol (0.12–3 μm)	PMS PCASP
In situ accumulation mode aerosol (0.3–20 μm)	PMS FSSP-300
Condensation nuclei	TSI 3025 CNC
Cloud droplets (2–40 μm)	PMS FSSP-100
Cloud particle 2D (25–800 μm)	PMS 2D Grey Scale probe
Liquid water content	PMS King probe, PMS FSSP-100
SO_2	TECO 43S (pulsed fluorescence)
NO_y	O_3 chemiluminescence, Mo converter
NO	O_3 chemiluminescence
H_2O_2	Kok, Fenton reagent, benzoic acid fluorescence
Total peroxide	Kok, PHOPAA fluorescence
O_3	TECO UV absorption
O_3 (fast response)	surface chemiluminescent reaction of O_3 with an organic dye absorbed on dry silica gel coated Al
CO	gas filter correlation
Soluble carbonyls	coil scrubber, derivitization with DNPH HPLC-UV/VIS detection
Hydrocarbons	stainless steel canisters, GC-FID
Inorganic ions, elemental carbon, trace metals, organic ions	47-mm filter sampling
Cloudwater sampling for inorganic ions, H_2O_2, $CH_2(OH)_2$, HCOOH, trace metals, elemental carbon	two modified Mohnen-type cloudwater collectors
UV irradiance (up and down)	two UV Eppley radiometers
Visible irradiance (up and down)	two Kipp and Zonen pyranometers
Formic, acetic, and nitric acids	wet scrubbing and IC
Dimethylsulphide	accumulation sampling and GC

The inlet was designed to minimize losses of nitric acid and particulate nitrate. A $\frac{3}{8}$-inch-OD Teflon tube led air under ram flow conditions to the inlet of the instrument. A straight piece of $\frac{1}{4}$-inch-OD Teflon tubing ~20 cm in length connected the inlet to the heated molybdenum converter. This arrangement has demonstrated rapid response to nitric acid in ground-based tests. Channels 1 and 2 were preceded by a 1-μm Teflon filter to remove particulate matter. During instrument operation in the vicinity of the airport, the $\frac{3}{8}$-inch inlet tubing was back flushed with air from a carbon-vane pump filtered through a charcoal filter and two 0.2-μm Teflon filters.

During the NARE intensive, several problems were observed with this instrument. Anomalous values of NO_2 were noted during early flights, and some unknown failure of the photolysis system was assumed. A significant shift in the zero baseline was noted in all three channels. The baseline shift was inversely related to the ambient water vapor and was identical in all three channels. By operating channel 2 in continuous zero, the zero levels in the other two channels were determined to within 20–50 ppt, depending on humidity. In the future this problem will be addressed by humidifying the sample stream. After August 25, the NO_y channel showed evidence of either a leak or contamination. The problem appeared to be sporadic and is the cause of several days of "missing" data.

CO measurements were made with a modified TECO Model 48 Gas-Filter-Correlation analyzer. The mirrors in the White cell were gold plated to improve reflectance in the infrared. Active temperature control of the White cell and the instrument interior reduced signal drift and noise. Tests have shown a zero shift of −40 ppbv/°C with the temperature inside the instrument. Sample air was taken from a $\frac{3}{8}$-inch-OD Teflon tube operating under ram flow conditions. The air passed through a 1-μm Teflon filter and then was dried in a molecular sieve cartridge. Zeroes were taken by passing the dried stream through a Hopcalite cartridge. For a 30-s averaging time the noise on the signal was ~15 ppbv equivalent. The absolute accuracy tended to be controlled by the zero drift and is estimated at ±30 ppb + 15% as judged by the repeatability of measurements in the same air mass.

Continuous O_3 mixing ratios were obtained with a TECO-49 analyzer, having a full response time of 20 s, calibrated against a transfer standard traceable to National Institute of Standards and Technology (NIST). The inlet for ambient air was a 0.8-cm-ID forward facing Teflon line permitting ram flow. Dried-aerosol number concentrations in 15 size bins covering the range 0.12–3 μm were measured continuously using a Particle Measuring Systems PCASP-100X.

Data was recorded at a frequency of 1 Hz. For the purpose of this study, concentrations and other parameters were averaged over 30-s time intervals. This figure is a compromise between faithfully representing the high-frequency components from fast response instruments such as PCASP and temperature and improving signal-to-noise ratios for slower responding instruments such as CO. At typical flight speeds and climb and descent rates, a 30-s interval is equivalent to 2 km in a horizontal direction and 100 m in the vertical. Data in this study have been further subjected to an averaging over 200 m altitude bins. Averages for wind speed and direction are done on the vector components. Part 2 presents the 30-s averaged data as well as averages taken over the 5-min or so intervals coincident with hydrocarbon samples. All chemical data are presented as mixing ratios, i.e., ppbv for gases and number per standard cubic centimeter for aerosol particles (T = 0°C, P = 1 atm).

Flight Summary

The primary mission of the Twin Otter was to measure the chemical and physical state of the atmosphere above the NARE surface site in Chebogue Point, Nova Scotia. A total of 48 research flights were conducted, of which 47 yielded useful data on O_3 and other trace substances. These flights occurred between August 6 and September 8, 1993, covering most of the primary operating period of the surface site. There were 95 total research flight hours.

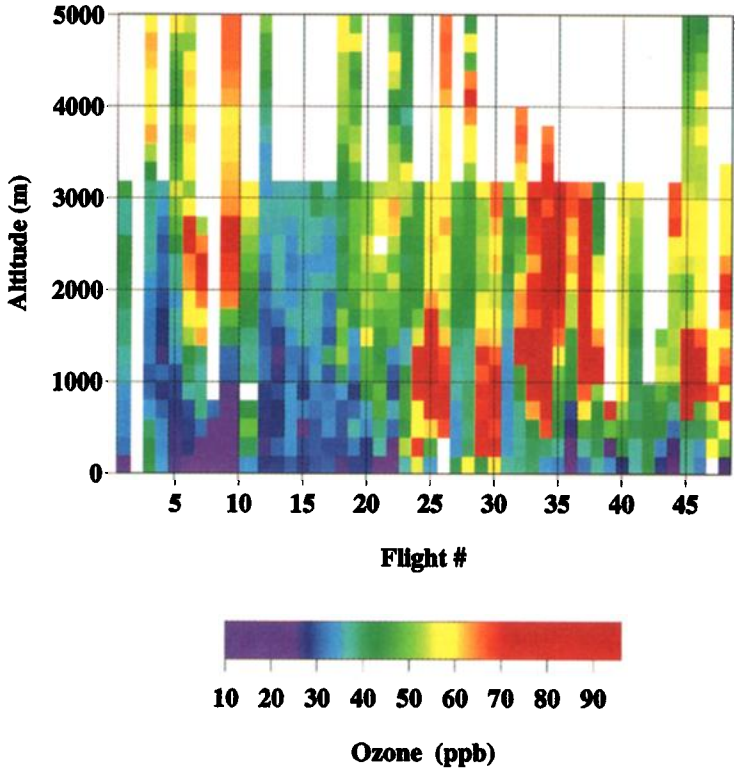

Plate 1. Ozone concentration as observed from the Twin Otter, averaged over 200 m altitude bins. Note that there is no flight 10; the color bars for flights 9 and 11 are 1.5 times the width of those for other flights. Correspondence between flight number and date is given in Table 2.

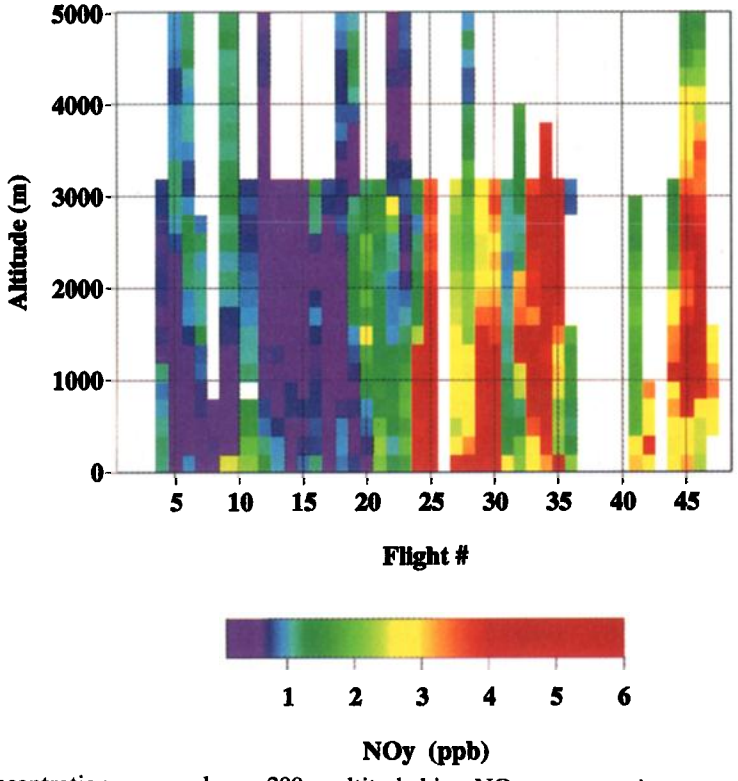

Plate 2. NO_y concentration averaged over 200 m altitude bins. NO_y concentration extends beyond values in color bar to 14.5 ppb.

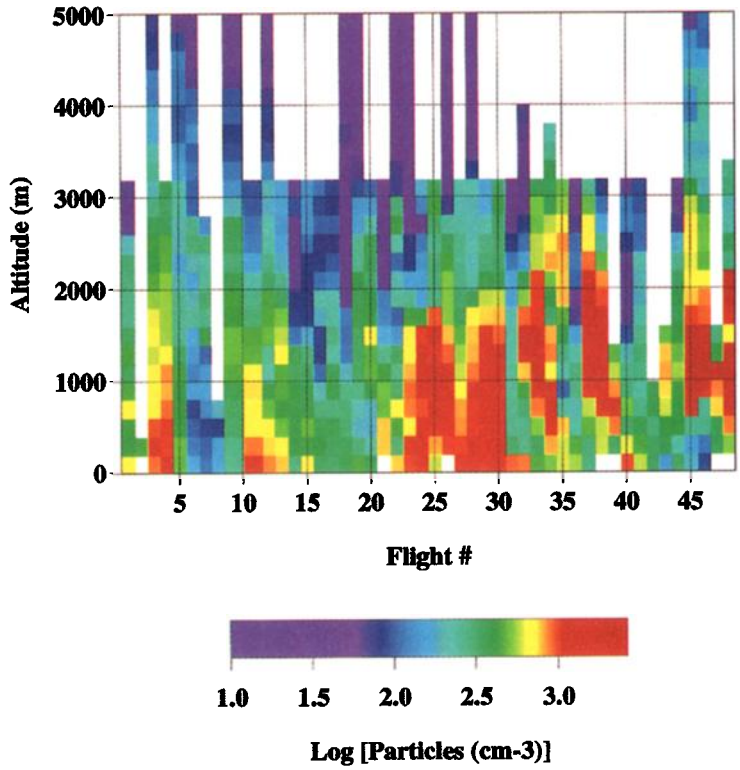

Plate 3. Logarithm of the number concentration of accumulation mode aerosol particles as determined from the PCASP detector. Diameter of dry particles ranges from 0.12 to 3 μm. Number concentration has been converted to standard conditions; P = 1 atm, T = 0°C. Values are averaged over 200 m altitude bins.

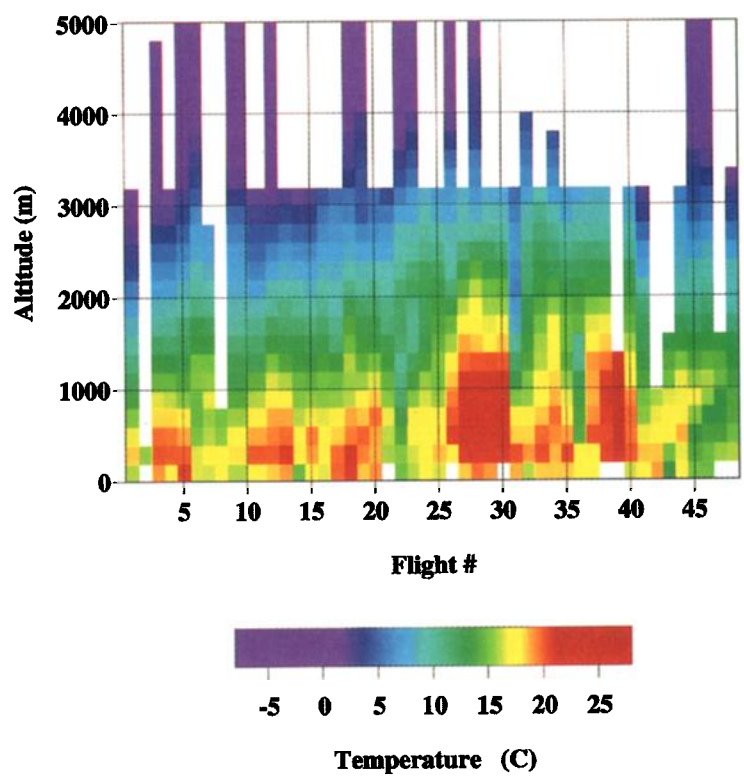

Plate 4. Temperature averaged over 200 m altitude bins.

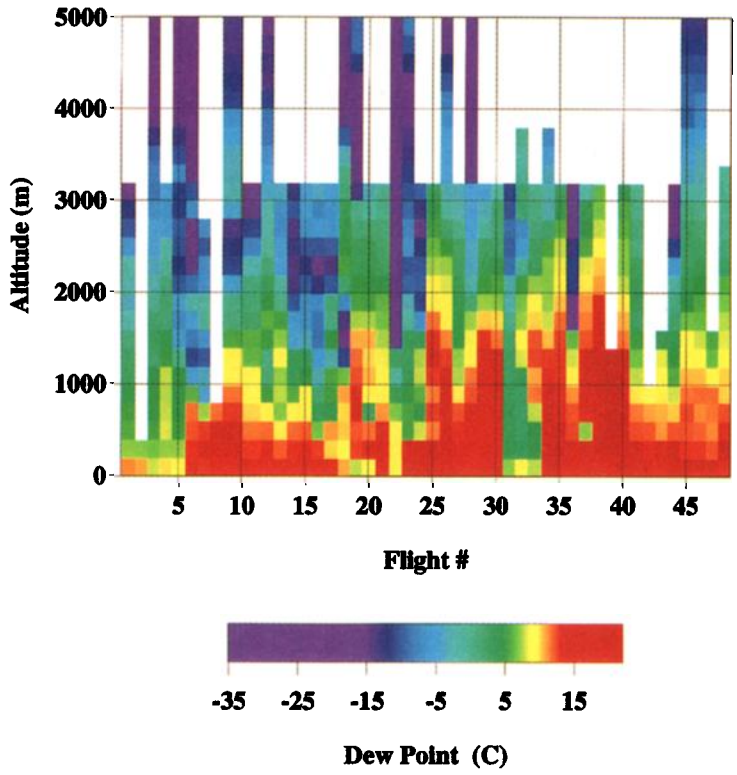

Plate 5. Dew point averaged over 200 m altitude bins.

A typical flight pattern consisted of a vertical profile to 3 or 5 km (ascent and descent rates ~200 m min^{-1}) and several horizontal transects. Usually, a low-altitude pass was made over Chebogue Point and/or over open waters of the Atlantic. Traverses were frequently done at altitudes of 0.3, 0.9, 1.5, 3, and 5 km. Additional traverses were added to the flight plan to investigate cloud or pollutant layers. Traverses typically lasted 5–20 min, during which time instruments were zeroed and hydrocarbon canisters filled. Longer traverses (~30–45 min) were required for cloud samples and filter collection. Most flights were conducted within a limited geographic area encompassing the southern tip of Nova Scotia and 50 km or less of the adjoining Atlantic Ocean.

Changes to this basic flight pattern were required to satisfy other experimental objectives. A standing objective, subject to weather conditions, was to measure cloud microphysical properties and collect cloud water for chemical analysis. The in-cloud penetrations usually did not interfere with performing a vertical profile near Chebogue Point. Several flights were directed toward measurements over Kejimkujik National Park, located 100 km inland from Yarmouth and Chebogue Point. There is a multiyear record of O_3 and peroxyacetylnitrate (PAN) from a surface station at Kejimkujik [*Bottenheim et al.*, 1994; *Sirois and Bottenheim*, 1995], and during the NARE experiment, O_3, CO, and volatile organic compounds (VOCs) were measured. Low-level traverses to and from Kejimkujik were used to measure O_3 deposition fluxes over a forested region. One flight was conducted over Yarmouth harbor and sampled pollution from local sources. Three flights were directed at sampling local air pollution in and around Saint John, New Brunswick. Table 2 presents a flight summary.

The National Center for Atmospheric Research (NCAR) King Air (KA) and the Department of Energy (DOE) ACP G-1 aircraft were deployed in the same general area as the Twin Otter. The KA was based in Portland, Maine, and its flights were concentrated in areas closer to the North American source region. The G-1 was stationed in Halifax, Nova Scotia, and its flights were concentrated farther downwind. Both aircraft complemented the Twin Otter by providing extended geographic coverage. Maps of the NARE region showing flight tracks of the Twin Otter, KA, and G-1 are contained in an overview article [*Fehsenfeld et al.*, this issue (b)].

3. Observations and Discussion

Plates 1–5 provide an overview of O_3, NO_y, PCASP, temperature, and dew point as observed from the Twin Otter. These plates were generated by averaging all data within a given flight over 200-m vertical intervals. Data taken below 200 m altitude on takeoff and landing have been removed, as they are influenced by the airport environment. Averages encompass multiple ascents and descents as well as horizontal traverses. With the possible exception of some near-surface data points, most of the vertical structure apparent in Plates 1–5 is not affected by systematic (i.e., location dependent) horizontal inhomogeneities, as the predominant flight pattern was confined to a limited distance (50 km) of Chebogue Point. Exceptions to this flight pattern have been noted in Table 2. There were, however, cases where concentrations changed by a factor of 2 over horizontal distances of 10 km or less, as described in part 2. Extreme gradients appear to be due to encounters with plume elements or convective bubbles, and we believe that averaging over that type of stochastic variable is a reasonable way to proceed.

We have elected to display the data using flight number rather than time as an independent variable. This was done to

give equal weight to each flight in the presentation and data analysis. The correspondence between flight number and date is more or less uniform, as specified in Table 2. There was an average of 1.4 flights per day over the 34-day experimental period. On 5 days, there were no flights, 13 days had one flight, and 14 days had two flights. Two days toward the end of the experiment had three flights apiece.

A purple-to-red rainbow code is used to specify parameter value. Scales are nonuniform in order to spread the data among the available distinct colors. The caption for Plate 2 indicates that NO_y values extend beyond the range of the color scale. The 200-m averaging procedure used to construct Plates 1–5 smooths over vertical gradients and removes some of the extreme values which will be evident in part 2 in figures that present individual data points. A color plate is not provided for CO because the precision of the measurements interferes with the interpretation of day-to-day trends and altitude variations within a single flight. CO data will be provided in a different format.

Plates 1–5 indicate many features that vary from flight to flight, as well as features with a multiday lifetime. In general, the first half of the experimental period (August 6–23, flights 1–23) had lower concentrations of particles, NO_y, and O_3 than the second half. A particularly clean period occurred between August 16 and 18, flights 12–17. Embedded within the first half of the experiment were also instances in which high O_3 concentration occurred in high-altitude, dry air (dew point $<-5°C$). These instances were observed in vertically narrow layers, as on flights 6, 7, and 9, August 12–13, between 2000 and 2800 m and also in broad layers typically extending upward from 3 km. A comparison of Plate 1 with Plates 2 and 3 indicates that concentrations of particles and NO_y are relatively low in these layers compared with those observed later in the program. There are, however, correlations between trace substances in the high-O_3 dry layers, which will be explored later on, that are not particularly evident in Plates 1–5 due to the data presentation format.

Beginning on August 24 (flight 24), compact plume-like regions with very high O_3 concentration became a common occurrence. These regions were located at relatively low altitude and had high dewpoints and high concentrations of NO_y, CO, and particles. On several occasions these regions were more or less continuous up to a 3200-m maximum sampling height. Similar layers were observed in this region in 1992 [*Berkowitz et al.*, 1995] and again in 1993 as part of the present campaign by the KA and G-1 sampling groups [*Angevine et al.*, this issue; *Berkowitz et al.*, this issue; *Buhr et al.*, this issue; *Daum et al.*, this issue]. In particular, an air pollution episode on August 28 (flights 29 and 30) was observed by the three aircraft and, unlike other episodes, resulted in high concentrations at the surface in Chebogue Point. Above 3 km, high O_3 levels were found in dryer air, similar to those seen in the first half of the field program.

Table 2. Summary of Twin Otter Flights

Flight	Date	Time, UT	Location[a]
1	Aug. 6	1628–1848	CP, OP
2	Aug. 7	1916–2043	CP
3	Aug. 9	1737–1918	CP, OP
4	Aug. 9	2012–2225	CP, K
5	Aug. 10	1809–2048	CP, K
6[b]	Aug. 12	1430–1705	CP, OP
7[c]	Aug. 12	1854–2117	CP, OP
8	Aug. 13	1447–1621	CP, OP
9	Aug. 13	1800–2031	CP
11	Aug. 14	1716–1931	CP, K
12	Aug. 16	1423–1654	CP, OP
13	Aug. 16	1847–2040	CP, OP
14	Aug. 17	1250–1453	CP, OP
15	Aug. 17	1655–1911	CP, K
16	Aug. 18	1355–1606	CP, OP
17	Aug. 18	1752–2024	CP, I
18	Aug. 19	1619–1850	CP, Y
19	Aug. 20	1819–2055	CP, I
20	Aug. 20	2358–0157	CP, OP
21	Aug. 21	1516–1655	CP, OP
22	Aug. 23	1619–1854	CP, OP
23	Aug. 24	1323–1508	CP, OP
24	Aug. 24	1850–2028	CP
25	Aug. 25	1020–1212	CP
26	Aug. 25	1620–1756	CP
27	Aug. 26	1652–1929	CP, K
28	Aug. 27	1752–2021	CP, OP
29	Aug. 28	1221–1403	CP, OP
30	Aug. 28	1547–1710	K
31	Aug. 30	1627–1858	CP, OP, K
32	Aug. 31	1622–1852	CP, OP
33	Aug. 31	2145–2344	CP, OP
34	Sept. 1	1524–1655	CP, OP
35	Sept. 1	1830–2044	CP, Y, I
36	Sept. 2	1312–1532	CP
37	Sept. 3	1527–1713	CP
38	Sept. 3	1905–2102	CP, OP
39	Sept. 3	2211–2325	CP, OP
40	Sept. 4	1848–2037	CP, OP
41	Sept. 5	1458–1657	Y–SJ
42	Sept. 5	1908–2146	SJ
43	Sept. 6	1355–1511	SJ–Y
44	Sept. 6	1740–1928	CP, OP
45	Sept. 6	1507–1702	CP, OP
46	Sept. 7	1832–2027	CP, OP
47	Sept. 7	2123–2242	CP, OP
48	Sept. 8	1340–1456	CP, OP

[a]Abbreviations are CP, Chebogue Point; OP, Ocean Point (sampling was done over the Atlantic Ocean more than 25 km away from Chebogue Point); K, Kejimkujik National Park; Y, Yarmouth; I, other inland locations; and SJ, Saint John, New Brunswick.
[b]Intercomparison with KA.
[c]Intercomparison with G-1.

3.1. Vertical Distributions

Composite vertical profiles based on the data in Plates 1–5 and similar data for CO and wind direction are shown in Figures 1–7. The distribution of data as a function of altitude is indicated by showing the 10, 25, 50, 75, and 90 percentile points on a frequency distribution. Also shown are data points lower than the 10 percentile or higher than the 90 percentile. For substances that primarily have an anthropogenic origin, the high-percentile values give information on the vertical distributions of relatively recent emissions and their reaction products. The low-percentile values are related to background concentrations or concentrations in photochemically aged air masses [*Wofsy et al.*, 1994].

The frequency distributions in Figures 1–7 are for the entire data set and therefore include contributions from flight segments near Kejimkujik National Park and Saint John, New Brunswick. We examined the data set for differences between these locations by considering flight segments south and north of 44° latitude, the northerly segments containing flights to Saint John, as well as the inland portions of flights to Kejimkujik. Comparisons were made for those flights which contained both southerly and northerly segments in the same altitude

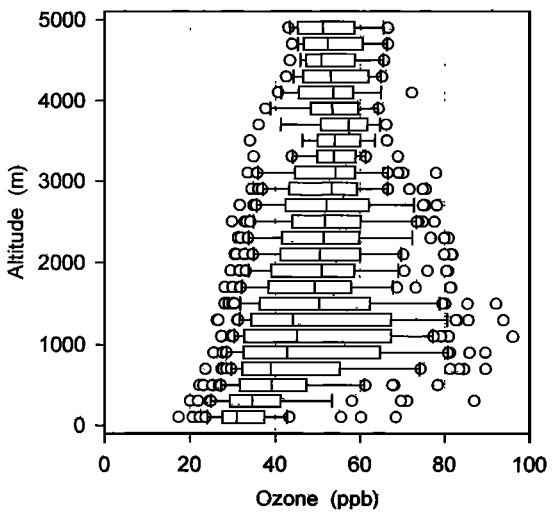

Figure 1. Vertical profile of O_3 frequency distribution. Data are in 200 m altitude bins. Circles are individual measurements below 10 percentile or above 90 percentile. Whiskers show 10 and 90 percentile values. Box covers interquartile range between 25 and 75 percentiles. Line in box is median.

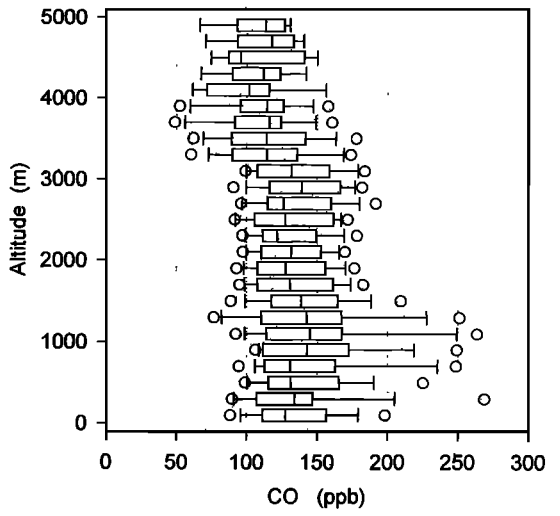

Figure 3. Vertical profile of CO frequency distribution. Circles show 5 and 95 percentile values. Otherwise, format is the same as Figure 1. Extreme values must be interpreted cautiously because of the limited number of 30-s measurement periods contributing to these values and the relatively large fractional uncertainty in CO, particularly at low concentrations.

bins. Systematic differences were small. O_3 south of 44° was 2 ppb higher than north. Corresponding values for NO_y and aerosol particles were 0.1 ppb and −0.1 particle cm^{-3}, respectively. On a few flights we also observed differences between low-altitude measurements made near Chebogue Point and measurements made tens of kilometers away over the Atlantic Ocean. We have elected not to focus on horizontal variations in this article because on average, they are not large, and our objective is to present an overview of the entire data set. However, the possibility of horizontal variations in chemical compositions should be kept in mind when making comparisons between the frequency distributions in Figures 1–7 and those observed at other specific locations.

Ozone. Median values for O_3 increase from 30 ppb near the surface to 50–55 ppb at 3 km and above (Figure 1). At the low end of the frequency distribution, concentrations increase more or less monotonically from 20 ppb near the surface to 45 ppb above 4 km. Highest O_3 concentrations are observed between 600 and 1600 m, with an absolute maximum of 96 ppb (200 m average value). A secondary region of high concentration, evident at the 90 percentile level, occurs between 1600 and 3200 m. A change in the frequency distribution at 3.2 km is, however, likely a result of the relatively small number of flights that continue to higher altitude. There is a strong vertical gradient near the surface, with only a few high-concentration values below 200 m.

NO_y. Median values are highest near the surface, 2.2 ppb between 0 and 200 m (Figure 2). The near-surface maximum persists when the data set is screened to remove flight segments north of 44° latitude, which eliminates the influence of

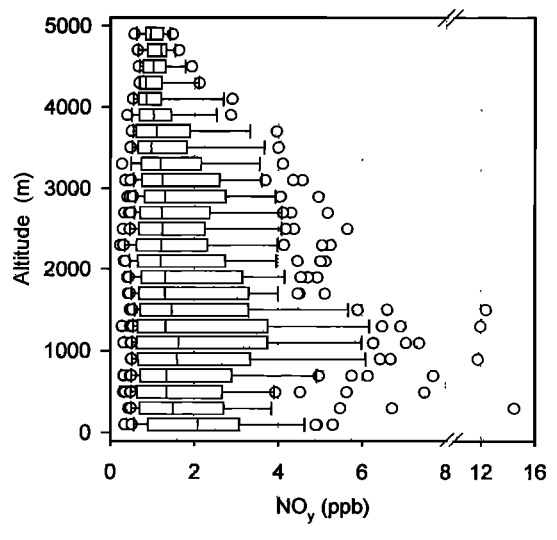

Figure 2. Vertical profile of NO_y frequency distribution. Format is the same as Figure 1.

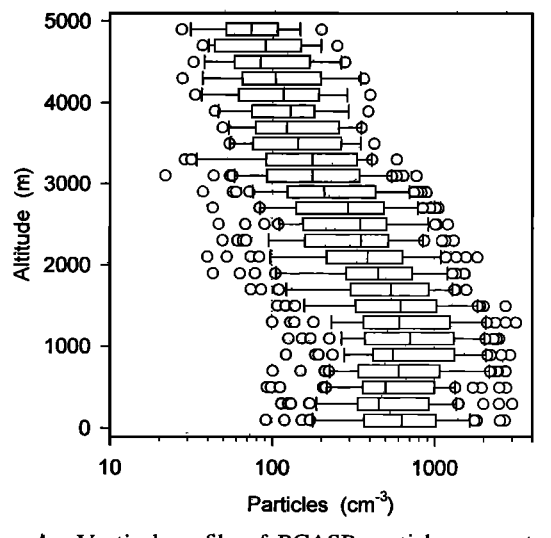

Figure 4. Vertical profile of PCASP particle concentration frequency distribution. Note log scale. Format is the same as Figure 1.

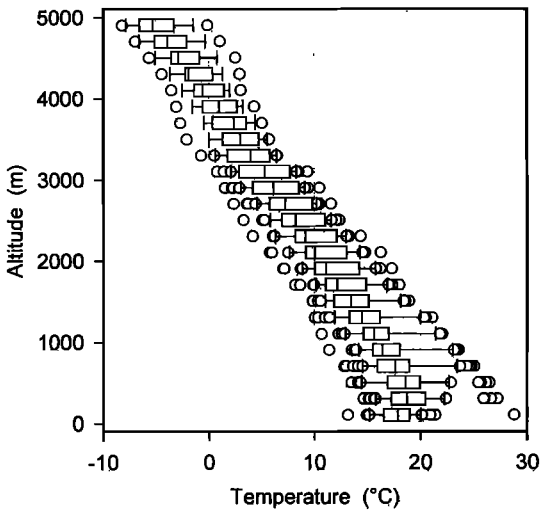

Figure 5. Vertical profile of temperature frequency distribution. Format is the same as Figure 1.

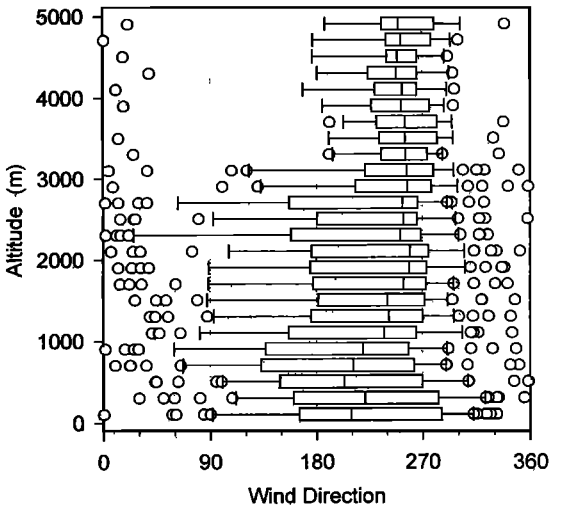

Figure 7. Vertical profile of wind direction frequency distribution. Format is the same as Figure 1.

Saint John and Kejimkujik. At the 10 percentile level, NO_y concentrations (~0.5 ppb) are nearly independent of altitude up to 4 km. As with O_3, highest concentrations occur between 600 and 1600 m. There is also a secondary region of elevated NO_y between 1600 and 3200 m.

CO. CO has a median concentration of about 140 ppb between the surface and 1800 m, decreasing to 110 ppb at 5 km (Figure 3). The 10 percentile values decrease from about 90–100 ppb at low altitude to 60 ppb at high altitude. Concentrations exceeding 200 ppb occur mainly in the band between 600 and 1600 m. A secondary region of high concentration (90 percentile values ~175 ppb) is located between 1600 and 3200 m.

Accumulation mode particles. The frequency distribution of accumulation mode aerosol particles is nearly the same from the surface to 1600 m (Figure 4). Highest concentrations ($N >$ 2000 cm^{-3}) are, however, concentrated in the altitude range between 600 and 1600 m. There is a nearly monotonic decrease in concentration at higher altitude, with values at 5 km a factor of 8 lower than at the surface. Very clean air ($N < 100$ cm^{-3}) is occasionally observed near the surface and becomes more common above 1800 m. Clouds account for some of these "clean" cases, as accumulation mode particles grow to cloud droplet size and are not counted by the PCASP detector.

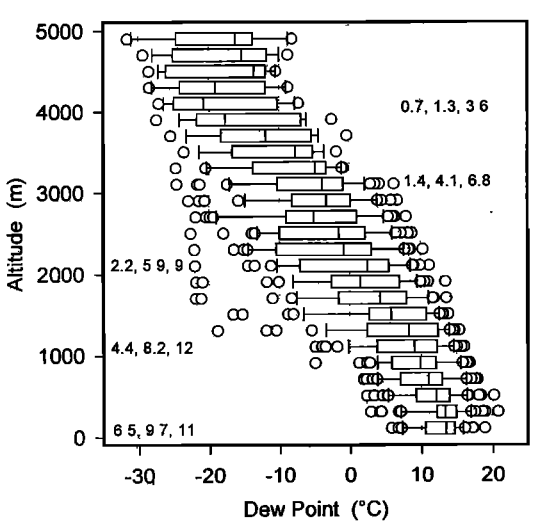

Figure 6. Vertical profile of dew point frequency distribution. Format is the same as Figure 1. Numbers on graph at 0, 1, 2, 3, and 4 km give 10, 50, and 90 percentile values for water vapor concentration (grams per kilogram).

Temperature. Median temperature decreases with altitude with a lapse rate of 5.5°C km^{-1} (Figure 5). Effects of a surface-based inversion can be seen in the lowest altitude bin. As discussed in a following section, an inversion was always present over the Atlantic; the high-percentile temperature data points not indicating an inversion were obtained on flight segments over land.

Dew point. The temperature structure of the atmosphere sets a strict upper bound on dew point and imposes a general decrease with altitude (Figure 6). For this reason, dew point is a useful indicator of air mass origin. However, dew point is not conserved with respect to vertical air motions, and it is sometimes preferable to consider water vapor mixing ratio, which is a conserved quantity, as long as there is no condensation. Mixing ratios are indicated in Figure 6 for selected altitudes at the median and at the 10 and 90% ranges. There is a factor of 5 decrease in median mixing ratio between the near-surface layer (0–600 m) and the colder air above 4 km. At a given altitude, temperature varies by about 10°C; dew point and water vapor variability is due mainly to relative humidity varying by as much as an order of magnitude. A wide range of conditions is possible, particularly in the midaltitude band from about 1.5–3 km, where dew point varies by more than 35°C and mixing ratio by an order of magnitude. There are occasions when very dry air with dew point below −20° occurs below 2 km.

Winds. Wind direction becomes more zonal at higher altitude. Median wind direction changes from 210° near the surface to 255° above 1.5 km (Figure 7). A second group of flights indicated as being outside of the 10–90 percentile range have wind directions from NW to NE. Median values of wind speed (not shown in figure) increase more or less monotonically with altitude, from about 4 m s^{-1} near the surface to about 10–12 m s^{-1} above 4 km. Calm conditions (speeds below

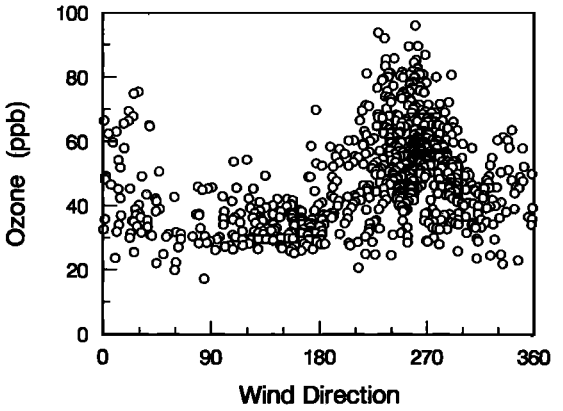

Figure 8. Relation between ozone concentration and wind direction.

2 m s^{-1}) exist at least some of the time at all altitudes. Maximum wind speeds are about 20 m s^{-1}, independent of altitude.

3.2. Winds

The major populated and industrialized regions which could contribute pollutants to the air arriving at Nova Scotia are located to the west and southwest. To the northwest and around to the northeast are located less populated land areas. Other directions face the Atlantic Ocean. In addition to calculating back trajectories, we use the local wind direction, measured from the Twin Otter, as an approximate measure of the "origin" of the air masses that were sampled.

Figure 8 shows the dependence of O_3 concentration on wind direction. Highest O_3 levels occur in southwesterly to westerly flow, with a broad peak between 220° and 300°. There is also a secondary maximum from the north. Points with high O_3 and flow from the north are mainly from flight 9, August 13. The O_3 vertical profile on this day is virtually identical to that observed a day earlier with southwesterly winds. This leads us to believe that transport is from the southwest but that there was a change in wind direction shortly before the sampling period. Back trajectories confirm this view. Figure 8 also shows that westerly and southwesterly winds are not always associated with high O_3. This may be a failing of the local wind direction as a surrogate for trajectory location or a reflection that these flow conditions do not always produce high O_3 concentrations at all altitudes.

The dependence of local wind speed on wind direction is given in Figure 9. Points with O_3 greater than 60 ppb are highlighted in this figure. The average wind speed for the high O_3 measurements is 11 m s^{-1}, 25% greater than the overall average wind speed. As *Berkowitz et al.* [this issue] point out, high O_3 concentrations in many areas are associated with stagnation conditions, but in the NARE region, high-O_3 levels are observed under conditions favoring rapid transport.

3.3. Measurements From a "Clean" Period

Most of the flights give some indication of anthropogenic influence by virtue of the high concentrations of O_3, NO_y, and/or particles observed through all or part of the altitude range. The 10 percentile values in Figures 1–4 provide one indication of the vertical trends in "clean air." Another view is obtained by singling out a period with low O_3 concentration, as occurred between August 16 and 18, flights 12 to 17. Back trajectories at 700 mbar are shown in Figure 10. Transport occurs from regions to the north and west that are relatively free of anthropogenic emission sources. Trajectories at 850 mbar are similar. Five-day back trajectories at lower altitude (925 and 1000 mbar) also traverse areas with relatively low emissions. At the start of the clean period, low-altitude trajectories originate nearby in New Brunswick and later on in the clean period originate to the north and east over the Atlantic Ocean.

Figure 11 shows O_3, NO_y, particles, and CO as a function of altitude during this six-flight period. Trace gas levels are seen to vary relatively little from flight to flight. Ozone concentration increases, nearly monotonically with altitude, from an average near-surface value of 29 ppb to 37 and 51 ppb at 3 and 5 km, respectively. NO_y decreases from the surface to 3 km, a trend opposite to that observed for O_3. On the one flight above 3.2 km (flight 12), NO_y and O_3 both increase in concentration above 3 km, but the increase in O_3 is more pronounced. There are several measurement points near the surface and near 3 km having enhanced NO_y (concentrations greater than 1 ppb). The near-surface points with NO_y greater than 1 ppb are due to flight segments near Yarmouth harbor, and therefore local pollution sources are suspected. The origin of high NO_y at 3 km is unclear. Variations in CO concentration above 3.2 km, in particular the data points below 75 ppb, are not associated with any atmospheric features; rather, they appear to be the result of statistical fluctuations in the single 30-s measurement periods contributing to those altitude bins.

Measurements from August 16–18 have been compared with the lowest 10 percentile values for the whole experimental period; results are shown in Table 3. Ozone concentrations are almost identical; NO_y is slightly higher between August 16 and 18; and CO and aerosol particles are appreciably higher, approaching the median values shown in Figures 3 and 4 for the whole period. However, as previously noted, the extrema in the frequency distribution for CO must be cautiously interpreted, as they are affected by the statistics of the measurements. Still, it appears that there is a CO–aerosol particle source affecting measurements in the clean period.

The ABLE 3B field campaign (see special section on The Arctic Boundary Layer Expedition in *Journal of Geophysical Research*, *99*(D1), 1421–1963, 1994) provides an extensive set of atmospheric trace gas measurements in a region that is near Nova Scotia (eastern Canada) but not directly influenced by

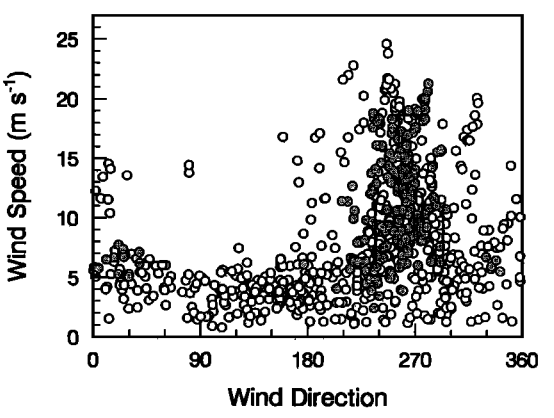

Figure 9. Relation between wind speed and wind direction. Data points with O_3 greater than 60 ppb are shaded.

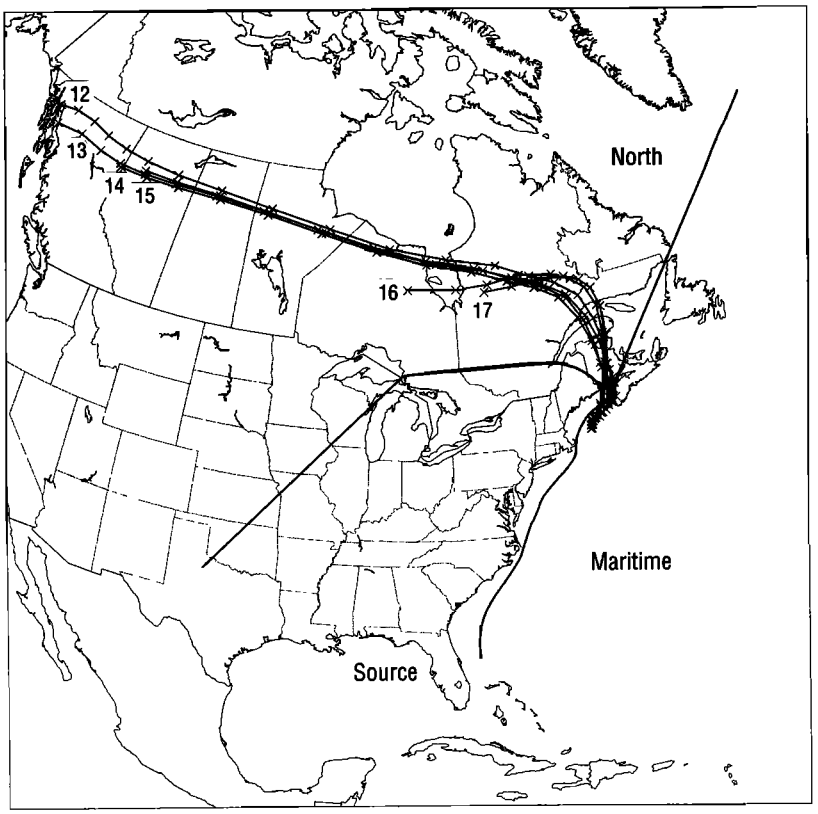

Figure 10. Back trajectories terminating in Yarmouth at 700 mbar for flights 12–17 during the "clean" period. Trajectories have been calculated by the three-dimensional method of *Olsen et al.* [1978]. Each trajectory is 5 days long and consists of segments of 6 hours duration. Flight number and corresponding trajectory termination times are flight 12, August 16, 1200 UT; flight 13, August 16, 1800 UT; flight 14, August 17, 1200 UT; flight 15, August 17, 1800 UT; flight 16, August 18, 1200 UT; and flight 17, August 18, 1800 UT. Emission sectors from *Banic et al.* [this issue] are indicated.

major anthropogenic emission sources. On the basis of tracer techniques and a meteorological analysis, the ABLE 3B data were split into subsets defined as regional background, biomass burning, tropical outflow, and stratospheric influence [*Talbot et al.*, 1994]. In Table 3 we compare trace gas concentrations from the "clean" air period (August 16–18) with the ABLE 3B background and biomass influenced measurements as summarized by *Fan et al.* [1994]. The biomass burning values are of particular interest because the ABLE 3B campaign was conducted during the same time of year as NARE and because clean-period trajectories traverse the same general region found to have biomass burning in ABLE 3B. Ozone concentrations during ABLE 3B (above 2.5 km) are seen to be appreciably higher than occurred between August 16 and 18. Our NO_y and CO measurements are between the ABLE 3B background and biomass influenced values. It is possible that our somewhat elevated NO_y, CO, and aerosol particle concentrations are due to biomass burning, but the signal is not nearly as pronounced as seen during ABLE 3B.

3.4. Measurements in the Continental Plume

A prevalent feature in the second half of the field program is that elevated concentrations of O_3, particles, and NO_y occur in well-defined layers, similar to those observed in this region during 1992 [*Berkowitz et al.*, 1995]. For the most part, these layers stand out as being red or orange on the O_3 plate as well as on the NO_y and/or particle concentration plates. Judging from the chemical mix, concurrent observations from the G-1 [*Daum et al.*, this issue] and KA [*Buhr et al.*, this issue], and back trajectory results, these cases clearly represent transport from the North American continent.

Air masses that have been influenced by the large emission sources on the North American continent can be identified in several ways, including chemical composition, photochemical age, tracer concentration, and meteorological analysis. *Daum et al.* [this issue] discriminated between plume and background measurements on the basis of $NO_y > 1$ ppb, with a further restriction that altitude be below 2 km. We adopt a similar pragmatic approach based on $O_3 > 60$ ppb, averaged over a 200 m altitude bin. Upper atmospheric sources of O_3 are discriminated against by requiring that dew point be above 0°C. In order not to split an apparently continuous layer with $O_3 > 60$ ppb into a plume and nonplume segment because dew point drops below 0°C in the top part of that layer, we add those dryer data points to our moist continental plume collection. Since our criterion is based on a concentration threshold, it discriminates against air parcels that arrive from less polluted continental regions. Our criterion also discriminates against boundary layer air parcels that have experienced vertical lifting resulting in precipitation and a drop in dew point to below our threshold value. Because air with a continental boundary layer origin can be found in moist or dry layers, we will refer to the data set having $O_3 > 60$ ppb and dew point >0°C as moist

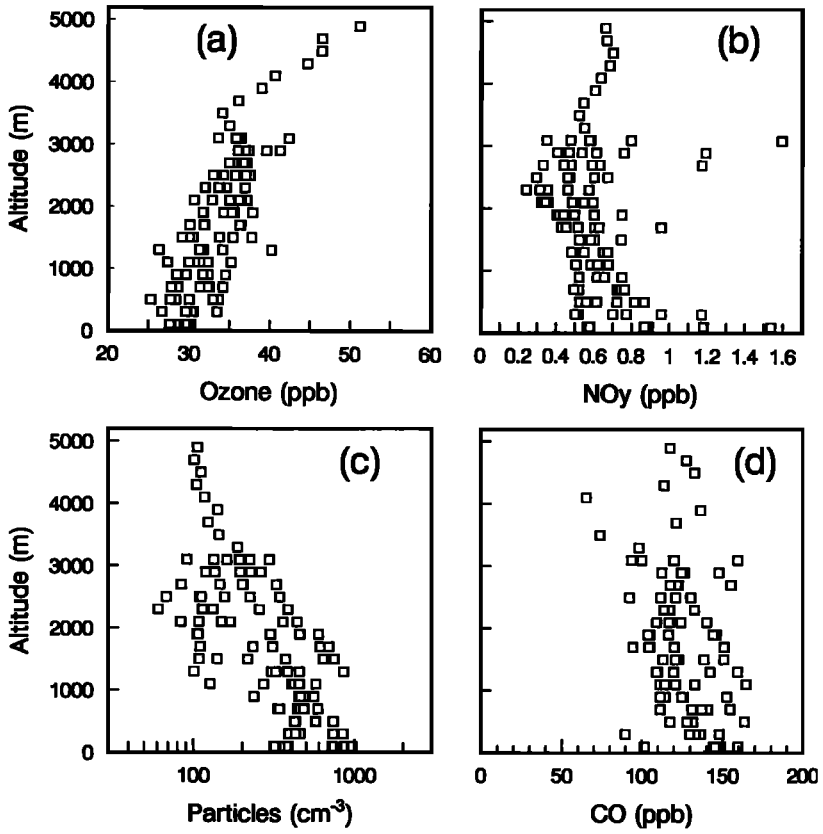

Figure 11. Vertical profiles of trace substances during the "clean" period, August 16–18, flights 12–17: (a) O_3 (b) NO_y, (c) aerosol particles, and (d) CO.

plume points, in contrast to dry plume points, which will be considered in a following section.

There are 17 flights on 9 days that satisfy our criteria for moist transport from source regions on the North American continent; see Table 4. A comparison of the vertical extent of the continental layers with the previously noted high-concentration bands at 600–1600 m and 1.6–3.2 km shows that the bands are the result of averaging over multiple layers having varying depths and base altitudes. However, 1400–1600 m does appear to be a frequent top altitude for the plume layers. The bases of the high-O_3 layers are usually a few hundred meters or more above the surface. In only one case, flight 28, does the highest O_3 occur in the lowest 200 m.

Plume concentrations and meteorological parameters are summarized in Table 4. Average values for CO, NO_y, and particle number density are quite high, consistent with the selection criteria that $O_3 > 60$ ppb (average is 73 ppb). A frequency distribution for wind direction is shown in Figure 12 and indicates a narrow range with a central value slightly to the south of west (~260°). Figure 13 is a composite diagram showing 850-mbar back trajectories for each flight with a continental plume layer at that altitude. Possible source regions are seen to include the northeast corridor (especially Boston), Ohio River valley, Great Lakes region, and portions of the central United States. Transport times range from less than 1 day to 3 or more days, depending on location of source region.

3.5. Relationship to Near-Surface Measurements

Vertical profiles over the cold ($T < 15$°C) Atlantic Ocean and over the coastal surface monitoring site at Chebogue Point indicate a persistent surface-based temperature inversion. This inversion typically extended to 200–300 m, and in it, temperature had a median drop of 4°C. Surface inversions can be seen in Plate 4 and Figure 5 but are not quantitatively represented because of the 200-m averaging used to construct those figures and also because of the inclusion of temperature measurements made over land and ocean.

We expect the inversion to strongly inhibit downward mixing to the surface. In agreement with this expectation, the plates indicate many flights in which the composition of air in the near-surface layer (0–200 m) is distinctly different than that observed several hundred meters overhead. This is particularly apparent on those flights where there is a continental plume layer with a base at several hundred meters causing a sharp vertical gradient in concentration. The correlation between near-surface O_3 and O_3 at altitude is indicated in Figure 14. At an altitude of only 500 m the r^2 correlation with surface observations is less than 0.3. Above 1500 m, there is essentially no correlation with surface measurements. According to Plate 1, the disappearance of correlation is caused by the occurrence of high-concentration layers which do not penetrate down to the surface.

Low-altitude measurements were made in part over the Atlantic Ocean and in part over the surface monitoring site at Chebogue Point located 250 m from the coastline. Both locations experience temperature inversions, and in both locations, near-surface air can have a very different composition than air at several hundred meters altitude. Focusing on O_3, which unlike NO_y and aerosol particles does not appear to be af-

Table 3. Characteristics of "Clean" Air

	August 16–18	10%	ABLE 3B[a] Background	Biomass Burning
		0–1.2 km		
O_3, ppb	30	27		
NO_y, ppb	0.72	0.51		
CO, ppb	132	99		
PCASP, cm^{-3}	489	225		
Temperature, °C	17.6	17.4[b]		
Dew point, °C	8.9	12.5[b]		
		1.2–2.4 km		
O_3, ppb	34	33		
NO_y, ppb	0.52	0.46		
CO, ppb	123	94		
PCASP, cm^{-3}	304	130		
Temperature, °C	10.9	11.1[b]		
Dew point, °C	−3.5	2.7[b]		
		2.4–3.6 km		
O_3, ppb	36	38	46	58
NO_y, ppb	0.59	0.49	0.26	0.9
CO, ppb	111	86	100	150
PCASP, cm^{-3}	174	77		
Temperature, °C	3.4	3.9[b]	−3	2
Dew point, °C	−6.6	−6.5[b]	−8	−3
		3.6–5 km		
O_3, ppb	43	42	54	63
NO_y, ppb	0.64	0.58	0.51	1.0
CO, ppb	117	58	99	140
PCASP, cm^{-3}	115	39		
Temperature, °C	−3.8	−0.5[b]	−6	−6
Dew point, °C	−12.5	−15.6[b]	−17	−13

[a]Regional background and biomass influenced data subsets as defined by *Talbot et al.* [1994]. Results tabulated by *Fan et al.* [1994].
[b]Averaged over data points with the lowest 10% of O_3.

fected by local emission sources, we find only one instance (flight 28 on August 27) where the near-surface layer is significantly more polluted than air aloft. On the following day (August 28, flights 29 and 30) the maximum O_3 concentration was still located within the surface inversion layer but not at the surface. The more common case was for high-pollutant layers to be located entirely above the surface inversion layer.

Near-surface air evidently has a different origin than air above, either coming from less polluted regions or having a greater admixture of unpolluted marine air. Wind speeds decrease near the surface, which would contribute to a greater photochemical aging of pollutants as they are advected toward Nova Scotia; but a difference in aging, by itself, is unlikely to account for the observed chemical differences between surface and plume layers. Nor can dry deposition account for all of the differences, especially for O_3, which was determined to have a near-zero deposition velocity over the ocean based on eddy correlation measurements made from the Twin Otter (J. I. MacPherson, personal communication, 1993).

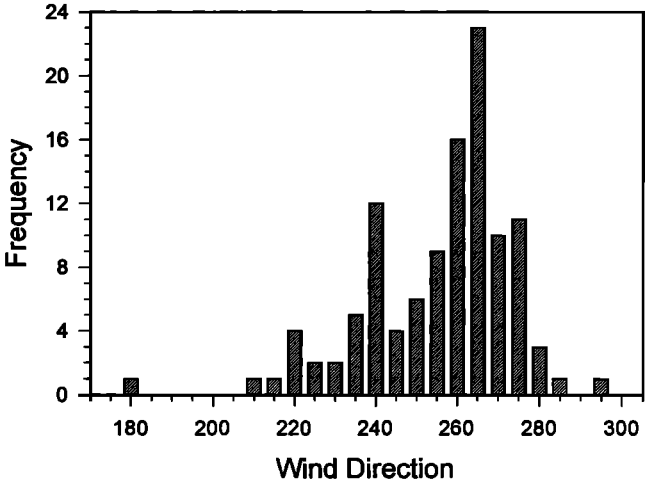

Figure 12. Frequency distribution of wind direction for moist plumes. Each data point represents a 200-m section of a single flight with O_3 > 60 ppb and dew point >0°C.

Chemical differences could be due to a coastal boundary layer effect that prevents continental air from being advected eastward at low altitude coupled with a shift in wind direction near the surface [*Angevine et al.*, this issue]. A shift to southerly flow at the surface would tend to expose our sampling location to oceanic regions with lower pollutant levels. Table 5 summarizes back trajectory results of *Banic et al.* [this issue] which indicate that there is a systematic shift in air mass origin between the surface (1000 mbar) and typical plume altitude (850 and 925 mbar). At the surface the most common origination

Table 4. Characteristics of Air Masses With O_3 Greater Than 60 ppb

	Moist Layer[a]			Dry Layer[b]		
	Average	Minimum	Maximum[c]	Average	Minimum	Maximum[c]
O_3, ppb	72.8	60.1	96.0	65.5	60.1	76.7
NO_y, ppb	5.23	3.07	14.5	1.26	0.82	2.76
CO, ppb	174	76	394	121	52	193
PCASP, cm^{-3}	1470	353	3193	201	28	610
PCASP mvd, μm[d]	0.27	0.20	0.32	0.23	0.20	0.36
Wind speed, m s^{-1}	11.9	4.8	19.1	8.8	2.4	21.3
Temperature, °C	15.4	4.4	28.8	4.2	−7.0	13.5
Dew point, °C	9.6	−7.2	18.9	−15.9	−27.7	−5.3
Relative humidity, %	69	43	90	26	9.2	57
Altitude, m	1602	100	3700	3337	1500	4900

[a]Dew point >0°C except for contiguous portions of layer with lower dew point (including two points with dew point < −5°C); 120 data points except for NO_y (87), CO (112) and PCASP mvd (105).
[b]Dew point < −5°C; 43 data points except for NO_y (29) and CO (15).
[c]All data averaged over 200 m altitude bins.
[d]Relative humidity <80%.

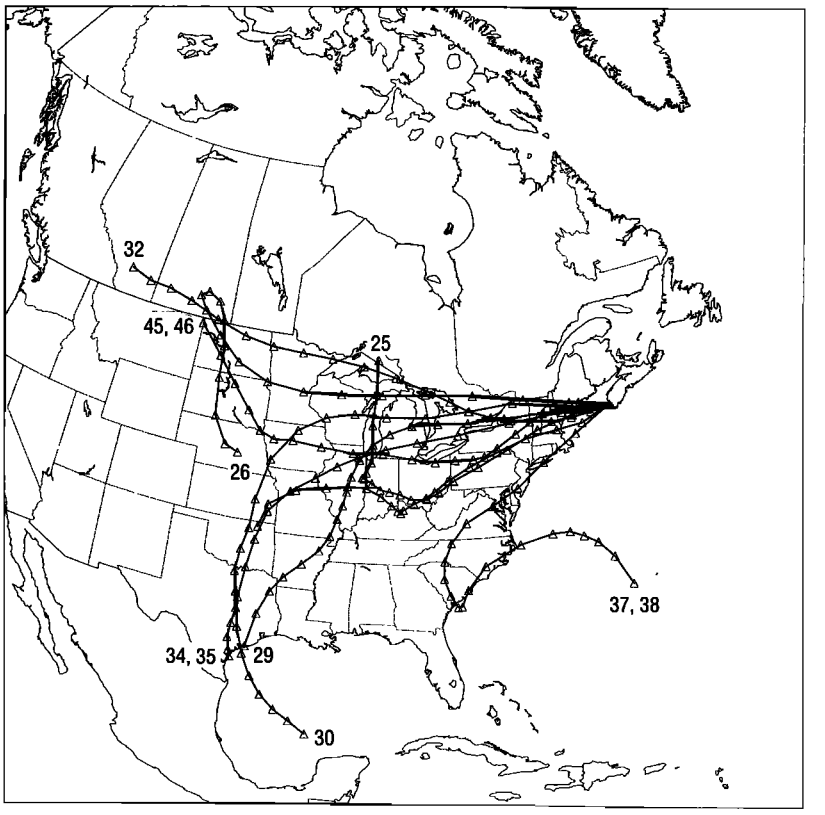

Figure 13. Plots of 850-mbar back trajectories terminating at Yarmouth on days with moist continental plumes. Each trajectory is 5 days long and consists of segments of 6 hours duration. There are trajectories for 12 flights that have a moist plume layer in an altitude range that includes 850 mbar (~1.5 km). On three occasions, a pair of flights in a single day is represented by a single trajectory. Trajectory termination times are either at 0000, 0600, 1200, or 1800 UT, whichever time is closest to the plume encounter.

point for an air mass 1 or 2 days before it arrives at Nova Scotia is the "maritime" sector (see Figure 10), whereas at higher altitude the most common origination point is the "source" sector. In addition, wind measurements from the Twin Otter indicate a southerly shift in direction on some, but not all, of the days that have continental plumes aloft.

3.6. Dry, High-O_3 Layers

High O_3 concentrations, in addition to occurring in air that is clearly of continental origin, are observed at higher altitude in dry air masses. Pollutant levels, as indicated by CO, NO_y, and aerosol particles, are typically lower than in the continental plumes. There is a potential ambiguity in the origin of O_3 in dry layers, as O_3 has an upper atmospheric source as well as an anthropogenic low-altitude source [*Logan*, 1985; *Fishman and Seiler*, 1983].

As with the moist O_3 layers, we adopt a pragmatic point of view in specifying criteria for the dry layers. Our selection rules are $O_3 > 60$ ppb and dew point <-5°C. We leave out a few flight segments that meet these criteria but have been put into the moist layer category by virtue of their continuity with air masses with dew point >0°C. Nine flights on 8 days meet the dry layer conditions. The altitude bases for the dry layers are at 2000 m or higher except for one data point at 1500 m on flight 7.

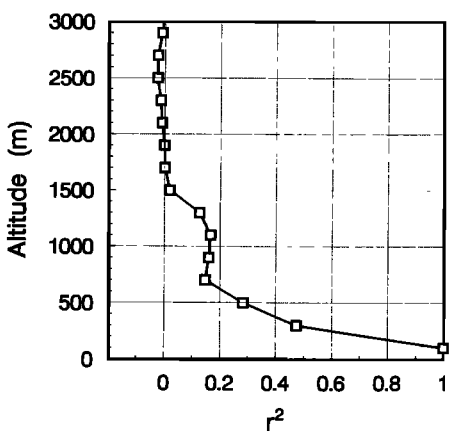

Figure 14. Graph of r^2 correlation for linear regression between surface layer O_3 concentration and O_3 concentration at altitudes up to 3 km. Regression variables are 200 m average values for O_3 near the surface (i.e., altitude between 0 and 200 m) and aloft. The term r^2 has been multiplied by the sign of r, resulting in several slightly negative values above 2 km. Flight segments are restricted to over Chebogue Point and over adjacent ocean, i.e., inland segments, and flights to Saint John are not included. The full data set gives essentially the same results.

Table 5. Percentage of Time Air Originated in a Given Sector

Altitude, mbar	Maritime	Source	North
	24-hour Back Trajectory		
1000	68	19	13
925	26	62	13
850	22	69	9
	48-hour Back Trajectory		
1000	62	30	9
925	17	66	17
850	16	69	16

Sectors are shown in Figure 10. Back trajectories are categorized by sector according to the method of *Banic et al.* [this issue]. Trajectories are from the days and altitudes that had aircraft coverage. Termination times are at either 0000, 0600, 1200, or 1800 UT, whichever is closest to flight time.

Chemical concentrations and meteorological parameters for the dry layers are summarized in Table 4. As compared with the moist layers, the dry layers occur at higher altitude and have significantly lower concentrations of NO_y, CO, and aerosol particles. The distribution of NO_y concentrations in the dry layers does not overlap that in the moist layer; there is minimal overlap for particle concentration and CO. Wind speeds are slightly lower in the dry layers and wind direction more variable. Compared with the "clean" air values above 2.4 km listed in Table 3, the dry layers on average have lower dew points and higher concentrations of O_3, NO_y, CO, and aerosol particles.

A composite of the 700-mbar back trajectories on flights with dry high-O_3 layers near 3 km is shown in Figure 15. Possible source regions include Boston and the Great Lakes region. A comparison with the 850-mbar moist plume trajectories shown in Figure 13 indicates that similar regions are traversed as far west as Lake Michigan. Farther back in time, there is a tendency for the moist trajectories to bend south and the dry trajectories to bend north. Most of the dry high-O_3 layers have transport times from large source regions greater than 3 days.

3.7. Relations Between O_3, NO_y, Aerosol Particles, and Dew Point

A wide range of O_3 concentrations are observed at different altitudes and with different combinations of other trace substances. We examine the relation between O_3, dew point, NO_y, and particles in order to gain insight into the origin of the O_3. Our objective in this section is to give an overview for the entire experimental period. In part 2 of this study we will show the relations between trace substances for selected flights and groups of flights.

Figures 16–18 are scatter diagrams showing the dependence of O_3 on dew point, particles, and NO_y. Data points from moist and dry plumes are indicated in these figures. The graphs of O_3 versus dew point and O_3 versus particle concentration also indicate points with NO_y concentration lower than the median value (1.23 ppb for the 200 m averaged data). A linear least squares regression calculation was done for the low-NO_y points. The r^2 correlations are 0.48 for O_3 versus dew point and 0.19 for O_3 versus particle concentration. Regression lines are included on the graphs.

A comparison of the moist and dry plume points in Figures

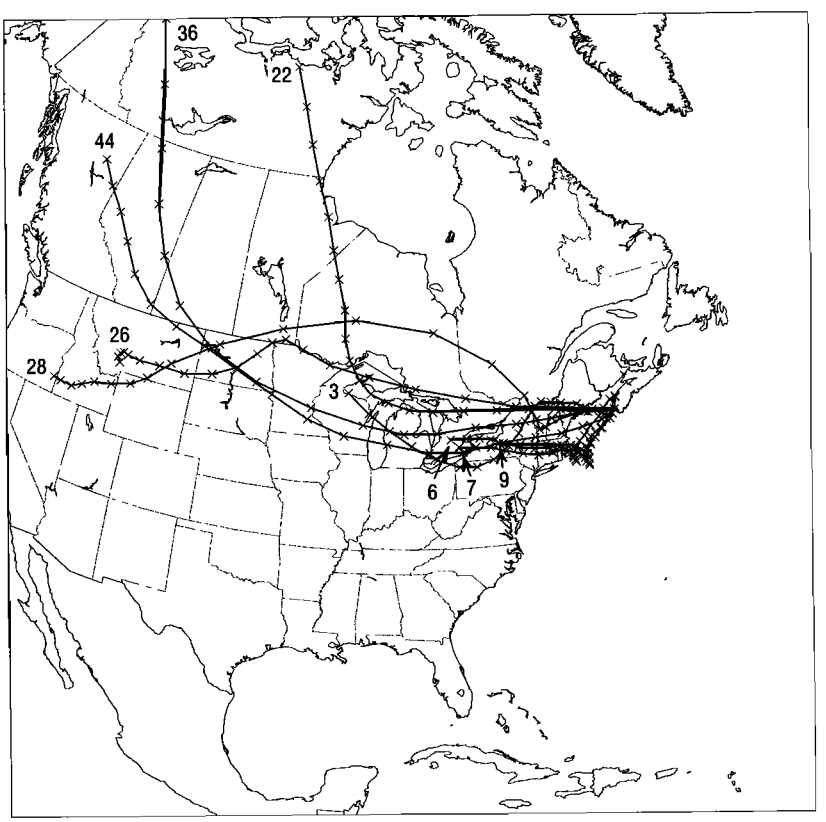

Figure 15. Plots of 700-mbar back trajectories terminating at Yarmouth on days with dry, high-O_3 plumes. Plumes are at altitudes ranging from 2.5 to 5 km. Format is the same as Figure 13.

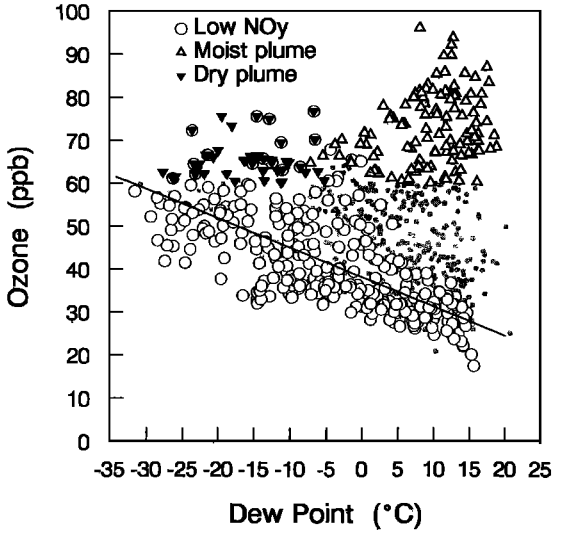

Figure 16. Scatter diagram showing the relation between O_3 and dew point. Regression line is for the low-NO_y subset.

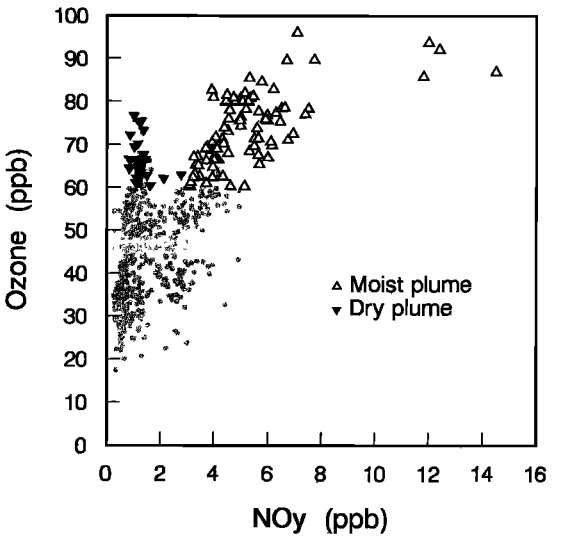

Figure 18. Scatter diagram showing the relation between O_3 and NO_y.

17–18 confirms that the dry plume points have significantly lower concentrations of NO_y and aerosol particles; there is minimal overlap between the two data subsets in the case of O_3 versus particles and no overlap in the case of O_3 versus NO_y. Plumes with low and high dew point evidently have qualitatively different compositions, and there are few intermediate cases. This is most dramatically shown in the O_3 versus NO_y diagram which has two distinct branches ending in the dry and moist plume points. There are two points with O_3 between 60 and 65 ppb that appear to bridge the branches; these points have a unique chemical signature which will be discussed in part 2.

The two branches in Figure 18, besides having dry and moist plume points at their tops, also mainly contain data points from dry and moist air masses at lower O_3 concentrations. Both branches show correlations between O_3 and NO_y which become more evident when the data set is sorted by dew point

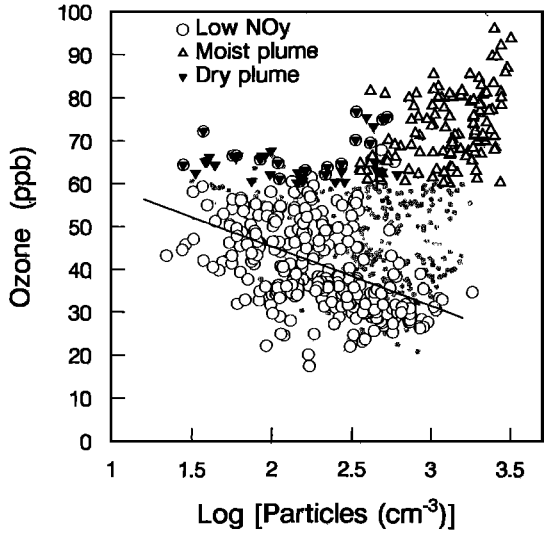

Figure 17. Scatter diagram showing the relation between O_3 and particle concentration measured with the PCASP. Regression line is for the low-NO_y subset.

and time period. The moist subset (not explicitly shown in Figure 18) has an O_3-NO_y correlation characteristic of continental boundary layer air, with a slope, $\Delta O_3/\Delta NO_y$, of about 10, similar to that observed at various continental sites with the same range of NO_y concentrations [*Trainer et al.*, 1993; *Kleinman et al.*, 1994; *Olszyna et al.*, 1994]. The slope decreases at high O_3 concentration as predicted from photochemical model calculations and as has been observed at Egbert, Ontario [*Trainer et al.*, 1993] and by the G-1 during NARE [*Daum et al.*, this issue]. Figure 18 also includes a subset (not explicitly shown) of dry data points with a slope, $\Delta O_3/\Delta NO_y \sim 30$, that is greater than the moist subset but still much less than observed in upper atmospheric air or at remote locations [*Hübler et al.*, 1992; *Murphy et al.*, 1993; *Ridley et al.*, 1994].

A low-NO_y subset has been included in Figures 16 and 17 because it has some of the properties of "background" air and can be compared with the plume data to assess the extent of anthropogenic influence in the plumes. The background-like characteristics of the low-NO_y subset are an anticorrelation between O_3 and water vapor, an anticorrelation (albeit statistically less significant) between O_3 and aerosol particles, and the defining relation that NO_y is low. Moist plume points are seen to be qualitatively different from the low-NO_y points, supporting the argument that these plumes are derived from polluted continental boundary layer air. The distinction between low-NO_y and dry plume points is less clear cut. There are dry plume points which are also low-NO_y points. A part of the dry plume family has O_3, dew point, and particle values placing it near the low-NO_y regression lines. However, another part has higher dew point and more particles, causing it to look dissimilar to the low-NO_y air masses.

While the correlations in moist air all tend to give a consistent picture relating O_3 to anthropogenic activity, the picture that we get from the dry air flight segments tends to vary, perhaps indicating multiple origins for the O_3. In some dry air masses, O_3 is strongly correlated with anthropogenic tracers (i.e., NO_y and particles) but with a different relation than in moist air. In other cases, correlations between O_3 and anthropogenic tracers are weak or absent, consistent with either highly processed boundary layer air or downward transport of

O_3 from high altitude. On many flights, correlations are dominated by vertical trends in which O_3 increases with altitude while dew point and particle concentration decrease. These altitude trends tend to obscure the positive correlations which are sometimes found within an atmospheric layer [*Fishman and Seiler*, 1983].

Several mechanisms for the formation of dry, high-O_3 layers in the free troposphere (2–6 km) have recently been discussed in conjunction with observations made during the ABLE 3B [*Talbot et al.*, 1994], CITE 3 (Chemical Instrumentation Test and Evaluation) [*Anderson et al.*, 1993a, b], and NARE [*Berkowitz et al.*, 1995] field campaigns. The dry, high-O_3 layers in those studies typically have dew points below −25°C and O_3 concentrations of about 60–70 ppb, placing them at the dry edge of the dry plume points shown in Figure 16. Talbot et al. assign an upper altitude origin to the dry air masses they observed in ABLE 3B based on back trajectories and potential vorticity calculations. A scenario for the formation of dry high-O_3 layers in the NARE region, involving the descent of upper level air on the south side of the polar front, has been outlined by *Berkowitz et al.* [1995]. *Anderson et al.* [1993b] observed layers with dew points between −30° and −40°C in the southern tropics, which was ascribed to subsidence of O_3-rich air from the upper troposphere or stratosphere. Several of the layers sampled showed a positive correlation between O_3 and CO which was attributed to mixing of upper level air with biomass burning plumes. Some of the dry plumes that we observed from the Twin Otter resembled the layers seen in ABLE 3B and CITE 3, while others tended to be in moister air and have higher concentrations of particles and NO_y. A combination of upper altitude and boundary layer sources seems likely; further discussion including hydrocarbon measurements and estimates of photochemical age will be given in part 2.

4. Summary

The NRC Twin Otter was used to sample trace gases, aerosol particles, cloud properties, and meteorological parameters during 48 flights conducted primarily in the vicinity of the surface monitoring site near the southern tip of Nova Scotia. A typical flight pattern included one or more vertical profiles to an altitude of 3 or 5 km. Our focus in this article is on presenting the O_3 measurements along with supporting chemical and meteorological data.

Because of the location of Nova Scotia relative to emission sources and because of meteorological variability, air masses that were sampled had a wide range of chemical signatures. As an aid to understanding the observed variability, we have considered four types of air masses: (1) clean background air, (2) moist plumes with high concentrations of O_3 and other anthropogenic pollutants, (3) near-surface air, and (4) dry layers at high altitude with elevated O_3. These situations are not mutually exclusive, and within each category there can still be a great deal of variability.

Characteristics of background air were considered from two viewpoints: as the lowest 10 percentile of all concentration measurements and as the concentrations observed during a multiday period (August 16–18) with a particularly low and constant O_3 concentration. Results were compared with measurements made in eastern Canada during the ABLE 3B field program. Concentrations of NO_y, CO, and aerosol particles during the clean period were somewhat higher than expected, based on the 10 percentile observations, and also higher than the regional background values observed in ABLE 3B. A comparison with ABLE 3B biomass burning data indicates the possibility that we are observing air masses with a dilute biomass burning influence.

A prominent feature of our observations is the existence of well-defined layers which contain high concentrations of anthropogenically generated pollutants. These layers were first noticed in a series of flights conducted in the vicinity of the Gulf of Maine in 1992. Within the pollutant layers, O_3, NO_y, particles, and CO are correlated. Maximum concentrations of these substances (O_3 = 96 ppb, NO_y = 14.5 ppb, particles = 3200 cm^{-3}, CO = 394 ppb; all averages over 200-m altitude bins) are comparable to those observed in urban pollution. Before averaging, the maximum O_3 concentration was 133 ppb. These pollutant layers have high dew points and appear to be sections of continental boundary layer air that have been advected out over the ocean, accompanied by modest lifting in most instances. According to local wind direction and back trajectories, these polluted air masses are coming from urban or industrial areas located to the west or southwest. Other directions face less populated portions of Canada or the Atlantic Ocean, giving rise to much lower concentrations of anthropogenic pollutants.

The vertical location of the plumes is markedly influenced by the temperature structure of the atmosphere. There is a persistent strong temperature inversion over the cold waters of the Atlantic and usually one or more inversions at higher altitude. Anthropogenic plumes can either be trapped within the surface inversion layer or more commonly be located above the inversion. In the latter case, downward mixing to the surface is strongly inhibited, and surface measurements are not representative of concentrations occurring within even the lowest half kilometer of the atmosphere.

At higher altitude we have observed dry layers with enhanced concentrations of O_3. Concentrations of NO_y, CO, and aerosol particles in these layers are significantly lower than in the moist continental plume layers but in most cases higher than background values. A subset of the data collected in dry air masses has a strong correlation between O_3 and NO_y, suggesting an anthropogenic origin for the O_3. The slope of the O_3-NO_y relation is ~30, about 3 times greater than observed in moist air but much lower than observed in air from the upper troposphere or lower stratosphere. In other cases, correlations in dry air between O_3 and anthropogenic tracers are weak or absent, suggesting a natural origin for the O_3.

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References

Anderson, B. E., G. L. Gregory, J. D. W. Barrick, J. E. Collins Jr., G. W. Sachse, D. Bagwell, M. C. Shipham, J. D. Bradshaw, and S. T. Sandholm, The impact of U.S. continental outflow on ozone and aerosol distributions over the western Atlantic, *J. Geophys. Res.*, *98*, 23,477–23,489, 1993a.

Anderson, B. E., G. L. Gregory, J. D. W. Barrick, J. E. Collins, G. W. Sachse, C. H. Hudgins, J. D. Bradshaw, and S. T. Sandholm, Factors influencing dry season ozone distributions over the tropical south Atlantic, *J. Geophys. Res.*, *98*, 23,491–23,500, 1993b.

Angevine, W. M., and J. I. MacPherson, Comparison of wind profiler and aircraft wind measurements at Chebogue Point, Nova Scotia, *J. Atmos. Oceanic Technol.*, in press, 1995.

Angevine, W., M. Trainer, S. McKeen, and C. Berkowitz, Mesoscale meteorology of the New England coast, Gulf of Maine, and Nova Scotia: Overview, *J. Geophys. Res.*, this issue.

Banic, C. M., W. R. Leaitch, G. A. Isaac, M. D. Couture, L. I. Kleinman, S. R. Springston, and J. I. MacPherson, Transport of ozone and sulfur to the North Atlantic atmosphere during the North Atlantic Regional Experiment, *J. Geophys. Res.*, this issue.

Berkowitz, C. M., K. M. Busness, E. G. Chapman, J. M. Thorp, and R. D. Saylor, Observations of depleted ozone within the boundary layer of the western North Atlantic, *J. Geophys. Res.*, *100*, 11,483–11,496, 1995.

Berkowitz, C. M., P. H. Daum, C. Spicer, and K. M. Busness, Synoptic patterns associated with the flux of excess ozone to the western North Atlantic, *J. Geophys. Res.*, this issue.

Bottenheim, J. W., A. Sirois, K. A. Brice, and A. J. Gallant, Five years of continuous observations of PAN and ozone at a rural location in eastern Canada, *J. Geophys. Res.*, *99*, 5333–5352, 1994.

Buhr, M., D. Sueper, M. Trainer, P. Goldan, B. Kuster, F. Fehsenfeld, G. Kok, R. Shillawski, and A. Schanot, Trace gas and aerosol measurements using aircraft data from the North Atlantic Regional Experiment (NARE 1993), *J. Geophys. Res.*, this issue.

Chylek, P., C. M. Banic, P. A. Damiano, G. A. Isaac, B. Johnson, W. R. Leaitch, P. S. K. Liu, D. Ngo, F. Said, S. R. Springston, and B. Winter, Black carbon: Atmospheric concentrations and cloud water content measurements over southern Nova Scotia, *J. Geophys. Res.*, this issue.

Daum P. H., L. I. Kleinman, L. Newman, W. Luke, J. Weinstein-Lloyd, C. M. Berkowitz, and K. Busness, Chemical and physical properties of plumes of anthropogenic pollutants transported over the North Atlantic during the North Atlantic Regional Experiment, *J. Geophys. Res.*, this issue.

Fan, S.-M., D. J. Jacob, D. L. Mauzerall, J. D. Bradshaw, S. T. Sandholm, D. R. Blake, H. B. Singh, R. W. Talbot, G. L. Gregory, and G. W. Sachse, Origin of tropospheric NO_x over subarctic eastern Canada in summer, *J. Geophys. Res.*, *99*, 16,867–16,877, 1994.

Fehsenfeld, F. C., A. Volz-Thomas, S. Penkett, M. Trainer, and D. D. Parrish, NARE 1993 summer intensive: Foreword, *J. Geophys. Res.*, this issue (a).

Fehsenfeld, F. C., P. Daum, W. R. Leaitch, M. Trainer, D. D. Parrish, and G. Hubler, Transport and processing of O_3 and O_3 precursors over the North Atlantic: An overview of the 1993 NARE summer intensive, *J. Geophys. Res.*, this issue (b).

Fishman, J., and W. Seiler, Correlative nature of ozone and carbon monoxide in the troposphere: Implications for the tropospheric ozone budget, *J. Geophys. Res.*, *88*, 3662–3670, 1983.

Hübler, G., et al., Total reactive oxidized nitrogen (NO_y) in the remote Pacific troposphere and its correlation with O_3 and CO: Mauna Loa Observatory Photochemistry Experiment 1988, *J. Geophys. Res.*, *97*, 10,427–10,447, 1992.

Kleinman, L., et al., Ozone formation at a rural site in the southeastern United States, *J. Geophys. Res.*, *99*, 3469–3482, 1994.

Kleinman, L. I., P. H. Daum, S. R. Springston, W. R. Leaitch, C. M. Banic, G. A. Isaac, T. Jobson, and H. Niki, Measurement of O_3 and related compounds over southern Nova Scotia, 2, Photochemical age and vertical transport, *J. Geophys. Res.*, this issue.

Leaitch, W. R., C. M. Banic, G. A. Isaac, M. D. Couture, P. S. K. Liu, I. Gultepe, S.-M. Li, L. I. Kleinman, P. H. Daum, and J. I. MacPherson, Physical and chemical observations in marine stratus during NARE 1993: Factors controlling cloud droplet number concentrations, *J. Geophys. Res.*, this issue.

Lee, Y.-N., X. Zhou, W. R. Leaitch, and C. M. Banic, An aircraft measurement technique for formaldehyde and soluble carbonyl compounds, *J. Geophys. Res.*, this issue.

Li, S.-M., C. M. Banic, W. R. Leaitch, P. S. K. Liu, G. A. Isaac, X.-L. Zhou and Y.-N. Lee, Water-soluble fractions of the aerosol and their relations to size distributions based on aircraft measurements during NARE 1993, *J. Geophys. Res.*, this issue.

Logan, J. A., Tropospheric ozone: Seasonal behavior, trends, and anthropogenic influence, *J. Geophys. Res.*, *90*, 10,463–10,482, 1985.

MacPherson, J. I., Wind and flux calculations on the NAE Twin Otter, *Rep. LTR-FR-109*, 38 pp., Natl. Res. Counc. Can., Ottawa, 1990.

Merrill, J. T., and J. L. Moody, Synoptic meteorology and transport during the North Atlantic Regional Experiment (NARE) intensive: Overview, *J. Geophys. Res.*, this issue.

Murphy, D. M., D. W. Fahey, M. H. Proffitt, S. C. Liu, K. R. Chan, C. S. Eubank, S. R. Kawa, and K. K. Kelly, Reactive nitrogen and its correlation with ozone in the lower stratosphere and upper troposphere, *J. Geophys. Res.*, *98*, 8751–8773, 1993.

Olsen, M. P., K. K. Oikawa, and A. W. MacAfee, A trajectory model applied to the long-range transport of air pollutants, *Rep. LRTAP 78-4*, Atmos. Environ. Serv., Air Qual. Res. Branch, Downsview, Ont., Can., 1978.

Olszyna, K. J., E. M. Bailey, R. Simonaitis, and J. F. Meagher, O_3 and NO_y relationships at a rural site, *J. Geophys. Res.*, *99*, 14,557–14,563, 1994.

Parrish, D. D., J. S. Holloway, M. Trainer, P. C. Murphy, G. L. Forbes, and F. C. Fehsenfeld, Export of North American ozone pollution to the North Atlantic, *Science*, *259*, 1436–1439, 1993.

Ridley, B. A., J. G. Walega, J. E. Dye, and F. E. Grahek, Distributions of NO, NO_x, NO_y, and O_3 to 12 km altitude during summer monsoon season over New Mexico, *J. Geophys. Res.*, *99*, 25,519–25,534, 1994.

Sirois, A., and J. W. Bottenheim, Use of backward trajectories to interpret the 5-year record of PAN and O_3 ambient concentrations at Kejimkujik National Park, Nova Scotia, *J. Geophys. Res.*, *100*, 2867–2881, 1995.

Talbot, R. W., et al., Summertime distribution and relations of reactive nitrogen species and NO_y in the troposphere over Canada, *J. Geophys. Res.*, *99*, 1863–1885, 1994.

Trainer, M., et al., Correlation of ozone with NO_y in photochemically aged air, *J. Geophys. Res.*, *98*, 2917–2925, 1993.

Wofsy, S. C., S.-M. Fan, D. R. Blake, J. D. Bradshaw, S. T. Sandholm, H. B. Singh, G. W. Sachse, and R. C. Harriss, Factors influencing atmospheric composition over subarctic North America during summer, *J. Geophys. Res.*, *99*, 1887–1897, 1994.

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