JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 101, NO. D22, PAGES 28,923–28,933, DECEMBER 20, 1996

Synoptic patterns associated with the flux of excess ozone to the western North Atlantic

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Abstract. Observations of O_3, CO, and aerosols taken in the vicinity of Halifax, Nova Scotia, during the summers of 1992 and 1993 indicate long-range transport of O_3 that was photochemically generated within urban areas of North America. We identify eastward moving cyclonic systems as the main synoptic-scale transport mechanism into this region with the consequence that transport events are highly episodic. The potential for further well-defined long-range transport was found to be slight as a result of subsequent mixing by these cyclonic systems. The ozone flux associated with these cyclones into the lowest 1.5 km of this region is estimated to be on the order of 1 Gmol per 24–hour cyclonic event. We conclude that the circulation patterns associated with these fronts are a major pathway for the export of pollutants from North America.

Introduction

Recent studies [*WMO*, 1986, 1990] have shown a 1% per year increase in tropospheric ozone over Europe. This increase has broad implications for atmospheric chemistry and the Earth's radiative balance. Ozone within the troposphere can trap long-wave radiation emitted from the surface of the Earth ("greenhouse warming"), and as an oxidant, ozone is intimately involved in the production and resulting concentration of many atmospheric compounds, including hydroxyl radicals and organic aerosols. Changes in the ozone concentration thus have impacts well beyond long-recognized health effects.

Concentrations of tropospheric ozone are generally associated with a combination of transport from the stratosphere, in situ tropospheric formation mechanisms involving a complex set of reactions between NO_2, NO, volatile organic compounds (VOCs), sunlight [*Logan*, 1985; *Lin et al.*, 1988; *NRC*, 1991], and transport within the troposphere. We will use the term "excess ozone" to refer to ozone produced in and downwind of large urban areas from human-made emissions of nitrogen and organic compounds since this term applies to ozone concentrations "in excess" of naturally occurring background amounts. For the United States, during the summer the flux of excess ozone to the free troposphere is estimated to be on the order of 35% of the cross-tropopause ozone flux with half of this excess ozone produced in the boundary layer, and half from the subsequent downwind production of ozone from emissions of NO_x [*Jacob et al.*, 1993].

A series of O_3, CO, NO_y and aerosol measurements made over the western North Atlantic near Halifax, Nova Scotia, and the Bay of Fundy during the summers of 1992 and 1993 are presented as evidence for long-range transport of excess ozone from North America. Ozone correlations with CO and aerosols will be the main feature used to identify excess ozone. Carbon monoxide concentrations are commonly used to identify air masses impacted by human activity because CO is a relatively long-lived species associated with the incomplete combustion of fossil fuels, primarily from auto exhaust; it does not have a significant ocean source [*Seiler and Fishman*, 1981]. *Fishman and Seiler* [1983] have observed that there has been considerable in situ production of tropospheric ozone where ozone and CO are positively correlated.

We next consider the meteorological conditions during which excess ozone transport occurred and show that these conditions are associated with relatively well-defined synoptic events. Forward trajectories are then used to consider the potential for subsequent long-range transport. Finally, scaling arguments are presented to evaluate the relative contribution of excess ozone to the tropospheric ozone budget over the sampling domain.

Field Campaign and Instrumentation

The field study was carried out with the International Global Atmospheric Chemistry Program's North Atlantic Regional Experiment (NARE). One of the objectives of NARE was to look for evidence of long-range transport of pollutants from North America to the offshore waters of the western North Atlantic. As part of this study, Pacific Northwest Laboratory (PNL) based its Gulfstream-I (G-1) aircraft at Halifax, Nova Scotia, and made eight sampling missions during 1992 and 6 sampling missions during 1993 within the dashed region in the vicinity of Halifax (Figure 1). One mission, carried out on the morning of September 10, 1992, was to the Bay of Fundy; all other flights were south of Halifax. Under conditions of southwesterly flow, which we will show to be the predominant direction associated with pollution events, the main sampling region is on the order of 1000 km from land. Measurements were taken over altitudes as

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Paper number 95JD03274.
0148-0227/96/95JD-03274$09.00

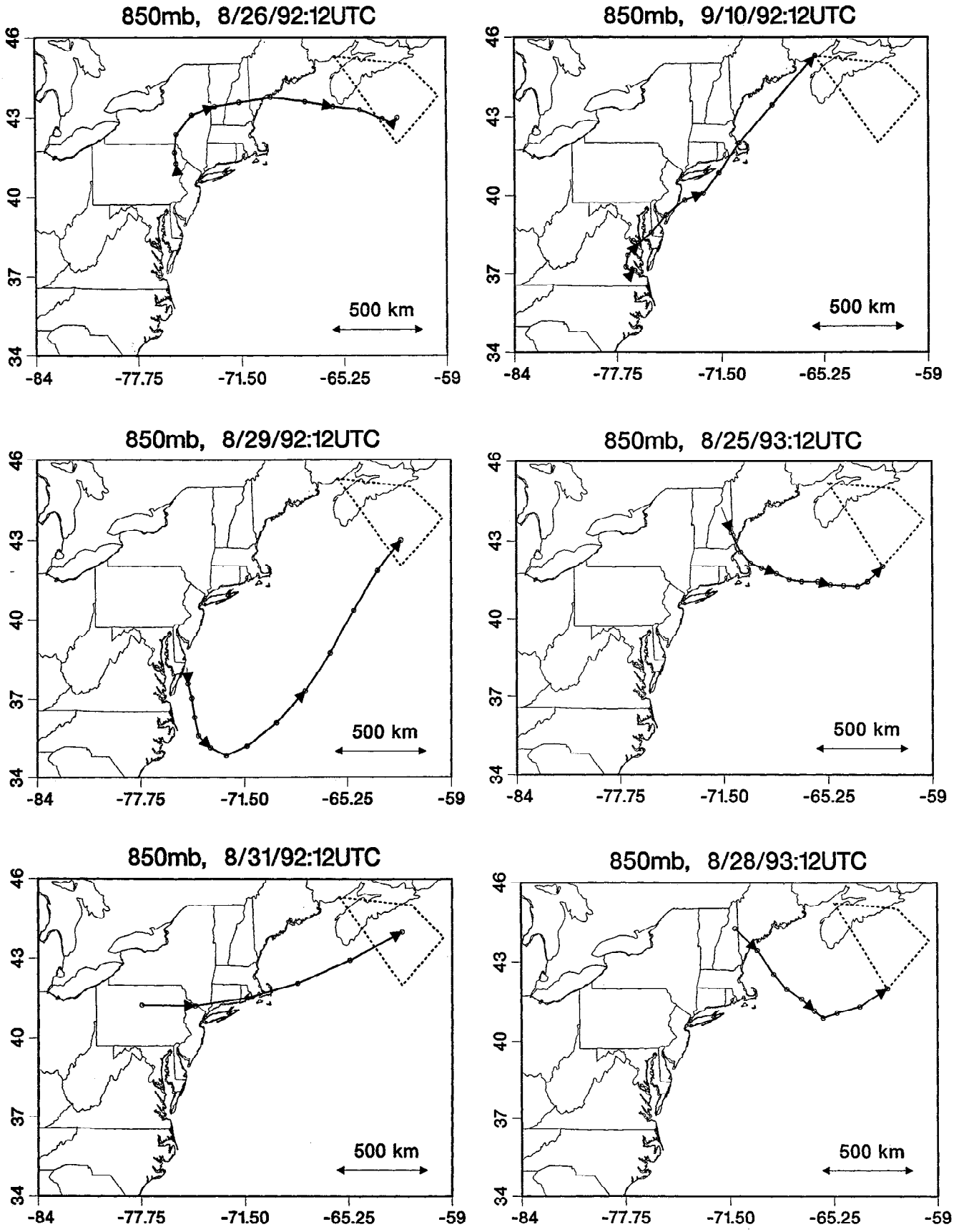

Figure 1. Figure shows a 24-hour isobaric back trajectories for 6 days when r^2 between O_3 and CO was greater than 0.5 ("pollution events"). Arrowheads are drawn at the receptor and source points, with circles shown for every 6 hours of transport. The dashed region on the right side of the map encompasses the sampling domain.

low as 100 m during both years. The maximum sampling height was 2.5 km during the 1992 campaign, but extended as high as 5.5 km during 1993.

The measurements reported here are O_3, CO, NO_y and total number density for aerosols between 0.1 and 3 μm. Ozone measurements were made with a Thermo Electron Corporation, model 49 dual-cell UV absorption system. Minimum detectable concentrations with this instrument are typically 2 to 3 ppb with a response time of 20 s for a 0 to 95% step change. Cycling intervals between the sample/zero mode for each cell provide measurement updates each 4 s. Field calibrations were performed using an ozone generator which was referenced to a laboratory-based ozone UV photometer.

Carbon monoxide was measured with a nondispersive detector (Thermo Electron Corporation, model 48) that had been modified according to the design of *Dickerson and Delaney* [1988]. The instrument was calibrated using a National Institute of Standards and Technology (NIST) standard gas mixture. Instrument uncertainty for the 1-min averaged data reported here is estimated to be 30 parts per trillion (ppt) ± 15% of the measured concentration.

The aerosol measurements reported were observed with an externally mounted Particle Measuring Systems axial-scattering aerosol spectrometer probe (ASASP-100X) particle probe which measures particles in the range of 0.1 to 3 μm diameter. Particle counting and sizing result from detection of scattered laser light by a photodiode device. This system was not calibrated in the field. Calibrations were performed at the aircraft's home base using dilutions of latex spheres in several sizes appropriate to the instrument's range.

Measurements of NO_y were made with a two-channel ozone chemiluminescent NO detector similar to the one described by *Kleinman et al.* [1994], with the exception of the addition of water vapor to minimize response changes of the instrument due to changes in relative humidity. During the field campaign, one of the two instrument channels was devoted exclusively to the measurement of NO_y; the other channel alternated between measuring NO and NO_2; for the vast majority of the measurements the instrument was used to measure NO_y and NO_2. Instrument response was determined by multipoint calibrations and by standard addition of a high concentration of NO (~90 ppb) in flight. Usually two such "standard additions" were done during each flight. In-flight instrument zeroes were performed by mixing ambient air with ozone in a prereaction chamber. Based upon uncertainties in determining instrument zero response and variations in the in-flight standard additions, the uncertainty in measurement of the NO concentration for 10-s averaged data is estimated to be 30 ppt ± 15% of the NO concentration. Uncertainties for NO_y and NO_2 are estimated to be 50 ppt ± 15% of the measured concentration.

Volatile organic compounds (VOCs), and in particular, nonmethane hydrocarbons (NMHCs) play an important role in determining the nonlinearity of ozone production with respect to the loss of NO_X. VOCs were measured in samples collected from the G-1 aircraft. Whole air samples were collected in six liter passivated stainless steel canisters. The samples were collected over approximately 5-min periods by filling the evacuated canisters to approximately 24 psig using a stainless steel Metal Bellows pump. Samples were drawn from an external gas sampling probe to the pump and canister through one-eighth-inch stainless steel tubing. Before the field study, the entire sampling apparatus was cleaned and tested for contamination by sampling zero air. Three different analyses were performed on each sample. A 1.0-mL sample was withdrawn from the canisters and analyzed for methane by gas chromatography with flame ionization detection (GC/FID). A separate 525-mL sample was analyzed for C_2-C_4 hydrocarbons by GC/FID. This sample was cryogenically preconcentrated at -185°C, and separated using a phenylisocyanate on a Porasil C column. Higher molecular weight VOCs were analyzed by GC with both flame ionization and electron capture detection. A 320-mL sample was cryogenically preconcentrated at -160°C and the VOCs were separated using a 50-m OV-1 fused silica capillary column. Calibrations were performed by dilution of ppb level standards of the VOCs. The standards were referenced to NIST primary standard gas mixtures.

Temperature was measured with a Rosemount 102U2U/510BF instrument with a range of -50°C to +5°C. Pressure was measured with a Rosemount 1201F1 absolute transducer instrument.

Observations

We use two related measurements in this study to identify chemical loading over the western North Atlantic associated with air masses coming from urban areas of eastern North America. The first is the concurrent presence of elevated values of daily mean O_3 and CO. A second, related measure is the linear correlation coefficient between the 10-s average values of ozone and CO during each flight, as suggested by the work of *Fishman and Seiler* [1983]. Support for ozone in excess of naturally occurring amounts also comes from an examination of the corresponding correlations between ozone and aerosols within the 0.1- to 3-μm diameter range, and correlations between ozone and NO_y. Ancillary support for identification of "pollution" events comes from a day-to-day examination of the air mass history, defined by 3-day back trajectories into the sampling domain.

We have partitioned the data collected within the sampling region into a set from the mixed layer and another from aloft. *Luria et al.* [1990] demonstrated that different photochemical regimes can exist near the surface relative to the free troposphere. Air within the surface mixed layer is subject to surface removal and exchange processes between the atmosphere and underlying surface, whereas air in the free troposphere is likely to have undergone transport from longer distances as a result of the generally greater wind speeds aloft.

The height of the mixed layer, Z_{stable}, is defined as the first elevation above the surface for which the atmospheric stability,

$$S = \left(\frac{1}{\theta}\right)\frac{d\theta}{dz} \tag{1}$$

[*Lyons and Scott*, 1990] had a maximum relative to other values in the profile, where θ is the potential temperature. All data collected below Z_{stable} are classified as mixed layer measurements; all data collected above Z_{stable} are classified as free tropospheric measurements. A third classification was defined for missions when there was no clear maximum in S, indicating the absence of any significant stable layer.

Table 1 summarizes the resulting mixed layer mean values, standard deviations, and median values for ozone, CO, NO_y and aerosol for all flights within the sampling domain during

Table 1. Observations Taken Within the Domain Shown on the Right Side of Figure 1 During the 1992 and 1993 Summer Campaigns

Missions	r^2 (O_3 and CO)	$\frac{\Delta O3}{\Delta CO}$	median CO, ppb	$\frac{\sigma CO}{[\overline{CO}]}$, ppb	median O_3, ppb	$\frac{\sigma O3}{[\overline{O3}]}$, ppb	r^2 (O_3 and ASASP)	$\overline{ASASP}$ counts $cm^{-3}\ s^{-1}$	z_{stable}, km	median NO_y, ppb	r^2 (O_3 and NO_y)	$\frac{\sigma NOy}{\overline{NOy}}$, ppb
						1992						
Aug. 26	0.6	0.19	144	19.0/196	70	7.1/80	na	na	1.0	3.8	na	na/4.1
Aug. 29	0.9	0.28	104	59.1/130	58	21.3/62	na	na	z_{max}	1.3	na	na/2.7
Aug. 30	0	0	96	19.2/102	57	11.5/55	0	213	z_{max}	3.0	na	na/3.0
Aug. 31	0.9	0.30	110	11.3/130	56	3.0/68	0.9	1260	1.4	2.1	na	na/3.9
Sept. 5	0	0	105	29.5/112	35	2.6/35	0	120	1.5	0.6	na	na/0.6
Sept. 10	0.5	0.21	140	37.8/119	65	11.9/45	0.6	787	z_{max}	4.0	na	na/4.0
Sept. 11	0.1	0	117	13.9/115	37	8.1/37	0	80	1.2	0.8	na	na/0.8
Sept. 14	0.1	0	123	16.2/126	36	3.8/37	0	120	1.0	0.6	na	na/0.7
						1993						
Aug. 17	0.2	0	147	38.0/147	33	5.1/34	0.1	273	1.8	0.3	0	0.2/0.4
Aug. 18	0	0	142	48.5/142	42	9.6/41	0.5	107	1.5	0.5	0.1	0.1/0.5
Aug. 22	0.1	0	141	40.5/141	35	7.3/33	0.1	93	z_{max}	0.4	0	0.3/0.4
Aug. 25	0.6	0.22	172	1.5/172	52	16.3/56	0.5	560	z_{max}	1.5	0.6	1.5/1.9
Aug. 28	0.7	0.27	268	3.8/268	72	24.7/83	0.8	1280	1.8	4.6	0.2	3.8/5.8
Aug. 29	0	0	152	40.0/152	39	14.3/45	0.6	200	z_{max}	0.8	0.5	0.4/1.1

In the table na indicates not available. $\Delta O_3/\Delta CO$ is the slope of the line of best fit for 10-s average values of ozone and CO. "z_{max}" indicates that no well-defined mixing height was identified below the maximum sampling altitude. ASASP is axial-scattering aerosol spectrometer probe.

1992 and 1993. Also included are the elevation of the top of the mixed layer, the linear correlation coefficients between O_3 and CO and between O_3 and aerosol. The linear correlation coefficients between ozone, CO, NO_y and ASASP exhibit a series of high (August 26, 29, and 31, September 10, 1992, and August 25 and 28, 1993) and low values, which we take as a measure of day-to-day variations in pollutant loading over the sampling domain. Consistent with these maxima in correlation coefficients are the mean and median values. Those days having large mean values are associated with linear correlation coefficients greater than 0.5. We will refer to days with relatively large mean and median values, and having correlation coefficients greater than 0.5, as "pollution events."

A strong height dependence was observed in the correlation between ozone and CO when a well-defined stable layer could be identified at the top of the mixed layer. On those days when Z_{stable} could be defined, measurements above Z_{stable} in the free troposphere showed a negligible correlation between ozone and other species although measurements below Z_{stable} showed a relatively high correlation. The scatter plots on the left side of Figure 2 show the 10-s mean values of ozone and CO taken above Z_{stable}; the correlation is non-existent or weak for this subset of the data. In contrast, the scatter plots for these same days below Z_{stable} show correlation coefficients greater than 0.5. On days when no stable layer could be identified, there appeared to be no height dependence on the correlation between ozone and CO. That a height dependence was seen in the plume structure only when there was a stable layer is consistent with what would be expected from a photochemical plume emanating from surface sources; when a well defined "top" exists, mixing would occur up to this height. In the absence of such a stable layer, the mixing would continue upward with no height dependent sensitivity seen in the mixing ratios.

The contrast in plume structure in the presence and absence of a well-defined stable layer is consistent with the earlier observations of *Van Valin and Luria* [1988] that the mixed (or "boundary") layer is the more important conduit than the free troposphere for the direct long-range transport of pollutant gases over the western North Atlantic. Transport above the marine mixed layer certainly can occur as a consequence of exchange processes between the boundary layer and free troposphere, for example, cloud mixing [*Pickering et al.*, 1992]. However, identifying plumes in the free troposphere is difficult due to their weaker intensity relative to the variable background mix of ozone and CO.

Synoptic maps (Figure 3) and the corresponding 850 hPa back trajectories (Figure 1) show that a common synoptic pattern and source region can be associated with each of these "pollution" events. The trajectories are derived from the Global Data Assimilation system [*Kanamitus*, 1989], which uses the National Meteorological Center's Medium Range Forecast Model. The associated calculations take into account changes in the wind field over space during a fixed time and changes in the wind field over time at a fixed location by using information at the starting times/locations and at the final time/approximate location. However, because each back trajectory calculation began near a synoptic-scale front, with the associated discontinuities in pressure and wind fields, they can be looked upon only as approximations to the actual air mass history.

The August 26 and August 29, 1992, missions were carried out under conditions of southwesterly flow within the warm sector of a cold front. Sampling on August 30, 1992, was done shortly after a cold front had passed over the sampling domain, while sampling on August 31, 1992, was again prefrontal. The mission of September 10, 1992, was carried out within the warm sector of a cyclone north of Nova Scotia moving into the sampling domain from the southwest. High pressure or the absence of an organized circulation pattern characterized the synoptic conditions over the smaller sampling domain on August 17, 18 and 22, 1993. The warm sector of a cold front passed north of this region on August 25-28, 1993, resulting in back trajectories with southwesterly flow from along the coast of North America. Another cold front passed through the region on August 29, 1993, with aircraft sampling done after the passage over the sampling domain. This data set suggests that high values of excess ozone occur only under conditions of well-defined flow from the west or southwest which are associated with the synoptic patterns shown in Figure 3.

The role of cyclones in the ozone budgets of the western Atlantic has not, to our knowledge, been extensively considered within the context of air quality. Previous work has focused on anticyclonic systems and their role in the regional scale distribution of O_3 [e.g., *NRC*, 1991; *Vukovich*, 1994]. Previous studies over the North Atlantic have emphasized effects of the Bermuda-Azores high on long range transport. For example, *Pszenny et al.* [1990], in their description of the 1988 Global Change Expedition/Coordinated Air-Sea Experiment/Western Atlantic Ocean Experiment (GCE/CASE/WATOX) note that much of the atmosphere over the Atlantic is dominated by this anticyclone, with the result that air over this region will spend at least 5 days circulating over ocean areas; they detected pollution near Norfolk, Virginia, and for short periods of time, near Bermuda.

In contrast, the prefrontal sampling reported here indicate the potential for long range transport as ozone and its predecessor species from populated portions of North America are quickly advected from the southwest to the northeast in advance of eastward moving cyclones. These results show that transport in advance of such patterns can be significant, with the potential to quickly transport pollutants from the region defined by *Hansen et al.* [1990] in their analysis of aerosol black carbon and ^{222}Rn, as "inhabited continental areas of North America."

Discussion

Our observations indicate that excess ozone was transported into the sampling domain by cyclonic circulations in advance of frontal systems. To evaluate where these air masses went after leaving the sampling domain, we calculated forward trajectories along the 850 hPa surface. Two "pollution" events showed evidence of long-range transport. The August 26 and September 10, 1992, episodes (Figure 4) were followed by relatively fast transport, with air from the sampling domain estimated to reach the mid-Atlantic 3 days after the measurements were taken. The August 26, 1992, event was of particular interest because of its predicted intersection with a sampling site in Ireland. *Derwent et al.* [1994] have recently presented hourly carbon monoxide and ozone measurements taken at the Mace Head site on the Atlantic coast of the Republic of Ireland, a site close to the predicted receptor location shown in Figure 4. Although the surface winds were south westerly during the expected arrival time of this air mass, no chemical signatures indicative of

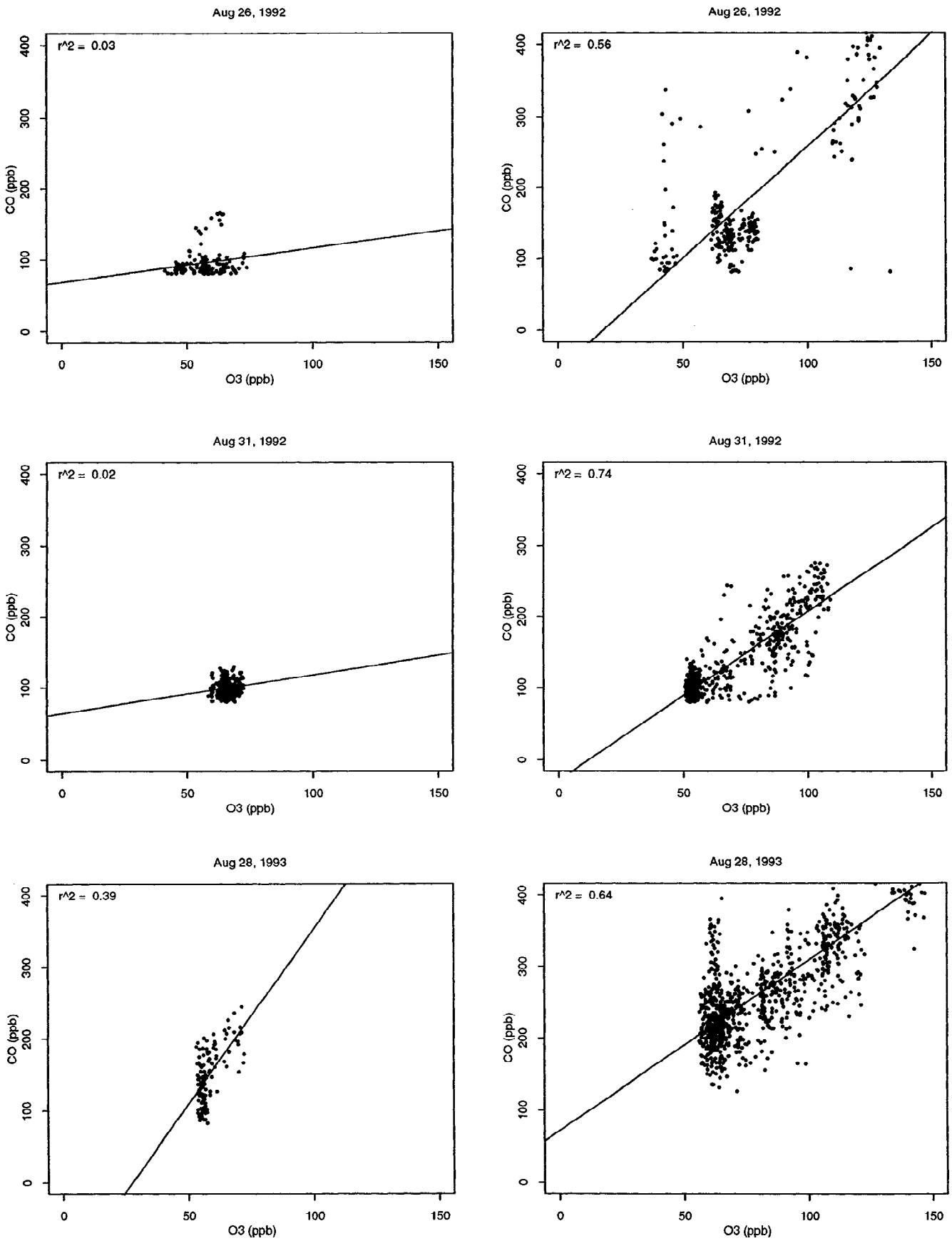

Figure 2. Scatter plots of ozone and CO on "pollution" days, as identified in Table 1. Figures on the right side are based on data taken within the mixed layer on days when a stable layer could be defined. Figures on the left side are for these same days only using data collected above the stable layer.

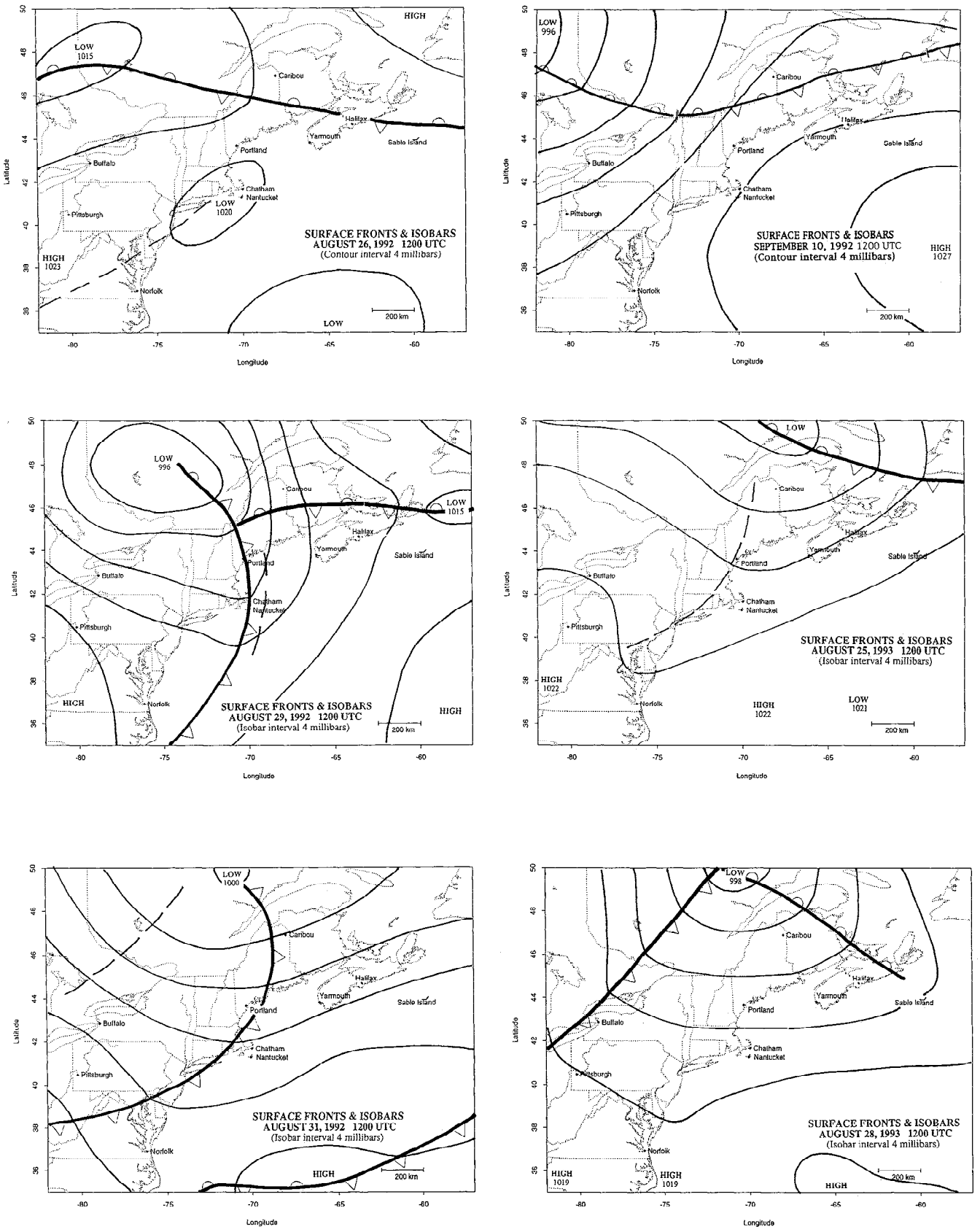

Figure 3. National Weather Service analysis of frontal positions on 6 days when r^2 between O_3 and CO was greater than 0.5 ("pollution events").

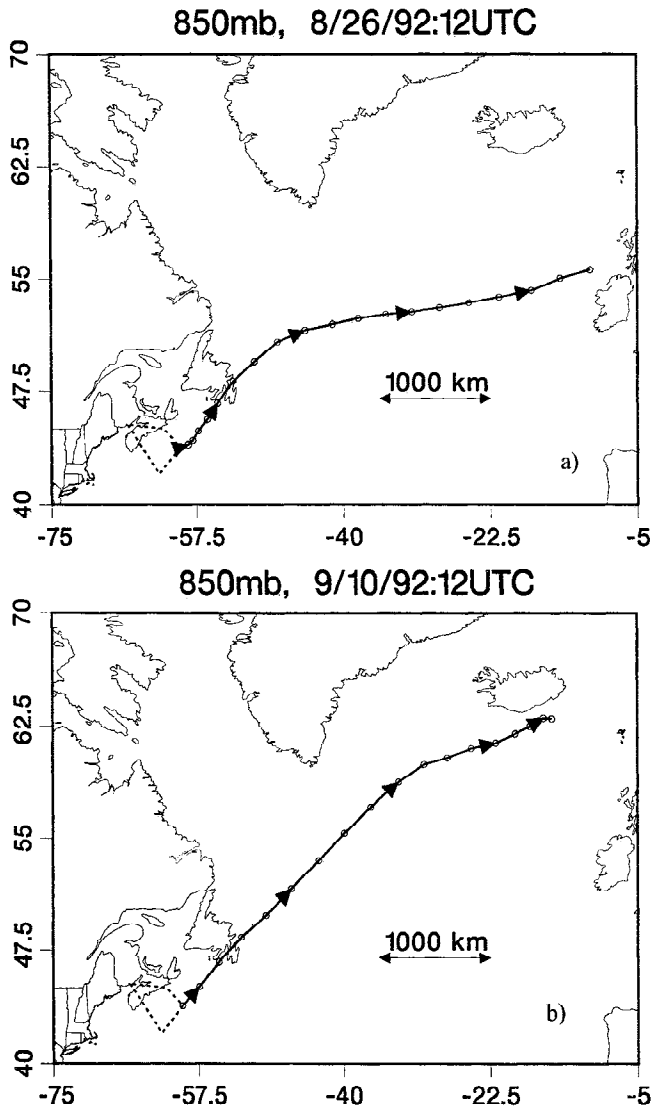

Figure 4. Isobaric forward trajectories for (a) August 26, 1992, and (b) September 10, 1992, from the easternmost point of the sampling domain, showing subsequent eastward transport of air after a "pollution event." The sampling domain is within the dashed lines shown at the start of the trajectory. Arrowheads are drawn at the release time and every subsequent 24 hours. Open circles are drawn every 6 hours.

polluted air were noted [*R. G. Derwent*, personal communication, 1995].

Forward trajectories for all of the other "pollution" events detected in the sampling domain during 1992 and 1993 showed little movement, were directed northward, or encountered frontal activity shortly after the sampling period. This last category of forward trajectories would begin moving within strong westerly or southwesterly flow, but within 2 to 3 days, the paths were characterized by a relatively tight cyclonic motion (Figure 5), indicating that the frontal region, with its associated region of strong wind shear, had overtaken the air being tracked. The resulting mixing of pollutants into the atmosphere does not mean these trace gases cannot undergo subsequent long-range transport or make a contribution to the air chemistry east of North America. Rather, it indicates that mixing will cause these air masses lose their identity as previously defined "pollution" events. We find that there is a high probability such mixing will occur, making it difficult or impossible to identify such plumes and conclude that the same mechanism responsible for the presence of high mixing ratios of excess ozone off the coast of North America is also responsible for extensive mixing shortly after such events, making the likelihood of detecting in Europe the excess ozone that originated in North America relatively remote.

The relation between cyclonic synoptic patterns and the observations of O_3, CO, aerosols, and NO_y during the 14 observations reported here suggest that the frequency of these "pollution" events within the boundary layer off the coast of Nova Scotia can be approximated by the frequency of southerly flow associated with precold front warm sector circulations moving into the area. We will make use of this observation to evaluate the seasonal flux of excess ozone into the sampling domain through cyclonic activity.

There are two sources for excess ozone over the North Atlantic. The first source, which we will refer to as "primary," results from the advection of preexisting, excess ozone from over North America. A "secondary" source is the generation of ozone over the western North Atlantic associated with the subsequent photochemical generation of ozone from associated NO_x and hydrocarbons. The number of molecules of excess ozone, N^e, transferred into a region defined by a horizontal extent of Δy and vertical extent Δz during time interval Δt is given by

$$N^e = N^{primary} + N^{secondary} \tag{2}$$

$$= \int\int\int_{\Delta y \Delta z \Delta t} dy\,dz\,dt [O_3]_{total}\, \beta u(y,z,t)$$

$$+ \int\int\int_{\Delta y \Delta z \Delta t} dy\,dz\,dt [NO_x]_{total}\, \varepsilon_g(NO_x, NMHC)\, u(y,z,t) \tag{3}$$

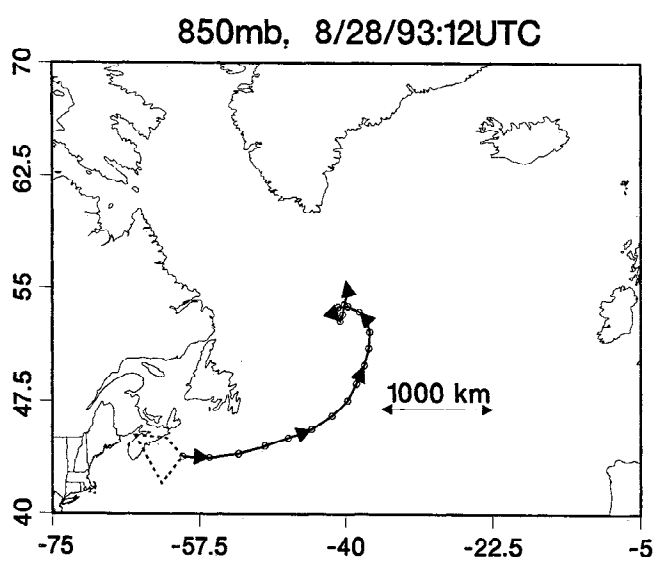

Figure 5. As in Figure 4, for August 28, 1993, illustrating the cyclonic shear zone associated with an eastward moving front overtaking air that was initially in the sampling domain.

where $u(y, z, t)$ is a spatially and time varying wind speed into the region of interest, β is the fraction of the total ozone in excess of the natural, or background, amount,

$$\beta = \frac{[O_3]_{excess}}{[O_3]_{total}} = \frac{[O_3]_{total} - [O_3]_{natural}}{[O_3]_{natural} + [O_3]_{excess}} \quad (4)$$

and $\varepsilon_g(NO_x, NMHC)$ is the gross ozone production efficiency, defined as the number of ozone molecules produced per molecule of NO_x consumed [*Lin*, 1988; *Jacob et al.*, 1993]; it does not account for ozone chemical loss.

Part of our motivation for limiting the analysis to the dashed domain shown in the right side of Figure 1 was to consider conditions that were more horizontally homogeneous than would be expected over a larger domain, and would therefore facilitate evaluation of the terms within (3). We will also limit our analysis to measurements within the mixed layer where photochemical plumes were identified. With these restrictions, we mathematically assume horizontal and vertical homogeneity.

Under these conditions, we obtain the following expression for the number of molecules of excess ozone advected into this smaller domain per kilometer, within a boundary layer of height Δz:

$$N^e = \Delta y \Delta z \Delta t \, \bar{u} \times \left\{ \overline{[O_3]}_{total} \times \bar{\beta} + \overline{[NO_x]}_{total} \times \varepsilon_g\left(\overline{NO_x}, \overline{NMHC}\right) \right\} \quad (5)$$

We now use the values in Table 1 to evaluate the terms in (5) for the cyclonic events associated with episodes of high ozone. Typical ozone mixing ratios during these events were 70 ppb. Although not included in the table, representative meteorological conditions include warm sector wind speeds of 10 m s^{-1}, temperatures 25°C, and a pressure of 1010 hPa. A characteristic vertical length scale is given by the height of the stable layer as defined earlier to partition the measurements into a subset taken in the free troposphere and another subset taken within the mixed layer; we use the mean observed value of 1.5 km. The mean value of the ozone mixing ratio was 40 ppb on days when r^2 was less than 0.5 with the result that $\beta = (70 - 40)/70 = 43\%$. Using these values in the first term within the brackets on the right-hand side of (5) results in an estimate of 18.5 mol km^{-1} s^{-1} of excess primary ozone transferred into the boundary layer of this region during the synoptic events described above.

The second term within brackets on the right-hand side of (5) is more difficult to evaluate, and must await additional observations. *Jacob et al.* [1993] noted that the value of ε_g depends on a number of variables, in particular the concentration of NO_x. Our NO_y instrument had two channels; one channel used to measure NO_y, the other channel switched between NO and NO_2 (NO was measured about one third of the time and NO_2 about two thirds of the time). There were no simultaneous measurements of NO and NO_2 (= NO_x). However, *Daum et al.* [this issue] presents median ratios of NO_2/NO_y and NO/NO_y of 0.16 and 0.04 for the 1993 measurements, suggesting that a relatively small fraction (~20%) was present as NO_x, and takes this, in conjunction with other observations reported in that paper, as evidence of extensive photochemical processing of the sampled air masses having already occurred. Three NMHC samples were taken within the sampling domain shown in Figure 1 with total NMHC values of 2.2 ppb, 1.8 ppb, and 1.2 ppb within the boundary layer on August 30 and 31 and September 5, 1992. Given that the NO_y observations suggest extensive aging, and that the limited NMHC samples suggest relatively high variability from one mission to the next, we assume that the contribution of North American "primary" ozone is much greater than that of ozone formed from subsequent photochemical reactions of NO_x and hydrocarbons and do not consider it in the following calculations. A more quantitative evaluation must await future investigations.

A characteristic time and length scale are necessary to compare our estimate of the transport of primary ozone per cyclonic event with similar estimates made by other investigators. We will follow the recommendation of *Atkinson* [1981] in characterizing fronts as meso-α phenomenon with representative timescales of one day. We estimate the horizontal spatial scale by the width of the sampling domain, approximately 500 km. We thus estimate the transport of excess ozone into a 1.5-km deep boundary layer region shown in the right side of Figure 1 during summer as 18.5 mol km^{-1} s^{-1} per cyclonic event x 500 km x 24 h ≈ 1 Gmol per 24-hour cyclonic event.

This number is larger than two previous estimates of the daily mean export of excess ozone along the coastline of the eastern United States, a geographic region on the order of 2000 km. *Parrish et al.* [1993] estimated the seasonal export of primary ozone by assuming that all of the CO emitted from the states and provinces east of the Mississippi River, E_{CO}, was exported to the troposphere over the North Atlantic. The observed slope of a line of best fit to the ratio of ozone and carbon monoxide, $m = \Delta O_3/\Delta CO$, from three surface sites along the western North Atlantic coast (Seal Island, Sable Island, and Cape Race) was then used to evaluate the ozone flux via $F_{O3} = E_{CO} \times m$. By using the observed 30% molar ratio of ozone to CO, they estimated the quantity of ozone photochemically produced and transported to the North Atlantic to be approximately 100 billion moles per summer (91 days). This corresponds to a mean daily flux of 1.1 Gmol of ozone for the coastline of North America, or 500 km/2000 km × 1.1 = 0.3 Gmol, in contrast to our estimate of 1 Gmol within the boundary layer of the sampling domain shown in Figure 1. Certainly a large part of this difference is because our analysis focused on "pollution events" that were clearly identified by daily maxima in ozone. *Jacob et al.* [1993] estimate the flux of ozone from the United States between the surface and 2.6 km to be of order 4 Gmol d^{-1}. Normalizing this to a boundary layer of 1.5 km and a coastline of 500 km produces a daily flux of 0.6 Gmol d^{-1}, also smaller than the events associated with synoptic transport reported here. However, the estimates of *Parrish et al.* [1993] and of *Jacob et al.* [1993] were intended to characterize mean values and not the extreme cases associated with frontal transport.

Our aircraft observations of CO and O_3 are similar to the earlier patterns reported by *Parrish et al.* [1993] to estimate the transport of excess ozone to the western North Atlantic. Lines of linear best fit were used to evaluate the ratio of $\Delta O_3/\Delta CO$, shown in Table 1, for the sampling domain using only measurements within the mixed layer, as defined by Z_{stable}. The slope of a line of best fit for "pollution" days was in good agreement with the surface observations of *Parrish et al.* [1993], who reported slopes of approximately 0.3, suggesting

that the two data sets are consistent. However, no statistically significant correlations were observed using aircraft data taken above the mixed layer of this region during the sampling reported here.

An estimate of the seasonal contribution by these cyclonic systems can be made by considering the frequency of occurrence of these open waves over the western North Atlantic. *Barchet and Davis* [1984] present a statistical summary of nine weather patterns over the 48 conterminous United States. The daily synoptic weather pattern was classified into nine types for the 10-year period January 1, 1969, to December 31, 1978. Weather pattern types were defined relative to the classical polar front model of a midlatitude cyclonic storm system and its associated air masses. Also, 3,652 daily surface weather maps were used to produce a time series of weather pattern types at grid points on a 3° latitude by 4° longitude array.

During this 10-year period, cyclones of the type shown in Figure 3 were observed at 45°N latitude and 66°W longitude on an average of 6 days during the 92 days of summer. Thus an estimate of the summer flux of excess ozone into the sampling domain may be approximated as 6 days of cyclonic events at approximately 1 Gmol per 24-hour cyclonic event ≈6 Gmol of "primary" ozone as a result of transport associated with eastward moving cyclonic systems.

These estimates of the exported ozone by cyclonic systems applies only to the boundary layer within the sampling domain shown on the right side of Figure 1. Extending this estimate to the coastline of North America is complicated by several factors. First, the frequency of eastward transport by synoptic storms is sensitive to latitude. *Barchet and Davis* [1984] give the summer frequency of warm sector passage at 66°W and at 48°N, 45°N and 42°N as 4.6, 6.2 and 5.1; this frequency is zero north and south of this range for the summer months. Second, background ozone is a function of latitude, and an important factor in evaluating the influx of excess ozone. And finally, the mean outflow of NO_x, NMHC and excess primary ozone would be expected to vary with latitude as a result of the geographical distribution of emissions over North America. For these reasons, extrapolating our results to a larger area by scaling these results from the spatial domain shown in Figure 1 to the coastline of North America is not valid. However, it does appear that fronts and the associated cyclones are a major outflow pathway for pollutants coming from North America into the western North Atlantic.

Summary and Conclusions

Observations of O_3, CO, NO_y and aerosols, taken in the vicinity of Halifax, Nova Scotia in conjunction with NARE during the summers of 1992 and 1993 are presented as evidence for long-range transport of O_3 photochemically generated downwind of urban areas of North America. Pollution events were noted during 6 out of 14 aircraft sampling missions.

The presence of excess ozone was determined by looking for the concurrent presence of elevated values of mission mean ozone and CO, and $r^2 > 0.5$ for the 10-s average values of ozone and CO during each flight. Ancillary support for excess ozone came from an examination of aerosol concentrations and NO_y. Measurements taken in the free troposphere or in the absence of local cyclonic flow showed no evidence of urban-related ozone.

Each of the pollution events was detected within the mixed layer in advance of eastward moving cyclonic systems. The potential for further transport during these events was evaluated with isobaric forward trajectories from the sampling domain. Two such "pollution events" out of the six appeared to be associated with subsequent long-range transport. A more typical scenario had the polluted air caught up in the circulation of the eastward moving cyclone, suggesting that subsequent identification of long-range transport would be difficult as a result of mixing with ambient air by the frontal system.

Observations are used to estimate that approximately 1 Gmol of ozone per 24-hour cyclonic event is transported into the boundary layer of the sampling domain south of Halifax (Figure 1) by individual storms. This estimate does not take into account the subsequent formation of ozone from additional photochemical reactions. Previous estimates of ozone transport, [*Parrish et al.*, 1993; *Jacob et al.*, 1993], when scaled to the spatial and temporal domain reported here, are less. However, these earlier estimates were intended to characterize mean values and not the pollution events associated with prefrontal transport.

Acknowledgments. We gratefully acknowledge Bob Hannigan and Mike Warren for their efforts in piloting the G-1 aircraft and translating scientific needs into safe flight patterns; Terry Dana for onboard scientific support, Dick Easter for assistance in planning and data reduction, and Len Peters for assistance in study design and mission planning. We also wish to acknowledge the forecasting staff at Bedford, Nova Scotia AES, the staff at the Hanford Meteorological Station, and Sylvan Murdock and staff at IMP Flight Services. Grateful acknowledgment is made to John Thorp of PNL for preparation of the synoptic maps shown in Figure 3 and to Jeff McQueen of the National Oceanic and Atmospheric Administration/Air Resources Laboratory, Silver Springs, Md. for providing the meteorological data used in the trajectory calculations. Funding for this work was provided by the U.S. Department of Energy's Atmospheric Chemistry Program. Pacific Northwest National Laboratory is operated for the U.S. Department of Energy by Battelle Memorial Institute under contract DE-AC06-76RLO 1830.

References

Atkinson, B. W., *Meso-scale Atmospheric Circulations*, Academic, San Diego, Calif., London, 1981.

Barchet, W. R., and W. E. Davis, A weather pattern climatology of the United States, *Rep. PNL-4889*, Pacific Northwest Lab., Richland, Wash., 1984.

Daum, P. H., L. I. Kleinman, W. Luke, J. Weinstein-Lloyd, C. M. Berkowitz, and K. M. 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, *95500316*3.

Derwent, R. G., P. G. Simmonds, and W. J. Collins, Ozone and carbon monoxide measurements at a remote maritime location, Mace Head, Ireland, from 1990 to 1992, *Atmos. Environ.*, *28*(16), 2,623–2,637, 1994.

Dickerson, R. R., and A. C. Delaney, Modification of a commercial gas filter correlation CO detector for enhanced sensitivity, *J. Atmos. Ocean Technol.*, *5*, 424-431, 1988.

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*(C6), 3,662–3,670, 1983.

Hansen, A. D. A., R. S. Artz, A. A. P. Pszenny, and R. E. Larson, Aerosol black carbon and radon as tracers for air mass origin over the North Atlantic Ocean, *Global Biogeochem. Cycles*, *4*(2), 189–199, 1990.

Jacob, D. J., J. A. Logan, G. M. Gardner, R. M. Yevich, C. M. Spivakovsky, S. C. Wofsy, S. Sillman, and M. J. Prather, Factors regulating ozone over the United States and its export to the global atmosphere, *J. Geophys. Res.*, *98*(D8), 14,817–14,826, 1993.

Kanamitus, M., Description of the NMC global data assimilation and forecast system, *Weather Forecastor, 4*, 335–342, 1989.

Kleinman, L. K., et al., Ozone Formation at a rural site in the southeastern United States, *J. Geophys. Res., 99*(D2), 3,469–3,482, 1994.

Lin, X., M. Trainer, and S. C. Liu, On the nonlinearity of tropospheric ozone production, *J. Geophys. Res., 93*(D12), 15,879–15,888, 1988.

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

Luria, M., C. C. Van Valin, R. L. Gunter, D. L. Wellman, W. C. Keene, J. N. Galloway, H. Sievering, and J. F. Boatman, Sulfur dioxide over the western North Atlantic Ocean during GCE/CASE/WATOX, *Global Biogeochem. Cycles, 4*, 381–393, 1990.

Lyons, T. J., and W. D. Scott, *Principles of Air Pollution Meteorology*, CRC Press, Boca Raton, Fla., 1990.

National Research Council (NRC), *Rethinking the Ozone Problem in Urban and Regional Air Pollution*, National Academy Press, Washington, D.C., 1991.

Parrish, D. D., J. S., Holloway, M. Trainer, P. C. Murphy, G. L. Forbes, and F. Fehsenfeld, Export of North American ozone pollution to the North Atlantic Ocean, *Science, 259*, 1436–1438, 1993.

Pickering, K. E., A. M. Thompson, J. R. Scala, W-K Tao, R. R. Dickerson, and J. Simpson, Free tropospheric ozone production following entertainment of urban plumes into deep convection, *J. Geophys. Res., 97*(D16), 17,985–18,000, 1992.

Pszenny, A. A. P., J. N. Galloway, R. S. Artz, and J. F. Boatman, Overview of the 1988 GCE/CASE/WATOX studies of biogeochemical cycles in the North Atlantic region, *Global Biogeochem. Cycles, 4*(2), 121–131, 1990.

Seiler, W., and J. Fishman, The distribution of carbon monoxide and ozone in the free troposphere, *J. Geophys. Res., 86*, 7,255–7,265, 1981.

Van Valin, C. C., and M. Luria, O_3, CO, hydrocarbons, and DMS over the western Atlantic Ocean, *Atmos. Environ., 22*(11), 2,401–2,409, 1988.

Vukovich, F. M., Boundary layer ozone variations in the eastern United States and their association with meteorological variations: Long-term variations, *J. Geophys. Res., 99*(D8), 16,838–16,850, 1994.

World Meteorological Organization (WMO), Atmospheric ozone 1985, *Atmospheric Ozone Assessment of Our Understanding of the Processes Controlling its Present Distribution and Change, Rep. 16*, vol. 1, Global Ozone Res. and Monit. Proj., World Meteorol. Org., Geneva, 1986.

United Nations Environment Program and World Meteorological Organization (WMO), Scientific assessment of stratospheric ozone: 1989, *World Meteorological Organization Global Ozone Research and Monitoring Project, Rep. 20*, vol. I, 486 pp., World Meteorol. Org., Geneva, 1990.

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(Received January 13, 1995; revised September 14, 1995; accepted October 3, 1995.)