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Transport and processing of O_3 and O_3 precursors over the North Atlantic: An overview of the 1993 North Atlantic Regional Experiment (NARE) summer intensive

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Abstract. In the summer of 1993, airborne and ground-based measurements of O_3 and O_3 precursors were made in the North Atlantic region. These studies were made by an international team of scientists collaborating as part of the North Atlantic Regional Experiment, an activity of the International Global Atmospheric Chemistry project of the International Geosphere-Biosphere Program. Previous measurements [cf. *Fehsenfeld et al.*, this issue] have indicated that the amount of O_3 produced from anthropogenic sources is greater than that reaching the lower troposphere in this region from the stratosphere and that ozone derived from anthropogenic pollution has a hemisphere wide effect at northern temperate latitudes. In this special issue the recently acquired data are used to better quantify the contribution of continental sources to the ozone levels over the North Atlantic. The aim of this overview is to provide the operational and logistical context of the study and to introduce the principal findings and conclusions that have been drawn from the results.

1. Introduction

The industrial regions on the continental rim of the North Atlantic are major global sources of gases that influence the oxidizing capacity and the radiative balance of the Earth's atmosphere. The 1993 intensive of the North Atlantic Regional Experiment (NARE) was designed to investigate how these sources are affecting the ozone distributions over the North Atlantic. The foreword to this special section reviews the background work that prompted this field program. This overview provides the framework and context of the measurements that were carried out as part of NARE in the summer of 1993 and presents a summary of some of the findings and conclusions from the study.

2. 1993 Summer Intensive Measurements

The geographical scope of the 1993 summer measurement campaign is indicated in Figure 1. The measurements can be grouped into six distinct activities. First, an intensive series of measurements was carried out in the continental fringes of the western Atlantic, including the East Coast of the United States, the Gulf of Maine, and the Maritime Provinces of Canada. The aim of these experiments was to better quantify the contribution of North American continental sources to the ozone levels over the North Atlantic. This study collected measurements of a large set of compounds throughout the planetary boundary layer (PBL) and the lower free troposphere (FT) to investigate the transport and chemical processing that occurs at the interface in the lower atmosphere between the continental and the marine regions. (Herein, the term "boundary layer" is applied to that part of the troposphere that is directly influenced by the presence of the Earth's surface and responds to surface forcing with a timescale of about an hour or less [*Stull*, 1988]. Over much of the NARE domain, strong surface-based temperature inversions restrict turbulent mixing to about 200 m. Accordingly, the term "lower atmosphere" is used to describe the air from the surface to about 3 km above the mean sea level.) Second, comprehensive measurements of ozone and ozone precursors were gathered on Tenerife in the Canary Islands in order to investigate the amount of ozone attributable to the transport of ozone and ozone precursors from the European and African continents. Third, a more limited set of measurements of ozone and some ozone precursors were carried out on the island of Terceira in the Azores to provide some information on the chemical composition of the lower marine atmosphere in the central Atlantic. Fourth, as a complement to surface monitoring, ozonesondes were released from the Canary Islands, Azores, and Bermuda to obtain more information concerning the vertical distribution and source of ozone above these sites. Fifth, ozone and ozone precursors were measured from the National Oceanic and Atmospheric Administration (NOAA) research vessel *Malcomb Baldridge* during the course of a cruise between Iceland and Miami, Florida, to obtain a latitudinal transect of those compounds in the lower marine atmosphere of the study region. Finally, the United Kingdom Meteorological Office (UKMO) Hercules C-130, carrying a comprehensive suite of meteorological and chemical measurements, was flown from Farnborough, England, across the North Atlantic to Halifax, Nova Scotia, Canada, returning to Farnborough via the Azores and Canary Islands. These flights provided a larger picture of the chemical composition of the midfree troposphere in transit across the North Atlantic.

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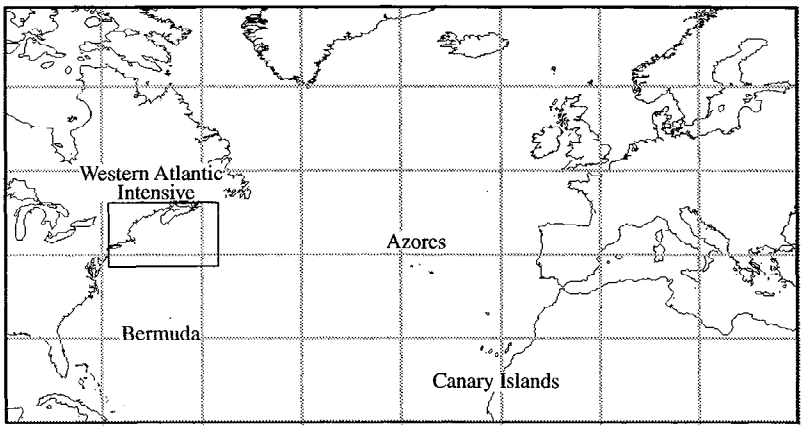

Figure 1. Map indicating the location of the measurement stations and platforms in the North Atlantic which were operated during the 1993 North Atlantic Regional Experiment (NARE) summer intensive.

2.1. Measurements Made at the Western North Atlantic Rim

The study in the region of the Maritime Provinces of Canada was carried out between July 20 and September 5, 1993. During this season, high pressure centered over the northeastern United States tends to favor the photochemical production of ozone in that region. Ozone formed over the continents during high-pressure pollution events is transported ahead of advancing cold fronts. This, combined with the summertime circulation around the Bermuda high, leads to episodic transport of pollution plumes over the Maritime Provinces of Canada [cf. *Merrill and Moody*, this issue; *Angevine et al.*, this issue (b)]. Such production and transport can lead to high levels of ozone and ozone precursors even in the most remote locations in this region.

The study region centered off the Maritime Provinces of Canada is illustrated in Figure 2. Two highly instrumented ground stations located at Chebogue Point and Sable Island, Nova Scotia, were established especially for this study. The Chebogue Point site was instrumented by NOAA, the Atmospheric Environment Service of Canada (AES), and Brookhaven National Laboratories (BNL), while the measurements made at Sable Island were operated by AES, the University of Michigan (UMi), and NOAA. The instruments operated at these sites are listed in Table 2 (Table 1 lists the abbreviations and acronyms used to identify the measurements). Measurements were also made at stations that had been established in connection with other programs: Kejimkujik National Park, located in central Nova Scotia (AES); Acadia National Park, located on the coast of Maine (National Park Service of the United States); Harvard Forest, located in west central Massachusetts (Harvard University); and several air pollutant monitoring stations in Maine (State of Maine, Department of Environmental Protection). See Figure 2 for the relative location of these sites.

In addition to the surface sites, four aircraft were instrumented: National Center for Atmospheric Research (NCAR) King Air 250; National Research Council of Canada (NRCC) Twin Otter; U. S. Department of Energy (DOE) Grumman Gulfstream G-1; and the UKMO Hercules C-130. Additional airborne measurements were made during the study period by the University of Colorado (CU) using kite-borne instruments. The instruments carried by each aircraft are listed in Table 3. Three aircraft were operated from sites in the western Atlantic region: the Twin Otter from Yarmouth, Nova Scotia (NRCC, AES, BNL); the Grumman G-1 from Halifax, Nova Scotia (Battelle Pacific Northwest Laboratories (BPNL), BNL); and the King Air from Portland, Maine (NCAR, NOAA). The UKMO Hercules C-130 was operated from several sites on both sides of the Atlantic by UKMO .

The most highly instrumented ground site (see Table 2) was located at Chebogue Point, Nova Scotia, Canada (43.75°N latitude, 66.12°W longitude, 15 m elevation), on the grounds of the Canadian Coast Guard Maritime Communication Station near the tip of a peninsula approximately 10 km south of Yarmouth, Nova Scotia. The instruments were located in a cluster of trailers located approximately 250 m to the east of the shoreline of the Gulf of Maine and 200 m to the northwest of the communications facility.

The Chebogue Point site was as isolated as possible from immediate anthropogenic pollution, but separation of signals

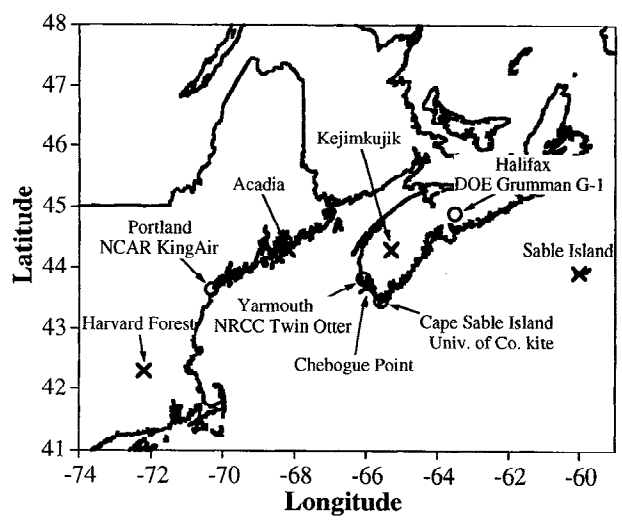

Figure 2. Location of the ground stations, the aircraft base sites, and the kite-borne measurement site which were operated in the western North Atlantic region during the 1993 NARE summer intensive. Ground stations are indicated with crosses, aircraft base sites and the kite-borne site with circles.

Table 1. Abreviations and Acronyms Used to Identify Various Measurement Techniques

Acronym	Definition
AD	aqueous denuder with flow injection analysis
ASASP	active scattering aerosol spectrometer probe
Au-CO	gold catalyzed reduction of NO_y to NO by carbon monoxide
Canister	air sample drawn into evacuated container, later analyzed by GC-FID
CL	chemilumenescence detection of NO by reaction with added O_3
Chemi (O_3)	chemilumenescence detection of O_3 by reaction with added NO
CNC	condensation nuclei counter
DNPH	dinitrophenylhydrazene (absorbant compound)
ECD	electron capture detector
FID	flame ionization detector
FP	filter pack
FSSP	forward scattering spectrometer probe
GC	gas chromatography (compound separation)
HPLC	high-pressure liquid chromatography (compound separation)
IC	ion chromatograph (anion, cation separation)
Imp.	1-10 μm aerosol impactor
MESIR	matrix isolation and electron spin resonance spectroscopy
MoO-R	reduction of NO_y compounds to NO using heated molybdenum oxide
NDIR	nondispersive infrared
P	photolysis of NO_2 to NO
UVA	ultraviolet absorption
UVRF	ultraviolet resonance fluorescence

of local origin from those due to long-range transport is a significant problem. The site was selected to avoid local upwind sources to the south through the northwest sector, the direction of the prevailing winds and the long-range transport source of interest. However, there was some ship traffic to the west of the site associated with Yarmouth Port, which produced isolated spikes in the data. More distant shipping may contribute to the measured concentrations and may simply represent a characteristic North Atlantic source. The communication station itself was automated and needed no on-site personnel but required only an occasional (approximately once weekly) maintenance visit. All vehicle parking was at that facility. A rural road ran parallel to the eastern edge of the grounds, approximately 400 m from the location of the sampling trailers, and reached a dead end at the end of the peninsula. Scattered houses were located along the road, and a dairy farm was located at the south edge of the Communication Station, approximately 700 m from the instrument trailers. The area surrounding the Coast Guard property comprised fields where dairy cows grazed and hay was grown. When winds were from the northeast through south, occasional spikes from vehicles and farm machinery were evident, and the dairy farm was a source of ammonia and other reduced nitrogen species during southerly winds. The town of Yarmouth (population approximately 10,000) with associated harbor facilities, including petroleum and liquid natural gas storage and

Table 2. Instruments at Ground Sites During the 1993 NARE Intensive

Species	Chebogue Point, Nova Scotia, Canada	Sable Island, Nova Scotia, Canada	Izaña, Tenerife Canary Islands, Spain	Terciera, Azores, Portugal
O_3	UVA	UVA	UVA	UVA
CO	NDIR	NDIR	NDIR	NDIR
NO	CL	CL	CL	CL
NO_2	P/CL	P/CL	P/CL	-
PAN, peroxy nitrates	GC/ECD	-	-	-
Other organic nitrates	Tenax/GC/ECD	-	-	-
HNO_3	Teflon/nylon FP	-	-	-
NO_y	Au-CO/CL	Au-CO/CL	Au-CO/CL	Au-CO/CL
NMHC	canister	canister	canister	canister
Carbonyls	DNPH/HPLC	-	-	-
C_y	GC/FID	-	-	-
H_2O_2	AD/HPLC	-	-	-
SO_2	UVRF	-	-	-
Peroxy radicals	-	-	MEISR	-
Aerosols	FP/IC	CNC,FP/IC, Imp.	-	-

Table 3. Instruments Aboard Aircrafts Operated During the 1993 NARE Intensive

Species	NCAR KingAir	AES Twin Otter	DOE Grumman G-1	UKMO Hercules C-130
O_3	chemi (O_3)	UVA	UVA	chemi (O_3)
CO	NDIR	NDIR	NDIR	NDIR
NO	CL	CL	CL	CL
NO_y	Au-CO/CL	MoO/R	-	Au-CO/CL
NMHC	GC/FID	canister	canister	GC-FID
Aerosols	ASASP, FSSP, CNC	ASASP, FSSP, CNC	ASASP, FSSP, CNC	ASASP, FSSP, CNC

distribution equipment, was located approximately 10 km to the north of the site; the influence of emissions from this complex could be discerned under northerly winds.

The suite of measurements provided a comprehensive indication of the chemical composition of the air reaching the location. Most of these measurements were made with inlets located atop 10-m towers erected next to the instrument trailers. Along with the usual chemical measurements the fraction of "modern" carbon in formaldehyde samples was also determined by accelerator mass spectrometry [cf. *Tanner et al.*, this issue].

The meteorology and dynamics of the site were investigated using standard meteorology measurements (temperature, dew point, precipitation occurrence, extinction coefficient of fog, wind speed and direction, solar UV radiation) and a 915-MHz boundary layer wind profiler equipped with a radio acoustic sounding system (RASS). This instrument gave a continuous recording of the vertical profiles of temperature, vertical and horizontal winds, and radar reflectivity (which gives information concerning atmospheric layering) above the site. The meteorology of the coastal site was found to be complex [cf. *Angevine et al.*, this issue (a,b)]. A strong surface-based temperature inversion was almost always present, contributing to a strongly stratified lower atmosphere. A low-level jet was also often present [*Angevine et al.*, this issue (b)].

The chemical composition and physical structure of the atmosphere over the region was investigated in a series of 48 flights by the AES Twin Otter. The regional coverage afforded by these flights is indicated in Figure 3. The aircraft carried a wide range of chemical (see Table 3) and dynamical measurements. Besides gas phase chemical composition the Twin Otter studied aerosol chemistry and microphysics in order to improve our understanding of aerosols and their interaction with clouds in this region. Condensation nuclei (CN) and cloud condensation nuclei (CCN) were measured and filter samples were collected for major inorganic and organic ions, carbon, and trace metals analysis. The aircraft measurements contributed greatly to the understanding of the meteorological results at Chebogue Point which were described above. The aircraft, which operated out of the Yarmouth Airport, concentrated on a routine schedule of flights over the Atlantic immediately south of Yarmouth, Nova Scotia, with two flights over the Gulf of Maine to New Brunswick, and others to the Kejimkujik site in the interior of Nova Scotia. During most flights the aircraft completed one or more profiles over the Chebogue Point ground site.

Additional profiles of ozone mixing ratio, temperature, and water vapor concentration were taken by kite-borne instruments that were flown from Cape Sable Island, Nova Scotia. This island is just at the southern tip of Nova Scotia, approximately 55 km to the southeast of the Chebogue Point site. The profiles made by the kite, the Twin Otter, and the King Air in the vicinity of the ground sites gave a great deal more information concerning the vertical structure and composition of the atmosphere above the surface. They clearly indicated the complexity and layering of the atmosphere in the region [cf. *Angevine et al.*, this issue (a, b)].

A second, highly instrumented (see Table 2) ground site was operated during the NARE intensive [cf. *Wang et al.*, this issue] at the AES weather station on Sable Island, Nova Scotia (43.93°N latitude, 60.02°W longitude). Sable Island is located some 300 km east of Halifax, Nova Scotia, and is reasonably isolated from human emissions. The measurement instruments were located in a building located approximately 150 m to the northeast of the shoreline and 100 m to the southwest of the AES weather station.

The only significant source of pollution on Sable Island is the exhaust from the diesel generators used to supply power to the weather station, which is the only inhabited facility on the island, and to the lighthouses. These generators are approximately 400 m to the northeast of the instrument building, so that they are downwind during the prevailing winds and from the direction of the eastern seaboard of the United States. Access to the island can only be obtained by permission of the Canadian Coast Guard. A single small aircraft provides for transportation of personnel and supplies to the island on an intermittent basis. A petroleum production platform is located approximately 20 km offshore to the

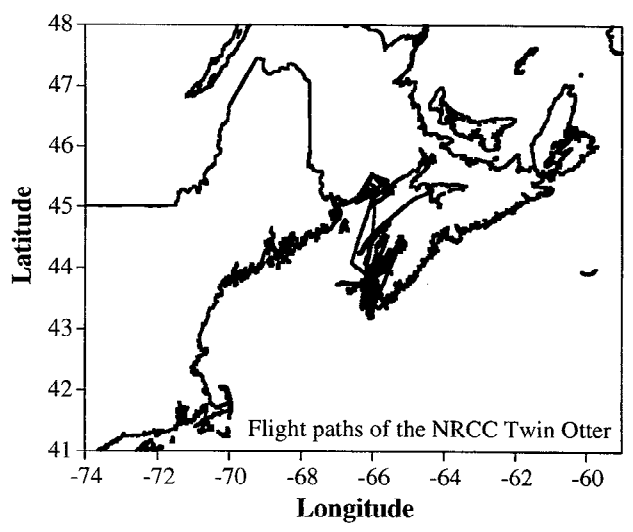

Figure 3. On a map of the region are projected all flight tracks of the National Research Council of Canada Twin Otter that were made during the 1993 NARE summer intensive.

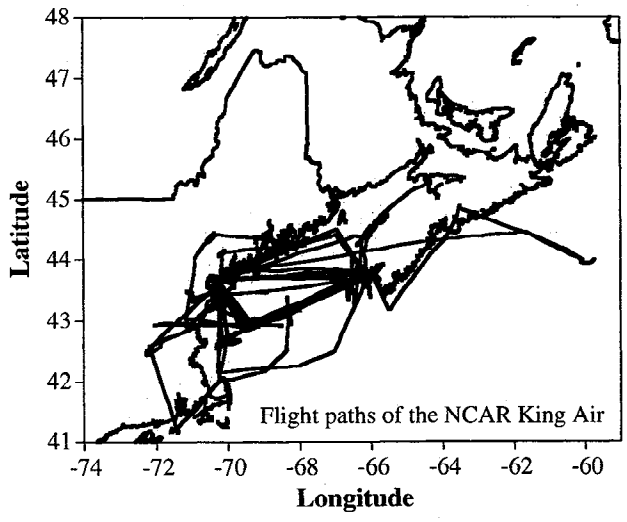

Figure 4. On a map of the region are projected all flight tracks of the National Center for Atmospheric Research King Air that were made during the 1993 NARE summer intensive.

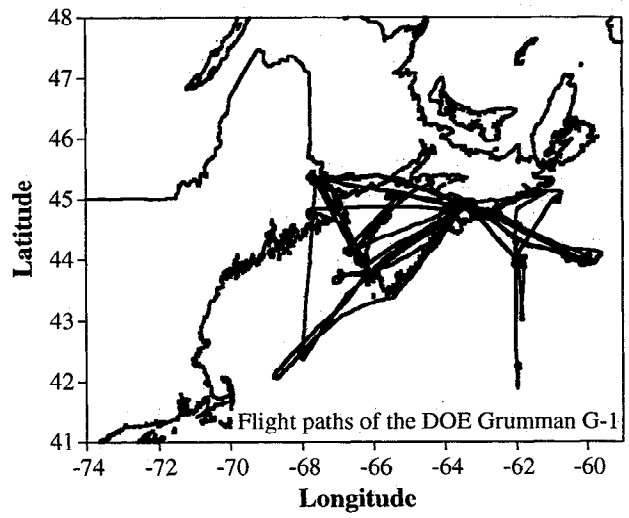

Figure 5. On a map of the region are projected all flight tracks of the Department of Energy Grumman G-1 that were made during the 1993 NARE summer intensive.

southwest; it was in operation during the measurement period. Emissions from this facility, as well as passing ships, may have influenced the measured levels of atmospheric species [cf. *Wang et al.*, this issue].

The suite of measurements at Sable Island (see Table 2) provided a reasonably complete picture of ozone and its precursors as well as the physical and chemical characteristics of aerosols reaching the site. Most of these measurements were made through inlets located atop a 10-m tower erected next to the instrument building. Measurements of NO, NO_2, total reactive oxidized nitrogen (NO_y), and nonmethane hydrocarbons (NMHCs) were added for the intensive to the ongoing measurements of aerosols, CO, and O_3 [cf. *Fehsenfeld et al.*, this issue; *Parrish*, 1993; *Parrish et al.*, 1993] that are being made at the site.

The AES operates an air quality monitoring site in Kejimkujik National Park in central Nova Scotia. At this site, from mid-July to mid-September 1993, ground level ozone, carbon monoxide, and selected (C_2-C_5) volatile organic carbon compounds (VOCs) were measured [cf. *Beauchamp et al.*, 1994]. Also, an enhanced air quality monitoring site was operated by the National Park Service of the United States in Acadia National Park, Maine. Measurements at this site included ozone, NO, NO_y, VOCs and standard meteorology parameters [cf. *Ray et al.*, this issue].

While the NRCC Twin Otter provided detailed information concerning the chemical composition and physical structure of the atmosphere over southern Nova Scotia, the other two aircraft operating in the western North Atlantic were investigating more regional aspects of the chemical processing and transport. The NCAR King Air flew 16 flights from Portland, Maine. The aircraft instrument complement is listed in Table 3, and the regional coverage provided by these flights is indicated in Figure 4. These flights focused on the composition and transport patterns of air leaving the continental environment of the East Coast of the United States and entering the marine environment over the Gulf of Maine, as well as the chemical processing that occurred in this air as it passed from the northeastern coast of the United States, over the Gulf of Maine, and into the western North Atlantic. Generally each flight was planned to include profiles, over the Gulf of Maine southeast of Portland, and over the Chebogue Point site. Individual flights were made to measure at least one profile over the sites at Harvard Forest, Acadia, and (on one long-range flight) Sable Island. Horizontal flight tracks on individual days were planned to intercept plume directions inferred from predicted trajectories, and altitudes during the horizontal transects were chosen to sample within, above, and below transport layers identified in the vertical profiles.

The U. S. DOE Grumman G-1 flew 14 flights from Halifax, Nova Scotia. The regional coverage afforded by these flights was concentrated to the south and southeast of Nova Scotia, as indicated in Figure 5. The purpose of these flights was to sample photochemically aged air masses well downwind of the North American source regions. In coordination with flights of the other two aircraft the G-1 flights enabled sequential sampling of the photochemical processing that occurred in air masses as they were transported eastward over the North Atlantic. Flights consisted of combinations of vertical soundings to determine the thermodynamic structure of the atmosphere and to locate layers of transported pollutants, and horizontal transects to establish the horizontal extent of any pollutant layers that were identified. Vertical profiles typically extended from within 100 m of the surface to altitudes of 3-5 km. Horizontal fixed altitude legs extended for distances as long as several hundred kilometers. A substantial number of flights sampled air in conjunction with the surface measurements at Chebogue Point and Sable Island for the purpose of examining the relationship between air composition aloft and at the surface.

2.2. Measurements Made off the Eastern Perimeter of the North Atlantic

Comprehensive measurements of ozone and ozone precursors were undertaken at Izaña, Tenerife, in the Canary Islands (28.30°N latitude, 16.50°W longitude, 2370 m elevation) in order to investigate the ozone and the ozone

formation from precursors attributable to transport from the European and African continents. Previous measurements have shown that during summer at Izaña the ozone levels frequently exceeded 60 parts per billion by volume (ppbv) and have approached 100 ppbv, but the causes for this elevated ozone are not well understood. Elevated ozone levels were correlated with elevated ^{7}Be, a stratospheric tracer, when the transport to the site was from the north and northwest [*Prospero et al.*, 1995]. On the other hand, during the summer, ozone was found to be correlated with anthropogenic CO_2, methane, PAN, NMHC, and CO and to be associated with long-range transport from northern latitudes, especially the European and North American continents [*Schmitt*, 1994]. When the transport was from the south and southwest, a sector that has been identified to correspond with transport from Africa, ^{210}Pb, a continental tracer, correlated with low levels of O_3 and high levels of $SO_4^=$ and NO_3^-.

During August 1993 at Izaña, ground-based measurements were made of a variety of chemical species (see Table 2) and meteorological parameters. Along with the measurement of the listed compounds, measurements were made of peroxy radicals that are most closely associated with direct photochemical production of ozone. Peroxy radical concentrations were determined by using the chemical amplifier technique and by using matrix isolation with electron spin resonance (MIESR) spectroscopy detection. The MIESR technique consists of cryogenic sampling of the radicals in an ice matrix at 77 K, followed by ESR spectroscopic detection and quantification of the radicals in the laboratory [*Mihelcic et al.*, 1990]. With the MIESR technique it was possible to distinguish between HO_2 and its organic homologues (RO_2), because of their different spectroscopic signature. In addition to the surface measurements, balloon-borne sondes were used to measure profiles of ozone, water vapor, and temperature. During the study period, 25 soundings were obtained.

2.3. Other Measurements Supporting the 1993 Intensive

The measurements at Izaña were complemented by measurements made at Ny Ålesund on Spitsbergen, Norway (78.91°N latitude, 11.88°E longitude, 474 m elevation). This sampling site is an air monitoring station of the Norwegian Institute for Air Research (NILU) and is located on Mount Zeppelin. Measurements of NO, NO_2, NO_y, O_3, $J(NO_2)$, peroxy acetyl nitrate (PAN), NMHCs, and other atmospheric constituents were made from February 15 to May 31, 1994. The measurements were aimed at quantifying the transport of ozone and ozone precursors transported into and from northern Europe during the winter and spring seasons.

Continuous monitoring of CO and O_3 was begun in April 1993 on Santa Bárbara, Terceira, in the Azores (38.73°N latitude, 27.32°W longitude, 1010 m elevation). These measurements were intended to augment a similar study in the Maritime Provinces of Canada that began in 1991. The systematics and trends in O_3 and CO observed at this central North Atlantic site are more representative of the region as a whole compared to the other available island locations, which are near the continents. Also, because of their central location the anthropogenic compounds delivered to the Azores can originate from either North America or Europe. For 3 weeks of the 1993 summer the CO and O_3 measurements were augmented by measurements of other ozone precursors (see Table 2). The NO and NO_y measurements represent the first fixed-location nitrogen oxides measurements made in the central North Atlantic troposphere.

The Terceira site is located at the highest point on the island, a volcanic peak near the island's western edge. Radio and television transmission antennas dominate the peak with a small dead-end road as access. The instruments were housed in a small concrete building provided by the Universidade dos Azores. Instrument inlets were mounted approximately 5 m above the ground on a pole adjacent to the building. There is little on-site pollution (only occasional vehicle emission spikes), but emissions from lower elevations on the island impact the measurements. During the majority of the time the site receives air from the marine boundary layer. Air flows up and over the peak with the very frequent formation of clouds, which enclose the sampling site. The lower elevations are primarily rural, farming areas with dairy cow herds and sparse population, primarily along the coast in the vicinity of the peak. The majority of the population (approximately 90,000 total) live in Angra do Heroismo (12 km to the southeast) and near Lajes air field (20 km to the east) at the opposite end of the island. Thus the island impact is strongly dependent upon wind direction; minimum impact is expected during the prevailing winds, which are from the northwest, the expected direction of transport from North America.

Although most of the aircraft measurements were aimed at determining the chemical composition and transport of compounds as they were carried off the coast of North America, limited studies also were undertaken to determine the distribution of ozone and its precursors over wider reaches of the North Atlantic. A series of ozone radiosonde profiles were obtained from Bermuda and the Azores [cf., *Oltmans et al.*, this issue]. At each location, 25 soundings were made during the campaign. The sondes were intended to indicate the systematics of the ozone distribution at locations that are thousands of kilometers downwind from the North American continent in order to provide a basis for checking the accuracy of any extrapolation based on the near-continental results.

In addition to the ozonesonde measurements the UMKO Hercules C-130 flew transect flights over the North Atlantic during late August. Figure 6 shows the regional coverage of profiles taken from these flights during the NARE campaign. The measurements made from this aircraft are listed in Table 3. The purpose of the flights was to indicate the distribution of ozone and ozone precursors across the entire domain encompassed by the study.

Finally, atmospheric trace species, including ozone, carbon monoxide, nitrogen oxides, and aerosols, were measured in the lower atmosphere of the North Atlantic aboard the NOAA *Malcolm Baldridge* during September 2-22, 1993, on a cruise from Reykjavik, Iceland, to Miami, Florida. Ozone was measured by UV absorption, carbon monoxide by gas chromatography, nitrogen oxides by chemiluminescence, and aerosol ions by ion chromatography.

2.4. Model Simulations and Inventory Development

The meteorological conditions during the NARE intensive period, August 1 to September 13, 1993, are summarized by *Merrill and Moody* [this issue]. Using trajectory analysis, synoptic charts, and other meteorological products, the origin of the air masses arriving at the two ground sites in the Maritime Provinces of Canada are discussed. Backward trajectories were also computed from Chebogue Point for the

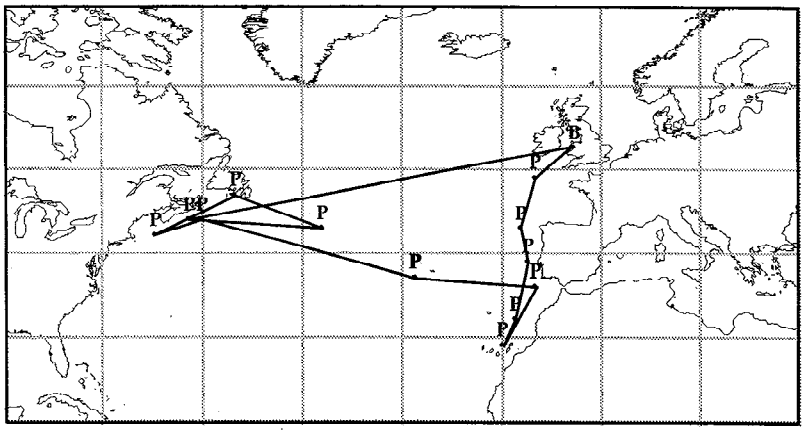

Figure 6. On a map of the region is the location of all altitude profiles of the United Kingdom Meteorological Office Hercules C-130 that were made during the 1993 NARE summer intensive. The profile locations are indicated with a P, the base in Farborough, England, with a B. The profile locations are connected by a line in the order in which the profiles were taken.

month of August 1993 using two different three-dimensional approaches to evaluate the compatibility of isentropic and kinematic trajectories [*Draxler*, this issue]. Both studies show that peak concentrations of pollutants are more frequently associated with flow ahead of advancing cold fronts during periods with transitions of the flow regime, when trajectory uncertainty is the greatest.

Wild et al. [this issue] examined the origin of specific layers of ozone and precursors that were observed during UKMO C-130 flights over the eastern North Atlantic. Backtrajectory calculations were used to identify source regions for these layers. Photochemical calculations along the trajectories from the source regions were used to evaluate the photochemical production of ozone during transport and the parameters affecting it.

The three-dimensional Eulerian regional transport model developed by the Aeronomy Laboratory of NOAA [*McKeen et al.*, 1991] was used to simulate the distribution of ^{222}Rn during the 1993 NARE intensive and the results have been compared with measurements of ^{222}Rn made onboard the Grumman G-1 aircraft that was flown from Halifax, Nova Scotia [*Lin et al.*, this issue]. The model simulates soil emissions of ^{222}Rn over the continent, radioactive decay in the atmosphere, and transport by advection, cloud and convective mixing, and diffusion.

A mesoscale chemistry transport model driven by meteorological data from a numerical weather prediction model was used to calculate ozone and related trace species over the North Atlantic for a 13-day period during the NARE experiment (August 18-30, 1993). The model [*Flatoy and Hov*, this issue] has a circumpolar grid to minimize problems associated with the definition of boundary conditions, includes treatment of cloud transport, and treats the photochemical conversion of anthropogenic and natural emissions of NO_x and the NMHCs. The model was evaluated by comparison with measurements made onboard the UKMO Hercules C-130. In addition, the model was used to provide information about the chemical and meteorological processes that gave rise to concentrations observed during specific aircraft flights.

A Lagrangian [*Atherton et al.*, this issue] as well as an Eulerian [*Kasibhatla et al.*, this issue] global chemistry-transport model was used to study tropospheric ozone over the North Atlantic and the effects of changes in the continental emissions from a global and climatological perspective. In contrast to the episodic mesoscale model by *Flatoy and Hov* [this issue] the transport in these two global models is driven by meteorological fields from general circulation models.

The Lagrangian parcel model by *Atherton et al.* [this issue] does include the emission and the gas phase chemistry of anthropogenic NO_x and hydrocarbons, wet and dry deposition, and transport due to advection, diffusion, and convection. The model was evaluated by comparison to global O_3 observations and by comparison with species correlations observed over the North Atlantic Ocean. The model was then used to characterize the photochemistry and transport over different regions of the North Atlantic Ocean. These simulations indicated that during August, tropospheric ozone appears to be transported from North America across the Atlantic Ocean in "events" and that the North Atlantic Ocean may be characterized by three regions (western, central, and eastern) with distinct photochemical and transport signatures. In the western Atlantic, emissions are fresh and O_3 and CO, O_3 and NO_y, and O_3 and (NO_y - NO_x) show a strong positive correlation. As air travels eastward across the Atlantic Ocean, it photochemically ages, selected species are deposited, and the degree of correlation tends to decrease. Finally, there appears to be a region within the central Atlantic (35°-45°N, 35°-50°W) that is not affected by episodic transport from North America.

The Eulerian global chemical transport model developed jointly by the Georgia Institute of Technology and the Geophysical Fluid Dynamics Laboratory was used to examine the export of photochemically produced O_3 to the North Atlantic Ocean basin from adjacent continental regions [*Kasibhatla et al.*, this issue]. The model includes a layered chemical scheme which uses calculated NO_x and NO_y concentrations and O_3 versus (NO_y-NO_x) relationships observed at midlatitude continental sites to calculate the photochemical production of O_3 in the boundary layer. Free tropospheric chemistry based on off-line calculations using the standard CH_4-CO-NO_x-O_3 chemistry is also included. The model was first evaluated by comparing the results of the simulations with summertime ozone measurements taken in and near the North Atlantic Ocean basin as well as with the

relationships of ozone and CO. The model was then used to examine the impact of anthropogenic emissions on the distribution of ozone over the North Atlantic region by a comparison of present-day and preindustrial emission scenarios. From the comparision it is estimated that present-day O_3 levels in the lower troposphere over the North Atlantic are at least twice as high as corresponding preindustrial O_3 levels. Moreover, the anthropogenic impact is substantial even in the midtroposphere, where modeled present-day O_3 mixing ratios are at least 1.5 times higher that preindustrial O_3 levels.

In addition to the summertime model studies, the frequency and magnitude of events that transport Arctic air over the North Atlantic during springtime were assessed through the development of a climatology of isentropic forward trajectories originating in the Arctic during the period 1984-1994 [*Honrath et al.*, this issue]. This climatology, in combination with estimated levels of NO_y and VOC compounds in the Arctic troposphere available from the published literature, was used to estimate the importance of Arctic outflow events to the budgets of nitrogen oxides and hydrocarbons in the North Atlantic region. The analysis shows that these fluxes are seasonally significant relative to other sources of ozone precursors to the North Atlantic troposphere. Moreover, they can influence the concentration of these compounds in air parcels which are not associated with direct transport from source regions. Assuming that a significant fraction of the PAN and alkyl nitrates, which compose most of the advected NO_y, decomposes over the North Atlantic, the transport of anthropogenic pollutants through the Arctic may play a significant role in the ozone budget of the North Atlantic troposphere.

Finally, a global inventory of anthropogenic emissions of sulfur oxides (SO_x) and NO_x for circa 1985 was produced in support of regional and global modeling done in connection with the NARE study [cf. *Benkovitz et al.*, this issue]. This inventory, done on a 1° by 1° latitudinal/longitudnal grid, shows that the spatial distributions of emissions of SO_x and NO_x are strongly localized in the highly populated and industrialized areas of eastern North America and across Europe. The inventory indicates that the global anthropogenic emissions of nitrogen oxides are 21.0 Tg N yr^{-1} and of sulfur-containing compounds are 65.1 Tg S yr^{-1}.

3. Findings and Conclusions

3.1. Intercomparisons

In a field campaign such as the 1993 NARE intensive, which involves measurements of the same species or parameters by different groups at different sites and from different platforms, it is essential that the different measurements be consistent and comparable with each other. This consistency and comparability can only be demonstrated by comparing simultaneous measurements by the different groups in the same air mass. Although it was not possible to bring all the investigators and their instrumentation together at the same time in one location prior to the 1993 activities, considerable emphasis and effort was placed upon intercomparisons before, during, and after the intensive period. Similarly, intercomparison of theoretical calculations by different models can yield much information. An overview of the experimental and theoretical intercomparison efforts are given below; some of the results are included in the Appendix and other papers of this issue.

The standards used to calibrate the instruments at many of the various sites and platforms that made the measurements of NMHC, NO, NO_2, NO_y, CO, and SO_2 were compared during the campaign. The NMHC standards used by the King Air were compared to those used for the NMHC measurements made at Acadia National Park, Chebogue Point, Sable Island, the Azores and from the Twin Otter and the *Malcolm Baldridge*. Standards for CO, SO_2, and NO were circulated to the measurement groups at Chebogue Point and aboard the King Air, the Twin Otter, and the Grumman G-1; each group completed a blind comparison of its field standards to the circulated standards. The UKMO Hercules C-130 was not able to participate in the standard intercomparison at that time, so after the field intensive, the Hercules investigators sent a NO calibration standard to the NOAA Aeronomy Lab where it was compared to the King Air standards.

Chebogue Point was the focal point for much of the intercomparison activity. Immediately before the intensive, an informal ground-based intercomparison [cf. *Wang et al.*, this issue] between the University of Maryland (UMd), the University of Michigan (UMi), and the Aeronomy Laboratory (NOAA) was conducted at the Chebogue Point site. During the intercomparison, air parcels representative of both polluted continental and clean marine origin were sampled. Measurements of ambient mixing ratios of O_3, CO, NO, NO_2, and NO_y by the three groups were compared. Near the end of the intensive period the CO measurement system from Kejimkujik National Park was operated at Chebogue Point for 2 days.

An opportunity to intercompare aircraft and ground data was given by the frequent passes of the aircraft close to the Chebogue Point site. Antenna towers located near the site prevented direct overflights at low altitude, but the site is close to the shore and the aircraft flew over the water, as close as possible and parallel to the shore. The Twin Otter passed the ground site on most flights and the King Air came to Chebogue Point on several of the flights at its easternmost point.

Intercomparison flights between pairs of aircraft were conducted. These included Twin Otter - King Air, Twin Otter - Grumman G1, and King Air - Hercules C-130. The flight plans were designed to accommodate sampling of the same air masses, even though the aircraft flew at different speeds.

The measurement groups from the Azores, the *Malcolm Baldridge*, and Harvard Forest intercompared their NO, NO_2, and NO_y instrumentation at the Harvard Forest site in November after the intensive.

During the course of the campaign, wind speed and direction measured by the 915-MHz wind-profiling radar at Chebogue Point were compared with those quantities measured by instruments aboard the Twin Otter [cf. *Angevine and MacPherson*, 1995]. In the height range between 300 m and 2000 m, the random difference between wind direction measurements was 9° with no systematic difference ($\Delta \leq 0.5°$). Likewise, the random difference between the wind speed measurements was 0.9 m/s with a small systematic difference of 0.14 m/s that was probably due to the uncertainty in the zenith angles of the radar.

In addition to comparisons of measurement techniques, a comparison was made of predicted air parcel trajectories [*Draxler*, this issue] using two separate three-dimensional trajectory calculation approaches: diagnostic vertical velocity fields (kinematic) and an isentropic assumption. In this

comparison, 4/day backward air trajectories were computed using the two approaches. Draxler et al. found that 90% of all the kinematic-isentropic pairs were displaced after 2 days within ± 75 hPa vertically and differed by about 10% in the horizontal. Comparison of the simulations with CO measurements indicated that both approaches identified known source regions, but peak CO concentrations were generally observed during flow transition periods when the trajectory uncertainty was the greatest.

3.2. Atmospheric Structure and Air Mass Transport Patterns

3.2.1. Near the continents. Elevated O_3 and CO levels were found to correlate and be the highest in the warm sectors of low-pressure systems to the northwest of the region. This produced a weak pressure gradient, modest southwesterly flow, and clear skies above the near marine surface in advance of the approaching cold front. Surface (1000 mbar) trajectories indicated transport from the Boston-New York corridor in advance of the cold front. Vertical mixing of ozone and precursors may have been limited by a persistent inversion that was located over the Gulf of Maine.

The meteorology of the NARE region is quite complex, with vertical layering on scales of tens of meters and substantial horizontal inhomogeneity being dominant features [cf. *Angevine et al.*, this issue (b)]. This complexity must be taken into account when attempts are made to model the domain or interpret measurement results. The measured concentrations of ozone and its precursors indicate the complicated structure of the lower atmosphere in the interface region along the coast of the North Atlantic. At the surface sites in the Maritime Provinces, vertical mixing of ozone and precursors are limited by the presence of marine inversions over the Gulf of Maine. During the daytime, over North America, the compounds emitted at the surface are mixed through the highly developed continental lower atmosphere. However, at the coast, when the prevailing airflow is from the west, these continental air masses can override the more shallow marine lower atmosphere carrying the air out over the North Atlantic. Under these conditions the highest concentrations of O_3 and its precursors would be found well above the surface [cf. *Angevine et al.*, this issue (b)].

Airborne measurements from the aircrafts and kite were obtained in the region under a variety of meteorological conditions. Depending on the wind direction and strength, these measurements often show pronounced differences between near- surface ozone concentrations and those measured several hundred meters aloft. Near- surface ozone concentrations were often poorly correlated with ozone concentrations aloft. A tracer for air transported from the continent, ^{222}Rn, which was measured aboard the Grumman G-1 aircraft, was found to vary as a function of altitude and according to the history of the air mass where the samples were collected [*Zaucker et al.*, this issue]. High radon concentrations in the marine environment were generally associated with back trajectories from the westerly sectors and with high concentrations of photochemical pollutants. For example, boundary layer radon concentrations were well correlated with both NO_y and accumulation mode aerosol number densities. This pattern was consistent with the transport of these pollutants (and the radon) to the North Atlantic from the continent. However, free tropospheric radon measurements were generally much lower than boundary layer measurements and thus were consistent with a surface source for radon and only sporadic mixing of the boundary layer with the free troposphere.

Measurements made with the 915-MHz boundary layer wind profiler at the Chebogue Point site as well as a variety of airborne and surface site measurements indicated the complexity of the meteorology at this coastal site [cf. *Angevine et al.*, this issue (b)]. These measurements showed that a strong surface-based temperature inversion was almost always present, producing strong layering in the lower atmosphere. In addition, a low-level jet was also frequently present. These measurements underline the need for continuous vertical profiling of some chemical species when undertaking atmospheric chemistry experiments in a coastal environment.

3.2.2. Remote Atlantic. The measurements of NO and NO_y carried out in the Azores during this period indicated that the central North Atlantic region was isolated from large-scale anthropogenic sources by transport of air from industrial North America during the August time frame [*Peterson and Honrath*, 1994], a feature captured by the global model of *Atherton et al.* [this issue]. Backtrajectory analyses support this conclusion. Statistical analyses of the data show that NO_y mixing ratios in the central North Atlantic near-surface mixing layer are similar to those found in near-surface mixing layer in the Pacific [*Hübler et al.*, 1992]. The relationship between CO and O_3 at the site offers insights into the photochemical histories of the sampled air parcels. For example, positive correlations during some episodes, particularly during the spring, indicate the transport of pollution from industrialized regions to the central North Atlantic troposphere, while small O_3 to CO ratios observed in summer during periods of relatively high CO are interpreted to be due to the influx of biomass burning plumes.

Ozonesonde measurements were made over an extended period in order to characterize the annual and seasonal verticle profiles of tropospheric ozone over the western North Atlantic. A number of ozonesonde profiles were obtained from Bermuda during the spring and summer of 1993 [cf. *Merrill et al.*, this issue; *Moody et al.*, this issue]. The measurements revealed a pattern of tropospheric ozone characterized by spring and summer maximum in the North Atlantic with periods of lower O_3 column mixing ratios in the fall and winter. The observations are in general agreement with the patterns of tropospheric ozone column densities over the North Atlantic inferred from satellite data by *Fishman et al.* [1990]. However, the ozonesonde measurements indicated slightly more ozone in the spring than the summer, while the tropospheric ozone inferred from the satellite measurements was higher in the summer. In addition, the sonde data clearly show that a majority of the tropospheric ozone is contained in the upper troposphere, and the variance of the total column is primarily attributable to upper tropospheric ozone. Two case studies, where elevated O_3 mixing ratio was observed in the middle and upper troposphere, were analyzed using isentropic trajectories. These results suggested that stratospheric O_3 transported into the troposphere over North America may have strongly influenced middle and upper tropospheric O_3 in the western North Atlantic Ocean.

In recent years a number of aircraft profiles taken by the UKMO Hercules aircraft have revealed relatively high levels of primary and secondary pollutants in the midtroposphere in

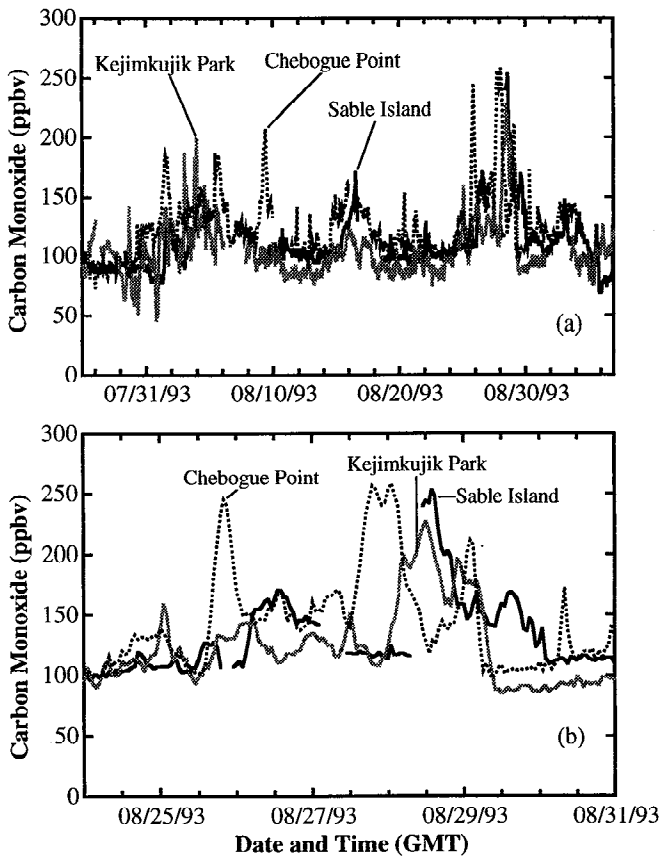

Figure 7. Time series of CO measured at the three ground sites in Nova Scotia for the whole intensive period (a) and on an expanded timescale for the most extensive episode of transport of polluted air to the region (b).

the eastern North Atlantic. Analyses suggested that pollutants in the lowest 2.5 km originate from Europe, whereas the higher-altitude pollution layer may originate over North America [cf. *Wild et al.*, this issue]. Layers of high pollution that probably originated within the boundary layer over the North American continent were detected south of Newfoundland. Other layers of enhanced CO and NO_y concentrations were found west of Portugal at an altitude of approximately 6 km.

3.3. Transport and Processing of Anthropogenic and Natural Emissions

The atmosphere over the Atlantic near the continental fringes of North America is strongly impacted by anthropogenic emissions. The correlation of O_3 with CO measured at surface sites in Maritime Canada [*Parrish et al.*, 1993] indicates the influence of anthropogenic sources of O_3 precursors on the distribution of O_3 in this region. The seasonality observed in the relation between O_3 and CO [*Parrish*, 1993] indicates that this ozone is being photochemically produced during the summer. The relation between O_3 and CO suggests that much of the O_3 observed in the lower troposphere over the temperate North Atlantic can be attributed to production from human sources. Many of the measurements during the 1993 NARE intensive were focused upon elucidating the transport and processing of anthropogenic emissions within the NARE region.

3.3.1. CO time series and CO, O_3 correlations. In the western North Atlantic region, CO was found to be an effective indicator of anthropogenic pollutant transport from emission source regions. Figure 7a presents time series through the study period of the CO levels measured at the three ground sites in Nova Scotia. Each of the sites showed elevated levels for multihour or longer periods during three general episodes: August 1-6, August 14-17, and August 24-29. The last of these periods was the most pronounced and is shown in greater detail in Figure 7b. During this last period all three of the aircraft also observed extensive, transported layers of polluted air, both at or near the surface and in the lowest 1 or 2 km of the troposphere. It is clear that the transported air masses were quite extensive; they encompassed the whole region during each of these three periods. However, the arrival times, the varying intensity, and the duration of the influence of the transported air varied between the sites. This variablity indicates that the transport patterns can be better described as large, meandering rivers of polluted air, rather than a reservoir flooding the entire region.

A strong correlation between O_3 and CO during periods of elevated levels was a common feature of all of the data sets collected at the three ground sites in Nova Scotia and from the three aircraft that operated in the western North Atlantic region. Table 4 summarizes these correlations. The correlation coefficients are significantly less than unity for all of the platforms. Thus there is uncertainty in the fitting of the slope, which is reflected in the different results derived from the two regression techniques used. Given this uncertainty, three limited conclusions can be drawn. First, there are no significant differences between the correlations determined from the surface data and those derived from the aircraft data; at least for this relationship, surface data appear to be representative of the lower troposphere as a whole. Second, all of the correlations are consistent with those reported previously [*Parrish et al.*, 1993; *Chin et al.*, 1994] for this region. Second, the one inland site, Kejimkujik Park [*Beauchamp et al.*, 1994], exhibited the poorest correlation

Table 4. Parameters of Linear Regressions Between O_3 and CO and Maximum observed O_3 Levels for Measurement Platforms in the Western North Atlantic Region

Measurement Platform	r	Slope[a]	Slope[b]	Max O_3, ppbv
Ground Sites[c]				
Chebogue Point	0.71	0.35	0.40	93
Kejimkujik Park	0.58	0.27	0.32	76
Sable Island	0.77	0.29	0.40	86
Aircraft[d]				
King Air	0.84	0.28	0.40	140
Twin Otter	0.77	0.25	---	96
G-1	0.80	0.26	---	145

[a] Standard, one-sided linear regression.
[b] Two-sided linear regression; weighting varied between platforms.
[c] Includes all 1-hour average data collected July 2-September 5, 1993.
[d] Includes plume data only (selected as King Air, all data below 1500 m altitude; Twin Otter and G-1, NO_y > 1 ppbv). Each aircraft employed different averaging periods, which affects derived linear regression parameters.

and the lowest maximum O_3 level; this likely reflects the effects of relatively rapid surface deposition of O_3 to the forested surroundings, coupled with the diurnal evolution of the continental boundary layer, which is absent at the other two surface sites.

Additional measurements of ozone and the ozone precursors, volatile organic compounds, and nitrogen oxides, were made at Acadia National Park, Cape Elizabeth, and other coastal Maine locations during the NARE intensive [cf. *Ray et al.*, this issue]. At Arcadia, peak ozone concentrations reached approximately 90 ppbv on August 24 and 110 ppbv on August 27. During the study, ozone also was measured from a commercial ferry, the *Scotia Prince*, in the Gulf of Maine where ozone concentrations up to 129 ppbv were observed during the late August pollution period described above.

3.3.2. Flux estimates. Observations of O_3, CO, NO_y, and aerosols, taken 300 to 600 km southeast of Halifax, Nova Scotia, by the DOE Grumman G-1 indicate long-range transport of O_3 photochemically generated within urban areas of North America. Eastward moving cyclonic systems are identified 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 into this region is estimated to be of the order of 130 Gmol per summer season. This corresponds to approximately 1.4 Gmoles per day, which is in reasonable accord with the 1.6 Gmol per day derived by *Chin et al.* [1994].

From an analysis of O_3, SO_2, and particulate sulfate measurements made during NRCC Twin Otter flights, the horizontal transport of O_3, SO_2, and non-sea-salt (nss) particulate $SO_4^=$ over the ocean near Nova Scotia was determined [*Banic et al.*, this issue]. The average mass of O_3 transported through an area 1 m in horizontal extent and 5 km in the vertical is 2.8 g/s, moving from west to east. In addition, the data indicated that anthropogenic O_3 accounted for 50% of the transport below 1 km, 35-50% from 1 to 3 km, 25-50% from 3 to 4 km, and 10% from 4 to 5 km.

Although the compounds over the NARE region were heavily impacted by the flux of anthropogenic compounds from North America, natural compounds from the ocean were also emitted into the atmosphere. In a separate study made from the G-1 that was done during August and September 1992, a tandem mass spectrometer was used to determine the concentration of dimethyl sulfide (DMS) over the western North Atlantic [*Spicer et al.*, this issue]. DMS mixing ratios between the detection limit of the instrument (1-2 pptv) and 332 pptv were observed. The concentrations were highly varible both horizontally and vertically. The formation of the stable layer above the ocean surface may serve to trap DMS and its oxidation by-products facilitating the removal of the latter by deposition. The DMS measured in the free troposphere was lower than in the marine surface layer. However, there was sufficient DMS to suggest significant transport from the surface to the free troposphere.

3.3.3. Investigations of photochemical processing. At Chebogue Point the levels of several photochemical products, including O_3 and the alkyl nitrates, correlate well with CO throughout the study period [cf. *Roberts et al.*, this issue]. These correlations are taken as evidence of the primarily anthropogenic origin for the precursors of these photochemical products. PAN and HNO_3 present contrasting behavior; although their concentrations were often found to correlate with CO and the other photochemical products, frequently their concentrations dropped well below the levels expected from these correlations. The evidence suggests that PAN and HNO_3 are strongly removed from an air mass by passage of the air mass through fog banks, while O_3, alkyl nitrates, and CO are not similarly affected. No evidence of such removal was found in the aircraft data, pointing to the importance of low-level fog banks, as well as dry deposition to the ocean surface, in the removal processes.

Quantifiable levels of a wide range of carbonyls including formaldehyde, acetaldehyde, acetone, propionaldehyde, methyl ethyl ketone, and benzaldehyde were consistently found at the Chebogue Point site [cf. *Tanner et al.*, this issue]. In addition, the soluble oxygenated organic compounds including formaldehyde, glycolaldehyde, pyruvate, propionate, formate, and glyoxalate were found to be present on aerosols [*Liu et al.*, this issue]. The largest formaldehyde mixing ratios were found during periods when the site was influenced mainly by local sources, or when air masses transporting precursors from the northeastern United States were sampled. A large fraction of contemporary carbon (of the order of 80%) was found in formaldehyde sampled from all transport regimes and for the full range of observed formaldehyde mixing ratios, suggesting the dominance of biogenic rather than anthropogenic, sources of hydrocarbon precursors to formaldehyde [cf. *Tanner et al.*, this issue].

Filter measurements of the chemical and physical properties of aerosols were made at Chebogue Point [*Liu et al.*, this issue]. The major organic and inorganic ions quantitated were $SO_4^=$, nss $SO_4^=$, NH_4^+, Na^+, Cl^-, NO_3^-, oxalate, methanesulfonate, and acetate. Lesser amounts of the organic species formaldehyde, glycolaldehyde, pyruvate, propionate, formate, and glyoxalate were occasionally detected. The nss $SO_4^=$ and NH_4^+ were correlated in all size ranges. Na^+, Cl^-, and NO_3^- were typically found on the larger particles. An analysis of the measurements grouped the particles into three distinctive categories that were associated with their chemical and physical properties. The three categories grouped according to their diameter: 0.15-0.3 μm, 0.25-0.35 μm, and 0.25-0.5 μm. The two largest of these categories were identified to be aerosols that had been processed through clouds, while the smallest had been derived through gas phase processes.

At Sable Island, measurements of NO, NO_2, and total reactive oxidized nitrogen (NO_y) were added to ongoing measurements of aerosols, CO, and O_3 during the NARE 1993 summer intensive [cf. *Wang et al.*, this issue]. At this site, "background" air of marine origin was characterized by low and constant levels of O_3 and CO. However, a multiday pollution episode occurred in late August (see Figure 7) during which elevated NO_x and NO_y were observed along with enhanced levels of O_3, CO, nonmethane hydrocarbons, and condensation nuclei. The relation of O_3 and NO_x oxidation products as determined from (NO_y - NO_x) appears to indicate that wet and/or dry deposition processes played a significant role in the removal of NO_y in air masses reaching Sable Island during the period of study.

Measurements made from the NCAR King Air 250 focused on a region over the Gulf of Maine [cf. *Buhr et al.*, this issue]. These flights detected polluted air masses leaving the coastline of northeastern North America with the most polluted air generally confined to altitudes between the surface and 1500 m. However, principal component analysis [*Buhr et al.*, this

issue] of the relationships observed between ozone and its precursors indicated that photochemical production of ozone was an important factor shaping the ozone distribution in this region throughout the range of altitudes investigated.

A wide variety of air masses were observed in measurements made from the NRCC Twin Otter operating near the southern tip of Nova Scotia [*Kleinman et al.*, this issue (a)]. The chemical composition reflected the location of upwind emission sources. Plumes containing high concentrations of O_3 and other anthropogenic pollutants were generally found either immediately above the ocean within the near-surface inversion layer or, more commonly, in layers located somewhat above the surface inversion. Additional ozone strata were found at higher altitudes. For a subset of these layers in which the O_3 was high and the water vapor low, a strong correlation between O_3 and NO_y was observed, as well as elevated levels of CO and aerosols, suggesting an anthropogenic source for this O_3. However, for this subset, the slope of a linear fit to the correlation between O_3 and NO_y was much higher than observed for the boundary layer plumes. In addition, at higher altitudes, O_3 layers were observed that had little correlation between O_3 and anthropogenic tracers, suggesting a natural origin for O_3.

The measurements aboard the NRCC Twin Otter indicated that the concentrations of the carbonyls decreased with increasing altitude [*Lee et al.*, this issue]. The photochemical products and multioxygenated carbonyls of formaldehyde, glycolaldehyde, glyoxal, and methylglyoxal were found to be correlated. By contrast the acids glyoxylic acid and pyruvic acid were correlated but exhibited a distinct diurnal pattern decoupled from photochemical reactivities.

Measurement of the chemical composition of aerosols made aboard the NRCC Twin Otter [*Li et al.*, this issue] indicated the presence of watersoluble inorganic and organic compounds. Although $SO_4^=$ and NO_3^- were found in abundance on the aerosols, formate, acetate, propionate, methanesulfonate, glyoxylic acid, and formaldehyde accounted for a significant portion of the total aerosol mass (20% on average). Trajectory analysis showed that these compounds were associated with the oxidation products of anthropogenic compounds transported from major source regions on the continent.

Filter samples of air and cloud water samples from these flights [cf. *Chylek et al.*, this issue] indicated that the highest black carbon concentrations over southern Nova Scotia were located between 1 and 3 km. In these layers the average carbon concentration was approximately 0.22 $\mu g/m^3$ compared to the average concentration of 0.06 $\mu g/m^3$ below 1 km and 0.11 $\mu g/m^3$ near the surface at Chebogue Point. The black carbon concentration in continental air masses was 0.23 $\mu g/m^3$, compared to 0.03 $\mu g/m^3$ for maritime air. Sulfate and nitrate were the dominant anions measured in the cloud water samples collected in marine stratus [*Leaitch et al.*, this issue]. The correlation of the cloud water concentrations of sulfate and nitrate and the droplet density in these strataform clouds was found to depend on the presence of weak turbulent mixing in the cloud.

The DOE Grumman G-1 aircraft flying from Halifax sampled plumes of photochemical pollutants over the North Atlantic Ocean at distances up to 1000 km downwind of the industrialized regions of the northeastern United States and eastern Canada [*Berkowitz et al.*, this issue; *Daum et al.*, this issue]. These plumes were found in well-defined layers up to 1 km thick in the lowest 2 km of the atmosphere, and under some conditions were sampled for distances in excess of several hundred kilometers. Plume composition was consistent with the occurrence of extensive photochemical processing during transit from source regions as indicated by high O_3 concentrations (O_3 max~150 ppbv), high fractional conversion of NO_x to its oxidation products (> 85%), and generally high peroxide concentrations (median 3.6 ppbv, max 11 ppbv).

These plumes exhibited strong correlation between CO and O_3 concentrations, between CO and accumulation mode particle number densities, and CO and NO_y. O_3 was found to depend nonlinearly on the NO_x oxidation product concentration. At low concentrations of (NO_y - NO_x) the slope (14) was within the range of values measured previously in photochemically aged air masses; at higher concentrations the slope was much lower (4.6). The low slope at high concentrations is attributed to reduced loss of NO_x oxidation products by gas phase surface deposition during transport because of strong atmospheric stability imposed by transport over cold North Atlantic waters.

Measurements made in the marine free troposphere during periods when backtrajectories indicated that the sampled air masses were transported from the southwest and west (i.e., over regions containing large continental sources) indicated elevated mixing ratios of O_3 and compounds usually associated with human sources such as nss $SO_4^=$ and HNO_3. For air masses with back trajectories indicating transport from the north and east (i.e., over maritime regions or continental without significant human sources), the O_3 and the O_3-precursor mixing ratios were typically lower.

Peroxide concentrations measured on the Grumman G-1 were found to vary between the detection limit and ~11 ppbv [cf. *Weinstein-Lloyd et al.*, this issue]. The highest concentrations occurred above the surface inversion in well-defined layers of photochemical pollutants that had been advected to the sampling region from the North American continent. In clean free tropospheric air, a strong correlation between H_2O_2 and the product H_2O*O_3 was observed that appeared to depend predominantly on variations in water vapor concentration. In plumes of photochemical pollutants, this correlation was lower and depended most strongly on the variation in the O_3 concentration. In plumes a strong linear correlation was found between O_3 and the concentration of radical sink species as represented by the quantity ((NO_y - NO_x) + 2 H_2O_2). This correlation indicates that O_3 photolysis is the principal source of radicals in the sampled air.

3.3.4. Analysis concerning photochemical age. Measurements of C_2-C_7 hydrocarbons that were made at several locations during the course of the study were used to determine the systematics of the photochemical aging of air advected from the North American continent [*Jobson et al.*, 1994]. The sampling locations include aerial surveys, ground-based locations at Chebogue Point, Sable Island, Kejimkujik, Acadia, and the Azores, and on the *Malcolm Baldridge*. Because of the effects associated with atmospheric mixing and diffusion the ratio of hydrocarbon concentrations derived from these measurements cannot be reproduced using the simple kinetic ratios that are inferred from HO reaction kinetics. However, it is found that a simple analytic expression

Table 5a. Results of Field Calibration Standard Intercomparsion

Gas	King Air, Portland	Ground site, Chebogue	Twin Otter, Yarmouth	G-1, Halifax
NO, ppmv	3.96±.11	3.80	4.10	3.84
HNO_3, ng/min	34.3 (300°C)	27.2 (300°C)	57.3/40[a]	27.22
CO[b], ppmv	42.1±2.5	42.3	42.6±4.8	41.4/45.3
SO_2, ppmv	NA	85.5	93.5	75.2

[a] signal stable for 45 min, then sudden drop to new level.
[b] Thanks to *Al Fried* (NCAR) for providing the standard.

can be derived assuming a Gaussian distribution of photochemical ages that reproduces the results obtained at the various sites.

Hydrocarbon measurements from the NRCC Twin Otter were used to examine the data in the context of the photochemical age [*Kleinman et al.*, this issue (b)]. Hydrocarbon concentration ratios were interpreted with due consideration given to the effects of dilution (above) on the compounds in the transported air masses. Four age groups were defined and the vertical profiles and relations between ozone and other trace species were examined as a function of their age. Hydrocarbon samples taken above 2.5 km were all in the older half of the data, as were all samples with dew points < 0°C. Boundary layer plumes having high dew points and high (>85 ppbv) concentrations of O_3 and related species were found to have the lowest photochemical ages. Air masses with moderately elevated concentrations of O_3 (60-85 ppbv) were found to exhibit a wide range of photochemical ages consistent with transport times of 1-4 days.

Appendix

The accurate measurement of ambient trace gas concentrations relies most often on calibrations by standard addition. Since the instruments need to be calibrated close to ambient concentrations, standards with low concentrations are involved. These standards are difficult to handle and in the past have been shown to have different concentrations than that certified by their commercial vendors. Therefore calibration standards similar to those used by the different groups were intercompared in the field with the instrumentation that was deployed by the different groups during the NARE intensive. In early August, Standard Reference Materials (SRMs) of NO, CO, and SO_2 prepared by the National Institute for Standards and Technology (NIST) in small cylinders and a temperature stabilized HNO_3 permeation source were brought to a ground site and to the various bases of aircraft operation (Chebogue Point, Yarmouth, Halifax, and Portland).

Tables 5a and 5b summarizes the results of the intercomparisons. While the agreement for NO and CO is good, there are discrepancies in the SO_2 and HNO_3 determinations. It is well known that HNO_3 is very difficult to handle at low concentrations. The differences in SO_2 were not expected.

Table 5b. Results of Laboratory Calibration Standard Intercomparison

Standard	KFA, Jülich	NOAA Aeronomy Lab
NO, ppmv	9.16 ± 0.1	9.33 ppmv ± 4%

The Jülich group, responsible for reactive odd nitrogen measurements aboard the UKMO C-130, sent a NO standard after the field measurement to the NOAA Aeronomy Lab where it was compared with several standards from NIST.

Aircraft instrumentation can only be truly intercompared in flight. The NRCC Twin Otter and the Grumman G-1 usually conduct their research flights at significantly different speeds. Since inlets and operating conditions of instruments are tailored to normal aircraft research speeds, no side-by-side intercomparison was attempted. Instead, the aircraft were directed to fly consecutively through the same air mass. Dew point and ozone measurements showed that significant atmospheric variability was encountered by both aircraft. Yet together they indicate good consistency of the measurements. The differences in total peroxide were larger than expected. A comparison of the NO and NO_y instruments was not possible due to instrument failure on this flight.

For the in-flight intercomparison the King Air and UKMO Hercules C-130 flew wingtip to wingtip at four different altitudes. They simultaneously encountered the same air masses. Temperature and dew point data from both platforms track each other very well. The NO data show good agreement. The Hercules NO data show larger scatter, reflecting a higher detection limit and lower sensitivity of the Hercules NO instrument. The Hercules NO_y instrument consistently reported significantly lower values. A two-sided linear regression of the averaged NO_y data shows a slope of less than 1 and a large offset. The small slope can be rationalized as a result of tests that found significant losses of HNO_3 in the used Hercules inlet. The offset could be due to a high "NO_y artifact" (about 400 pptv) that was subtracted from the Hercules data. Both aircraft experienced problems with air conditioning on this flight leading to unusually high cabin temperatures and failure of NMHC and CO instrumentation.

Additional comparison of measurement techniques was also made in connection with Oxidizing Capacity of Tropospheric Atmosphere. A formal intercomparison of the different peroxy radical measurement methods was organized at the Kernforschungsanlage's field observatory at Schauinsland in 1994. Five chemical amplifiers (CAs) from the United States and European countries and a MIESR participated in this campaign. In general, for atmospheric measurements the instruments agreed within a factor of 2. When comparing the results of the CAs with those of MIESR, there were indications for a reduced sensitivity of most CAs toward organic RO_2,

which is not fully explained by our current understanding of the chemical processes involved.

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