IGACtivities Newsletter

of the International Global Atmospheric Chemistry Project

A Note From the IGAC Chair: *Guy Brasseur*

Towards a Second Phase of IGAC

When IGAC was created in the late 1980's, clear scientific objectives were established with the purpose of solving important issues related to global atmospheric chemistry and global change. At that time, very little information on the global budgets of chemical species was available, and the global distribution of key compounds in the troposphere was virtually unknown. The photochemical theory for the lower atmosphere, especially in remote environments, had not been tested *in situ*, and chemical transport models were in their infancy. In fact, most of the efforts by the scientific community in the 1980's had focused primarily on issues related to stratospheric ozone; time had come to investigate how changes in the chemical composition of the *troposphere* would affect the Earth system. The importance of biosphere/atmosphere interactions was soon identified as a priority for the Project, and the role of aerosols became another important IGAC focus. Several field experiments were organized under the IGAC umbrella in various parts of the world, with superb results published in different special issues of professional journals. The two most recent experiments endorsed by IGAC are ACE-Asia (supported by NSF in the United States as well as agencies in several Asian countries) and TRACE-P (supported by NASA), both in the western Pacific and with a strong international participation.

The major success of IGAC is probably that a large international scientific community with focus on global atmospheric chemistry has been formed and has become very active. International scientific conferences sponsored by IGAC (with various partners) have presented exciting results on several occasions. A synthesis of many efforts conducted by this community is nearing completion and will appear in a few months in a volume prepared by a large group of experts. It has been reviewed extensively and can be considered as a first international assessment on global tropospheric chemistry. This integration/synthesis document is a major milestone in IGAC history, and it will conclude the first phase of the Project.

Time has therefore come to start defining the scientific objectives and an organizational structure for a new phase of IGAC. This second phase is expected to begin in , 2003. A "transition team" to guide preparation of the new phase of IGAC is being formed now and will be co-chaired by Mary Scholes (South Africa) and Tim Bates (United States). Both are world-class scientists who have contributed very substantially to IGAC's science. The task of the transition team will be to establish new priorities for research in atmospheric chemistry on the regional to global scale. Issues like upper troposphere/lower stratosphere processes, long-range transport of pollutants, multiphase chemistry, cloud-chemistry interactions and chemistry-climate couplings are examples of topics that the new IGAC will have to consider. A workshop will be held in Sweden late this year or early in 2002 to develop scientific themes and priorities for the next 10 years. Because of the breadth of the new themes for IGAC in the future, it is hoped that, in addition to IGBP and CACGP, the two parent organizations of IGAC, stronger links will be established with other related programs, in particular the World Climate Research Programme (WCRP) and its SPARC Project.

GLOBAL IGBP CHANGE

CACGP

SCIENCE FEATURES

The North Atlantic Regional Experiment (NARE)

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Background

Industrial emissions to the atmosphere are highly concentrated in the northern temperate latitudes. The EDGAR emission inventory, for example, suggests that about 90% of NO_x from fossil fuel combustion is released there [Olivier *et al.*, 1999]. The temperate North Atlantic Ocean covers about 16% of the northern temperate region or about 4% of the global surface. It is unique in that it is bordered on the west and east by the globe's most highly concentrated industrial emissions, located in eastern North America and western Europe. Consequently, the troposphere over the North Atlantic is expected to be the region of the marine troposphere most impacted by industrial emissions. NARE was established by IGAC to study the chemical processes occurring there. The primary objective was to investigate the chemical and transport processes that shape ozone distribution over the North Atlantic and to estimate the impact of human-induced emissions from North America, and Europe on the production of tropospheric ozone and related parameters. NARE was not the first research initiative to focus on the photochemistry of the North Atlantic troposphere. In 1988, the Global Change Expedition/Coordinated Air-Sea Experiment/Western Atlantic Ocean Experiment (CCE/CASE/WATOX) [Pszenny *et al.*, 1990] was conducted in this region. Its results were a useful guide for planning NARE research. Also at the time of the inception of NARE, the Atmosphere-Ocean Chemistry Experiment (AEROCE) (see Prospero, this issue) was underway in the region. AEROCE was incorporated from the start as an explicit component of NARE.

The first NARE Co-conveners—Fred Fehsenfeld in North America and Stuart Penkett in Europe—organized four meetings from 1989 to 1992 to plan research activities. Initial research was begun in 1991 with measurements of outflow of North American pollution at surface sites in the Maritime Provinces of Canada [Parrish *et al.*, 1993]. The first major intensive field study was conducted in the summer of 1993; two special sections of *J. Geophys. Res.* [101, D22 and 102, D11] were devoted predominantly to the results. Two additional field intensives were conducted in early spring, 1996 and late summer/early fall, 1997.

Current research

The following articles review the current state of progress in NARE investigations, focusing on work from the latter two field studies. Peterson *et al.* describe the transport of anthropogenic pollution within the marine boundary layer of the western North Atlantic, the region most immediately impacted by the pollution export from North America. Cooper *et al.* detail the transport mechanisms and the photochemical and physical processing of pollutants as they are transported out of the North American continental boundary layer, where the pollutants are initially injected. Stohl and Trickl survey the important experimental evidence for the trans-Atlantic transport of North American pollution. Li *et al.* use a global chemical transport model to describe the effects of anthropogenic pollution on the ozone budget of the North Atlantic. Law *et al.* describe the anthropogenic influence upon the photochemical environment of the central North Atlantic, the region presumably most remote from anthropogenic emissions.

Future plans

Ongoing NARE investigations will continue under a new IGAC Activity: Intercontinental Transport and Chemical Transformation (ITCT). This initiative was begun in response to the recognition that atmospheric pollution now has a global scale. Thus NARE has been combined with its sister IGAC Activity, East Asian/North Pacific Regional Experiment (APARE) to provide at least a hemisphere-wide perspective. The conveners are the original NARE and APARE conveners: Fred Fehsenfeld, Stuart Penkett, and Hajime Akimoto. Development of the science plan for ITCT is currently underway. The first research activity being conducted under ITCT in the North Atlantic region will be the establishment of a surface site to provide measurements in the free troposphere in the central North Atlantic. It is located at an altitude of 2225 m on the summit of Pico mountain in the Azores. Honrath and Fialho (this issue) more fully describe the planned research.

The Atmosphere-Ocean Chemistry Experiment (AEROCE): Background and major accomplishments

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AEROCE was a comprehensive multi-disciplinary and multi-institutional research program that focused on a variety of aspects of the atmospheric and marine chemistry over the North Atlantic Ocean (NAO) region. Major objectives were to gauge the impact of anthropogenic sources on the chemical and physical properties of the atmosphere, to assess the consequences of these perturbations on natural processes including climate, and, through the use of models, to predict longer term effects. Research focused on two theme areas:

Theme 1: Ozone and oxidants
To understand the role of anthropogenic emissions and natural processes in the ozone budget and the oxidizing capacity of the troposphere over the NAO.

Theme 2: Aerosols and climate
To characterize the chemical and physical properties of aerosols important to the radiative properties of the atmosphere and climate; to study the processes that affect these properties; and to assess the relative importance of natural vs. human sources.

Within the context of these two main themes, a substantial effort was made to study atmosphere/ocean chemical fluxes and their effects on biogeochemical processes in the ocean.

AEROCE began in 1988. Sponsored mainly by the U.S. National Science Foundation, the program involved both continuous measurements and intensive field programs, some of which were carried out in conjunction with activities such as NARE and ACE-2. Activities focused to a large extent on field stations: Barbados, West Indies; Bermuda; Izaña, Tenerife, Canary Islands; Mace Head, Ireland; Heimaey, Iceland; Miami, Florida. Several targeted studies were conducted with aircraft. AEROCE facilities have served a broad scientific community beyond AEROCE itself. Although AEROCE ended in 1998, its sites continue to operate independently, although at reduced levels, with support provided from the international community.

Some major findings and accomplishments are listed below.

- *Characterized role of US East Coast frontal passages on vertical distribution of pollutants over the western NAO*

Springtime aircraft measurements coupled with an ozonesonde network showed substantial NO$_Y$, CO, VOC's, and aerosols in layers in the free troposphere between the east coast and Bermuda. Ozone layers were also observed, some of which were attributed to pollution while others originated in the upper troposphere/lower stratosphere (UT/LS). Layering was driven by a mechanism that linked cyclones and associated cold fronts. Convective activity over the east coast in the warm sector (ahead of cold fronts) lifts pollutants from the boundary layer into the free troposphere where ozone can become moderately enhanced through chemical processing. In post cold-front areas subsiding air forms layers that have low specific humidity, high potential vorticity, and elevated ozone from the UT/LS. Subsidence behind a cold front encounters convective clouds ahead of the following cold front. Thus, parcels of polluted continental boundary layer air are found close to layers of air from the UT/LS containing high mixing ratios of O$_3$. These studies show how complex vertical structures evolve during frontal passage and they help clarify the relationship of ozone to pollutants [Prados *et al.*, 1999].

- *Characterized the meteorological factors associated with pollution transport from the eastern United States to Bermuda and the western NAO.*

Seasonal cycles in the concentrations of pollution-derived elements in aerosols at Bermuda were mainly driven by transport; they were not strongly related to variations in source emissions. Spring maxima in pollutants were caused by rapid transport from North America while fall maxima were the result of air that was slowly transported from North America by large high-pressure systems that stagnated over the lower mid-Atlantic states. Ozone and CO and the tracers ^{210}Pb and [7]Be exhibited seasonal cycles similar to those of the pollution-derived trace elements. The springtime maximum in ozone over the western NAO is largely driven by transport from the UT/LS over eastern North America [Moody *et al.*, 1995].

- *Developed an ozone climatology for the NAO.*

A network of ozonesonde stations provided a multi-year picture of ozone distributions over the NAO, which has led to a better understanding of the factors that drive the large-scale variability of ozone over this region and the relative importance of natural and anthropogenic sources [Oltmans *et al.*, 1996].

- *Linked atmospheric transport to water column processes.*

Records of dust deposition in deep-sea sediment traps in the Sargasso Sea were found to be consistent with measured atmospheric dust loadings measured at Bermuda. The seasonality of the fluxes differed in the atmosphere and the ocean as a result of biological cycles in the surface water. Annual variations in the sediment trap fluxes were linked to changes in the atmospheric transport efficiency from source regions in Africa as opposed to changes in the strengths of the dust sources [Jickells *et al.*, 1998].

- *Documented the large-scale temporal (daily, seasonal, interannual) and spatial variability of aerosols, precipitation, and selected gases over the NAO.*

The AEROCE data set has been widely used for testing large-scale chemical transport models; it was the only NAO data used in aerosol forcing models in the recent (third) IPCC climate assessment [IPCC, 2001].

- *Provided estimates of anthropogenic impacts on the atmospheric cycles of S and N and other substances.*

Human activities accounted for a maximum of 85-90% of particulate sulfate (in the westerly winds at Mace Head, Ireland). Even at Barbados, in the easterly Trade Winds, about half of the sulfate was from anthropogenic sources. Similar impacts were observed for particulate nitrogen species (nitrate and ammonium) and selenium [Savoie *et al.*, 1992].

- *Showed that mineral dust is the dominant light scattering aerosol over a large region of the tropical and subtropical NAO.*

On an annual basis, dust accounts for 56% of the light scattering over the tropical Atlantic, sea-salt 33% and non-sea-salt sulfate 11%. These measurements demonstrate that dust (the most prominent aerosol constituent visible in satellite imagery over the oceans) can have a great impact on radiative processes and (possibly) climate [Maring *et al.*, 2000].

- *Documented long-term trends in pollutant transport.*

Bermuda data indicate that there has been no substantial change in the concentration of nss-sulfate and nitrate in aerosols and precipitation over the period 1988-1998 although a slight downward trend is suggested. Over this time period the SO_2 emissions in the US have decreased about 15%. Such a small change may not be readily discernable because of the confounding effects of transport variability noted above. In contrast, aerosol Pb concentrations decreased by a factor of 4 during AEROCE and a factor of 10 since the 1970s. Similar changes in Pbconcentrations were observed in seawater from the NAO [Arimoto *et al.*, 1999].

- *Provided aerosol and deposition data that enabled as assessment of the impact of atmospheric inputs on nutrient cycles and primary productivity in the NAO.*

AEROCE dust deposition measurements served as a basis of a current working hypothesis – that African dust, by providing the micronutrient Fe, has strongly impacted the nitrogen cycle by enhancing the growth of *Trichodesmium sp*, a prominent colonial cyanobacterium in the central NAO. The large temporal-spatial variability of African dust could provide a strong modulation to N-nutrient budgets in the NAO. AEROCE aerosol and precipitation data have been widely used by the oceanographic community in their biogeochemical models. The dust-Fe data are central to the current focus on the effects of dust on ocean primary productivity. By modulat-

ing ocean productivity, mineral dust could have a substantial impact on the global carbon cycle and atmospheric CO_2. Finally, AEROCE measurements show that direct inputs of N-species to the surface ocean via wet deposition can lead to episodic enhancements in primary production [Michaels *et al.*, 1996].

- *Showed the impact of long range transport on air quality in the southeastern (and Gulf Coast) United States.*

Aerosol studies at Barbados and Miami show that during the summer, on a mass basis, African dust is the major sub-2.5 mm diameter aerosol. Furthermore dust is carried throughout the southeastern United States where it could have implications for air-quality enforcement. Although African dust in itself is unlikely to cause an exceedance of the new EPA PM 2.5 standard, dust in combination with local pollution aerosols could well exceed the new standards. These data suggest that African dust can be a health issue in the southeastern states [Prospero, 1999].

- *Showed that long-range dust transport is linked to large-scale climate processes.*

AEROCE African dust measurements (and the long term record from Barbados) show that dust concentrations vary greatly from year to year. Concentrations increase sharply (a factor of 3-4) during periods of severe drought. The long-term record at Barbados has been shown to be strongly related with the North Atlantic Oscillation. This relationship can provide the basis for linking dust to paleoclimate forcing processes [Prospero, 1996].

- *Provided a unique aerosol data set to the remote sensing community.*

AEROCE aerosol data has been widely used by the remote sensing community to develop and test aerosol algorithms. AEROCE data is currently being used as a part of the NASA Global Aerosol Climatology Project. The value of the AEROCE data set lies in the fact that the data were obtained on a daily basis (and thus could be linked to synoptic meteorology) and the data are available as an integrated data set over a large ocean region [Diaz *et al.*, 2001.

- *Provided (in conjunction with satellite data) information on global dust sources and the processes that affect dust mobilization.*

The linking of the AEROCE mineral dust record to the TOMS absorbing aerosol product has led to a global assessment of dust sources. The major dust sources are shown to be associated with topographical lows in arid regions. All major dust sources are associated with deep alluvial soils that were deposited during Pleistocene pluvials. This study shows that the paleoclimate record of dust (from ocean sediments and ice cores) must be reinterpreted. Dust does not necessarily imply arid conditions; for significant production, aridity must follow upon a relatively recent (in a geological sense) pluvial period [Ginoux *et al.*, 2001].

- *Demonstrated that sea-salt aerosol is a major reaction medium and sink in the chemical evolution of S and N over the NAO.*

Scavenging by sea salt is a potentially important shunt in the S cycle that could limit production and growth of new submicrometer aerosol. Sea salt must be explicitly considered in assessing relationships between S emissions and the associated direct and indirect radiative effects of S-containing particles in marine regions. Studies also led to the first reliable estimates of marine aerosol pH as a function of particle size and implications for S oxidation, N phase partitioning, and associated radiative effects. HCl and HNO_3 phase partitioning strongly buffers the pH of supermicrometer marine aerosol [Keene *et al.*, 1998].

- *Investigated the importance of halogen radical chem-istry in the cycling of S, N, O_3, and alkanes over the NAO.*

Demonstrated that most particulate Br is efficiently volatilized from sea-salt aerosol. This observation is consistent with predictions based on the autocatalytic halogen activation mechanism. Showed that HCl produced from Cl-atom reactions in the gas phase can be efficiently recycled through acidic aerosol [Milne *et al.*, 2000].

- *Developed predictive tools to relate chemical and optical properties of precipitation at Bermuda and Barbados with aerosols properties of corresponding scavenged air parcels.*

These tools can be used to model the influences of precipitation on the optical properties of marine air over the Western NAO [Todd *et al.*, 2001].

AEROCE was uniquely conceived to investigate a broad array of atmosphere-ocean chemistry issues over a large ocean region for an extended time period. The results demonstrate the value of combining long-term measurements with intensive campaigns, highlight the important role that the atmosphere plays in linking continental and ocean chemistry processes, and lay the foundation for future programs in this region.

Transport of anthropogenic pollutants within the marine boundary layer of the Central and Northwestern North Atlantic

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Long-range transport of anthropogenic emissions appears to be transforming the composition of much of the remote troposphere. For example, North America exports a large amount of ozone to the North Atlantic [Parrish *et al.*, 1993; Chin *et al.*, 1994]. However, this flux is not the total impact on the remote troposphere, since ozone formation continues in airflows with levels of NO_X (=NO + NO_2) above about 80 pptv [Moxim *et al.*, 1996]. Determining the influence of long-range transport of anthropogenic pollution on the composition of the North Atlantic troposphere, especially with regard to the ozone budget, is one of the primary goals of NARE. In this paper we summarize the results from three ground-based measurement campaigns organized by Michigan Technological University. We also present results from modeling studies of the fate of reactive nitrogen oxides and ozone production within the North Atlantic marine boundary layer (MBL).

We conducted campaigns during the NARE intensives in 1993, 1996, and 1997 to determine reactive nitrogen oxide levels and investigate photo- and physicochemical processes in remote regions of the North Atlantic MBL. The 1993 study was in the summer at the 1 km peak of Santa Barbara volcano (27.322^{o}W, 38.732^{o}N) on the Azores island of Terceira. The Azores provide the only location for making extended observations of background trace gas levels and long-range transport events over the central North Atlantic Ocean [see Honrath and Fialho, this issue]. During the winter/spring of 1996, measurements were conducted at the Canadian Coast Guard's Cape Norman lighthouse (55.90^{o}W, 51.60^{o}N, 30 m elevation) at the northern tip of Newfoundland. This site maximized exposure to airflows from the Arctic, provided direct exposure to the unmodified marine troposphere, minimized impacts from local emissions, and provided opportunities to sample long-range transport events from the heavily populated regions of North America. The fall 1997 NARE intensive was located at the Canadian Coast Guard's Cape Pine lighthouse (53.31^{o}W, 46.37^{o}N, 100 m elevation) at the southern tip of Newfoundland. This location was chosen so that local and regional emissions from Newfoundland would not interfere with analysis of long-range transport events from more southerly portions of North America. The species measured in all three studies included NO and NO_Y (the sum of all reactive nitrogen oxides), O_3, CO and non-methane hydrocarbons. The 1996 and 1997 measurements also included NO_2, nitric acid , nitrate aerosol, peroxyacyl nitrates (PANs) and alkyl nitrates.

Measurements and modeling of reactive nitrogen oxide levels at Terceira in the Azores demonstrate the importance of downward transport of NO_Y-rich air from the free troposphere (FT) to the MBL, and also demonstrate the importance of considering the MBL lifetimes of trace gas species. Observations indicate that NO_Y levels in the overlying FT were 300 to 500 pptv at Terceira during NARE 1993 [Peterson *et al.*, 1998]. When combined with transport of this NO_Y-rich air, relatively simple modeling shows that the lifetime of NO_Y in the MBL must be

0.6 to 1.8 days in order to explain background MBL NO_Y levels of 59 to 93 pptv [Peterson *et al.*, 1998; see also Table 1 in Cooper *et al.*, this issue]. These low MBL NO_Y levels, and lack of CO and O_3 correlations, indicate an absence of long-range transport events in this region during the period of the NO_Y measurements [Peterson *et al.*, 1998]. This is not always the case. Parrish *et al.* [1998] show that CO and O_3 are correlated at Terceira during short periods in other seasons. However, it is important to note that the simple modeling results show that caution is needed when interpreting correlations between CO and O_3 levels observed in the MBL, as these correlations will be degraded relative to those in the FT due to the different lifetimes of these species in the MBL.

A chemically explicit model, free of the simplifications required in models that use lifetimes to compute mixing ratios, and not dependent on interpretations of correlations, was also used to study trace gas levels in subsiding air. The cycling of reactive nitrogen oxides and their effect on ozone during long-range transport from the high latitude FT to the North Atlantic MBL was followed with the NCAR Master Mechanism employed as a Lagrangian box model advecting on the path of typical (subsiding) isentropic trajectories [Hamlin and Honrath, 2001]. In these simulations, subsidence-induced warming releases NO_X from air rich in the NO_X-reservoir species peroxyacetyl nitrate (PAN) as it enters the North Atlantic MBL. The situation representing our best estimate of the upper-limit of PAN decomposition is depicted in Figure 1. When generalized to all airflows, this process is responsible for more than 80% of the NO_X found in portions of the North Atlantic MBL during winter [Moxim *et al.*, 1996]. Thus, anthropogenic emissions that form PAN enhance NO_X levels in the remote MBL. Although the NO_X released from PAN is oxidized to nitric acid in a few days (Figure 1) and deposited, elevations in NO_X levels are responsible for increasing the ozone tendency by as much as 1 ppbv/day, relative to the ozone tendency without NO_X release from PAN [Hamlin and Honrath, 2001].
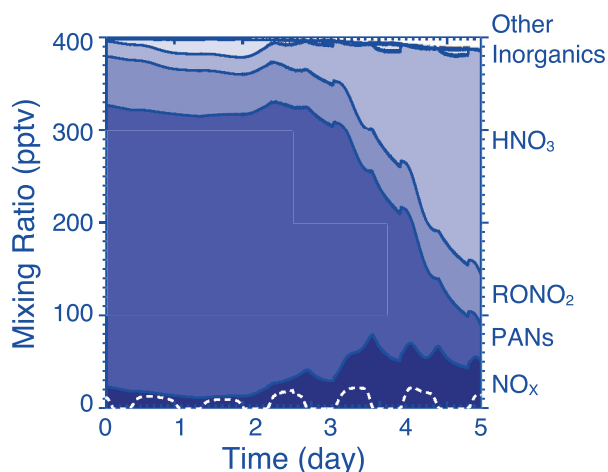

Figure 1. Transformations in NO_Y speciation during subsidence from the high latitude free troposphere in May.

While current models and measurement techniques are becoming increasingly sophisticated and accurate, discrepancies between model results and observations are significant in some cases. One such example involves our NO_X measurements from Cape Norman in northern Newfoundland and an explicit set of global chemical transport model (GCTM) simulations of the influence of long-range transport on NO_X levels over the North Atlantic [Moxim *et al.*, 1996]. The observed median NO_X level of 24 pptv in the MBL of this region is similar to anthropogenically-impacted levels observed in the western Pacific MBL, and is 35%-48% higher than previous observations in the clean midlatitude MBL [Peterson and Honrath, 1999]. Despite this, observed monthly average NO_X levels at this site are about one-half of those predicted for the northwestern North Atlantic MBL by this GCTM [Peterson and Honrath, 1999]. Reactive nitrogen oxide levels observed within the MBL at Terceira in the Azores are also much smaller than predicted by this and another GCTM [Kasibhatla *et al.*, 2000; Lawrence and Crutzen, 1999], both including ship emissions [Corbett and Fischbeck, 1997]. Analysis of NO_X and NO_Y observations made during background MBL airflow periods at Cape Norman in Newfoundland supports this result. Although NO_X/ NO_Y ratios were greater than 0.25 during half of these periods, elevations in NO_X of just 20 pptv above background levels are sufficient to explain this high NO_X/ NO_Y ratio. While we are not certain of the origin of this NO_X enhancement, it is much smaller than expected from ship emission impacts, based on the results of the two GCTMs [Kasibhatla *et al.*, 2000]. Taken together, these results indicate that current GCTMs overestimate reactive nitrogen oxide levels in the North Atlantic MBL. Kasibhatla *et al.* [2000] suggest that this may be due to, "the lack of parameterized representations of plume dynamics and chemistry in these models". Peterson and Honrath [1999] state that, "the durations of simulated events of elevated NO_X are much longer than are observed". In both cases the authors conclude that simulations of relatively short events with high levels of reactive nitrogen oxides (i.e., long-range transport events, ship emissions) are currently inadequate.

The magnitude of nitrogen oxide export from source regions is a key determinant of global ozone production. Measurements at Cape Pine, southern Newfoundland during fall 1997 indicate significant NO_Y export, but less than calculated by a regional model [Liang *et al.*, 1998]. Nevertheless, the influence of the exported NO_Y upon the O_3 budget is likely greater than the influence of direct O_3 export. To fully assess the ultimate impacts of anthropogenic emissions on ozone levels and production rates over the North Atlantic, additional measurements are needed. One goal of our program at Michigan Technological University is to extend the available data. This is the goal of the PICO-NARE study [Honrath and Fialho, this issue] at a FT site in the Azores.

The influence of synoptic scale transport mechanisms on trace gas relationships above the western North Atlantic Ocean

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A goal of the North Atlantic Regional Experiment (NARE) is to determine the synoptic scale meteorological mechanisms that transport pollutants from North America to the western North Atlantic Ocean (WNAO). Mid-latitude cyclones tracking from west to east are believed to be responsible for the bulk of the trace gas transport throughout the year, even in summer when these systems are weaker [Merrill and Moody, 1996]. Over the past 30-40 years precipitation and clouds have been studied in terms of the component airstreams of mid-latitude cyclones [Carlson, 1998]. Recently, both the origin and evolution of individual airstreams have been shown to influence trace gas mixing ratios and relationships in the troposphere [Bethan *et al.*, 1998; Cooper *et al.*, 2001a]. This article interprets *in situ* trace gas measurements and their relationships in terms of the airstreams of mid-latitude cyclones.

The typical mid-latitude cyclone is composed of four major airstreams (Figure 1). The warm conveyor belt (WCB), cold conveyor belt (CCB) and dry airstream (DA) produce the distinctive comma cloud of a mature mid-latitude cyclone [Browning and Monk, 1982; Browning and Roberts, 1994; Bader *et al.* 1995; Bethan *et al.*, 1998; Carlson, 1998]. To a first approximation, these airstreams move along sloping isentropic surfaces. The CCB originates north of the cyclone's warm front, and relative to the cyclone center, ascends as it heads westward, with a component heading eastward at higher altitudes. The WCB is located on the eastern side of the cyclone, ahead of the surface cold front. The air originates at low altitudes in the warm sector of the cyclone and travels northward, ascending into the mid- and upper troposphere, above the CCB. In contrast the DA originates at high altitudes on the poleward side of the cyclone and descends into the mid- and lower troposphere west of the cold front. Cooper *et al.* [2001a] introduced the concept of the post cold front airstream (PCF) to explain the lower and mid-tropospheric flow that follows a cold front, beneath the DA.

Initially, NARE focused on two synoptic scale transport mechanisms, the tropopause fold and the cyclone warm sector of mid-latitude cyclones. The cyclone warm sector constitutes the lower portion of the WCB. In eastern North America, this feature develops on the western side of surface anticyclones where stable and often stagnant conditions allow for the accumulation of photochemically active trace gases in the lower troposphere [Comrie and Yarnal, 1992; Comrie, 1994; Cooper and Moody, 2000]. As the cyclone moves off shore it carries the warm sector with it, exporting the polluted air mass to the WNAO [Berkowitz *et al.*, 1996; Merrill and Moody, 1996; Moody *et al.*, 1996].

Tropopause folds embody the isentropic decent of stratospheric air on the polar side of upper level cold fronts. They occur within the dry airstream and are associated with every mid-latitude cyclone, their depth of penetration roughly proportional to the strength of the cyclone [Danielsen, 1968; Shapiro, 1980; Johnson and Viezee, 1981]. These intrusions of stratospheric air into the mid- and upper troposphere lead to irreversible stratosphere/troposphere exchange (STE), enriching the ozone content of the DA. Tropopause folds are easily identified when isentropic potential vorticity, a quasi-conservative dynamic tracer of stratospheric air, is contoured on an altered water vapor image [Moody *et al.*, 1999; Wimmers and Moody, 2000]. This product is derived by correcting the GOES satellite 6.7 μm water vapor channel for temperature and zenith angle bias, resulting in a depiction of specific humidity, rather than relative humidity [Soden and Bretherton, 1993] in the mid- to upper troposphere. Tropopause folds have their greatest impact during spring when cross-tropopause exchange and ozone mixing ratios in the lower stratosphere reach their seasonal peaks; their weakest impact occurs in late summer/au-
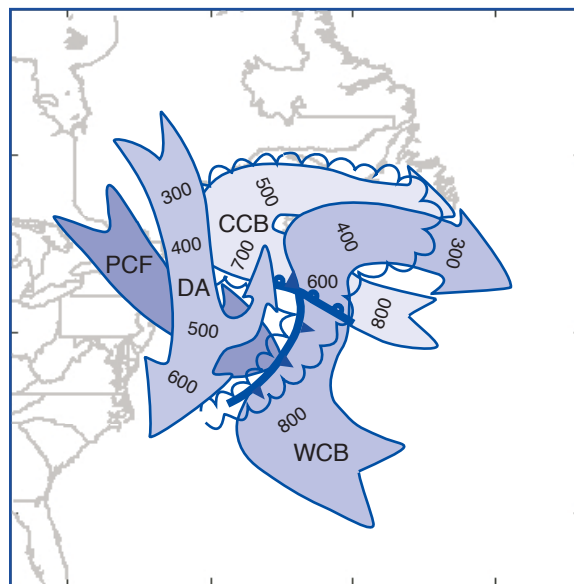

Figure 1. Model of a mid-latitude cyclone. The scalloped lines indicate the border of the comma-cloud about the cyclone center (L). The numbers on the warm (WCB) and cold (CCB) conveyor belts indicate the pressure at the top of these airstreams, while the numbers on the dry air stream (DA) indicate the pressure at the bottom of this airstream. The post cold front (PCF) airstream flows beneath the DA.

Figure 2. Spring 1996 ozone vs. CO for all

	Spring 1996	Summer-Autumn 1997
1. Percent of NO_Y emissions lost from boundary layer or during transport from it	33-76%	78-91%
2. Percent of NO_Y emissions reaching altitudes above 3 km.	5.3%	2.8%
3. Percent of total NO_Y above 3 km originating at the surface	41%	35%
4. Mean e-folding lifetime of NO_Y	1.8 days	1.7 days

tumn [Appenzeller *et al.*, 1996; Fahey and Ravishankara, 1999; Monks, 2000]. Several NARE [Berkowitz *et al.*, 1995; Merrill and Moody, 1996; Moody *et al.*, 1996; Oltmans *et al.*; Parrish *et al.*, 2000; Cooper *et al.*, 2001a] and Atmosphere Ocean Chemistry Experiment (AEROCE) studies [Moody *et al.*, 1995; Cooper *et al.*, 1998; Prados *et al.*, 1999] have described the influence of tropopause fold events on the chemistry of the WNAO atmosphere. NARE aircraft and ozonesondes have routinely detected mid- and upper troposphere ozone enhancements on the polar side of cold fronts during all seasons; ample meteorological and chemical data indicate that tropopause folds produced these enhancements. Moody *et al.* [1995] found that post-frontal transport, descending from the mid-troposphere above North America, produced surface ozone enhancements at Bermuda with greatest frequency and intensity during spring.

The interpretation of *in situ* trace gas measurements and their relationships in terms of the airstreams of mid-latitude cyclones requires two components: a climatology of the airstreams, including their frequency, origin and transport routes, and an understanding of the chemical and physical processing of the trace species in each airstream. Stohl [2001] has established a climatology of WCBs and DAs by calculating a large set of trajectories with initialization points equally distributed over the Northern Hemisphere over a year's period. The trajectories were classified by airstream according to certain criteria [Wernli and Davies, 1997; Wernli, 1997]. The results indicate that WCB inflow occurs only at latitudes below 50° N; during winter and spring inflow only occurs below 40° N. Inflow frequency maxima occur at the southeastern seaboards of North America and Asia. The proximity to the continental east coasts is significant since the highest global anthropogenic emissions of sulfur, nitrogen oxides, and other pollutants are located there. The air masses entering WCBs traverse both the high-emission continental regions and the neighboring, relatively source free Gulf of Mexico, Caribbean, and tropical Pacific. Thus the chemical characteristics of WCB air masses range from very clean [Grant *et al.*, 2000] to highly polluted [Stohl and Trickl 1999], depending on their exact

path. DAs originate from a belt around the Northern Hemisphere between approximately 30° and 60° N, in the vicinity of the polar front jet stream. The most striking feature is the seasonal cycle with high DA activity during the winter and very low activity in the summer.

The chemical and physical processing of the trace species in each airstream has been characterized by Cooper *et al.* [2001a,b,c]. They 1) give examples of trace gas signatures from all four major midlatitude cyclone airstreams, 2) develop a conceptual model for systematically investigating the trace gas relationships in the airstreams, and 3) discuss the seasonal differences in these relationships. Cooper *et al.* [2001a] describe how modeled, remotely sensed and *in situ* meteorological data were used to identify airstreams during the late summer-early autumn 1997 NARE campaign above the Canadian Maritimes, and present a limited number of case studies. Cooper *et al.* [2001b] analyze the chemical measurements of all the airstreams sampled during NARE 1997, amalgamate the data into a single composite cyclone, and develop a conceptual model of the chemical and physical processing within a mid-latitude cyclone. The model separates the meteorological influences on airstream trace gas signatures from the influence of surface emissions heterogeneity. The meteorological influences on airstream trace gas composition during late summer–early autumn above the WNAO are: 1) The DA always has a stratospheric component that brings ozone into the mid- and upper troposphere. 2) The PCF originates to the northwest, is unaffected by wet deposition and the sunny conditions may allow for some photochemical ozone production. 3) Both the CCB and WCB experience wet deposition, but because of its southerly origin and association with the western side of surface anticyclones the WCB draws from regions more favorable for photochemical activity than either the CCB or PCF. 4) The CCB is generally cloudy and does not show signs of significant photochemical production of ozone. 5) Very little of the oxidized nitrogen species (NO_Y) is exported from the lower troposphere, due to wet and dry deposition. 6) Airstreams in the mid-troposphere are the most susceptible to mixing with other air masses, which blurs the distinction between airstream trace gas signatures. The remainder of the chemical variation between and within airstreams is largely controlled by surface emission heterogeneity; for example a WCB that draws from the polluted mixed layer will have higher mixing ratios of ozone and CO than one that draws from the clean marine boundary layer.

Stohl *et al.* [2001] have investigated the extent and time scale of the removal of NO_Y by wet and dry deposition during transport from the North American continental surface, where the sources are located, to the free troposphere of the WNAO. Their analysis utilized aircraft-based measurements of NO_Y and CO from the NARE
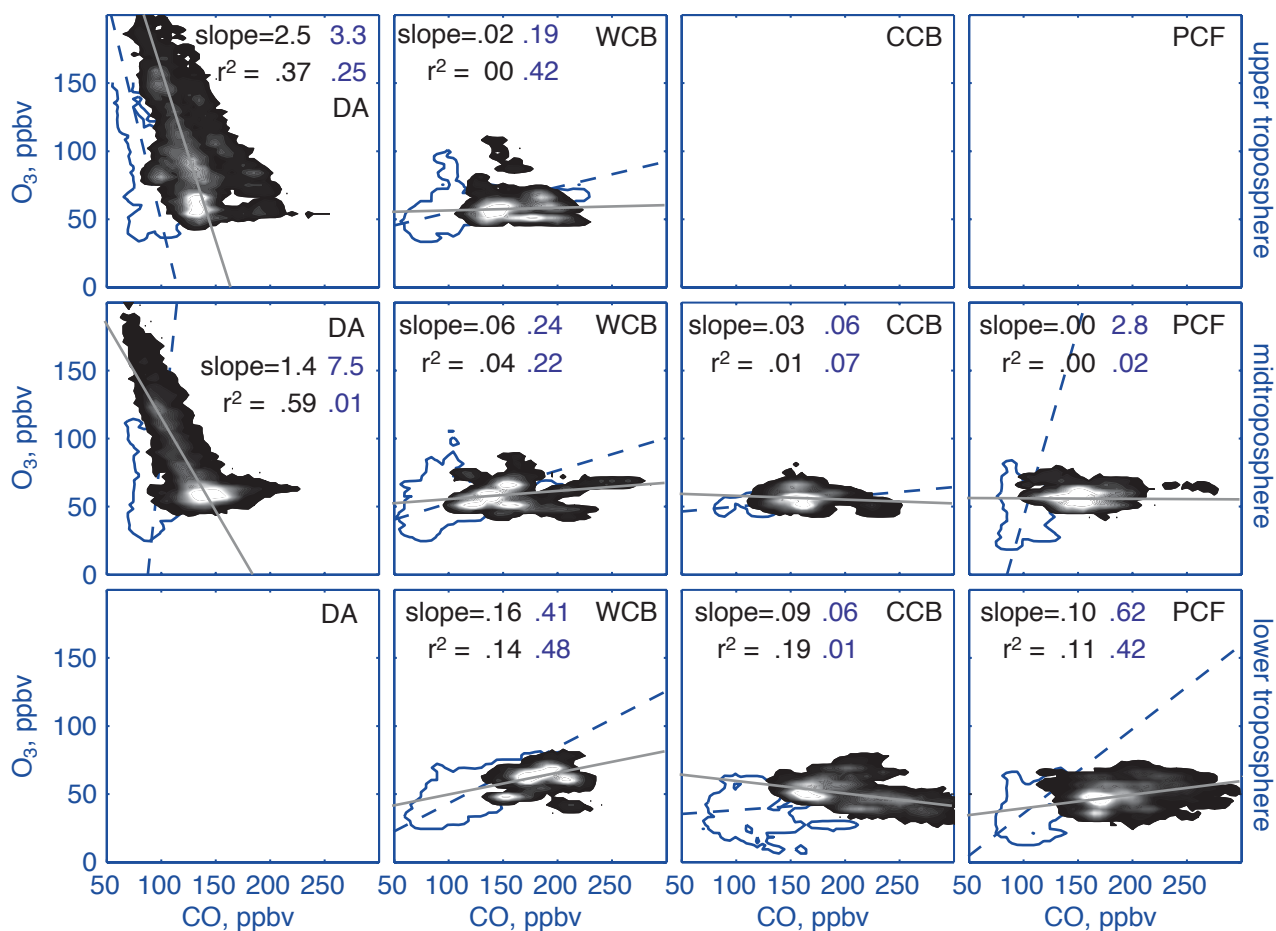
Figure 2. Spring 1996 ozone vs. CO for all four cyclone airstreams at three levels of the troposphere. The lighter (darker) shading corresponds to relatively higher (lower) data density. The range of the late summer-early autumn 1997 data for each airstream is outlined in blue. The linear regression lines for each airstream are shown for spring 1996 (gray lines) and summer-autumn 1997 (blue dashed lines), with the slope and r-squared values labeled in black (spring) and blue (summer-autumn).

1997 and early spring NARE 1996 studies, combined with a particle transport model. Extensive and rapid removal of NO_Y was found in both seasons. The major findings of the study are summarized in Table 1.

Cooper *et al.* [2001c] show that seasonal variation of photochemistry and meteorology affect the characteristic trace gas mixing ratios of the conceptual cyclone. During spring background ozone and CO are at their maximum, cyclones track farther south where continental surface emissions are greater, and STE injects more ozone into the troposphere. Ozone and CO are compared by airstream for early spring and late summer-early autumn conditions over the WNAO in Figure 2. Using the positive (negative) O_3/CO slope as an indicator of photochemical ozone production (destruction), ozone production during late summer-early autumn is associated with the lower troposphere PCF and all levels of the WCB, especially the lower troposphere. During early spring, significant ozone production is not associated with any airstream at any level, with the lower troposphere CCB associated with ozone destruction. The negative slopes of the DA indicate STE increases ozone in the mid- and upper troposphere.

Building a more complete picture of the seasonal and spatial variation of the trace gas relationships in midlatitude cyclones will require additional analyses. Emmons *et al.* [2000] have compiled an extensive data set of chemical measurements from many aircraft campaigns over the past 20 years, indicating regions of the globe where additional composite cyclones could be constructed. The upcoming Intercontinental Transport and Chemical Transformation (ITCT) aircraft campaign will be conducted over the eastern North Pacific Ocean and western North America in spring, 2002. The differences in chemical composition of cyclones entering North America from the Pacific and exiting the continent into the WNAO will provide a more comprehensive picture of North American cyclones. Ultimately the trace species relationships in cyclone airstreams, and their variation with season and region will be very useful for comparison to the output of chemical transport models that have the ability to resolve cyclone structure.

Experimental Evidence for Trans-Atlantic Transport of Air Pollution

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Introduction

With increasingly costly measures taken to reduce ambient concentrations of air pollutants at a regional level, pollution sources far upwind are receiving more and more attention. There is particular concern that rising emissions in regions with growing industrialization could offset the positive effects on regional air quality of emission reductions made in other parts of the world. It is suggested that Eurasian pollution transported by westerly winds across the Pacific Ocean basin can increase concentrations of CO, peroxyacetyl nitrate (PAN), O_3 and aerosols in North America [Jaffe *et al.*, 1999; Wilkening *et al.*, 2000]. Model studies indicate the contribution of Asian emissions to pollutant concentrations over North America will be significant in the future [Berntsen *et al.*, 1999; Jacob *et al.*, 1999; Yienger *et al.*, 2000].

Trans-Atlantic transport of pollution is of equal concern for Europe as trans-Pacific transport is for North America. In fact, because of the smaller dimension of the North Atlantic as compared to the North Pacific, intercontinental transport between North America and Europe may be even more important. This paper summarizes the experimental evidence for trans-Atlantic air pollution transport.

Evidence for trans-Atlantic transport of O_3 and its precursors

The NARE campaigns have provided comprehensive evidence of the strong influence that pollution export from North America has on the air chemistry over the western part of the Atlantic Ocean, both within and above the boundary layer [Petersen *et al.*, this issue].

Detection of air pollution from North American sources is more difficult as one proceeds eastwards over the Atlantic Ocean. Parrish *et al.* [1998] reported a clear influence on O_3 and CO at 1 km altitude over the Azores in the central Atlantic Ocean. Correlation of O_3 with tracers of anthropogenic pollution (PAN, CO, VOCs, etc.) at Izaña on Tenerife led Schmitt [1994] to suggest a common anthropogenic source of these substances, but due to the complexity of the transport processes a clear attribution to North American emissions was impossible. During the OCTA campaign, polluted air with relatively high concentrations of O_3, CO and NO_y was found both at low levels and in the middle troposphere off the coast of Portugal [Wild *et al.*, 1996]. While the lower-level pollution could be attributed to European sources, the higher-altitude pollution was likely of North American origin.

Detection of North American pollution at surface sites in Europe has been particularly elusive. At Mace Head on the west coast of Ireland an unequivocal attribution to North American sources is difficult even for inert chlorofluorocarbons (CFCs). Comparing Mace Head measurements with modeled transport of CFCs, Ryall *et al.* [1998] estimated "that, on average, North American sources may account for only a few per cent of the CFC-11 enhancements over the Northern Hemisphere baseline values. During long-range transport events, North American sources may contribute CFC peaks at Mace Head which are about one order of magnitude smaller in concentration than those from European sources." During such episodes, CO concentrations at Mace Head are also enhanced [Jennings *et al.*, 1996]. However, few such episodes have been identified, and corresponding O_3 enhancements are marginal. Derwent *et al.* [1998] therefore concluded "that either the North American O_3 and CO plume does not intersect the European coastline over Mace Head or that this plume had become merged into the Northern Hemisphere background in transit." Similar difficulties in the definite detection of pollutant plumes from North America have been faced at other stations, for instance at Porspoder, on the French Atlantic coast, where a North American influence on PAN and VOC concentrations was suggested, especially in spring-time [Dutot *et al.*, 1997; Fenneteaux *et al.*, 1999].

Despite these difficulties in detecting an influence of North American emissions on European O_3, model studies clearly indicate the possibility of O_3 transport across
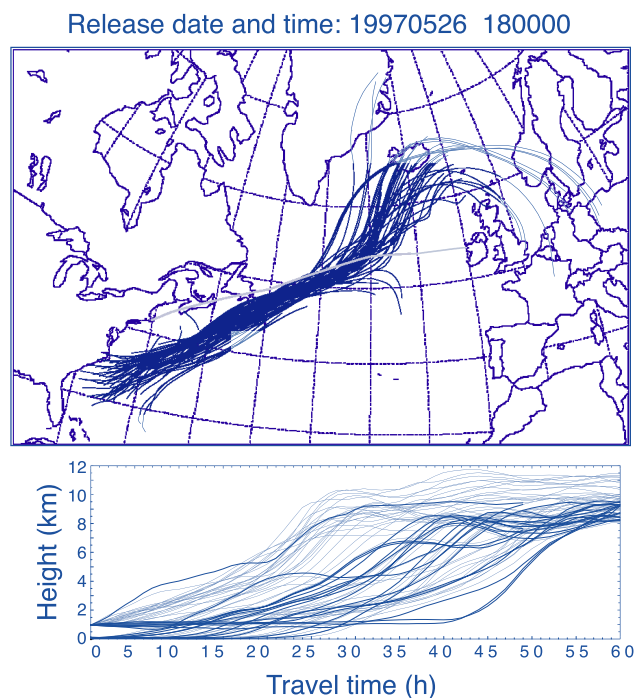
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Figure 1. Three-dimensional trajectories with strong ascent that visualize the WCB. The upper part of the figure shows a horizontal projection, the lower part shows a time-height profile of the trajectories. The black line marks the leg of the MOZAIC aircraft that flew through the WCB and measured about 100 ppb O_3.

the North Atlantic [Wild *et al.*, 1996; Schultz *et al.*, 1998], and suggest that reductions in North American NO_X emissions would decrease the O_3 concentrations throughout the North Atlantic basin [Atherton, 1996]. Schultz *et al.* [1998] have shown that O_3 is destroyed en route. The O_3 destruction rate depends on both the chemical and meteorological conditions of the transport but is, in any case, slow enough to allow intercontinental O_3 transport. Wild *et al.* [1996] demonstrated the possibility of even net O_3 production during transit. The studies of Schultz *et al.* [1998] and Wild *et al.* [1996] agree on the key factor that favors intercontinental O_3 transport: Lifting of the polluted air to higher altitudes. The wind speeds are much faster there so transport to Europe takes less time, plus the photochemical environment and thermal changes favor release of photochemically active NO_X from PAN and HNO_3, thereby allowing O_3 formation during transport. Ultimately, the ozone-forming capacity of an airmass is determined by the emission input of NOY_Y and the amount of NO_Y removed by dry deposition and by wet deposition during the ascending phase of the transport. As wet removal of NO_Y is highly efficient upon export from the boundary layer [Stohl *et al.*, 2001], it is likely that most of the O_3 is formed in the North American boundary layer and is subsequently slowly destroyed en route, as suggested by Schultz *et al.* [1998].

The model studies cited above suggest that the best chances of detecting O_3 plumes from North America over Europe are not at the surface, but in the upper troposphere. Stohl and Trickl [1999] presented an example of such an episode. Polluted, ozone-rich (almost 100 ppbv at the east coast) air left North America and was rapidly transported to the upper troposphere by a warm conveyor belt (WCB) [see Cooper *et al.*, this issue, for an explanation of WCBs] over the North Atlantic (Figure 1). Measurements aboard a commercial aircraft flying through the WCB showed O_3 maxima of about 100 ppbv. The polluted air then rode the jet stream to Europe, arriving after 2 days. Lidar measurements in the outflow of the WCB over Europe again showed O_3 maxima up to 100 ppbv in moist air, located above a stratospheric intrusion (Figure 2).

Other examples of intercontinental O_3 transport can be found in Stohl and Trickl [2001] and Kreipl *et al.* [2001]. A common feature of these episodes is that the polluted air from North America arrives in the upper troposphere over Europe in the outflow of a WCB associated with a low-pressure system tracking over the Atlantic. It overrides the dry intrusion airstream of a preceding cyclone. Thus the normal atmospheric stratification is inverted: Boundary layer air from North America is found in the European upper troposphere, while air of stratospheric origin is found in the lower troposphere. Eventually the polluted air descends, although we have no evidence yet that it reaches the surface.

The reason that these episodes are quite frequent is that North American anthropogenic emissions occur at relatively low latitudes, from where WCBs draw their inflow [Stohl, 2001, and Cooper *et al.*, this issue]. In contrast, emissions released at more northerly latitudes are less affected by WCB transport and tend to remain in the lower troposphere. Indeed, Forster *et al.* [2001] recently found an example where emissions from boreal forest fires in Canada were transported to Europe at lower altitudes. Aerosols caused a dense haze layer over Germany that weather observers erroneously described as cirrus clouds. O_3 concentrations in the polluted airmass were 25 ppbv higher than in the unpolluted airmasses above and below. Model simulations carrying passive CO tracers from both European and North American anthropogenic emissions and from the forest fires showed that the largest contribution to European CO above the baseline value came from the forest fires. At Mace Head (see Figure 3) North American anthropogenic emissions had little influence on the measured CO, whereas Canadian forest fire emissions dominated the CO variations. This was not so much because the CO emissions of the fires were larger than the anthropogenic emissions, but because anthropogenic emissions from more southerly latitudes were transported to the upper troposphere while the forest fire emissions partly remained in the lower troposphere. Tropospheric NO_2 columns derived from satellite data showed that NO_X was also transported across the North Atlantic during this episode [Spichtinger *et al.*, 2001].
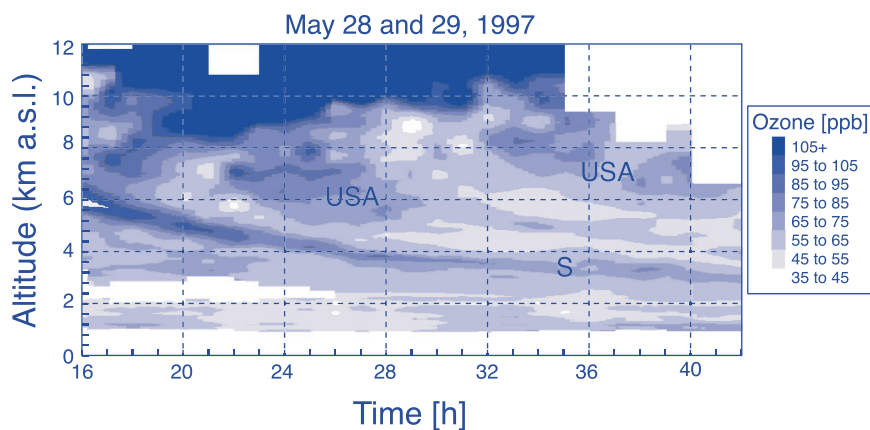

Figure 2. Time-height section of ozone as captured by lidar measurements in Garmisch-Partenkirchen. The white areas correspond to thin cloud layers, for which no useful data have been obtained. The stratospheric intrusion is labeled with "S", the North American boundary layer air with "USA".
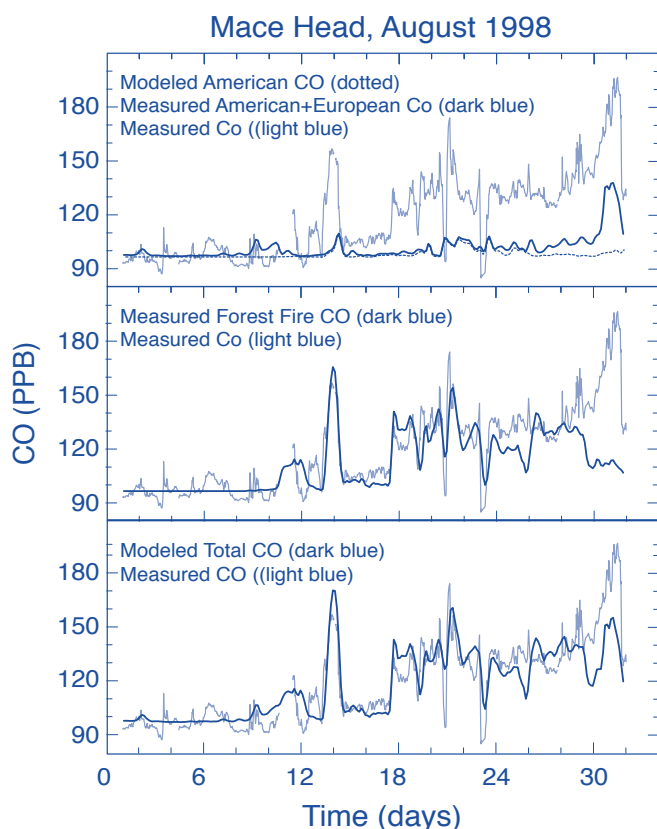
Mace Head, August 1998

Figure 3. Measured (light blue curves in each panel) and simulated CO concentrations in ppb at Mace Head during August 1998. (a) Model results for the American anthropogenic CO tracer (dotted curve) and the American plus European anthropogenic CO tracer (dark blue curve). (b) Modeled CO concentrations for the forest fire emissions (black curve). (c) Modeled CO concentrations from American and European emissions plus forest fires (dark blue curves). A background of 97 ppb was added to the simulated CO concentrations.

Conclusions

There is little evidence that North American anthropogenic emissions exert a strong influence on the concentrations of air pollutants at European surface sites. Some episodes have been identified, but still lack unequivocal attribution to North American sources. In contrast, in the European upper troposphere several cases were found with significantly enhanced O_3 concentrations that could be attributed clearly to transport from North America. During August 1998, boreal forest fires in Canada had a strong influence on European air chemistry. The climatological relevance of intercontinental transport, however, still lacks quantification, and the timescale of mixing into the hemispheric background is also unknown.

Sources of ozone over the North Atlantic and trans-Atlantic transport of pollution: A global model perspective

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Introduction

There is considerable interest in understanding the linkages between regional ozone pollution and global atmospheric chemistry because of the implications for the oxidizing power of the atmosphere, greenhouse radiative forcing by ozone, and intercontinental transport of pollution. Particular focus over the past decade has been placed on the North Atlantic Ocean (NAO) atmosphere through a series of field programs [Parrish, this issue]. We have recently applied the GEOS-CHEM global 3-D model of tropospheric chemistry [Bey *et al.*, 2001a] driven by assimilated meteorological observations for 1993-1997 from the NASA Data Assimilation Office (DAO) [Schubert *et al.*, 1993] to a detailed analysis of observations from the 1997 North Atlantic Regional Experiment (NARE) [Fehsenfeld *et al.*, 1996], the Atmospheric Chemistry Studies in the Oceanic Environment (ACSOE) [Sturges *et al.*, 1996], and the 2nd Aerosol Characterization Experiment (ACE-2) [Raes *et al.*, 2000], as well as ozonesonde and surface measurements over the NAO. Model budget analyses, tagging of species by source region, and sensitivity simulations are offering new insights on the sources of tropospheric ozone over the NAO and the trans-Atlantic transport of pollution. This work is being prepared for publication in the Journal of Geophysical Research [Li *et al.*, 2001a, b]. We present here a few of the major results.

Sources of ozone over the North Atlantic

There has been long-standing debate over the contributions of anthropogenic pollution and transport from the stratosphere to the tropospheric ozone budget over the NAO. Oltmans *et al.* [1992, 1994] have argued for a major stratospheric influence on surface ozone at Bermuda in spring on the basis of strong subsidence indicated by trajectory analyses. However, the relationship of subsiding trajectories to the actual origin of ozone is ambiguous [Moody *et al.*, 1995]. Other studies have found evidence for a major contribution from North American pollution to the springtime ozone maximum at Bermuda [Dickerson *et al.*, 1995; Prados *et al.*, 1999]. A positive O_3:CO correlation at Sable Island and other Canadian

Atlantic sites in summer was reported by Parrish *et al.* [1993] and implies a dominance of pollution over stratospheric influence at least for that season. Negative O_3:CO correlations in winter at the same sites have been attributed to ozone titration by NO_X and hydrocarbons [Parrish *et al.*, 1998]. Similar correlations between ozone and CO have been observed at Mace Head on the western coast of Ireland [Derwent *et al.*, 1994].

The observed O_3:CO correlations at Sable Island and Mace Head are well simulated by our model (Figure 1), providing support for the model representation of photochemistry and transport over the NAO. Further comparison of observed and simulated time series of ozone and CO concentrations at Bermuda and Mace Head in 1996-1997 are shown in Figure 2; the success of the model in capturing both background values and high events is apparent. In that figure we have decomposed model ozone and CO into contributions from different source regions by using tagged tracers [Wang *et al.*, 1998; Bey *et al.*, 2001b]. We find that most of the surface ozone observed at Bermuda in spring originates from the lower troposphere over North America, while transport from the upper troposphere/lower stratosphere plays only a minor role (Figure 2a). Similarly, our simulations indicate that most of the ozone observed at Mace Head in spring is produced in the lower troposphere over Europe (Figure 2b), and this is further supported by decomposition of the time series of CO concentrations in the model (Figure 2c). The "other" contributions in Figure 2a and 2b are mainly from ozone production in the lower troposphere over the NAO. Considering that the ozone precursors over the NAO are largely from North America and Europe, the anthropogenic influence from North America on surface ozone in Bermuda and from Europe on surface ozone in Mace Head may be even larger.

Prospero *et al.* [1995] found that summertime ozone at Izaña in the Canary Islands (28°N, 16°W, 2.4 km) is positively correlated with aerosol [7]Be, and negatively correlated with aerosol ^{210}Pb, and viewed these relationships as evidence for a high-altitude source of ozone, possibly from the stratosphere. We examined the ability of the GEOS-CHEM model to reproduce these correlations, using the radionuclide simulation previously reported by Liu *et al.* [2001]. We find that simulated ozone at Izaña is correlated with [7]Be (r=0.80; slope=0.39) and anti-correlated with [210]Pb (r=0.50, slope=-0.01) [Li *et al.*, 2001b]. Tagged ozone tracer simulations show that these correlations are mostly

driven by ozone production in the middle and upper troposphere, with transport from the stratosphere contributing less than 5 ppbv ozone at the site.

There has been considerable recent interest in the effect of ship NO_X emissions on ozone production over the NAO [Lawrence and Crutzen, 1999; Kasibhatla *et al.*, 1999]. In our standard simulations we use ship emission estimates from the Global Emissions Inventory Activity (GEIA) [Benkovitz *et al.*, 1996], which are sufficently low that ships play little role in the ozone budget. A recent ship emission inventory by Corbett *et al.* [1999] indicates much larger values, implying a large influence from ships on ozone and OH over the NAO [Lawrence and Crutzen, 1999]. Kasibhatla *et al.* [1999] compared the 1997 NARE aircraft observation statistics for NO and NO_Y with results from a global 3-D model driven by GCM meteorology, and concluded that the high ship emissions of Corbett *et al.* [1999] are inconsistent with the aircraft observations. By comparing to specific 1997 NARE observations removed from continental influence, our simulations show indeed that when the ship emission inventory of Corbett *et al.* [1999] is included, the marine boundary layer NO and NO_Y concentrations are overestimated by a factor of 2; ozone concentrations are increased by about 10 ppbv. We conclude that the aircraft observations were inconsistent with the representation of the high ship NO_X emissions of Corbett *et al.* [1999] in their model.
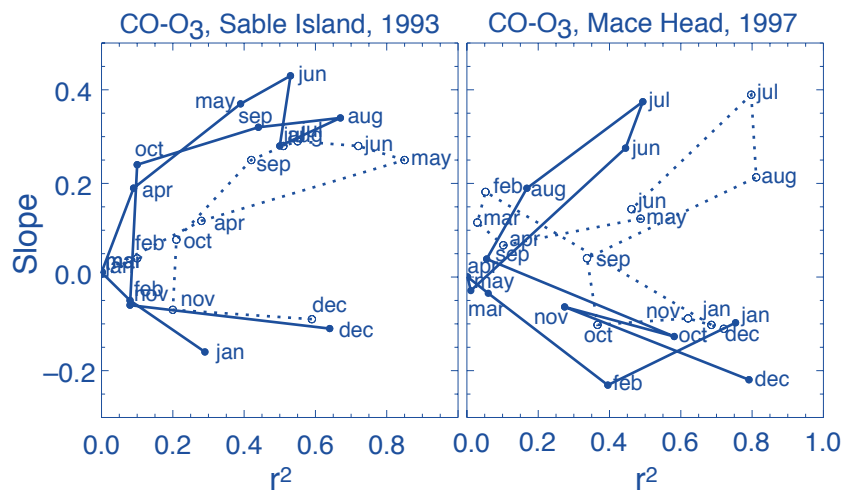

Figure 1. Correlations between ozone and CO concentrations at Sable Island on the east coast of Canada (44°N, 60°W) and at Mace Head on the west coast of Ireland (53°N, 10°W). The figure shows monthly correlation coefficients and slopes in the observations (solid circles) and in the GEOS-CHEM model (open circles). The Sable Island observations are for 1993 [Parrish *et al.*, 1998] and the Mace Head observations are for 1997 (Peter Simmonds and Gerard Spain, personal communication). Model results are for the corresponding years.
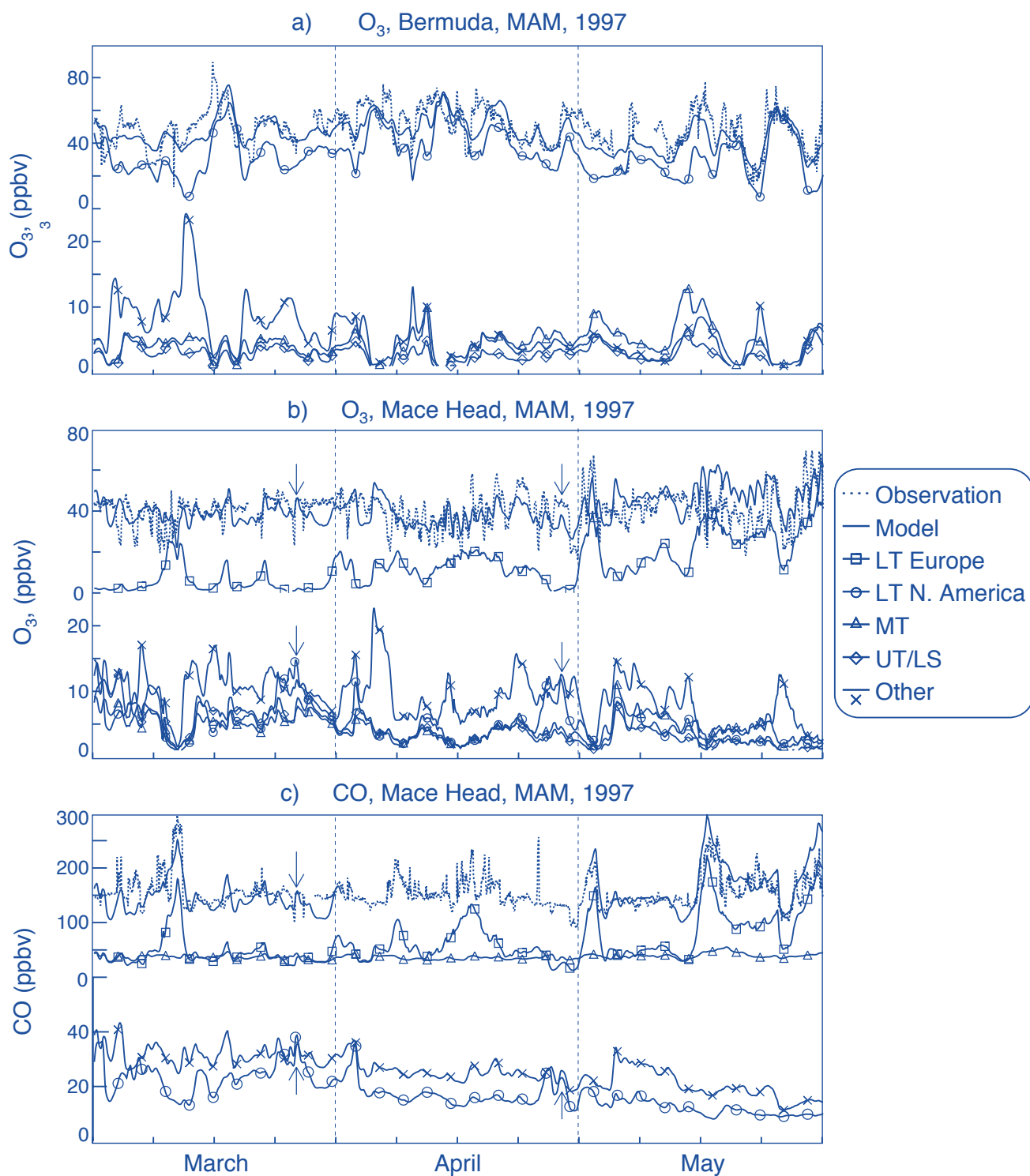
Figure 2. Observed (dotted line) and simulated (solid line) time series of surface concentrations of (a) ozone in spring 1996 at Bermuda and (b) ozone in spring 1997 at Mace Head, and (c) CO in 1997 at Mace Head. Contributions from different sources are isolated in the model with tagged ozone and CO tracers [Wang *et al.*, 1998; Bey *et al.*, 2001b]. In this manner, total ozone concentrations are decomposed into contributions from production in (1) the upper troposphere (< 400 hPa) and lower stratosphere (UT/LS); (2) the middle troposphere (MT; 400-700 hPa); and (3) the lower troposphere (LT; > 700 hPa) over North America and Europe separately. Total CO concentrations are decomposed into contributions from direct anthropogenic emissions in different continents and chemical production within the atmosphere. Ozone data for Bermuda were provided by Samuel Oltmans. Ozone and CO data for Mace Head were provided by Peter Simmonds and Gerard Spain, respectively. The arrows highlight North American pollution events at Mace Head discussed in the text.
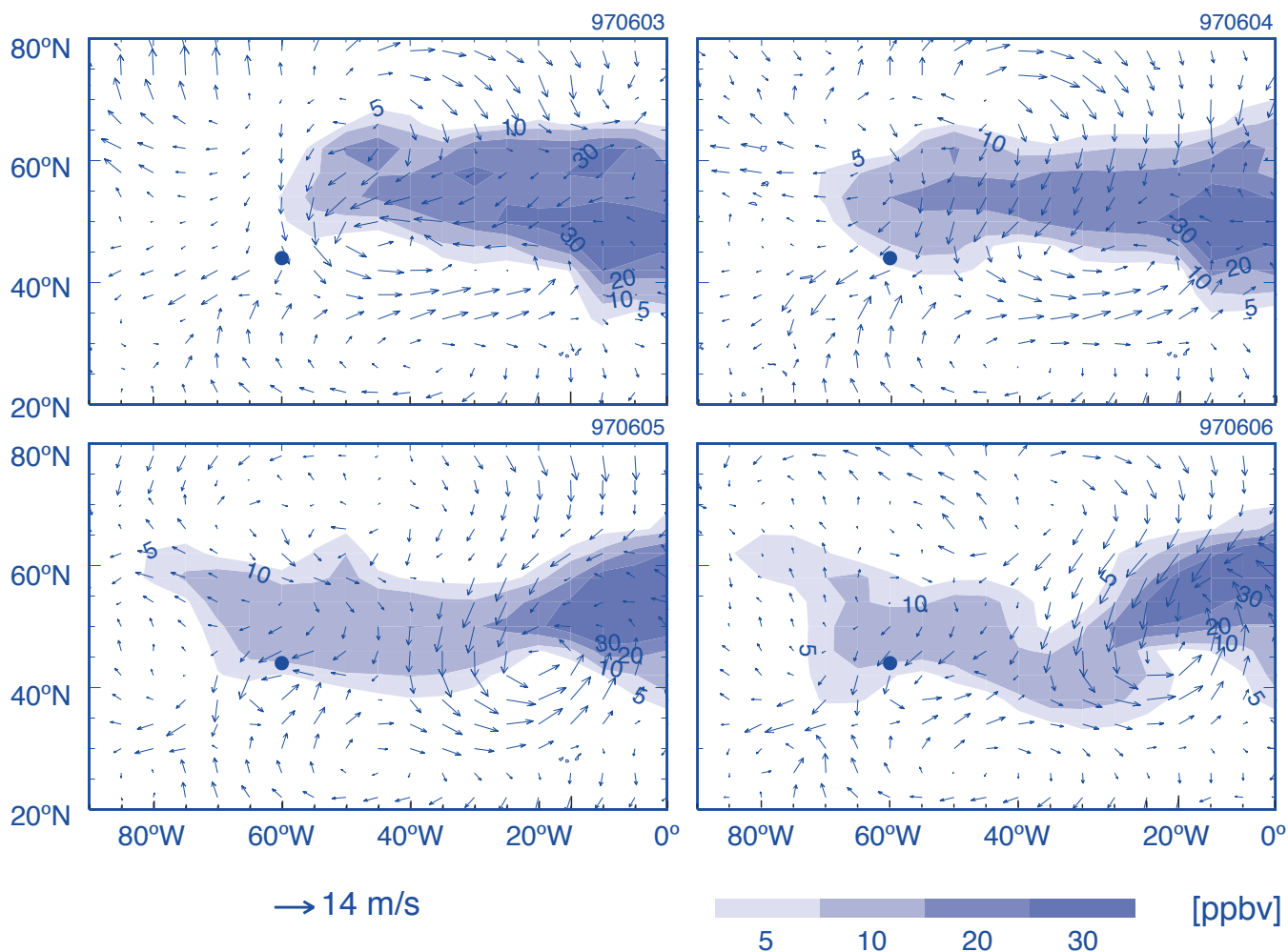
Figure 3. Simulated surface concentrations on June 3-6, 1997 of the European pollution ozone tracer produced in the lower troposphere over Europe on June 3-6, 1997. GEOS surface wind fields are also shown. The location of Sable Island is indicated by the solid circle.

Trans-Atlantic transport of pollution

Analyses of observations have shown evidence for long-range transport of North American ozone pollution to the middle and upper troposphere over Europe, but little effect at the surface [Stohl and Trickl, this issue]. Tagging of ozone and CO enable us to diagnose trans-Atlantic transport of pollution in the GEOS-CHEM simulation. We find that ozone produced in the lower troposphere (>700 hPa) over North America contributes on average about 5 ppbv to the surface ozone at Mace Head, but as much as 10-15 ppbv during some trans-Atlantic transport events. Figures 2b and 2c show such events on March 23-26 and April 26-29, 1997. We find that these trans-Atlantic pollution transport events are less frequent in summer than in other seasons [Li *et al.*, 2001b].

A remarkable result of our simulation is the occasional occurrence of trans-Atlantic transport of European pollution to North America. We show in Figure 3 one such event during June 3-6, 1997. On June 2-3, a high pressure system formed between the Hudson Bay and the North Sea along 60°N while a low pressure system was

developing between Newfoundland and the eastern NAO along 45°N. Between the two systems a low level (below 2 km) easterly flow was established, bringing European pollution directly to northeastern North America. This easterly flow stopped on June 4 as the low pressure system moved eastward. However, the European pollution cloud persisted over northeastern North America until June 8, with large effects on simulated ozone and CO at Sable Island (Figure 4). The "other" contribution in Figure 4a is mainly from ozone production in the lower troposphere over the NAO, which was particularly large during the June 3-6 event. Under the flow pattern discussed above, it is likely that the "other" contribution during the June 3-6 event was due to European pollution being transported to the NAO and subsequent ozone production. As a result, the European influence during the June 3-6 event may be even larger. Unfortunately, no observations were available for that period, and the anomalous circulation pattern did not recur for the remainder of the summer. However, we find similar events occurred almost every spring and some-
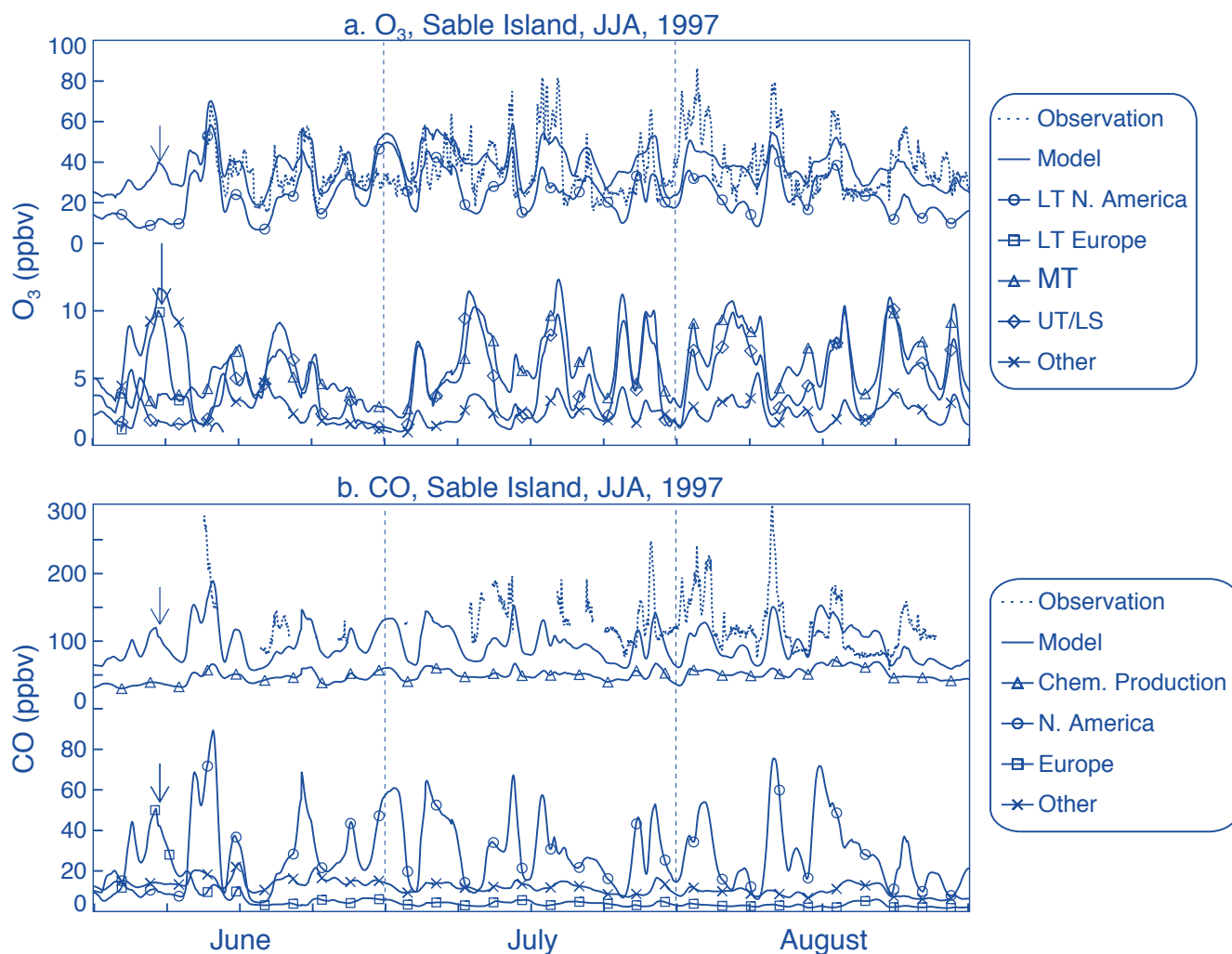
Figure 4. Observed (dotted line) and simulated (solid line) time series of surface concentrations of ozone and CO at Sable Island in the summer of 1997. Contributions from different sources are isolated in the model with tagged tracers as in Figure 2. The arrows indicate the European pollution event in the model on June 7-8, 1997. Observations are from David Parrish (personal communication).\

times fall for the time period that we simulated, i.e., 1993-1997.

In sensitivity simulations with either North American or European fossil fuel emissions shut off, we find that anthropogenic sources in North America enhance July mean ozone concentrations in surface air over Europe by 2-4 ppbv, with maxima over the British Isles (Figure 5, left panel). Greater North American influence is actually found over North Africa and the Middle East because of the deep mixing in these arid regions [Li *et al.*, 2001c]. Anthropogenic sources in Europe enhance July surface ozone over North America by only 1-2 ppbv (Figure 5, right panel).
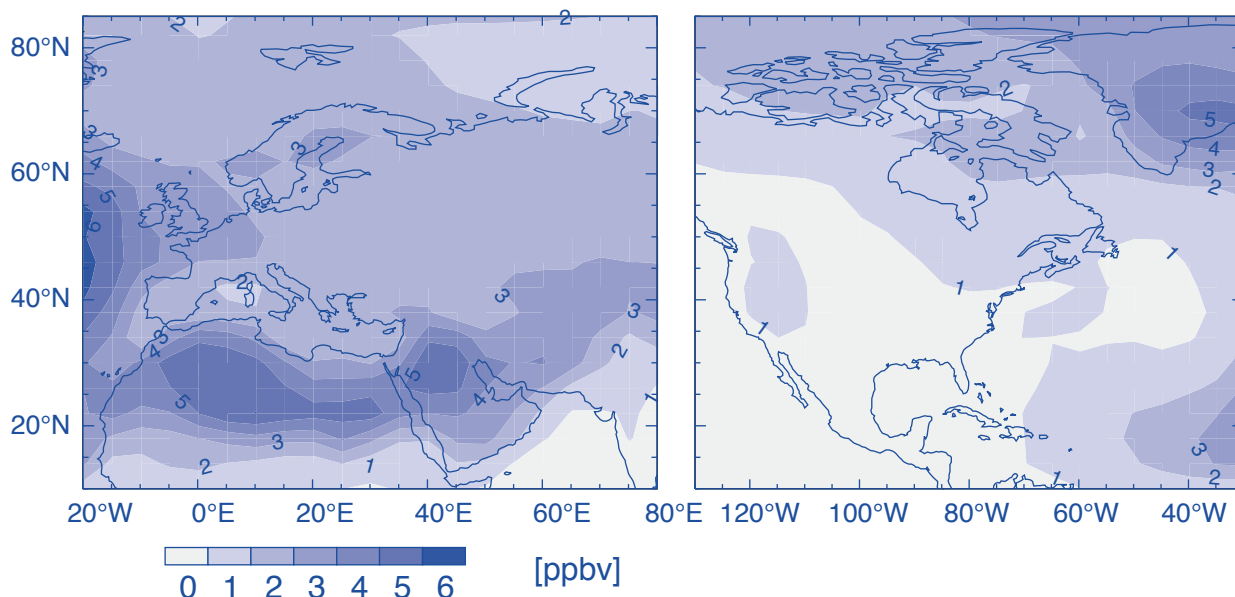
Figure 5. Decrease in simulated monthly mean ozone concentrations in surface air in July over Europe when North American fossil fuel emissions are shut off (left panel) and over North America when European fossil fuel emissions are shut off (right panel).

Evidence for anthropogenic influence over the central North Atlantic

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Introduction

In this article, we report on observations of widespread layers of air pollution over the central and eastern North Atlantic, particularly between 3km and 8km altitude in summer 1997 as part of the NARE2 campaign. The focus here is on results collected by the United Kingdom (UK) C-130 aircraft during detachment from its base in southern England to the island of Santa Maria in the Azores in September 1997. There was also a spring campaign based in the Azores in April 1997. The study was carried out as part of the UK NERC community program Atmospheric Chemistry Studies in the Oceanic Environment (ACSOE), which also included extensive ground-based and ship experiments studying many aspects of the chemistry of the atmosphere over the Atlantic Ocean. This article presents a summary of some of the results from several papers that are being prepared for submission to the Journal of Geophysical Research [Penkett *et al.*, 2001; Law *et al.*, 2001; Reeves *et al.*, 2001; Schmitgen *et al.*, 2001; Bauguitte *et al.*, 2001 and Edwards *et al.*, 2001].

The Azores summer detachment

The UK Meteorological Office C-130 aircraft flew to the island of Santa Maria (35°N, 25°W) on 13 September 1997

and returned on 23 September 1997. From this base it completed 6 flights over the middle of the North Atlantic Ocean. The main chemical objectives of the flights included a study of ozone/CO relationships in changing water vapor regimes, *in situ* photochemical ozone production and loss rates, perturbation of the photochemical equilibrium of peroxides, a study of NO_Y/ozone relationships, and of the chemical form of NO_Y. Another major objective was to survey the composition of air over the North Atlantic Ocean between the North American and European/North African continents and the extent to which it is impacted by air pollution. The flights therefore contained many vertical profiles from the surface up to 8 km to detect the presence of polluted layers seen previously on flights over the North Atlantic in 1993 during the NARE1 campaign (e.g. see Wild *et al.*, [1996]).

Evidence for long-range pollution transport

During all the flights, to a greater or lesser extent, there was clear evidence for long-range transport of pollutants from continental regions, especially in the mid-troposphere, over the North Atlantic. One of the most dramatic examples was observed on 14 September 1997 when the C-130 flew into air circulating around Hurricane Erika which had moved north-eastwards from the West Indies to the Azores. This produced some spectacular effects, including the transport of polluted air from the south-eastern USA into the mid-Atlantic free troposphere south of the Azores. Trajectory analysis (not shown) suggests that frontal systems situated over the North American continent 5-6 days earlier had contributed to the uplift of pollution into the free troposphere over the North Atlantic and into the path of Hurricane Erika.
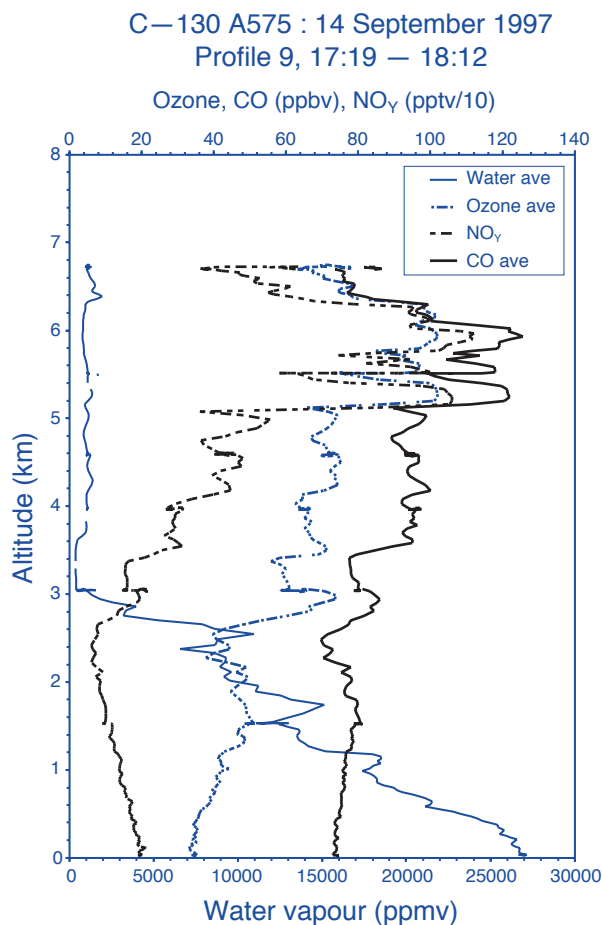
C—130 A575 : 14 September 1997
Profile 9, 17:19 — 18:12

Ozone, CO (ppbv), NO_Y (pptv/10)

Figure 1. Vertical profile of trace gas concentrations measured on the United Kingdom C-130 Meteorological Research Flight aircraft on 14 September 1997 as part of the UK ACSOE NARE2 campaign (see Penkett *et al.* [2001]) for details).

On 14 September 1997 the aircraft initially flew southwards from Santa Maria, then west into the cloud streamers emanating from the eye of the Hurricane, and then back to Santa Maria through air that had clearly been uplifted. The aircraft also cut vertically through the outflowing air and a profile of the concentration of ozone, CO and total reactive nitrogen (NO_Y) are shown in Figure 1. High concentrations of these pollutants are clearly visible in layers at altitudes between 5 and 7 km. The ozone concentration in these layers reaches 100 ppbv, the NO_Y concentrations exceed 1 ppbv and both are highly correlated with CO indicating a boundary layer rather than a stratospheric source.

The trajectory analysis showed that the polluted layers observed between 5 and 7 km had been uplifted from the polluted boundary layer over the southeastern United States. The air was uplifted to about 9 km over 2 days, then it slowly subsided for about 4 days before being intercepted by the aircraft. Lower down in the profile the air had been slowly subsiding over several days or had traveled in the marine boundary layer, where ozone is

destroyed efficiently by sunlight and high water vapor concentrations. The ozone concentration close to the surface was only 40 ppbv. This is typical of ozone concentrations measured during the ACSOE Mace Head (Ireland) experiment in the summer of 1996 in air from North America that had crossed the Atlantic close to the surface (e.g., see Evans *et al.* [2000]). Pollution therefore does appear to be mostly transported from the continents in the mid-troposphere over the North Atlantic.

A further point worth emphasizing is the marked anticorrelation between ozone and water vapor seen in the profiles. This is also shown in Figure 1 although the detail is difficult to discern because above 3 km the water concentration is close to the detection limit of the sensor, that is, it is very dry air. This is not stratospheric air though, as shown by the high CO and CN (not shown) concentrations, by the trajectories, and by the low PV values calculated along their course that did not exceed 1 PV unit over the 6 days. The conclusion to be reached here is that an anticorrelation between ozone and water vapor does not necessarily indicate a stratospheric origin for the ozone.

The general picture of the atmosphere over the Atlantic Ocean during the sampling periods is therefore of long-range transport of ozone pollution from the continents at altitudes between 3 and 8km interspersed with uplifted marine boundary layer air. There is also evidence, at least in the spring, that ozone production can still take place in the free troposphere in plumes of polluted air. Only rarely was any trace of stratospheric influence detected. Below 3 km there is evidence both for less polluted air being transported from the African continent, and for clean marine air in which photochemical destruction of ozone appears to dominate. The layering, seen in all the ACSOE flights, is a very general feature and is undoubtedly related to the overall vertical and horizontal transport processes that occur in the troposphere. See Penkett *et al.* [2001], Bauguitte *et al.* [2001], Reeves *et al.* [2001] and Edwards *et al.* [2001] for further discussion of these results.

The relationship between ozone and CO has been used previously to estimate the amount of ozone being exported from the continent into the background troposphere (e.g., see Parrish *et al.*, [1993]; Chin *et al.*, [1994]). This is because CO is a major precursor to ozone and is emitted in large quantities in industrial regions. Here, O_3:CO relationships were examined in air masses sampled during the 1997 summer C-130 campaign to investigate factors affecting the concentration of summertime ozone in the troposphere between ~1 and 8 km. In particular, we attempted to discern whether it is possible to separate out the effects of photochemical processes from mixing processes. Results are described more fully in Law et al [2001].

Figure 2 shows a composite of all ozone and CO from flights out of the Azores. What is interesting is that dif-

ferent ozone and CO concentrations and ratios (varying from 0.3 to 0.8) exist at different levels of water vapor (not shown). In particular, higher ratios are evident in drier air masses. As well as higher ozone, these air masses also had higher levels of CO, CN, NO_Y and NO, indicating that they were more polluted and generally they were sampled in the mid rather than the lower troposphere (see earlier discussion). Air masses with lower ratios were moist and had lower ozone and CO concentrations and originated largely over the North Atlantic. What is leading to these differences? Is it photochemistry or mixing with 'background' air?

The Cambridge Lagrangian photochemical model, CiTTyCAT, described by Evans *et al.* [2000], was run along 5-day, three-dimensional back trajectories calculated using meteorological analyses from the European Centre for Medium Range Weather Forecasts (ECMWF). Two typical cases were examined based on the analysis of data described earlier. Firstly, air originating from the polluted North American boundary layer that was uplifted, most probably by frontal systems [see Cooper *et al.*, 2001] was considered and, secondly, air originating from the clean marine boundary layer over the North Atlantic. Results were compared to observed O_3:CO ratios and their dependence on precursor concentrations, water vapor and mixing with background air were examined.

The most important result is that a combination of both photochemistry and mixing are required to reproduce the observed O_3: CO ratios and concentrations. In polluted airmasses ozone can increase due to photochemical production but also due to lower water vapor, in air that has been uplifted and dried, leading to less photochemical destruction (also see Wild *et al.* [1996]). However, CO concentrations, which are not really affected by photochemistry over a 5-day period, were calculated to be much higher than observed over the North Atlantic, suggesting that mixing with background air must also occur. Mixing parcels with typical 'background' concentrations leads to increased O_3:CO ratios and decreased ozone and CO concentrations in line with observed values. In the case of clean marine boundary layer air, transported in the lower troposphere, mixing serves to maintain the observed ratio of O_3:CO around 0.2-0.4 by mixing in higher ozone descending from aloft. Therefore, the observed distribution of ozone and CO shows that both chemical and dynamical processes are important in determining the distribution and ratios of these tropospheric trace gases.

Conclusions

The quality of trajectory analysis is now such that many individual features of the chemical composition of air along the flight tracks of research aircraft such as the UK C-130 can be accounted for with confidence. This includes uplift of continental boundary layer air, transport of marine boundary layer air, and long-range trans-
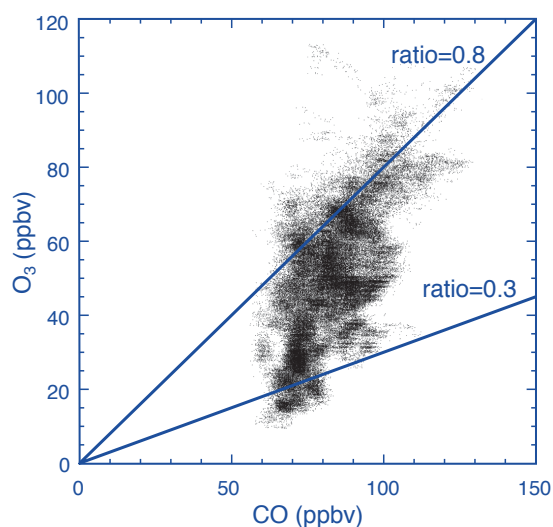

Figure 2. Plot of ozone and CO concentrations measured from UK C-130 aircraft during flights from Santa Maria, Azores over the central North Atlantic in September 1997 as part of the UK ACSOE NARE2 campaign (see Law *et al.* [2001] for details).

port of pollution in the troposphere across the North Atlantic Ocean.

High concentrations of ozone are present in layers over the Atlantic between 3 and 8 km in association with elevated concentrations of anthropogenic tracers such as CO, CN and NO_Y. The ozone concentration declines in the marine boundary layer, probably due to increased removal efficiency.

There is evidence that a significant part of the ozone observed over the North Atlantic in summer (and spring) has a pollution origin. The influence of ozone from the stratosphere appears to be small, at least below altitudes of 8 km.

Transport and mixing processes within the troposphere, as well as photochemistry, are clearly important in generating observed trace gas distributions over the central North Atlantic.

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The Azores Islands: A unique location for ground-based measurements in the MBL and FT of the central North Atlantic

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The Azores Islands—the only islands in the central North Atlantic that are distant from all surrounding continents—have historically been important for studies of the North Atlantic atmosphere. Prior to the advent of satellite observations, they provided weather data critical to the accuracy of forecasts of European weather. Today, they provide a unique base for observations of the impacts on atmospheric composition of emissions from the surrounding continents. As part of the NARE program, ground-based measurements of CO and O_3 [Parrish *et al.*, 1998] and NO_Y [Peterson *et al.*, 1998], as well as ozone sondes [Oltmans *et al.*, 1996] were made in 1993 on the island of Terceira. The Azores have also served as a base for airborne studies (e.g., those described by Law *et al.*, this issue) and shipboard studies [e.g., Huebert *et al.*, 1996]. Here, we briefly discuss Azores ground-based measurements, with an emphasis on a new mountaintop site designed to probe the free troposphere.

The 1993 measurements were made at 1000 m on the island of Terceira. This was low enough that the air sampled originated in the surrounding marine boundary layer (MBL), with the exception of short periods of active vertical mixing due to frontal passages. Periods of correlated variations in CO and O_3 were observed during spring, indicating significant impacts from pollutant transport [Parrish *et al.*, 1998]. However, this signature of long-range transport was much weaker during summer. NO_Y measurements were made during August only, and were similarly unaffected by long-range transport [Peterson *et al.*, 1998]. Interpretation of measurements in the MBL to identify impacts of long-range transport is not straightforward for three reasons. First, the structure of the near-shore boundary layer over oceans and other large water bodies is largely determined by land-water temperature differences, and this can result in the lofting of continental emissions above the MBL and a disconnection between surface-air composition and that of the air above [Angevine *et al.*, 1996; Honrath *et al.*, 1997]. This process restricts North American pollutant export into the Atlantic MBL during summer. Second, pollutant lifetimes in the MBL are shorter than those in the free troposphere (FT), as a result of the presence of the ocean-water surface, high concentrations of water vapor and therefore of OH radical, and elevated aerosol levels. This reduces the spatial scale of impacts from long-range transport in the MBL, relative to that of transport in the overlying FT. Finally, in remote midlatitude marine regions like the central North Atlantic, MBL composition and structure are largely determined by subsidence from the FT. For this reason, concentrations in the MBL of compounds like O_3,

nitrogen oxides, and CO are determined by a balance between the source from the FT (which depends on concentrations in the FT) and the sink in the MBL. Events of changing concentrations in the overlying FT, which may be caused by long-range transport, are therefore reflected by changing concentrations in the MBL, but the magnitude and timing of these changes is different for each compound because of differences in their lifetimes in the MBL. The result is that interspecies correlations in the MBL must be interpreted with caution [Peterson *et al.*, 1998]. Nevertheless, ground-based measurements can be an extremely valuable complement to aircraft studies. In particular, the opportunity for continuous observations for an extended period of time allows determination of the frequency and duration of pollutant transport events and calculation of the distribution of concentrations in background air.

The Pico International Atmospheric Chemistry Observatory (PICO-NARE) was developed with these issues in mind to provide information on the frequency and duration of events carrying O_3 and O_3 precursors to the lower FT of the Azores region, and to determine regional background levels of these compounds for comparison with global model predictions. PICO-NARE is the result of a collaboration between Michigan Tech and the University of the Azores, and was set up in July 2001 on the summit of Pico mountain on the Azores island of Pico. At an altitude of 2225 m, this is the only location in the central North Atlantic high enough for ground-based observations frequently in the FT. (Water vapor soundings deployed from the adjacent island of Terceira indicate that the MBL height during August typically ranged from 1 to 2 km [Oltmans *et al.*, 1996], and the summit of Pico is often observed above the MBL-capping cloud layer.)

Measurements on Pico mountain are logistically difficult, as the nearest road ends 1000 m below the summit, and the mountain is a restricted area for both environmental and safety reasons. Equipment on the mountaintop is limited to a 2 by 2.5 by 2 m instrument enclosure and instrument inlets. The system is powered by a small diesel generator located 1000 m lower in elevation, via a 2.5 km power cable. All instruments are fully automated and are controlled and accessed via a GSM (cellular) internet connection. The regional government of the Azores has granted permission for 2 years of operation.

Measurements during the first year will focus on the relatively simple and reliable observations of O_3 and the combustion tracers CO and aerosol black carbon, plus standard meteorological parameters and automated sampling of whole air for determination of non-methane hydrocarbons. However, the site was designed with capacity for a limited number of additional measurements, and it is our hope that the potential value of PICO-NARE as a platform for observations of the impacts of continental emissions on the lower FT and MBL of the central North Atlantic region will be fully realized. Scientists wishing to conduct collaborative research during Year 2 (June 2002–2003) and those desiring additional information on

PICO-NARE may contact the project's web site for additional information (www.cee.mtu.edu/~reh/pico).