

LOSSES AND TRANSPORT OF ODD NITROGEN SPECIES (NO_y) OVER THE WESTERN ATLANTIC OCEAN DURING GCE/CASE/WATOX

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Abstract. Aircraft and shipboard measurements of mixing ratios for odd nitrogen species (NO_y) were made over the western Atlantic Ocean during the summer of 1988. NO_y in boundary layer air ranged from 4.8 ppbv near the U.S. east coast to 1.7 ppbv near a research ship 160 km from the coast. A vertical NO_y gradient was observed near shore; mixing ratios decreased with altitude from 3.0 ppbv at 150 m to 1.3 ppbv at 2600 m. A smaller NO_y gradient was observed near the ship, with

mixing ratios also decreasing with altitude. During the observation period of this experiment, a high-pressure system over the mid-Atlantic limited advection of polluted continental air to a band just along the coast, thus preserving less polluted conditions to the east of the band. Loss rates for NO_y advected from the continent, based on 3 eastward flights from the U.S. east coast, were estimated to be $2.0 \pm 1.5\%$ hour⁻¹. Measurements near Bermuda were in marine air with average mixing ratios near the surface of 0.8 ppbv for NO_y and 0.3 ppbv for total NO_3^- . No significant vertical gradient was observed for NO_y near Bermuda, where the high-altitude NO_y mixing ratio was 0.7 ppbv. Overall, NO_y mixing ratios near Bermuda were higher than would be expected on the basis of either measurements or computer modeling for remote marine air, suggesting possible influence from local anthropogenic sources.

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INTRODUCTION

Eastward advection of anthropogenic pollutants (nitrogen and sulfur species) from North America is considered to be the main cause of air quality reduction over the western Atlantic Ocean [Galloway et al., 1984]. Because few monitoring stations exist in the Atlantic Ocean region, accurate information on reactive nitrogen species concentrations and lifetimes is sparse. The effect of advected air from

North America on the troposphere and the oceans has been studied in a series of Western Atlantic Ocean Experiment (WATOX) programs in which nitrogen species were measured from surface sites on the U.S. east coast and on Bermuda [Wolff et al., 1986a,b], from aircraft and surface sites during 1985 [Hastie et al., 1988], and from two aircraft during 1986 [Luke and Dickerson, 1987; Misanchuk et al., 1987]. The present study is a continuation of the WATOX programs during summertime. This program may help provide information for models of tropospheric chemistry that make predictions of changes in global tropospheric ozone and radiative balances.

Previous literature has differing definitions for the sum of odd nitrogen species, mainly because of the difference in instrument responses, which can make comparisons difficult. Wolff et al. [1986b] converted NO to NO₂ for detection, but the luminol-chemiluminescence analyzer used to detect NO₂ also responded to peroxyacetyl nitrate (PAN) and CH₃ONO, which were thus included in the sum as NO_x. Luke and Dickerson [1987] used a chemiluminescence analyzer with a hot-molybdenum converter and expected NO_y to be NO + NO₂ + HNO₃ + 2N₂O₅ + HONO + PAN + R-ONO_x + fine p-NO₃⁻. Both Luke and Dickerson and Misanchuk et al. [1987] defined NO_x' as the sum of NO plus the species detected from an FeSO₄ converter (that is, NO + NO₂ + ~0.7 PAN). A consistent definition of total odd nitrogen is important, since NO_y mixing ratios are usually 2 to 3 times or more the NO_x or NO_x' mixing ratios. Most of the difference between NO_y and NO_x generally is HNO₃ and NO₃⁻, but it can include significant amounts of organic nitrates as well [Hubler et al., 1989; Buhr et al., 1989]. In this article we define NO_y to be the sum of odd nitrogen species as determined with a hot-molybdenum converter [Fehsenfeld et al., 1987].

During prior WATOX experiments, wintertime NO_y mixing ratios were measured along the U.S. east coast and at Bermuda [Wolff et al., 1986b] that were similar to rural continental mixing ratios [Altshuller, 1986; Fahey et al., 1986; Logan, 1983]. NO_y mixing ratios observed from aircraft flights parallel to and 50-300 km off the U.S. east coast varied highly with latitude (0.6-4.0 ppbv) in the boundary layer and were >1.0 ppbv in the free troposphere [Luke and Dickerson, 1987; Misanchuk et al., 1987]. Global modeling of NO_y distribution by Levy and Moxim [1989] sug-

gests that NO_y mixing ratios decrease rapidly eastward from the continental United States. Average NO_y mixing ratios for the western Atlantic Ocean were predicted to be from 0.1 to 1.0 ppbv as yearly averages in the surface layer (>990 mbar).

Literature reports of NO mixing ratios measured over the Atlantic Ocean were usually <1.0 ppbv in the boundary layer. NO was reported to be approximately 0.2 ppbv in the free troposphere near the U.S. east coast [Misanchuk et al., 1987] and to be <0.02 ppbv in the free troposphere farther from the east coast [Luke and Dickerson, 1987]. Other NO measurements in the western Atlantic region indicated mixing ratios of 0.03-0.20 ppbv for marine air near the surface at Wallops Island, Virginia [Torres, 1985; Carroll et al., 1985], and 0.005-0.02 ppbv in the boundary layer near Bermuda [Drummond et al., 1988]. For comparison, reported NO mixing ratios over the Pacific Ocean tend to be quite low (<0.01 ppbv) [Ridley et al., 1987].

Measurements of HNO₃ and NO₃⁻ over the Atlantic Ocean confirmed that these species are a major portion of NO_y. Huebert and Lazrus [1980] reported HNO₃ mixing ratios of 0.01-0.27 ppbv with a mean of 0.070 ppbv. Observations of surface HNO₃ in Bermuda [Wolff et al., 1986b] averaged 0.04 ppbv or 0.13 ppbv, depending on air mass origin; Hastie et al. [1988] reported a mean value of 0.067 ppbv. Much higher mixing ratios of 0.38-0.71 ppbv were reported for surface NO₃⁻ [Wolff et al., 1986a]. Aircraft measurements of HNO₃ near Bermuda, however, averaged 0.061 ppbv in the boundary layer and 0.041 ppbv in the free troposphere. Higher HNO₃ mixing ratios of 0.28 ppbv in the boundary layer and 0.11 ppbv in the free troposphere were observed from aircraft along the U.S. east coast [Hastie et al., 1988]. Whelpdale et al. [1987] reported mean mixing ratios of 0.15 ppbv for NO₃⁻ and 0.10 ppbv HNO₃ in the boundary layer off the U.S. east coast; the mixing ratios in the boundary layer were 1.5-4.5 times higher than in the free troposphere at the same location.

The contribution of PAN to NO_y in a remote marine environment may be of about the same magnitude as the contribution of HNO₃. PAN mixing ratios of 0.01-0.10 ppbv were reported for the Pacific and Atlantic oceans [Singh and Salas, 1983; Singh et al., 1986; Rudolph et al., 1987]. Slightly higher PAN mixing ratios were observed near the U.S. east coast [Bottenheim and

Gallant, 1987]; the mean values were 0.184 ppbv for the boundary layer and 0.094 ppbv for the free troposphere.

Several estimates of NO_x and NO_y decay times and distances have been made at various locations: over the northeastern Atlantic Ocean [Helas and Warneck, 1981], off the U.S. east coast (over the western Atlantic Ocean) [Spicer, 1982], over the western Atlantic Ocean in the 1985 WATOX program [Hastie et al., 1988], and over the eastern Pacific Ocean [Ridley et al., 1988]. NO_x and NO_y lifetimes of 1-5 days were most often assumed. That range is rather large, a result of different definitions of the odd nitrogen group, uncertainty in the measurements, different methods of determination, and spacial and temporal variability in factors that influence atmospheric lifetimes.

In this report we examine the transport of odd nitrogen species from the continental United States under summertime conditions dominated by a high-pressure system over the mid-Atlantic Ocean, estimate the loss rate of NO_y over the ocean, and discuss the contribution of individual odd nitrogen species to NO_y . This July 1988 study was a part of the Global Change Expedition/Coordinated Air-Sea Experiment/Western Atlantic Ocean Experiment (GCE/CASE/WATOX).

EXPERIMENTAL DETAILS

Eight research flights were conducted by the National Oceanic and Atmospheric Administration (NOAA) King Air C-90 aircraft to the NOAA ship Mt. Mitchell. Four flights were made from Newport News, Virginia, to the ship while it was located offshore at approximately 35.5°N latitude, 74.4°W longitude. Four additional flights were made later from Bermuda to the ship, then located upwind of the island at approximately 32.0°N, 63.3°W. Each flight consisted of a high-altitude leg with the intent of making free troposphere measurements of about 90 min at 2600 m (740 mbar). This was followed by a stepwise descent of 5-15 min at each of two or three intermediate altitudes, and a low-altitude leg in the marine boundary layer of about 90 min at 150 m (1010 mbar). Greater detail on the flight tracks, ship track, aircraft operation, and meteorology are given by Boatman et al. [1990] and Gunter and Boatman [1989].

Nitrogen species were measured by several different techniques. The NOAA King

Air carried a modified Thermo Environmental Instruments, Inc., model 14B/E chemiluminescence analyzer for measuring NO and NO_y [Dickerson et al., 1984]. This instrument used a 375°C molybdenum catalyst to convert NO_y to NO ; the technique is consistent with other accepted methods for measuring NO_y [Fehsenfeld et al., 1987]. NO_3^- and HNO_3 were measured from the aircraft with a dichotomous filter pack system [Bardwell et al., 1990]. SO_2 , O_3 , H_2O_2 , aerosol size distribution, meteorological parameters, location, and position were also measured continuously on board the aircraft [Wellman et al., 1989].

The NO/NO_y analyzer was calibrated at several concentrations between 0 and 10 ppbv before the first flight using certified 0.25-ppm NO in N_2 (Scott Specialty Gases) that was diluted with NO -free zero air. A span check was made before each flight and repeated during flight to normalize for any altitude dependence in response. Span gas was introduced at a Teflon tee just before the 5- μm Teflon filter and the molybdenum converter that were mounted approximately 50 cm from the sample-air intake. The instrument baseline varied with aircraft cabin temperature and pressure, therefore, zero-mode readings (a dynamic zero using a prereactor prior to the detection chamber) were taken every 20 min. Cycle time for the NO and NO_y modes was 4 min each. The minimum detection limit based on a signal-to-noise ratio of 2 for the NO analyzer was 0.070 ppbv; under field conditions the instrument resolution for either NO or NO_y was 0.1 ppbv. The absolute accuracy under field conditions for this type of instrument was estimated to be plus or minus 30% [Fehsenfeld et al., 1987]. NO_y mixing ratios were well above the detection limit for the analyzer; however, NO was generally <0.1 ppbv except at locations close to shore.

The ship carried a similar filter pack sampler [Bardwell et al., 1990] and an NO_2 -luminol-chemiluminescence analyzer [Hastie et al., 1990] to measure NO_2 , NO_x , and NO_y . NO_y was measured by conversion to NO using CO reduction on a hot-gold catalyst and then oxidation by reaction with CrO_3 to NO_2 for detection. NO_x was measured similarly by conversion of NO to NO_2 and measuring the sum of the NO_2 concentration. A timer switched on a regular cycle between the 3 species modes NO_y , NO_x , and NO_2 and the zero-air mode. Daily calibrations were made using an NO stan-

ard introduced at the sample inlet. The data were corrected for O₃ interference and temperature dependence of the luminol detector.

RESULTS

Meteorology

A general description of the meteorology during the GCE/CASE/WATOX experiment is presented by Stunder et al. [1990] and Gunter and Boatman [1989]. Isobaric air mass back trajectories indicated that two different regimes were sampled. Flights out of Newport News encountered both continental and marine air; flights out of Bermuda encountered only marine air. On July 17, continental air extended out to the ship at 74.4°W longitude. However, on July 18-19 a near-surface continental-to-marine transition zone was observed between 75.0° and 75.4°W (based on measurements of oxidant trace gases and potential temperature; see Ray et al. [1990]). Air samples taken from the ship were thus of marine origin from July 18 to 29. By July 21 the transition zone had moved westward and therefore only marine-origin air was observed during the low-altitude flight segments from the coast to the ship. Air mass back trajectories to the Bermuda area were of marine origin for at least 10 days at altitudes between the surface (1000 mbar) and 700 mbar for July 26-28.

Table 1 presents low-altitude average measurements by day for NO_y mixing ratios, wind direction and speed, temperature, dew point, and water mixing ratio (WMR) as measured from the aircraft. The air masses sampled are divided into nearshore (76.0°-75.1°W) continental-influenced air; nearshore marine air (75.1°-74.4°W); and near-Bermuda marine air. Table 1 indicates both the daily differences and the changes between air masses. Winds, for example, were from the southwest during all of the low-altitude flight segments from the U.S. east coast. However, wind speed, temperature, and NO_y were lower on the marine-air side of the transition zone near 75.1°W. Different wind direction was observed near Bermuda, mostly from the south and southeast; wind speed, temperature, and water mixing ratio values were lower near Bermuda than along the U.S. east coast. High-altitude values (Table 2) for NO_y, wind speed, wind direction, and water mixing ratio were generally lower near Bermuda than near the U.S. east coast.

Aircraft NO_y Data

Spatial differences in NO_y mixing ratios were observed. At low altitude, the highest average NO_y mixing ratios of 3.0 ppbv were near shore, and the lowest average NO_y mixing ratio of 1.0 ppbv was near Bermuda (Table 1). Average NO_y mixing ratios at high altitude were 1.0 ppbv near shore and 0.7 ppbv near Bermuda; in low-altitude marine air they were 1.9 and 1.0 ppbv, respectively (Tables 1 and 2). A trend of decreasing NO_y mixing ratio by day was observed at low altitude near the U.S. east coast.

NO_y mixing ratios in marine air near Bermuda (Figure 1) showed both day-to-day and longitudinal variations at low altitude of 0.5-1.6 ppbv and at high altitude of 0.1-2.2 ppbv. Longitudinal dependence for NO_y was small at low altitude near Bermuda, but at high altitude, NO_y had an increasing gradient from west to east on July 27 and a strong peak at 64.3°W on July 28.

U.S. east coast NO_y mixing ratios at high and low altitudes (Figure 2) were both higher and more variable than NO_y mixing ratios near Bermuda. Each successive day between July 17 and 21 showed decreased NO_y at low altitude (Figure 2b), especially close to shore. Overall NO_y mixing ratios along the U.S. east coast were approximately twice as high as the Bermuda mixing ratios where only marine air was sampled. At low altitude, east coast NO_y mixing ratios decreased with distance from shore slightly on July 17 and more significantly on July 18-19. During the latter 2 days, NO_y mixing ratios were at marine levels eastward from the transition zone (at 75.1°W). A similar decrease in NO_y mixing ratio at high altitude was observed on July 18-19. The lowest NO_y mixing ratios were observed on July 21 at both altitudes; the change with distance from shore was not significant on that date. At the upper altitude (Figure 2a), a sharp peak in NO_y at 74.5°W was observed on July 17; decreasing NO_y gradient from the coast out to 75.5°W was observed on July 18 and 19.

Variation in NO_y mixing ratios with altitude near the ship is presented for both the U.S. east coast and Bermuda in Figure 3. Vertical profiles near the coast showed that the mixing ratios were highest at low altitude and decreased with altitude up to 2600 m (740 mbar). Overall, the NO_y mixing ratio declined at each altitude between July 17 and 21. By con-

TABLE 1. Observation Averages for Low Altitude (150 m)

		Near U.S. East Coast (76.0-75.1°W)				U.S. East Coast (75.1°-74.4°W)				Near Bermuda (64.5°-63.4°W)				
		July 17	July 18	July 19	Average	July 18	July 19	July 21	Average	July 26	July 27(1)	July 27(2)	July 28	Average
n		5	6	5	16	15	19	7	41	23	23	23	22	91
Average		3.5	3.2	2.2	3.0	2.1	2.1	1.7	1.9	1.4	0.9	0.8	0.7	1.0
Std. dev.		0.1	0.7	0.3	0.4	0.3	0.3	0.2	0.3	0.2	0.2	0.2	0.2	0.3
		<u>NO_y, ppbv</u>												
n*		29	37	25	91	81	97	38	216	122	119	124	113	478
Average		206	233	212	217	213	218	212	214	189	176	124	150	160
Std. dev.		5	42	4	17	31	11	16	20	76	63	80	45	73
		<u>Winds, deg</u>												
Average		10.8	6.0	13.1	10.0	16.1	13.5	11.1	13.4	14.5	3.9	4.1	6.2	7.2
Std. dev.		2.0	3.0	1.7	2.2	7.8	2.2	2.9	5.1	19.1	1.8	2.4	2.7	10.8
		<u>Wind Speed, m s⁻¹</u>												
Average		28.1	27.0	28.0	27.7	25.9	26.0	26.0	26.0	25.1	25.5	25.4	25.7	25.4
Std. dev.		1.1	0.5	0.3	0.6	0.5	0.3	0.4	0.4	0.5	0.7	0.6	0.4	0.6
		<u>Temperature, °C</u>												
Average		23.2	22.7	22.3	22.7	23.2	22.9	22.4	22.8	20.7	20.7	21.0	21.6	21.0
Std. dev.		0.5	0.2	0.5	0.4	0.6	0.3	1.1	0.8	0.5	0.4	0.7	0.3	0.6
		<u>Dew Point, °C</u>												
Average		18.3	17.8	17.2	17.8	18.3	17.9	17.3	17.8	15.5	15.5	15.9	16.0	15.7
Std. dev.		0.6	0.3	0.6	0.5	0.7	0.3	1.1	0.9	0.4	0.3	0.6	0.6	0.6
		<u>Water Mixing Ratio, g kg⁻¹</u>												

*Values of n apply to winds, wind speed, temperature, dew point, and WMR.

TABLE 2. Observation Averages for High Altitude (2600 m)

		Near U.S. East Coast (76.0-74.4°W)				Near Bermuda (64.5°-63.4°W)					
		July 17	July 18	July 19	July 21	Average	July 26	July 27(1)	July 27(2)	July 28	Average
n		17	18	18	15	68	17	16	13	13	59
Average		0.7	1.5	0.9	0.6	1.0	0.5	0.8	0.9	0.6	0.7
Std. dev.		0.4	0.2	0.5	0.2	0.5	0.3	0.3	0.5	0.8	0.5
<u>NO_y, ppbv</u>											
n*		115	114	101	102	432	101	101	99	95	396
Average		221	231	241	219	228	175	197	178	186	184
Std. dev.		27	38	17	8	27	45	72	59	49	58
<u>Winds, deg</u>											
Average		7.9	8.6	11.7	17.3	11.1	6.5	4.2	22.5	5.3	9.3
Std. dev.		2.7	3.4	3.6	3.4	4.9	2.6	1.4	25.6	2.3	14.4
<u>Wind Speed, m s⁻¹</u>											
Average		13.7	12.0	11.8	10.6	12.1	11.3	12.4	12.0	10.2	11.5
Std. dev.		0.8	0.6	0.4	0.3	1.3	0.4	0.3	0.4	0.2	0.9
<u>Temperature, °C</u>											
Average		-3.0	6.3	3.2	6.0	2.9	-1.6	-7.0	-5.2	3.2	-2.7
Std. dev.		5.6	1.3	3.5	0.8	5.2	5.6	4.3	5.2	1.4	5.9
<u>Dew Point, °C</u>											
Average		4.5	8.1	6.7	7.9	6.7	4.9	3.2	3.7	6.5	4.6
Std. dev.		1.8	0.7	1.6	0.4	2.0	1.6	1.0	1.6	0.7	1.8
<u>Water Mixing Ratio, g kg⁻¹</u>											

*Values of n apply to winds, wind speed, temperature, dew point, and WMR.

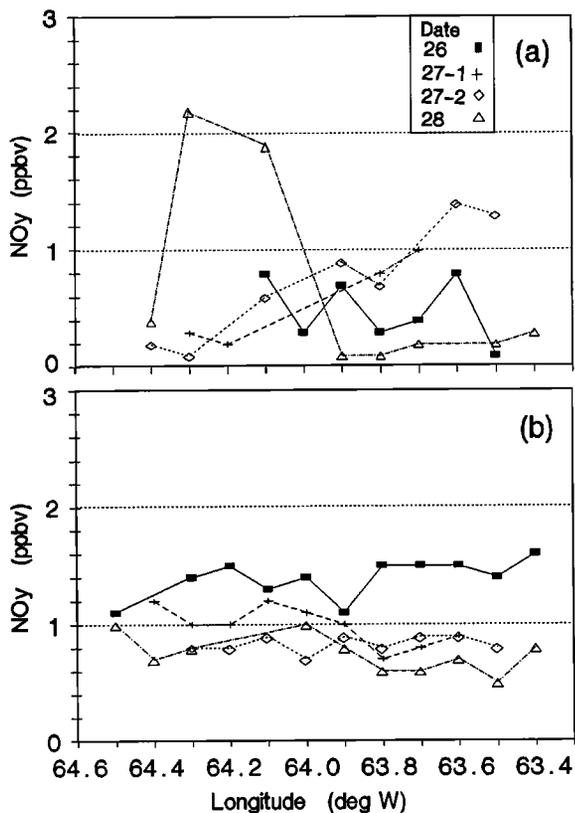


Fig. 1. Averaged NO_y mixing ratios by longitude, measured during flights from Bermuda in July 1988: (a) 740 mbar and (b) 1000 mbar.

trast, vertical profiles near Bermuda showed no obvious NO_y gradient with altitude; daily variation was about the same at all altitudes.

Shipboard NO_y Data

Shipboard averages of NO_y and NO₂ mixing ratios from the continuous analyzer and T-NO₃⁻ (total nitrate, the sum of p-NO₃⁻ and HNO₃) from the filter pack sampler are shown in Table 3 by location for daytime measurements only. NO_y averaged 1.7 ppbv in marine air near the east coast but decreased to <1.0 ppbv as the ship neared Bermuda. The highest T-NO₃⁻ mixing ratios (1.4 ppbv) were obtained near the U.S. east coast and decreased with distance from the coast. Shipboard average values for HNO₃ (0.04 ppbv) and T-NO₃⁻ (0.3 ppbv) measured in predominantly marine air were about the same near the east coast and near Bermuda. Aircraft averages

of T-NO₃⁻ were generally lower than the shipboard averages, and the aircraft relative distributions of HNO₃ and p-NO₃⁻ were quite different from the shipboard distributions; a larger percentage of T-NO₃⁻ was HNO₃ at higher altitude. The difference between measured NO_y and NO_x should be approximately equal to the T-NO₃⁻. However, this difference was considerably larger than T-NO₃⁻ for the east coast samples and nearly the same for the Bermuda area samples. The measured NO₂ mixing ratios were more constant with longitude (0.4-1.0 ppbv), and there was no indication of a daily cycle.

The longitudinal distribution for NO_y and NO_x is presented in Figure 4 for ship-

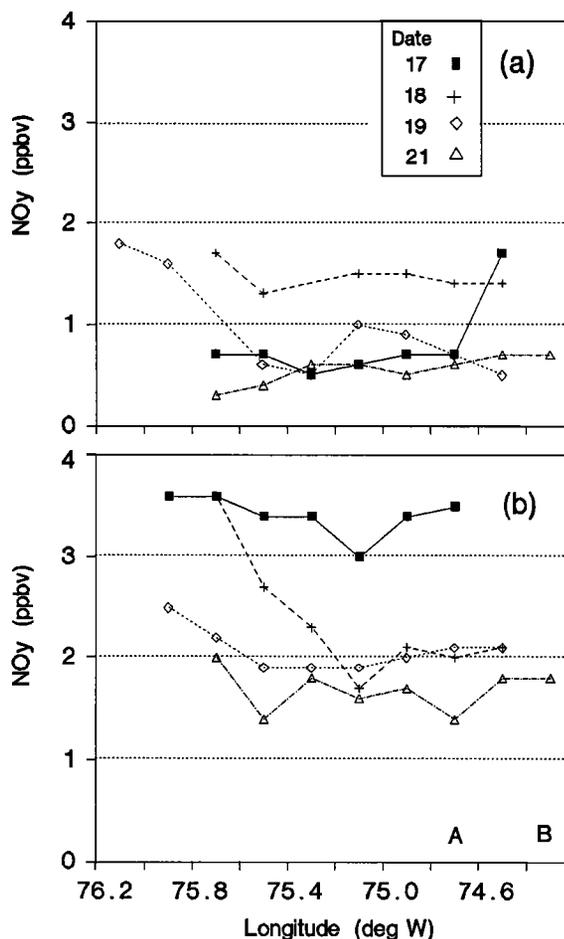


Fig. 2. Averaged NO_y mixing ratios by longitude, measured during flights from the U.S. east coast in July 1988: (a) 740 mbar and (b) 1000 mbar. Approximate ship position is indicated by "A" for July 17-19 and by "B" for July 21.

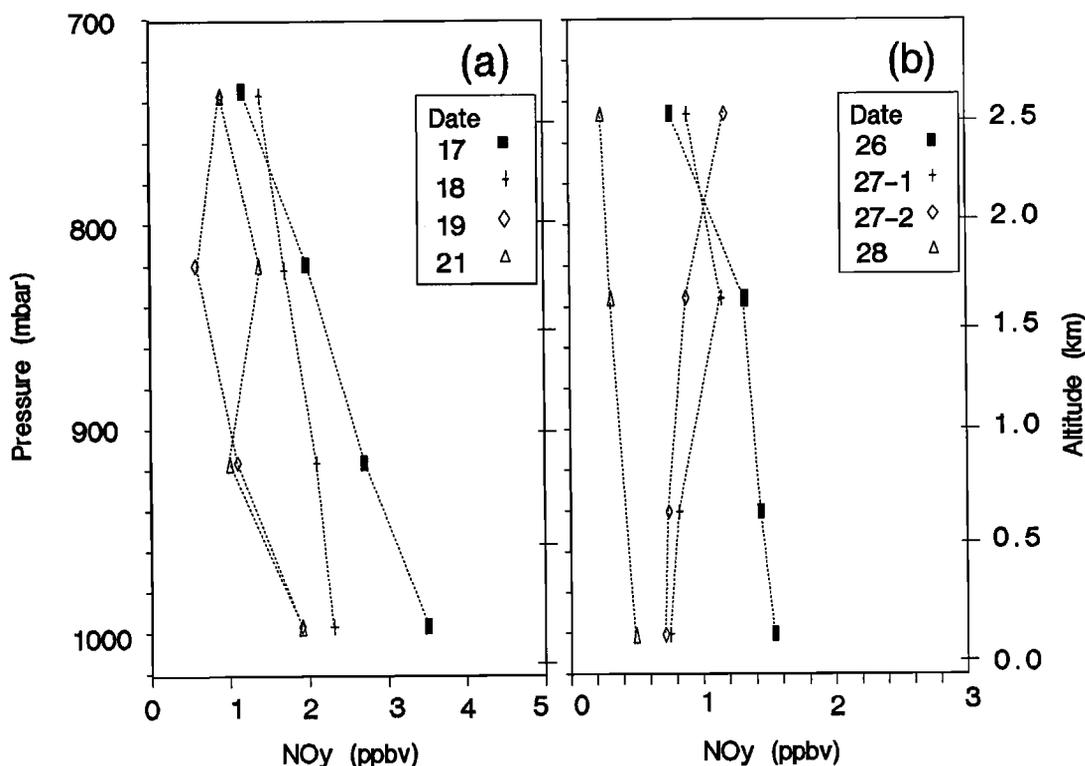


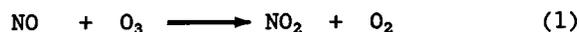
Fig. 3. Vertical profiles for each flight in July 1988 of averaged NO_y mixing ratios: (a) near the U.S. coast and (b) near Bermuda.

board measurements between the east coast and Bermuda. Each point represents the average for 0.5° of longitude. NO_y mixing ratios decreased from 1.8 ppbv near the east coast to approximately 0.8 ppbv near Bermuda. Between 69° and 70°W , the ship appears to have passed through plumes from heavy ship traffic [Keane et al., 1990]. NO_x mixing ratios remained at 0.4 ± 0.2 ppbv, except for near 70°W , showing no systematic change with longitude.

DISCUSSION

All odd nitrogen species in the atmosphere ultimately originate from oxidation of N_2 through high-temperature combustion, electrical discharges, or biogenic conversion. The principal removal mechanism for odd nitrogen is dry and wet deposition to the surface. Absorption and reaction of HNO_3 on sea-salt aerosols may also contribute [Sievering et al., 1990]. Odd nitrogen species can be categorized according to atmospheric cycling times into chemically active species (NO , NO_2 , NO_3 ,

N_2O_5), reservoir species (PAN, organic nitrates, HONO, HO_2NO_2), and sink species (HNO_3 , particulate NO_3^-). Active species rapidly convert through



or convert into reservoir species



or convert into sink species



Both reservoir and sink species can reconvert to active species. However, the rate constants for back conversion are much

TABLE 3. Summary of Odd Nitrogen Sink Species Mixing Ratios by Location and Air Mass Type

Sampling Platform	Species	Continental Nearshore (July 17)		Marine Nearshore (July 18, 19, 21)			Marine Bermuda (July 26, 27, 28)		
		Average	n	Average	Std. Dev.	n	Average	Std. Dev.	n
Aircraft	HNO ₃	0.463	1	0.092	0.035	3	0.049	0.006	8
Aircraft	p-NO ₃ ⁻	0.105	1	0.126	0.040	3	0.026	0.008	8
Ship	HNO ₃	0.831	1	0.036	0.011	3	0.039	0.020	6
Ship	p-NO ₃ ⁻	0.610	1	0.235	0.042	3	0.293	0.155	6
Aircraft	T-NO ₃	0.568	1	0.218	0.074	3	0.075	0.008	8
Ship	T-NO ₃	1.441	1	0.271	0.046	3	0.332	0.168	6
Ship	NO _y	1.56	48	1.71	0.19	111	0.90	0.18	156
Ship	NO _x	1.06 ^a	48	0.73	0.10	111	0.66	0.22	156
Ship	NO ₂	1.15 ^b	47	0.50	0.16	111	0.50	0.02	156

HNO₃ and p-NO₃⁻ were determined by University of Virginia filter packs and NO_y, NO_x and NO₂ were determined by York University instruments; p-NO₃⁻ is particulate nitrate and T-NO₃⁻ is total nitrate, the sum of p-NO₃⁻ and HNO₃. All mixing ratios are in ppbv.

^aNO_x mixing ratios are upper limits; see text for discussion.

^bNO_x and NO₂ were determined individually by separate methods.

higher for reservoir species. Sink species, on the other hand, are removed much faster by deposition processes, primarily because of their greater solubility. Conversion of reservoir species to sink

species usually proceeds through the active species.

The rapid decrease in NO_y as it was transported in air from the U.S. east coast suggests rapid conversion of active

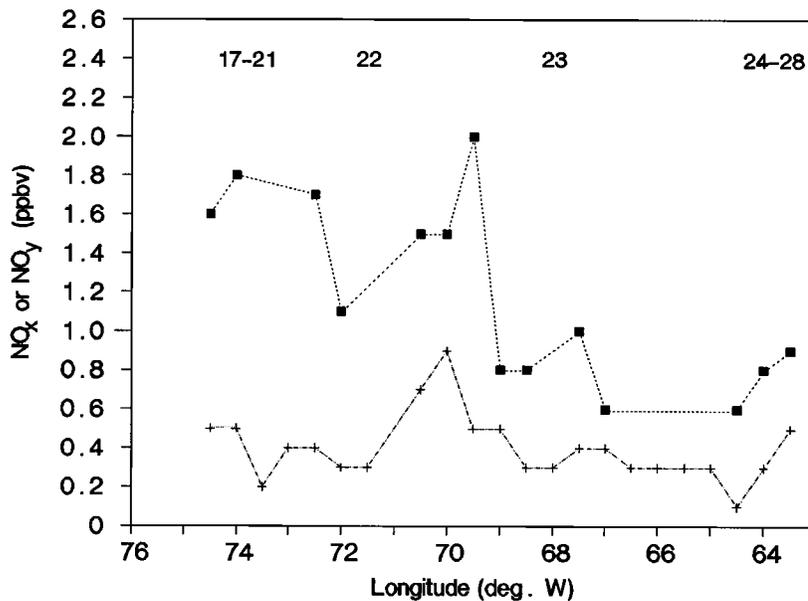


Fig. 4. Longitudinal variation in daily averages for each nitrogen species NO_y (square) and NO_x (plus symbols) measured on the ship. Dates for July 1988 are indicated along the top for approximate ship location.

species and losses of sink species to the ocean during July 18-19. Eastward of 75.1°W longitude, the NO_y mixing ratios at low altitude were nearly constant at 2 ppbv for July 18 and July 19 (Figure 2). The transition zone between continental and marine air had shifted west of the ship location on those days, and therefore surface mixing ratios no longer reflected advection from the U.S. east coast. West of 75.1°W longitude, a strong NO_y gradient with longitude was still observed for those 2 days. By July 21 the transition zone had shifted west to the coastline, and aircraft measurements of NO_y were about 2 ppbv from the coast to the ship.

All the NO_y vertical profiles near the U.S. east coast in the present study showed NO_y decreasing with altitude (Figure 3a). Since most NO_x emissions are from near the surface, this profile is consistent with that of an anthropogenic continental plume. Kley et al. [1981] and Misanchuk et al. [1987] reported similar NO_x profiles downwind from urban centers. The NO_y profiles shifted to lower mixing ratios with each flight, the largest change occurring near the ocean surface. In a prior WATOX program [Luke and Dickerson, 1987], similar decreases in NO_y were observed with altitude. NO_y mixing ratios as high as those in this study were observed in plumes coming off the continent between 44°N and 37°N latitude. The highest NO_y mixing ratios were below 800 mbar, decreasing above that altitude. One example showed 3 ppbv near the surface and approximately 0.6 ppbv at 750 mbar. We observed low-altitude NO_y mixing ratios of 1.9-3.5 ppbv and upper altitude mixing ratios of 0.6-1.5 ppbv. The range of mixing ratios for NO_y and the profile trends were comparable with those of Luke and Dickerson, even though their data were for winter.

The NO_y vertical profiles near Bermuda (Figure 3b) did not have the vertical gradient observed along the U.S. east coast. There were significant variations in NO_y between flight days; on July 27 both the morning and later afternoon flights had similar profiles. The location of the profile could have a significant impact on its shape; for example, consider projections from Figure 1. Thus the NO_y vertical profiles in Figure 3 imply good mixing up to 2600 m and a lack of surface sources, whereas Figure 1 suggests that horizontal distribution was uneven and contained plumes of polluted air.

NO_y Loss Rates

Under clear skies in the marine environment, removal from the atmosphere of NO_y is primarily by deposition of sink species (HNO₃ and p-NO₃⁻) to the ocean. Loss rates or lifetimes of odd nitrogen species over the ocean are not well known. NO_x loss rates, presumably by conversion to reservoir and sink species, reported in the literature vary from 3% hour⁻¹ to 35% hour⁻¹ [Hastie et al., 1988; Helas and Warneck, 1981; Spicer, 1982]. Summers and Fricke [1989] estimated sink species' (T-NO₃⁻) decay times that corresponded to a loss rate of 6.3% hour⁻¹ in an urban plume over eastern Canada. The dry deposition rate for p-NO₃⁻ is thought to be an order of magnitude less than that of HNO₃ [Huebert and Robert, 1985], so the loss rate for HNO₃ should be greater than 6% hour⁻¹. Dry deposition velocities for HNO₃ of 2-3 cm s⁻¹ to grassland were reported by Huebert and Robert [1985]; however, the overall deposition rate of nitrates over the ocean were estimated to be 0.3-0.6 cm s⁻¹ [Logan, 1983; Levy and Moxim, 1989]. Translation of deposition velocities to loss rates depends on mixing height, wind velocities, aerosol size distribution, and even time of day. Presumably, loss rates by dry deposition over the ocean will follow a similar trend and be 10-50% of the loss rate over land.

Three methods were used in the present program to calculate the NO_y loss rate $k(\text{NO}_y)$ from NO_y measurements at low altitude near the U.S. coast (Table 4). For calculations of the NO_y loss rate, an estimate for transport time of the air mass from the continent to the observation point over the ocean was needed. The first method presumed that the U.S. coastline was at a 30° angle from north, that NO_y mixing ratios measured near the coast were representative of NO_y mixing ratios in the air mass as it left the coast, and that the wind speed and direction measured on the aircraft could be used to calculate an air parcel trajectory. Great-circle distances from the U.S. coast were calculated to the aircraft measurement sites, and the transport time was estimated using the measured wind speed. The end point for the transport was taken to be 75.2°W rather than the ship, which was in marine air after July 18. The natural logarithm of NO_y mixing ratio was plotted against estimated air mass travel times in Figure 5 to estimate NO_y loss rate. The slope of

TABLE 4. Comparison of NO_y Loss Rates Computed by Different Methods

Data Set	Loss Rate, % hour ⁻¹	R ²	Method ^a	Dates used, July 1988
Aircraft	2.0±1.5	0.66	extrapolated winds	17 - 19
Aircraft	0.18	0.99	radon transport	17 - 21
Ship	0.51	0.43	radon transport	16 - 18
Aircraft	15.0±6.2	0.31	850-mb back trajectories	18, 19

^aSee text for explanations.

the linear regression fit represents the NO_y loss rate, presuming a first-order decay rate [Summers and Fricke, 1989].

Calculated NO_y loss rates were 0.6%, 1.8%, and 3.5% hour⁻¹ for July 17, 18, and 19, corresponding to lifetimes of 1.2-7.0 days. The averaged loss rates give a lifetime of 2.1 days. Two problems contributed to the uncertainty in the estima-

tion method. Because of the extreme angle of the winds to the coast, the presumed coastal source was far from the shore position where measurements were actually made. Had the winds been more westerly, the assumptions in this method would have more obvious validity. Further, the validity of the air mass back trajectory used in this method was questionable for transport periods of several days.

The second method for calculating air mass transport time used the radon data collected on the ship. The decrease in ²²²Rn, which has only continental sources, was due to radioactive decay and to dilution from mixing with marine air. An estimate of NO_y loss rate can be obtained from the slope of the ln-ln plot of NO_y mixing ratio versus radon counts. The radon served as an indicator of transport time of that air mass from its last contact with land. The 4 days of aircraft flight data over the ship and the radon data from the ship were used to obtain a loss rate of 0.2% hour⁻¹. Shipboard NO_y data from July 16-18 (while the ship was in continental air) were also used with the radon data to obtain an estimated NO_y loss rate of 0.5% hour⁻¹. This was in good agreement with the loss rate calculated for July 17 by the first method. The relative contribution of HNO_3 to NO_y was much smaller in the marine air, so the NO_y loss rate should be smaller. It is uncertain whether the assumptions required for this method strictly hold for the circumstances of this study. The longer back trajectories to a land mass during the first days and the complications resulting from the transition between continental air and marine air introduce uncertainty into the estimated loss rates.

The third method of estimating air mass transport times to calculate NO_y loss rate was to use the air mass back trajectories [Stunder et al., 1990; Ray et al., 1990]

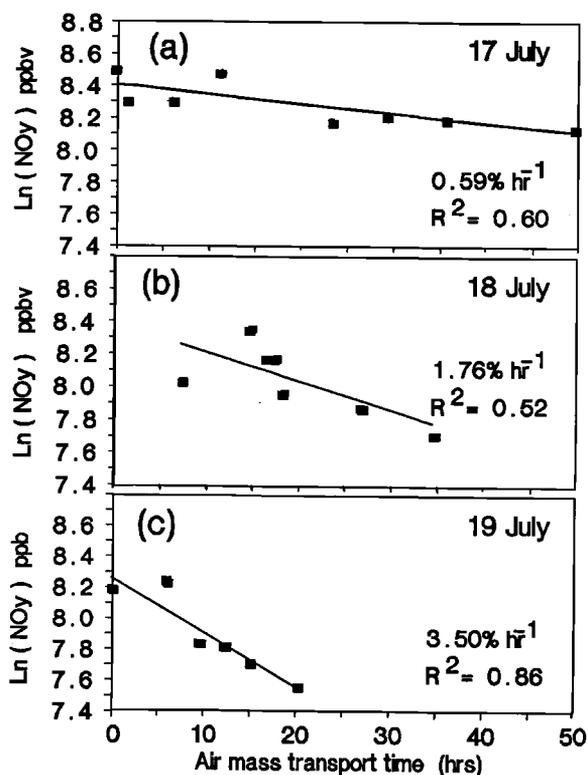


Fig. 5. NO_y loss rates $k(\text{NO}_y)$ for (a) July 17, (b) July 18, and (c) July 19, calculated from the slope of $\text{Ln}(\text{NO}_y)$ versus air mass transport time estimated from aircraft wind observations.

to the ship. However, the surface back trajectories to the ship on July 17 and July 21 were from the ocean. Since only the 850-mbar air mass back trajectories to the ship showed continental history, they were used to estimate air mass transport times. Transport times from the coast were estimated by linear interpolation and plotted against the natural logarithm of NO_y mixing ratios to calculate NO_y loss rates. No net loss was showed for July 17, whereas July 18 and July 19 showed loss rates of 19% and 11% hour^{-1} , respectively. This corresponded to NO_y lifetimes of only 5 and 9 hours, which seem far too short. The main problem here appears to be the air mass back trajectories to the ship. The 850-mbar trajectories that had overland components were not representative of airflow at 150 m. From previous discussions, we expected surface back trajectories out to 75.2°W longitude to have overland components, but trajectories with a finer end point resolution were unavailable.

Results of the above calculations yield very different estimates for NO_y loss rates. Wind direction and speed measured by the aircraft were fairly steady from the U.S. east coast out to the ship during the 4 flight days. The estimated travel times from extrapolated winds were probably reasonable in this study. Thus the loss rate average of $2.0 \pm 1.5\%$ hour^{-1} from the first method is favored, corresponding to an average lifetime of 2.1 days. The wide variation in NO_y loss rates suggests that a single value for loss rate may not define all conditions over the ocean.

Luria et al. [1990] concluded from computer modeling of SO_2 loss rates that atmospheric mixing and chemical reactions were of less importance than dry deposition to the ocean in predicting the decrease in SO_2 concentration with distance from shore. That conclusion was dependent on the marine boundary layer height and was specific for the conditions observed in the GCE/CASE/WATOX experiment. Although the reaction sequence to produce HNO_3 from NO_x is different from that of SO_2 , dry deposition rates for both HNO_3 and SO_2 in the marine boundary layer are expected to be high. Ultimately, deposition of HNO_3 and p-NO_3^- to the ocean should be the primary loss mechanism for NO_y .

Partitioning of Species

A comparison of NO_y mixing ratios observed on the aircraft during low-altitude flights near the ship and on the ship at the same time shows general agreement [Boatman et al., 1990]. However, on July 17-18, NO_y measured from the aircraft was a factor of 2 higher than NO_y measured from the ship. Large differences were also observed in the HNO_3 mixing ratios measured on the ship and aircraft for those dates [Keene et al., 1990]. During the 6 following intercomparison periods, the agreement for NO_y mixing ratios was better than $\pm 10\%$. The low NO_y values observed on the ship for July 18 were, however, consistent with the drop in shipboard T-NO_3^- from 1.4 ppbv on July 17 to 0.27 ppbv on July 18 (Table 3). A continental-to-marine air transition that occurred on that day near the surface [Ray et al., 1990] may explain the higher concentrations of trace gases observed on the aircraft at 150-m altitude.

The calculated NO mixing ratios from the shipboard analyzer (the difference between NO_x and NO_2) were always higher than the aircraft upper limit estimate of NO (<0.1 ppbv). The overestimation of shipboard NO mixing ratio may result from conversion of species other than NO to NO_2 by the CrO_3 converter [Wolff et al., 1986b]. If we presume that nighttime NO mixing ratios should be nearly zero, then an NO offset of approximately 0.20 ppbv can be inferred from the data. The luminol detector has an NO_2 interference from PAN [Fehensfeld et al., 1990] and maybe some from O_3 due to the different averaging times of the two instruments; therefore the NO_x mixing ratios reported here (Table 3) should be considered as upper limits.

Averages of the odd nitrogen species observed on the ship over three different periods are presented in Table 3. Both NO_y and NO_x mixing ratios decreased between the U.S. east coast and Bermuda. During July 16-21 the NO_x mixing ratio near the U.S. east coast was 35% of the NO_y mixing ratio, and the remainder of the NO_y species is presumed to be mostly HNO_3 , NO_3^- , and PAN. The NO_x active-species fraction of NO_y increased to $70 \pm 2\%$ near Bermuda. The high relative and absolute magnitude of active species near Bermuda was unexpected, since the air mass back

trajectories suggested a well-aged marine air mass. These observations suggested that there may be some sources of NO_x near Bermuda. Possible NO_x sources within the region include civil and military aviation activity, ship traffic, and fossil fuel combustion on Bermuda. Contributions from natural sources, such as lightning, cannot account for the observed levels, especially when compared with the low NO_y mixing ratios observed at other remote marine locations [Ridley et al., 1987].

A clear trend of decreasing HNO_3 and NO_3^- is evident in going from the U.S. coast to Bermuda (Table 3). Total NO_3^- concentration in the continental-influenced air near shore on July 17 was 1.44 ppbv. Concentrations of T- NO_3^- in marine air near shore on July 18-21 were lower by a factor of 4 (0.27 ppbv) and were similar to average T- NO_3^- in marine air near Bermuda (0.33 ppbv). T- NO_3^- was about 40% of the aircraft NO_y mixing ratios in continental air near the U.S. east coast and in marine air near Bermuda. It was lower in marine air near the U.S. east coast. By comparison, these marine air values were similar to the mean values of 0.07 ppbv HNO_3 and 0.23 ppbv NO_3^- reported by Huebert and Lazrus [1980] for Pacific marine boundary layer air and are comparable with previous WATOX values discussed earlier.

Comparison of Observations With Modeling Results

Although the agreement for the NO_y mixing ratios observed by two different methods is good, the distribution of individual NO_y species seems inconsistent with the expected photochemical equilibrium. The main question is why the relative contribution of NO_x to NO_y is so large. It is expected that a photochemically aged air mass would contain a higher T- NO_3^- fraction of NO_y . We modeled the partitioning of odd nitrogen species for different NO input rates and transport times [Luria and Meagher, 1988]. The photochemical smog reaction scheme was taken from Atkinson and Lloyd [1984], and the meteorological parameters were chosen to match the Bermuda portion of the GCE/CASE/WATOX experiment. The first computer model run was used as a reference; it presumed a constant, low NO input (1.0×10^{10} molecules $\text{cm}^{-3} \text{ s}^{-1}$) and allowed for photochemical aging and dry deposition processes.

The boundary layer height was taken as 2500 m, the photolysis constant ($j(\text{NO}_2)_{\text{max}}$) was set at 0.54 min^{-1} to fit the location and the date, cloud coverage was assumed to be 20%, and exchange between the boundary layer and the free troposphere was assumed to be $12\% \text{ day}^{-1}$. The model did not calculate HNO_3 and NO_3^- separately; thus a combined deposition velocity of 1 cm s^{-1} was used. The reference model run reproduced the main features of the sulfur cycle and the O_3 mixing ratios and slightly overestimated H_2O_2 [Luria and Sievering, 1990]. After a 10-day simulation the photochemical system reached equilibrium; NO_y mixing ratios were about one-half of the experimentally observed mixing ratios. NO_y consisted of T- NO_3^- (70%), NO_x (20%), and PAN and organic nitrates (10%).

In the second model run, the constant NO input was doubled to reproduce the observed NO_y mixing ratios, while all other parameters remained unchanged. The results showed that NO_y was nearly doubled, T- NO_3^- fraction increased slightly to 76%, and NO_x and PAN decreased accordingly. But the increase in NO_y also enhanced the photochemical activity so that O_3 was 50% higher than in the previous model run. Thus increasing NO, as though from a nearby source, leads to model predictions that nearly match the NO_y mixing ratios observed, but greatly exceed the O_3 and NO_x observed.

The third model run started with high NO (10 ppbv) to simulate a polluted air mass that is transported to a clean environment. A constant low input of NO (1.0×10^9 molecules $\text{cm}^{-3} \text{ s}^{-1}$) was assumed. After 12 hours of model simulation, NO_x mixing ratios were similar to the experimental NO_x observations; however, T- NO_3^- was more than a factor of 10 higher. After 10 days of simulation, at photochemical equilibrium, predicted NO_x was <15 pptv and T- NO_3^- was 40 pptv. O_3 and H_2O_2 increased initially and then decreased to equilibrium values of 12 ppbv and 1.0 ppbv, respectively, which were within the range of the experimentally observed mixing ratios [Ray et al., 1990].

The model predictions were able to match only 1 of the 3 species NO_x , NO_y , or T- NO_3^- at a time by adjustments in the initial NO or in the NO input rate. When the predicted NO_x matched the observed NO_x mixing ratios, the predicted oxidants and T- NO_3^- mixing ratios were too high. When

the predicted NO_y matched, the predicted NO_x was too low and the predicted O_3 was too high. When the predicted T-NO_3^- matched, NO_y and NO_x were too low by an order of magnitude. The clue to the discrepancy between the model and the observations is the difference between NO_y and T-NO_3^- . This difference is too large to be accounted for by organic nitrate reservoir species and active species. Since we have no direct measurements of the reservoir species and there may have been a discrepancy between the NO measured on the ship and the aircraft, it is not possible to independently verify the concentrations of species that make up the difference between our observed NO_y and T-NO_3^- . We believe that the difference consists largely of reservoir species plus the accumulated uncertainty in the measurements of both NO_y and T-NO_3^- . This assumption is based on the modeling results that neither a well-aged nor a recently polluted air mass can account for the observed odd nitrogen species without the other pollutant mixing ratios being outside the observed ranges.

The net result is that we cannot easily explain, at least from computer modeling, the relatively high NO_y mixing ratios and the partitioning of NO_y species around Bermuda. Meteorology during the GCE/CASE/WATOX study effectively prevented advection of pollution from North America to Bermuda, and the air mass back trajectories indicated only oceanic source regions for at least 10 days. Despite those indicators of remote marine air, low-altitude NO_y mixing ratios varied by a factor of 2, and the high-altitude NO_y mixing ratios varied by a factor of 10 over the observation area. In the absence of nearby NO_y sources or significant changes in air mass trajectories, such large variations are unlikely, and only low background-level mixing ratios would be expected. Although it would be easy to invoke NO_y sources in the Bermuda area as an explanation, that would not also explain the steady decrease in NO_y mixing ratio in marine air from 74°W to Bermuda observed from the ship (Figure 4) and therefore seems unlikely. In the present study, transportation-related NO_y sources, and perhaps high-altitude advection with downward mixing, provide the most likely explanations for the observed NO_y mixing ratios. The limited data set and the short observation periods of leg 1 of the GCE/CASE/WATOX cruise preclude making broad generaliza-

tions. A future publication with a more extensive analysis of data by participants on the whole cruise throughout the Atlantic Ocean region may provide additional insight into the NO_y distribution and partitioning.

CONCLUSIONS

NO_y mixing ratios of >3.0 ppbv were observed off the U.S. east coast during summertime measurements. The NO_y mixing ratio decreased with distance from shore to about 1.7 ppbv at 160 km. This decrease is believed to be due to conversion of active nitrogen species to HNO_3 and p-NO_3^- and subsequent deposition to the ocean. The NO_y loss rate was estimated to be $2 \pm 1.5\%$ hour^{-1} , which is consistent with a T-NO_3^- removal rate of approximately 3-6% hour^{-1} .

The NO_y and T-NO_3^- mixing ratios in marine air near Bermuda were comparable with those in marine air off the U.S. east coast (0.6-1.5 ppbv for NO_y and 0.27-0.33 ppbv for T-NO_3^-). These relatively high mixing ratios in the boundary layer near Bermuda, combined with the rapid NO_y loss rates calculated for transport over the ocean, lead to the conclusion that sources of NO_y species exist in this portion of the Atlantic Ocean.

The difference between NO_y and T-NO_3^- was high near Bermuda, both in absolute amount (0.5 ppbv) and as a fraction of NO_y (60%). On the basis of predictions from a photochemical model, we conclude that only a small fraction of the difference between NO_y and T-NO_3^- was reactive species (NO and NO_2). The remaining difference is presumed to be reservoir species and cumulative uncertainty in both measurements. Although the data on both NO and NO_2 over the Atlantic Ocean are inconclusive, the present observed NO_y , HNO_3 , and p-NO_3^- mixing ratios are consistent with previously reported mixing ratios.

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