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Ship-based nitric acid measurements in the Gulf of Maine during New England Air Quality Study 2002

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[1] Gas phase nitric acid (HNO_3) was measured at 5-min resolution on board the National Oceanographic and Atmospheric Administration (NOAA) research vessel *Ronald H. Brown* during the second leg (29 July to 10 August) of the New England Air Quality Study (NEAQS) 2002 cruise. A primary objective of the cruise was to improve understanding of the oxidation of NO_x in, and removal of the oxidation products from, the polluted marine boundary layer east of northeastern North America. For the first 9 days of this leg the ship remained north of Cape Cod, and the cruise track did not extend much farther north than the New Hampshire-Maine border. During this period, HNO_3 averaged 1.1 ppb and accounted for 19% of total reactive nitrogen oxides (measured NO_y). On all days, peak HNO_3 mixing ratios were observed in the early afternoon (average 2.3 ppb), at levels twofold to fourfold higher than the minima around sunrise and sunset. In these daytime peaks, HNO_3/NO_y averaged 28%. There were secondary nighttime peaks of HNO_3 (0.9 ppb average), when HNO_3 accounted for 16% of total reactive nitrogen oxides. This pronounced diurnal pattern confirms that production, and subsequent deposition, of HNO_3 in the polluted marine boundary layer downwind of New England removes a significant fraction of the NO_x exported to the atmosphere over the Gulf of Maine. Nitric acid was correlated with O_3 , particularly during the early afternoon interval when both molecules reached maximum mixing ratios ($R^2 = 0.66$). The ozone production efficiency (OPE) inferred from the slope (10 ppb O_3 /ppb HNO_3) was similar to the OPE of 9 estimated at the Atmospheric Investigation, Regional Modeling, Analysis and Prediction (AIRMAP) Thompson Farm station in coastal New Hampshire during the study period. **INDEX TERMS:** 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; **KEYWORDS:** nitric acid production, nitric acid deposition, polluted marine boundary layer, New England Air Quality Study, Gulf of Maine

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1. Introduction

[2] The emission of nitric oxide (NO) by anthropogenic activity plays a major role in regional air quality, primarily by controlling the photochemical production of ozone (O_3). There is growing recognition that export of NO_x (NO plus nitrogen dioxide (NO_2)) and its oxidation products perturbs the composition of the troposphere long distances down-

wind of major source areas [e.g., Liang *et al.*, 1998; Li *et al.*, 2004].

[3] Northeastern North America represents a significant source of anthropogenic NO_x on a global scale. However, Munger *et al.* [1998] estimated that conversion of NO_x to HNO_3 , which is rapidly lost by deposition, within the continental boundary layer of this region is a very effective sink, removing approximately 45% of emitted NO_x within 24 hours during the summer. Simulations with the three dimensional global chemical transport model GEOS-CHEM predict that approximately 80% of the anthropogenic NO_x emitted into the North American boundary layer is quickly deposited as HNO_3 , with the remainder exported to the

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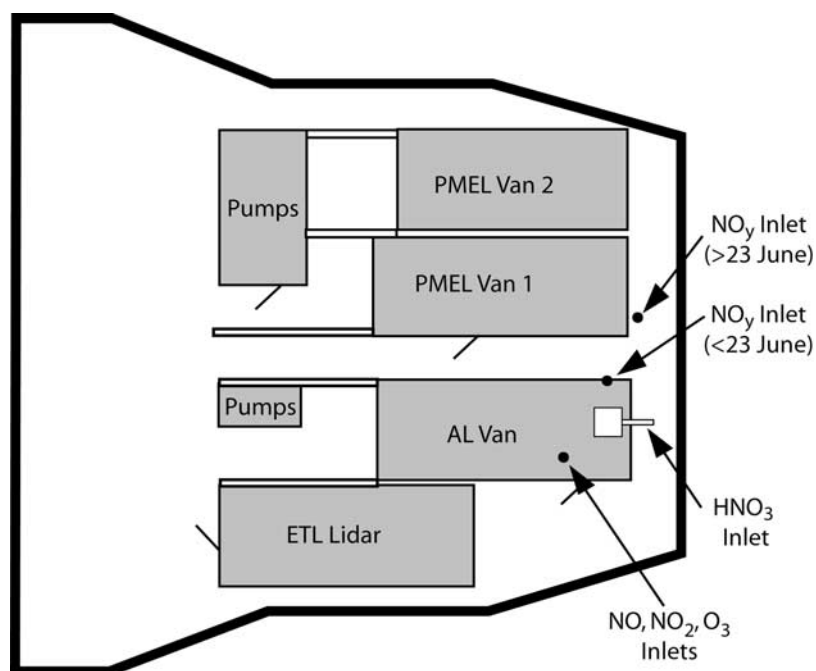


Figure 1. Plan view of the instrumentation vans and sampling inlets discussed herein. The bow of the ship was to the right, approximately 10 m forward of the leading edge of the HNO₃ inlet. Decking on top of the vans was 10.5 m above the waterline; all inlets were at least 1 m above the decking. To provide horizontal scale, it is noted that the large vans (PMEL 1, AL, and ETL) are 2.4 m wide by 6.1 m long.

atmosphere over the Atlantic Ocean as NO_x and peroxyacyl nitrates (PANs) [Li *et al.*, 2004]. Interestingly, the importance of HNO₃ deposition as the primary sink for NO_x has largely been inferred from NO_x/NO_y relationships, because accurate measurements of HNO₃ have been difficult, hence sparse.

[4] It is likely that a larger fraction (>80%) of the NO_x emitted along the urban/industrial corridor of the east coast of the United States is exported eastward over the Atlantic Ocean as NO_x than is the case for all anthropogenic emissions of NO_x, simply because of the very short transport distances. It is expected that production of HNO₃ in the marine boundary layer will remove much of this NO_x quickly, much as it does over the continent.

[5] The New England Air Quality Study in the summer of 2002 (NEAQS 2002) provided the opportunity to test this hypothesis. The NOAA research vessel *Ronald H. Brown*, carrying an extensive suite of in situ and remote sensing atmospheric chemistry instrumentation, conducted a month long cruise as part of NEAQS 2002. The primary study region was the coastal zone of the Gulf of Maine, offshore of New England and southeastern Canada. This paper presents measurements of gas phase HNO₃ made during the second half of the cruise, when the ship remained directly offshore of Massachusetts, New Hampshire, and Maine. Particular attention is directed toward demonstrating that HNO₃ is rapidly produced, and subsequently deposited to the ocean, in polluted air masses advected from the continent.

2. Methods

2.1. Nitric Acid

[6] Sampling was conducted with an automated dual mist chamber system, coupled to dual ion chromatographs that

provided near-real-time analyses. The system is modeled on the airborne instrument developed by the University of New Hampshire and described most recently by Scheuer *et al.* [2003]. For deployment on the *Ronald H. Brown*, the samplers and ion chromatographs were mounted inside a shipping case, along with the computer controlling both sampling and analysis and all associated air handling and measuring hardware. This shipping case was mounted at the forward edge of a platform on top of the NOAA Aeronomy Laboratory (AL) sampling van that was situated as far forward on the 02 deck of the ship as possible (Figure 1). The computer inside the shipping case was also connected via ethernet cable to a second computer in the main laboratory two decks below, allowing system operation and the ion chromatograph traces to be monitored remotely.

[7] Ambient air was pulled into the shipping case through a 75-cm-long heated manifold constructed of 1.27-cm OD PFA tubing. The flow rate through the manifold was in excess of 150 standard liters min⁻¹ (slpm). Particles were excluded from the manifold with a 9-cm diameter, 2- μ m pore size, Zeflour Teflon filter that was changed frequently. Extensive experimentation during the cruise demonstrated that the filter caused no measurable artifact in the collection of HNO₃, likely because of the very low abundance of sea-salt aerosols under the generally light wind conditions encountered during the study period.

[8] The mist chambers sampled from the manifold at a rate of 40 slpm for integration intervals of 5 min. When one mist chamber stopped sampling, the second immediately started, while the first automatically injected its sample into the ion chromatograph. Sampling was interrupted periodically (at least once every 36 hours) to replenish supplies of ultra pure water and eluent. The ion chromatographs were

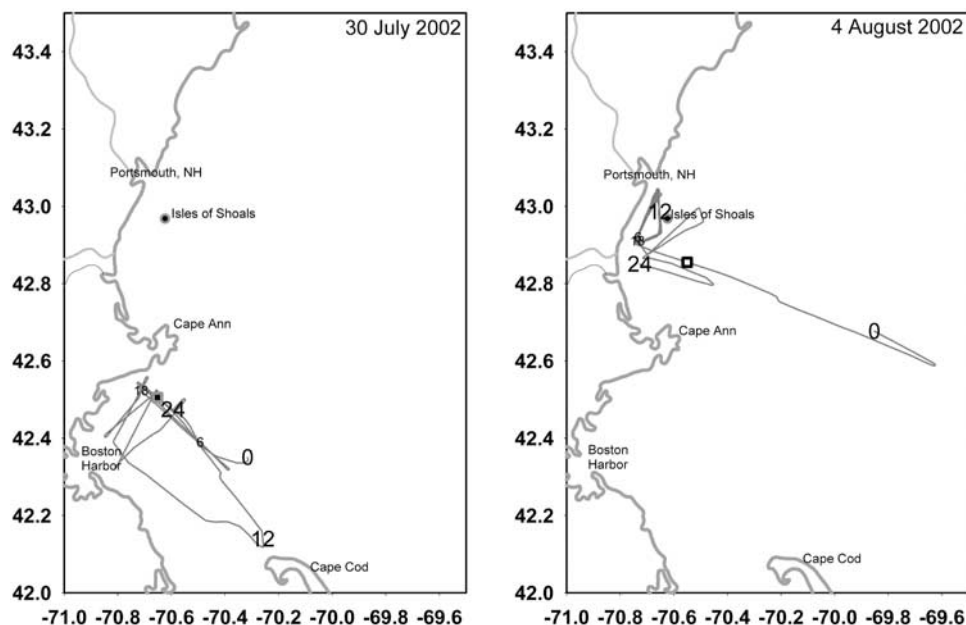


Figure 2. Cruise tracks of the *Ronald H. Brown* on 30 July and 4 August. These 2 days are selected to illustrate the two primary sampling areas (Boston Harbor and the Isles of Shoals) during leg 2. The ship did not traverse significantly outside the regions sampled on these two days until heading south past Cape Cod on the afternoon of 6 August. Figure 2 of *Brown et al.* [2004] presents the cruise track for all of legs 1 and 2. See color version of this figure at back of this issue.

recalibrated each time the eluent was refreshed, resulting in data gaps of several hours.

[9] Shortly after the ship left Charleston, South Carolina, on 12 July 2002 an uncontrolled heater partially melted the high-flow manifold inside the shipping case. Repairs were attempted and the instrument was operated throughout the first leg of the cruise, but agreement between the two samplers was generally poor. During the port call at Portsmouth, New Hampshire, midway through the cruise (26–29 July), all damaged parts were replaced. The improvement in data quality during the second leg confirmed that the original manifold had been leaking for most of the first leg, so all data from the first leg were discarded. During the second leg of the cruise (29 July until 10 August 2002) 3032 five-minute samples were collected. The complete data set is part of the NEAQS 2002 archive and is also available from the authors. This paper focuses only on the 2188 samples collected the first nine days of the second leg (ending 6 August) while the ship was north of Cape Cod in the Gulf of Maine, offshore of Massachusetts, New Hampshire, and southwestern Maine (Figure 2).

[10] The detection limit for HNO₃ using a 5-min integration time is better than 5 parts per trillion (ppt). All samples during the second leg of the NEAQS 2002 cruise were well above detection limit. We estimate that precision is approximately 30% below 50 ppt, improving to 15% for mixing ratios greater than approximately 300 ppt. The absolute accuracy of HNO₃ measurements is, in general, unknown [Crosley, 1996]. Our technique for measurement of HNO₃, as deployed on board NASA's DC-8, compared very well to measurements by chemical ionization/mass spectrometry on board the P3 in "wingtip to wingtip" flight legs during the

Transport and Chemical Evolution Pacific (TRACE P) campaign [Eisele et al., 2003].

2.2. Ozone and Nitrogen Oxides

[11] Nitric oxide (NO), nitrogen dioxide (NO₂), and total reactive nitrogen oxides (NO_x) were all measured with similar NO/O₃ chemiluminescence instruments. For NO₂ the sampled air was taken from a high-flow manifold and passed through a small (~17 cc) glass cell that was illuminated with UV light from a broadband 500W Xe lamp. This lamp photolyzed a fraction (~0.3–0.8) of the NO₂ in the sample, which was then measured as an increase in the signal from ambient NO. The instrument used to measure NO had identical plumbing, including a blackened photolysis cell, that also sampled from the high-flow manifold. The flows of the two instruments were matched so that subtraction of the NO data from the NO₂ data did not produce any spurious results. Calibrations were done as standard additions of NO or NO₂ to the sampled air. Sampling was conducted every second, but data were reported as 1-min averages. For this study the total uncertainty for NO was approximately ±(4% + 6 pptv) and for NO₂ was approximately ±(7% + 24 pptv). Detection limit (for the 1 s raw data at 1 sigma uncertainty) for NO was approximately 7 pptv and for NO₂ (also for 1 s data with no NO present) was approximately 30 pptv. The NO₂ Xe lamps failed numerous times during the study for unknown reasons, otherwise the systems operated normally. For NO_x, the sampled air was mixed with a small amount (0.3%) of pure CO within a short Teflon inlet and then drawn into a heated (325°C) gold tube converter. This converter was mounted on a post on the forward edge of the roof of one of the Pacific Marine Environmental Laboratory (PMEL) sam-

Table 1. Summary of 5-min Averages of Nitrogen Oxides and Ozone Mixing Ratios Measured on the *Ronald H. Brown* in the Period 29 July Through 6 August 2002^a

	HNO ₃	HNO ₃ /NO _y	NO _x	NO _y	O ₃
Mean (σ)	1.10 (1.02)	0.19 (0.15)	4.91 (5.48)	7.86 (7.47)	46.7 (20.5)
Median	0.81	0.15	3.24	5.93	43.8
Range	0.02–7.10	0.01–0.79	0.06–60.9	0.45–87.47	2–108
<i>n</i>	2188	2043	1913	2043	2182

^aMixing ratios in parts per billion (ppb); σ is 1 standard deviation, and *n* is number of 5-min intervals with ambient measurements for the given molecule.

pling vans (Figure 1). The sample was then sent through Teflon tubing at low pressure to the chemiluminescence detector in the AL van. Calibrations were performed as standard additions of NO and NO₂ to ambient air. The conversion efficiency of the gold tube for NO₂ was evaluated with every calibration. Conversion efficiency for HNO₃ was evaluated periodically by addition of HNO₃ from a permeation tube source. When conversion fell below 80% the gold tube was baked out under zero air flow at high temperature (500°C). Originally the converter was mounted on the roof of the AL van (Figure 1), but it became clear that air from ship operations (exhaust stack, galley exhaust, etc.) was contaminating the NO_y sampling. The converter was then moved to the second location (roof of PMEL van (Figure 1)), which reduced, but did not eliminate, the sampling contamination. Such contamination was not observed nearly as often in the NO/NO₂ data as in the NO_y data. The difference was likely due to the higher location of the NO/NO₂ inlet than the NO_y inlet, but this could not be confirmed. In any case, the contamination was easily observed as extremely high-mixing-ratio plumes (>100 ppbv) of short duration (2–5 s) so these events could be eliminated from the data set. For this study, the 1 s NO_y data were averaged to 1-min data points. Total uncertainty for NO_y is estimated at $\pm(15\% + 20 \text{ pptv})$ and the detection limit (1 s as NO; 1 sigma) was approximately 10 pptv.

[12] Ozone was measured with a commercial UV absorbance instrument (Thermo Environmental Instruments, Inc. Model 49c). This instrument sampled from the same high-flow manifold as the NO/NO₂ systems. The 10 s data from this instrument were averaged to 1-min data points. Detection limit for this instrument is estimated at 1–2 ppbv.

2.3. Hydrocarbons

[13] A gas chromatograph with flame ionization and mass spectrometric detectors was operated on board the *Ronald H. Brown*. Details of sampling and analysis are provided by *Goldan et al.* [2004]. This paper uses selected hydrocarbons to identify distinct changes in air mass. No attempt to merge the ozone and nitrogen oxide data sets to the gas chromatograph sample collection intervals is made herein.

3. Results

[14] Gas phase HNO₃ mixing ratios averaged 1.1 parts per billion (ppb) and accounted for 19% of measured NO_y during the 9 days of interest (Table 1). The average during this short period was 300–700 ppt higher than summertime averages (based on 24-hour filter-pack sam-

ples) measured at a coastal station immediately upwind of the NEAQS 2002 study area in Portsmouth, New Hampshire (43°2'N, 70°43'W), in 1994–1997 [*Jordan et al.*, 2000]. Close inspection of Plate 2 of *Jordan et al.* [2000] suggests that there were several weeklong intervals in summer 1994 when HNO₃ average mixing ratios were near 1 ppb, but in the other years just a few daily samples exceeded the overall average in the present study. On the other hand, it should be noted that the highest 5-min average measured from the *Ronald H. Brown* (7.1 ppb) was only about twofold higher than the peak 24-hour averages in 1994 and 1996 (3.6 and 3.2 ppb, respectively) and about threefold higher than the peaks at the coast in 1995 and 1997 (2.1 and 2.4 ppb, respectively) reported by *Jordan et al.* [2000].

[15] Nitric acid measurements have also been conducted in several studies further upwind in northeastern North America. *Lefer et al.* [1999] used the same mist chamber/ion chromatographic technique employed for this study to collect 45-min samples at Harvard Forest (42°32'N, 72°11'W) in central Massachusetts. Composite mean mixing ratios of HNO₃ during the summers of 1991–1995 were found to depend strongly on wind direction, decreasing from 2.0 ppb when transport was from the southwest to about 0.5 ppb under flow from the northwest. Faster, and more continuous, measurements were made at the same site in 2000 by *Horii et al.* [2001] using a tunable diode laser absorption spectrometer. That study found HNO₃ to average approximately 1.0 ppb in the polluted southwest flow. *Hayden et al.* [2003] measured HNO₃ at 2-hour resolution with filter packs at the Sutton research station (45°5'N, 72°33'W) during 2-week intensive sampling campaigns in the summers of 1998 and 1999. At that site just north of the Vermont-Quebec border the average HNO₃ mixing ratio was 0.5 ppb. In all of these studies, HNO₃ was found to peak in the middle of the day; the daytime maximum at Harvard Forest was 3–4 times higher than the nighttime minimum, while at Sutton the amplitude of the diurnal cycle was approximately a factor of two. A downwind comparison can be made to measurements conducted at Chebogue Point, Nova Scotia (43°45'N, 66°7'W), during the North Atlantic Regional Experiment (NARE) 93 [*Roberts et al.*, 1996]. That study used 2-hour exposures of filter packs to quantify total inorganic nitrate (HNO₃ + aerosol NO₃⁻ (TIN)), with HNO₃ estimated to contribute approximately 80% of the total. The maximum measured TIN reached 2.2 ppb, but most samples were well below 0.5 ppb. No mean was reported, but an estimate near 200 ppt can be made from plots given by *Roberts et al.* [1996]. It is not possible to discern any consistent diurnal variation in TIN at this site from the presented data.

[16] The continuous, high-resolution sampling during NEAQS 2002 revealed that HNO₃ varied widely over timescales of hours (Figure 3). Midday maxima above 4.0 ppb were observed both days when sampling was conducted in Boston Harbor (30 and 31 July) and on two of the days when the ship was circling near the Isles of Shoals offshore of Portsmouth, New Hampshire (4 and 5 August). (See Figure 2 for sample cruise tracks and the locations of named regions.) In all of these cases, HNO₃ mixing ratios increased from low (<0.5 ppb) levels just 6–

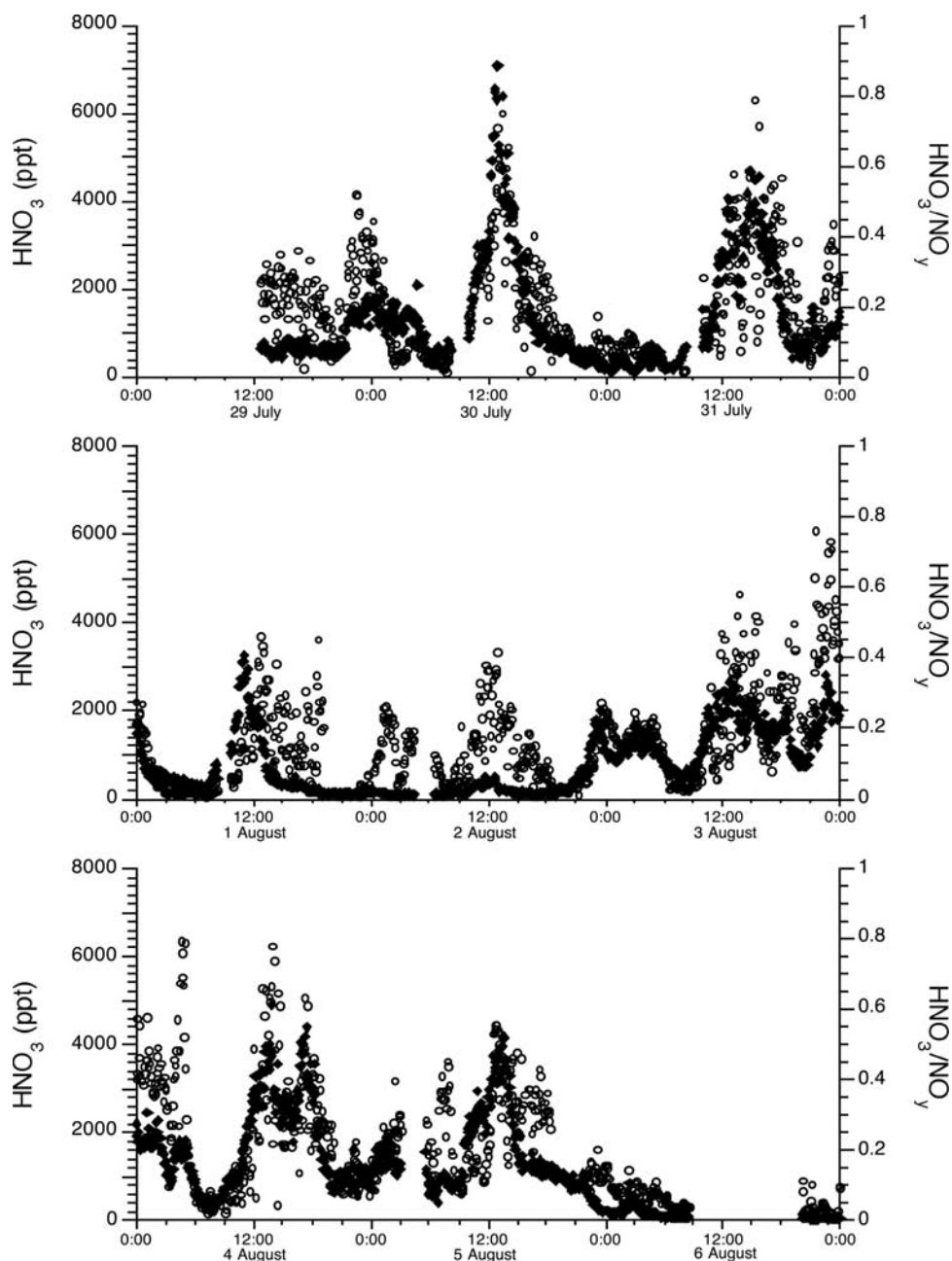


Figure 3. Time series of HNO₃ (solid diamonds) and HNO₃/NO_y (open circles) for the first 9 days of the second leg of the NEAQS 2002 cruise. All times in this paper are reported as eastern daylight time.

8 hours prior to the peak and decreased below 1 ppb shortly after sunset (Figure 3). In fact, all sampling days except 2 August were characterized by pronounced early afternoon peaks in HNO₃ exceeding 2 ppb. The much lower mixing ratios through the night of 1 August and much of 2 August reflect sustained winds from the southeast advecting cleaner air from the Atlantic Ocean to the sampling region. During the rest of the study period, the prevailing westerlies clearly carried polluted continental boundary layer air over the Gulf of Maine.

[17] The relatively clean interval on 2 August highlights the consistent diurnal pattern in HNO₃/NO_y that occurred on all days (Figure 3) but was sometimes noisier and obscured when mixing ratios were elevated. (There

was a 2.5-fold increase in HNO₃ mixing ratios between sunrise and midday on 2 August, though the scaling of Figure 3 makes this peak hard to appreciate.) Nitric acid constituted a small fraction (<5%) of NO_y shortly after sunrise each day, increasing to greater than 40% in some samples collected in the late morning and early afternoon each day (Figure 3). On average, HNO₃/NO_y exceeded 23% each day for the interval between 1100 and 1500 local time (LT) (Table 2). On all days except 3 August, HNO₃ and HNO₃/NO_y smoothly decreased to secondary minima with the setting sun and then increased again at night (Figure 3 and Table 2).

[18] The pronounced diurnal variations of HNO₃ can be attributed to significant photochemical production (NO₂ +

Table 2. Median Values of the Mixing Ratios of Nitric Acid and Ozone, and the Contribution Nitric Acid Makes to NO_y (HNO₃/NO_y), During Four Selected Times of Day^a

Date	Midnight ^b			Sunrise ^c			Midday ^d			Sunset ^e		
	HNO ₃	HNO ₃ /NO _y	O ₃	HNO ₃	HNO ₃ /NO _y	O ₃	HNO ₃	HNO ₃ /NO _y	O ₃	HNO ₃	HNO ₃ /NO _y	O ₃
All	0.93	0.16	50.2	0.44	0.04	24.6	2.27	0.28	59.4	0.64	0.11	48.8
29 July							0.58	0.26	54.8	0.58	0.13	45.7
30 July	1.41	0.30	56.6	0.56	0.04	24.4	3.86	0.43	88.2	0.66	0.10	51.8
31 July	0.30	0.07	39.1	0.26	0.03	24.7	2.84	0.32	70.6	0.65	0.12	45.9
1 Aug.	0.92	0.22	45.4	0.28	0.02	13.6	1.28	0.24	45.8	0.11	0.24	29.1
2 Aug.	0.12	0.09	28.5	0.10	0.06	27.5	0.26	0.23	34.2	0.25	0.03	40.3
3 Aug.	1.07	0.17	37.0	0.59	0.04	16.1	2.06	0.26	63.6	0.91	0.20	59.9
4 Aug.	1.90	0.45	68.0	0.46	0.05	21.4	2.78	0.31	72.6	1.03	0.21	81.6
5 Aug.	1.16	0.14	63.9	0.83	0.23	45.7	2.83	0.30	66.3	0.94	n.d. ^f	66.9
6 Aug.	0.23	0.12	54.2	0.07	0.04	26.0						

^aValues are given in ppb.^b2200–0200 LT, with date corresponding to the morning end time.^c0600–0800 LT.^d1100–1500 LT.^e1900–2100 LT.^fHere, n.d., no data.

hydroxyl radical (OH)) during the day and heterogeneous production (hydrolysis of dinitrogen pentoxide (N₂O₅) on particles) at nearly the same rate during the night, coupled with a continuous strong sink by dry deposition to the ocean surface. *Brown et al.* [2004] combined the results discussed herein with measurements of nitrate radical (NO₃) and N₂O₅ to show that the heterogeneous production of HNO₃ during the 9.5 hours of darkness accounted for at least one third of the NO_x lost by HNO₃ production over a full 24 hours. It should be noted that *Munger et al.* [1996, 1998] inferred the need for a similar contribution from nighttime heterogeneous production of HNO₃ to explain observations of NO_y deposition and the NO_x budget at Harvard Forest. In contrast to the secondary maximum of HNO₃ and HNO₃/NO_y at night during NEAQS 2002 (Table 2 and Figure 3), at Harvard Forest, HNO₃ was lowest and accounted for only 5–10% of NO₃ at night [*Lefer et al.*, 1999; *Horii et al.*, 2001]. Diurnal evolution of the boundary layer has been shown to control the nighttime build up and daytime decrease of NO_x and NO_y at Harvard Forest [*Munger et al.*, 1996, 1998], suggesting that rapid deposition of HNO₃ from the shallow nighttime boundary keeps mixing ratios low. Relatively stable boundary layer conditions throughout the day over the Gulf of Maine allowed the temporal variation in HNO₃ production to be more clearly manifested during NEAQS 2002 [*Brown et al.*, 2004].

[19] The early morning minima in HNO₃ generally coincided with distinct minima in O₃ as well (Table 2). On average over the 9-day period, O₃ was twofold higher around midnight than in the 2 hours just after sunrise and reached maximum levels just after noon. This pattern was apparent on most individual days as well (Table 2). In contrast, NO_x and NO_y tended to be higher in the early morning than around midday and were generally even lower around midnight (Table 3). The positive relationship between O₃ and HNO₃ is apparent in the full 29 July to 6 August data set as well (Figure 4). The slope (10 ppb O₃/ppb HNO₃) during the afternoon when both molecules are being photochemically produced has been suggested to indicate O₃ production efficiency (OPE) per emitted NO_x molecule in previous studies [e.g., *Hayden et al.*,

2003; *Roberts et al.*, 1996, and references therein]. In most cases the calculated parameter NO_y – NO_x (often denoted NO_z) has been used because of the lack of direct measurements of HNO₃ and PANs. (Even when HNO₃ and PANs have been measured, NO_z is often used because of the higher temporal resolution of the data.) *Griffin et al.* [2004] report an OPE of approximately 9 based on the O₃ – NO_z relationship at the Atmospheric Investigation, Regional Modeling, Analysis and Prediction (AIRMAP) Thompson Farm station 20 km inland from the coast during the NEAQS 2002 study. The relationship around midnight is not as strong, but shows that other processes beside production can cause linear trends in such plots, suggesting caution when using them to estimate OPE.

[20] The early morning minima in O₃ and HNO₃ (Table 2) raise an important issue. The decrease in HNO₃ is readily explained by dry deposition to the ocean surface, at a time when both the nighttime and daytime sources are very weak [*Brown et al.*, 2004]. For O₃,

Table 3. Median Mixing Ratios of NO_x and NO_y During the Same Intervals as in Table 2^a

Date	Midnight ^b			Sunrise ^c			Midday ^d			Sunset ^e		
	NO	NO ₂	NO _y	NO	NO ₂	NO _y	NO	NO ₂	NO _y	NO	NO ₂	NO _y
All	bd ^f	2.73	4.66	0.89	5.26	8.50	0.51	2.17	7.49	0.002	3.25	5.55
29 July							0.16	0.64	2.45	0.033	n.d. ^g	4.55
30 July	bd	3.39	5.59	1.69	8.25	14.44	0.51	2.95	8.94	bd	3.95	6.50
31 July	bd	2.59	4.06	2.41	5.69	7.63	0.88	3.81	8.91	0.026	3.73	4.90
1 Aug.	0.005	2.65	4.57	5.75	9.37	18.09	0.42	1.57	4.48	bd	0.15	0.48
2 Aug.	bd	0.42	1.69	0.18	0.65	1.58	0.09	0.29	1.02	0.004	7.61	9.53
3 Aug.	bd	5.16	7.27	3.23	7.72	15.75	0.65	2.13	6.89	0.001	2.75	4.25
4 Aug.	bd	1.89	4.27	0.97	5.30	10.93	0.96	3.26	9.42	0.003	2.65	4.86
5 Aug.	0.004	4.83	7.60	0.15	2.09	3.30	0.83	3.57	9.06	0.001	2.27	n.d.
6 Aug.	0.003	1.10	2.20	0.12	1.08	1.79						

^aValues are given in ppb.^b2200–0200 LT with date corresponding to the morning end time.^c0600–0800 LT.^d1100–1500 LT.^e1900–2100 LT.^fHere, bd, below detection limit.^gHere, n.d., no data.

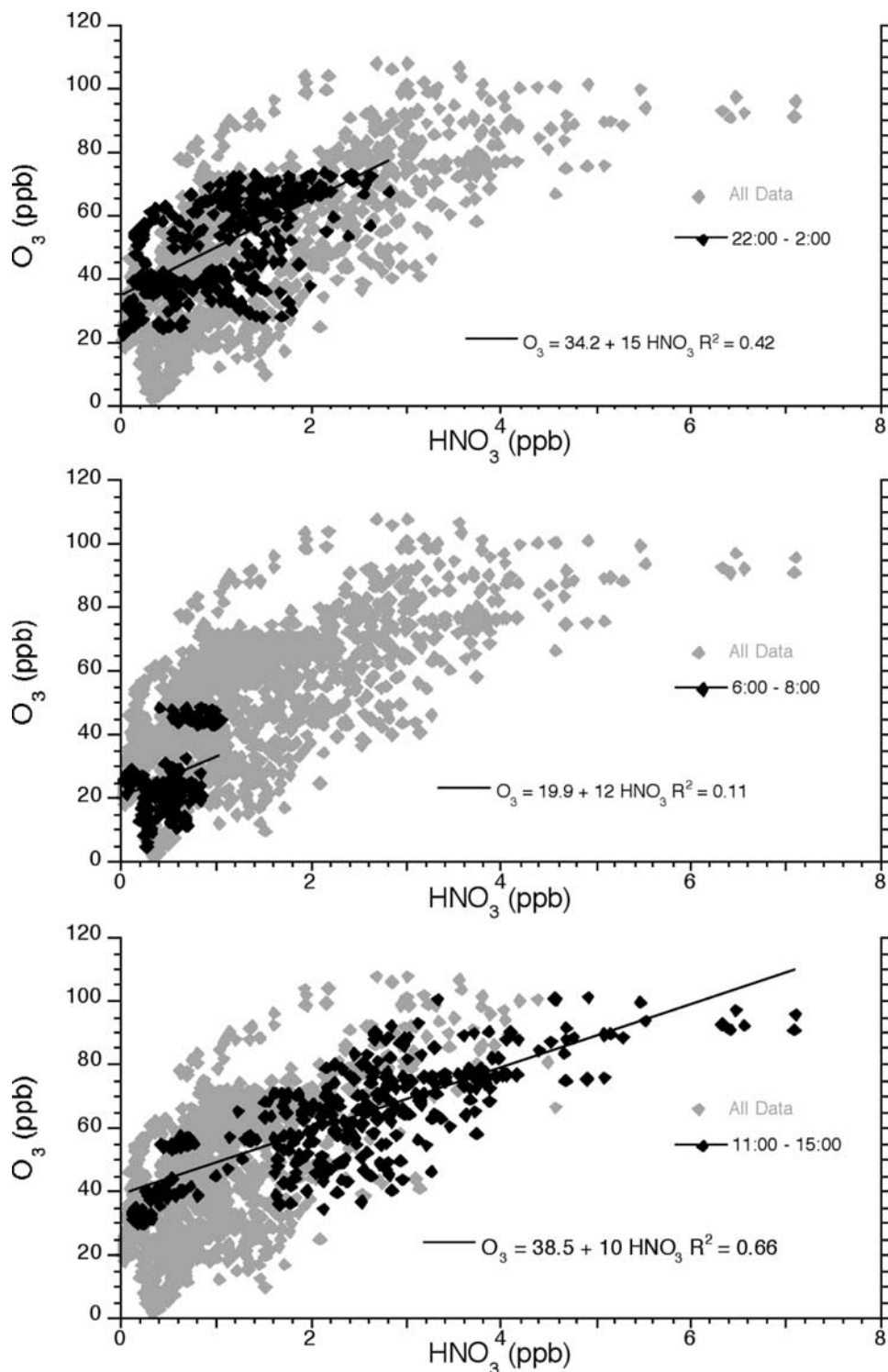


Figure 4. Scatterplot of O₃ versus HNO₃. The top panel highlights samples collected around midnight with the black diamonds, samples collected just after sunrise are highlighted in the middle panel, and those collected around noon are highlighted in the bottom panel. Lines in each panel are least squares fits through the black diamonds.

deposition to the ocean is not an effective sink [Roberts *et al.*, 1996; Kleinman *et al.*, 1996]; hence some other processes must be involved in causing the minima. Close examination of the middle panel of Figure 4 shows that, while all of the

early morning samples are characterized by low HNO₃ and O₃, there are two clusters of data. One has O₃ mixing ratios between 45 and 50 ppb. The second cluster has very low O₃, <30 ppb and reaching a minimum below 5 ppb. The cause of

the very low O₃ in this group of samples will be examined in the following discussion.

4. Discussion

[21] The high-resolution HNO₃ data collected during NEAQS 2002 confirm that production and loss of HNO₃ within the marine boundary layer is a strong NO_x sink, as is the case in the continental boundary over the northeastern United States [Munger *et al.*, 1996, 1998; Li *et al.*, 2004]. On average, the observed decreases of nearly 2.0 ppb of HNO₃ during the afternoon and early evening, and more than 0.5 ppb in the early morning, each day, define a lower limit to the magnitude of the NO_x sink. It is likely that HNO₃ is being deposited at comparable rates throughout the day, with the sources overwhelming the sink much of the time. If it is assumed that the measurements on the *Ronald H. Brown* are representative of a 100 m deep mixed layer [Brown *et al.*, 2004], daily loss of 2.5 ppb of HNO₃ implies a flux of 11.2 μmol N m⁻² d⁻¹, with a more realistic estimate possibly being twice as high. In comparison, Jordan and Talbot [2000] estimated that if all of the HNO₃ present in air masses leaving the New Hampshire coast subsequently was deposited to the Gulf of Maine the median flux would have been 16 μmol N m⁻² d⁻¹ (ranging from 1 to 144 μmol N m⁻² d⁻¹).

4.1. O₃ Depletion

[22] As noted earlier, parallel increases in O₃ and HNO₃ during the day were expected, as they are both photochemically produced in polluted air masses. However, these compounds do not share sinks, hence coincident decreases in the early morning are less readily explained. Titration by NO will generally not be a factor in O₃ depletion in the dark over the ocean relatively far from strong sources, and loss by dry deposition also appears to be a minor sink at best [Roberts *et al.*, 1996; Kleinman *et al.*, 1996]. Production of NO₃ radical by the reaction of NO₂ + O₃ does constitute a sink of O₃ (along with initiating the nighttime production of HNO₃). Brown *et al.* [2004] estimate that production of NO₃, and subsequently N₂O₅ (from the reaction of NO₃ with NO₂), could consume 2.4 to 3.6 ppb of NO₂ during a night under the conditions prevailing in NEAQS 2002. The impact on O₃ would be smaller than on NO₂, so this would make only a modest contribution to the average 25 ppb decrease in O₃ seen between the middle of the night and sunrise (Table 2). Ozone will also react with a wide range of hydrocarbons, particularly those with unsaturated carbon-carbon bonds, which might, in aggregate, explain the magnitude of the decrease of O₃ observed, though it would be an unusual situation.

[23] Seeking to explain the loss of 25 ppb O₃ over 4–5 hours (Table 2) without invoking titration by NO is challenging. Examining the 5-min O₃ record for the study period initially appears to make the challenge even harder (Figure 5). Frequently, a large fraction of the O₃ decrease between midnight and 0600 LT was seen to occur over a very short period, usually less than 1 hour. Titration by NO, or possibly halogen radical chemistry, would seem to be the only viable chemical mechanisms to cause such rapid O₃ destruction.

[24] Further examination reveals that all of the downward steps (decreases > 5 ppb in less than 1 hour) in O₃ mixing

ratio (Figure 5) were accompanied by similarly rapid increases in NO₂ and a host of anthropogenic hydrocarbons. Two cases are presented in Figures 6 and 7, using toluene as an example hydrocarbon, but many other alkenes and alkanes display nearly identical behavior (e.g., ethyne, ethene, *iso*- and *n*-ibutane, *iso*- and *n*-pentane all increase simultaneously in all of the O₃ depletion events, with the enhancements exceeding 1 ppb in most cases). It should be noted that NO does not increase above background levels when O₃ drops and NO₂ and the hydrocarbons increase. Rather, NO reappears shortly after sunrise (0531 LT on 30 July and 0536 LT on 4 August) and increases rapidly because of photolysis of NO₂. Any impact on HNO₃ from these events is hard to discern in the two cases illustrated (Figures 6 and 7).

[25] These events are not the result of unusual nighttime NO₂ and hydrocarbon explosions, rather, they reflect dramatic changes in air mass over short distances/times. It appears that the ship moved from regionally polluted marine boundary layer air directly into a concentrated plume, likely originating from the Boston metropolitan region. On 30 July the highly polluted air was first encountered just south of Cape Ann. (The solid square in the 30 July panel of Figure 2 indicates the ship's position at 0200 LT.) Later in the morning, as the ship cruised toward Cape Cod, the drop in toluene indicates that the ship passed out of the plume by 1000 LT (Figure 6). The situation on 4 August was similar, with that day's cruise track beginning further offshore than any other day on leg two. While steaming toward "station" near the Isles of Shoals, a plume was entered just north of Cape Ann. (The solid square in the 4 August panel of Figure 2 indicates the ship's position at 0500 LT.) In this case, the *Ronald H. Brown* remained in the same region for the rest of the day, but the plume shifted position in the afternoon (toluene decreased to 92 ppt by 1400 (not shown)). Onshore breezes in the afternoon apparently pushed the plume west of the ship track and over coastal New England.

[26] Recognition of heavily polluted plumes in the NEAQS 2002 study region allows the dramatic nighttime decreases in O₃ to be attributed to upwind titration by NO. By the time these urban air masses reached the ship all of the NO had reacted away, but the impacts on O₃ and NO₂ were still very much apparent. However, the frequent encounters with these plumes does raise concern over the validity of analyzing an average day constructed from the entire leg as representative of conditions in the region during the campaign.

4.2. Impact of Plumes on Diel Averages

[27] The fact that the plumes are characterized by large simultaneous increases in NO₂ as well as a suite of hydrocarbons makes them easy to identify. We chose a threshold of 200 ppt toluene to define plume encounters, but all other hydrocarbon tracers examined gave very similar results. Using any hydrocarbon tracer limits precise definition of plume start and end times to the 30-min resolution of that data set, but the signals of plume ending are much less ambiguous than is the case for either O₃ or NO₂ (Figures 6 and 7). To avoid including spikes from very local pollution (e.g., ship plumes), we also required that toluene remain above 200 ppt for at least 2 consecutive samples to qualify as a plume encounter. This definition identified 13 plume

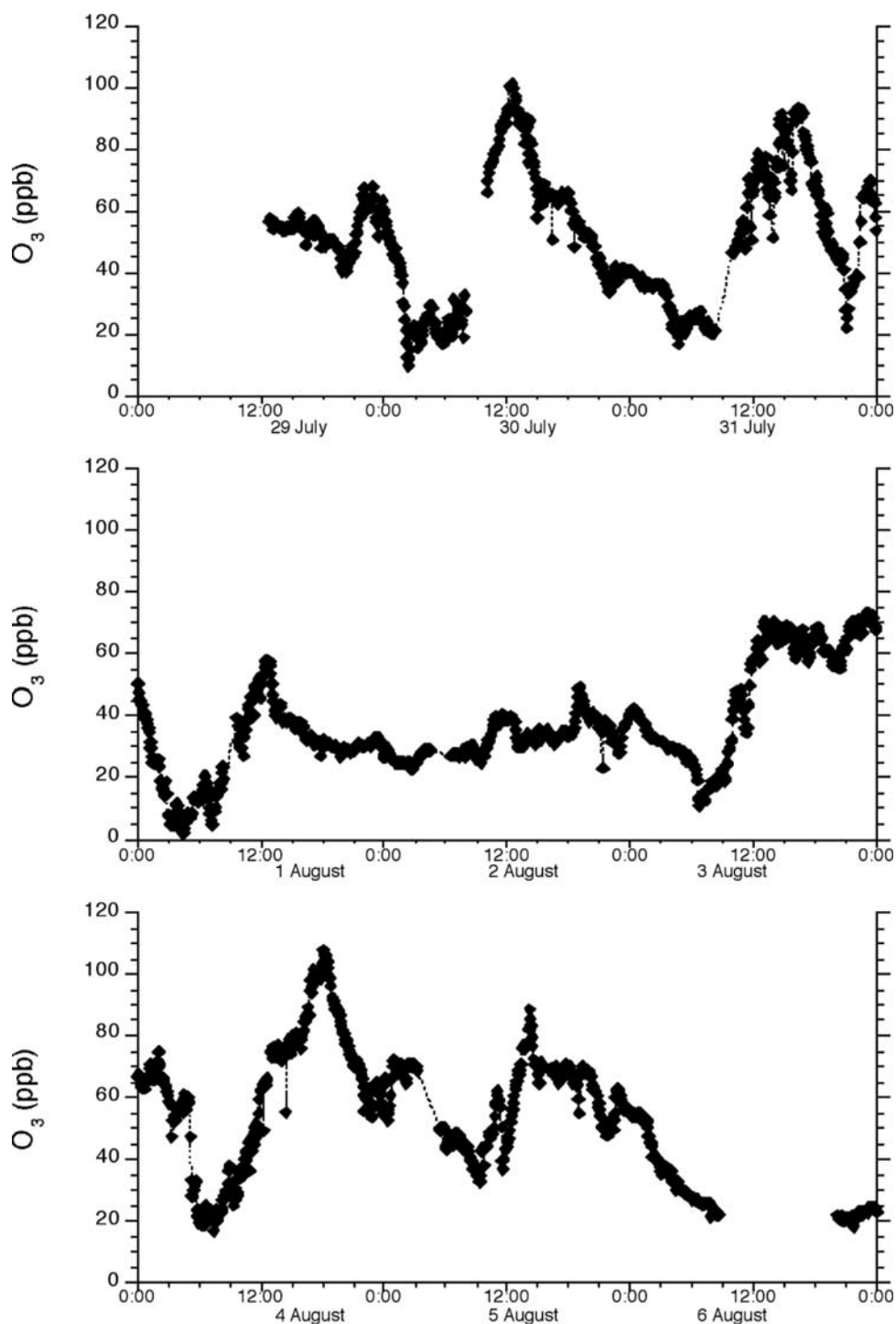


Figure 5. Time series of O₃ for the first 9 days of the second leg of the NEAQS 2002 cruise.

encounters, accounting for 47.5 hours of sampling time (24% of total sampling time during the first 9 days of leg two). No plume encounters were noted between 1500 and 2000 LT, and 82% of sampling in plume-impacted air occurred between midnight and noon. Put another way, 39 out of the 96 morning (0000–1200) hours, and 18 out of the 76 dark hours, in this study were impacted by plumes defined in this manner.

[28] The impact of plumes on atmospheric composition in the NEAQS 2002 study region was quantified by comparing

the diurnal averages for the first 9 days of leg two calculated in 1/2 hour bins for all data and for a filtered subset with all plumes removed (Figure 8). Not surprisingly, NO_x and O₃ differ substantially throughout the interval 0000–1200 LT. For the period between 0200 and 1000 LT, O₃ averaged 6.5 ppb higher in the filtered data set, while NO_x was 4.3 ppb higher in the full data set. Between 0200 and 0600 LT, when essentially all of the NO_x was NO₂, the plumes depressed average O₃ by 7.3 ppb and enhanced average NO₂ by 4.0 ppb.

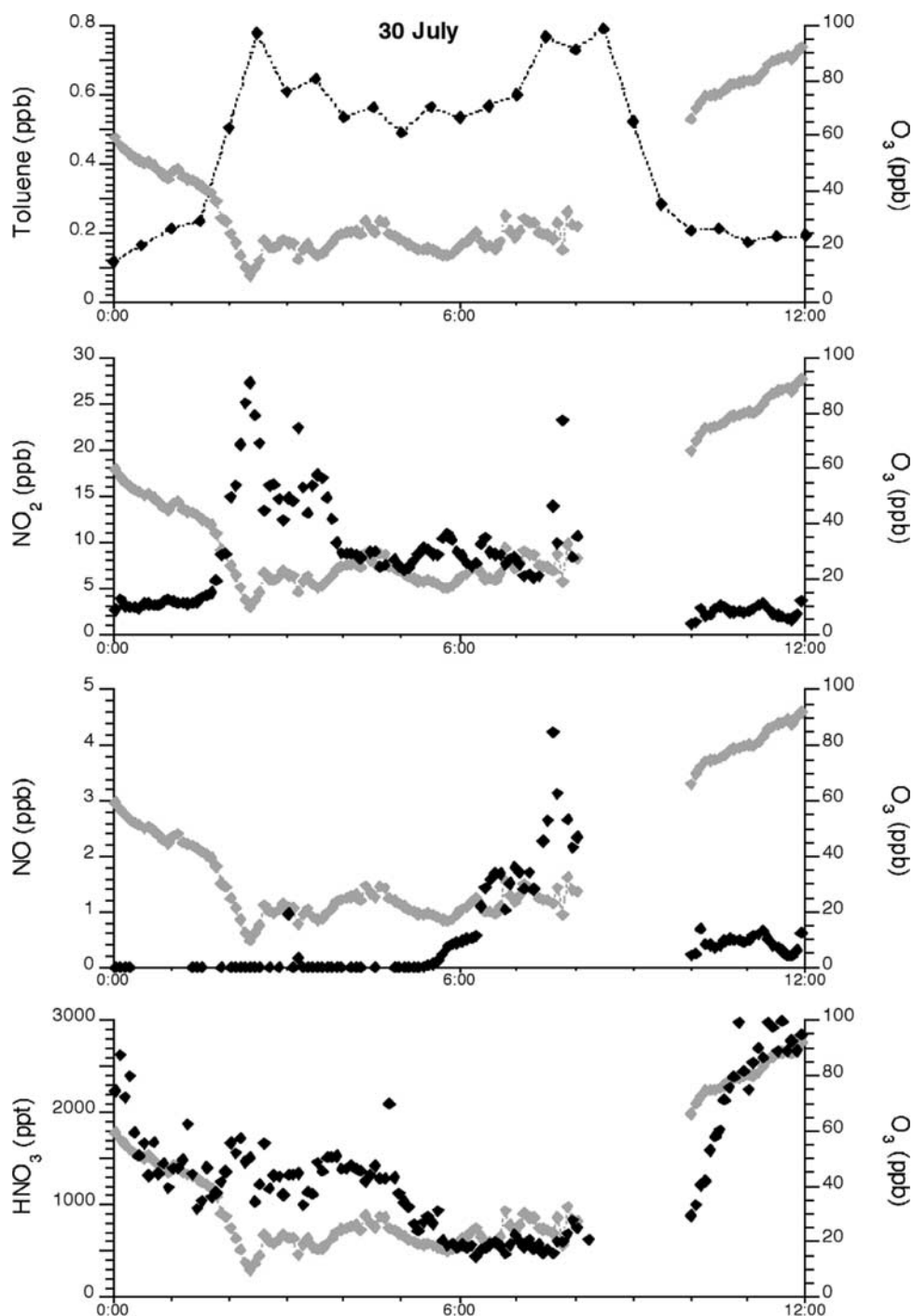


Figure 6. Case study of an encounter with an urban plume over the Gulf of Maine on 30 July. Ozone is shown with gray diamonds and is repeated in all four panels.

[29] If titration of O₃ by NO was the only plume impact, the decrease in O₃ should match the enhancement in NO₂. As noted earlier, the plumes also had very large enhancements in reactive hydrocarbons, perhaps contributing to the excess O₃ depletion observed. Perhaps the most striking feature in Figure 8 is the lack of impact on HNO₃ mixing ratios. The average difference (filtered – full data set) was 37 ppt between 0200 and 1000 LT and just –3 ppt between 0200 and 0600 LT (both of which are well within the uncertainty of any individual mea-

surement). Taken separately, the large decrease in O₃ would be expected to reduce production of NO₃ (from the reaction of O₃ with NO₂), hence N₂O₅ (from NO₂ + NO₃) and ultimately HNO₃, while increasing NO₂ should enhance production of NO₃, N₂O₅ and HNO₃. Apparently, on average, O₃ in plume-impacted air decreased just enough to balance the NO₂ increase, yielding no difference in the nighttime formation of N₂O₅ and the subsequent heterogeneous production of HNO₃. The average mixing ratios of NO₃ and N₂O₅ in the morning decreased

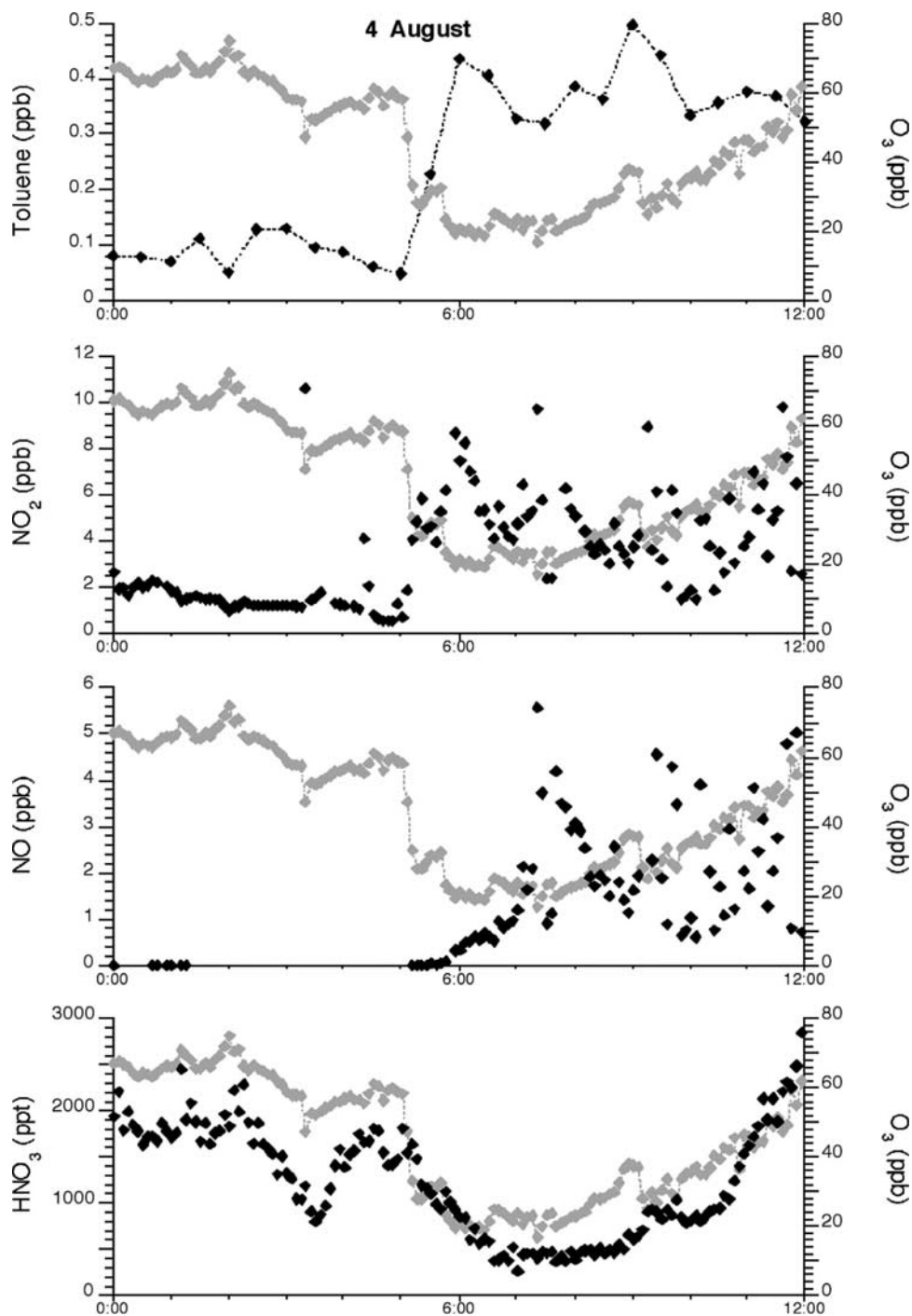


Figure 7. As in Figure 6, but for 4 August.

just 0.9 and 11.6 ppt when the plume-impacted samples were excluded.

5. Conclusions

[30] High-resolution measurements of gas phase HNO₃ in the polluted marine boundary of the southern Gulf of Maine revealed pronounced diel variations in the late July and early August period of the NEAQS 2002. On average, the increase in HNO₃ mixing ratios during the daytime exceeded 1.5 ppb; on four days mixing ratios increased more than 3.0 ppb from the minima just after sunrise in

about 6 hours. Ozone mixing ratios followed a similar diel pattern, with the strongest correlation of O₃ versus HNO₃ observed between 1100 and 1500 LT (slope = 10 ppb O₃/ppb HNO₃, $R^2 = 0.66$). Dry deposition of HNO₃ to the ocean surface was an effective sink, reducing HNO₃ mixing ratios to secondary minima near 0.5 ppb around sunset each day. Heterogeneous production at night supported a broad secondary maximum approaching 1.0 ppb on average.

[31] The observed decreases leading to the dawn and dusk minima in HNO₃ mixing ratios provide a lower bound estimate of the flux of N, exported as NO_x, to the surface waters of the Gulf of Maine on the order of

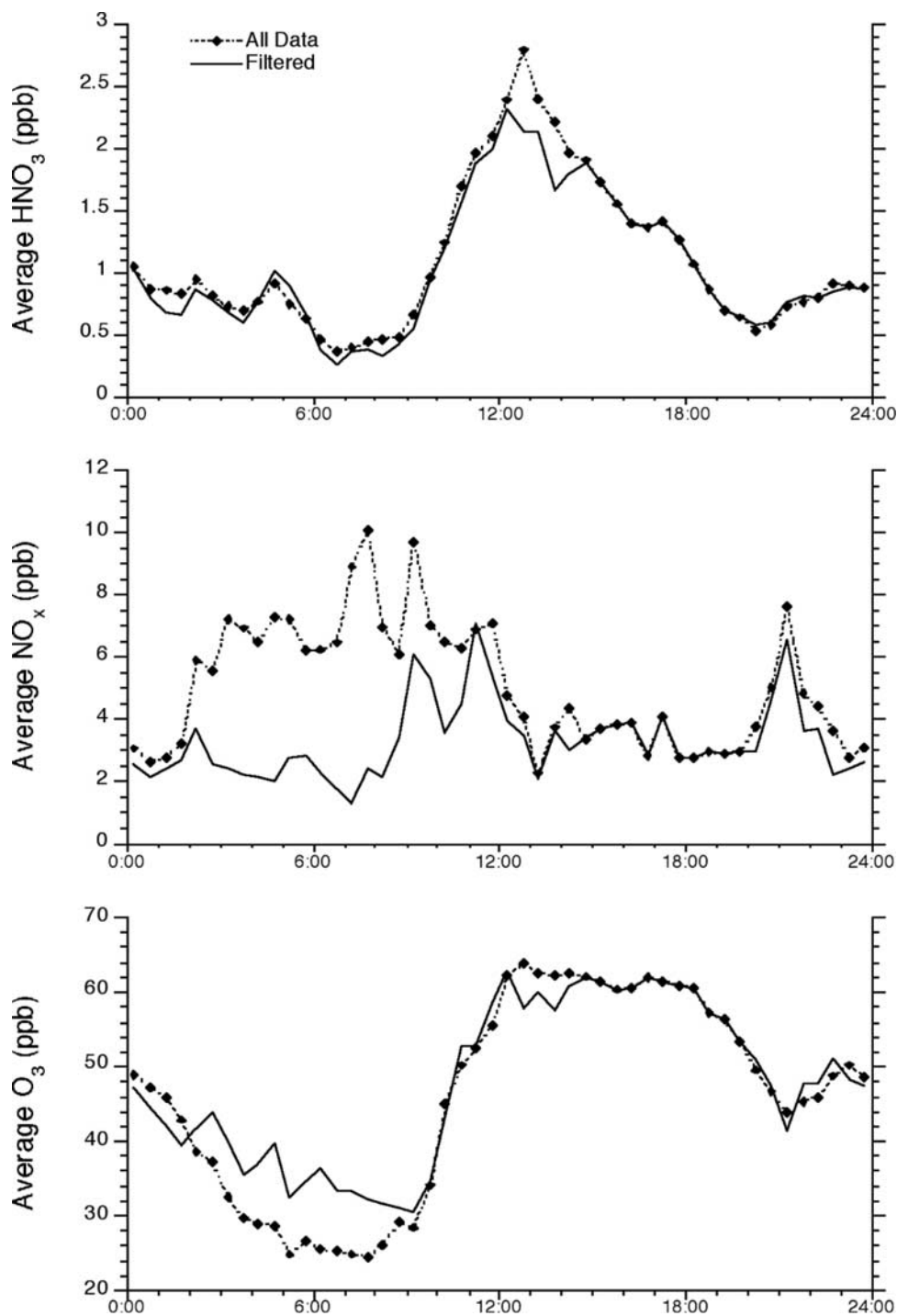


Figure 8. Comparison of the diel patterns of HNO₃, NO_x, and O₃ based on 1/2 hour intervals for the full data set (solid diamonds) and for a filtered data set (open circles) from which all plume-impacted samples have been removed.

11 $\mu\text{mol N m}^{-2} \text{d}^{-1}$. This estimate of the deposition of HNO₃ produced above the Gulf of Maine represents 70% of an earlier flux estimate based on the quantity of HNO₃ exported from the New Hampshire coast to the same receiving waters. Assuming that dry deposition of HNO₃ is similarly efficient throughout the extended periods each day when atmospheric mixing ratios were increasing or constant suggests that deposition of HNO₃ that formed in

the marine boundary layer represents the dominant fraction of atmospheric HNO₃ directly delivered to the ecosystem.

[32] Our analysis has shown that under the westerly and southwesterly winds that prevailed 29 July to 6 August, the coastal boundary layer of the Gulf of Maine is pervasively influenced by anthropogenic emissions from eastern North America. Within this generally polluted region, distinctive

plumes were frequently encountered in close proximity to the coast of Massachusetts and New Hampshire. Within these plumes, large enhancements of NO_x and reactive hydrocarbons resulted in significant depletion of O₃. Surprisingly, and likely fortuitously, the opposing changes in NO_x and O₃ balanced, such that the mixing ratios of HNO₃ were not significantly impacted within the plumes.

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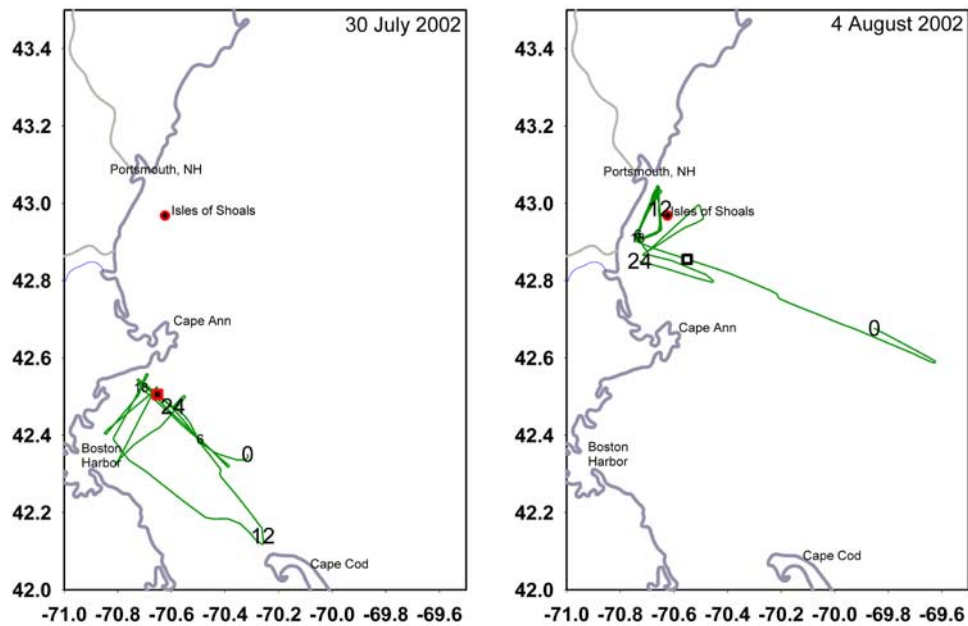


Figure 2. Cruise tracks of the *Ronald H. Brown* on 30 July and 4 August. These 2 days are selected to illustrate the two primary sampling areas (Boston Harbor and the Isles of Shoals) during leg 2. The ship did not traverse significantly outside the regions sampled on these two days until heading south past Cape Cod on the afternoon of 6 August. Figure 2 of *Brown et al.* [2004] presents the cruise track for all of legs 1 and 2.