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MEASUREMENTS OF TROPOSPHERIC NITRIC ACID OVER THE WESTERN UNITED STATES AND NORTHEASTERN PACIFIC OCEAN

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Abstract. During the August-September 1986 GTE/CITE 2 aircraft mission, more than 240 measurements of nitric acid (HNO_3) were made in the free troposphere as well as in the boundary layer over the northeastern Pacific Ocean and western continental United States. Marine HNO_3 measurement results were strikingly similar to results from GAMETAG and other past atmospheric field experiments. The marine boundary layer HNO_3 average, 62 parts per trillion by volume (pptv), was one third lower than the marine free tropospheric average, 108 pptv, suggesting that the boundary layer is a sink for tropospheric nitric acid, probably by dry deposition. Nitric acid measurements on a nighttime continental flight gave a free tropospheric average of 218 pptv, substantially greater than the daytime continental free tropospheric five-flight average of 61 pptv. However, the nighttime results may have been influenced by highly convective conditions that existed from thunderstorms in the vicinity during that night flight. Our continental boundary layer HNO_3 average of 767 pptv is an order of magnitude greater than the free tropospheric average, indicating that the boundary layer is a source of free tropospheric HNO_3. The distribution of continental boundary layer HNO_3 data, from averages of 123 pptv over rural Nevada and Utah to 1057 pptv in the polluted San Joaquin Valley of California suggests a close tie between boundary layer HNO_3 and anthropogenic activity.

Introduction

Nitric acid (HNO_3) is one of the most abundant trace nitrogen species in the troposphere. A reactive nitrogen species, HNO_3 plays a key role in the photochemistry and chemistry of the troposphere as well as in the biogeochemical cycling of nitrogen between the atmosphere and the biosphere [Levine, 1984; Logan et al., 1981; Stedman and Shetter, 1983]. In addition, HNO_3 is a rapidly growing component of acid precipitation [Galloway and Likens, 1981]. The atmospheric removal of HNO_3 by rainout or dry deposition is the major sink for NO_x in the troposphere [Logan, 1983]. Unfortunately, knowledge of the chemistry and photochemistry of HNO_3 and other reactive nitrogen species is limited by the availability of techniques capable of rapid, reliable measurements at low species concentrations. To assess the capabilities of existing and emerging measurement technology, an aircraft intercomparison of HNO_3 sensing techniques was undertaken as part of the Chemical Instrumentation Test and Evaluation (CITE 2) mission under the auspices of the NASA Global Tropospheric Experiment (GTE) project.

The CITE 2 flight mission took place over the western United States and northeastern Pacific Ocean during August/September 1986. CITE 2 involved measurement of a number of atmospheric chemical species and meteorological parameters with several scientific and instrument related goals [Hoell et al., this issue]. This paper describes the results of the measurement of HNO_3 during CITE 2. A companion paper [Huebert et al., this issue] relates HNO_3 concentrations to NO_x concentrations measured in several different regimes. A related paper [Gregory et al., this issue] describes the intercomparison of three HNO_3 measurement techniques during CITE 2.

Experimental

On August 11, 1986, the NASA Electra aircraft departed Wallops Flight Facility (WFF), Wallops Island, Virginia, on a transcontinental flight to Ames Research Center, Moffett Field, California. The two legs of this flight, with a refueling stop at Wichita, Kansas, represented the first two CITE 2 data-taking missions. Moffett Field, located approximately 50 km southeast of San Francisco, was the base for nine additional missions between August 15 and September 2. These flights, typically 5 hours in duration and covering a radius up to 800 km from Moffett Field, included both continental and marine, free troposphere and boundary layer regimes. While most flights took place during midmorning to midafternoon, one nighttime mission was also undertaken. On September 5, 1986, the aircraft departed Moffett Field on a return transcontinental flight to WFF, with a refueling stop at Oklahoma City, Oklahoma. Further details of each flight mission including specific flight paths can be found in the paper by Hoell et al. [this issue]. Meteorological conditions during CITE 2 are described by Shipham et al. [this issue].

The CITE 2 nitric acid measurement techniques included a tungsten oxide denuder sampler (DENUDER) (NASA Langley Research Center, P. J. LeBel, principal investigator), a Teflon/nylon filter pack sampler (FILTER) (Stanford Research Institute, B. J. Huebert, principal investigator), and a tunable diode laser spectrometer (TDL) (York University, H. Schiff, principal investigator). The denuder sampler [Braman et al., 1982; LeBel et

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TABLE 1. Characteristics of HNO_3 Instruments

Technique	Integration Time	Detection Limit	Accuracy,%	Precision,%
Tungsten oxide denuder/chemiluminescence	5-10 min	20 pptv (10 min)	15-20	8
Nylon filter/ion chromatography	0.5-2 hours	8 pptv (1.5 hours)	20	10
Tunable diode laser	2-3 min	75 pptv (3 min)	15	10

al., 1985] consisted of a 6-mm OD quartz tube with an interior coating of tungsten oxide to chemisorb HNO_3 in an atmospheric sample. Typical sampling times were 5-10 min. Collected samples were analyzed on board the aircraft immediately after collection. Sample analysis involved thermal desorption of collected HNO_3 as nitric oxide (NO) and detection by chemiluminescent reaction of NO with ozone [Bollinger, 1982]. The filter pack sampler [Goldan et al., 1983] consisted of two 90-mm-diameter filters, a Teflon prefilter to retain aerosols followed by a nylon filter to collect HNO_3. Typical filter pack sampling times were 1/2 to 2 hours. Filters were analyzed after completion of each flight, generally within 48 hours of collection, by ion chromatography nitrate analysis. The tunable diode laser system [Schiff et al., 1983, 1987, this issue] measured HNO_3 directly, in real time, through its absorption of infrared radiation from a lead-salt solid state laser.

Characteristics of the three HNO_3 instruments are shown in Table 1. Note that HNO_3 detection limits ranged from 8 parts per trillion by volume (pptv) for a 120 min filter sample to 75 pptv for a 3-min TDL sample. The three techniques estimate similar accuracy and precision. Additional details of the measurement techniques can be found in the references cited above as well as in the CITE 2 HNO_3 instrument intercomparison paper [Gregory et al., this issue].

Because of the aircraft configuration and space limitations, each HNO_3 instrument was located in a different area of the Electra aircraft, and each used its own probe and manifold system to sample outside air. To insure that all instruments were sampling free stream air, the probes were designed to extend beyond the aircraft boundary layer.

More than 240 HNO_3 measurements were made on 13 flight missions during the 3 1/2 week CITE 2 experiment. The majority of the HNO_3 measurements were made by the denuder and filter instruments; during most of the flight missions the TDL system was dedicated to measurement of nitrogen dioxide. In fact, nearly the entire TDL HNO_3 data set comes from measurements during a portion of one flight within the boundary layer of California's San Joaquin Valley. Only the denuder system made measurements during aircraft descents and ascents; these measurements are described later as "spiral."

Observations

Marine Free Tropospheric Measurements

Nitric acid measurements were made in the marine free troposphere during CITE 2 missions 6,7,8,10, and 12 over a 2-week period from August 15 to August 30, 1986. Flight routes [Hoell et al., this issue] ranged over the Pacific Ocean from northwest through southwest of Moffett Field. The results of denuder and filter HNO_3 measurements made on August 15 during mission 6 are shown in Figure 1. (The horizontal lines on the filter data points indicate the extent of the filter sampling time; the denuder sampling time is less than the width of the data point symbols. Note the excellent agreement between the two techniques on this mission, despite a quite large difference in integration times.) On this flight, two different air masses were encountered, both with significant levels of species suggesting continental origin [Shipham et al., this issue]. During the initial portion of mission 6 the HNO_3 levels are high. Further along the flight route we encounter a second air mass with lower, but still significant, HNO_3 concentrations. The return flight route, beginning at approximately 2100 GMT, retraced the outgoing route and the HNO_3 concentrations measured tend to mirror the initial measurements.

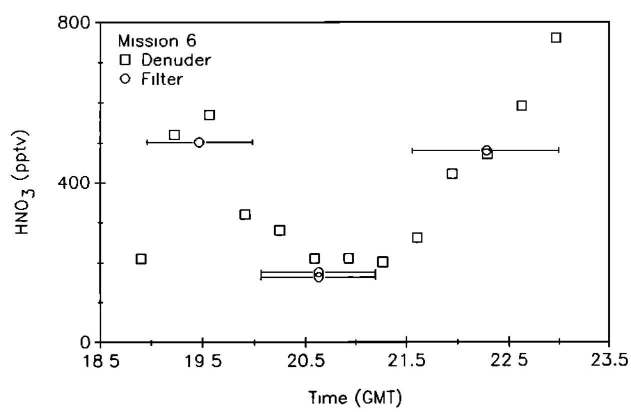

Fig. 1. Marine tropospheric HNO_3 concentrations measured by denuder and filter instruments during mission 6.

TABLE 2. Summary of HNO_3 Marine Measurements

Mission	Date	n	Nitric Acid Concentrations, pptv Minimum	Maximum	Median	Mean	s.d.
			Marine Free Troposphere				
6	Aug. 15	17	162	760	320	372	173
7	Aug. 19	12	45	200	95	104	42
8	Aug. 21	14	<20	140	60	69	42
10	Aug. 26	10	50	136	82	87	23
12	Aug. 30	17	30	159	90	92	32
All data		70	<20	760	100	157	152
All except part of mission 6 (see text)		62	<20	320	90	108	62
			Marine Boundary Layer				
7	Aug. 19	5	38	100	70	69	20
10	Aug. 26	4	30	104	40	53	29
All data		9	30	104	60	62	26

Here, n is number of measurements; s.d. is standard deviation.

The HNO_3 marine measurements are summarized in Table 2. If we exclude that portion of the mission 6 data that would appear to have recent continental origin, the 62 remaining HNO_3 marine free tropospheric measurements give a mean concentration (108 ± 62 pptv) remarkably similar to the GAMETAG HNO_3 results of 110 ± 70 pptv [Huebert and Lazrus, 1980]. The results are also in quite good agreement with the 97 ± 59 pptv summertime (August) marine tropospheric HNO_3 concentration reported from measurements at Mauna Loa Observatory in Hawaii [Galasyn et al., 1987].

Marine Boundary Layer Measurements

Nine HNO_3 measurements were made in the marine boundary layer during missions 7 and 10 (August 19 and 26). The mean measured HNO_3 concentration (62 pptv) is in close agreement with GAMETAG results (70 pptv) [Huebert and Lazrus, 1980], but our measurements show less variability (±26 pptv) than reported for GAMETAG (±60 pptv). Note that for the two missions (7 and 10) with measurements in both free troposphere and boundary layer the marine boundary layer HNO_3 concentrations tend to be about one third lower than marine free tropospheric concentrations.

Marine Profiles

Figure 2 shows HNO_3 mixing ratios measured by the denuder instrument during portions of the four marine flights (missions 7, 8, 10, and 12), which included a "spiral" altitude change between free troposphere and boundary layer. These flights took place between August 19 and August 30, 1986. Keeping in mind that Figure 2 is not a precise altitude profile because of the instrument's integration time and that the four missions were flown over a 12-day period in somewhat different

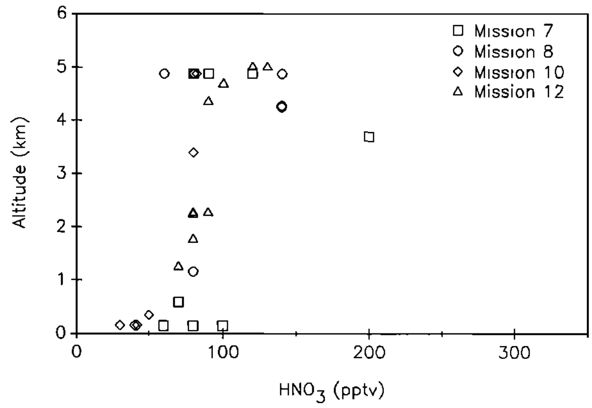

Fig. 2. Marine nitric acid concentrations measured by the denuder instrument during aircraft "spirals" between free troposphere and boundary layer on four CITE 2 missions.

areas, the data show a decrease in HNO_3 concentration with decreasing altitude, suggesting a sink for tropospheric HNO_3 within the marine boundary layer, probably from dry deposition. While the (mission 7) data point at 200 pptv/3.7 km would seem to be an anomaly, it correlates well with the detailed NO_y profile measured on mission 7 (G. Huebler, private communication, 1989) which shows a layer of elevated nitrogen species concentrations at that altitude.

Continental Free Tropospheric Measurements

Nitric acid continental measurements are summarized in Table 3. Daytime measurements were made during three missions (11, 13, and 14) from Moffett Field, as well as on the transcontinental

TABLE 3. Summary of HNO_3 Continental Measurements

			Nitric Acid Concentrations, pptv				
Mission	Date	n	Minimum	Maximum	Median	Mean	s.d.
			Continental Free Troposphere				
4,5	Aug. 11	15	<20	560	128	154	149
11	Aug. 28	25	20	174	61	73	41
13	Aug. 30	15	<20	216	80	78	63
14	Sept. 2	9	<20	70	40	40	22
15,16	Sept. 5	30	<20	153	40	46	35
9 (night)	Aug. 23-24	19	140	374	219	218	66
All Data		113	<20	560	70	99	94
Daytime		94	<20	560	58	75	80
Western U.S./ Day		67	<20	216	53	61	47
Nighttime		19	140	374	219	218	66
			Continental Boundary Layer				
4,5	Aug. 11	10	280	590	470	457	140
11	Aug. 28	24	300	1721	988	1057	437
14	Sept. 2	6	30	238	120	123	60
All Data		40	30	1721	645	767	507

Here, n is number of measurements; s.d. is standard deviation.

flights (missions 4,5 and 15,16). Nighttime measurements were made during mission 9. The result of all (113) continental free tropospheric measurements over a 3 1/2 week period is a mean HNO_3 concentration of 99 ± 94 pptv. Considering daytime measurements only, 94 measurements give a mean HNO_3 concentration of 75 ± 80 pptv. If we eliminate the measurements made over the eastern United States (where significant free tropospheric pollution was encountered on one of the transcontinental flights (see discussion below)), the result is a "western U.S." continental daytime tropospheric HNO_3 concentration of 61 ± 47 pptv based on 67 measurements. By comparison, during the GAMETAG experiment [Huebert and Lazrus, 1980], 23 continental free tropospheric measurements gave an HNO_3 concentration of 160 ± 110 pptv, nearly 3 times our western U.S. value. Nineteen measurements on August 23-24 during mission 9 established a nighttime HNO_3 average of 218 ± 66 pptv, nearly 4 times the 61 pptv daytime concentration.

Continental Boundary Layer Measurements

Continental boundary layer HNO_3 measurements were made during three missions. During mission 5, the western portion of the August 11 transcontinental flight (discussed below), 10 measurements gave a mean HNO_3 concentration of 457 ± 140 pptv in an elevated boundary layer over the Rocky Mountains. During mission 11 in the polluted San Joaquin Valley boundary layer, 24 measurements resulted in a concentration of 1057 ± 437 pptv. During mission 14, six measurements gave a boundary layer HNO_3 concentration of 123 ± 60 pptv. The mission 14 flight path was east across California and Nevada, including over an hour in the planetary boundary layer, a spiral up to the free troposphere over western Utah, and a return flight leg that retraced the outgoing leg but at an altitude of 6.1 km. The HNO_3 concentration measured on this free tropospheric leg was 40 ± 22 pptv, one third of the boundary layer concentration. The entire continental boundary layer data set consists of 40 measurements giving a mean HNO_3 concentration of 767 ± 507 pptv, quite variable, strongly influenced by the San Joaquin Valley measurements and, as expected, significantly higher than the free tropospheric values measured during CITE 2. Nitric acid measurements during GAMETAG showed northern mid-latitude boundary layer concentrations always greater than 250 pptv [Huebert and Lazrus, 1980]. Our measurements during mission 14 over remote areas of Nevada and Utah showed concentrations always less than 238 pptv. This would suggest that both the CITE 2 HNO_3 continental boundary layer results and the GAMETAG results are influenced by choice of sampling location, and that neither is totally representative of the entire northern mid-latitude boundary layer. It does seem clear, from the distribution of HNO_3 concentrations on our three boundary layer missions, that HNO_3 in the continental boundary layer is closely tied to anthropogenic activities.

Longitudinal Variation

Figure 3 shows HNO_3 mixing ratio versus longitude from denuder and filter measurements during the August 11 (missions 4 and 5)

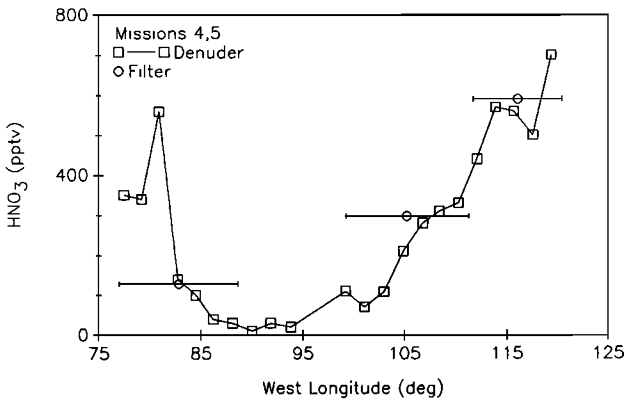

Fig. 3. Longitudinal variability of HNO_3 between Wallops Island, Virginia and Moffett Field, California, measured by denuder and filter instruments during the August 11 transcontinental mission.

transcontinental flight from WFF (75.5°W longitude) to Moffett Field (122°W longitude). As in Figure 1 the horizontal lines show the extent of the filter sampling time, with the denuder sampling period hidden by the data point symbols. All measurements were made at an altitude of 4.9 km. During the transcontinental flight we encountered a wide range of HNO_3 concentrations, from less than 20 pptv to over 700 pptv. The high concentrations east of longitude 82° were measured in an air mass that had spent substantial time over the southeastern United States and contained high levels of carbon monoxide and ozone [Shipham et al., this issue]. West of the Appalachian mountains the aircraft penetrated a cold front, and we immediately saw a substantial reduction in HNO_3 (and other species as well). Over the Rocky Mountains, significant HNO_3 levels were measured, not in tropospheric air but in an elevated planetary boundary layer which the aircraft had penetrated over the mountains [Shipham et al., this issue]. The concentration of HNO_3 (and other species) remained elevated through the remainder of the flight. By contrast, the return transcontinental flight from Moffett Field to WFF, which took place 3 1/2 weeks later over a similar flight route, showed some of the lowest HNO_3 (and other species) free tropospheric concentrations encountered during CITE 2.

Conclusions

During CITE 2, more than 240 tropospheric nitric acid measurements were made, significantly increasing the available tropospheric HNO_3 data base. Approximately one third of the measurements were made over the northeastern Pacific Ocean with the remainder over the continental United States. Our marine results, both free tropospheric and boundary layer, agreed remarkably well with results from the GAMETAG atmospheric experiment conducted 9 years earlier. Our average marine boundary layer HNO_3 concentration (62 pptv) was one third lower than the free tropospheric average (108 pptv), indicating a loss of tropospheric HNO_3 within the marine boundary layer. Marine and continental free tropospheric concentrations were roughly comparable, although surprisingly, the continental levels were somewhat lower (mean 75 pptv, median 58 pptv) than marine values (mean 157 pptv, median 100 pptv). Our continental free tropospheric HNO_3 average is substantially less (by a factor of 3) than the GAMETAG results, perhaps due to the variability of HNO_3 with location. Our measured nighttime tropospheric HNO_3 average of 218 ± 66 pptv is significantly greater than measured daytime values, possibly because the highly convective conditions that existed during that night flight from thunderstorms in the area may have brought boundary layer air into the free troposphere. Like the GAMETAG results our continental boundary layer measurements were much (3-12 times) higher than free tropospheric concentrations suggesting that nitric acid in the boundary layer is a source of free tropospheric HNO_3. The distribution of HNO_3 in the continental boundary layer from low concentrations in rural areas to much higher concentrations in air coming from a large urban area suggests a close tie between boundary layer HNO_3 and anthropogenic activity. We also note that in some of the measurement regimes the standard deviation of the measurements is significant, sometimes comparable to the average. This atmospheric variability has been observed in past field experiments involving measurement of atmospheric HNO_3 and is not surprising for a gas with potential for rapid removal by heterogeneous processes.

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