

Measurements of the Nitric Acid to NO_x Ratio in the Troposphere

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Nitric acid concentrations, measured by both teflon/nylon filter packs (FP) and the tungstic oxide denuder (DEN), are compared with the average NO_x concentrations from laser-induced fluorescent and chemiluminescent methods. The HNO₃/NO_x ratio based on filter packs ranged from 0.8 to 10.4, with a mean of 3.4. The DEN nitric acid concentrations produced ratios ranging from <0.3 to 9.8, with a mean of 2.6. Average marine ratios were larger than those from continental regions, in part due to continental anthropogenic sources of NO_x. Although we collected very few boundary layer samples, their average ratios were smaller than those in the free troposphere, apparently because of the effect of dry surface removal of nitric acid. The nitric acid to NO_x ratio was greatest when the NO_x/NO_y ratio was smallest, such that the nitrogen photochemistry was nearing completion.

INTRODUCTION

The ratio of nitric acid concentration to NO_x (the sum of NO and NO₂) depends on both the production and loss rates for nitric acid. During the daytime, nitric acid is formed by the gas-phase reaction of NO₂ and OH [Crutzen, 1979; Logan, 1983; Parrish *et al.*, 1986]. At night, NO₂ can generate N₂O₅, which reacts with water on surfaces to continue the nitric acid production in darkness [Heikes and Thompson, 1983; Logan, 1983; Parrish *et al.*, 1986]. Although the source of oxidized nitrogen in both of these mechanisms is NO₂, the rapid daytime interconversion between NO and NO₂ makes it convenient to ratio observed nitric acid to NO_x.

Most nitric acid is lost through heterogeneous processes. The high solubilities of both nitric acid vapor and nitrate aerosol lead to large washout ratios for the wet deposition of both species [McMahon and Denison, 1979; Levine and Schwartz, 1982; Huebert *et al.*, 1983; Misra *et al.*, 1985; Sperber and Hameed, 1986; Savoie *et al.*, 1987]. In the absence of precipi-

itation, the dry surface deposition of nitric acid can also lead to its rapid removal from the atmosphere [Huebert and Robert, 1985; Huebert *et al.*, 1988]. The nitric acid to NO_x ratio is determined by the relative rates of nitric acid's formation from NO₂ and its removal by wet and dry deposition.

Models have often been used to estimate this ratio, in part because of a paucity of reliable measurements. Naturally, their results are strong functions of the modelers assumptions regarding OH and NO_x concentrations and wet and dry removal parameters. Fishman and Crutzen [1977] used a one-dimensional model to estimate the ratio at 0 and 6 km, with and without heterogeneous removal. The heterogeneous removal parameterization used in their study might be described as a slow, continuous rainout. They predicted a minimum ratio of about 0.5 at the surface with heterogeneous removal and a maximum of about 12 at 6 km without heterogeneous losses. Crutzen [1979] also modeled the change in the ratio with OH concentration, predicting ratios of 100 (at 107 OH/cm³), 25 (106 OH/cm³), and 3 (105 OH/cm³).

Logan *et al.* [1981] also modeled the odd-nitrogen cycle. From their figures one can compute approximate ratios as small as 1 (at the surface in the mid-latitudes) or as large as 5 (at 6 km in the tropics). Again, heterogeneous loss was modeled as a slow, continuous rainout. Thompson and Cicerone [1982] modeled these heterogeneous processes in much greater detail, taking care to represent the episodic nature of wet removal events. As it happens, their nitric acid to NO_x ratios were also in the range of 1-5, with the exception of smaller values noted just after rainfall events.

Some groups have incorporated limited measurements into models from which we can estimate the nitric acid to NO_x ratio. Liu *et al.* [1983] combined a model with surface measurements of HNO₃ and NO in the equatorial Pacific to estimate NO_x concentrations of about 10-15 parts per trillion by volume (pptv). Since nitric acid measured at the same time

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averaged around 35 pptv, the inferred ratio was about 3.

Most other measurements have been over continents. *Kelly et al.* [1984] report both nitric acid and NO_x at Whiteface Mountain, and *Kelly et al.* [1980] measured the same at Niwot Ridge, Colorado. Although the ratio was almost always much less than 1 (0.2 was a typical value), the use of a hot molybdenum converter caused some fraction of peroxyacetyl nitrate (PAN) to be included in their operational definition of NO_x. Thus the ratio of nitric acid to NO_x as we have defined it would be somewhat larger than what they reported. *Parrish et al.* [1986] and *Fahey et al.* [1986] also report continental measurements of this ratio, based on (PAN-free) data from Niwot Ridge. Again the continental surface ratio seldom exceeded 1, typically ranging from 0.1-0.4.

The results of the GTE/CITE 2 nitric acid instrument intercomparison are presented by *Gregory et al.* [this issue]. This paper evaluates the HNO₃/NO_x ratio, based on the airborne nitric acid and NO_x measurements made as a part of this program. Most of the measurements were made in relatively clean air above either the eastern Pacific Ocean near San Francisco or the western United States. Since they were made at altitudes of 0.1-6 km, they should be less affected by local sources and surface sinks than most of the other measurements of this ratio which have been published to date.

EXPERIMENT

The techniques by which NO, NO₂, and nitric acid were measured are described elsewhere in this volume (see CITE 2 intercomparison papers).

Most of the NO_x data which we use here were compiled at York University as 1-min. averages of the reported values from each operating NO and NO₂ technique. The flight 4 NO_x data were compiled at the National Center for Atmospheric Research (NCAR). We averaged these values over each filter pack sampling interval. Each NO_x average reported in Table 1 has a "percent coverage" tabulated to its right. This represents the fraction of the total sampling interval during which NO_x data were available, and it ranged from 22% to 82%. If this percent coverage was greater than 33%, the NO_x average was retained and included in our analysis. If the coverage was less than 33%, the average was only retained if the NO_x data were evenly spread over the entire interval (as evidenced by a lack of gaps exceeding 15 min.).

Although they generally agreed at high concentrations, the filter pack (FP) and tungstic oxide denuder (DEN) frequently found quite different nitric acid values below 100 pptv. Since the intercomparison provided us with no basis for preferring one over the other, we chose not to average the values but rather to compute and plot the ratios from both techniques. This permits readers to evaluate each set of ratios for reasonableness, in view of the

possibility that the two methods apparently have different interferences and biases. The DEN values were averaged over the FP sampling interval, to ensure comparability. The results are listed in Table 1. The standard deviation of the DEN values during each interval is included because it gives some idea of the atmospheric variability of nitric acid during the averaging period.

RESULTS

The raw data and computed nitric acid to NO_x ratios for each of the sampling periods are listed in Table 1. Both the range and the average values are slightly higher when the FP data are used than when the DEN results are included. We sampled in marine and continental areas, in both the boundary layer and the free troposphere. The boundary layer/free troposphere assignment was based largely on observed changes in dew-point depression and other variables during soundings. Table 2 lists the number of samples in each of the four resulting categories, as well as the average ratios from each technique in that category.

It should be noted that the three lowest ratios for the DEN system (<0.3) were from samples where the reported nitric acid concentrations were often "<MDL," meaning less than the minimum detection limit. Thus both the concentrations which we have used and the resulting nitric acid/NO_x ratios should be thought of as upper limits.

The highest ratios were found in the marine free troposphere, averaging about 4 using either technique. In the marine boundary layer, where we collected only two samples, the ratio was about 2. Although this is just half the free troposphere average, it is well within the range of free troposphere values. A third marine sample, collected at 789 m altitude, was determined not to represent the boundary layer. Its dew-point depression was 12°C, whereas a sample collected in the boundary layer just below it had a depression of only 3°C. Layered clouds also indicated that the higher sample was in an air mass isolated from the surface.

Only one sample was collected in the continental boundary layer (CBL). The FP ratio was 1.8, while that for the DEN was 0.7. The 21 ratios from the continental free troposphere (CFT) yielded an average of 3.0 for the FP system and 2.0 for the DEN. In each case the single CBL value was smaller than the average for the free troposphere, reflecting the same "smaller near the surface" behavior as the marine samples. (It should be noted, though, that the two CBL ratios lie within the range of CFT values.) Furthermore, the continental ratios were smaller than those in marine areas. Clearly, the ratios from the two nitric acid techniques differed more in continental than marine regions.

Figure 1a demonstrates that there is some variation in the ratio with longitude. The marine samples (west of 123°) generally exhibit higher ratios than the continental ones. The lowest average values were

TABLE 1. Nitric Acid/NO_x Ratios

Flight	Sampling Location	Altitude, km	Time, GMT		HNO ₃ /NO _y		NO _x		DEN HNO ₃		FP HNO ₃
			Start	Stop	FP	DEN	pptv	Percent Coverage	pptv	s.d.	pptv
0	F, C	4.9	132553	153937	0.8	1.4	160	22	223	184	128
0	F, C	4.9	183839	205207	5.8	4.2	51	37	213	92	297
0	F, C	4.8	205712	223451	8.1	7.6	73	34	554	86	590
1	F, M	4.8	185710	195848	10.4	9.8	48	52	470	108	501
1	F, M	4.9	200338	211204	2.7	3.6	63	39	230	33	169
1	F, M	4.9	213028	230245	7.0	7.4	68	29	500	168	478
2	F, M	4.9	174950	185241	1.2	2.2	52	30	113	19	63
2	F, M	4.9	185924	200814	1.6	3.5	28	27	97	17	45
2	B, M	.5	204239	221348	1.2	2.4	33	25	80	16	38
3	F, M	4.9	175313	192542	1.5	1.3	32	32	43	29	47
4	F, C	4.6	041911	051847	4.0	3.8	46	20	173	29	184
4	F, C	4.6	051938	061630	3.1	2.2	122	82	267	37	374
4	F, C	4.9	062145	071555	3.3	2.6	73	76	193	65	239
4	F, C	4.9	071644	082237	2.8	2.3	77	81	180	49	219
5	B, M	.2	194200	205101	3.7	1.3	28	33	37	5	104
5	?, M	.8	205633	220219	8.5	5.4	16	36	87	19	136
6	F, C	2.6	183940	191122	3.4	0.6	39	45	25	5	134
6	F, C	4.7	193920	201006	1.2	0.7	55	56	40	10	63
6	F, C	4.7	201122	204121	4.5	2.5	16	26	40	NA	72
6	F, C	3.8	204518	211618	3.7	2.5	18	50	45	5	66
6	F, C	3.8	211721	214612	2.8	1.4	46	40	65	5	129
7	F, M	5.0	175126	192237	3.7	3.2	28	47	90	39	103
7	F, M	2.3	200415	210637	5.1	2.8	30	60	83	5	152
8	F, C	4.7	181043	191132	1.8	<0.3	52	61	<13	NA	92
8	F, C	5.0	211307	223411	3.4	1.6	63	52	100	40	216
9	B, C	2.3	175745	191541	1.8	0.7	131	78	95	38	238
9	F, C	6.1	201140	215340	1.0	1.3	34	30	43	22	34
10	F, C	5.7	150350	160318	2.7	0.4	56	49	20	0	153
10	F, C	5.1	160547	170610	2.0	<0.3	32	45	<10	NA	65
10	F, C	5.1	170924	184423	1.9	<0.3	32	59	<10	NA	61
10	F, C	5.2	210556	220421	4.3	4.3	18	38	77	39	77
10	F, C	5.2	220632	230909	1.7	1.2	23	63	28	8	40
10	F, C	5.2	231314	240939	1.0	1.1	79	47	90	NA	76
Average					3.4	2.6	48	43	121	36	151
Standard deviation					2.5	2.4	32	14	144	45	142

The s.d. column contains the standard deviation for the DEN samples during each filter sampling interval. F refers to free troposphere, B to boundary layer, M to marine, and C to continental sampling locations. NA, not applicable.

TABLE 2. Average HNO₃/NO_x Ratios by Region

Region	N	FP Ratio	DEN Ratio
Marine boundary layer	2	2.4 + 1.3	1.9 + 0.6
Marine free troposphere	8	4.1 + 3.0	4.2 + 2.7
Continental boundary layer	1	1.8	0.7
Continental free troposphere	17	3.0 + 1.7	2.0 + 1.7

found over the eastern United States, during ferry flights to and from the Electra's home base at Wallops Island, Virginia.

Clearly, any conclusions concerning boundary layer ratios will have to be qualified because of the very

small number of boundary layer samples. While the altitude variation is not obvious in Figure 1b the average boundary layer ratios in each regime were indeed smaller than those in the free troposphere in that regime (Table 2). For both nitric acid techniques the very lowest marine ratio was found in the boundary layer.

Figure 2 contains three plots of the nitric acid to NO_x ratio versus concentrations or the ratios of concentrations. It is not surprising that the ratio is largest when NO_x (the denominator) is small. (Figure 2a is included for the reader's information, even though the axes are not truly independent.) It should also be noted, however, that equally small ratios are found in air with very low concentrations of NO_x. Likewise, the largest values of the ratio occur for large values of the numerator, nitric acid. There appears to be no correlation between the ratio and ozone (Figure 2b) concentrations, although high values of ozone are associated with high ratios.

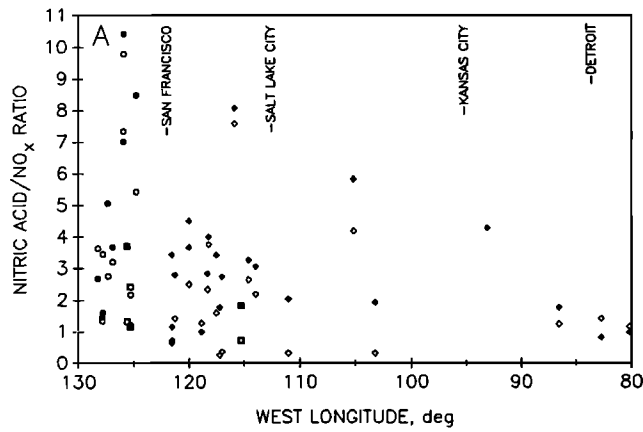


Fig. 1a. Nitric acid/NO_x ratio versus longitude. Circles represent marine data, diamonds continental data, and squares boundary layer data. Solid symbols use FP data, while open ones use DEN data.

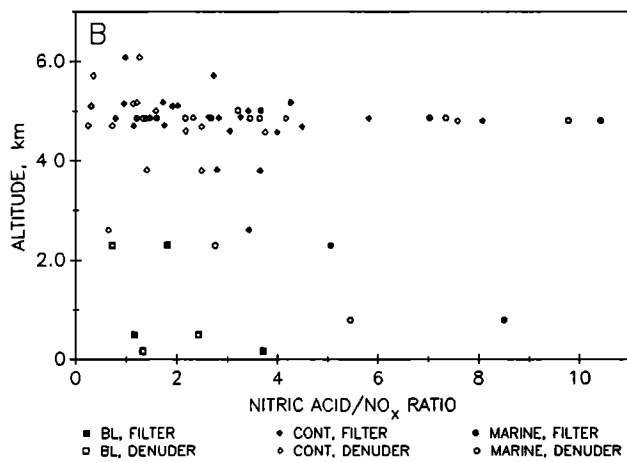


Fig. 1b. Nitric acid/NO_x ratio versus altitude.

The ratio NO_x/NO_y (the sum of all odd-nitrogen compounds) can be thought of as an index of the completeness of odd-nitrogen photochemistry, since it represents that fraction of NO_y which still has the potential to be oxidized further. The nitric acid/NO_x ratio is plotted against NO_x/NO_y in Figure 2c, with predictable results: nitric acid/NO_x is greatest when the photochemistry is most complete, at small NO_x/NO_y ratios. Six nitric acid/NO_x ratios (mostly from flights 0 and 1) do not appear on this plot because no NO_y data exist for those time intervals.

DISCUSSION

The measured HNO₃/NO_x ratios agree quite well with the models. Logan [1983], Fishman and Crutzen [1977], and Thompson and Cicerone [1982] all predicted surface mid-latitude ratios of around 0.5-1. Our few boundary layer values are only slightly larger, ranging from 0.7 (DEN, CBL) to 3.71 (FP, MBL). The average measured boundary layer ratios are smaller than the free troposphere averages, and this finding also agrees with the larger FT ratios predicted

by the models. Presumably, the difference is due in part to the more rapid removal of nitric acid in the BL by dry deposition, a process which cannot occur in the FT. The continental BL also contains NO_x sources, which might further reduce the CBL ratios relative to the CFT.

The measured FT ratios also agree quite well with those predicted by the models. The MFT average ratios of 4.1 (FP) and 4.2 (DEN) are remarkably close to the estimates based on the work of Logan *et al* [1981] and Thompson and Cicerone [1982]. The

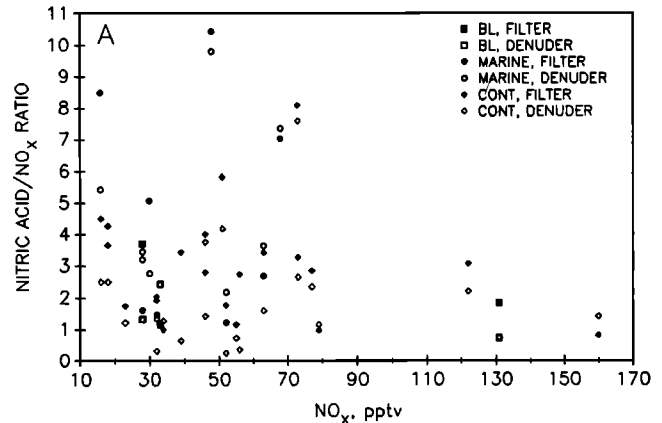


Fig. 2a. Nitric acid/NO_x ratio versus NO_x concentration.

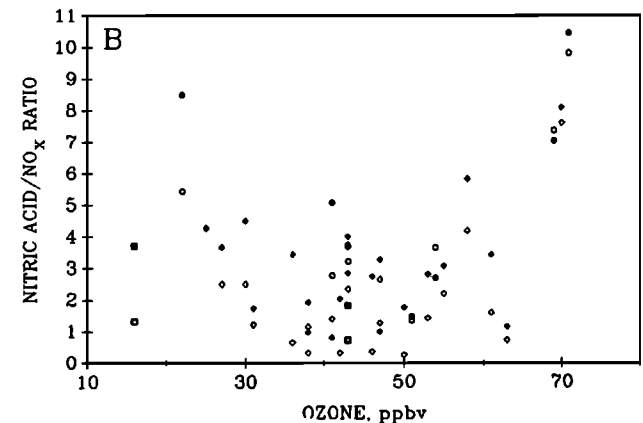


Fig. 2b. Nitric acid/NO_x ratio versus ozone concentration.

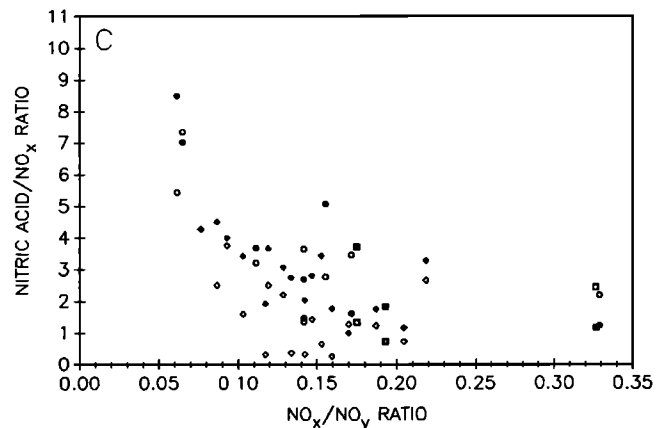


Fig. 2c. Nitric acid/NO_x ratio versus the NO_x/NO_y ratio.

highest individual ratios measured (around 10) would agree with *Fishman and Crutzen's* [1977] prediction if the diurnally averaged OH concentration were in the vicinity of $3\text{--}5 \times 10^5/\text{cm}^3$. OH values computed from the actual conditions encountered on CITE 2 [*W.L.Chameides et al.*, this issue], tend to be slightly larger, implying that still larger ratios could be achieved if air were free of scavenging for a long enough period of time.

While the models do not explicitly predict a difference between marine and continental areas, their boundary conditions implicitly include this difference. Continental areas are likely to be closer to anthropogenic NO_x sources, so that the chance of encountering fresh, unreacted NO_x is greater over the continents. Our average measured marine ratios were larger than those from continental areas, presumably because the odd-nitrogen photochemistry was more nearly complete in marine areas, far from anthropogenic NO_x sources.

It is worth noting that many of the FT continental samples were collected from marine air that had only recently crossed the California coastline. This is particularly true in flight 8, where we tried over land to sample roughly the same air which we had sampled the day before (flight 7) over the ocean. The ratios did decrease over land (going from 4.4 FP and 3.0 DEN to 2.6 FP and 0.9 DEN), due largely to a doubling of the NO_x concentration. As we moved farther east on the ferry flights (flights 0 and 10), the ratios became smaller still, in part due to higher NO_x values.

We also had the opportunity to compare tropical marine air (flight 2, and to some extent 3) with marine air that may have contained both stratospheric air and aged continental pollution (flight 1). The first and last samples of flight 1, which contained both elevated ozone and very little humidity, were almost certainly influenced by a recent tropopause fold. The tropical air had much lower ratios (1.4 FP and 2.3 DEN) than the more polluted (in terms of aerosols and ozone) air (6.7 FP and 6.9 DEN). The NO_x concentrations were similar on all three flights, but nitric acid was elevated in the polluted/stratospheric air mass. While one might expect high tropical OH concentrations to increase the ratio relative to that in mid-latitude air, it is possible that precipitation scavenging of nitric acid kept our tropical ratios low.

Since the range of possible ratios is an important result of such a study, we should examine the lowest values carefully. Four of the ratios calculated from the DEN measurements were less than 0.5. Since three of these values contain measurements of <MDL, the ratios we have computed here are maximum values for those ratios. The small ratios in each case are the result of very small nitric acid concentrations, since the NO_x levels are all fairly typical. It is certainly possible that recent scavenging of nitric acid could have reduced its concentration to

the very low reported levels, but the meteorological analyses of these flights do not support that explanation. Although these low ratios are similar to values measured in ground-based experiments [*Parrish et al.*, 1986; *Fahey et al.*, 1986], they are somewhat lower than the 6-km predictions of the models by *Fishman and Crutzen* [1977], *Logan* [1981], and *Thompson and Cicerone* [1982].

CONCLUSIONS

The measured ratios of nitric acid to NO_x agreed nicely with predictions from models, ranging generally from 1 to 5. The average free tropospheric ratios were larger than those in the boundary layer, as a result of boundary layer NO_x sources and dry surface nitric acid removal. Marine ratios tended to be greater than those over the North American continent, presumably because of the longer distance (and time) between anthropogenic NO_x sources and marine areas. This is consistent with the idea that more NO_x is converted to nitric acid the longer NO_x emissions are allowed to age in the atmosphere.

While the filter pack and tungstic oxide denuder nitric acid measurements yielded similar ratios in marine areas, the average filter pack ratios were substantially larger for continental samples. The lowest ratios were also quite different for the two techniques: 0.8 for the filter pack and <0.3 for the tungstic oxide denuder.

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