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AIRCRAFT NO_x HAD NO UNIQUE FINGERPRINT ON SONEX; LIGHTNING DOMINATED FRESH NO_x SOURCES

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Abstract. Key questions to which SONEX was directed were the following: Can aircraft corridors be detected? Is there a unique tracer for aircraft NO_x? Can a "background" NO_x (or NO_y) be defined? What fraction of NO_x measured during SONEX was from aircraft? How representative was SONEX of the North Atlantic in 1997 and how typical of other years? We attempt to answer these questions through species-species correlations, probability distribution functions (PDFs), and meteorological history. There is not a unique aircraft tracer, largely due to the high variability of air mass origins and tracer ratios, which render "average" quantities meaningless. The greatest NO and NO_y signals were associated with lightning and convective NO sources. Well-defined background CO, NO_y and NO_y/ozone ratio appear in subsets of two cross-track flights with subtropical origins and five flights with predominantly mid-latitude air. Forty percent of the observations on these 7 flights showed NO_y/ozone to be above background, evidently due to unreacted NO_x. This NO_x is a combination of aircraft, lightning and surface pollution injected by convection. The strongly subtropical signatures in SONEX observations, confirmed by pv (potential vorticity) values along flight tracks, argues for most of the unreacted NO_x originating from lightning. Potential vorticity statistics along SONEX flight tracks in 1992-1998, and for the North Atlantic as a whole, show the SONEX meteorological environment to be representative of the North Atlantic flight corridor in the October-November period.

1. Introduction

The SONEX mission had as major objectives detection of corridors, fingerprinting of aircraft NO_x (and NO_y) and evaluation of the fractional contributions of aircraft, surface, lightning and stratospheric NO_x during the deployment period. Flight planning focused on identification of air masses with varying sources through meteorological forecasts, use of daily OTS (Organized Track System) map assignments, satellite imagery and specialized trajectory-based model products [Thompson et al, 1999]. In this paper, examples of meteorological characteristics and tracer statistics address the key SONEX NO_x questions. Unless otherwise specified, 10-s data from upper tropospheric segments (8-12 km) of SONEX are used, with merges done with Goddard Science System programs. Filtering of stratospheric air, which was significant but not dominant on 9 of 14 SONEX science flights, was accomplished using observations at times for which ozone < 100 ppbv.

The conclusion from our statistical analyses is that "fresh" NO on SONEX was ubiquitous (40% of NO_y on the most chemically uniform flights without recent lightning), but NO_x and NO_y from aircraft do not coincide with a unique chemical tracer. The unexpected frequency of lightning NO and frequently subtropical nature of air parcels sampled on SONEX, however, implicate lightning as the major fresh NO_x source. This agrees with Liu et al [1999], who used a different statistical approach to SONEX data. SONEX meteorological characteristics show that mission sampling was representative of North Atlantic climatology, so our conclusion about NO_x sources should hold generally for this region in mid-autumn.

2. Detection of Aircraft in Corridors

Although it will be shown that it is difficult to generalize about NO and NO_y sources during SONEX, three dedicated cross-track flights on SONEX were conducted to quantify the aircraft contribution (18 and 23 October; 9 November 1997). *Can aircraft corridors be detected?* The answer is yes and no. The affirmative refers to two flights from Shannon in which NO and NO_y spikes of recently expired tracks stand out against a relatively low background environment. The negative refers to the 9 November flight in which NO and NO_y were enriched by contributions from both subtropical and localized lightning episodes. Figure 1a shows that it was easy to detect the corridor on the 23 October 1997 flight from Shannon. Fresh NO (denoted by high NO/NO_y) and similar increases in volatile particles signify ascent into the corridor and sampling along Flight Levels 330, 350 and 370 (10-11.3 km); the NO mixing ratio is shown. Back trajectories (Figure 1c) show that subtropical origins were combined with recirculation near the eastern Atlantic, which brought relatively clean air to sampling altitudes.

The flight of 9 November 1997 was loaded with fresh NO from convective injection of surface pollution and lightning (hours to 1-2 day transport time), as well as aircraft (Figure 1b). The latter appeared as spikes superimposed on broad lightning or pollution NO sources, making it difficult to select aircraft NO spikes definitively. The NO/NO_y ratio was > 0.5 for most of the flight. Flight-track back-trajectories (Figure 1d) show sub-tropical origins for this flight with high exposure to Mexican Gulf lightning [Thompson et al., 1999; Pfister et al, 1999]. Spikes of NO and NO_y during the dark last hour of the flight could only have come from a nearby source; marine origins were seen in tracers, eg halogenated hydrocarbons, methyl nitrate [Thompson et al., 1999; Snow et al, 1999; Pickering et al, 1999].

This brings up the question: *is there a unique tracer for aircraft NO?* Fresh aircraft spikes are identified by aerosol characteristics [Anderson et al., 1999], but closer examination shows that the answer to the aircraft uniqueness question is no. Two approaches are used. First, we performed a flight-by-flight correlation of CN (fine aerosol, "condensation nuclei") with NO/NO_y, NO_y and CO, to look at aircraft and/or lightning connections, and to see if aerosol injected from the surface was unique. There was no consistent pattern as two Shannon cross-track flights illustrate. Frequency of occurrence of CN and of the volatile fraction for the 18 and 23 October1997 flights differ. Volatility is obtained by dividing heated fine aerosol particles by the total measured without heating. The most probable volatility of CN, strongly peaked in each case, is 0.2 for the 18 October flight and 0.05 for the 23 October flight. NO_y and aerosol volatility are positively correlated for 18 October and negatively correlated for the 23 October flight.

Second, in Section 3, it is shown that NO_y, CO and tracer ratio probability distribution functions (PDFs) across SONEX can be classified into statistically well-defined subsets of flights. Aerosol properties do not show these distinct populations. Figure 2 shows that fine, unheated (UH) and ultrafine (UF) aerosols display overall distributions (gray shaded areas) similar to those from subsets which are distinguishable for NO or NO_y. Fine aerosol volatility (third panel in Figure 2) is broadly distributed for the composite and all subsets. The cross-track fine aerosols resemble the subtropical UH, but cross-track ultrafine aerosols have a secondary peak coincident with mid-latitude continental UF.

3. No "Average" Tracer Composition on SONEX; Categorization of Flights by NO and NO_y

The previous section showed that the dedicated cross-track flights on SONEX were highly diverse. However, they were typical in showing that upper tropospheric air sampled during the mission was highly heterogeneous and that "average" properties are not representative of the SONEX environment. To investigate this more thoroughly for all the science flights (Nos. 3-16, from 13 October to 12 November 1997), we compared the most probable value and the mean value for NO_y , ozone, CO, NO_x/NO_y, NO_y/O_3 and NO/NO_y. Except for CO, the divergence of most probable and mean values was often very large. On 5 flights the most probable ozone mixing ratio was much higher than the mean because significant stratospheric sampling time occurred. For example, Flight 10 (29 October 1997) was planned south of the Azores to capture subtropical air, but took off into a cutoff low. The differences between the mean and most probable NO_y and NO_y/ozone on 29 October, even with stratospheric segments removed, exceeded a factor of 2 because convection and lightning led to high NO and NO_y episodes. Mean-most probable discrepancies show how variable reactive nitrogen is by any measure: NO_y, NO/NO_y; NO_x/NO_y; NO_y/ozone. Extreme examples occur when the least probable value corresponds to the mean, as for NO_y on 28 October 1997.

Upper tropospheric CO, unlike other tracers, has mean and most probable values coinciding for every flight. Furthermore, values fall into a bimodal pattern: distinctly subtropical ("clean," < 80 ppbv) and mid-latitude values (80-100 ppbv). These categories roughly describe the first 6 and last 8 SONEX flights and appear as two peaks in the gray-shaded aggregate CO PDF frame in Figure 2.

Given that NO and NO_y display complex tracer correlations on SONEX and that "average" values are meaningless, alternative statistical approaches are used to give insight into NO_x sources on SONEX flights. Four subsets of flights emerge as distinct distributions when classified with tracer PDFs and air parcel history. The two Shannon cross-track flights had strongly peaked distributions (purple in Figure 2), once stratospheric segments were eliminated on the 18 October 1997 flight. Although their most probable CO and NO/NO_y peaks resemble those labeled "subtropical" (green in Figure 2), the cross-tracks have better-defined peaks for NO_y/O_3 and NO_y. Trajectory origins [Thompson et al, 1999] suggest that the reason is an absence of high NO_y values from lightning in Shannon cross-tracks compared to the subtropical flights. The latter, with low CO and one NO_y cluster < 100 pptv are the flights of 15, 20, 25 October 1997. The 25 October flight was the dedicated northern survey from Shannon to capture stratospheric air. With stratospheric flight segments removed, signatures of subtropical air become apparent. A 4th flight (13 October) with strongly subtropical influences has a broad NO_y distribution due to convectively injected pollution and lightning (probably some aircraft also), and is classified with three other lightning-dominated NO_y flights: 29 October, 3 and 9 November 1997 (yellow in Figure 2). The fourth sub-group (red in Figure 2) consists of flights in which the reactive nitrogen has a high fraction of HNO_3 and PAN - signs of mid-latitude continental influence - and the lowest NO/NO_y peak: 28 and 31 October, 5, 10 and 12 November 1997.

4. "Background" and Perturbed NO_y on SONEX; Most Likely Sources of NO_x

Given that aircraft NO_x has no unique signature, what can be said about NO_x sources on SONEX? Chemical and dynamic features are used to answer this question.

Chemical Signatures

First, the most useful tracers have to be isolated. The gray shading in Figure 2 shows that, over all SONEX, NO_y and NO_y/ozone define a background reference state, against which perturbations in subsets can be assessed. Background NO_x is not defined because the NO/NO_y and NO_x/NO_y ratios show no single peak emerging in the distribution. For SONEX as a whole, NO_x/NO_y (not shown) has a nearly uniform probability between 0.1 and 0.6.

The overall population of NO_y has a distinct most probable value (225 pptv), as does the NO_y/ozone ratio. Note that "background" is not a single number, but is a distribution which characterizes chemical variability on time scales longer than transient perturbations from lightning, aircraft, and convective injection. In other words, it is the equilibrium distribution toward which the SONEX region is tending [Sparling, 1999]. The subsets labeled continental midlatitude and cross-track are close to the overall distributions for NO_y and NO_y/ozone, but subtropical and lightning, of course, are not. The strong influence of lightning suggests that this is a major NO_x source on SONEX, but the yellow and green PDFs in Figure 2 have too many maxima for quantitative analysis.

Carbon monoxide has two distinct background reference values over all SONEX (gray, Figure 2). One resembles the Shannon cross-tracks (purple); the other has a CO fingerprint similar to the midlatitude continental distribution (red). Both of these subsets, which together account for 45% of SONEX sampling, therefore, characterize SONEX sampling as a whole. Figure 3 shows that NO_y and NO_y/ozone in the cross-track and midlatitude continental subsets are one-sided Gaussian distributions with long tails representing recent NO_y inputs. The most probable values are given along with the 2-sigma standard deviation (eg 200 ± 57 pptv). The shading represents the fraction of NO_y that is still reactive, ie NO_x. This is 39-43% of NO_y and is implied as 33-37% by NO_y/ozone. For the cross-track set, one might assume that this fraction is aircraft but the resemblance to the subtropical subset (green, Figure 2) does not rule out lightning. The 40% of unreacted NO_y (NO_x) in the midlatitude fraction represents a mixture of aircraft, lightning and surface pollution, that can only be deconvoluted with labeled modeling (Allen et al, 1999; Meijer et al, 1999).

Meteorological Signatures

The chemical fingerprints of SONEX air parcels point to subtropical origins (low CO) for the first 6 of 14 flights. Of the remainder, Flights 10, 12, and 14 (29 October, 3 and 9 November) have back-trajectories and flight-level PV indicating subtropical origins (see RD and CP "Model Products" at telsci.arc.nasa.gov/~sonex; Thompson et al, 1999). The most probable NO, NO_y, NO/NO_y (also NO_y/ozone) for these three flights reflect enrichment by lightning. This degree of subtropical influence on SONEX was unexpected. These findings suggest active dynamics with considerable mixing and lead to two last questions.

How representative was SONEX of the mid-Fall 1997 North Atlantic region? How representative were SONEX dynamics (and by extension, NOx sources) for the time of year of the mission? The PV field is selected as a tracer for the degree of subtropical (low PV, < 1.5 pv unit) or stratospheric (PV> 2 or 3 pvu) influence. The PV PDF for the North Atlantic (35-55N, 0-75W, 15 October-15 November) at the 330 K level, typical of DC-8 altitudes for the chemical statistics presented here, shows a strong peak. The overall distribution is virtually the same for the years 1992-1998, as shown by the cumulative PDF in Figure 4a. The individual years overlie one another. The PV PDF along SONEX flight tracks, a subsample of the North Atlantic, is similar (thick gray line in Figure 4b) to the regional North Atlantic PV for 1997, as well as for 1998 and the 5 years immediately prior to SONEX. By this measure of dynamical mixing, SONEX is representative of the North Atlantic as a whole. However, Figure 4b also shows that along SONEX flight paths, the PV distribution is more weighted toward low values than sampling would have been during other years. Half of the air parcels during SONEX were subtropical, ie < 1.5 pvu; fewer than 20% were intensely stratospheric, if PV > 3.0 is the criterion. Sampling along SONEX flight tracks during other years would have encountered 15-40% subtropical parcels, with a 35-65% probability of capturing stratospheric air.

5. Conclusions

Statistical analysis of chemical and meteorological signatures on SONEX has answered the key questions about NO and NO_y origins during the mission. The outstanding messages from this analysis are:

-> Aircraft corridors are readily detected but absence of a unique tracer for aircraft NO precludes quantitative assignment of the aircraft NO_x fraction.

-> Heterogeneity on nearly every flight as well as among SONEX flights renders the concepts "average" or "typical" North Atlantic air meaningless. Broad distributions of NO/NOy, NO_x, and particles on 30-40% of flights resulted from mixtures of mid-latitude, aged continental air and subtropical air.

-> Marked most probable values for NO_y and NO_y/ozone define a background SONEX distribution. 40% of air parcels sampled on SONEX are outside of this equilibrium due to aircraft, lightning and convective injection of surface NO_x.

-> Using PV as an additional tracer for air parcel origins confirms the strongly subtropical signature of the SONEX observations and points to lightning as the most likely major NO_x source during the mission. Origins of the underlying NOy can only be determined with a coupled chemical-transport model.

-> PV statistics over the North Atlantic show SONEX sampling to be representative of the region as a whole for the period of the mission. Furthermore, PV along SONEX flight tracks during mid-October-mid-November 1997 resembles climatology for the years 1992-1998, indeed more so than the other six years in that period.

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Figure Captions

Figure 1. (a) Vertical distribution of NO on SONEX flight of 23 October 1997, during which DC-8 traversed freshly expired eastbound OTS tracks between Ireland and Scotland; (c) clusters of back-trajectories run from locations along the flight track with the GSFC trajectory model; + denotes 24-hour segments over 5 day total transit. Trajectories are similar to those of kinematic models used by Fuelberg et al [1999] and KNMI during SONEX and POLINAT [Meijer et al, 1999]; (b, d) same as (a,c) except for the 9 November

1997 flight across fresh westbound tracks over Newfoundland. Note that NO (also NOy concentrations, not shown) during the latter flight were much higher and that high values also appear in ascent and descent, signifying convection/pollution and lightning NO as a background against which aircraft are an additional source. See Jeker et al [1999].

Figure 2. Composite probability of occurrence for the upper tropospheric segments of all 14 SONEX (non-test) flights in gray, and for subsets: Flight Nos. 3-16, from 13 October to 12 November 1997. Fraction of observations in each subset and key are in NOy/ozone panel. Basis of statistics is 10-s data merged with the GSFC Science System. Cross-track: 18 and 23 October 1997; Subtropical: 15, 20, 25 October. Mid-latitude: 28 and 31 October, 5, 10 and 12 November 1997; Lightning: 13 and 29 October, 3 and 9 November. Unheated fine aerosol ("UH", in natural log of molecules/cm^3) from the NASA/Langley instrument [Anderson et al, 1999, and references therein]; ratio of heated fine aerosol to unheated fine aerosol from same instrument; Log UF = natural log of ultrafine aerosols from Anderson et al [1999]. NO/NO$_y$; NO$_y$ mixing ratio in pptv; NO$_y$/ozone in pptv/ppbv; CO mixing ratio in ppbv.

Figure 3. Background NO$_y$, NO$_y$/ozone, CO from the two SONEX subsets that are closest to background values for the entire SONEX upper tropospheric distribution. Note that average NO$_y$/ozone occurs at a local minimum in the cross-track distribution. Disequilibrium from a Gaussian, denoted in the higher values, represents still reacting NOy (assumed to be NO$_x$). Using either NO$_y$ or the ratio NOy/ozone gives this fraction as ~40% of NO$_y$. Liu et al [1999] use NO$_y$/ozone statistics in a different way to infer a similar conclusion about SONEX NO$_y$ reactivity.

Figure 4. (a) Cumulative PDF, the probability that sampling exceeds the given potential vorticity (PV) for years 1992-1998 averaged over 35-55N, 0-75W at 330K surface. This is region of most upper tropospheric sampling on SONEX. (b) Cumulative PDF for pv for 1992-1998 on 330K surface, along flight track positions of SONEX. Values < 1.5 pvu correspond to troposphere. The uniformity in (a) shows that variability across the domain, which would have been captured by sampling along SONEX flight tracks (b), averages out when the entire region is considered. Assuming that lower pvu signifies less high-latitude air, SONEX showed greater sub-tropical and less stratospheric influence than the other years considered. Statistics from UK Meteorological Office analyses, which are similar to the GSFC/DAO PV analyses used during SONEX [Thompson et al., 1999].

Running Head:
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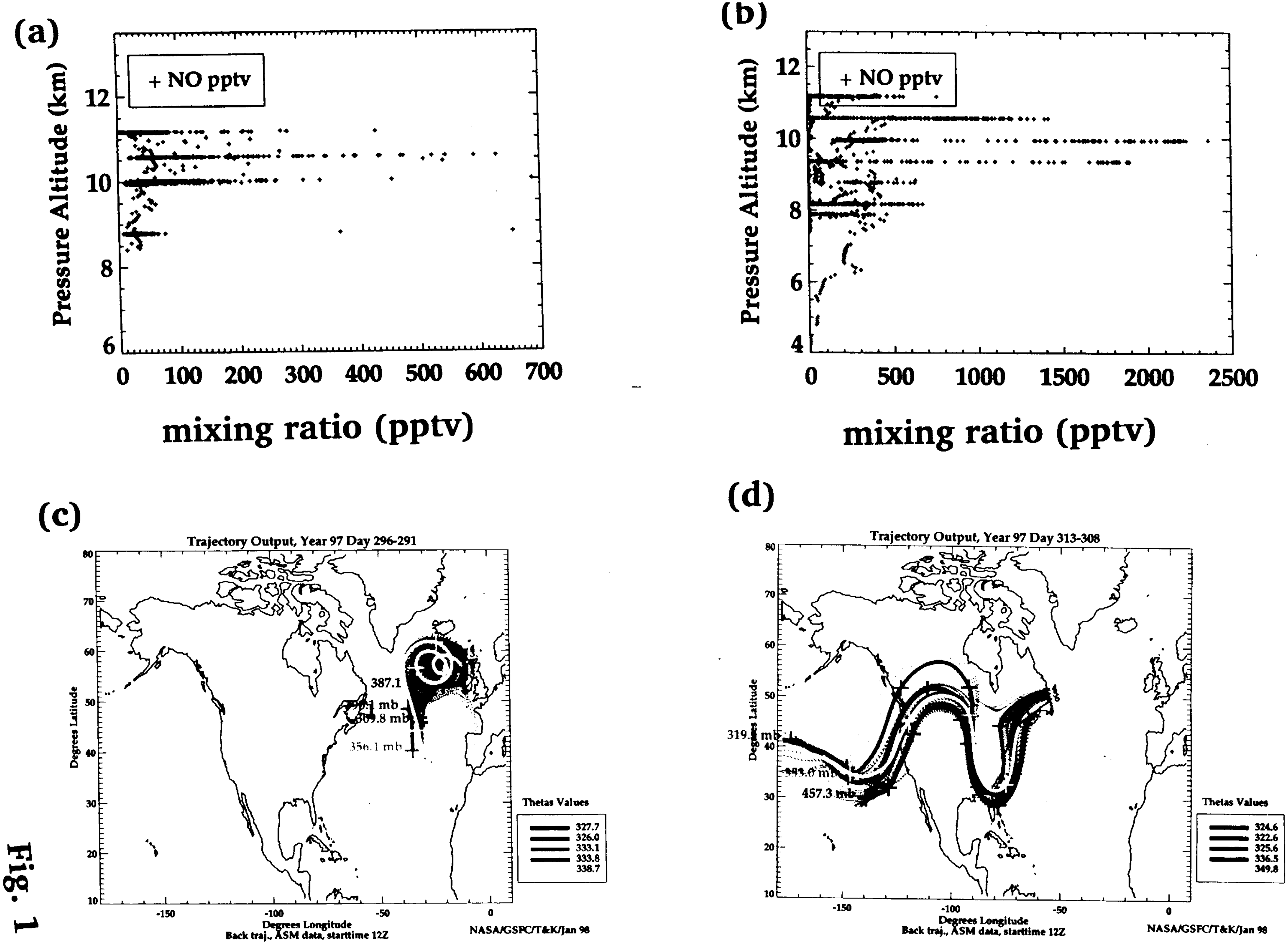
(a)
+ NO pptv
Pressure Altitude (km)
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8
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mixing ratio (pptv)
(b)
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Pressure Altitude (km)
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6
8
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12
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500
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1500
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mixing ratio (pptv)
(c)
Trajectory Output, Year 97 Day 296-291
Degrees Latitude
Degrees Longitude
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NASA/GSFC/T&K/Jan 98
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Thetas Values
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(d)
Trajectory Output, Year 97 Day 313-308
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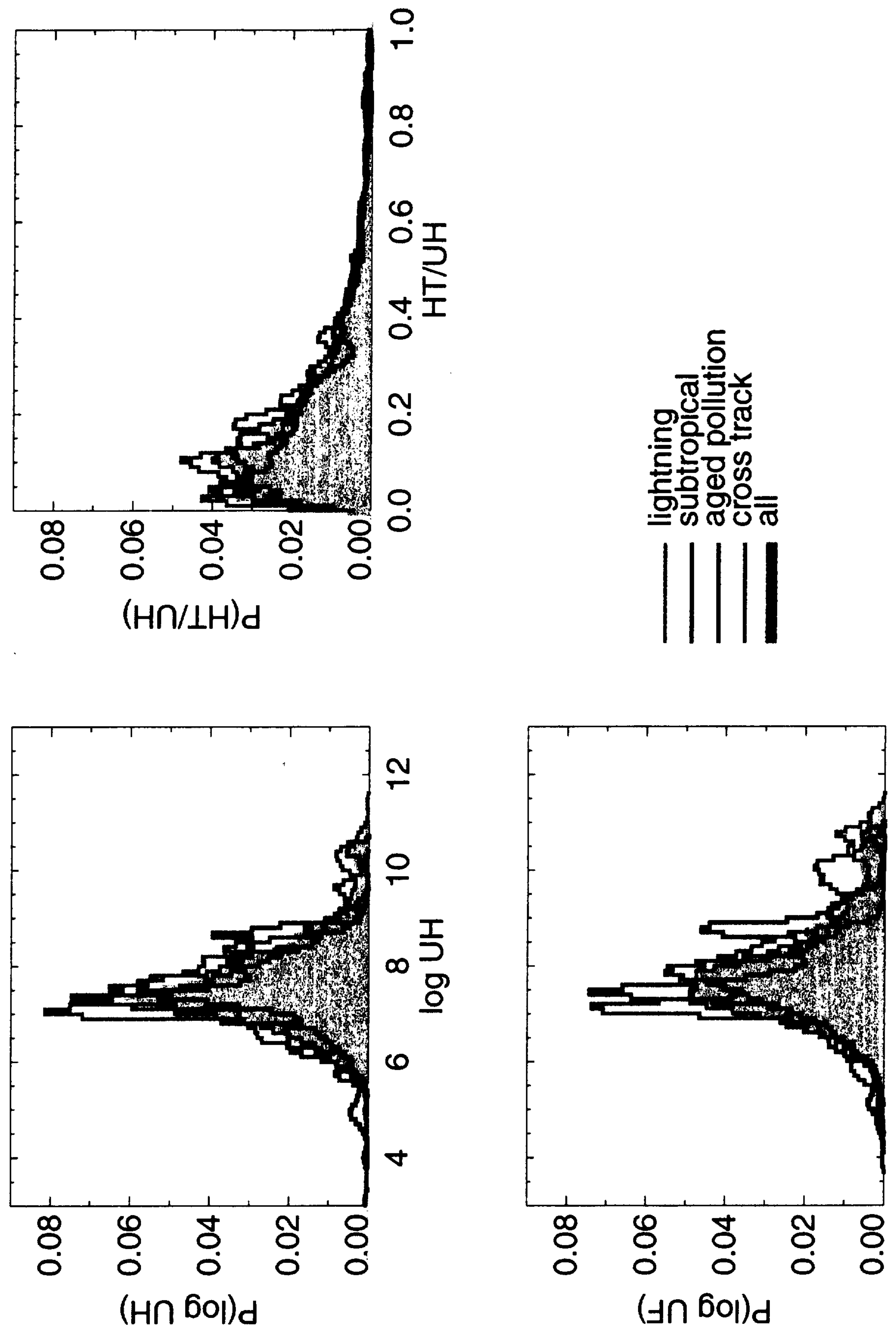
Fig. 1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P(log UF)
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cross track
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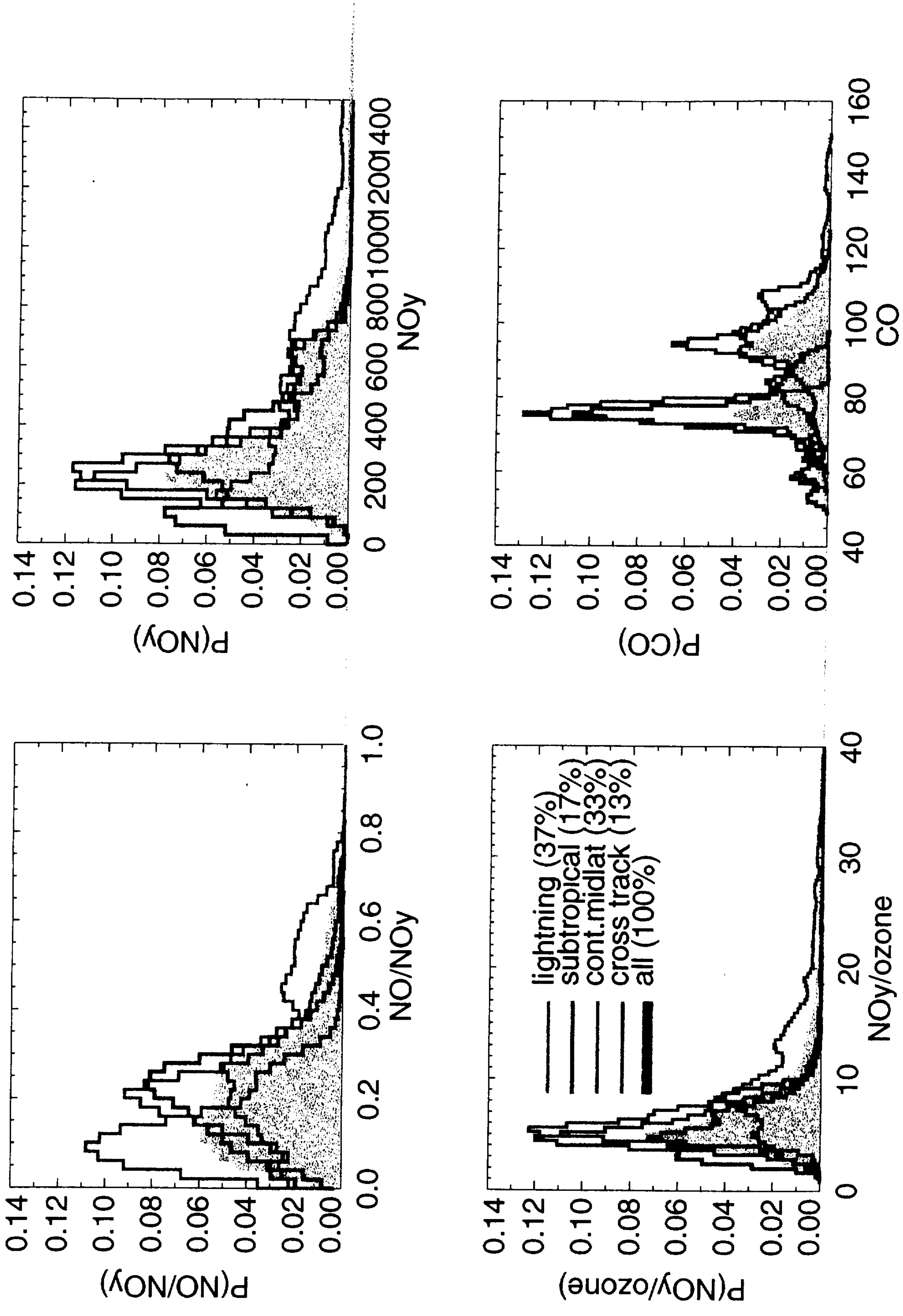
Fig. 2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0.8
1.0
NO/NOy
P(NOy)
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600
800
1000
1200
1400
NOy
P(NOy/ozone)
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20
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40
NOy/ozone
lightning (37%)
subtropical (17%)
cont.midlat (33%)
cross track (13%)
all (100%)
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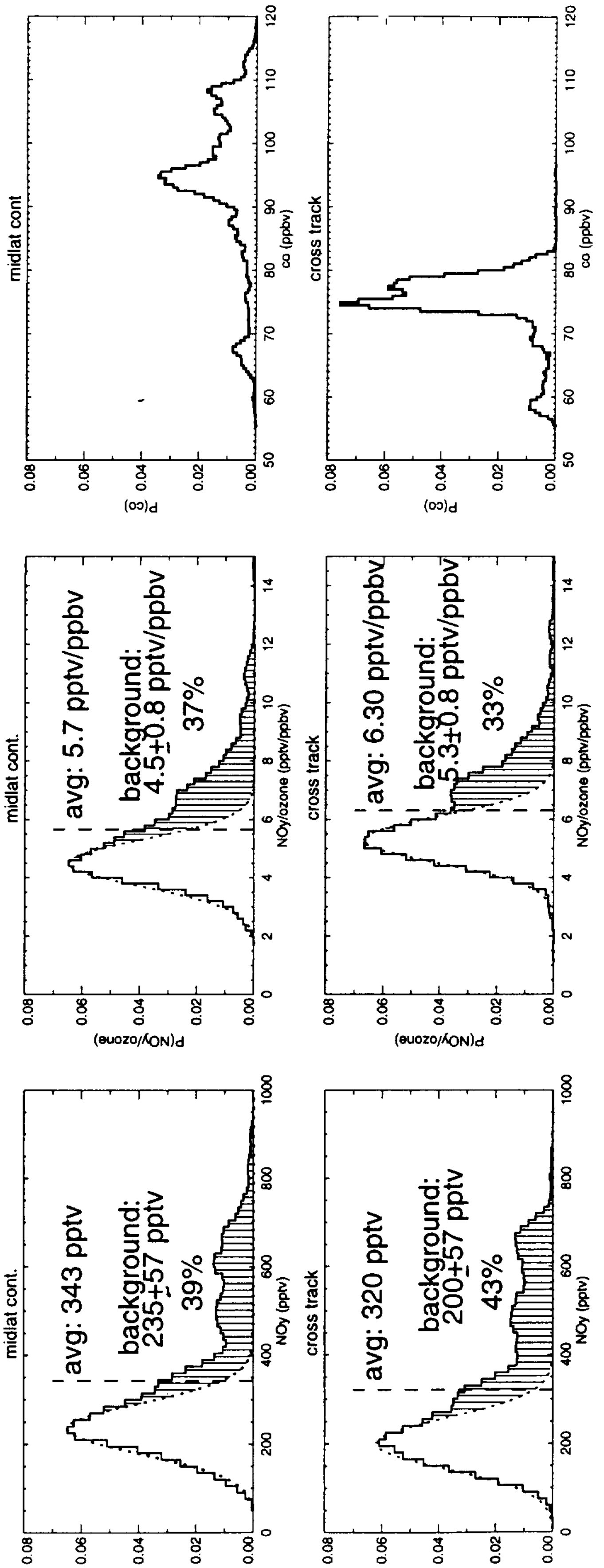
120
140
160
CO

Fig. 2, cont'd.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background: 235±57 pptv
39%
cross track
avg: 320 pptv
background: 200±57 pptv
43%
P(NOy)
NOy (pptv)
0
200
400
600
800
1000
0.00
0.02
0.04
0.06
0.08
midlat cont.
avg: 5.7 pptv/ppbv
background: 4.5±0.8 pptv/ppbv
37%
cross track
avg: 6.30 pptv/ppbv
background: 5.3±0.8 pptv/ppbv
33%
P(NOy/ozone)
NOy/ozone (pptv/ppbv)
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2
4
6
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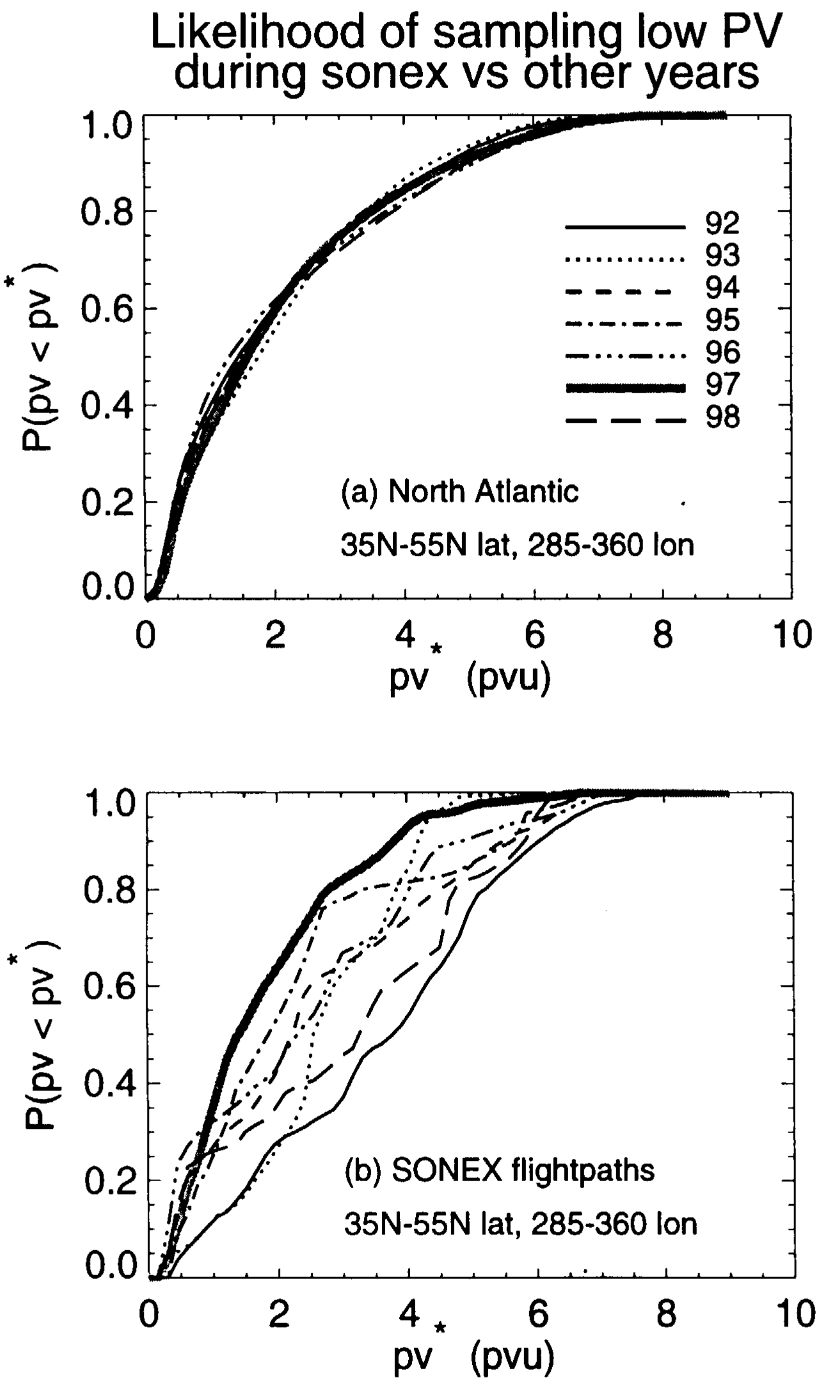
Fig. 3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0.2
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P(pv < pv*)
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2
4
6
8
10
pv* (pvu)
92
93
94
95
96
97
98
(a) North Atlantic
35N-55N lat, 285-360 lon
(b) SONEX flightpaths
35N-55N lat, 285-360 lon

Fig. 4