

# Nonmethane hydrocarbon measurements in the North Atlantic Flight Corridor during the Subsonic Assessment Ozone and Nitrogen Oxide Experiment

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**Abstract.** Mixing ratios of nonmethane hydrocarbons (NMHCs) were not enhanced in whole air samples collected within the North Atlantic Flight Corridor (NAFC) during the fall of 1997. The investigation was conducted aboard NASA's DC-8 research aircraft, as part of the Subsonic Assessment (SASS) Ozone and Nitrogen Oxide Experiment (SONEX). NMHC enhancements were not detected within the general organized tracking system of the NAFC, nor during two tail chases of the DC-8's own exhaust. Because positive evidence of aircraft emissions was demonstrated by enhancements in both nitrogen oxides and condensation nuclei during SONEX, the NMHC results suggest that the commercial air traffic fleet operating in the North Atlantic region does not contribute at all or contributes negligibly to NMHCs in the NAFC.

## 1. Introduction

Subsonic aircraft fly mainly in the upper tropospheric/lower stratospheric (UT/LS) region of the atmosphere. Jet fuel comprises 3% of the total fossil fuel usage [Friedl *et al.*, 1997], and elevated levels of nitrogen oxides (NO<sub>x</sub>), water vapor (H<sub>2</sub>O), and other species have been measured both directly in the wake of aircraft [Schulte *et al.*, 1997; Campos *et al.*, 1998] and in the corridors of commercial air traffic [Schlager *et al.*, 1997]. Other gases that are emitted from subsonic aircraft include carbon dioxide (CO<sub>2</sub>), carbon monoxide (CO), and nonmethane hydrocarbons (NMHCs) [Slemr *et al.*, 1998; Vay *et al.*, 1998].

The emissions from subsonic aircraft are expected to impact the atmosphere in at least three ways. First, background mixing ratios of the emitted gases may be perturbed. For example, experimental and model studies both have found that NO<sub>x</sub> emitted from aircraft contribute significantly to the total NO<sub>x</sub> in the UT/LS region of the atmosphere, especially between 30°N and 60°N [Ehhalt *et al.*, 1992; Friedl *et al.*, 1997]. Second, the aircraft emissions of NO<sub>x</sub>, CO, and NMHCs may impact both upper tropospheric and lower stratospheric ozone (O<sub>3</sub>) [Johnston *et al.*, 1989; Beck *et al.*, 1992; Johnson *et al.*, 1992; Fabian and Kärcher, 1997]. Third, H<sub>2</sub>O, CO<sub>2</sub>,

sulfur oxides, and other emitted species may affect both the production and the characteristics of clouds and aerosols, thereby influencing both global temperature and the radiative forcing in the UT/LS [Fabian and Kärcher, 1997; Friedl *et al.*, 1997; Singh and Thompson, 1997].

The hydrocarbon emissions from aircraft are believed to be small (~0.3 Tg yr<sup>-1</sup>), and most of the emitted hydrocarbons are in the form of NMHCs (by comparison, total NMHC emissions from anthropogenic and biogenic sources are ~600 Tg yr<sup>-1</sup>) [Friedl *et al.*, 1997]. However, few experiments have characterized aircraft emissions of NMHCs, especially for higher molecular weight (>C<sub>3</sub>) species [Friedl *et al.*, 1997] and in the cruise conditions under which most air traffic occurs [Slemr *et al.*, 1998]. Ehhalt *et al.* [1985] measured elevated levels of ethene (C<sub>2</sub>H<sub>4</sub>) and propene (C<sub>3</sub>H<sub>6</sub>) in air sampled over parts of the trans-Atlantic flight tracks of that day. However, Ehhalt *et al.* argued against jet exhaust as the cause of the enhancements, citing a National Academy of Sciences report that most of the NMHCs emitted from jet engines contain more than seven carbon atoms, with few emissions in the C<sub>2</sub>-C<sub>5</sub> range [National Academy of Sciences (NAS), 1976]. By contrast, Slemr *et al.* [1998] have recently reported that ethene, ethyne (C<sub>2</sub>H<sub>2</sub>), benzene (C<sub>6</sub>H<sub>6</sub>), and propene had the highest emission indices for NMHCs emitted from a German research aircraft. Emissions of toluene and other alkenes and alkynes were also observed. The findings by Slemr *et al.* are in agreement with work conducted in a test facility by Spicer *et al.* [1994], who found that a wide variety of NMHCs were emitted from two different aircraft turbine engines.

To date, no serious attempt has been made to model the atmospheric impact of aircraft NMHC emissions [Friedl *et al.*, 1997]. Of the carbon-containing compounds emitted from aircraft (CO<sub>2</sub>, CO, and hydrocarbons), CO and hydrocarbons are the most likely to perturb NO<sub>x</sub>/O<sub>3</sub> chemistry [Friedl *et al.*, 1997], because net O<sub>3</sub> production in the troposphere occurs via OH-induced oxidation cycles involving CO, CH<sub>4</sub>, and NMHCs [Ehhalt *et al.*, 1991]. However, the field measurements by Slemr *et al.* [1998] showed that total NMHC

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Paper number 1999JD900750.  
0148-0227/00/1999JD900750\$09.00

emissions from a German research aircraft were below levels required to substantially affect the total amount of  $O_3$  produced in the aircraft emission plume. Although the aircraft emissions of NMHCs are likely to have little impact on the atmosphere [Friedl *et al.*, 1997], it is important to know the background mixing ratios of NMHCs in the flight corridor region. In model calculations, omitting the hydrocarbon chemistry significantly changes the distribution of  $NO_x$  in the troposphere and appreciably reduces the sensitivity of  $O_3$  to aircraft  $NO_x$  [Friedl *et al.*, 1997].

In the fall of 1997, our research group from the University of California, Irvine (UC Irvine) participated in the NASA-sponsored Subsonic Assessment (SASS) Ozone and Nitrogen Oxide Experiment (SONEX). The goal of SONEX was to investigate the atmospheric impact of emissions from subsonic aircraft operating in the North Atlantic Flight Corridor (NAFC). A detailed overview of the SONEX mission is given by Singh *et al.* [1999]. The main UC Irvine objective was to determine whether or not NMHCs are enhanced in the NAFC as a result of subsonic aircraft emissions, with consideration of the location and season in which the samples were collected. In addition, the UC Irvine NMHC and halocarbon data set was used to help identify the origin of the various air masses encountered during the SONEX flights. The NMHC data set also provides background mixing ratios at cruising altitudes, for input into models that estimate the effects of aircraft  $NO_x$  on  $O_3$ .

## 2. Experimental Techniques

During the SONEX mission, 16 research teams flew aboard the NASA DC-8 aircraft on 14 science flights in and around the NAFC, deploying from bases in Bangor, Maine; Shannon, Ireland; and Lajes, Azores (see Singh *et al.* [1999] for flight paths). The NAFC is a major commercial air traffic route, with the 45°-65°N Atlantic region featuring some of the densest air traffic [Singh *et al.*, 1999]. Commercial aircraft operate within an organized tracking system (OTS), whose flight levels are defined every 1000 feet (305 m) from 31,000 to 39,000 feet (9.4 to 11.9 km). The commercial traffic is distributed on those levels every day, although the loading at each level varies from day to day. The most heavily traveled levels are 31,000 feet (9.4 km), 33,000 feet (10.0 km), 35,000 feet (10.7 km), 37,000 feet (11.3 km), and sometimes 34,000 feet (10.4 km). In the NAFC, the main eastbound traffic arrives in Europe in the early morning and the main westbound traffic departs from Europe later in the morning. The results presented here are based upon the three SONEX flights that were specifically designed to sample within and below recently traveled OTS airspace, with deployments between October 18 and November 9, 1997.

The DC-8 payload included equipment to measure meteorological parameters, ozone, nitrogen species, hydrogen oxides, aerosols, and condensation nuclei. The UC Irvine group was responsible for the measurement of NMHC, halocarbon, and alkyl nitrate mixing ratios in ~140 whole air samples collected during each research flight. Seven canister arrays, each consisting of twenty-four 2-L stainless steel canisters, were loaded onto the aircraft prior to each flight. During sampling, outside air was collected from beyond the laminar boundary layer of the aircraft, pressurized by a two-stage metal bellows pump, and distributed via 0.25-inch stainless steel tubing to a gas-handling manifold. The gas-

handling manifold allowed the air to be selectively directed into any given canister. The samples were collected in individual canisters and pressurized to 40 pounds per square inch gauge (psig) (275 kPa).

The whole air samples were collected throughout each flight, roughly every 4 min during horizontal flight legs and every 1.5 to 2 min during vertical legs. The sample collection times ranged from 0.75 to 2.5 min. The longer collection times were used on horizontal flight legs for better spatial coverage, and shorter sampling times were used on vertical flight legs in order to maximize the vertical resolution. On the basis of typical cruising velocities of 830-850 km hr<sup>-1</sup> during horizontal flight legs, a 2-min collection time covered a sampling distance of ~28 km. The vertical sampling distances were of the order of several hundreds of meters. During SONEX, the actual number of samples collected per flight ranged from 134 to 144. A few of the samples were not used in our data analysis, for example, because they were contaminated or became depressurized. A total of 1874 whole air samples were available from the 14 SONEX flights, of which 405 were collected during the three OTS flights.

After each flight, the canister arrays were couriered to our laboratory at UC Irvine for analysis. Within 7 days of being collected, the air samples were analyzed for the NMHCs, halocarbons, and alkyl nitrates using a four-gas-chromatograph (GC), six-column, six-detector analytical system. For each sample, 1772 ± 1 mL (STP) of canister air were used for analysis. The condensable trace gases (including all hydrocarbons except CH<sub>4</sub>) were preconcentrated in a loop that was filled with glass beads and immersed in liquid nitrogen. The loop was then isolated before being warmed to revolatilize the gases. The contents of the loop were flushed using a carrier gas (hydrogen) and were quantitatively split to the six different columns. The fractional split to each column was determined from standards run intermittently with the air samples (every fourth sample). Three flame ionization detectors (FIDs) and three electron capture detectors (ECDs) were used, producing six separate chromatograms for each air sample. More information about the analytical system used during SONEX and in previous airborne missions is given by Sive [1998] and Blake *et al.* [1996a].

The baselines on each chromatogram were individually inspected for selected compounds, including 18 C<sub>2</sub>-C<sub>9</sub> NMHCs, 16 C<sub>1</sub>-C<sub>2</sub> halocarbons, and 5 C<sub>1</sub>-C<sub>4</sub> alkyl nitrates. A complete list of the compounds reported by the UC Irvine group is given in Table 1. The range of accuracies for these 39 gases is 2-20%. The precision of the halocarbon measurement varies by compound and by mixing ratio. For example, the precision for CFC-12 at 550 parts per trillion by volume (pptv) was ±3 pptv, while that for methyl iodide (CH<sub>3</sub>I) at 0.02 pptv was ±0.01 pptv. The measurement precision for the NMHCs was ~1% or 1.5 pptv (whichever was larger) for the alkanes and alkynes and 3% or 3 pptv (whichever was larger) for the alkenes. The limit of detection (LOD) is different for each halocarbon, but none of the 16 halocarbons was below its detection limit at any time during SONEX. We imposed a conservative LOD of 2 pptv for the NMHCs.

## 3. Results and Discussion

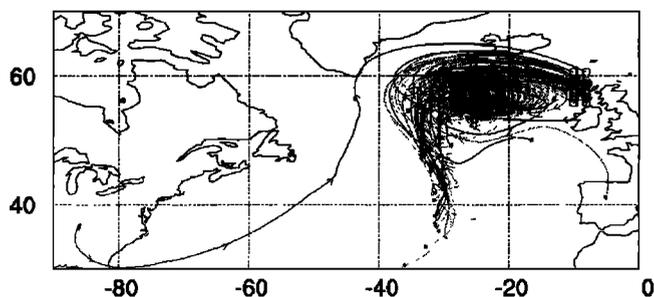
The 14 SONEX flights traced routes both in and around the main NAFC, with additional excursions north as far as 70°N and south to 20°N. On the three OTS flights, the path included

**Table 1.** Compounds Reported by the University of California, Irvine Group During SONEX

Archive Name	Common Name	Chemical Formula
<i>Nonmethane Hydrocarbons</i>		
Ethane	ethane	C <sub>2</sub> H <sub>6</sub>
Ethene	ethylene	C <sub>2</sub> H <sub>4</sub>
Ethyne	acetylene	C <sub>2</sub> H <sub>2</sub>
Propane	propane	C <sub>3</sub> H <sub>8</sub>
Propene	propylene	C <sub>3</sub> H <sub>6</sub>
<i>i</i> -butane	iso-butane	C <sub>4</sub> H <sub>10</sub>
<i>n</i> -butane	<i>n</i> -butane	C <sub>4</sub> H <sub>10</sub>
<i>i</i> -pentane	iso-pentane	C <sub>5</sub> H <sub>12</sub>
<i>n</i> -pentane	<i>n</i> -pentane	C <sub>5</sub> H <sub>12</sub>
me-cyclohexane	methyl cyclohexane	C <sub>7</sub> H <sub>14</sub>
Heptane	<i>n</i> -heptane	C <sub>7</sub> H <sub>16</sub>
Octane	<i>n</i> -octane	C <sub>8</sub> H <sub>18</sub>
Nonane	<i>n</i> -nonane	C <sub>9</sub> H <sub>20</sub>
Benzene	benzene	C <sub>6</sub> H <sub>6</sub>
Toluene	toluene	C <sub>7</sub> H <sub>8</sub>
<i>p</i> -xylene	paraxylene	C <sub>8</sub> H <sub>10</sub>
Ethylbenzene	ethyl benzene	C <sub>8</sub> H <sub>10</sub>
<i>o</i> -xylene	ortho-xylene	C <sub>8</sub> H <sub>10</sub>
<i>Halocarbons</i>		
F-11	CFC-11	CCl <sub>3</sub> F
F-12	CFC-12	CCl <sub>2</sub> F <sub>2</sub>
F-113	CFC-113	C <sub>2</sub> Cl <sub>3</sub> F <sub>3</sub>
F-114	CFC-114	C <sub>2</sub> Cl <sub>2</sub> F <sub>4</sub>
F-22	HCFC-22	CHClF <sub>2</sub>
CH <sub>3</sub> Cl	methyl chloride	CH <sub>3</sub> Cl
CH <sub>2</sub> Cl <sub>2</sub>	methylene chloride	CH <sub>2</sub> Cl <sub>2</sub>
C <sub>2</sub> HCl <sub>3</sub>	trichloroethylene	C <sub>2</sub> HCl <sub>3</sub>
C <sub>2</sub> Cl <sub>4</sub>	perchloroethene	C <sub>2</sub> Cl <sub>4</sub>
CH <sub>3</sub> Br	methyl bromide	CH <sub>3</sub> Br
CH <sub>2</sub> Br <sub>2</sub>	methylene bromide	CH <sub>2</sub> Br <sub>2</sub>
CHBr <sub>3</sub>	bromoform	CHBr <sub>3</sub>
H-1301	halon 1301	CBrF <sub>3</sub>
H-1211	halon 1211	CBrClF <sub>2</sub>
H-2402	halon 2402	C <sub>2</sub> Br <sub>2</sub> F <sub>4</sub>
CH <sub>3</sub> I	methyl iodide	CH <sub>3</sub> I
<i>Alkyl Nitrates</i>		
MeONO <sub>2</sub>	methyl nitrate	CH <sub>3</sub> ONO <sub>2</sub>
EtONO <sub>2</sub>	ethyl nitrate	C <sub>2</sub> H <sub>5</sub> ONO <sub>2</sub>
<i>i</i> -PrONO <sub>2</sub>	<i>i</i> -propyl nitrate	(CH <sub>3</sub> ) <sub>2</sub> CHONO <sub>2</sub>
<i>n</i> -PrONO <sub>2</sub>	<i>n</i> -propyl nitrate	C <sub>3</sub> H <sub>7</sub> ONO <sub>2</sub>
<i>i</i> -BuONO <sub>2</sub>	<i>i</i> -butyl nitrate	(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> CHONO <sub>2</sub>

five or six flight legs at different altitudes, both within and below the designated OTS levels. For example, Flight 7 was a 7-hour local flight off the west coast of Scotland, departing from Shannon on October 23, 1997, at 0600 UT. (As will be described below, the air masses encountered during Flight 7 offered the best opportunity for observing aircraft emissions.) The flight included legs at five standard altitudes, three within the OTS and two below. The timing of Flight 7 sought to intercept emissions from eastbound OTS aircraft, and samples were taken at the end of the peak traffic from that morning. During SONEX, the Goddard Space Flight Center (GSFC) provided plots of 5-day histories of flight corridor encounters over the North Atlantic. For Flight 7, the GSFC plot showed that the levels of aircraft exposure over the previous 5 days exceeded 110 aircraft hours within the sampling area (data accessible at [http://telsci.arc.nasa.gov/~sonex/models\\_gif/](http://telsci.arc.nasa.gov/~sonex/models_gif/)). The more than 110 aircraft hours represents maximum air traffic exposure for air parcels arriving at the sampling region, and they indicate that Flight 7 is well suited for investigating enhancements that result from aircraft emissions.

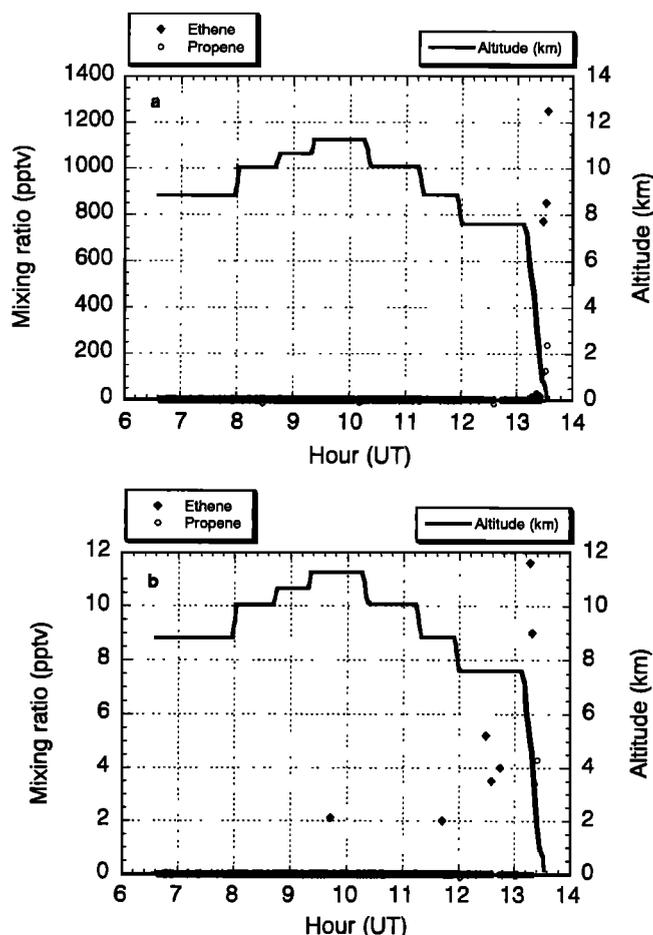
The suite of meteorological and chemical data collected aboard the DC-8 were used to characterize the air masses



**Figure 1.** Florida State University (FSU) 5-day backward trajectories for air encountered in the Flight 7 sampling region north of Ireland for October 23, 1997. Axes are degrees latitude and longitude.

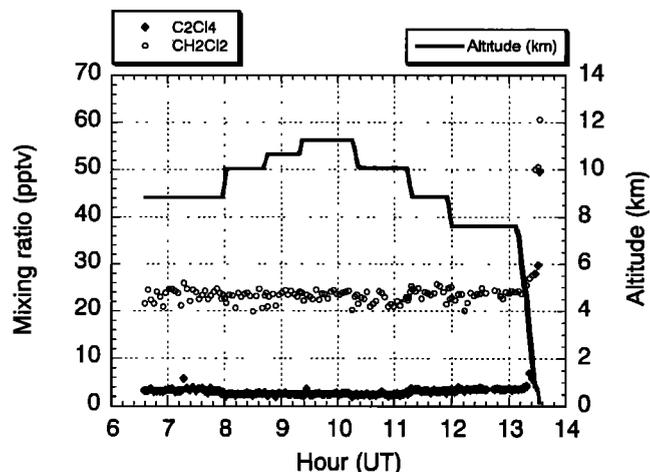
encountered during Flight 7. Several methods were available to estimate the age of the sampled air, i.e., the time since the last contact with anthropogenic emission regions. Five-day backward trajectory plots prepared independently at Florida State University (FSU) and GSFC each showed that typical air encountered during Flight 7 had been recirculating over the Atlantic for at least the past several days (the FSU plot is shown in Figure 1; the GSFC plot is very similar. The procedures used to calculate the FSU trajectories are described by *Fuelberg et al.* [1999]). The mixing ratios of various short-lived NMHCs such as ethene and propene were very low (almost exclusively below detection) at altitude (Figures 2a and 2b), also suggesting that the air was aged. In addition, the [ethyne]:[CO] ratio for Flight 7 samples collected at altitude was 0.8 pptv/ppbv, suggesting that the air was photochemically aged (an [ethyne]:[CO] ratio below 1 pptv/ppbv indicates aged air [*Smyth et al.*, 1996]). Finally, the ratio of a daughter alkyl nitrate to the parent hydrocarbon increases as air ages. For the SONEX data, the ratio of [*i*-butyl nitrate]:[*n*-butane] was around 0.01 pptv/pptv for fresh emissions and around 0.1 pptv/pptv for aged air masses. The Flight 7 ratios clustered around 0.1 pptv/pptv, confirming that the air was well aged. Mixing ratios of anthropogenic halocarbons such as perchloroethene (C<sub>2</sub>Cl<sub>4</sub>) and methylene chloride (CH<sub>2</sub>Cl<sub>2</sub>) were low and showed little variability, indicating that very little recent continental pollution was encountered during Flight 7, with the exception of the landing into Shannon (Figure 3). Further, the sampled air does not appear to have been marine boundary layer air, because none of the marine tracers (e.g., CH<sub>3</sub>I; methyl nitrate - CH<sub>3</sub>ONO<sub>2</sub>; bromoform - CHBr<sub>3</sub>) was elevated (CH<sub>3</sub>I is shown in Figure 4). For example, CH<sub>3</sub>I became elevated only during descent through the marine boundary layer during landing, contrasting with the lower CH<sub>3</sub>I mixing ratios encountered during the remainder of the flight (Figure 4). The low, fairly constant mixing ratios of the marine tracers indicate a lack of recent oceanic convection. Overall, the background air encountered during Flight 7 was found to be clean, well aged, and not recently influenced by surface sources. Thus Flight 7 provides a clean, uniform background against which any NMHC enhancements from aircraft emissions may most readily have been observed.

Analysis of the data collected during SONEX has shown that there is no unique tracer for aircraft emissions [*Thompson et al.*, 1999]. However, nitric oxide (NO) and fine condensation nuclei (CN) enhancements were sometimes correlated in the



**Figure 2.** Mixing ratios of the short-lived gases ethene and propene during Flight 7 of SONEX, October 23, 1997, (a) including high mixing ratios during landing into Shannon and (b) showing detail for the low mixing ratios encountered during most of the flight. Mixing ratios of zero represent values below our detection limit of 2 parts per trillion by volume (pptv).

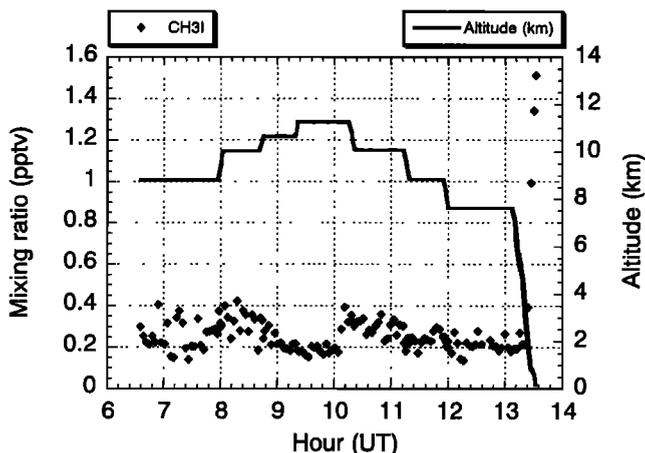
vicinity of flight corridors [Thompson *et al.*, 1999]. During Flight 7, elevated NO and CN were observed throughout the corridor region (altitudes above 9.4 km; Figures 5a and 5b). A combination of elevated NO and CN can result from a variety of sources, including urban influence, biomass burning, lightning, and/or aircraft. The low, constant mixing ratios of the urban tracers  $C_2Cl_4$  and  $CH_2Cl_2$  (Figure 3) and the oceanic (rather than continental) 5-day air mass history together indicate minimal urban influence. Further, the mixing ratios of CO,  $O_3$ , and ethane also were low (for comparison, see Reichle *et al.* [1990], Blake *et al.* [1996b], and Grant *et al.* [this issue] and displayed very little variation (Figures 6a and 6b). Together, these results indicate that the NO and CN enhancements did not result from surface sources. No lightning exposure was forecast for the region throughout Flight 7, and the elevated NO and CN are most likely to have been caused by aircraft. Indeed, Flight 7 showed the highest percentage contribution of aircraft to modeled  $NO_y$  during SONEX, excluding two tail-chase flights of the DC-8's own exhaust (K. E. Pickering *et al.*, unpublished manuscript, 1999).



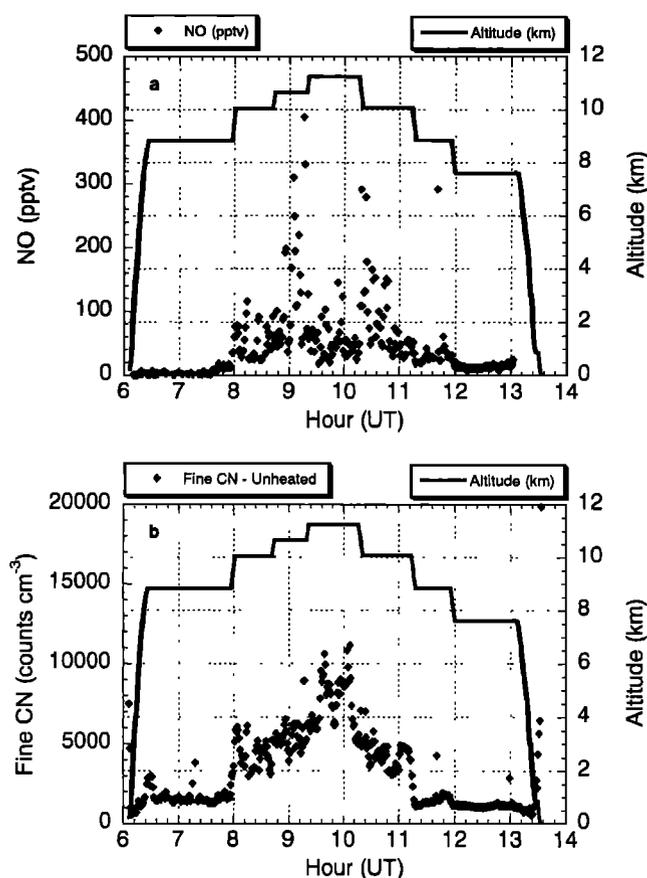
**Figure 3.** Mixing ratios of the urban tracers perchloroethene ( $C_2Cl_4$ ) and methylene chloride ( $CH_2Cl_2$ ) during Flight 7 of SONEX, October 23, 1997.

The hydrocarbons that Slemr *et al.* [1998] identified with the highest aircraft emission indices in jet exhaust have approximate local lifetimes (in days) of 6 (ethene), 145 (ethyne), 56 (benzene), and 1.7 (propene). These lifetimes were calculated for November 1 at  $55^\circ N$  and at a 10-km altitude, i.e., for conditions similar to those of Flight 7 (lifetimes provided by L. Jaeglé, Harvard University, personal communication, 1999). Therefore each gas has a sufficiently long chemical lifetime to remain in the atmosphere between any emission from the main eastbound air traffic of the morning of October 23 and sampling during Flight 7.

In addition to chemical reactivity, plume dispersion is another mechanism by which aircraft emissions become attenuated prior to sampling. However, the question of an aircraft exhaust plume dispersing into the free troposphere applies to both NO and the hydrocarbons, yet NO enhancements remained during Flight 7 despite plume dispersion (Figure 5a). The local lifetime of  $NO_x$  ( $= NO + NO_2$ ) with respect to conversion to nitric acid ( $HNO_3$ ) was 4–6 days for the conditions during the SONEX mission (L. Jaeglé, personal communication, 1999) and is comparable to the local



**Figure 4.** Mixing ratios of the oceanic tracer methyl iodide ( $CH_3I$ ) during Flight 7 of SONEX, October 23, 1997.



**Figure 5.** (a) Nitric oxide (NO) mixing ratios and (b) fine condensation nuclei (CN) counts during Flight 7 of SONEX, October 23, 1997. Each data point represents a 1-min average of 1 Hz data.

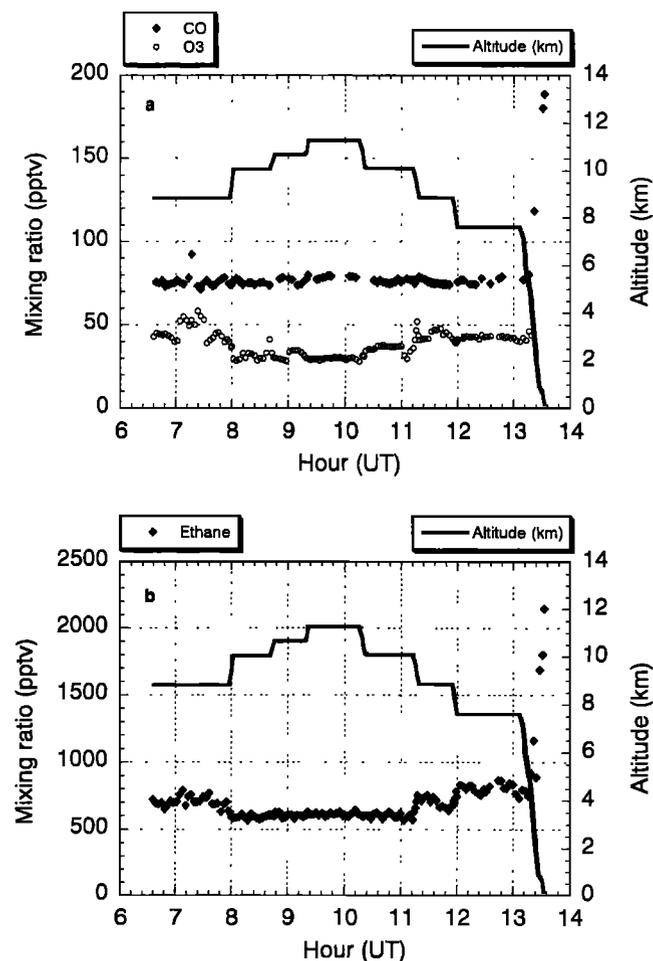
lifetime of ethene, the hydrocarbon with the highest aircraft emission index [Slemr *et al.*, 1998]. Therefore we do not believe that plume dispersion is the reason why hydrocarbon enhancements were not detected during the mission. (We note that NO and NO<sub>2</sub> are interchanged quite rapidly when there is reasonable sunlight, and the lifetime of NO<sub>x</sub> is considered here rather than the very short (seconds) lifetime of NO.)

The mixing ratios of ethyne and benzene remained low and fairly constant throughout Flight 7, with the exception of landing into Shannon (Figures 7a and 7b). (The landing data have been included in order to contrast the low mixing ratios at altitude with the high mixing ratios near an urban area.) The propene mixing ratios were consistently below our detection limit of 2 pptv during Flight 7, again except for landing into Shannon (Figures 2a and 2b). The ethene mixing ratios during Flight 7 were almost exclusively below our detection limit, with the exceptions of the landing and of three episodes of small, nonzero values encountered at altitude (Figures 2a and 2b). Two of the three episodes at altitude were at our detection limit of 2 pptv. The third episode (ethene mixing ratios of 3.2–5.2 pptv) occurred at an altitude below the OTS during the return to Shannon, and it does not appear that the nonzero ethene mixing ratios resulted from aircraft exposure. In previous missions, our group has experienced ethene growth within our sampling canisters. Here it has not been possible for us to determine whether the nonzero ethene mixing ratios

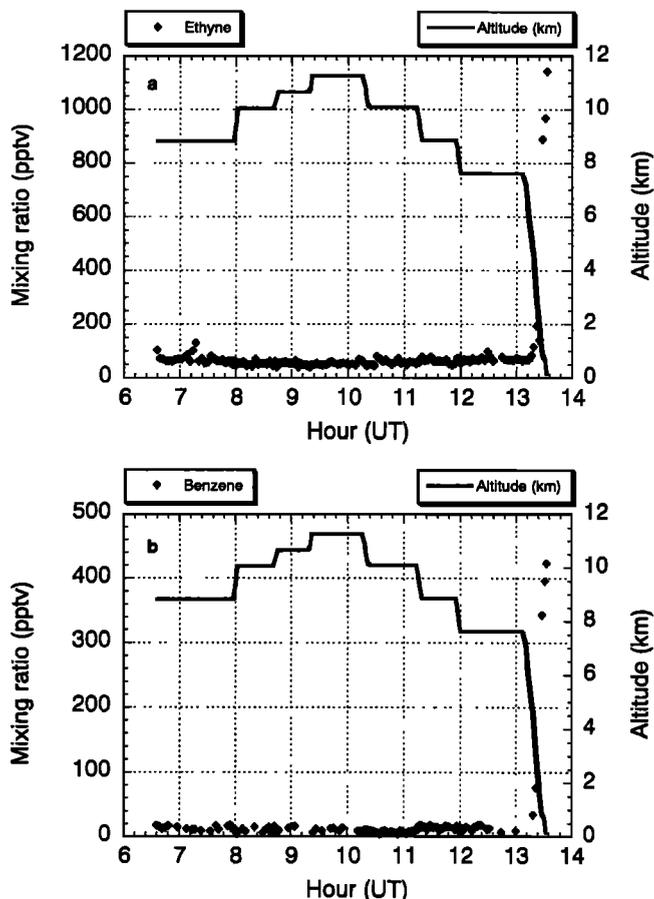
at altitude are artifacts from our canisters or real values. We have chosen to include these five mixing ratios in Figures 2a and 2b for completeness. The C<sub>2</sub>–C<sub>9</sub> alkanes also remained low and fairly uniform at altitude during Flight 7 (e.g., ethane, see Figure 6b). Overall, we did not observe enhancements from aircraft in any of the measured NMHCs during Flight 7, including four major NMHCs (ethene, ethyne, benzene, and propene) which aircraft have been reported to emit.

In addition to using a combination of NO, CN, whole air samples, and meteorological data to identify aircraft emissions, Thompson *et al.* [1999] have used the ratio of NO to total nitrogen (NO<sub>y</sub>) in cases where there is no evidence for lightning or recent convective influence (e.g., Flight 7). Thompson *et al.* tried limits of both [NO/NO<sub>y</sub>] > 0.2 and [NO/NO<sub>y</sub>] > 0.3 as cutoffs for aircraft influence. Here we compared pairs of means for CN, CO, ethene, ethyne, propene, and benzene for data conservatively binned by [NO/NO<sub>y</sub>] < 0.2 (no aircraft exposure) and [NO/NO<sub>y</sub>] > 0.3 (aircraft exposure). The fine condensation nuclei was the only one of these six compounds to show statistical enhancements for [NO/NO<sub>y</sub>] > 0.3 versus [NO/NO<sub>y</sub>] < 0.2 (Table 2). These results confirm that aircraft emissions did not give rise to enhancements in NMHCs or CO during Flight 7.

In addition to Flight 7, Flights 5 and 14 also featured encounters within and below recently traveled OTS airspace.



**Figure 6.** Mixing ratios of (a) carbon monoxide (CO) and ozone (O<sub>3</sub>) and (b) ethane during Flight 7 of SONEX, October 23, 1997.



**Figure 7.** Mixing ratios of (a) ethyne and (b) benzene during Flight 7 of SONEX, October 23, 1997.

Flight 5 was a local deployment from Shannon in the region west of Ireland, just after the peak of westbound traffic. Flight 14 was a local excursion from Bangor, also after the peak of westbound traffic. For both flights, we attempted to identify enhancements of NO and CN caused by aircraft exposure in a manner similar to that for Flight 7. However, we were unable

**Table 2.** Mean ( $\pm 1$  Standard Deviation) Fine Condensation Nuclei (CN), Carbon Monoxide (CO), Ethene, Ethyne, Propene, and Benzene During Episodes of Aircraft Exposure ( $\text{NO}/\text{NO}_y > 0.3$ ) and Episodes Without Aircraft Exposure ( $\text{NO}/\text{NO}_y < 0.2$ )

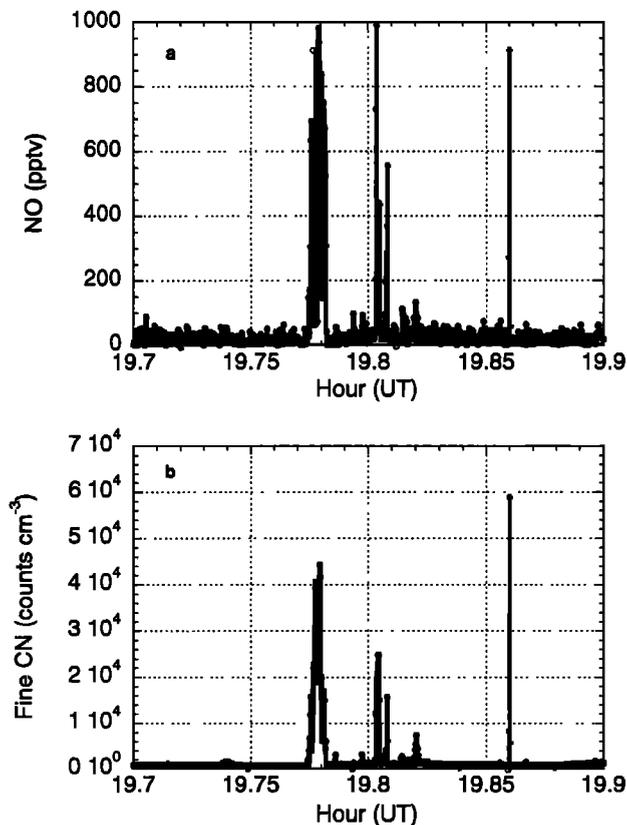
Species	Mean and Standard Deviation	$[\text{NO}/\text{NO}_y]$
CN	$1548 \pm 657$ (40)	$< 0.2$
	$5630 \pm 1751$ (22)	$> 0.3$
CO	$75.6 \pm 1.5$ (30)	$< 0.2$
	$76.3 \pm 1.8$ (16)	$> 0.3$
Ethene	$0.7 \pm 1.7$ (13)	$< 0.2$
	$0.0 \pm 0.0$ (16)	$> 0.3$
Ethyne	$66 \pm 8$ (31)	$< 0.2$
	$53 \pm 6$ (22)	$> 0.3$
Propene	$0.0 \pm 0.0$ (31)	$< 0.2$
	$0.0 \pm 0.0$ (22)	$> 0.3$
Benzene	$13 \pm 3$ (18)	$< 0.2$
	$10 \pm 3$ (13)	$> 0.3$

The data used in this analysis were retrieved from the SONEX 5-min data merge for Flight 7. The number of data points in each average is given in parentheses.

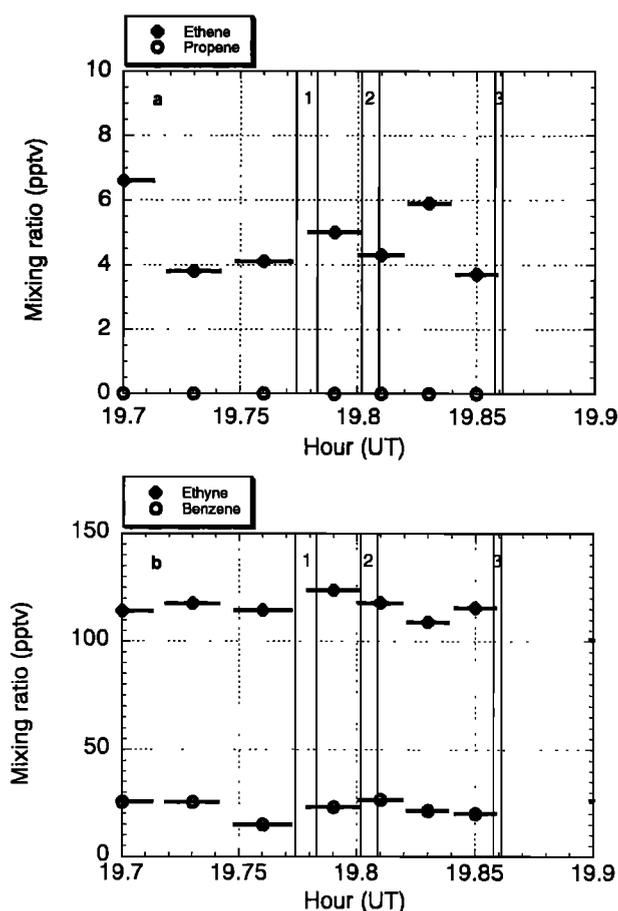
to clearly interpret the Flight 14 data because considerable convection and lightning influence confounded the aircraft signatures. During both Flights 5 and 7, no instances of elevated NMHC mixing ratios were observed during episodes of enhanced NO and CN that were determined to result from aircraft exposure (data from Flight 5 are not shown). That is, aircraft emissions did not cause enhancements in NMHC mixing ratios in the North Atlantic Flight Corridor during the fall.

Similarly, Slemr *et al.* [1998] did not detect enhancements of individual NMHCs within a few kilometers of emitting aircraft. However, Slemr *et al.* measured elevated NMHC mixing ratios in the direct wake of a German research aircraft, at a following distance of 75–1300 m. Specifically, benzene, toluene, and several alkenes and alkynes were enhanced by about an order of magnitude in the exhaust plume of the emitting aircraft. In order to directly encounter an aircraft exhaust plume during SONEX, Flights 13 and 15 included "tail chases" of the DC-8's own exhaust. Encounters with the exhaust plumes were clearly identified by elevated NO and CN (e.g., Flight 13; Figures 8a and 8b). By contrast, enhancements were not detected for any of the measured NMHCs for either tail chase (selected NMHCs from Flight 13 are shown in Figures 9a and 9b).

The plume encounters were short (2 to 25 s) compared to the 50 to 80 s collection times for the whole air samples. The horizontal lines in Figures 9a and 9b represent these whole air sampling times, and the enclosed areas labeled 1, 2, and 3 denote the intervals of the three prominent NO and CN



**Figure 8.** (a) Nitric oxide (NO) mixing ratios and (b) fine condensation nuclei (CN) counts during the tail chase of Flight 13 of SONEX, November 5, 1997. Encounters with the DC-8 exhaust plumes are evident in the elevated NO and CN data.



**Figure 9.** Selected nonmethane hydrocarbon (NMHC) mixing ratios during the tail chase of Flight 13 of SONEX, November 5, 1997, showing (a) ethene and propene and (b) ethyne and benzene. The propene mixing ratios of zero represent values below our detection limit of 2 pptv. The enclosed areas labeled 1, 2 and 3 indicate overlap with the three prominent NO and CN enhancements seen in Figures 8a and 8b.

enhancements seen in Figures 8a and 8b. Together, they indicate which whole air samples coincided with the aircraft exhaust plumes (in the discussion that follows, the coincident whole air samples are correspondingly named 1, 2, and 3). The NMHC mixing ratios were not elevated in the three Flight 13 whole air samples that featured some overlap with the aircraft plumes (Figures 9a and 9b). Indeed, in both Flights 13 and 15, no NMHC enhancements were encountered that were large enough to be detected within the diluted whole air sample.

To better understand the effect of dilution of the exhaust sample within the longer canister fill time, we have calculated the temporal overlap of the NO enhancements and the canister samples in more detail. We recall that there is no unique tracer for aircraft emissions [Thompson *et al.*, 1999], and we used the limits of both  $[\text{NO}/\text{NO}_y] > 0.2$  and  $[\text{NO}/\text{NO}_y] > 0.3$  that were applied above as cutoffs for aircraft exposure. The three canister samples that overlapped with the plume encounters of Flight 13 had fill times of 77, 64, and 59 s, for canister samples 1, 2, and 3, respectively (Figures 9a and 9b). The NO and  $\text{NO}_y$  data were collected at 1 Hz, and an  $[\text{NO}/\text{NO}_y]$  ratio was calculated for each second of canister fill time. The number of 1 s  $[\text{NO}/\text{NO}_y]$  ratios greater than 0.2 were summed as were the

number of ratios greater than 0.3. For example, for canister sample 1, 13 out of 77  $[\text{NO}/\text{NO}_y]$  ratios were greater than 0.3 and 16 were greater than 0.2. That is,  $13/77 = 17\%$  of the canister fill time overlapped with exhaust plumes when the more conservative aircraft influence cutoff of  $[\text{NO}/\text{NO}_y] > 0.3$  was used, and  $16/77 = 21\%$  overlap was calculated when the cutoff was relaxed to include  $[\text{NO}/\text{NO}_y] > 0.2$ . Similarly, canister sample 2 featured 16-27% temporal overlap with the plume encounter, and canister sample 3 had 7-19% overlap.

The whole air samples 1 and 2 overlapped with the plume encounters at the start of sampling, whereas the whole air sample 3 overlapped at the end of sampling (Figures 9a and 9b). There is a nonlinear relation between sample size and sample time as the canister fills to 40 psig (275 kPa) and the pumping capacity diminishes. That is, the measured mixing ratios are effectively weighted toward the values in the air that was collected at the start of the sample. Thus samples 1 and 2 offer the best opportunity for detecting hydrocarbon enhancements, both because they feature more overlap with the plume encounters than sample 3 and because the overlap occurred at the start of the canister filling, rather than at the end. We do not know the nonlinear function that describes how the sample filling changes with time (the relationship is complicated by flow-regulating valves on our gas-handling manifold). However, at altitude our experience is that filling the last 10 psig (70 kPa) takes as long as the first 45 psig (310 kPa) (the starting pressure inside the canisters is -15 psig (-105)). If we consider only samples 1 and 2 and use the calculated (linear) temporal overlaps of roughly 20% as the most conservative scenario (the maximum possible dilution within these canisters), the samples would feature 1 part of plume air diluted by 4 parts of background air. During the plume encounters, the NO mixing ratios reached values as high as 1000 ppbv against background values of less than 100 ppbv or roughly an order of magnitude increase. For the hydrocarbons, a similar order of magnitude enhancement of 20 pptv against a background of 2 pptv, would give a measured mixing ratio of at least 5.6 pptv. That is, hydrocarbon enhancements of the order of those of NO are larger than the precision of our measurement and would have been detected within the diluted whole air samples, even within this conservative scenario. The nonlinearity of the canister filling would have caused any hydrocarbon enhancements to appear even more prominently in whole air samples 1 and 2. However, such enhancements were not evident in the tail-chase data.

The NMHC results are in agreement with CO data that were collected during SONEX. Carbon monoxide is an excellent indicator of incomplete combustion, and CO was sampled at a high frequency (1 Hz). Therefore any aircraft emissions resulting from incomplete combustion would have been detected in the CO signal. The precision of the CO measurements was 1 ppbv, based upon a 1-s sampling period. However, CO enhancements caused by aircraft were rarely encountered during SONEX (the enhancements ranged from 1.4 to 2 ppbv, and they occurred with concurrent increases in  $\text{CO}_2$  and  $\text{NO}_y$  mixing ratios). Only one case of elevated CO resulting from aircraft was detected during the two tail chases (NMHCs collected at the same time did not exhibit mixing ratio enhancements). Just two additional episodes of enhanced CO resulting from aircraft were identified during the entire SONEX mission. The results suggest that the air fleet in the NAFC is clean burning with respect to both NMHCs and CO.

The SONEX mission was deployed during the fall of 1997, and the results must be considered with respect to seasonality. Although seasonal variations in aircraft emissions are generally small, summer emissions of aircraft  $\text{NO}_x$  in the North Atlantic area are up to 35% larger than winter emissions [Friedl *et al.*, 1997]. During the time frame of the SONEX campaign,  $\text{NO}_x$  emissions were within a few percent of the annual average in the North Atlantic region [Friedl *et al.*, 1997]. Therefore the SONEX results presented in this paper may be considered as close to neutral with respect to seasonal differences. During summer, the 35% larger  $\text{NO}_x$  emissions raise the question of seasonality in NMHC emissions. However, given that no NMHC enhancements were measured even during the DC-8 tail chase, we expect that dispersion and efficient summertime photochemistry would prevent any additional summertime NMHC emissions from being detected in the general NAFC. During winter, any gases emitted from commercial aircraft may be expected to persist longer because of the reduced oxidative capacity in the north temperate and polar zones. For example, a northern survey (to 70°N) along the Norwegian coast during SONEX showed higher mixing ratios of numerous NMHCs (e.g., alkanes, alkenes, alkynes, benzene), most likely because of less efficient removal by hydroxyl (data not shown). Any NMHCs emitted from aircraft during the winter would be expected to persist longer, superimposed upon a higher background mixing ratio.

The NMHC results discussed in this paper were dominated by measurements in the upper troposphere. However, 17% of aircraft emissions are reported to occur in the lower stratosphere [Baughcum, 1996]. The atmospheric residence times for NMHCs are expected to be longer in the lower stratosphere than in the upper troposphere, in part because of less efficient removal by hydroxyl. During SONEX, one of the three OTS flights (Flight 5) included encounters with stratospheric air. NMHC enhancements over background mixing ratios were not detected in either the upper troposphere or in the lower stratosphere (data not shown). That is, NMHC enhancements resulting from less efficient removal in the stratosphere were not evidenced in our samples.

We anticipate that aircraft emissions into the stratosphere will occur predominantly during the winter, because the tropopause height is lower. The emissions of NMHCs into the stratosphere may persist longer in the winter not only because NMHC residence times are longer in the lower stratosphere than in the upper troposphere but also because NMHC residence times are longer in the winter than during the summer. The direct emissions by aircraft into the stratosphere may become increasingly important in the near future, because of new engines that will allow commercial aircraft to operate at higher altitudes [Fabian and Kärcher, 1997].

Aviation is one of the fastest growing economies in the world, and global jet fuel consumption is expected to grow by ~3% per year over the next decade [Fabian and Kärcher, 1997]. The SONEX mission took place in the North Atlantic Flight Corridor, where 7% of the global jet fuel is burned [Friedl *et al.*, 1997]. Three other major geographical regions (North America, Europe, and the North Pacific) comprise 30, 17, and 9% of the total aircraft fuel burned, respectively [Friedl *et al.*, 1997]. The largest growth rates for future global jet fuel consumption are expected in the east Pacific [Fabian and Kärcher, 1997]. The NMHCs emitted in a given region will depend upon both the total amount of fuel consumed and the efficiency at which the aircraft engines operate. The SONEX

results showed that aircraft operating in the NAFC are clean burning with respect to NMHCs. However, it is possible that the commercial air fleets operating in other geographical regions are less efficient with respect to fuel combustion or may emit higher levels of NMHCs for a given amount of fuel consumed. By contrast, if aircraft efficiency and fuel usage are similar in all geographical regions, then little or no NMHC emissions may be expected. Continued studies will be needed to monitor possible changes of aircraft emissions and their impact on the atmosphere.

#### 4. Summary and Conclusions

Nonmethane hydrocarbon (NMHC) emissions from commercial aircraft were investigated between October 18 and November 9, 1997, in the North Atlantic Flight Corridor (NAFC). The results presented here are a subset of 1874 whole air samples collected during 14 flights aboard the NASA DC-8 research aircraft. The investigation was part of the larger Subsonic Assessment (SASS) Ozone and Nitrogen Oxide Experiment (SONEX). The flights spanned a large part of the North Atlantic region, and samples were collected both in and below the organized tracking system (OTS) and in the upper troposphere and lower stratosphere. The samples were analyzed in our laboratory at the University of California, Irvine, for 18  $\text{C}_2$ - $\text{C}_9$  NMHCs, 16  $\text{C}_1$ - $\text{C}_2$  halocarbons, and 5  $\text{C}_1$ - $\text{C}_4$  alkyl nitrates. Episodes of aircraft exposure were identified using a combination of elevated nitrogen oxides, elevated condensation nuclei, whole air sampling data, backward trajectories, and aircraft and lightning exposure plots. NMHC enhancements were not detected within the OTS of the NAFC nor on a finer scale during two tail chases of the DC-8's own exhaust. The results suggest that the commercial air traffic operating in the NAFC is clean burning with respect to NMHCs.

**Acknowledgments.** It is a pleasure to thank the research team at UC Irvine for their outstanding work throughout the SONEX mission, especially Pasquale Avino, John Bilicska, Nancy Ciszkowski, Adam Hill, Paul Holler, Jenn Lapierre, Brent Love, Murray McEachern, and Barbara Yu. We are also grateful to the ground and flight crews from NASA Ames, who were always available and willing to help. We would like to thank Brian Ridley, Hanwant Singh, and Jonah Colman for helpful consultations during the preparation of this manuscript, and two anonymous reviewers for their constructive input. The SONEX 5-min data merge and the NMHC and NO lifetimes were generated by Lyatt Jaeglé. The research was funded by NASA grant NAG-2-1102.

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(Received April 8, 1999; revised June 30, 1999;  
accepted July 9, 1999.)