

# The seasonal evolution of NMHCs and light alkyl nitrates at mid to high northern latitudes during TOPSE

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**Abstract.** The Tropospheric Ozone Production about the Spring Equinox (TOPSE) experiment was designed to follow the evolution of the previously observed springtime maximum of tropospheric ozone in the Northern Hemisphere (NH) at high latitudes. The tropospheric ozone (O<sub>3</sub>) maximum is thought to have a combination of in-situ photochemical and dynamic origins. Mixing ratios of a large number of C<sub>2</sub>-C<sub>10</sub> nonmethane hydrocarbons (NMHCs), selected C<sub>1</sub>-C<sub>2</sub> halocarbons, and C<sub>2</sub>-C<sub>4</sub> alkyl nitrates were quantified in whole air samples collected aboard the NCAR C-130 aircraft between early February and mid May 2000. These measurements revealed strong latitudinal, vertical, and temporal gradients for the NMHCs. In the mid-troposphere north of Churchill (58°N), ΣNMHCs decreased by ~ 6.2 ppbC between February and March (1.6 ppbC/month). This change diminished with altitude. At the same time, mid-

tropospheric O<sub>3</sub> levels increased by ~ 16 ppb (4.2 ppbv/month). The alkyl nitrates, which are a reservoir species for tropospheric reactive odd nitrogen (NO<sub>y</sub>), revealed similar latitudinal, vertical, and temporal gradients to their parent NMHCs. Their total decreased by ~4 ppt/month and they constituted 10% or less of NO<sub>y</sub>. In conjunction with meteorological trajectory analysis, different trace gas signatures provided significant clues to the origins of individual polluted air masses. Several of these air masses were rapidly advected across the Pole from source regions in Northeastern and Western Europe, as well as an air mass that originated over the southwestern US/Baja California that contained unusually high levels of alkanes. In addition, episodes of low boundary layer O<sub>3</sub> associated with low NMHC mixing ratios and trajectories from over the Arctic Ocean were frequently sampled towards the latter part of the experiment. Overall, the TOPSE experiment provided a macroscopic picture of N.H. trace gas evolution from winter to summer and demonstrated that the build-up of anthropogenically released light NMHCs have the potential to play a major role in high latitude ozone chemistry.

## **1. Introduction**

One of the major stated goals of TOPSE was to determine the composition and seasonal evolution of volatile organic carbon (VOC) species in the troposphere at northern mid-latitudes and their significance to a springtime ozone maximum. Organic carbon provides fuel for ozone production, and nitrogen oxides (NO<sub>x</sub> = NO + NO<sub>2</sub>) act as photochemical catalysts. Therefore, NMHCs are key species in the photochemical production of tropospheric ozone, and directly influence hydroxyl radical concentrations. Atmospheric measurements indicate a buildup of a wide range of NMHCs in late winter

to early spring in the lower, middle, and even in the upper Northern Hemisphere (NH) troposphere [e.g., *Singh and Salas*, 1982; *Hov et al.*, 1984; *Blake and Rowland*, 1986; *Penkett et al.*, 1993; *Anderson et al.*, 1993; *Blake et al.*, 1997]. This buildup appears to prime the atmospheric chemical system for a burst of photochemical oxidant production when insolation, temperatures, and circulation patterns change in early spring. Previous aircraft measurements by *Penkett et al.* [1993] showed that the maximum in ozone lags the maximum in NMHC by several months, and is thus qualitatively consistent with enhanced photochemistry contributing to the spring maximum in O<sub>3</sub>. However, this conclusion was based on relatively few measurements.

NMHC sources are predominantly land based [*Singh and Zimmerman*, 1992; *Plass-Dulmer et al.*, 1995], and the main sink for hydrocarbons and halocarbons with abstractable hydrogen atoms, denoted below as RH, is through oxidative reaction with hydroxyl radicals (OH):



Because the rate of reaction (1) differs significantly among the various NMHCs, their tropospheric lifetimes vary widely. Concentration ratios of the different gases offer important information about their sources [e.g., *Blake et al.*, 1994] while changing concentrations can provide insight into photochemical processing and mixing [e.g., *McKeen et al.*, 1996; *Wingenter et al.*, 1996, 1999].

Abundant sunlight and high humidity favor the photochemical production of OH, so its concentration varies diurnally, seasonally, and spatially. Minimum OH levels are found at high latitudes during winter, causing significantly reduced removal rates for many trace gases. Consequently, those gases with substantial emissions maintained

throughout the year exhibit maximum background levels in late winter, with minimum levels occurring during late summer. This seasonal variation in boundary layer (BL) concentrations has been reported for many NMHCs and  $C_2Cl_4$  [e.g., *Singh and Salas*, 1982; *Singh et al.*, 1988; *Hov et al.*, 1984; *Blake and Rowland*, 1986; *Lightman et al.*, 1990; *Hov et al.*, 1991; *Penkett et al.*, 1993; *Jobson et al.*, 1994a; *Goldstein et al.*, 1995; *Wang et al.*, 1995; *Blake et al.*, 1997; *Gupta et al.*, 1998]. Relatively few seasonal airborne, or non-boundary layer, measurements have been made [*Lightman et al.*, 1990; *Ehhalt et al.*, 1985, 1991; *Penkett et al.*, 1993; *Anderson et al.*, 1993; *Blake et al.*, 1997].

Many of the trace gases we report are uniquely anthropogenic and are released predominantly in urban areas, so that their levels can be used to estimate recent anthropogenic influence on an air mass. Industrial activity is indicated by elevated concentrations of gases such as  $C_2Cl_4$  [*Crutzen*, 1980; *Rasmussen*, 1982; *Blake et al.*, 1994, 1996a; *Blake et al.*, 1997]. Natural gas emissions are associated with elevated levels of methane, ethane, and other light alkanes, with no accompanying halocarbons [*Blake et al.*, 1994]. Liquefied petroleum gas (LPG) leakage is likely the largest source of atmospheric propane and the butanes [*Blake and Rowland*, 1995], and petroleum refining activities emit mostly ethane, propane and other alkanes [*Sexton and Westberg*, 1979]. Methyl nitrate has a tropical ocean source [*Atlas et al.*, 1997; *Ridley et al.*, 1997; *Blake et al.*, 2001a] in addition to a small atmospheric photochemical source [*Roberts et al.*, 1998].

## 2. Experiment

During TOPSE, we collected more than 2500 whole air samples in 2-liter stainless steel canisters. Canisters were filled on the NCAR C-130 aircraft, transported to our home laboratory, the samples were assayed, and then the canisters were evacuated and sent back to the field. We sampled every 6-7 minutes during the horizontal flight legs, and every 1-3 minutes during selected vertical profiles, filling a maximum of 96 canisters per flight.

Details of the analytical procedures employed by the UCI laboratory can be found in *Sive* [1998] and *Colman et al.* [2001]. For each sample  $1520 \pm 1$  cm<sup>3</sup> (STP) of air was preconcentrated in a liquid nitrogen-cooled loop. This sample was directed to five different gas chromatographic columns. The first column-detector combination (abbreviated as "DB5ms/MSD") was a DB-5ms column (J&W; 60 m, 0.25 mm I.D., 0.5- $\mu$ m film thickness) output to a quadrupole mass spectrometer detector (MSD) (HP-5973). The second combination ("DB1/FID") was a DB-1 column (J&W; 60 m, 0.32 mm I.D., 1- $\mu$ m film thickness) output to a flame ionization detector (FID) (HP-6890). The third combination ("PLOT-DB1/FID") was a PLOT column (J&W GS-Alumina; 30 m, 0.53 mm I.D.) connected in series to a DB-1 column (J&W; 5 m, 0.53 mm I.D., 1.5- $\mu$ m film thickness) and output to an FID. The fourth combination (Restek1701/ECD) was a RESTEK 1701 column (60 m, 0.25 mm I.D., 0.50- $\mu$ m film thickness), which was output to an ECD. The fifth combination (DB5-Restek1701/ECD) was a DB-5 (J&W; 30 m, 0.25 mm I.D., 1- $\mu$ m film thickness) column connected in series to a RESTEK 1701 column (5 m, 0.25 mm I.D., 0.5- $\mu$ m film thickness) and output to an ECD. The

DB5ms/MS, DB1/FID, PLOT-DB1/FID, Restek1701/ECD, and DB5-Restek1701/ECD combinations received 10.1, 15.1, 60.8, 7.2, and 6.8% of the sample flow, respectively.

Our analytical accuracy ranges from 2 to 20%. The precision of the measurements varies by compound and by mixing ratio. For example, the measurement precision is 1% or 1.5 pptv (whichever is larger) for the alkanes and alkynes, and 3% or 3 pptv (whichever is larger) for the alkenes [Sive, 1998]. The precision for the alkyl nitrates was better than 2% at the levels observed during TOPSE. The precision for  $C_2Cl_4$  at 5 pptv is  $\pm 0.05$  pptv [Colman *et al.*, 2001]. The limit of detection (LOD) is 3 pptv for the NMHCs.  $C_2Cl_4$  was present at mixing ratios well above its detection limit at all times. The canister air was also analyzed for CO using GC with FID, as described by Hurst [1990].

TOPSE made experimental observations over a very wide range of environmental and dynamic conditions during the entire winter-to-spring transition. The altitude range of the NCAR C-130 flying laboratory was 30 m to 8 km. Sampling took place at approximately biweekly intervals from early February to mid May 2000 in a series of 7 round trip deployments from Colorado (40°N) to Churchill, Canada (58°N); Thule (77°N) in northern Greenland; and as far north as 85°N [Atlas *et al.*, this issue]. The trips were as follows: Deployment 1, February 4-9 (Flights 5-8); Deployment 2, February 21-27 (Flights 9-13); Deployment 3, March 5-8 (Flights 14-17); Deployment 4, March 19-26 (Flights 18-23); Deployment 5, April 2-7 (Flights 24-30); Deployment 6, April 23-30 (Flights 31-36); and Deployment 7, May 15-23 (Flights 37-42). Most of these deployments got far enough north to land at Thule, but Deployments 1 and 3 were limited to local flights out of Churchill [Atlas *et al.*, this issue].

### 3. Large Scale Seasonal Evolution:

#### 3.1 Latitudinal Variation

To get a "big picture" view of the seasonal evolution of trace gases during the 7 TOPSE deployments the mid-troposphere data (1-6 km) for each deployment are divided by latitude into 5° bins. The median mixing ratios for each bin are plotted to reduce the impact of individual pollution plumes and stratospheric intrusions (Plates 1-4). (BL concentration trends are discussed in *Sive et al.*, this issue])

In general, the NMHCs show a strong latitudinal gradient, with consistently lower median mixing ratios south of 45°N for all gases (Plate 1). The rate of seasonal decrease in mixing ratios is proportional to OH reactivity, i.e., ethane, which is the longest-lived NMHC with a summer lifetime of about 70 days (much longer in winter) shows very little decrease until late in the project. In early April (Deployment 5), ethane still manifested high mixing ratios at all latitudes north of 50°N. The levels were reduced somewhat from early April to mid May (Deployment 7), but ethane maintained a slight latitudinal gradient, with higher northerly values. This is consistent with what we know from other projects [e.g., *Penkett et al.*, 1993; *Swanson et al.*, 2001] i.e., that long-lived ethane typically decreases relatively slowly in spring, and does not reach its summer minimum until August.

Ethyne, the next longest-lived gas shown (summer lifetime ~18 days), also did not change significantly until after the early April trip (Deployment 5), and its mixing ratios at the highest latitudes remained elevated into late April (Deployment 6) (Plate 1). By contrast, levels of propane (summer lifetime ~13 days) decreased faster and were depleted over a wider latitude range by Deployment 6. In fact, the latitude gradient for

propane disappeared by the end of the TOPSE period. This negative gradient is consistent with a strong NH mid-latitude continental source of propane, combined with a short summer lifetime relative to transport times to remote high latitudes.

Butane is removed much faster at all latitudes and is reduced to very low levels by early April (Plate 1). Its initially strong latitudinal gradient is almost gone by late April (Deployment 6) except at the highest latitudes. By mid May (Deployment 7), n-butane mixing ratios also established a negative latitude gradient, with even lower median levels in the Arctic troposphere than near Colorado. This is because the Arctic region late in the spring is relatively remote, i.e., the travel time of air masses from mid-latitude source regions is long compared to butane's summer atmospheric lifetime (about 5 days).

The change in total carbon over all C<sub>2</sub>-C<sub>8</sub> NMHCs (mixing ratio x number of carbons in molecule) as a function of latitude illustrates the composite picture of the winter reactive carbon reservoir being gradually depleted further and further north (Plate 2). In general, highest concentrations were sampled in early February and gradually decreased as the season progressed.

The sum of the light alkyl nitrates maintained a remarkably constant latitudinal gradient throughout Deployments 1-5, with generally highest levels to the north of 50°N (Plate 2). However, these high levels were significantly diminished by Deployment 6, and a slightly negative latitudinal gradient was observed in Deployment 7. This temporal change is comparable to that observed for n-butane (Plate 1) and is consistent with the strong NH mid-latitude continental source of the precursor NMHCs, combined with short summer lifetimes for the C<sub>3</sub> and C<sub>4</sub> alkyl nitrates. Not surprisingly, 2-butyl nitrate makes the largest contribution to the temporal mixing ratio change in total C<sub>2</sub>-C<sub>4</sub> alkyl nitrates at



high northern latitudes (Plate 3). By contrast, methyl nitrate only contributes a very small fraction (less than 1.5 pptv) (Plate 3), in accord with the observations of *Swanson et al.* [2001] from atop the Greenland ice sheet. Although methyl nitrate has only weak continental sources [*Roberts et al.*, 1998; *Blake et al.*, 2001a] this gas also exhibits a negative latitudinal gradient during Deployment 7 (Plate 3). The ocean, in particular the equatorial Pacific, is known to be an important source of methyl nitrate [*Atlas et al.*, 1997; *Blake et al.*, 2001a], so long-range transport from low-latitudes probably account for the observed methyl nitrate gradient.

CO is relatively long-lived, with a similar lifetime to that of ethane. However, Plate 4 shows a poorly defined temporal trend, except that the last deployment represents the lowest northern mixing ratios (see also *LaMarque and Hess* [this issue] and *Klonecki and Hess* [this issue]). Unlike ethane and the other NMHCs, atmospheric VOC oxidation contributes to the CO budget (40% over North America) [*Chin et al.*, 1994]. This CO production, especially during the mid-spring period of rapid reaction of short-lived NMHCs may be responsible for maintaining relatively high CO levels until late in the spring.

The principal source of CO in the NH is combustion, so typically it is tightly correlated with ethyne (also a combustion tracer). However, the different atmospheric lifetimes of the two gases mean that ethyne/CO ratios decrease with time compared to initial ratios near the source, or more accurately, with advancing “photochemical age” of an air mass. The ethyne/CO ratio has previously been used as an “index” against which to reference the atmospheric trends of the NMHCs and halocarbons [e.g., *Smyth et al.*, 1996; *Blake et al.*, 1997, 1999]. Ethyne/CO ratios tend to be low over Colorado (Plate 4)

because most air masses sampled here had been advected from further south, so had been subject to high levels of OH [Merrill *et al.*, this issue]. Although the southernmost ethyne/CO ratios decrease with increasing strength of sunlight, the biggest changes are seen further north. The long winter lifetime of ethyne explains the observation that ethyne/CO ratios are close to values that are typical of initial emissions (4 pptv/ppbv) to the north of 45°N for Deployment 1. Over the TOPSE period, the lifetime of ethyne gradually decreases until the ethyne/CO ratio indicates well processed/photochemically aged air at all latitudes by the final (mid May) Deployment (#7).

### **3.2. Vertical and Temporal Trends**

The strong latitudinal gradients presented above, especially during the early part of the TOPSE period (Plate 1) prompted us to segregate out the low latitude samples for the following analysis of vertical trends. We arbitrarily chose to focus on the data to the north of Churchill (58°N) and further divided these data into 1 km altitudinal bins (Plates 5-7). The temporal trend plots shown in Plates 8-10 further exclude data collected below 1 km (in order to avoid direct influence from ozone depletion events [Ridley *et al.*, this issue; Sive *et al.*, this issue]), as well as above 6 km (to reduce the direct impact of stratospheric air [Browell *et al.*, this issue; Dibb *et al.*, this issue]).

The early part of the TOPSE period was characterized by strong vertical gradients for ethane, propane, ethyne, and n-butane north of 58° (Plate 5). The high mixing ratios at mid-low altitudes gradually diminished during TOPSE until the gradient was gone for all gases by mid May. As with the latitudinal gradients described earlier, the vertical gradients disappeared faster for the shorter-lived gases such as n-butane (Plate 5).

Low median mixing ratios were observed below 1 km compared to the 1-2 km range for ethane, propane, ethyne, and n-butane during Deployments 4, 5, and 6 (Plate 5). BL ozone was also sharply lower below 1 km (Plate 6), however median benzene mixing ratios were similar or higher in the BL for these same deployments (Plate 6). Separate analysis of the NMHC and halocarbon data by *Sive et al.* [this issue] reveal that these BL NMHC and ozone losses are consistent with chlorine and bromine atom chemistry during the frequently encountered ozone depletion events, as reported previously for springtime Arctic studies [e.g., *Jobson et al.*, 1994b]. We also note that benzene (Plate 6) has low reactivity with both Cl and Br radicals, so was not influenced by these events.

For altitudes below 3 km, total carbon contributed by the NMHCs gradually declined over the TOPSE period, from an average of approximately 15 ppbC in mid February, to about 3.5 ppbC in mid May (Plate 7). The upper tropospheric change (3-6 km) was much less pronounced, going from about 9.5 ppbC to about 4 ppbC during the same period. At the highest altitudes (above 6 km), very little change was observed for any NMHCs during the TOPSE period.

The vertical gradients of total C<sub>2</sub>-C<sub>4</sub> alkyl nitrates were less pronounced during the early deployments compared to those for total NMHCs (Plate 7). For example during Deployment 2 there was a less than 20% drop between the median of total alkyl nitrates for the 0-1 km bin and that for the 5-6 km bin, compared to an approximately 45% decrease for total NMHCs (Plate 7). In addition, median alkyl nitrate values remained higher for longer, with the largest alkyl nitrate decrease occurring from late April to mid May (Deployments 6 and 7).

The temporal trend north of 58° and between 1-6 km reveals that total C<sub>2</sub>-C<sub>4</sub> alkyl nitrates decreased by ~4 pptv/month (Plate 9) compared with an increase of about 40 pptv/month for NO<sub>y</sub> [Flocke *et al.*, this issue]. As a result, the alkyl nitrates represented ~10% of NO<sub>y</sub> early in the experiment, decreasing to ~5% at the end of the TOPSE period [Flocke *et al.*, this issue; Ridley *et al.*, this issue]. We note that tertiary nitrates (and multifunctional nitrates) are not measured with this technique, so the reported values of sum are a lower limit (by perhaps 20 - 30%).

The average free tropospheric temporal trends in Plate 8 further illustrate that the rates of decrease of the C<sub>2</sub>-C<sub>4</sub> NMHCs proceed in order of their OH lifetimes, with ethane declining at the slowest pace, and n-butane mixing ratios diminishing at a considerably faster rate. Total NMHC mixing ratios north of 58° and between 1-6 km decreased by ~ 6.2 ppbC (1.6 ppbC/month), while O<sub>3</sub> increased by ~ 16 ppb (4.2 ppbv/month) (Plate 10). Depending on conditions, roughly 1 ppb of carbon from the photochemical consumption of light NMHCs can produce 1 ppbv of ozone, provided that sufficient NO<sub>x</sub> is available [see Flocke *et al.*, this issue and others still in preparation]. Therefore, in simplistic terms, this NMHC-ozone comparison indicates that the processes associated with the spring photochemical NMHC consumption may be responsible for a substantial fraction of the O<sub>3</sub> increase between 1-6 km (see Klonecki and Hess [this issue] and other modeling papers in preparation [this issue]).

#### **4. Comparison with previous work**

Our results are in general agreement with surface seasonal NMHC studies reported by Blake and Rowland [1986], Jobson *et al.* [1994a], Goldstein *et al.* [1995] and an Arctic aircraft-based winter experiment reported by Anderson *et al.* [1993]. In Plate

11 we directly compare our lower altitude results with those of *Penkett et al.* [1993] who made aircraft measurements over the North Atlantic, north of the Arctic Polar front up to altitudes of about 3 km in 1988-1989. The results agree remarkably well, indicating a similar seasonal cycle for NMHCs extending over a large portion of the NH, a conclusion that has been reached by several previous studies, including *Penkett et al.* [1993]. The comparison also suggests that there has been no significant large-scale temporal trend for light NMHCs at high northern latitudes during the past decade.

Our alkyl nitrate results compare well with measurements made at Alert [*Muthuramu et al.*, 1994] and on the Greenland ice sheet [*Swanson et al.*, 2001]. Early April total C<sub>2</sub>-C<sub>6</sub> alkyl nitrate mixing ratios at a surface site in interior Alaska [*Beine et al.*, 1996] were approximately 15 pptv higher than reported here (Plate 8), but were similar by mid-May. The contribution from the C<sub>5</sub> and C<sub>6</sub> alkyl nitrates, which can be quite large in winter [*Muthuramu et al.*, 1994] but decay at a fast rate during the winter-spring transition, accounts for much of the early spring difference.

## 5. Case Studies

### 5.1. Flight 22 (Deployment 4)

The previous sections have shown the large-scale changes encountered during the course of the TOPSE experiment. However, there is also a wealth of information to be obtained by scrutinizing the details of the many individual flights. Companion papers by *Sive et al.* [this issue], *Ridley et al.* [this issue] and others document individual flights focused on such features as boundary layer ozone depletion events (ODEs) during TOPSE.

Even employing median values, Plate 1 (and others) reveals evidence for individual pollution plumes. The most obvious example is observed in Deployment 4 between 60-65°N (Plate 1), where ethane, propane, and n-butane mixing ratios are elevated as the result of very high mixing ratios encountered on Flight 22. By contrast, ethyne levels were not unusually high. We have also chosen this flight to illustrate the power of combining our trace gas analysis with meteorological back trajectory analysis. Plate 12 displays the mixing ratios of selected NMHCs and methyl nitrate during Flight 22, which flew from Thule to Churchill on March 24. Two air masses with very different trace gas composition were encountered in the mid-troposphere (approximately 2-6 km) and are highlighted in Plate 12 as a and b.

Very high levels of ethane and propane were observed over the W shore of Hudson Bay (Plate 12, air mass b). N-butane was also elevated (not shown). This chemical signature is similar to that observed for cities such as Mexico City, which has high LPG usage, but surprisingly, the combustion tracers ethyne and benzene remained very close to background levels, not what would be expected for a mixed urban plume. This indicates an origin associated more closely with oil/gas production [*Sexton and Westberg, 1979; Blake et al., 1992*]. The 5-day back trajectories originate at low altitude over SW coastal US/Baja California, where there are both natural gas and oil fields (Plate 12, trajectory b).

High levels of the secondary alkyl nitrate 2-butyl nitrate in this Deployment 4 plume (Plate 3) suggest that significant photochemical activity produced this gas from its parent hydrocarbon n-butane along the path followed by air mass b. Because measured Arctic OH levels, and therefore photochemistry, were so low during Deployment 4

[*Mauldin et al.*, this issue] the observation of elevated 2-butyl nitrate compliments the southerly origin indicated by trajectory analysis (Plate 12).

If we contrast this plume with the mixing ratio signature from a similar altitude range earlier in the flight (Plate 12, air mass a), we find much lower levels of ethane and propane. Ethyne and benzene are again close to background levels, but there is a slight enhancement in methyl nitrate. Ethyl nitrate (not shown) is slightly elevated, but the other alkyl nitrates are not (not shown). The back trajectories for this small section of the flight show that the air masses have circulated over the North Pacific, including a period at low altitude, near 40°N for the past 10 days or so. Therefore, the methyl nitrate (and ethyl nitrate) is likely to reflect a small contribution from ocean sources.

We note that the back trajectories shown for Flight 22 are not meant to be representative of the TOPSE period (or of TOPSE as a whole). They instead represent some of the diverse conditions that were sampled. In fact, air masses that had been advected across the Arctic Ocean were more typical of the TOPSE period. Indeed, model analysis suggests that there was greater influence from the European continent than North America [*Merrill et al.*, this issue].

## **5.2. Flight 34 (Deployment 6)**

Flight 34 (north from Thule on April 27, 2000) was chosen to illustrate further the range of air mass transport conditions that contributed to the trace gas trends observed during TOPSE.

The first two highlighted sections of the flight were sampled exactly one hour apart and at 5.5 and 7.5 km altitude, respectively (Plate 13, air masses a and b). Both are characterized by high levels of the reactive combustion tracer ethene, as well as by

enhancements in the other combustion and fossil fuel-related NMHCs ethyne, ethane, and propane. However, the industrial tracer  $C_2Cl_4$  is not elevated in either plume. The trajectories for both plumes (Plate 13, trajectories a and b) have similar low altitude origins over Northeastern Europe from where they were transported within about 4 days, consistent with maintaining high levels of reactive ethene so late in the campaign. In fact, fast air mass transit clear across the Arctic Ocean occurred in less than 2 days.

The third plume, sampled between 4 km and 1 km was very different in chemical character, with low ethene and ethyne but relatively high  $C_2Cl_4$ , as well as ethane and propane (Plate 13, air mass c). This signature is consistent with trajectories that originate closer to industrialized Western Europe ( $C_2Cl_4$ ) and perhaps oil refining operations (propane and ethane (Plate 13, trajectory c).

The fourth highlighted section of the flight was sampled at low altitude in the Arctic boundary layer and is very different again, characterized by very low mixing ratios of all trace gases shown (Plate 13, air mass d). The trajectories remained at low altitude over the Arctic Ocean for at least the past 10 days (Plate 13, trajectory d). The very low ozone associated with this air mass makes it one of the ODEs that are studied in depth in several companion papers [*Ridley et al.*, this issue; *Sive et al.*, this issue].

## 6. Summary

Strong latitudinal, vertical, and temporal gradients were observed for NMHCs and alkyl nitrates as part of the most comprehensive airborne survey of the Arctic troposphere accomplished to date. Vertical and latitudinal gradients of all the measured NMHCs and alkyl nitrates diminished as photochemistry and dynamics increased during the winter-spring transition. In the northern part of the study region and between 1-6 km, NMHCs



decreased by  $\sim 6.2$  ppbC ( $1.6$  ppbC/month) over the nearly four-month long experiment, enough to account for a substantial fraction of the equivalent  $O_3$  increase.

Total light alkyl nitrates accounted for up to 10% of  $NO_y$ . Episodes of low BL  $O_3$  (ODEs) were frequently sampled and were strongly associated with low concentrations of NMHCs and certain halocarbons. We illustrated various examples of long-range transport of plumes with different trace gas signatures from sources that influenced the Arctic troposphere during TOPSE.

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## **References**

- Anderson, B. E., J. E. Collins Jr., G. W. Sachse, G. W. Whiting, D. R. Blake, and F. S. Rowland, AASE-II observations of trace carbon species distributions in the mid to upper troposphere, *Geophys. Res. Letts.*, *20*, 2539-2542, 1993.
- Atlas, E., et al., The TOPSE Experiment: Introduction, *J. Geophys. Res.*, this issue.

- Atlas, E., F. Flocke, S. Schauffler, V. Stroud, D. Blake, F. S. Rowland, Evidence for marine sources of atmospheric alkyl nitrates: Measurements over the tropical Pacific Ocean during PEM-Tropics, *EOS Transactions, AGU, Volume 78, Number 46*, 1997.
- Beine, H. J., D. A. Jaffe, D. R. Blake, A. Atlas, and J. Harris, Measurements of PAN, alkyl nitrates, ozone and hydrocarbons during spring in interior Alaska, *J. Geophys. Res.*, *101*, 12,613-12,619, 1996.
- Blake, D. R. and F. S. Rowland, Global atmospheric concentrations and source strength of ethane, *Nature*, *321*, 231-233, 1986.
- Blake, D. R., and F. S. Rowland, Urban Leakage of Liquefied Petroleum Gas and Its Impact on Mexico City Air Quality, *Science*, *269*, 953-956, 1995.
- Blake, D. R., D. F. Hurst, T. W. Smith, Jr., W. J. Whipple, T.-Y. Chen, N. J. Blake, and F. S. Rowland, Summertime measurements of selected nonmethane hydrocarbons in the Arctic and subarctic during the 1988 Arctic Boundary Layer Expedition (ABLE-3A), *J. Geophys. Res.*, *97*, 16,559-16,588, 1992.
- Blake, D. R., T. W. Smith, Jr., T.-Y. Chen, W. J. Whipple and F. S. Rowland, Effects of biomass burning on summertime nonmethane hydrocarbon concentrations in the Canadian wetlands, *J. Geophys. Res.*, *99*, 1699-1719, 1994.
- Blake, D. R., Chen, T. Y., Smith, T. W., and Wang, C. J. L., Three-dimensional distribution of nonmethane hydrocarbons and halocarbons over the northwestern Pacific during the 1991 Pacific Exploratory Mission, *J. Geophys. Res.*, *101*, 100-111, 1996.
- Blake, N. J., D. R. Blake, T.-Y. Chen, J. E. Collins Jr., G. W. Sachse, B. E. Anderson, and F. S. Rowland, Distribution and seasonality of selected hydrocarbons and

- halocarbons over the Western Pacific basin during PEM-West A and PEM-West B, *J. Geophys. Res.*, *102*, 28,315-28,331, 1997.
- Blake, N. J., D. R. Blake, O. W. Wingenter, B. C. Sive, G. H. Kang, D. C. Thornton, A. R. Bandy, E. Atlas, F. Flocke, J. Harris, and F. S. Rowland, Aircraft measurements of the latitudinal, vertical, and seasonal variations of NMHCs, methyl nitrate, methyl halides, and DMS during the First Aerosol Characterization Experiment (ACE 1), *J. Geophys. Res.*, *104*, 21,803-21,817, 1999.
- Blake, N. J., D. R. Blake, E. Atlas, F. Flocke, and F. S. Rowland, Latitudinal, vertical, and seasonal variations of C<sub>1</sub>-C<sub>4</sub> alkyl nitrates in the troposphere over the Pacific Ocean during PEM-Tropics A and B: Oceanic and continental sources, Submitted to *J. Geophys. Res.*, 2001a.
- Blake, N. J., D. R. Blake, I. J. Simpson, J. P. Lopez, N. A. Ciskowski, A. L. Swanson, A. S. Katzenstein, S. Meinardi, B. C. Sive, J. J. Colman, E. Atlas, F. Flocke, S. A. Vay, M. A. Avery, and F. S. Rowland, Large scale latitudinal and vertical distributions of NMHCs and selected halocarbons in the troposphere over the Pacific Ocean during the March-April 1999 Pacific Exploratory Expedition (PEM-Tropics-B), *J. Geophys. Res.*, in press, 2001b.
- Browell, E. V., et al., Ozone, aerosol, potential vorticity, and trace gas trends observed at high latitudes from February to May 2000 over North America, *J. Geophys. Res.*, this issue.
- Chin, M., D. J. Jacob, J. W. Munger, D. D. Parrish, and B. G. Doddridge, Relationship of ozone and carbon monoxide over North America, *J. Geophys. Res.*, *99*, 14,565-14,573, 1994.

- Colman, J. J., A. L. Swanson, S. Meinarde, B. C. Sive, D. R. Blake, and F. S. Rowland, Description of the analysis of a wide range of volatile organic compounds in whole air samples collected during PEM-Tropics A and B, *Anal. Chem.*, *73*, 3723-3731, 2001.
- Crutzen, P. J., Atmospheric Chemistry. The Atmospheric Sciences: National objectives for the 1980's, NRC, Washington DC, 1980.
- Crutzen, P. J. and M. O. Andreae, Biomass burning in the tropics: impact on atmospheric chemistry and biogeochemical cycles, *Science*, *250*, 1669, 1990.
- Dibb, J. E., R. W. Talbot, E. Scheuer, G. Seid, and L. DeBell, B. Lefer and B. Ridley, Stratospheric influence on then northern North American free troposphere during TOPSE:  $^7\text{Be}$  as a stratospheric tracer, *J. Geophys. Res.*, this issue.
- Ehhalt, D. H., J. Rudolph, F. Meixner, and U. Schmidt, Measurements of selected  $\text{C}_2\text{-C}_5$  hydrocarbons in the background troposphere: vertical and latitudinal variations, *J. Atmos. Chem.*, *3*, 29, 1985.
- Ehhalt, D. H., U. Schmidt, R. Zander, P. Demoulin, and C. Rinsland, Seasonal cycle and secular trend of the total column abundance of ethane above the Jungfrauoch, *J. Geophys. Res.*, *96*, 4985-4994, 1991.
- Flocke, F., et al., Measurements of PAN and PPN, and the budget of reactive oxidized nitrogen during TOPSE, *J. Geophys. Res.*, this issue.
- Goldstein, A. H., S. C. Wofsy, and C. M. Spivakovsky, Seasonal variations of nonmethane hydrocarbons in rural New England: Constraints on OH concentrations in northern midlatitudes, *J. Geophys. Res.*, *100*, 21,023-21,033, 1995.

- Gupta, M. L., R. J. Cicerone, D. R. Blake, F. S. Rowland, and I. S. A. Isaksen, Global atmospheric concentrations and source strengths of light hydrocarbons and tetrachloroethene, *J. Geophys. Res.*, *103*, 28,219-28,235, 1998.
- Hov, O., S. A. Penkett, I. S. A. Isaksen, and A. Semb, Organic gases in the Norwegian Arctic, *Geophys. Res. Lett.*, *11*, 425-428, 1984.
- Hov, O., N. Schmidbauer, and M. Oehme, C<sub>2</sub>-C<sub>5</sub> hydrocarbons in rural south Norway, *Atmos. Environ, Part A*, *25*, 1981-1999, 1991.
- Hurst, D.F., 1990, Dissertation: Seasonal variations in the latitudinal distribution of Tropospheric carbon monoxide, 1986-1988, Univ. of California, Irvine.
- Jobson, B. T., Z. Wu, H. Niki, and L. A. Barrie, Seasonal trends of isoprene, C<sub>2</sub>-C<sub>5</sub> alkanes, and acetylene at a boreal site in Canada, *J. Geophys. Res.*, *99*, 1589-1599, 1994a.
- Jobson, B. T., H. Niki, Y. Yokouchi, J. Bottenheim, F. Hopper, and R. Leitch, Measurements of C<sub>2</sub>-C<sub>6</sub> hydrocarbons during the Polar Sunrise 1992 Experiment: Evidence for Cl atom and Br atom chemistry, *J. Geophys. Res.*, *99*, 25,355-25,368, 1994b.
- Klonecki and Hess, Comparison of measured CO and NMHC with the HANK model for the TOPSE period, in preparation for this issue.
- Lightman, P., A. S. Kallend, A. R. W. Marsh, B. M. R. Jones, and S. A. Penkett, Seasonal variation of hydrocarbons in the free troposphere at mid latitudes, *Tellus, Ser. B*, *42*, 408-422, 1990.
- LaMarque, J. F, and P. Hess, Measured CO during TOPSE, in preparation for this issue.
- Mauldin, L., et al., Hydroxyl radical measurements during TOPSE, this issue.

- McKeen, S. A., S. C. Liu, E.-Y. Hsie, X. Lin, J. D. Bradshaw, S. Smyth, G. L. Gregory, and D. R. Blake, Hydrocarbon ratios during PEM-West A: A model perspective, *J. Geophys. Res.*, *101*, 2087-2109, 1996.
- Merrill et al., Air mass origins during TOPSE, this issue
- Muthuramu, K., P. B. Shepson, J. Bottenheim, B. T. Jobson, H. Niki, and K. G. Anlauf, Relationships between organic nitrates and surface ozone destruction during Polar Sunrise Experiment 1992, *J. Geophys. Res.*, *99*, 25,369-25,379, 1994.
- Parrish, D. D., C. J. Hahn, E. J. Williams, R. B. Norton, and others, Indications of photochemical histories of Pacific air masses from measurements of atmospheric trace species at Point Arena, California, *J. Geophys. Res.*, *97*, 15,883-15,901, 1992.
- Penkett, S. A., N. J. Blake, P. Lightman, A. R. W. Marsh, P. Anwyl, and G. Butcher, The seasonal variation of non-methane hydrocarbons in the free troposphere over the North Atlantic Ocean: Possible evidence for extensive reaction of hydrocarbons with the nitrate radical, *J. Geophys. Res.*, *98*, 2865-2885, 1993.
- Plass-Dülmer, C., R. Koppmann, M. Ratte, J. Rudolph J., Light nonmethane Hydrocarbons in seawater, *Global Biogeochem. Cycles*, *9*, 79-100, 1995.
- Rasmussen, R. A., M. A. K. Khalil, and J. S. Chang, Atmospheric trace gases over China, *Environmental Science & Technology*, *16*, 124, 1982.
- Ridley, B. A., E. L. Atlas, J. G. Walega, G. L. Kok, and others, Aircraft measurements made during the spring maximum of ozone over Hawaii: Peroxides, CO, O<sub>3</sub>, NO<sub>y</sub>, condensation nuclei, selected hydrocarbons, halocarbons, and alkyl nitrates between 0.5 and 9 km, *J. Geophys. Res.*, *102*, 18935-18961, 1997.

- Ridley, B.A., et al., "Ozone depletion events observed in the high latitude surface layer during the TOPSE aircraft program" *J. Geophys. Res.*, this issue.
- Roberts, J.M., S. B. Bertman, D. D. Parrish, F. C. Fehsenfeld, B. T. Jobson, and H. Niki, Measurement of alkyl nitrates at Chebogue Point, Nova Scotia during the 1993 North Atlantic Regional Experiment (NARE) intensive, *J. Geophys. Res.*, 103, 13569-13580, 1998.
- Sexton, K. and H. Westberg, Ambient air measurements of petroleum refinery emissions, *J. Air Poll. Control Assoc.*, 29, 1149-1152, 1979.
- Singh, H. B., and L. J. Salas, Measurements of selected light hydrocarbons over the Pacific Ocean: Latitudinal and seasonal variation, *Geophys. Res. Lett.*, 9, 842-845, 1982.
- Singh, H. B., and P. B. Zimmerman, Atmospheric distribution and sources of nonmethane hydrocarbons, in *Gaseous Pollutants: Characterization and Cycling*, edited by J. O. Nriagu, 177-235, John Wiley, New York, 1992.
- Singh, H. B., W. V. Viezee, and L. J. Salas, Measurements of selected C<sub>2</sub>-C<sub>5</sub> hydrocarbons in the troposphere: latitudinal, vertical, and temporal variations, *J. Geophys. Res.*, 93, 15861, 1988.
- Sive, B. C., Ph.D. Thesis, Analytical methods and estimated hydroxyl radical concentrations, *University of California Irvine*, 1998.
- Sive, B. C., O. W. Wingenter, N. J. Blake, A. S. Katzenstein, S. Meinardi, B. A. Ridley, D. Murphy, D. R. Blake, and F. S. Rowland, Nonmethane hydrocarbon and halocarbon measurements made over the Arctic and high northern latitudes: Impact of halogen chemistry on Arctic lower tropospheric ozone, this issue.

- Smyth, S. B., S. T. Sandholm, J. D. Bradshaw, R. W. Talbot, D. R. Blake, N. J. Blake, F. S. Rowland, H. B. Singh, G. L. Gregory, B. E. Anderson, G. W. Sachse, J. Collins, and A. S. Bachmeier, Factors influencing the upper free tropospheric distribution of reactive nitrogen over the South Atlantic during the TRACE-A experiment, *J. Geophys. Res.*, *101*, 24,165-24,186, 1996.
- Swanson A. L., N. J. Blake, D. R. Blake, F. S. Rowland, Seasonality of C<sub>2</sub>-C<sub>4</sub> NMHC and C<sub>1</sub>-C<sub>4</sub> alkyl nitrates on the Arctic ice-sheet at Summit, Greenland, submitted to *J. Geophys. Res.*, 2001.
- Wang, C. J.-L., D. R. Blake, and F. S. Rowland, Seasonal variations in the atmospheric distribution of a reactive chlorine compound, tetrachloroethene (CCl<sub>2</sub>=CCl<sub>2</sub>), *Geophys. Res. Lett.*, *22*, 1097-1100, 1995.
- Wingenter, O. W., M. K. Kubo, N. J. Blake, T. W. Smith Jr., D. R. Blake, and F. Sherwood Rowland, Hydrocarbon and halocarbon measurements as photochemical and dynamical indicators of atmospheric hydroxyl, atomic chlorine, and vertical mixing obtained during Lagrangian flights, *J. Geophys. Res.*, *101*, 4331-4340, 1996.
- Wingenter, O. W., D. R. Blake, N. J. Blake, B. C. Sive, and F. S. Rowland, Tropospheric hydroxyl and atomic chlorine concentrations, and mixing time scales determined from hydrocarbon and halocarbon measurements made over the Southern Ocean, *J. Geophys. Res.*, *104*, 21,819-21,828, 1999.



## Plate Captions

**Plate 1.** Latitude profiles for ethane, propane, ethyne, and n-butane. Each point is the median value for a 5° latitude increment and altitudes 1-6 km for each deployment (early February (#1) to mid May (#7)).

**Plate 2.** Same as Plate 1, but for total C<sub>2</sub>-C<sub>8</sub> NMHCs and total light (C<sub>1</sub>-C<sub>4</sub>) alkyl nitrates.

**Plate 3.** Same as Plate 1, but for methyl nitrate and 2-butyl nitrate.

**Plate 4.** Same as Plate 1, but for CO and ethyne/CO.

**Plate 5.** Vertical profiles for ethane, propane, ethyne, and n-butane. Each point is the median value for a 1 km altitude increment over the latitude range 58-85°N for each deployment (early February (#1) through mid May (#7)).

**Plate 6.** Same as Plate 4, but for ozone and benzene.

**Plate 7.** Same as Plate 4, but for total NMHCs and total light alkyl nitrates.

**Plate 8.** Temporal mid-tropospheric (1-6 km) trends at high latitudes (58-85°N) for ethane, propane, ethyne, and n-butane. Individual samples are shown as dots. Crosses represent the median values for each of the 7 deployments. Error bars are  $\pm 1\sigma$ . Median values are fitted with a polynomial curve to guide the eye.

**Plate 9.** Same as for Plate 7, but for total light alkyl nitrates.

**Plate 10.** Same as for Plate 7, but for total NMHCs and ozone.

**Plate 11.** Comparison between TOPSE data (mean  $\pm 1SD$ ) for 1-2 km and for 2-3 km and data collected over the North Atlantic in the Boundary Layer (BL, <150 m) and in the Free Troposphere (FT, <3 km) [*Penkett et al.*, 1993].

**Plate 12.** Propane, ethyne, ethane, benzene, methyl nitrate and altitude versus time for Flight 22, Thule to Churchill, March 24, 2000. Also shown are back trajectories showing the origins of the air masses sampled during the highlighted sections of the flight a and b.

**Plate 13.** Altitude (grey line), propane, ethyne,  $C_2Cl_4$ , ethyne, and ethene versus time for a section of Flight 34, north from Thule, April 27 2000. Four plumes a, b, c, and d, are highlighted and the trajectory plots for each of these plumes are shown.