In-Situ Measurements of of ΣANs During INTEX-NA

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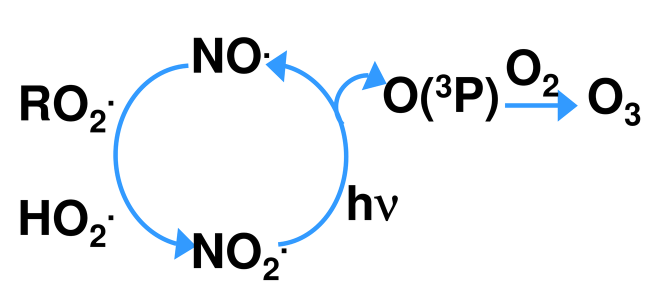
Abstract

Alkyl and multifunctional nitrates (ΣANs), produced by reactions of peroxy radicals with NO and reactions of the NO_3 radical with alkenes, have previously been observed at high mixing ratios and comprising large fractions of NO_y and NO_z at the surface (Day et. al, 2003). ΣANs were measured in real time aboard the NASA DC8 during INTEX-NA (6/1/04-8/14/04) by Thermal Dissociation Laser Induced Fluorescence (TD-LIF). Here we describe the first observations of ΣANs above the surface. Aircraft flights during INTEX-NA included extensive characterization of the continental and marine boundary layers as well as frequent vertical profiles Correlations between ΣANs and other hydrocarbon oxidation products, such as formaldehyde and ozone, were used to constrain isoprene nitrate yields and to examine factors governing ozone production efficiency in the troposphere.

The NO_x Cycle



Radical-chain termination reactions:

$NO_2\cdot + RO_2\cdot \longrightarrow RO_2NO_2$ ΣPNs
$NO_2\cdot + \cdot OH \longrightarrow HNO_3$
$NO\cdot + RO_2\cdot \longrightarrow RONO_2$ ΣANs

$NO_x = NO + NO_2$
$NO_y = NO_x + \Sigma PNs + \Sigma ANs + HNO_3 + \ldots$

Figure 1: Tropospheric ozone is produced through coupled HO_x and NO_x cycles in a radical chain of events that continues unless one of the chain-termination reactions occur.

ΣANs in the troposphere

Observations of ΣANs made during INTEX-NA show that ΣANs comprise a significant portion of NO_y throughout the lower troposphere. The observed concentrations of ΣANs indicate that they could be a NO_x sink of comparable importance to HNO_3. Figure 2 shows the NO_y distribution for a single low-altitude segment of flight 10 that occurred in the boundary layer over a forested area. Figure 3 shows NO_y partitioning as a function of altitude averaged over flight 7.

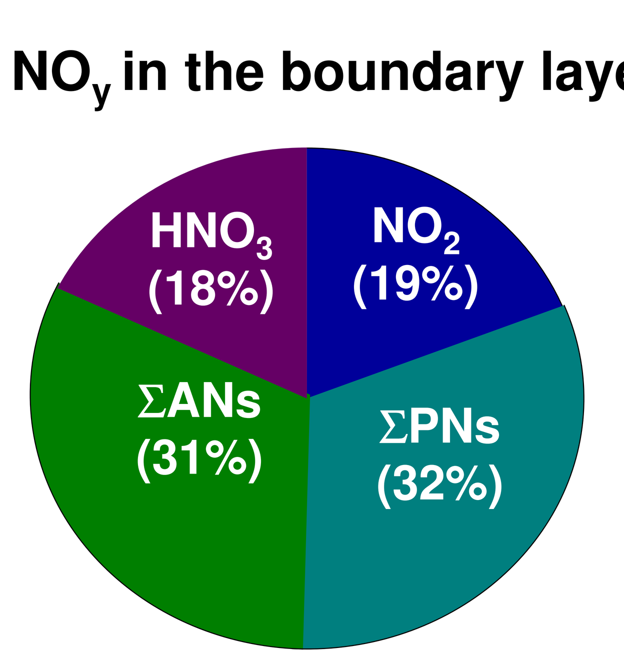


Figure 2: Low Altitude (<300 meters) Distribution of NO_y Measured by TD-LIF during the third low-level flight leg on 7/20/2004 while flying over a forested area. HNO3 data provided by Wennberg et al., CalTech

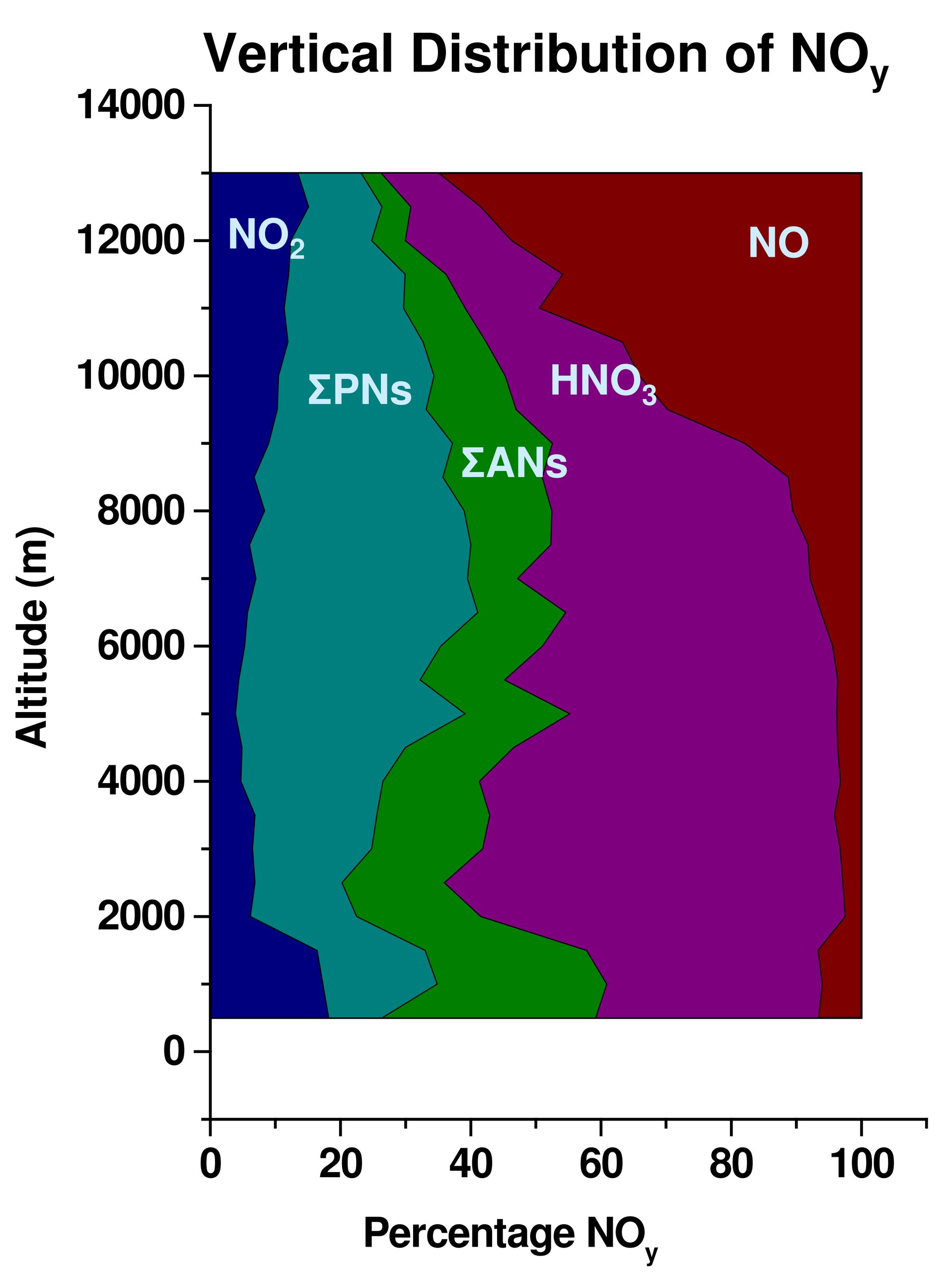


Figure 3: Profile of NO_y distribution on 7/12/2004 as a function of altitude. NO_2, ΣPNs and ΣANs measured by TD-LIF, HNO_3 by chemical ionization mass spectrometry (Wennberg et. al., CalTech) and NO calculated using steady state approximation.

The formation of ANs and the importance of isoprene nitrates

Alkyl nitrates are formed as a minor product of the reaction between peroxy radicals and NO:

a.) $RO_2 + NO \rightarrow RONO_2$
b.) $RO_2 + NO \rightarrow RO + NO_2$

The ratio $K_a/(K_a+K_b)$ is defined as the branching ratio and this sets the relative importance of chain termination and propagation. The branching ratio is dependent on the identity of R, increasing with size of the R group. The structural dependence of the branching ratio is well known for straight-chain alkanes and 1-alkenes but has been much harder to measure for certain other atmospherically relevant species such as isoprene. (Fig. 4)

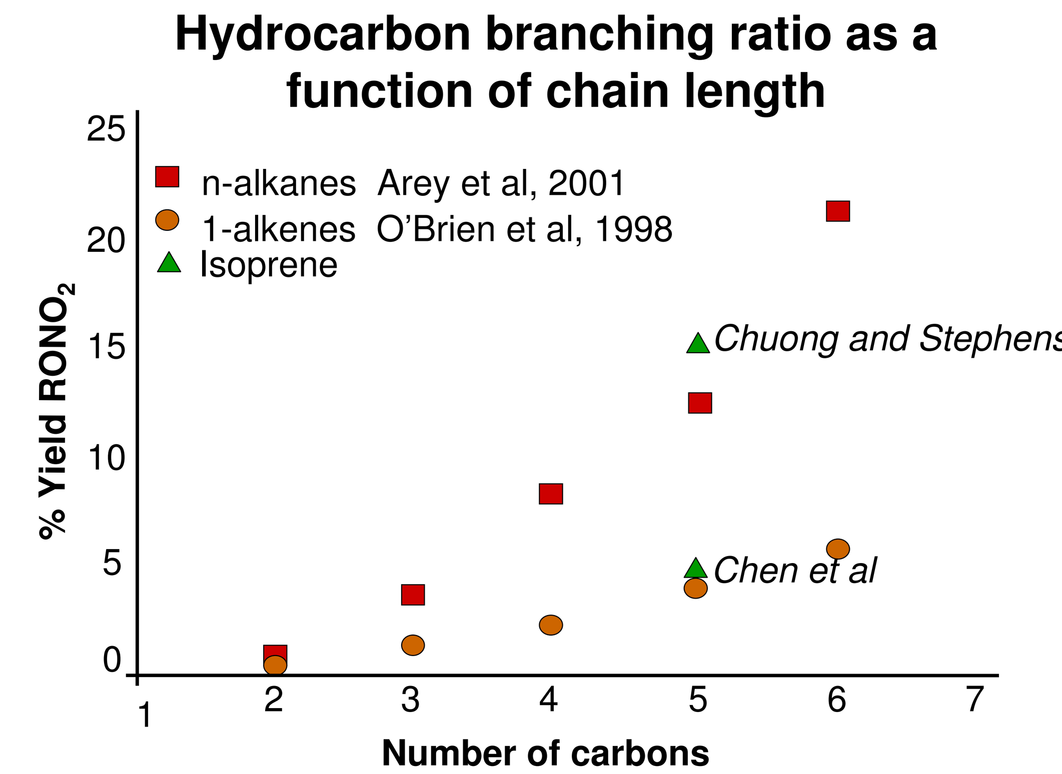


Figure 4: Carbon chain length v. published values of percent yield $RONO_2$ (branching ratio). Published values for isoprene vary from 4.4 - 15%.

Isoprene is a 5-carbon dialkene which plays a large role in the production of tropospheric ozone. Yearly emissions are estimated at 500 Tg/yr making it the most important biogenic non-methane hydrocarbon in the atmosphere. (Guenther et al. 1995). The relative importance of isoprene in the ozone production cycle as compared to other hydrocarbons can be assessed using an OH reactivity-weighted hydrocarbon budget.

By taking both the concentration of isoprene and its OH reactivity into account, it is possible to calculate the proportion of RO_2 that is isoprene derived. In some locations, as shown in Fig 5, observed isoprene concentrations imply that the majority of available RO_2 is isoprene-derived. Thus, isoprene nitrates will be a major component of ΣANs and of NO_y. Also, the high solubility of hydroxy-alkyl nitrates produced from isoprene makes them good candidates for both wet and dry deposition to the surface and onto aerosols.

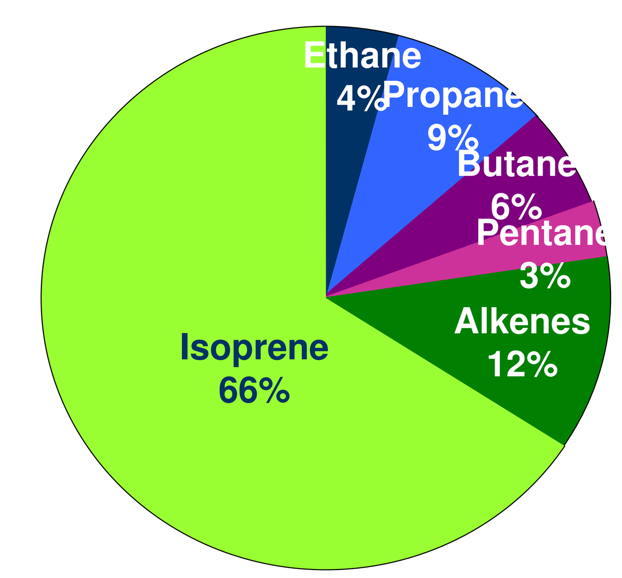


Figure 5: OH reactivity-weighted hydrocarbon budget from third low-level leg of flight on 7/20/2004 (same as Fig. 6). Indicates proportion of RO_2 that will result from a specified hydrocarbon (assuming the observed molecules represent a complete set). Hydrocarbon data provided by Blake et al, UC Irvine.

As an illustration of the importance of an accurate branching ratio for isoprene consider the following: if the lowest published nitrate yield of 4.4% is used in conjunction with EPA emission estimates, calculations indicate that up to 7% of NO emissions in the eastern US during the summer are removed through formation of hydroxy nitrates. If, on the other hand, the highest published yield (15%) is used, roughly 20% of the NO emitted is removed through this mechanism. (Chen et al, 1998, Sprengnether, et al., 2002).

Theoretical correlations between O_3, H_2CO and ΣANs

Isoprene oxidation yields for major products (O_3, H_2CO, MVK and MAC) are fairly well known (Sprengnether, et al., 2002) and the overall oxidation reaction for isoprene can be written as follows:

a.) $\alpha(C_5H_8 + OH + NO + O_2 \rightarrow C_5H_8(OH)ONO_2)$
b.) $(1-\alpha)\ (C_5H_8 + OH + 3O_2 \rightarrow 2O_3 + 0.6(H_2CO) + 0.32(MVK) + 0.22(MAC) + \text{other carbonyl products}\ldots)$

Where α is the branching ratio as introduced above $(k_a/(k_a+k_b))$. This overall equation implies the following relationships for an airmass where isoprene is the only important VOC:

$$\frac{\Delta O_3}{\Sigma ANs} = \frac{\gamma(1-\alpha)}{\alpha} \sim \frac{2}{\alpha} \qquad \frac{\Delta O_3}{\Delta H_2CO} = \frac{\gamma(1-\alpha)}{\beta} \sim \frac{2}{0.6} \qquad \frac{\Sigma ANs}{\Delta H_2CO} = \frac{\alpha}{\beta} = \frac{\alpha}{0.6}$$

Use of field data to constrain nitrate yields

Figures 6 and 7 show correlations between ΣANs and H_2CO (corrected for photolytic loss of H_2CO) and ΣANs and O_3 respectively with the best fit linear regression, confidence intervals and expected lines for extrema of published branching ratio values. The branching ratios calculated from each individual correlation agree with each other quite well and fall within the range of published values. The correlation between H_2CO and O_3 (not shown) has a slope of 3.4 which falls within 10% of the 3.17 slope that we would expect to see based on the relative yields. The following plots contain all points below 1 km with the exception of flight 16 on August 6th. Correlations made from flight 16 data were considerably different from all of the other flights but the reason for this anomaly is currently unknown.

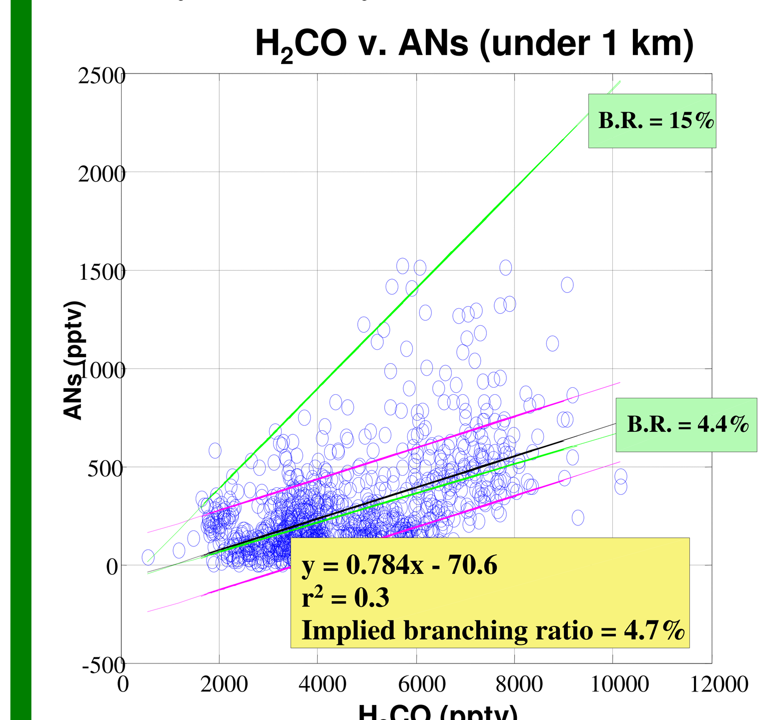


Figure 6: H_2CO v. ΣANs below 1km. Black line is best fit, pink lines show std deviation. Green lines show what the correlation should look like for maximum and minimum published branching ratio values.

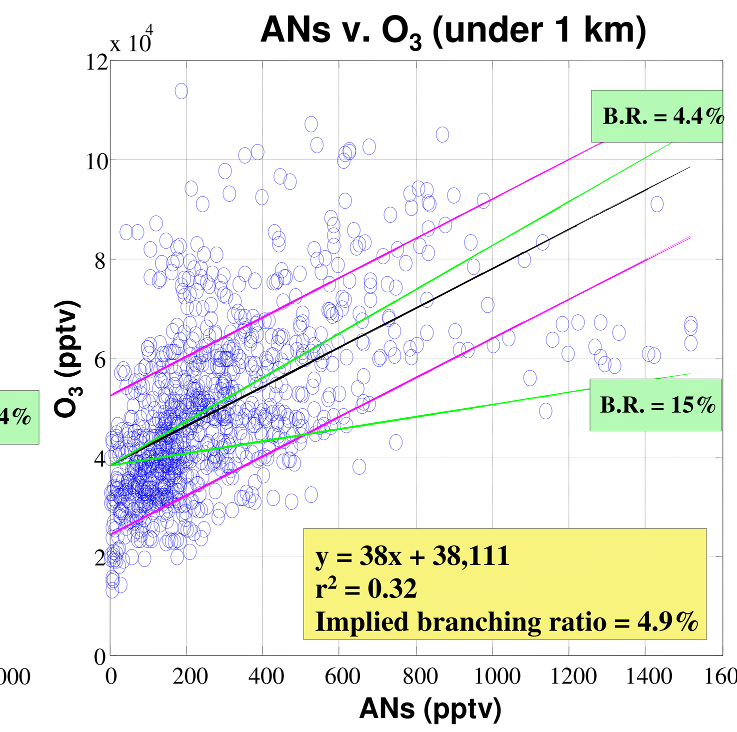


Figure 7: ΣANs v. O_3 below 1km. Black, pink and and green lines defined as in Fig. 6.

To examine the overall ratio of chain termination to propagation and the importance of ΣANs as a NO_x sink, we can use the correlation between the sum of all non-reactive NO_y reservoirs (HNO_3 + ΣANs) and odd oxygen (O_x = NO_2 + O_3). This plot is shown in Figure 8 at right. The radical chain is terminated through the production of either an AN or HNO_3 14.6% of the time. As we have seen in Figure 7 above, the radical chain is terminated by the formation of an AN ~5% of the time which implies that ΣANs are indeed acting as a significant NO_x sink and that this sink is about half as strong as that of HNO_3.

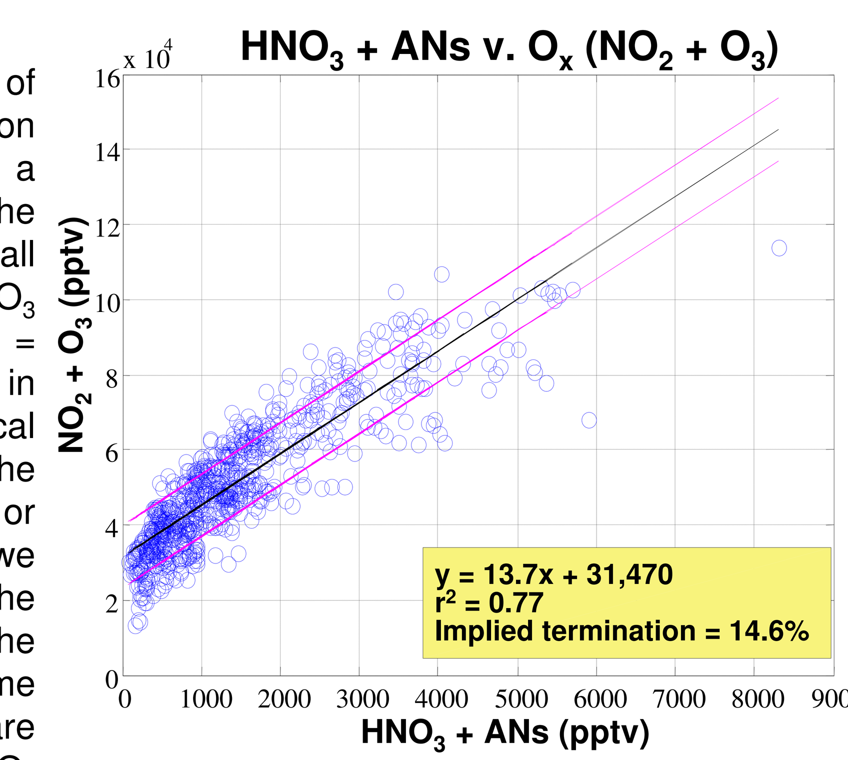


Figure 8: Non reactive NO_y (HNO_3 + ΣANs) v. O_x (NO_2 + O_3) below 1km with best fit line (black) and standard deviation (pink).

Acknowledgements

•Formaldehyde data provided by Fried et al., NCAR.
•Hydrocarbon data provided by Blake, et al. UC Irvine
•Nitric acid data courtesy of Dibb, et al. UNH.
•Ozone data courtesy of Avery et al.

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