Non-Methane Hydrocarbon and Oxy-Hydrocarbon Measurements Aboard the NOAA Research Vessel Ronald H. Brown During the New England Air Quality Study 2002

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The Cruise

As part of a consortium of research efforts from US government and university laboratories to explore ozone and particulate matter pollution in the New England coastal region, the NOAA ship Ron Brown was deployed off the NE coast of the U.S. during July and August 2002. Fig. 1 shows the ship track in the New England area from July 18th to August 06th, 2002.

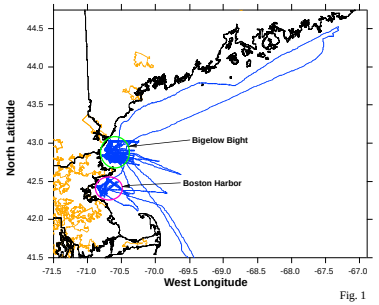

Fig. 1

As seen in the Figure, a large portion of the cruise time was spent in Bigelow Bight (shown on the map) in the vicinity of Portsmouth NH. Several days were also spent in Boston harbor (also shown) and New York harbor.

NMHC and Oxy HC Measurements

During the cruise, a wide range of non-methane hydrocarbons , oxy-hydrocarbons, alkyl nitrates and DMS were measured on a 1/2 hourly basis by an on-line GC/MS system. Large changes in local mixing ratios were seen as air masses with urban influence swept over the ships position.

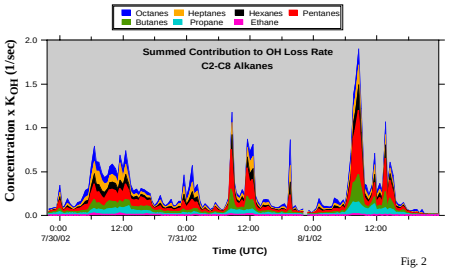

Fig. 2

Fig. 2 shows a portion of the cruise data for the C_2 through C_8 alkanes. The vertical width of each colored band in the Figure shows the contribution of each group of alkanes to the OH loss rate as a function of time. Several high pollution episodes are evident in the Figure. Some of these are discussed below.

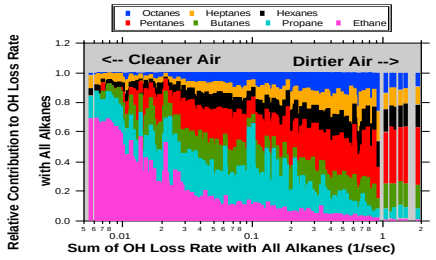

Fig. 3

Another useful method to display such data is shown in Fig. 3 in which data from the whole cruise are included. The ***relative*** contribution of each alkane group to the OH loss rate is displayed as a function of the net OH loss rate to all the compounds shown. As may be seen, ethane with its longer atmospheric lifetime, becomes the dominant alkane in the cleaner air masses while the pentanes are the largest contributors in the most polluted air masses. Compounds heavier than C_8 have been omitted as their contributions were observed to be negligible.

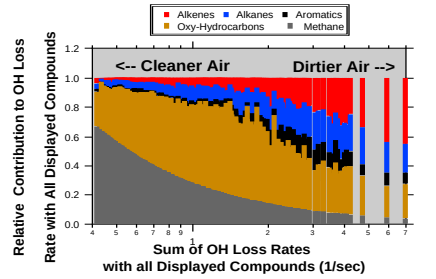

Fig. 4

A similar compilation of all measured anthropogenic compounds plus methane is shown in Fig. 4. [The OH loss rate with methane was calculated from an assumed 1.7 ppmv.] This figure shows the large role played in all but the most polluted air masses by the measured oxy-hydrocarbons which included only C_1-C_5 alcohols, C_2-C_5 aldehydes and C_3-C_5 ketones. This role would have been noticeably increased by the inclusion formaldehyde (which was not measured aboard the ship) and organic acids. [In the remote Atlantic marine troposphere, CO, at approximately 100 ppbv, would contribute an amount to the OH loss rate about 25% greater than that of methane.]

The Boston Downwind Plume

During July 22nd through 24th, the Bigelow Bight region experienced ozone levels in excess of 90 ppbv and significant increases in hydrocarbon loading. The air trajectory plots for that period, shown in Fig. 5, indicate that between 14:00 on July22nd and 16:00 on July 23rd the air passed directly over the Boston metropolitan area. This flow was also calculated to occur essentially at ground (sea) level.

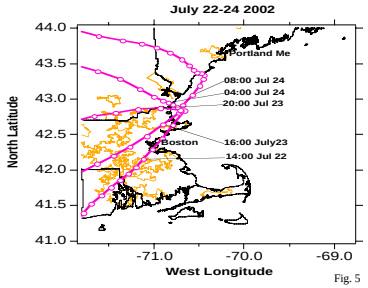

Fig. 5

Fig. 6 shows the OH loss rate with all measured hydrocarbons including the biogenic hydrocarbons, isoprene and the monoterpenes along with ozone, acetone and the true wind measured aboard the ship for the July 22nd through 24th period.

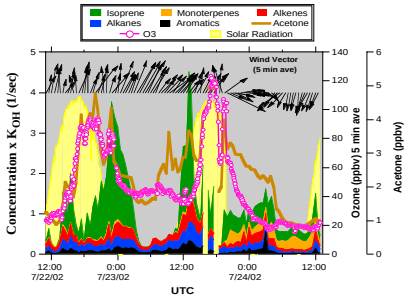

Fig. 6

The measured wind direction corroborates the air trajectory calculations. The ozone maxima during the afternoon hours are closely mirrored by acetone that is produced from similar oxidative chemistry. Anthropogenic hydrocarbon ratios were typical of auto tunnel studies implying mobile source emissions. The OH-hydrocarbon chemistry was often dominated by isoprene which shows large diminution during the most photo-chemically active part of the day. Similar hydrocarbon plumes from the Boston corridor were observed during the nights of Aug. 2-3 and Aug. 5-6. These were not associated with significant ozone increases due to the lack of sunlight driven photochemistry.

The Portsmouth/Kittery Plume

During the early morning of Aug.1st, a plume heavily laden with light alkenes was encountered in the NH coastal region. Both back trajectory calculations and ship-board wind measurements indicated the Portsmouth NH/Kittery ME complex as the source. Figure 7 shows the OH loss rate with the measured hydrocarbons for this time period together with ozone, ethanol and local (ship board) wind direction.

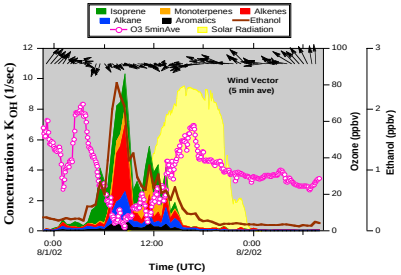

Fig. 7

The OH reactivity in this plume, was dominated by the C_4 and C_5 alkenes and Ozone was titrated out. The presence of significant amounts of very reactive alkenes and the lack of ozone indicated that this was a chemically "young" plume. The later ozone increase occurred predominantly due to changing air mass resulting from a wind shift. No significant hydrocarbon point sources are listed in the AIRS data base from this region. Comparison of the hydrocarbon profile with those from tunnel studies and gasoline headspace measurements indicated gasoline vapor venting as a possible source. Concurrent ethanol increases closely mirroring the hydrocarbon plume strengthen this conclusion. Similar plumes were encountered on the 3rd, 4th, and 6th of August.

Conclusions

- **OH loss rates in air masses near the New England coast are frequently dominated by biogenic emissions of isoprene.**
- **In air masses heavily influenced by anthropogenic emissions, the C_4 and C_5 alkenes play a dominant role followed by light oxy-hydrocarbons. In cleaner air masses, the OH loss rate with hydrocarbons is dominated by oxy-hydrocarbons, and methane.**
- **The New England coastal region is often influenced by significant hydrocarbon plumes of anthropogenic origin. Although these sometimes come from the Boston MA corridor, plumes from the Portsmouth NH / Kittery ME region were seen with about the same frequency.**
- **Plumes from the Boston corridor were chemically more "mature" and showed typical auto exhaust signatures.**
- **Plumes from the Portsmouth / Kittery complex were chemically "young" and possibly from gasoline vapor release.**