Measurements of HNO_3 on the NOAA Research Vessel Ronald H. Brown during NEAQS 2002

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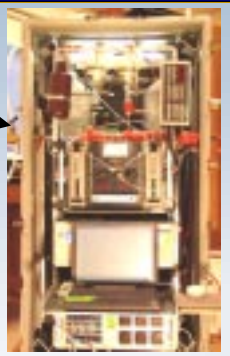
Introduction:
Nitric acid was measured at 5 minute resolution with an automated mist chamber/ion chromatograph sampling/analysis system. More than 3000 measurements were made from 29 July through 10 August, 2002, primarily in the Gulf of Maine but also during the transit to South Carolina at the end of the cruise. The focus here is the first 9 days when the ship was off the New England coast. Mixing ratios of HNO_3 varied over a wide range from day to day in response to synoptic conditions

HNO_3/NO_Y
The contribution HNO_3 made to total nitrogen oxides varied in response to synoptic changes and had a very clear diurnal pattern. In the early morning hours when HNO_3 mixing ratios were generally at their lowest, the average HNO_3/NO_Y was just 7% (median 4%). During the midafternoon photochemical peak in HNO_3 it represented 29% of total nitrogen oxides on average (median 27%). In the dark periods HNO_3/NO_Y averaged 17% (median 12%). At times HNO_3 represented the dominant fraction of NO_Y, particularly on the previously noted days when peak mixing ratios were observed. However, in these very polluted airmasses the partitioning of NO_Y varied markedly from one 5 minute sampling interval to the next.



The University of New Hampshire HNO_3 instrument was contained in a weather tight rack mount enclosure and installed above the bow of the ship. The inlet was generally kept facing into the wind. Data acquisition was internal to the instrument, but monitored continuously from a remote computer below deck.

Mist Chamber/Ion Chromatograph
Nitric acid was measured using 2 soluble gas aqueous scrubbers ("mist chambers") sub-sampling from a common heated high flow bypass manifold. Two custom ion chromatographs using Dionex detectors and columns were mated to the mist chambers for ion separation and detection. The mist chambers/ion chromatograph systems were operated alternately (sample/analysis) for continuous sampling at a 5 minute time resolution and low pptv detection limits.

HNO_3,N_2O_5, and NO_3 radical:
The morning hours between 6:00 - 8:00 almost always had the lowest HNO_3 mixing ratios each day, overall the mean during this period was 0.57 ppb. Interestingly, nitric acid increased after dark to a secondary maximum, averaging 0.98 ppbv for the 4 hours centered around midnight. The nighttime peak of HNO_3 was generally much broader than the daily maximum in the early afternoon, suggesting sustained production of HNO_3 in the dark from N_2O_5 and NO_3 radical (*see Brown et al., A41F-07, this session*).

Wind speed and direction are shown on the radial plots and colored according to time. The ship position tracks off the coast of New Hampshire and around Boston Harbor are shown in the same color/time scheme.

Mid-day peak HNO_3 mixing ratios greater than 4 ppb were observed while the ship was outside Boston Harbor again on 31 July, and also on 4 and 5 August just off the NH coast. Pronounced diurnal variability was superimposed on these synoptic changes. Peak mixing ratios around solar noon (mean for the interval 11:00 - 15:00 local time was 2.01 ppbv) indicate significant production of HNO_3 by the well established reaction of NO_2 and the OH radical.