Measurements of HNO₃ 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 HNO₃ varied over a wide range from day to day in response to synoptic conditions.

HNO₃/NOY
The contribution HNO₃ made to total nitrogen oxides varied in response to synoptic changes and had a very clear diurnal pattern. In the early morning hours when HNO₃ mixing ratios were generally at their lowest, the average HNO₃/NOY was just 7% (median 4%). During the midday photochemical peak in HNO₃, it represented 29% of total nitrogen oxides on average (median 27%). In the dark periods HNO₃/NOY averaged 17% (median 12%). At times HNO₃ varied markedly from one 5 minute sampling interval to the next.

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.

Mid-day peak HNO₃ mixing ratios greater than 4 ppb were observed while the ship was outside Boston Harbor on 1 and 2 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 HNO₃ by the well-established reaction of NO₂ by the OH radical.

HNO₃/N₂O₅ and NO₃ radical:
The morning hours between 6:00 - 8:00 almost always had the lowest HNO₃ mixing ratios each day, overall the mean during this period was 0.57 ppbv. 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 HNO₃ was generally much broader than the daily maximum in the early afternoon, suggesting sustained production of HNO₃ in the dark from N₂O₅ and NO₃ radical (see Brown et al., A41F-07, this session).

The University of New Hampshire HNO₃ instrument was contained in a weather tight rack instrument, but monitored continuously from a remote computer below deck.

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.