SUMMARY OF IMPROVE NITRATE MEASUREMENTS

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October 4, 2004

In November 2002 a number of questions arose regarding the accuracy of data obtained from the IMPROVE B Module, especially for nitrate. In particular, wintertime nitrate concentrations at many sites were below historical levels for about four years, from 1996-97 to 1999-2000. These questions were especially important due to the need to calculate reconstructed extinction under the Regional Haze Rule.

Since that time we have conducted a number of sampler tests and we have analyzed data from before, during, and after the late-90s period in question. Although we have not answered all the questions, we feel confident in drawing a number of important conclusions:

- IMPROVE nitrate data collected since mid-2000 are valid and accurate. These data can be used with confidence in data analysis, including Regional Haze Rule calculations.

- IMPROVE nitrate data collected prior to mid-1996 are also likely to be valid and accurate. However, we cannot state so with the same level of confidence as we can for recent data since we do not have nylon filters to test from that period.

- IMPROVE wintertime nitrate concentrations at some sites from 1996-97 to 1999-2000 appear to be anomalously low. We recommend treating these data with caution, although we have no definitive evidence to declare these data invalid. As with the earlier period, we do not have filters to test.

We have attempted to understand the reasons why nitrate concentrations may have decreased during the late 1990s. But since we do not have filters from that period and thus cannot replicate the conditions during that time, we may never find the answers. Hence, we have elected to proceed with this recommendation based on available information. We will continue to search for a solution, but it is likely that we will not succeed.

We now have routine IMPROVE data through February 2004, so we are able to examine several winters beyond the “reappearance” of nitrate in 2000-2001. The time series plots for five selected sites are shown in Figures 1 through 5. It is evident that the wintertime nitrate behavior has been consistent since 2000-2001.

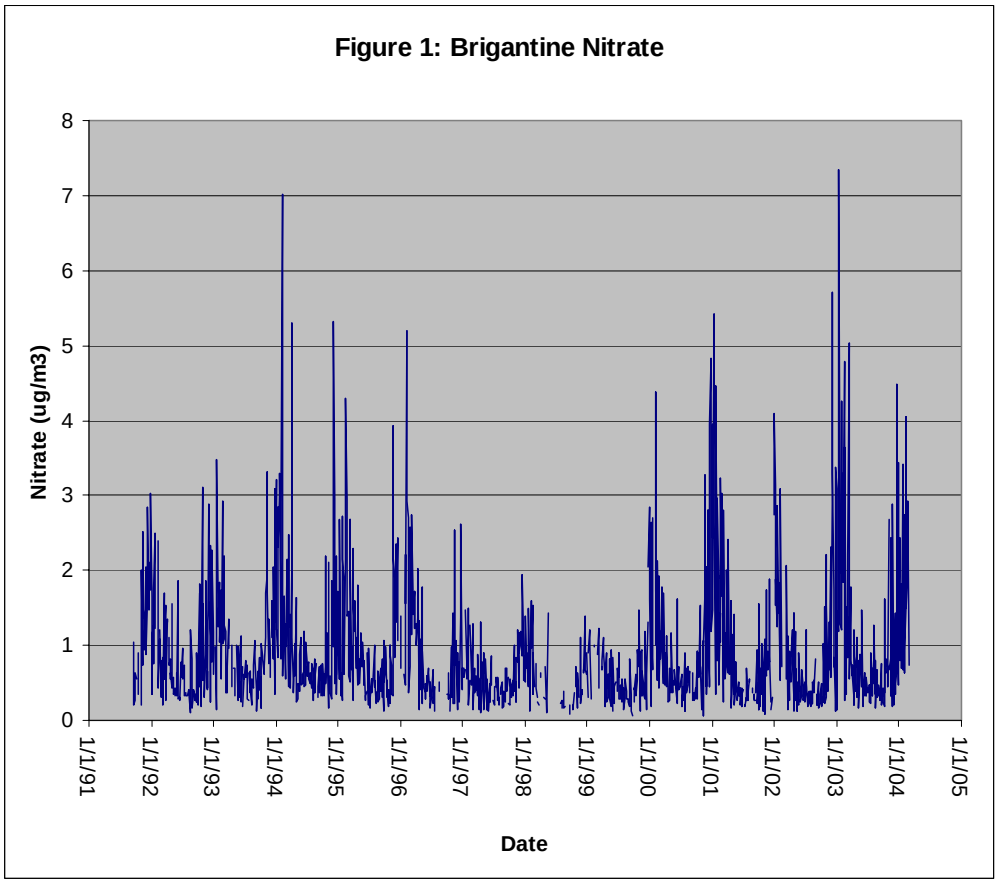


Figure 1: Brigantine Nitrate
Nitrate (ug/m3)
0
1
2
3
4
5
6
7
8
1/1/91
1/1/92
1/1/93
1/1/94
1/1/95
1/1/96
1/1/97
1/1/98
1/1/99
1/1/00
1/1/01
1/1/02
1/1/03
1/1/04
1/1/05
Date

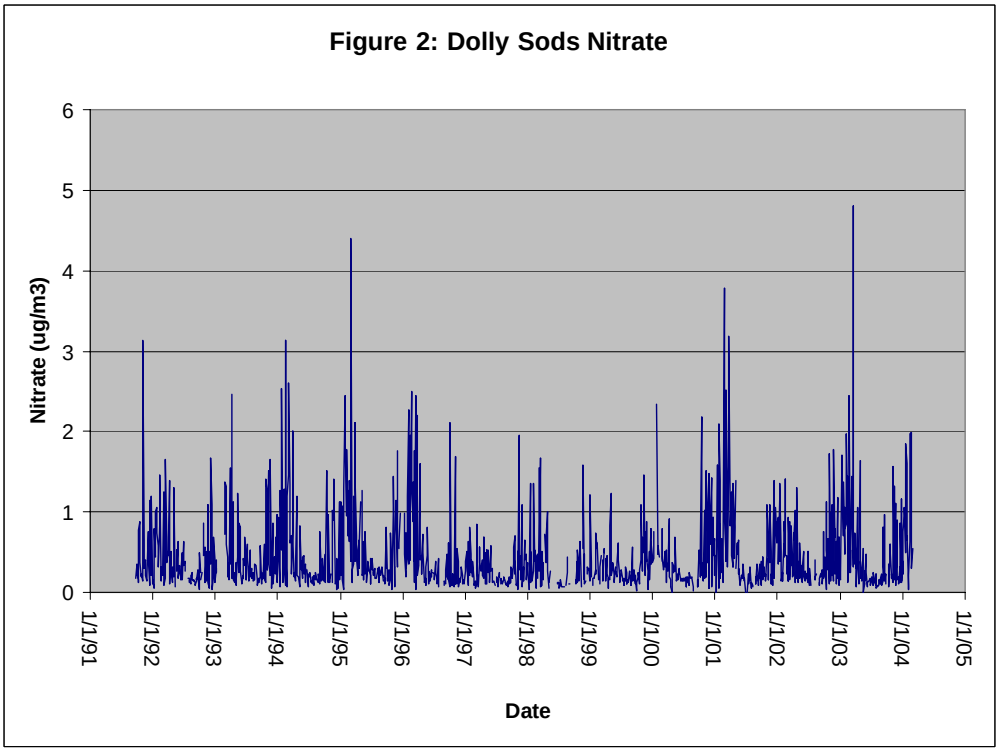


Figure 2: Dolly Sods Nitrate
Nitrate (ug/m3)
0
1
2
3
4
5
6
1/1/91
1/1/92
1/1/93
1/1/94
1/1/95
1/1/96
1/1/97
1/1/98
1/1/99
1/1/00
1/1/01
1/1/02
1/1/03
1/1/04
1/1/05
Date

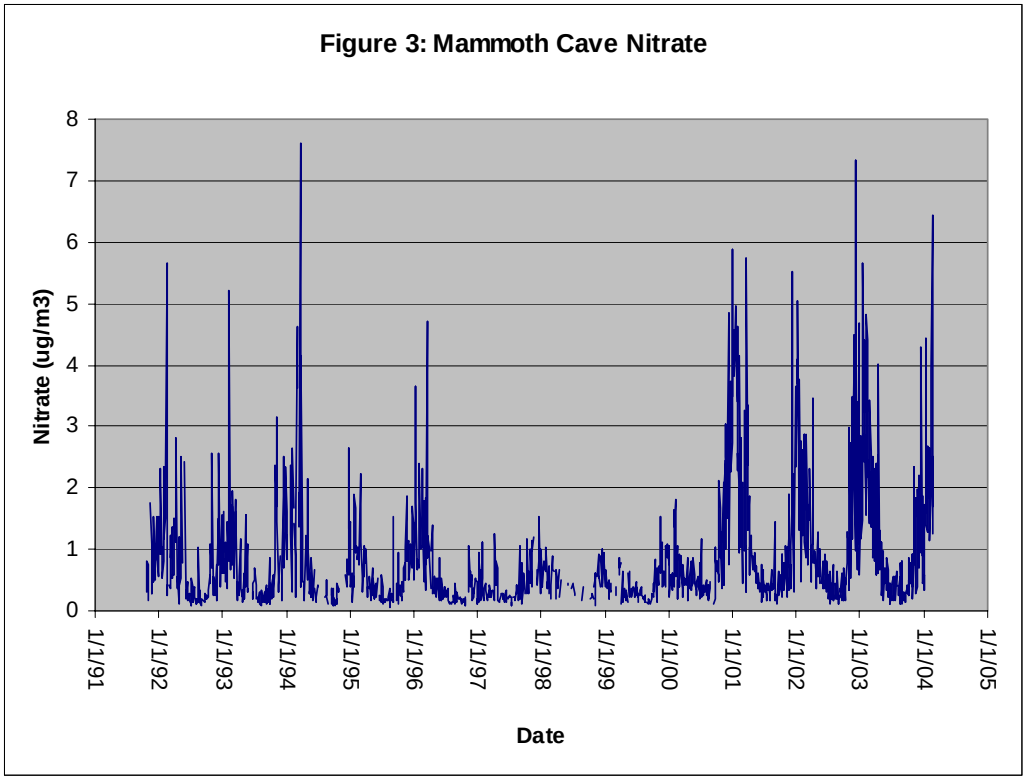


Figure 3: Mammoth Cave Nitrate
Nitrate (ug/m3)
0
1
2
3
4
5
6
7
8
1/1/91
1/1/92
1/1/93
1/1/94
1/1/95
1/1/96
1/1/97
1/1/98
1/1/99
1/1/00
1/1/01
1/1/02
1/1/03
1/1/04
1/1/05
Date

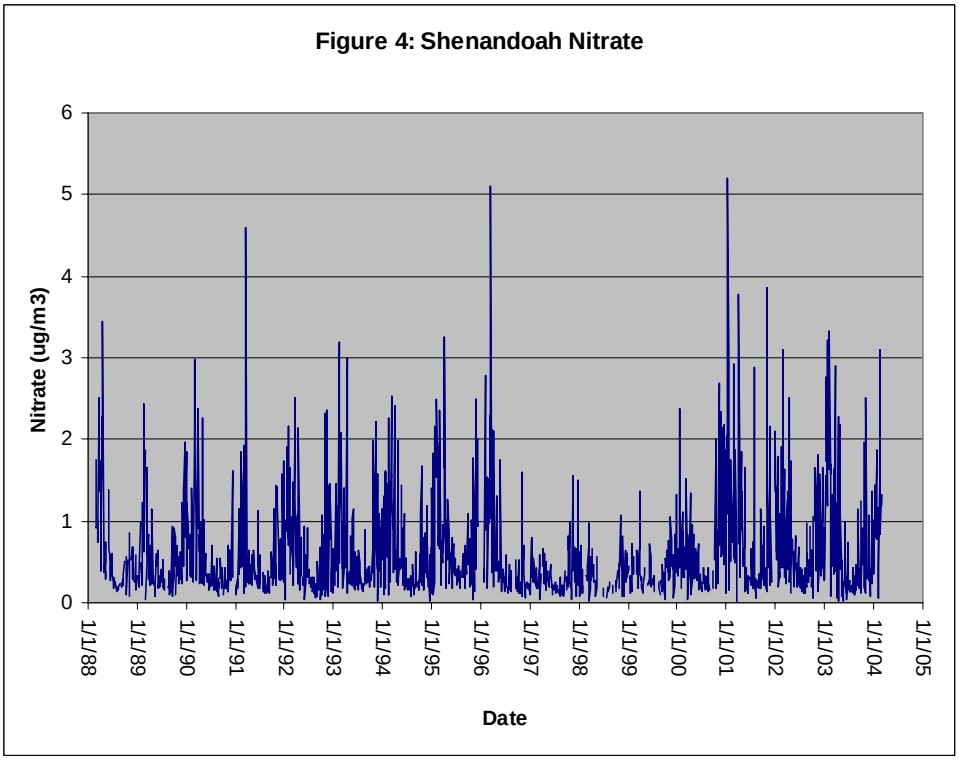
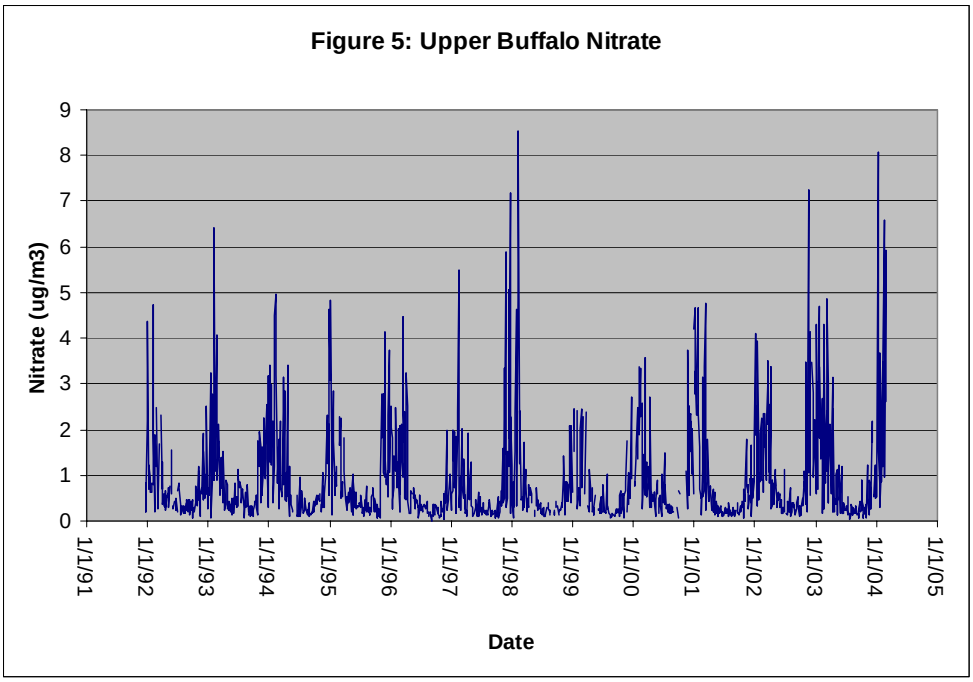


Figure 4: Shenandoah Nitrate
Nitrate (ug/m3)
0
1
2
3
4
5
6
1/1/88
1/1/89
1/1/90
1/1/91
1/1/92
1/1/93
1/1/94
1/1/95
1/1/96
1/1/97
1/1/98
1/1/99
1/1/00
1/1/01
1/1/02
1/1/03
1/1/04
1/1/05
Date



Several known or suspected changes in sampling were proposed in 2002 as possible reasons for the observed reduced nitrate levels. Our tests and findings for each one are summarized below.

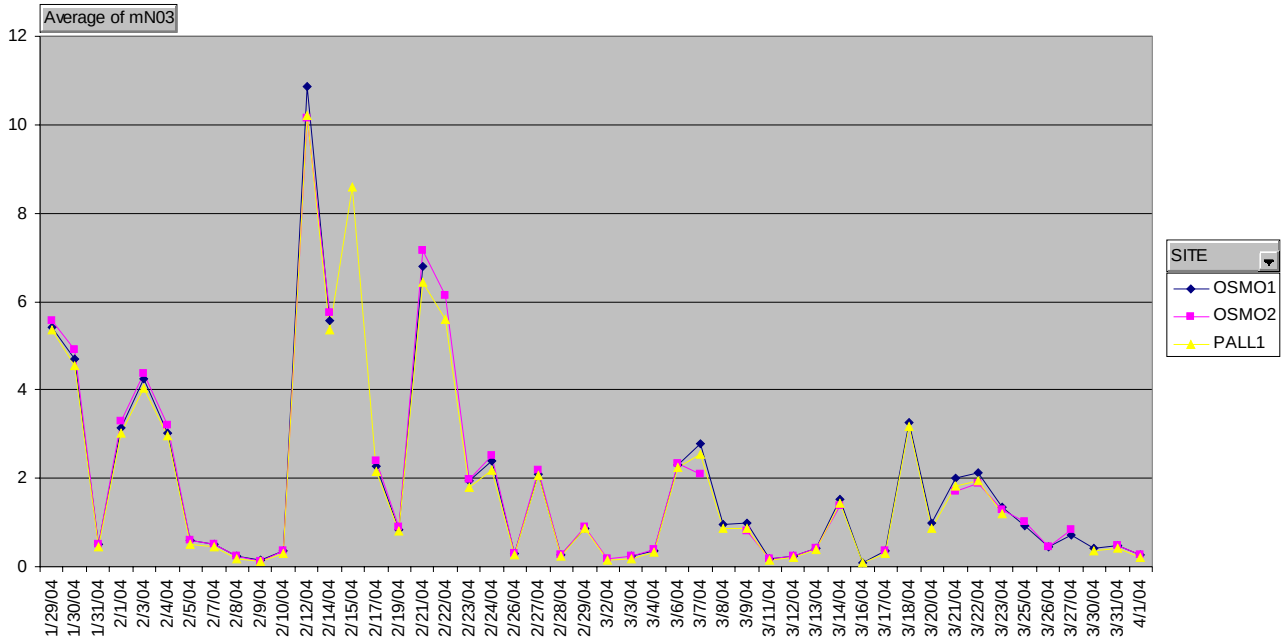
Filter Face Velocity: The size of the IMPROVE Nylon filter increased in 2000 from 25 mm to 37 mm, thereby decreasing the filter face velocity by over a factor of two. Nitrate values at many sites increased dramatically during the following winter, compared to the prior several winters.

To test the effect of filter face velocity, we operated collocated B Modules in early 2004 at the Davis test site, one with 25 mm filters and one with 37 mm filters. These filters were obtained from Osmonics, the same manufacturer as used in the late 90s. For comparison, we also included a 37 mm nylon filter obtained from Pall-Gelman, the manufacturer that we have used since January 2004.

The results of these filter face velocity tests are shown in Figure 6. OSMO1 is the 37 mm nylon filter, OSMO2 is the 25 mm nylon filter, and PALL1 Is the new Pall-Gelman nylon 37 mm filter. It is apparent from Figure 6 that neither filter size (i.e., face velocity) nor filter manufacturer had a significant effect on nitrate concentrations.

Figure 6

Concentration of NO3 in micrograms/cubic meter



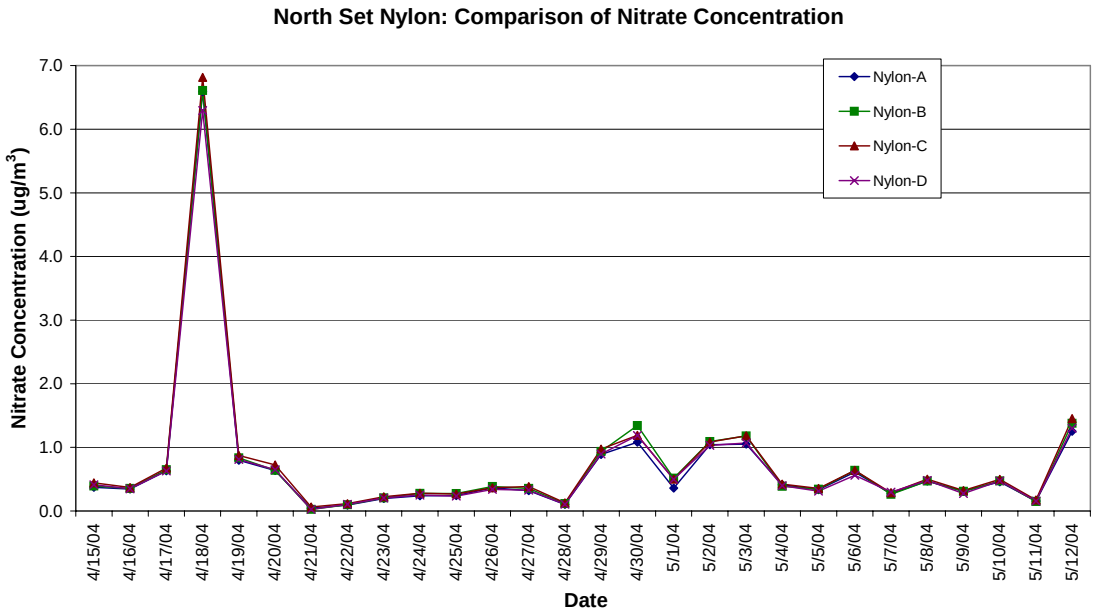
Filter Lots and Manufacturers: The Nylon filter manufacturer was changed from Gelman to Osmonics during 1996. The Osmonics filters exhibited several changes from Gelman, including high blank values that can vary from lot to lot, as well as visible changes in filter texture between lots. Lots are changed typically once a year, but sometimes more often.

Collocated sampling was conducted at the Davis test site in spring 2004, testing two different Osmonics lots side-by-side along with filters from two different manufacturers: Pall-Gelman (our current supplier) and Advantec (never used in IMPROVE, but included here for comparison). Unused filters were not saved in most prior years, so Osmonics lots are available for testing only from the past three years or so. The lots used in these tests were used routinely in IMPROVE in 2001 and 2002.

The test results are shown in Figure 7. It is apparent that all four filters gave the same nitrate concentration, so differences among lots and among manufacturers do not seem to

be controlling influences. Keep in mind, however, that we were unable to test the lots that were used in the late 90s.

Figure 7



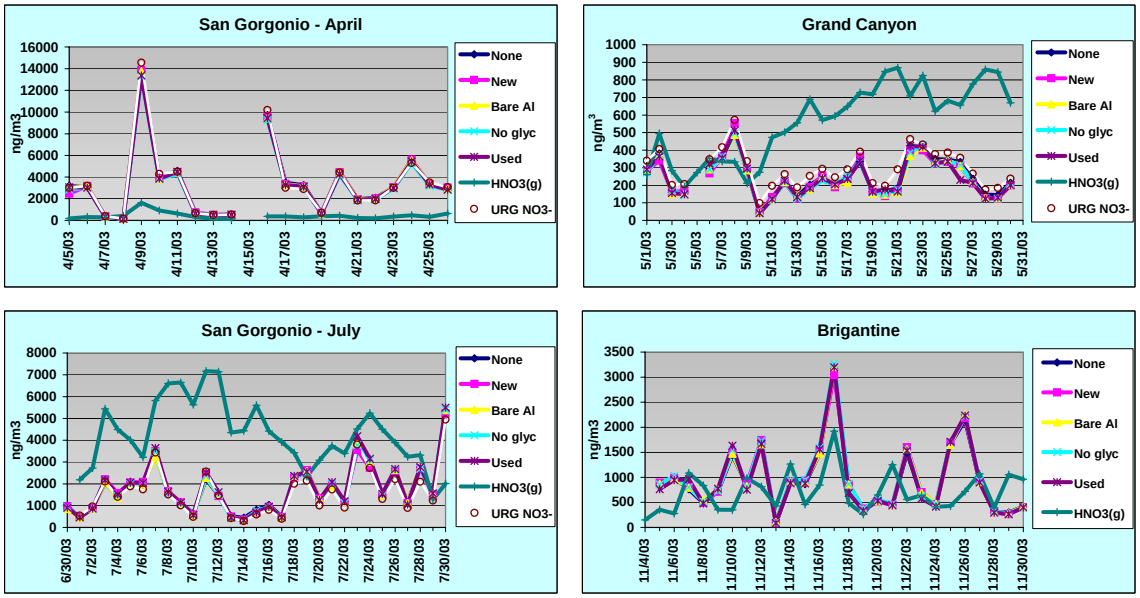
Denuder Characterization: Glycerin was added to the denuders during 1996, and it was feared that this change may have had an effect on nitrate concentrations. In particular, if denuder efficiency had been low prior to the addition of glycerol, it is possible that the apparently higher nitrate values prior to 1996 may have resulted from nitric acid breakthrough. However, no further changes in the glycerin coating were made prior to the resumption of higher nitrate values in 2000-2001, so denuder effects did not seem likely. Furthermore, breakthrough would likely be most prominent during the summer (when nitric acid concentrations are highest), but the peak concentrations were observed during the winter. Nevertheless, we conducted tests of denuder efficiency under several different conditions.

Tests were conducted throughout 2003 during four separate months at three sites: San Gorgonio (March and July), Grand Canyon (May), and Brigantine (November). Each experiment tested five separate configurations of the B Module sodium carbonate denuder:

1) No denuder
2) New denuder with carbonate and glycerol (IMPROVE standard denuder)
3) New denuder with no coating of any kind
4) New denuder with carbonate but no glycerol
5) Used denuder with carbonate and glycerol (brought from Joshua Tree site)

The results are shown in Figure 8. Nitric acid, measured concurrently by CSU, is shown as the bold green line. It is evident from this figure that all tested configurations were comparable in removing nitric acid from the sample stream. Efficiency was comparable even for the aluminum inlet with no added denuder. The Grand Canyon and San Gorgonio-July results demonstrate further that the nitrate values did not increase in the presence of high nitric acid concentrations, indicating that the denuders were working as designed. These tests suggest that the addition (or lack of) glycerol should have no effect on the observed nitrate concentrations.

Figure 8



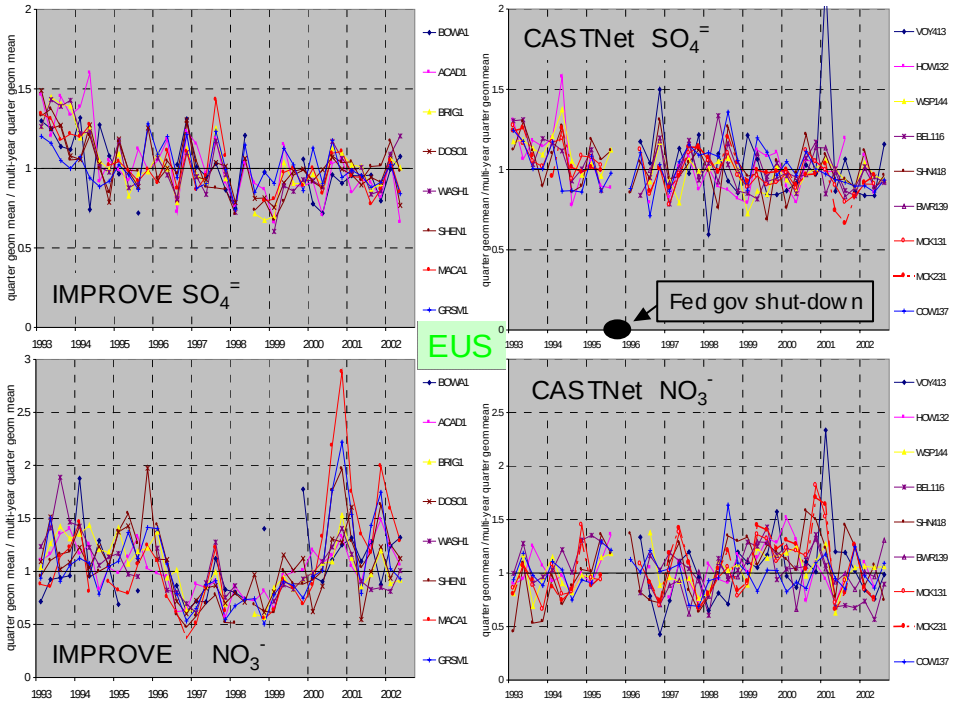
CSU is in the process of conducting laboratory tests on the efficiency of IMPROVE denuders. They are exposing denuders to known concentrations of nitric acid under controlled conditions of temperature and relative humidity. They are conducting these tests on a set of denuders removed from a variety of IMPROVE sites following about one year of field use.

Data Analysis: In addition to the sampler tests, we have also been examining routine IMPROVE data as well as data from other networks. Our findings are described below.

We examined data from CASTNet, which employs somewhat different protocols than does IMPROVE but which has been operating contemporaneously with IMPROVE for a number of years. Figure 9 shows IMPROVE and CASTNet sulfate and nitrate concentrations for the eastern U.S. in terms of the ratio of individual quarterly geometric means to multi-year quarterly geometric means. The peaks in these plots do not indicate

absolute concentrations, but rather the level of an individual quarter compared to long-term behavior.

Figure 9

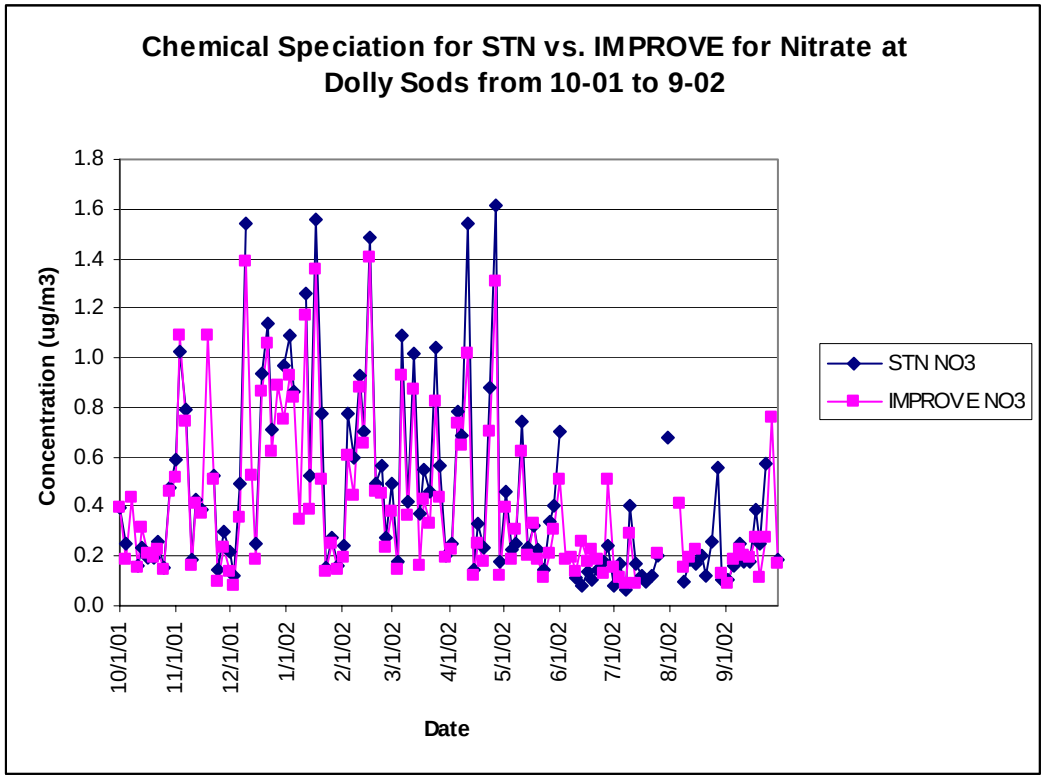


The bottom half of Figure 9 (nitrate) indicates two important observations: 1) Nitrate concentrations were higher than normal during the winter of 2000-2001 in both networks, suggesting a real atmospheric effect during that year, and 2) IMPROVE exhibited depressed concentrations during the prior four winters, whereas CASTNet did not. This second observation would suggest that the depressed IMPROVE concentrations were due to measurement abnormalities and not to atmospheric effects.

We have also compared IMPROVE nitrate data with data from collocated STN samplers at six sites (three urban and three rural). Thus far, STN data have been available from only one year, 2001-2002. But this year occurred after our nitrate "reappeared" so it should be an indicator of our present performance.

Figure 10 shows IMPROVE and STN nitrate at one of our collocated sites, Dolly Sods, WV. Although the STN values tend to be slightly higher than those from IMPROVE, it is apparent that both networks are measuring values at approximately the same level, indicating that our current concentrations are comparable to those recorded in STN. This observation is further evidence that our currently-reported concentrations are valid.

Figure 10



Summary*:* Wintertime IMPROVE nitrate concentrations have been at consistent levels since 2000-2001, and these levels are comparable to those observed prior to 1996-97. Current levels are also comparable to those measured independently in STN and CASTNet.

Special tests of the effects of filter differences indicate that changes in filter size and manufacturing lot during 2000 should not have been responsible for the increases in nitrate concentration that were observed in the following winter. Denuder tests also indicate that denuder changes in 1996 were not responsible for the drop in nitrate concentrations that occurred in the following winter.

All of this information taken together leads us to the conclusion that our current nitrate concentrations are valid. Low wintertime concentrations observed at some sites from 1996-97 to 1999-2000 may have resulted from measurement abnormalities during that period. However, we do not have definitive evidence to support that claim, and thus must consider those data valid until shown otherwise.