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## **Data Validation Historical Report NO<sub>3</sub>**

**Data Start:** March 1988

**Data End:** December 2003

**Retrieved from the VIEWS Database on Various Dates:** 11/2004-3/2005

### **Summary**

All of the recent special studies into nitrate measurements taken together lead to the conclusion that IMPROVE's current nitrate concentrations are in general valid. Isolated data anomalies reported here may be the result of isolated data quality problems.

Low wintertime nitrate concentrations observed at some sites from 1996-97 to 1999-2000 (anomaly 1 below) may have resulted from measurement abnormalities during that period. However, there is no definitive evidence to support that claim, and thus the data must be considered valid until shown otherwise.

### **Background**

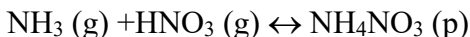
The background information provided here is a summary of the information found in several papers and reports, the reader is referred to the following documents for greater detail:

1. "Particulate nitrate measurement using nylon filters", Yu, X-Y., Lee, T., Ayres, B., Kreidenweis, S. M., Collett, Jr., J. L., and Malm, W. . J. Air Waste Manage. Assoc., 55, 1100-1110, 2005.
2. "Summary of IMPROVE Nitrate Measurements", Chuck McDade, internal report. 2004.
3. "Artifact Corrections in IMPROVE" Charles E. McDade, Robert A. Eldred, and Lowell L. Ashbaugh, internal report. 2004.
4. "Performance Evaluation—IMPROVE Laboratories" Michael S. Clark, Technical Memorandum, 2003

### ***Aerosol Nitrate Sampling Overview<sup>1,3</sup>***

Aerosol nitrate is present in the atmosphere in several forms, including NH<sub>4</sub>NO<sub>3</sub> which exists predominately in the fine mode and CaNO<sub>3</sub> and NaNO<sub>3</sub> which exist predominately

in the coarse mode. IMPROVE algorithms assume that all aerosol nitrate is in the form of ammonium nitrate and it is this form that is semi-volatile in the atmosphere.



Ammonium nitrate particles exist in the atmosphere in equilibrium with ammonia and nitric acid gases. The direction of the reaction is in part controlled by atmospheric temperature and relative humidity. Volatilization of  $\text{NH}_4\text{NO}_3$  increases with increasing temperature and decreases with increasing RH above the deliquescence point. Due to the semivolatile nature of ammonium nitrate, sampling efforts can be subject to significant positive and negative artifacts. These artifacts can be minimized through sampling design.

To reduce positive sampling artifacts, IMPROVE's sampling system includes a diffusion denuder prior to the collection filter to remove  $\text{HNO}_3 (\text{g})$  and  $\text{SO}_2 (\text{g})$ . Aerosol particles are collected on a single nylon filter intended to capture both nitrate aerosol particles and nitric acid volatilized from the collected ammonium nitrate particles. Nylon filters are efficient at collecting gaseous nitric acid, so the use of nylon filters is intended to reduce negative sampling artifacts due to particle volatilization and subsequent losses.

Dynamic field blank nylon filters are collected on a rotational basis at all sites in the network and used to correct for positive artifacts due to:

- contamination of the filter medium;
- contamination acquired by contact with the cassettes, in transportation, or in handling;
- adsorption of gases before and during collection that increase the mass measured on the filter;

The level of contamination has shown significant variation between manufacturers and also between filter lots.

### ***History of Changes***

Since IMPROVE sampling began in 1988, several important changes related to nitrate aerosol sampling have occurred:

<b>Start Date</b>	<b>End Date</b>	<b>Change Description</b>
<b>Changes in Filter Extraction Procedure</b>		
3/1988	6/1997	<ul style="list-style-type: none"> <li>• All nylon filters extracted using basic solution (IC eluent)</li> </ul>
6/1997	1/1999	<ul style="list-style-type: none"> <li>• Nylon filters from GRSM1, SHEN1, and DOSO1 extracted using deionized water</li> <li>• Nylon filters from all other sites extracted using basic solution (IC eluent)</li> </ul>
1/1999	10/2000	<ul style="list-style-type: none"> <li>• All nylon filters extracted using deionized water</li> </ul>
10/2000	4/2001	<ul style="list-style-type: none"> <li>• Nylon filters from GRSM1, SHEN1, and DOSO1 extracted</li> </ul>

		<ul style="list-style-type: none"> <li>using deionized water</li> <li>Nylon filters from all other sites extracted using basic solution (IC eluent)</li> </ul>
4/2001	current	<ul style="list-style-type: none"> <li>All nylon filters extracted using deionized water</li> </ul>
<b>Changes in Data Processing</b>		
4/2000	current	<ul style="list-style-type: none"> <li>Began reporting negative values resulting from blank/artifact subtractions (usually for chloride ion)</li> </ul>
6/2002	current	<ul style="list-style-type: none"> <li>Changed from quarterly to monthly medians to estimate artifact corrections from field blanks &amp; secondary filters</li> </ul>
<b>Changes in Contractor</b>		
3/1988	9/1990	<ul style="list-style-type: none"> <li>Switched ion analysis contractor from RTI to GGC</li> </ul>
5/1995	current	<ul style="list-style-type: none"> <li>Switched ion analysis contractor from GGC to RTI</li> </ul>
<b>Changes in Sampler Design</b>		
1996	current	<ul style="list-style-type: none"> <li>Added glycerin to Module B1 denuder</li> </ul>
1999-2001	current	<ul style="list-style-type: none"> <li>Sites transitioned from Version 1 to Version 2 IMPROVE samplers</li> <li>All new sites have received Version 2 samplers</li> </ul>
<b>Changes in filters</b>		
<i>Filter Size</i>		
3/1988	6/1994	<ul style="list-style-type: none"> <li>Module B filter size 47mm diameter</li> </ul>
6/1994	4/2000 - 1/2001	<ul style="list-style-type: none"> <li>Module B filter size 25mm diameter</li> </ul>
4/2000 - 1/2001	current	<ul style="list-style-type: none"> <li>Module B filter size 37mm diameter</li> </ul>
<i>Filter Manufacturer</i>		
3/1988	10/1996	<ul style="list-style-type: none"> <li>Module B filter supplier Gelman</li> </ul>
10/1996	1/2004	<ul style="list-style-type: none"> <li>Module B filter supplier Osmonics / MSI</li> </ul>
1/2004	current	<ul style="list-style-type: none"> <li>Module B filter supplier Pall-Gelman</li> </ul>

***Summary of Results from Recent Special Studies into Nitrate Sampling Procedures***  
*The information provided here are highly condensed excerpts from the referenced documents; please refer to those documents for additional detail and explanation.*

#### **Extraction method comparisons<sup>1</sup>:**

CSU conducted a field experiment including sample collection at four IMPROVE sites (Bondville, San Geronio, Grand Canyon and Brigantine) for 1 month each during times when high NO<sub>3</sub> concentrations were expected over the period 2/2003-7/2004. A key conclusion from this study was that the two extraction solutions used by IMPROVE (deionized water versus basic eluent) are equally effective for nitrate. This is not necessarily true if sonication is not used during the extraction process. Extraction with deionized water without sonication is not as effective as extraction with eluent and sonication. Extraction with eluent without sonication was not tested. IMPROVE's ion chromatography SOPs include sonication.

#### **Filter media comparisons<sup>1</sup>:**

The above study also looked at the effectiveness of nylon versus Teflon filters in preventing nitrate loss through volatilization. Nitrate losses from denuded nylon filters were extremely small with average losses for each campaign <1%. Whereas, Teflon filter losses were significant with average losses for each campaign ranging from 18-52%. These results were not unexpected, but represent one of the only thorough characterizations of the effectiveness of nylon filters in providing a single-filter sampling solution for the measurement of fine particle nitrate.

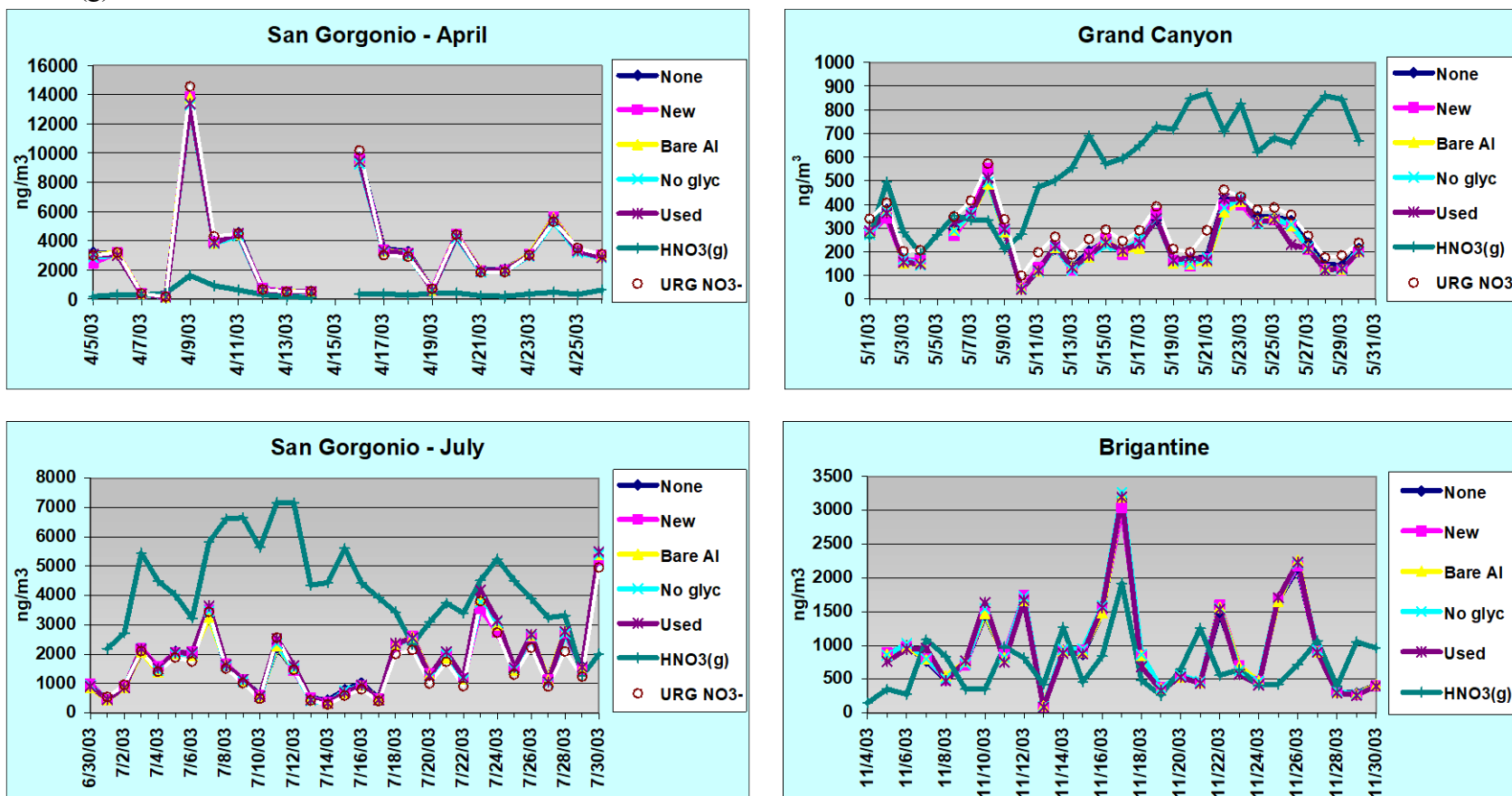
**Denuder coating comparisons<sup>2</sup>:**

The Crocker Nuclear Laboratory conducted tests throughout 2003 during four separate months at three sites: San Geronio (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 glycerin (IMPROVE standard denuder)
- 3) New denuder with no coating of any kind
- 4) New denuder with carbonate but no glycerin
- 5) Used denuder with carbonate and glycerin (brought from Joshua Tree site)

Efficiency was qualitatively comparable even for the aluminum inlet with no added denuder (Figure 1). These tests suggest that the addition (or lack of) glycerin should have no effect on the observed nitrate concentrations.

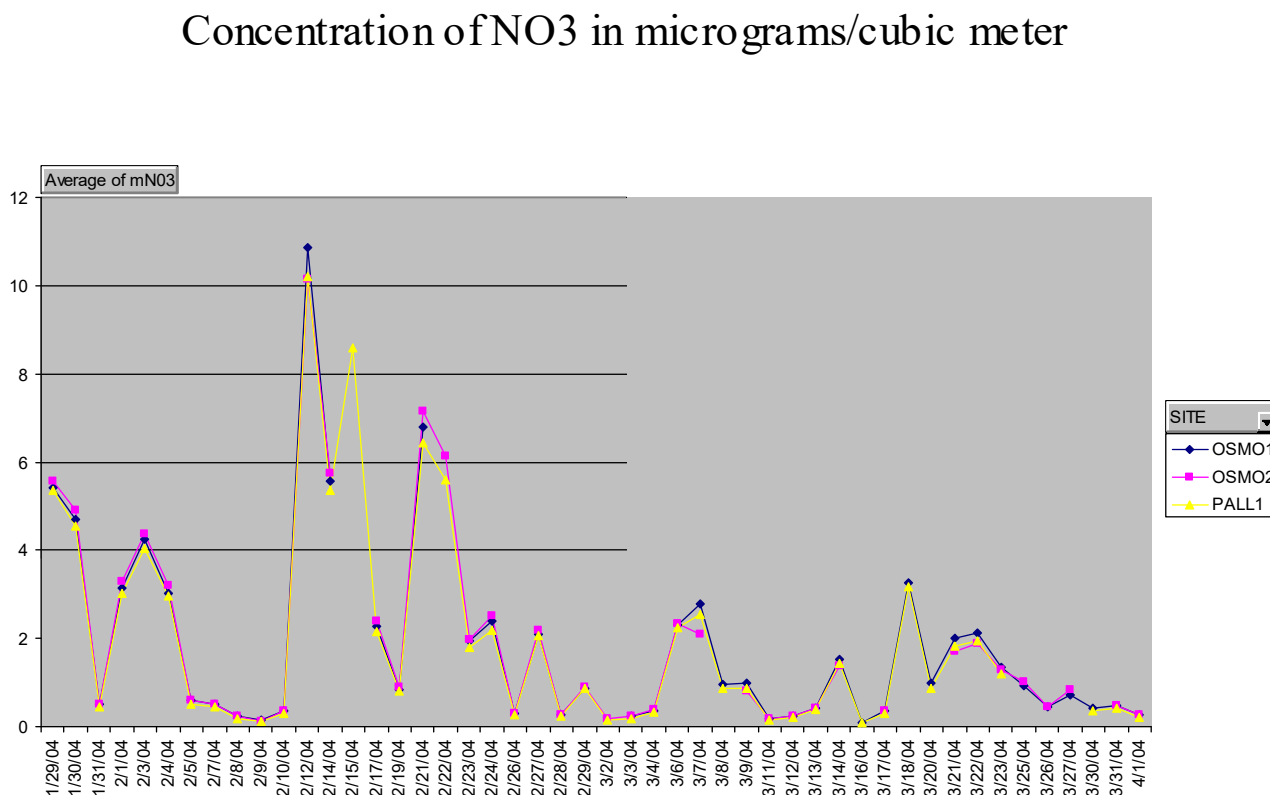
**Figure 1.** Nitrate concentrations measured with different denuder configurations were qualitatively comparable under even high  $\text{HNO}_3$  (g) concentrations



### Filter size comparisons<sup>2</sup>:

To test the effect of filter face velocity, the Crocker Nuclear Laboratory 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 1990s. For comparison, they also included a 37 mm nylon filter obtained from Pall-Gelman, the manufacturer that IMPROVE has used since January 2004. Neither filter size (i.e., face velocity) nor filter manufacturer had a significant effect on nitrate concentrations (Figure 2).

**Figure 2.** Comparisons of measured nitrate concentrations using different filter sizes



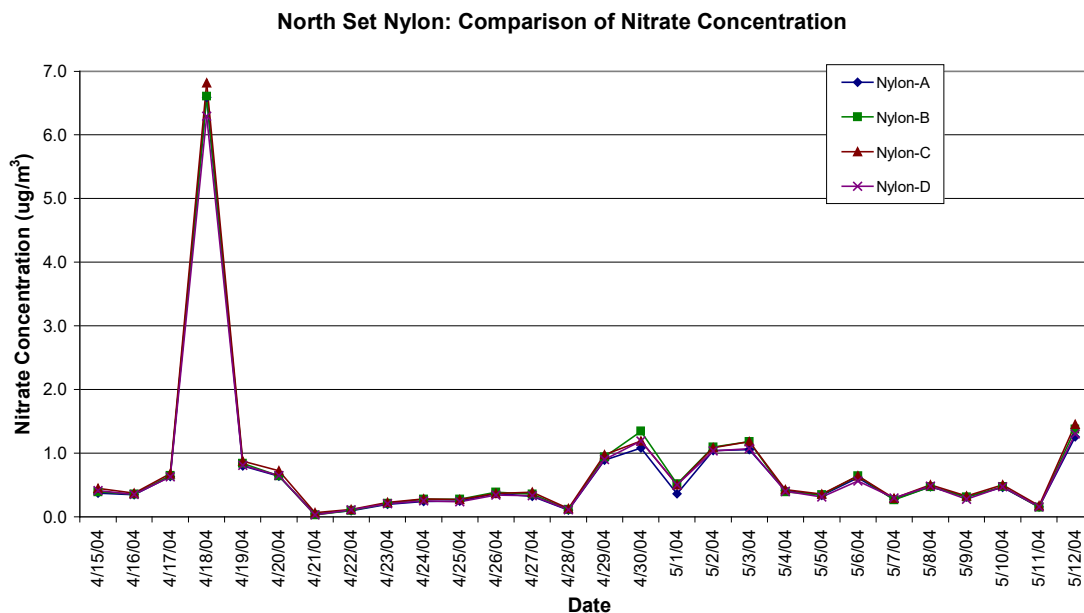
### Filter brand comparisons<sup>2</sup>:

Collocated sampling was conducted at the Davis test site by the Crocker Nuclear Laboratory in spring 2004, testing two different Osmonics lots side-by-side along with filters from two different manufacturers: Pall-Gelman (IMPROVE's current supplier) and Advantec (never used in IMPROVE, but included here for comparison). Osmonics lots are available for testing only from about the past three years. The lots used in these tests were used routinely in IMPROVE in 2001 and 2002. A proportion of unused filters is now routinely archived to permit future testing, but this was not typically done in prior years.

The test results are shown in Figure 3 (presented by Dyson and Ashbaugh at Asheville 2004). All four filter sets gave the qualitatively comparable nitrate concentrations, so differences among

lots and among manufacturers do not seem to be controlling influences. Keep in mind, however, that they were unable to test the lots that were used in the late 90s.

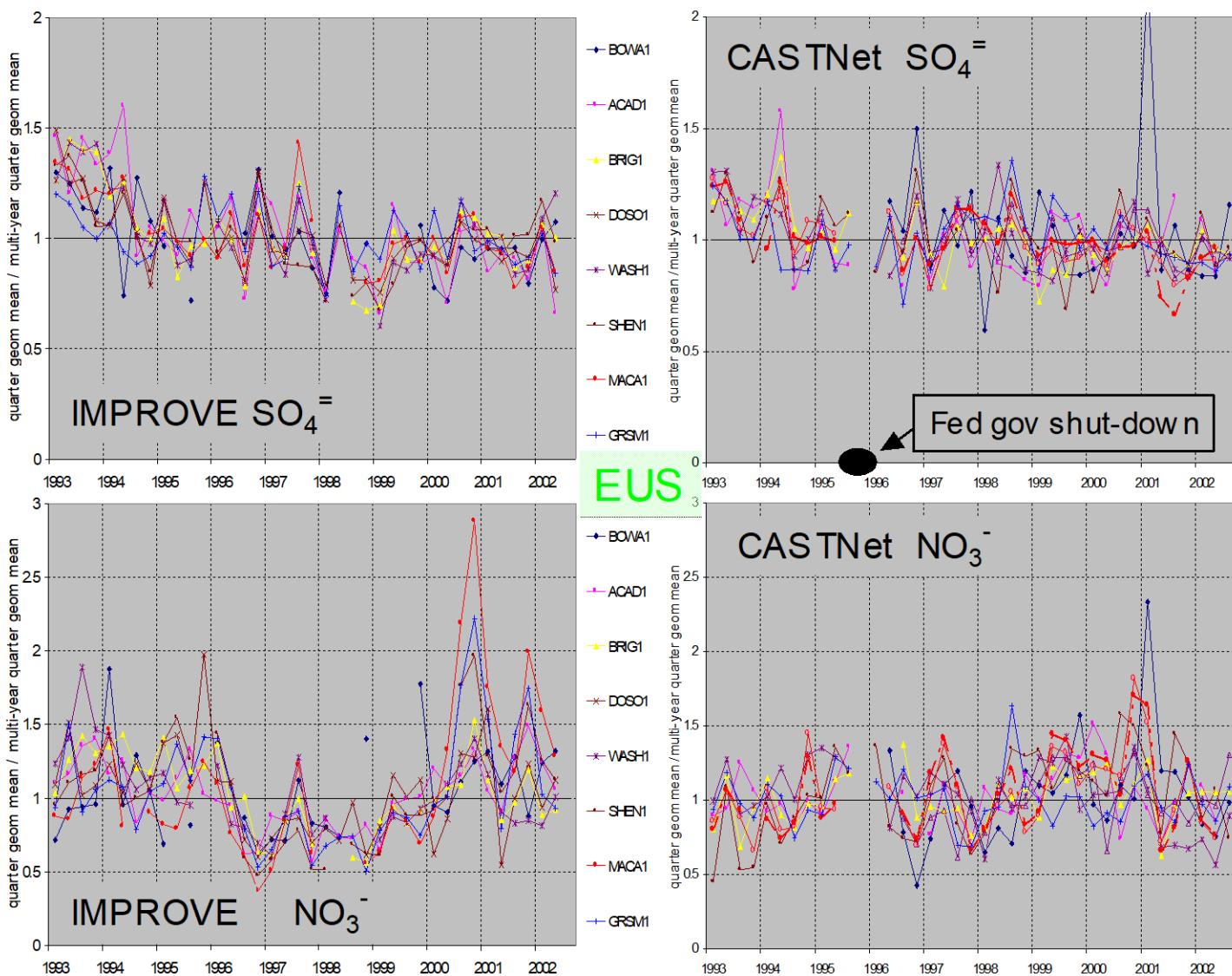
**Figure 3.** Comparisons of measured nitrate concentrations using different brands of filters.



#### Data comparability analysis<sup>2</sup>:

The Crocker Nuclear Laboratory examined data from CASTNet, which employs somewhat different protocols than IMPROVE but which has been operating contemporaneously with IMPROVE for a number of years. Figure 4 (presented by White et al. at Tucson 2002) 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 4.** Comparability of IMPROVE and CASTNet data



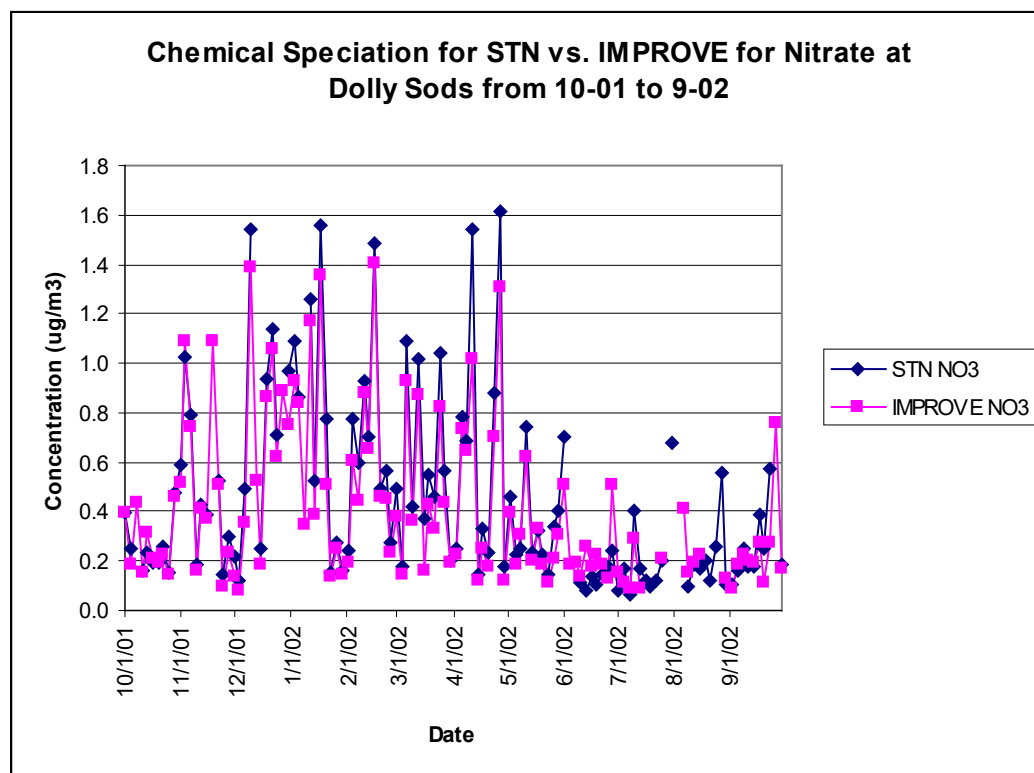


The bottom half of Figure 4 (nitrate) indicates two important observations: 1) Nitrate concentrations were higher than normal during the winter of 2000-2001 in both networks, suggesting a real atmospheric effect during that year, and 2) IMPROVE exhibited depressed concentrations during the prior four winters, whereas CASTNet did not. The authors concluded that the second observation suggested that the depressed IMPROVE concentrations were due to measurement abnormalities and not to atmospheric effects.

The Crocker Nuclear Laboratory 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. This year occurred after the period of unusually depressed wintertime nitrate concentrations, 1996-2000, observed by the IMPROVE program so it should be an indicator of IMPROVE's present performance.

Figure 5 shows IMPROVE and STN nitrate at a collocated site, Dolly Sods, WV. Although the STN values tend to be slightly higher than those from IMPROVE, it is apparent that both networks are measuring approximately the same values, indicating that IMPROVE's current concentrations are comparable to those recorded in STN. The authors concluded that this suggested that IMPROVE's currently-reported concentrations are valid.

Figure 5. Comparability of IMPROVE and STN data



**Laboratory performance evaluations<sup>4</sup>:**

A study was conducted in 2003 as part of the QA oversight for the IMPROVE program. This study was sponsored by the US Environmental Protection Agency as part of its joint commitment, along with several other agencies, to support IMPROVE. The purpose of this study was to evaluate specific performance of the laboratories that routinely analyze PM<sub>2.5</sub> samples collected at IMPROVE sites. Performance Evaluation (PE) samples were prepared at EPA's National Air and Radiation Environmental Laboratory (NAREL) and submitted to the participating laboratories for analysis. Those laboratories that participated in this study are the University of California/Davis campus (UC/Davis), the Desert Research Institute (DRI) located in Reno, NV, and the Research Triangle Institute (RTI) located in Research Triangle Park, NC.

The PE samples were designed to evaluate three analytical techniques as briefly described below. PE samples for XRF analysis will be included in a separate report at a later date.

<b>Laboratory</b>	<b>Analysis</b>	<b>PE Sample Components</b>
UC/Davis	Gravimetric Mass	ten Teflon® filters and three metallic weights
DRI	OC/EC by TOR	six Quartz filters and three spike solutions.
RTI	Ions by IC	six Nylon® filters, three anion spike solutions, and three cation spike solutions.

Excellent recoveries (99-103%) were obtained at RTI and at NAREL for the mid-level IC spikes. Good recoveries (96-115%) were also observed for the low-level spikes. Sample spike solutions identified as A-2 and C-2 were actually blank water. These blanks provided a mechanism to measure laboratory contamination from a variety of sources such as (1) the reagent water used to dilute every sample, (2) the “clean” filter extracted by the test solution which is normally provided to the field for PM<sub>2.5</sub> capture, and (3) containers used to hold and transfer the sample during the extraction and analysis process. No contamination was reported for the cation blank (C-2), but low levels of chloride (0.22 µg/filter) and sulfate (0.41 µg/filter) were reported for the anion blank (A-2). Both of these levels are above the reported MDL values for chloride and sulfate which may indicate the need for a more conservative estimate of the analytical uncertainty.

Replicate Nylon® filters from two sampling events were available for this study. The longer-than normal collection periods were necessary to provide a sample with all ions sufficiently above the detection threshold. The results reported by RTI show good agreement with the results produced at NAREL. A difference from the mean value was calculated for each analyte, and this Relative Percent Difference (RPD) is included in Table 6 and Table 7 of the report. Except for nitrite, all RPD's were well below 20 percent. This study indicates good analytical performance by the IC laboratory at RTI.

## Reported Nitrate Data Anomalies

**Anomaly 1:** Low NO<sub>3</sub> values and ammonium NO<sub>3</sub>/RCFM ratios from 1996-2000. This time period was clearly marked by very low NO<sub>3</sub> concentrations at 10 sites and possibly at an additional 12 of the ~74 sites in operation. The introduction of a new denuder design in 1996 was initially suspected as the cause for lower NO<sub>3</sub> levels. The new design added a glycerin coating in addition to the Na<sub>2</sub>CO<sub>3</sub> coating. The return to typical NO<sub>3</sub> levels in 2001 with the new denuder design still in use contradicted this explanation. A special study investigating the effect of changing the denuder design is currently underway.

Many of the sites with low NO<sub>3</sub> values during this period also had low and highly variable reconstructed fine mass to measured fine mass (RCFM/FM) ratios. There does not appear to be a correlation between cut point problems and the low NO<sub>3</sub> values. The low NO<sub>3</sub> values may be real rather than a result of sampling or analytical problems. There currently is no solid evidence of specific data quality problems.

The sites are identified in the attached PowerPoint file with blue rectangles.

### **Spatial Distribution: Affected Sites**

Site Code	Site Name	State	IMPROVE Region
SIPS1	Sipsy Wilderness	AL	Appalachia
LAVO1	Lassen Volcanic NP	CA	Oregon and Northern California
ROMO1	Rocky Mountain NP	CO	Central Rockies
MACA1	Mammoth Cave NP	KY	Ohio River Valley
BRIG1	Brigantine NWR	NJ	East Coast
GRSM1	Great Smoky Mountains NP	TN	Appalachia
SHEN1	Shenandoah NP	VA	Appalachia
CORI1	Columbia River Gorge	WA	Columbia River Gorge
SNPA1	Snoqualmie Pass	WA	Northwest
DOSO1	Dolly Sods Wilderness	WV	Appalachia

### **Possibly Affected Sites**

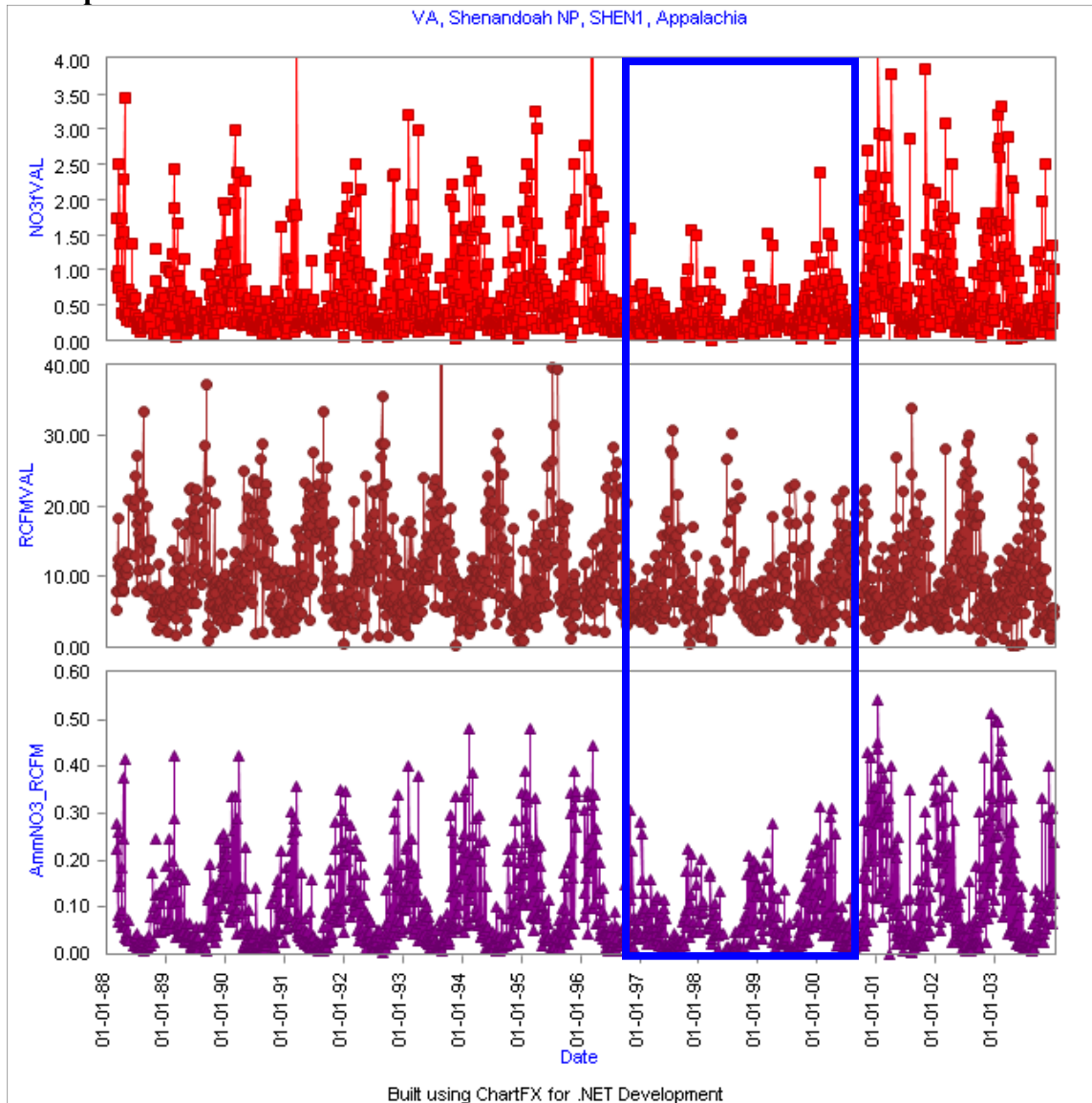
<b>Site Code</b>	<b>Site Name</b>	<b>State</b>	<b>IMPROVE Region</b>
CANY1	Canyonlands NP	UT	Colorado Plateau
GRCA2	Hance Camp at Grand Canyon NP	AZ	Colorado Plateau
COGO1	Columbia Gorge #1	WA	Columbia River Gorge
ACAD1	Acadia NP	ME	Northeast
MOOS1	Moosehorn NWR	ME	Northeast
BRID1	Bridger Wilderness	WY	Northern Rockies
GLAC1	Glacier NP	MT	Northern Rockies
YELL2	Yellowstone NP 2	WY	Northern Rockies
PUSO1	Puget Sound	WA	Puget Sound
CHAS1	Chassahowitzka NWR	FL	Southeast
OKEF1	Okefenokee NWR	GA	Southeast
ROMA1	Cape Romain NWR	SC	Southeast

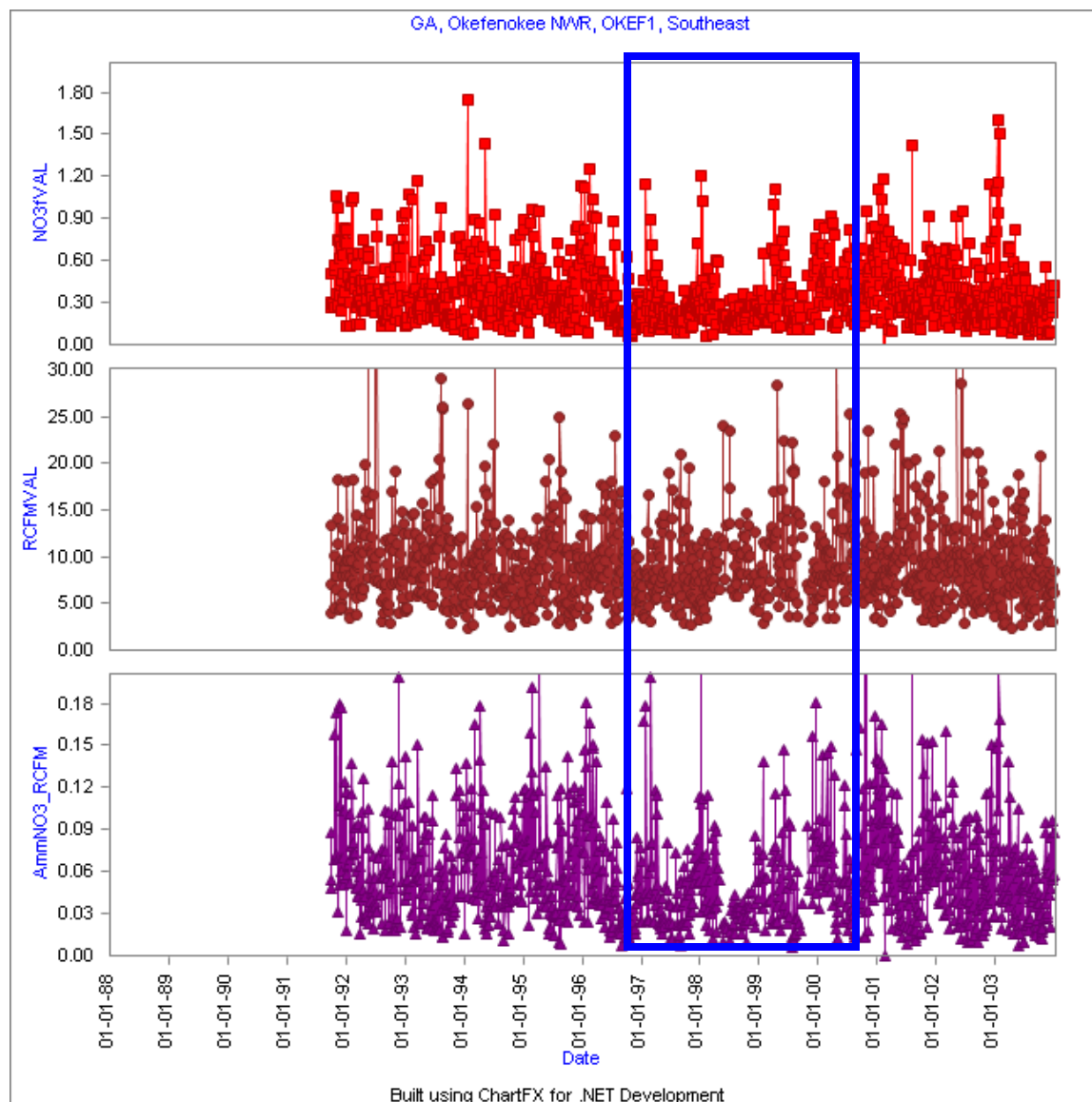
### **Unaffected Regions**

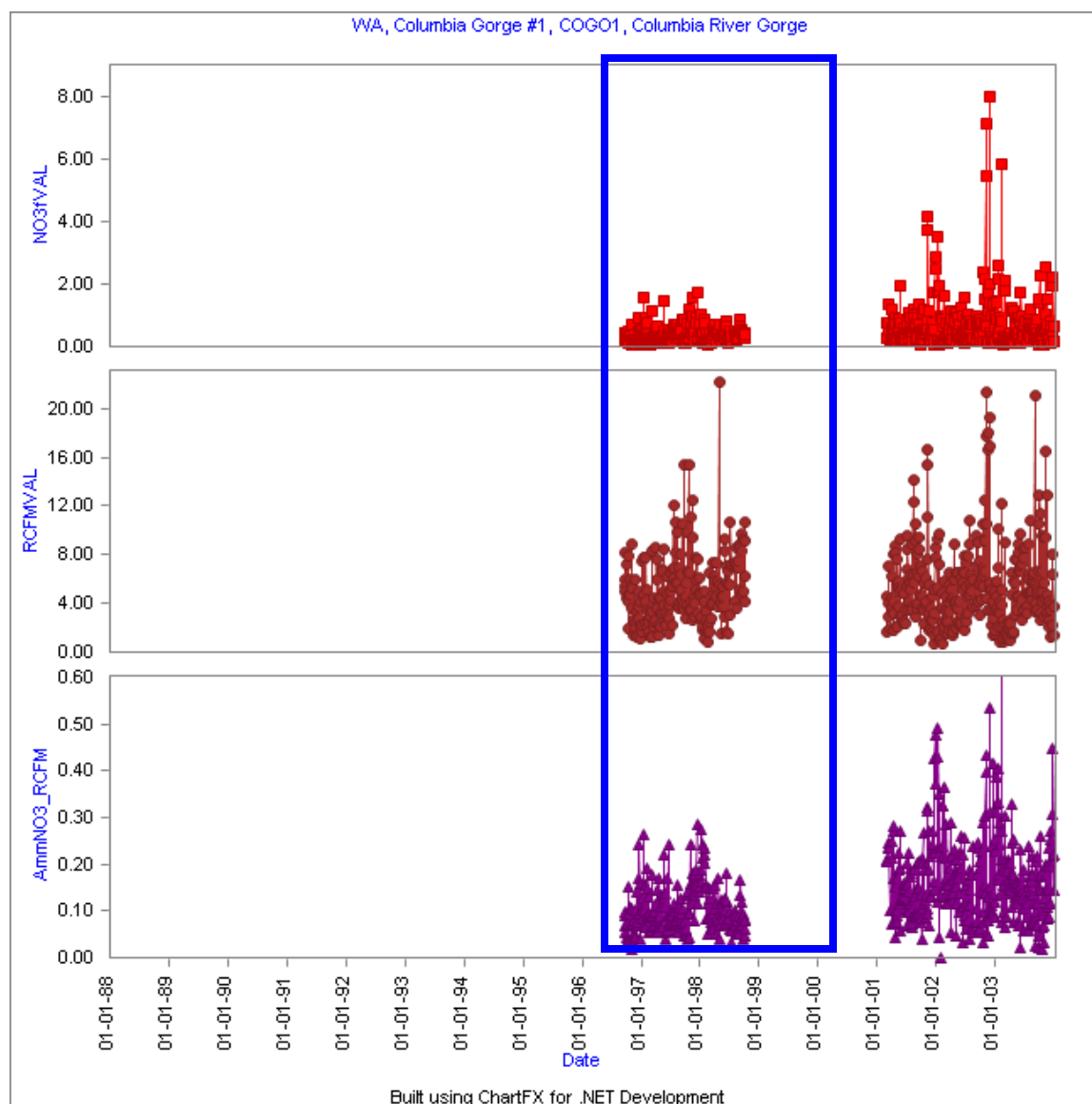
Alaska Region  
Boundary Waters Region  
California Coast Region  
Central Great Plains Region  
Death Valley Region  
Great Basin Region  
Hawaii Region  
Hells Canyon Region  
Lone Peak Region  
Mid South Region  
Mongollon Plateau Region  
Northern Region Great Plains Region  
Sierra Nevada Region  
Southern Arizona Region  
Southern California Region  
Virgin Islands Region

Washington DC Region  
West Texas Region

## Examples



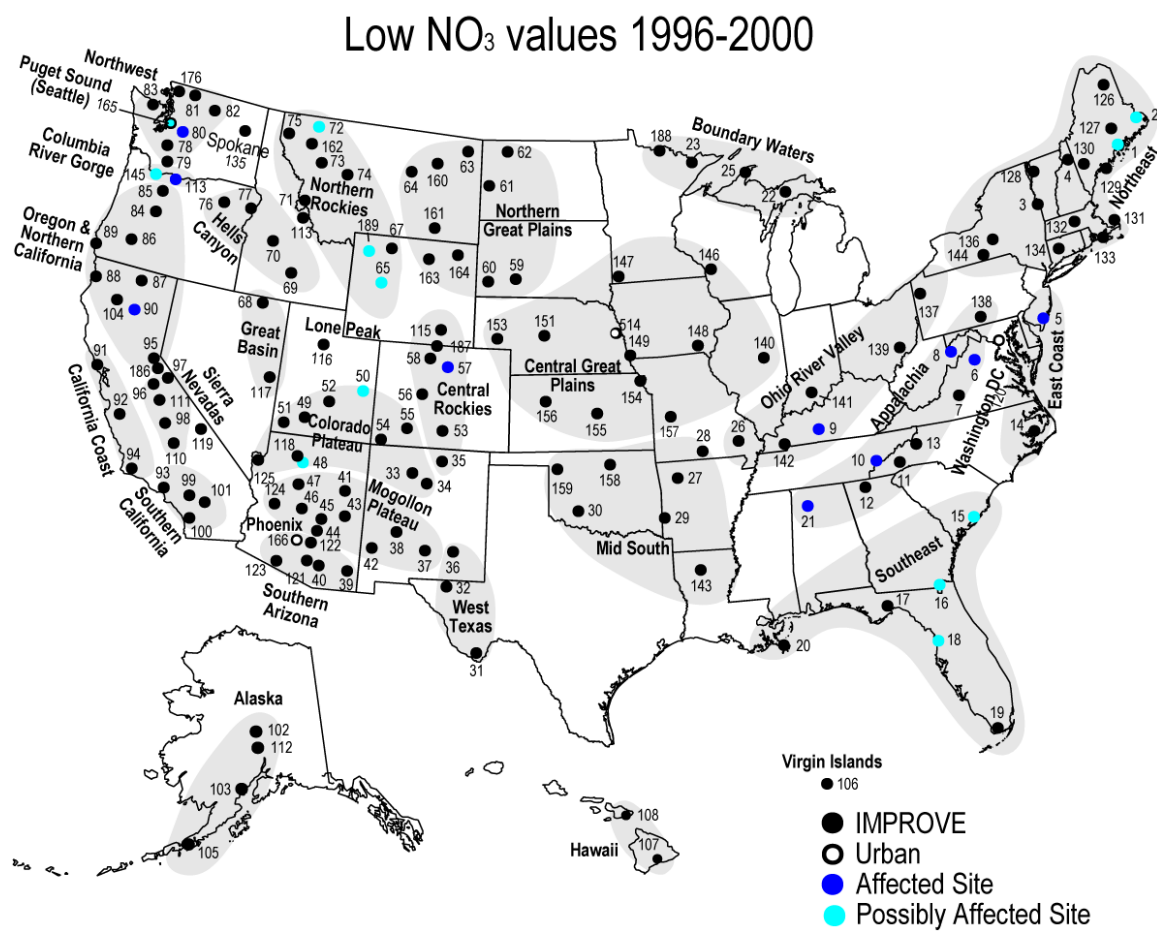




**Figure 1 a-c.** Examples of the unusually low absolute and relative NO<sub>3</sub> concentrations during 1996-2000.

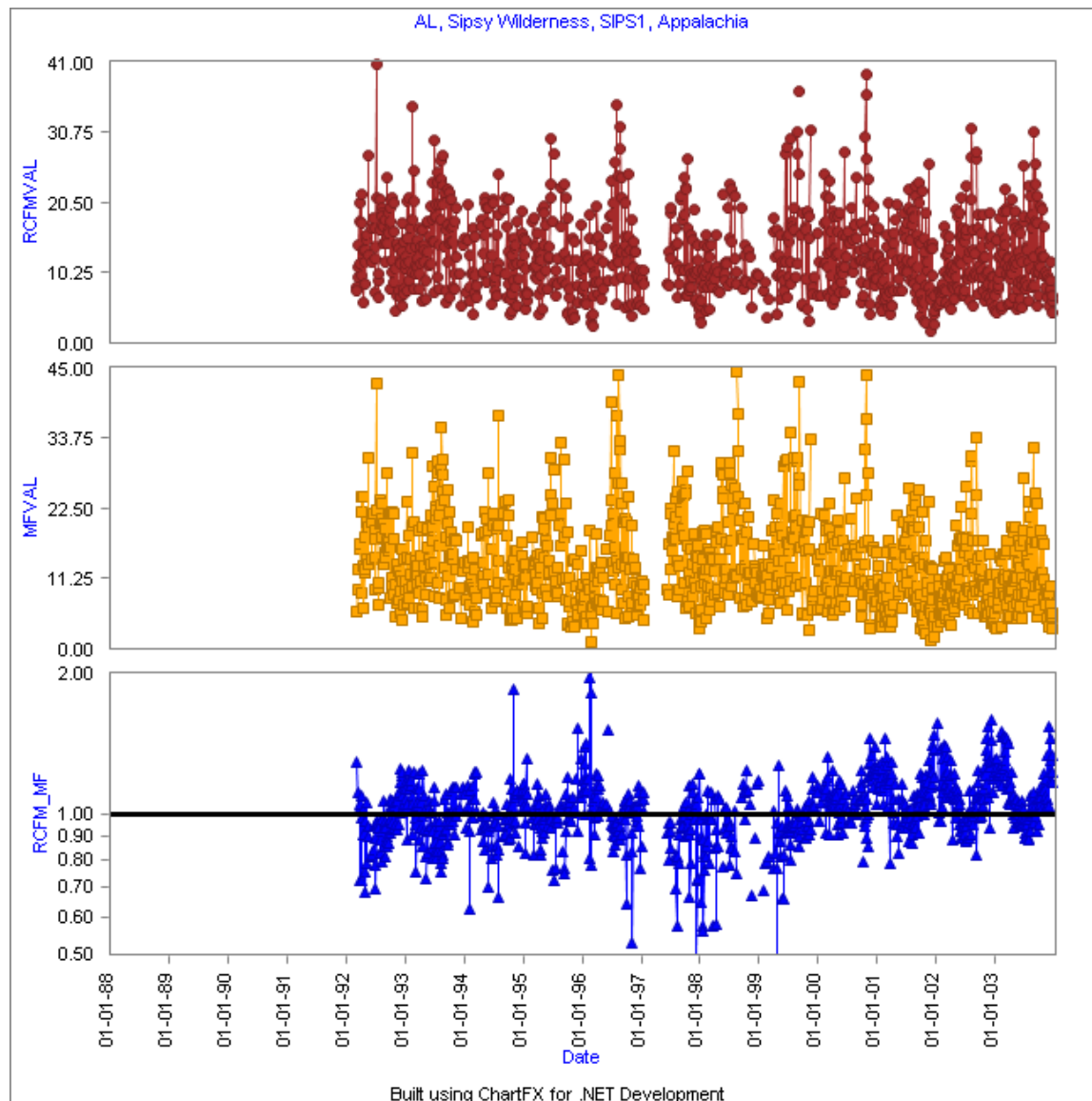
Legend:

- NO3fVAL: nitrate as measured by IC, [NO<sub>3</sub>] in ug/m<sup>3</sup>
- RCFM: reconstructed fine mass concentration calculated using the IMPROVE algorithm, [RCFM] in ug/m<sup>3</sup>
- ammNO3\_RCFM: ammonium nitrate concentration divided by the reconstructed fine mass concentration =  $1.29[\text{NO}_3]/[\text{RCFM}]$



**Figure 2.** Spatial Distribution of Anomaly 1





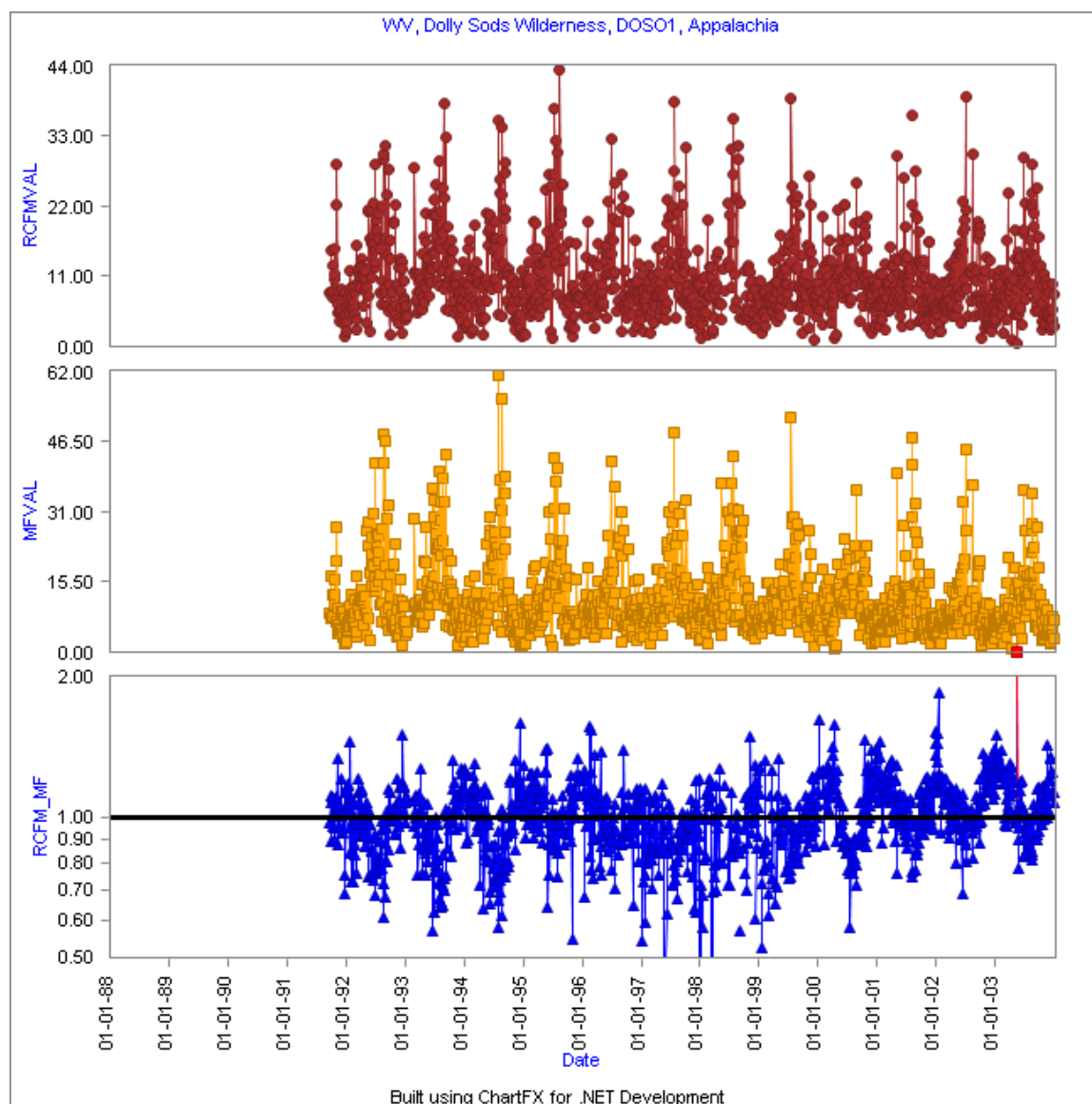


Figure 3 a-b) Examples of the low reconstructed fine mass to measured fine mass ratios and increased variability of the ratio from 1996-2000 at most sites with low  $\text{NO}_3$  values.

Legend:

- Ammonium Nitrate:  $\text{AmmNO}_3 = 1.29 \times [\text{NO}_3]$
- Ammonium Sulfate:  $\text{AmmSO}_4 = 4.125 \times [\text{S}]$
- Fine Soil:  $\text{SOIL} = 2.2 \times [\text{Al}] + 2.49 \times [\text{Si}] + 1.63 \times [\text{Ca}] + 2.42 \times [\text{Fe}] + 1.94 \times [\text{Ti}]$
- Organic Mass by Carbon:  $\text{OMC} = 1.9 \times ([\text{OC1}] + [\text{OC2}] + [\text{OC3}] + [\text{OC4}] + [\text{OP}])$
- Light Absorbing Carbon:  $\text{EC} = [\text{EC1}] + [\text{EC2}] + [\text{EC3}] - [\text{OP}]$
- Reconstructed Fine Mass:  $\text{RCFMVAL} = [\text{RCFM}] = \text{AmmSO}_4 + \text{AmmNO}_3 + \text{OMC} + \text{EC} + \text{SOIL}$
- Measured Fine Mass ( $\text{PM}_{2.5}$ ) =  $\text{MFVAL} = [\text{PM}_{2.5}]$
- Reconstructed to Fine Mass to Measured Fine Mass:  $\text{RCFM\_MF} = [\text{RCFM}] / [\text{PM}_{2.5}]$

**Anomaly 2:** High NO<sub>3</sub> values and ammonium NO<sub>3</sub>/RCFM ratios from 2000-2003. This time period was clearly marked by high NO<sub>3</sub> concentrations at 17 sites and possibly at an additional 17 of the ~165 sites in operation. Increased seasonality in the reconstructed fine mass to measured fine mass ratios was also present at most of these sites. There does not appear to be a correlation between cut point problems and the high NO<sub>3</sub> values. The high NO<sub>3</sub> values may be real rather than a result of sampling or analytical problems.

The sites are identified in the attached PowerPoint file with pink rectangles.

### **Affected Sites**

<b>Site Code</b>	<b>Site Name</b>	<b>State</b>	<b>IMPROVE Region</b>
DOSO1	Dolly Sods Wilderness	WV	Appalachia
GRSM1	Great Smoky Mountains NP	TN	Appalachia
SHEN1	Shenandoah NP	VA	Appalachia
SHRO1	Shining Rock Wilderness	NC	Appalachia
SIPS1	Sipsy Wilderness	AL	Appalachia
MOZI1	Mount Zirkel Wilderness	CO	Central Rockies
ROMO1	Rocky Mountain NP	CO	Central Rockies
MEVE1	Mesa Verde NP	CO	Colorado Plateau
WEMI1	Weminuche Wilderness	CO	Colorado Plateau
CORI1	Columbia River Gorge	WA	Columbia River Gorge
BRIG1	Brigantine NWR	NJ	East Coast
PEFO1	Petrified Forest NP	AZ	Mongollon Plateau
GLAC1	Glacier NP	MT	Northern Rockies
MORA1	Mount Rainier NP	WA	Northwest
SNPA1	Snoqualmie Pass	WA	Northwest
MACA1	Mammoth	KY	Ohio River

	Cave NP		Valley
GUMO1	Guadalupe Mountains NP	TX	West Texas

### **Possibly Affected Sites**

<b>Site Code</b>	<b>Site Name</b>	<b>State</b>	<b>IMPROVE Region</b>
BAND1	Bandelier NM	NM	Colorado Plateau
CANY1	Canyonlands NP	UT	Colorado Plateau
INGA1	Indian Gardens	AZ	Colorado Plateau
COGO1	Columbia Gorge #1	WA	Columbia River Gorge
GRBA1	Great Basin NP	NV	Great Basin
JARB1	Jarbridge Wilderness	NV	Great Basin
ACAD1	Acadia NP	ME	Northeast
MOOS1	Moosehorn NWR	ME	Northeast
BRID1	Bridger Wilderness	WY	Northern Rockies
YELL2	Yellowstone NP 2	WY	Northern Rockies
CRLA1	Crater Lake NP	OR	Oregon and Northern California
THSI1	Three Sisters Wilderness	OR	Oregon and Northern California
PUSO1	Puget Sound	WA	Puget Sound
YOSE1	Yosemite NP	CA	Sierra Nevadas
ROMA1	Cape Romain NWR	SC	Southeast
CHIR1	Chiricahua NM	AZ	Southern Arizona

### **Unaffected Regions**

Alaska Region

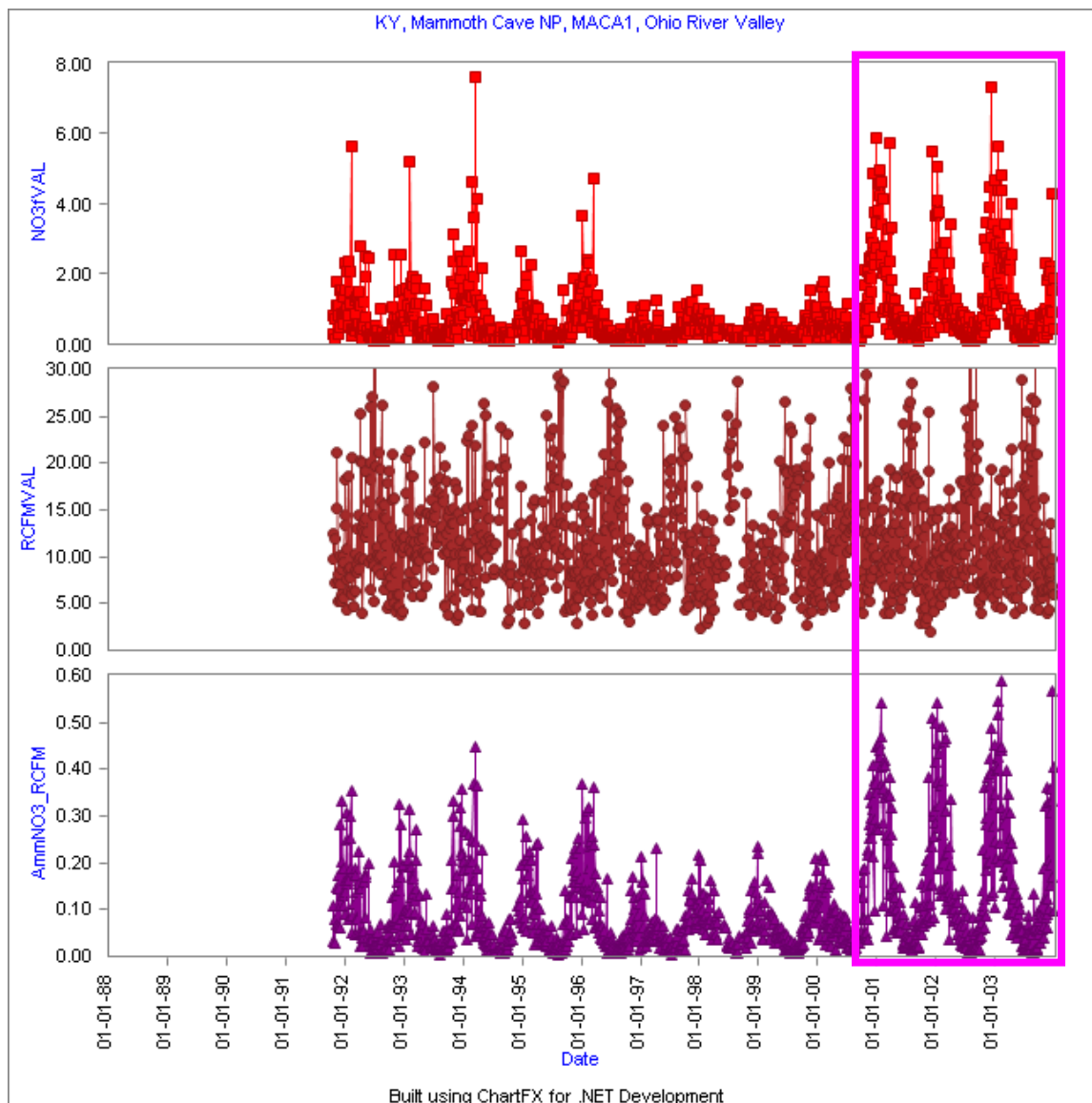
Boundary Waters Region

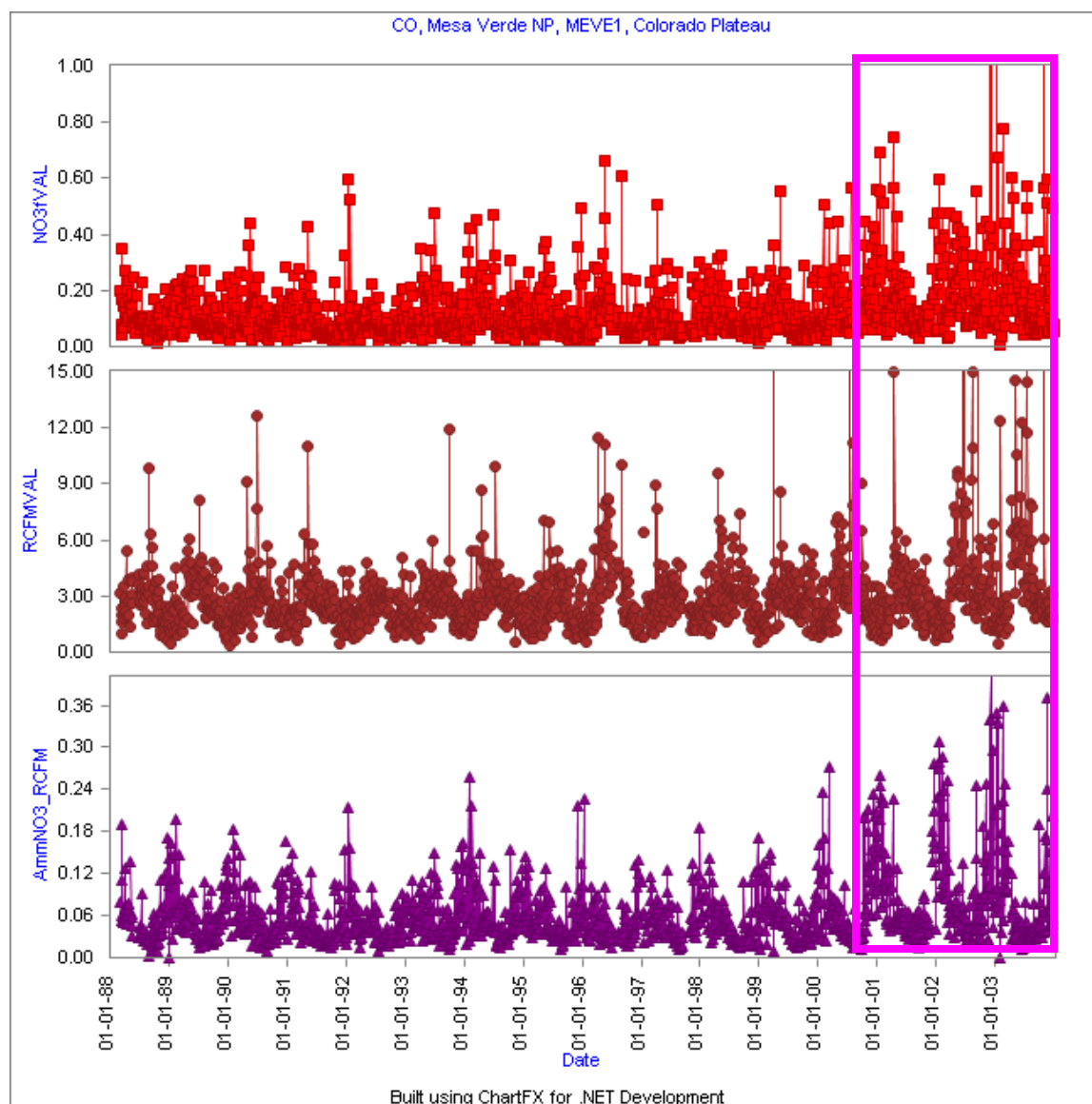
California Coast Region

Central Great Plains Region

Death Valley Region  
Hawaii Region  
Hells Canyon Region  
Lone Peak Region  
Mid South Region  
Northern Region Great Plains Region  
Southern California Region  
Virgin Islands Region  
Washington DC Region

### Example

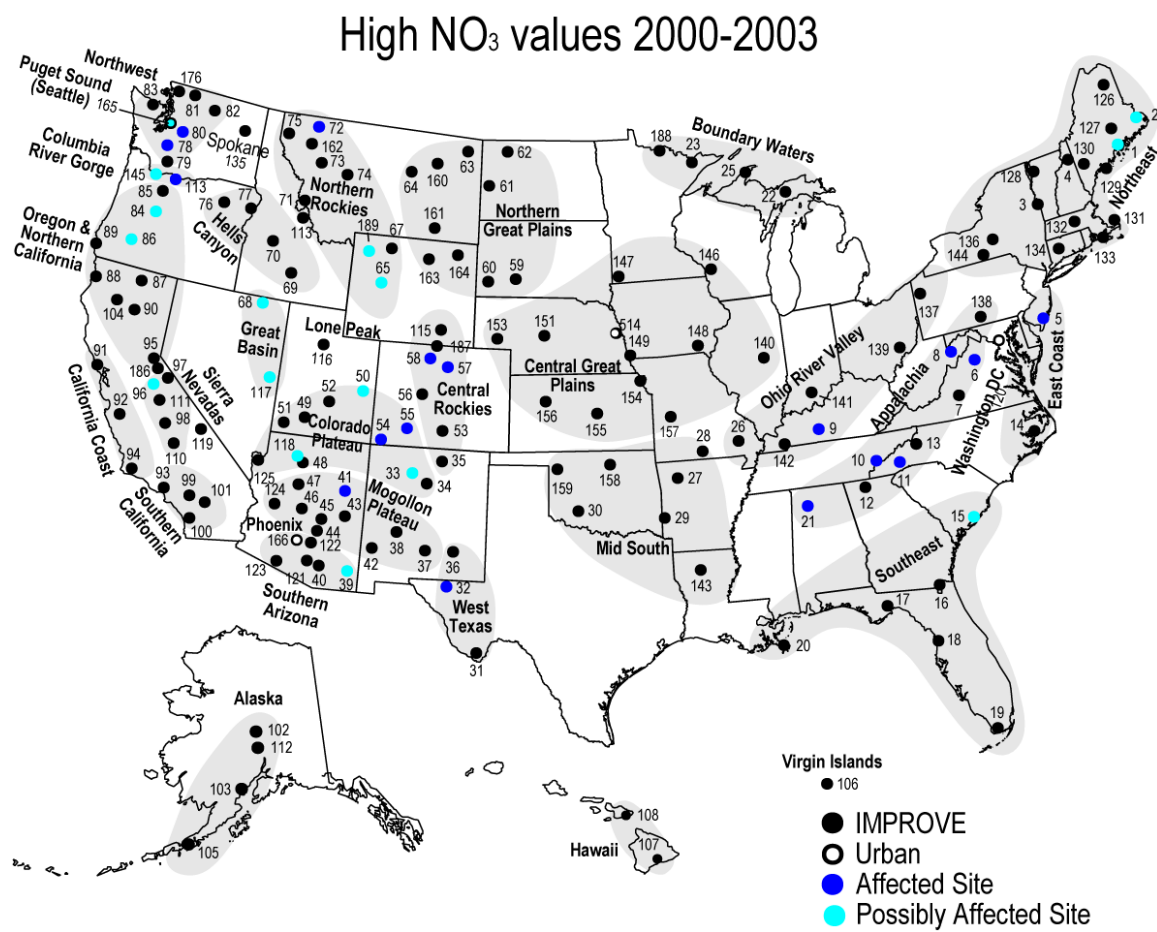




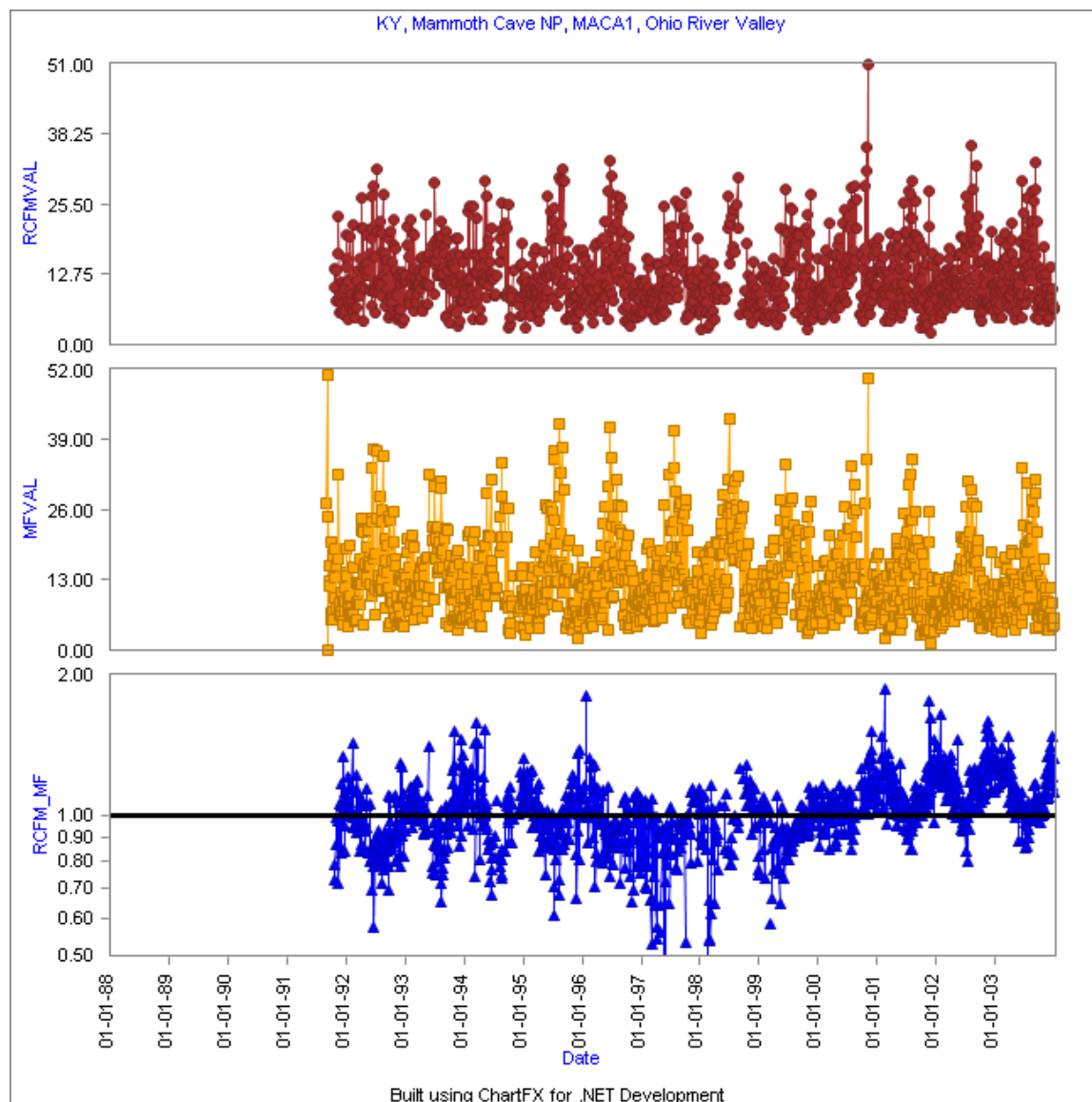
**Figure 4 a-b.** Examples of the unusually high absolute and relative NO<sub>3</sub> concentrations during 2001-2003.

**Legend:**

- NO3fVAL: nitrate as measured by IC, [NO<sub>3</sub>] in ug/m<sup>3</sup>
- RCFM: reconstructed fine mass concentration calculated using the IMPROVE algorithm, [RCFM] in ug/m<sup>3</sup>
- ammNO3\_RCFM: ammonium nitrate concentration divided by the reconstructed fine mass concentration =  $1.29[\text{NO}_3]/[\text{RCFM}]$



**Figure 5.** Spatial Distribution of Anomaly 2





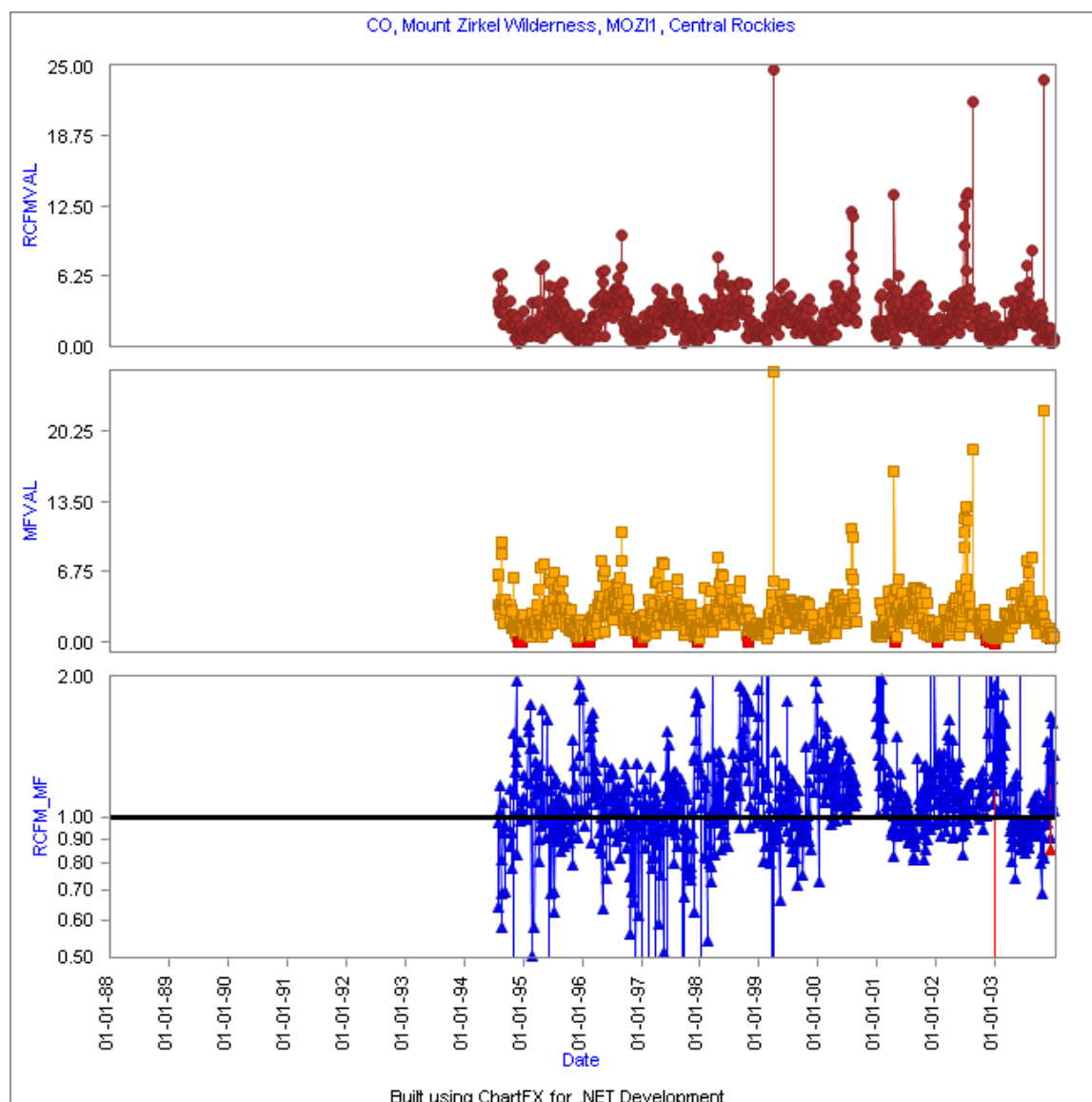


Figure 6 a-b) Examples of the very defined seasonality of the reconstructed fine mass to measured fine mass ratios from 2000-2003 at most sites with high  $\text{NO}_3$  values.

Legend:

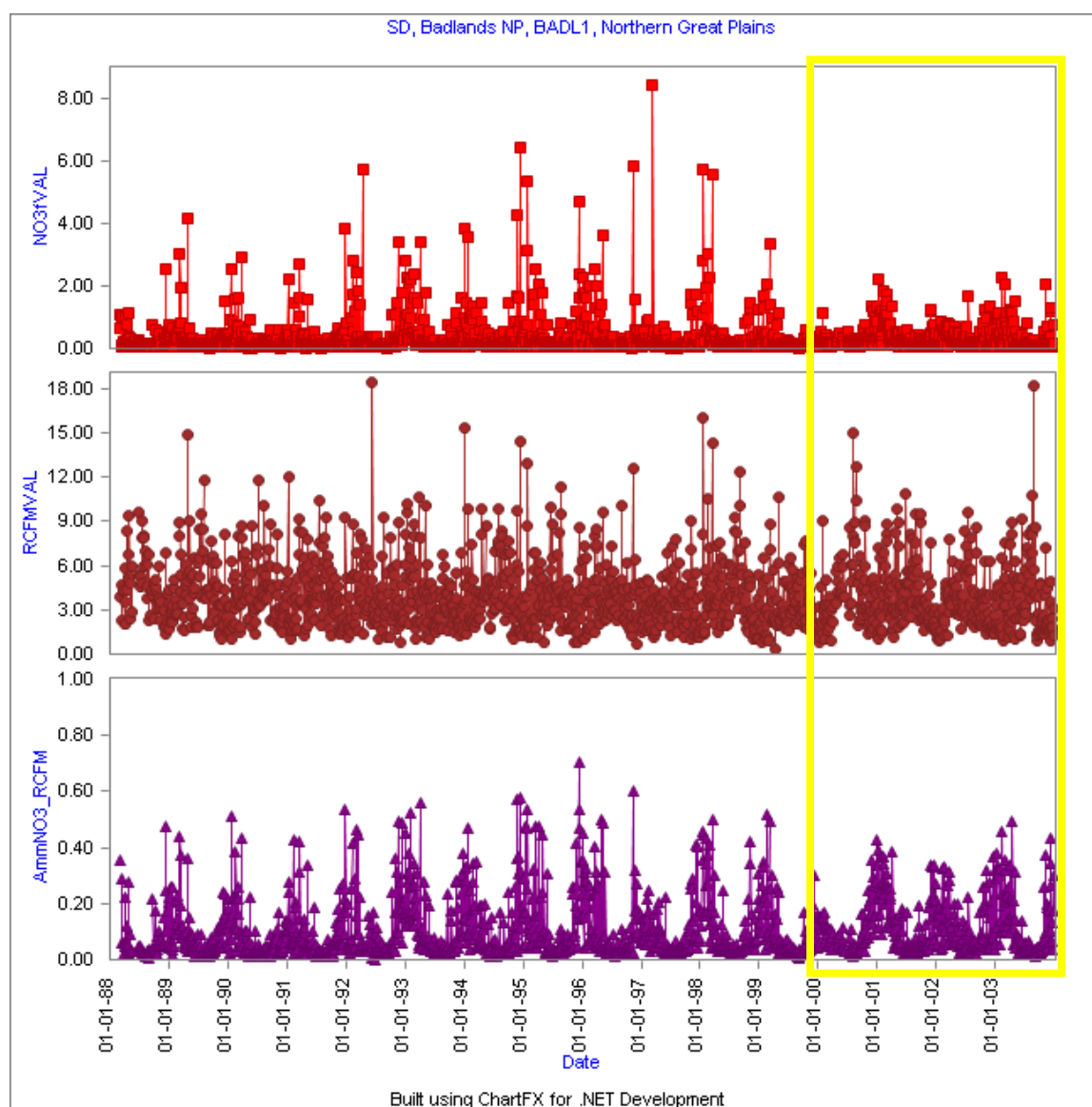
- Ammonium Nitrate:  $\text{AmmNO}_3 = 1.29 \cdot [\text{NO}_3]$
- Ammonium Sulfate:  $\text{AmmSO}_4 = 4.125 \cdot [\text{S}]$
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- Organic Mass by Carbon:  $\text{OMC} = 1.9 \cdot ([\text{OC1}] + [\text{OC2}] + [\text{OC3}] + [\text{OC4}] + [\text{OP}])$
- Light Absorbing Carbon:  $\text{EC} = [\text{EC1}] + [\text{EC2}] + [\text{EC3}] - [\text{OP}]$
- Reconstructed Fine Mass:  $\text{RCFMVAL} = [\text{RCFM}] = \text{AmmSO}_4 + \text{AmmNO}_3 + \text{OMC} + \text{EC} + \text{SOIL}$
- Measured Fine Mass ( $\text{PM}_{2.5}$ ) =  $\text{MFVAL} = [\text{PM}_{2.5}]$
- Reconstructed to Fine Mass to Measured Fine Mass:  $\text{RCFM\_MF} = [\text{RCFM}] / [\text{PM}_{2.5}]$

## Isolated Anomalies

**Anomaly 1:** There are no high outliers at BADL1 after 1999. The version 2 sampler was installed on 12/18/1999 which may have had some unforeseen impact on  $\text{NO}_3$  concentration ranges. Intermittent air conditioning was suggested by Kristi Gebhart as an issue worth exploring, metadata relating to the issue has not been identified.

The site is identified in the attached PowerPoint file with a yellow rectangle.

Site Code	Site Name	State	IMPROVE Region
BADL1	Badlands NP	SD	Northern Great Plains



**Figure 7.** Reduced range in  $\text{NO}_3$  concentrations from 2000-2003 at BADL1.

Legend:

- NO3fVAL: nitrate as measured by IC,  $[\text{NO}_3]$  in  $\mu\text{g}/\text{m}^3$
- RCFM: reconstructed fine mass concentration calculated using the IMPROVE algorithm,  $[\text{RCFM}]$  in  $\mu\text{g}/\text{m}^3$

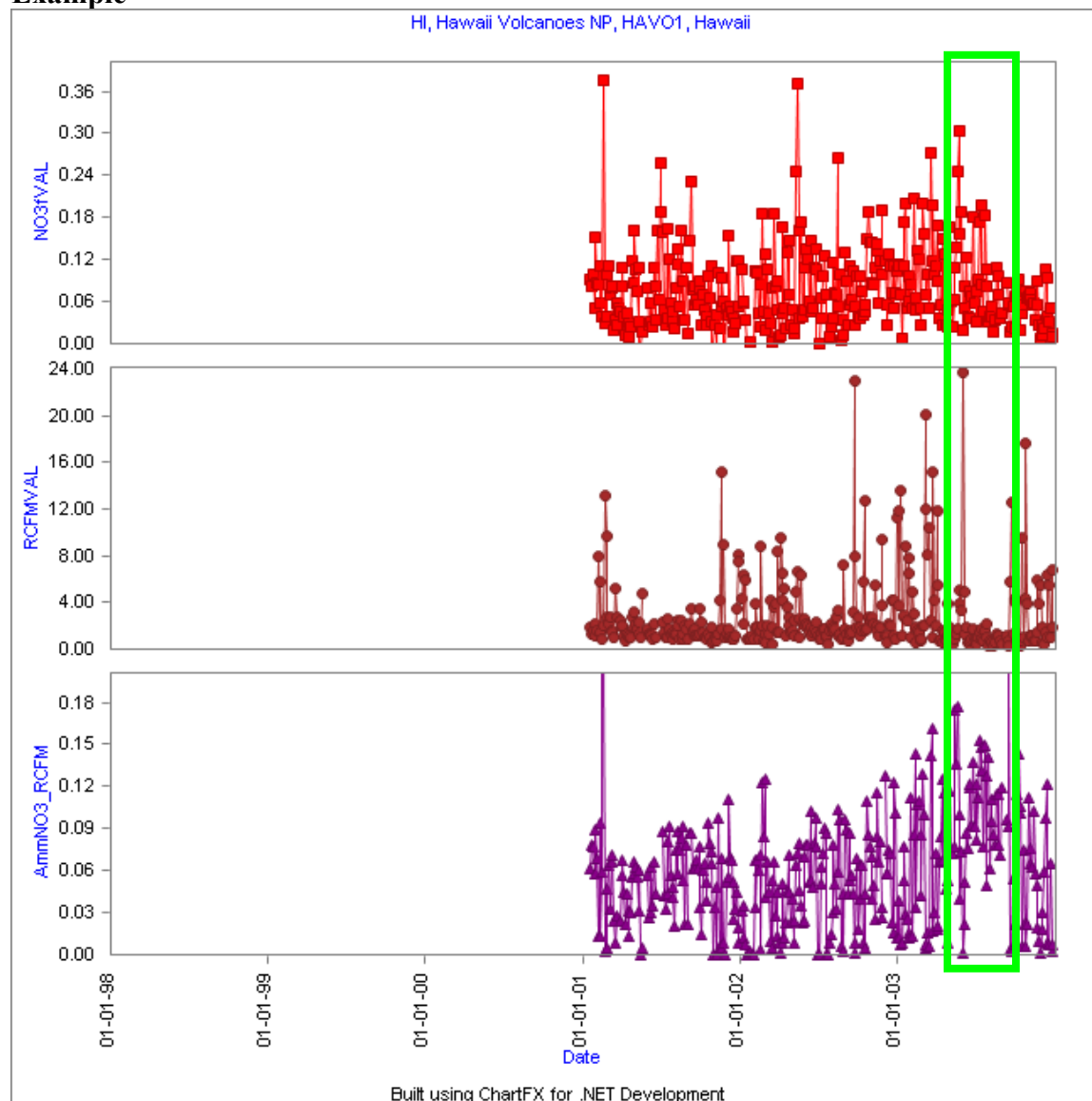
ammNO3\_RCFM: ammonium nitrate concentration divided by the reconstructed fine mass concentration =  $1.29[\text{NO}_3]/[\text{RCFM}]$

**Anomaly 2:** Unusually high ammonium nitrate to reconstructed fine mass ratios at HAVO1 during mid-2003.

The site is identified in the attached PowerPoint file with a bright green rectangle.

Site Code	Site Name	State	IMPROVE Region
HAVO1	Hawaii Volcanoes NP	HI	Hawaii

### Example



**Figure 8.** Reduced range in NO<sub>3</sub> concentrations from 2000-2003 at BAD11.

Legend:

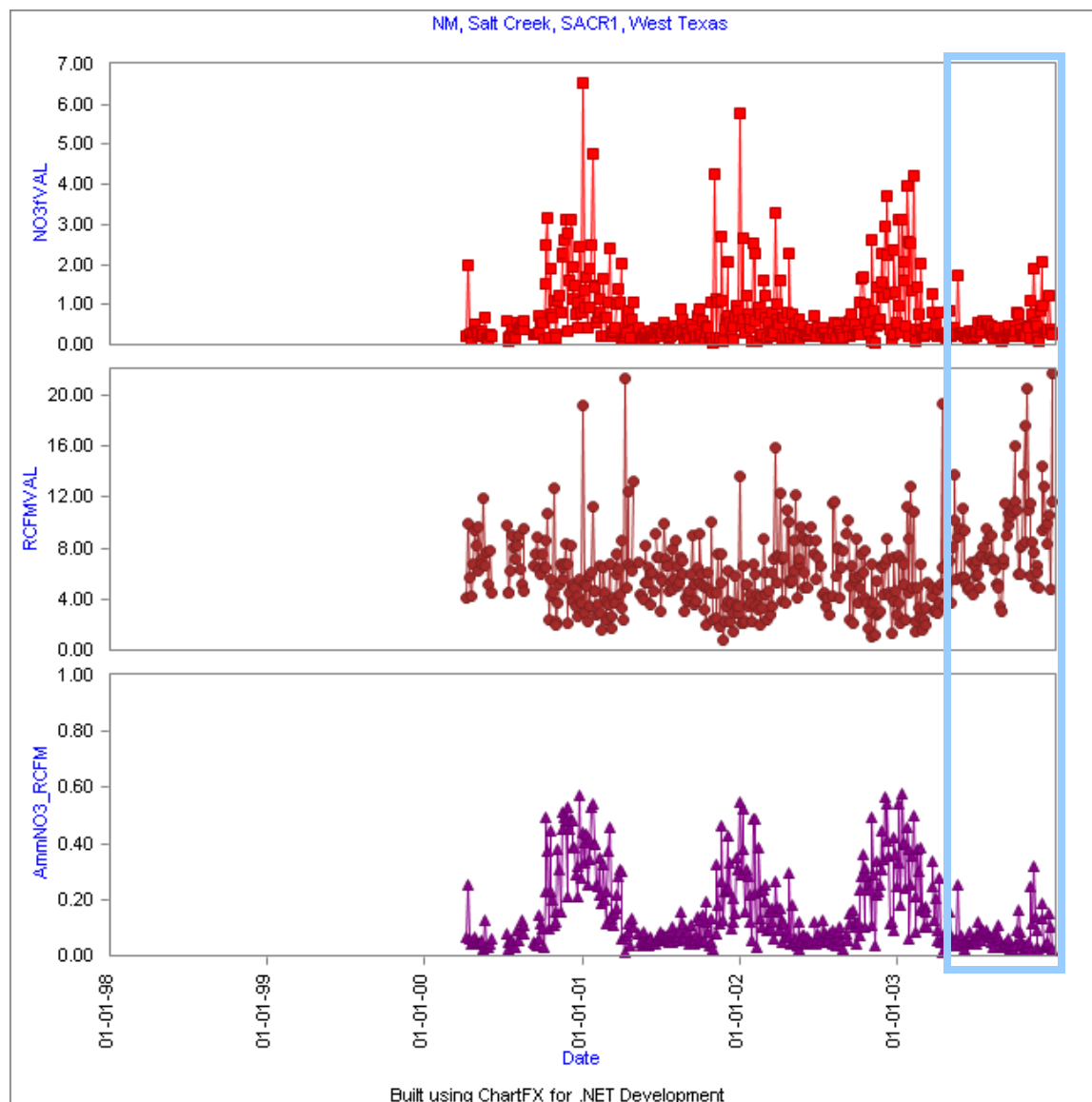
- NO3fVAL: nitrate as measured by IC, [NO<sub>3</sub>] in ug/m<sup>3</sup>

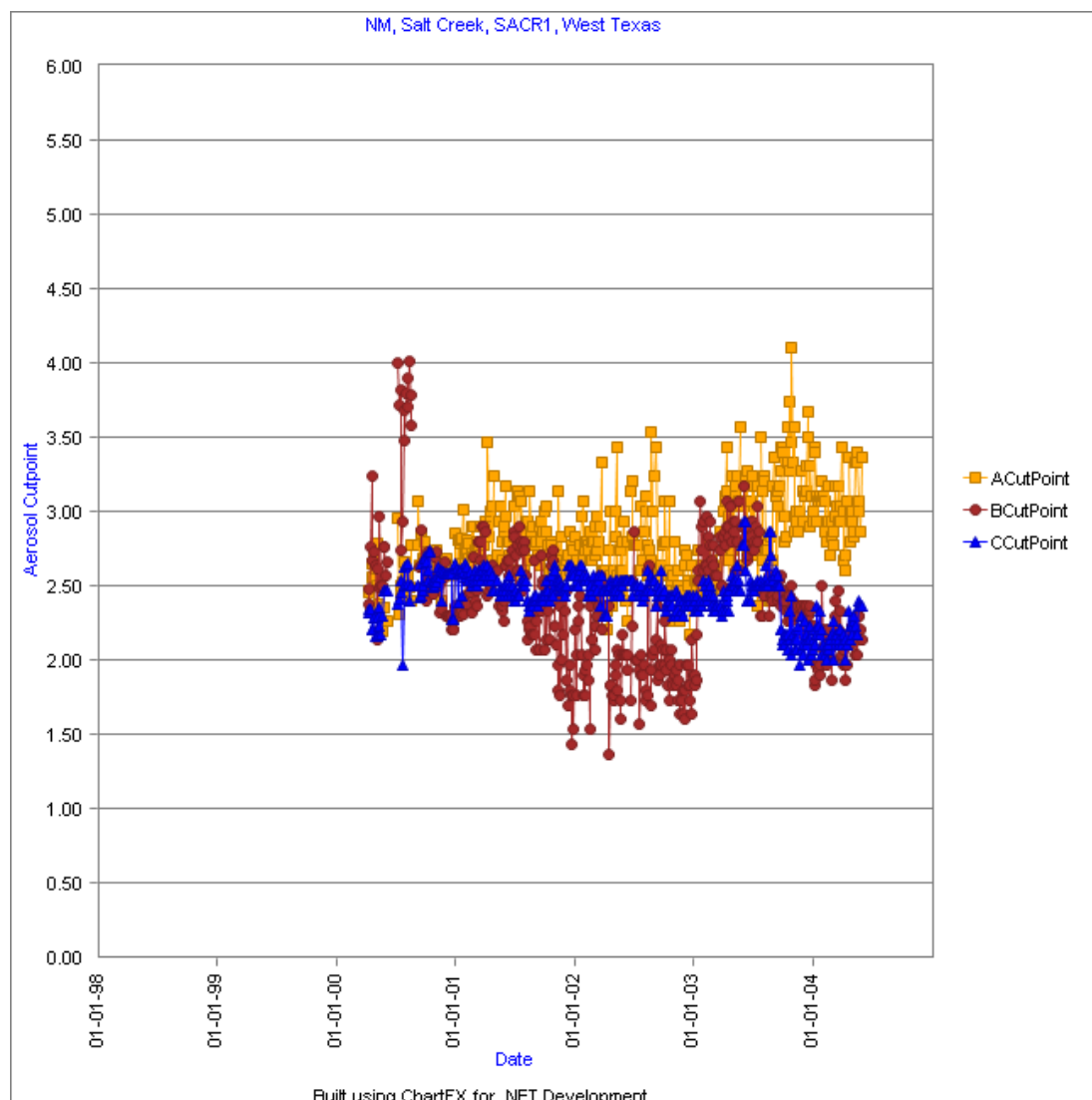
- RCFM: reconstructed fine mass concentration calculated using the IMPROVE algorithm, [RCFM] in  $\mu\text{g}/\text{m}^3$
- ammNO3\_RCFM: ammonium nitrate concentration divided by the reconstructed fine mass concentration =  $1.29[\text{NO}_3]/[\text{RCFM}]$

**Anomaly 3:** Ammonium nitrate to reconstructed fine mass (RCFM) ratios were unusually low during 2003 at SACR1 due to unusually high RCFM values. At SACR1 increasing trends in SOIL concentrations and relative SOIL contributions to reconstructed fine mass (SOIL/RCFM) look to be correlated to increasing trends in the A module cut point. However the B module was not similarly affected, in fact the B module cut point was consistently below the ideal of 2.5  $\mu\text{m}$ . The offset in cut points between the modules looks to be causing the change in relative  $\text{NO}_3$  concentrations during 2003 as compared to previous years.

The site is identified in the attached PowerPoint file with a light blue rectangle.

Site Code	Site Name	State	IMPROVE Region
SACR1	Salt Creek	NM	West Texas





**Figure 9 a-b.** Higher than nominal cut points on the A module lead to elevated soil and RCFM values and therefore depressed relative  $\text{NO}_3$  levels.

Legend:

- $\text{NO}_3\text{fVAL}$ : nitrate as measured by IC,  $[\text{NO}_3]$  in  $\mu\text{g}/\text{m}^3$
- RCFM: reconstructed fine mass concentration calculated using the IMPROVE algorithm,  $[\text{RCFM}]$  in  $\mu\text{g}/\text{m}^3$
- $\text{ammNO}_3\_RCFM$ : ammonium nitrate concentration divided by the reconstructed fine mass concentration =  $1.29[\text{NO}_3]/[\text{RCFM}]$
- ACutPoint: A module cut point, aerodynamic diameter at which 50% of the particles are collected ( $\mu\text{m}$ )
- BCutPoint: B module cut point, aerodynamic diameter at which 50% of the particles are collected ( $\mu\text{m}$ )
- CCutPoint: C module cut point, aerodynamic diameter at which 50% of the particles are collected ( $\mu\text{m}$ )