

Artifact Corrections in IMPROVE

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Paper #15

ABSTRACT

IMPROVE adjusts for positive sampling artifacts by subtracting nylon filter field blank values and quartz afterfilter values from measured ion and carbon concentrations, respectively. Artifacts have been observed to vary substantially among filter manufacturing lots, especially for nylon filters. Sulfate and nitrate artifact corrections are currently less than 10% of the measured values, but organic carbon artifacts can exceed 50% of the measured values.

INTRODUCTION

The IMPROVE (Interagency Monitoring of Protected Visual Environments) network collects fine particles (PM_{2.5}) on nylon filters for ion analysis and on quartz fiber filters for carbon analysis.¹ Data from both filters have been corrected for sampling artifacts since the beginning of IMPROVE measurements in 1988. Artifacts are defined as any increase or decrease of material on the filter that positively or negatively biases the measurement of ambient concentration. The five major types of artifacts are:

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

Citation Insert

Paper No. 15. Artifact Corrections in IMPROVE. Regional and Global Perspectives on Haze: Causes, Consequences, and Controversies – Visibility Specialty Conference, Air & Waste Management Association, Asheville, NC, October 25-29, 2004.

- volatilization during collection and in handling;
- loss of material during handling after collection.

The first three types are positive artifacts and the last two are negative.

For ions, dynamic field blank nylon filters are collected at all sites throughout the 164-site network. For carbon, dynamic field blank quartz filters are collected at all sites in the network and quartz afterfilters are collected at six selected sites. Dynamic field blank Teflon filters are also collected throughout the network. Dynamic field blanks are treated the same as standard network filters, including being placed in the sampler, but they are not sampled.

The nylon filter field blank or quartz afterfilter value is subtracted from the raw measured value to provide an artifact-corrected ambient concentration. By subtracting these values, IMPROVE corrects for the positive sampling artifacts. Because the gravimetric mass and elements measured on the Teflon field blanks are statistically insignificant, no artifact correction is made for the measurements on the Teflon filter. Blanks that are not used for artifact correction nonetheless serve a useful function in identifying unusual behavior in the network.

For sulfate and nitrate ions, the negative artifacts are negligible. The only volatile ionic species of interest is ammonium nitrate, and if any of the ammonium nitrate were to be converted to nitric acid through volatilization it would be retained on the nylon filter. Furthermore, only the first two positive artifacts (contamination) are believed to be significant, since gaseous species (nitric acid and SO₂) are captured by a sodium carbonate denuder upstream of the filter.

For carbon sampling, IMPROVE assumes that negative artifacts are insignificant compared to positive artifacts. Contamination and gas adsorption positive artifacts are accommodated by subtraction of the quartz afterfilter concentration. There is evidence that both positive adsorption artifacts and negative volatilization artifacts can compete under some conditions, and it cannot be known which dominates during a 24-hour sampling period.² Nevertheless, measured mass and light extinction are reproduced reasonably by the artifact-adjusted IMPROVE chemical components, lending credibility to the IMPROVE approach of subtracting positive organic artifacts.³

The artifact corrections do not distinguish among changes that may occur before, during, or after sample collection. All filters are analyzed once when they are returned to the laboratory, so all aspects of sample gain or loss are incorporated in a single artifact correction.

For both nylon and quartz filters, the seasonal or monthly median concentration value of all blanks or afterfilters is determined each season or month, and this median value is subtracted from each ion and organic carbon concentration to account for positive sampling artifacts. Artifact corrections are made separately for each reported ion and for each component of organic carbon.

Prior to June 2002, IMPROVE data were processed seasonally (e.g., March, April, May), so the median artifact value for each three-month season was used to adjust the data for that season. Beginning in June 2002, IMPROVE data have been processed monthly, so a monthly median artifact value is applied to each month's data.

When the artifact values are of comparable magnitude to the laboratory-measured filter concentration, then the artifact subtraction can result in negative reported concentrations. These

negative numbers are physically meaningful, as they represent the variability of the artifact. Negative concentrations are reported to the IMPROVE data base.

IMPROVE also collects particles on Teflon filters for gravimetric and elemental analysis. Teflon field blanks are collected routinely at all sites. The Teflon field blank levels are consistently very small compared to the ambient concentrations. Thus, although the Teflon field blanks are examined routinely to identify potential problems, they are not used for artifact corrections in the IMPROVE data base.

MEASUREMENTS

Filters to assess sampling artifacts are collected routinely in IMPROVE. For ions, a field blank nylon filter is placed in an unused port in the sampling plenum, so it is exposed to all aspects of the filter handling process except it does not have sample air drawn through it. Approximately 70 field blanks are collected each month, constituting around 4% of the total filters collected. Each site receives a nylon filter field blank every two to three months, on average. Quartz filter field blanks are also collected at approximately the same frequency, and they are analyzed for the components of organic and elemental carbon.⁴ These field blanks are examined routinely to identify potential problems, but they are not used for artifact corrections in the IMPROVE data base. Rather, secondary filters (afterfilters) are collected at six sites to determine the artifact corrections for organic and elemental carbon. These afterfilters are placed directly behind the primary quartz filter, which captures the particulate material. The afterfilter is designed to capture organic gases that have traversed the primary filter.

Although quartz field blank filters and afterfilters typically display similar concentrations, it was deemed prudent to use afterfilters for artifact correction because they are directly exposed to the airstream that may contain organic gases.

Quartz afterfilters are collected during every sampling period at six sites: Chiricahua, AZ; Grand Canyon, AZ; Yosemite, CA; Okefenokee, GA; Shenandoah, VA; and Mount Rainier, WA. These sites were selected to cover a variety of regions and aerosol conditions. The afterfilters at the Chiricahua and Okefenokee sites were added in 2001. Prior to that time, the organic artifact was determined from afterfilter measurements at four sites. The sites are limited within the network due to financial and logistical constraints.

RESULTS AND DISCUSSION

Ions (Nylon Filters)

Nylon filter field blanks are used to determine an artifact correction for each of the ions that are routinely reported in IMPROVE: sulfate (SO_4^-), nitrate (NO_3^-), nitrite (NO_2^-), chloride (Cl^-), and ammonium (NH_4^+). In each case, the artifact value is subtracted from the measured concentration to account for filter contamination.

The nylon filter artifacts that have been applied in IMPROVE since 1995 are shown in Figures 1, 2, and 3 for sulfate, nitrate, and chloride, respectively. Artifact corrections have been applied since the beginning of IMPROVE measurements in 1988, but only the more recent years are shown here to illustrate the variability with better visual clarity on an expanded time scale. Each data point represents the network median artifact value applied for that season or month. The

vertical bars represent the standard deviation of the field blank values during the season or month.

Variability of the artifact values is evident, especially in the chloride blanks. In late 1996 IMPROVE was forced to change filter manufacturers because the existing manufacturer ceased production of the nylon filters used in the network. Filters are purchased in manufacturing lots, and the lot changes with the new manufacturer are indicated by the green dots along the horizontal axis. Furthermore, IMPROVE switched from 25 mm to 37 mm diameter filters with the second lot change in 2000, giving a filter area more than twice as large as before. This size change corresponded to a redesigned IMPROVE sampler, deemed the Version 2 sampler. One would expect the artifact values to approximately double with this change in filter size, since the artifacts are determined by the amount of contaminant on the entire filter. However, the chloride artifact values more than doubled, suggesting that the 37 mm filters were not only larger but more contaminated, as well.

The larger standard deviations occur when a lot was changed during a season and the blank concentrations differed substantially from the beginning to the end of the season. An example would be the sulfate artifact during the first lot change of 1997.

The original IMPROVE filter manufacturer (pre-1996) recently resumed the manufacture of nylon filters. IMPROVE purchased a lot of these filters and began using them in the network in January 2004. It is evident from Figures 1, 2, and 3 that the new filters have much lower blank concentrations than did the old filters. Consequently, the artifact corrections will be substantially smaller beginning in 2004.

Figures 4 and 5 show the artifact corrections in comparison to the measured concentrations for sulfate and nitrate, respectively. Artifact-corrected chloride values are typically zero at most sites, so they are not shown here. The ambient concentrations in Figures 4 and 5 are the median reported (i.e., artifact-corrected) values for the entire IMPROVE network for the specified season or month. The artifact values are the seasonal or monthly medians expressed as ambient concentrations by converting the measured artifacts ($\mu\text{g}/\text{filter}$) using the nominal sampler flowrate (23 liters/minute) and nominal sampling time (24 hours). Figures 4 and 5 also show the percentage of the reported value represented by the artifact.

Sulfate artifacts typically represent less than 10% of the ambient concentration, whereas nitrate artifacts typically lie in the range of 10 to 20%. Beginning with the new filters in 2004, artifact corrections for both of these ions should typically lie well below 10%.

Figure 1. Sulfate artifacts used in the IMPROVE network since 1995, based on the median values of the field blanks. The vertical bars represent the standard deviation. The points along the horizontal axis indicate filter lot changes.

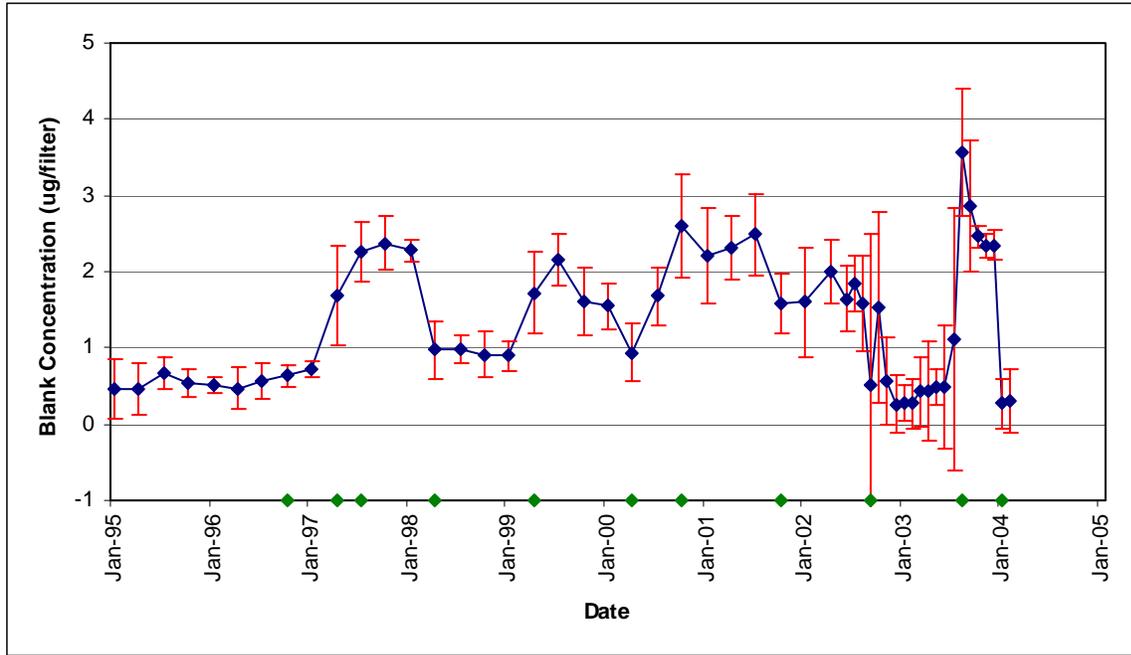


Figure 2. Nitrate artifacts used in the IMPROVE network since 1995, based on the median values of the field blanks. The vertical bars represent the standard deviation. The points along the horizontal axis indicate filter lot changes.

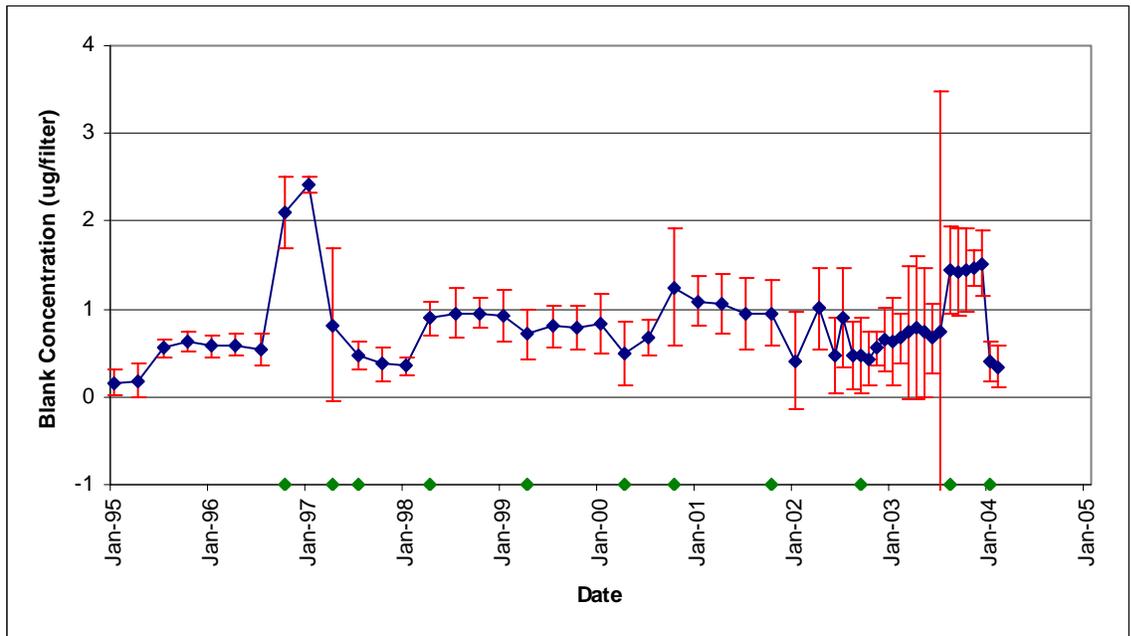


Figure 3. Chloride artifacts used in the IMPROVE network since 1995, based on the median values of the field blanks. The vertical bars represent the standard deviation. The points along the horizontal axis indicate filter lot changes.

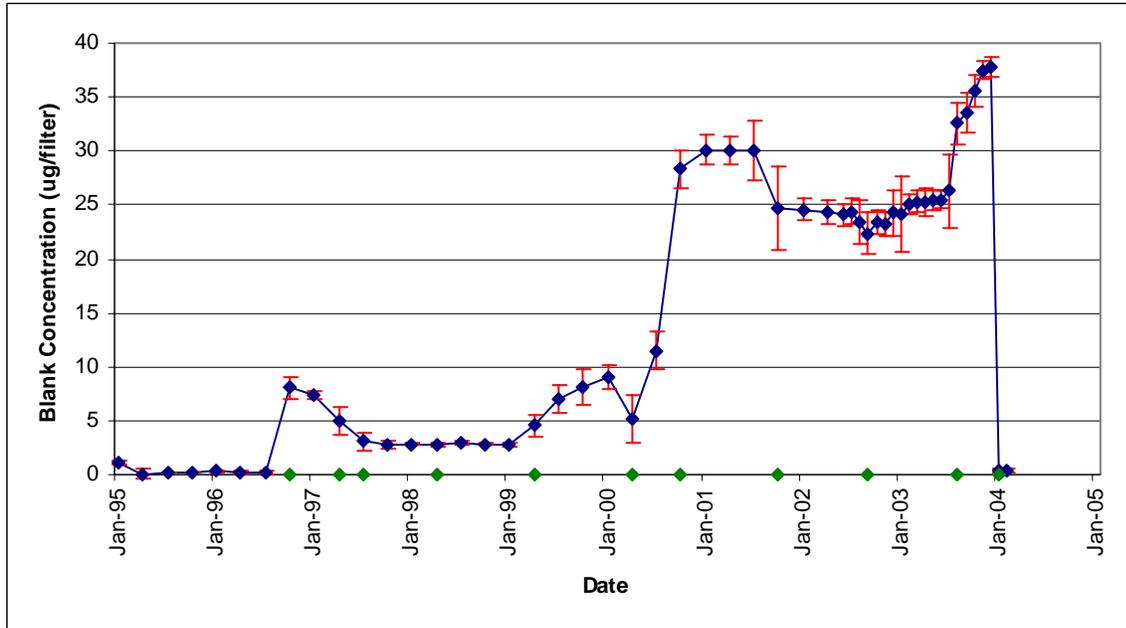


Figure 4. Comparison of the median ambient sulfate concentration to the median sulfate artifact. The units are $\mu\text{g}/\text{m}^3$. The artifact was converted to these units assuming the nominal sample volume.

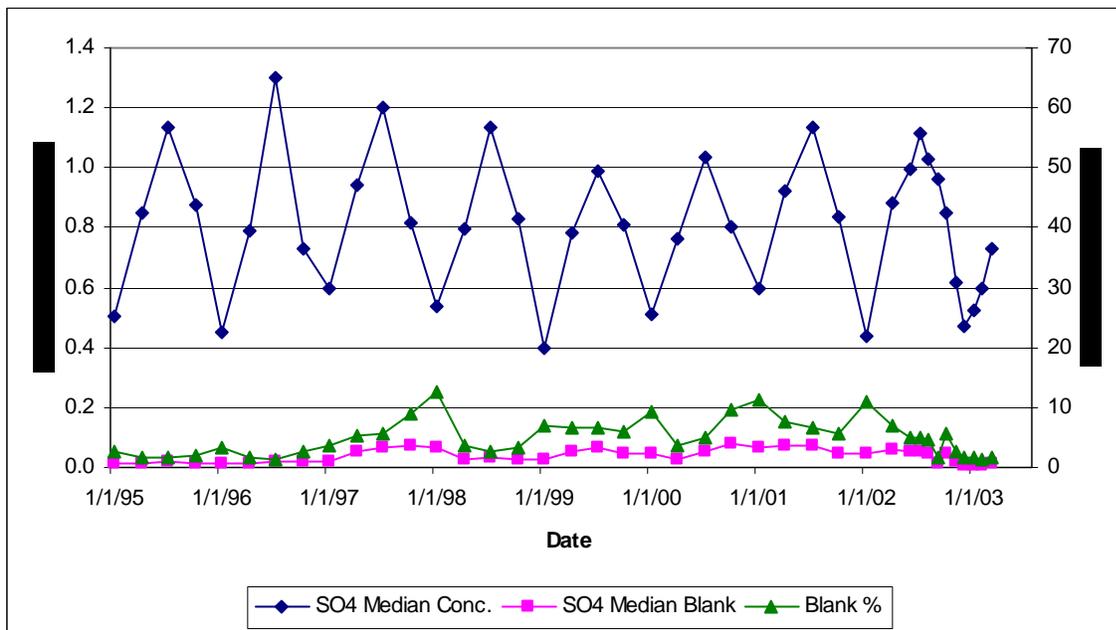
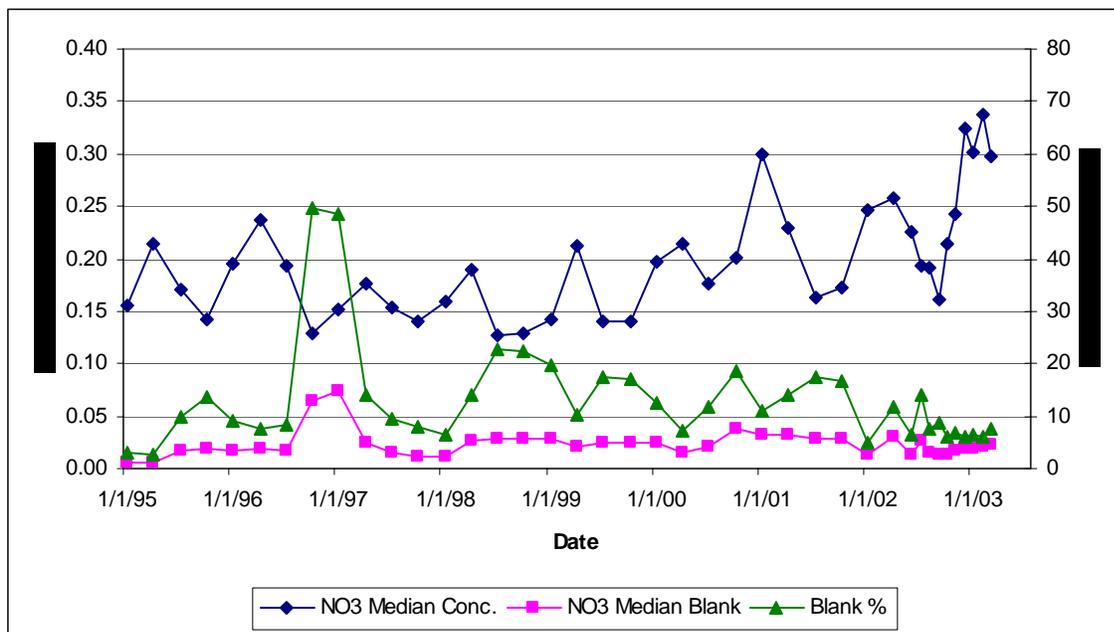


Figure 5. Comparison of the median ambient nitrate concentration to the median nitrate artifact. The units are $\mu\text{g}/\text{m}^3$. The artifact was converted to these units assuming the nominal sample volume.



Organic and Elemental Carbon (Quartz Filters)

Artifacts for organic and elemental carbon are applied separately for each of the temperature-defined components of the measurement. The quartz filter artifacts that have been applied in IMPROVE since 1995 are shown in Figures 6 and 7 for O₃ and E₂, two of the more prominent fractions of organic and elemental carbon, respectively. Each data point represents the network median artifact value applied for that season or month. The vertical bars represent the standard deviation of the artifact values during the season or month.

The O₃ artifact is substantial and typically represents around half of the reported ambient concentration, ranging to higher proportions when concentrations are low. The monthly O₃ artifact increased during the summer of 2002, compared to prior summers. However, most of this increase was due to the switch to monthly data reporting, with the highest median corresponding to a single month, July 2002. The median for the equivalent season (June, July, and August 2002) is $6.1 \pm 2.7 \mu\text{g}/\text{filter}$, which is not statistically different from the prior summer's median O₃ artifact (5.8 ± 2.9).

The E₂ artifacts decreased substantially following the introduction of the Version 2 IMPROVE samplers in 2000. The Version 1 sampler cassette employed a Viton o-ring which is absent in the Version 2 samplers. This o-ring apparently resulted in an elemental carbon artifact. The E₂ artifact represented around half of the reported ambient concentration in the Version 1 sampler, but is typically less than 10% of the reported ambient concentration in the Version 2 sampler.

Due to the expense of the measurement, quartz afterfilters are collected at only six sites. Figures 8 and 9 show the site-by-site median artifact values for O₃ and E₂, respectively, along with the network median for comparison. Both plots demonstrate some outlier values. The Okefenokee

site, in particular, tends to have higher artifact concentrations than the other sites. However, using the median value, rather than the mean, diminishes the influence of high or low points.

The network median artifact value is considered to be representative of the entire network. As an illustration, Figure 10 shows O₃ for Grand Canyon National Park as reported in the IMPROVE data base (blue diamonds) as well as O₃ calculated using the seasonal or monthly median as measured at Grand Canyon (pink triangles). The green squares show the percent difference between these two values, defined as the new Grand Canyon-adjusted concentration minus the original concentration, divided by the absolute value of the original concentration. Much of the time the network median-determined concentration is a close representation of the Grand Canyon median-determined concentration, with the two concentrations typically agreeing within 20% (the median is 15%). But in some cases the differences are substantial, rising well over 100%. These deviations typically occur when the actual ambient concentration is approaching zero, so that differences in the artifact corrections are magnified. Furthermore, the percent differences in Figure 10 are almost always positive, representing the tendency of the Grand Canyon afterfilter values to fall below the median value (see Figure 8).

Figure 6. Artifacts for the O₃ organic carbon fraction used in the IMPROVE network since 1995, based on the median values of the secondary filters. The vertical bars represent the standard deviation.

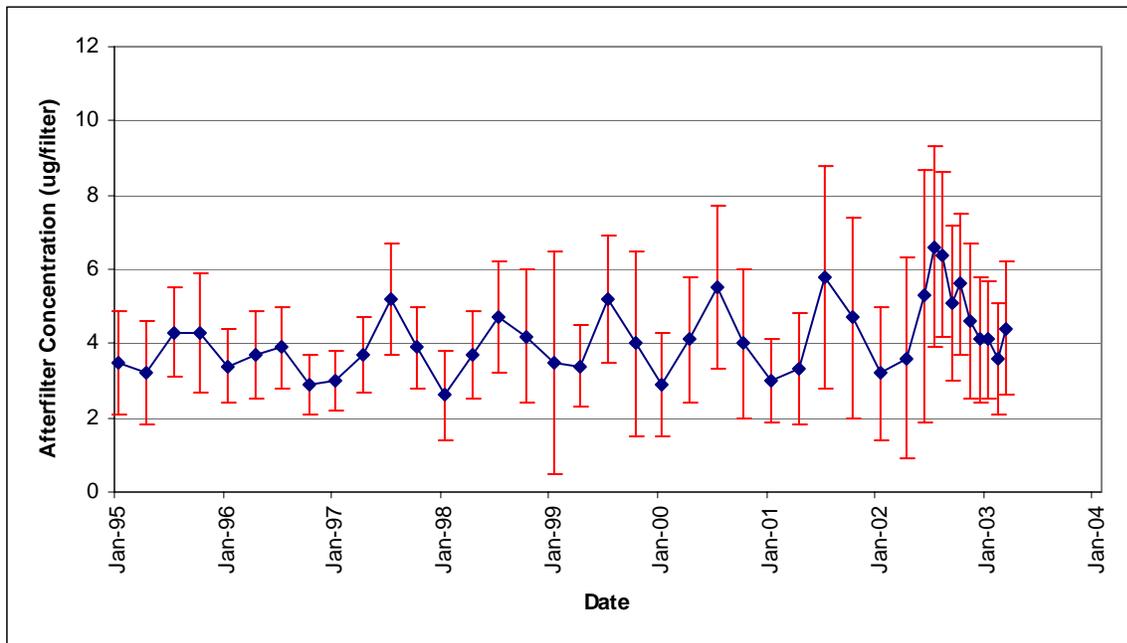


Figure 7. Artifacts for the E2 elemental carbon fraction used in the IMPROVE network since 1995, based on the median values of the secondary filters. The vertical bars represent the standard deviation.

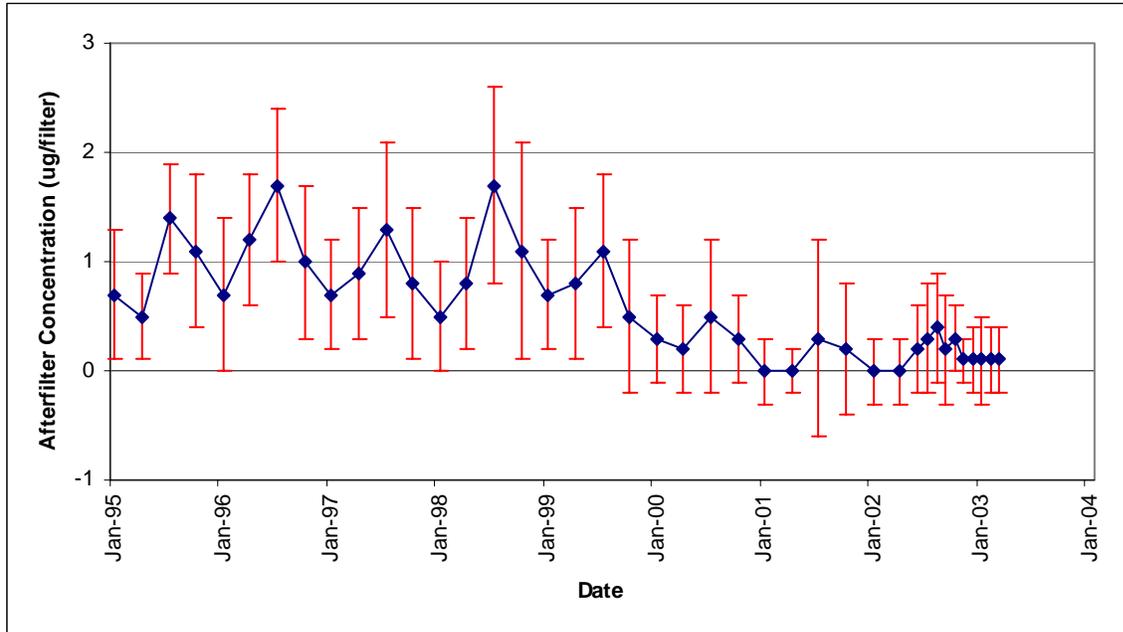


Figure 8. Comparison of the seasonal median artifact concentrations for the O3 organic carbon fraction for each of the six sites. Note that the data for Okefenokee and Chiricahua begin in 2001.

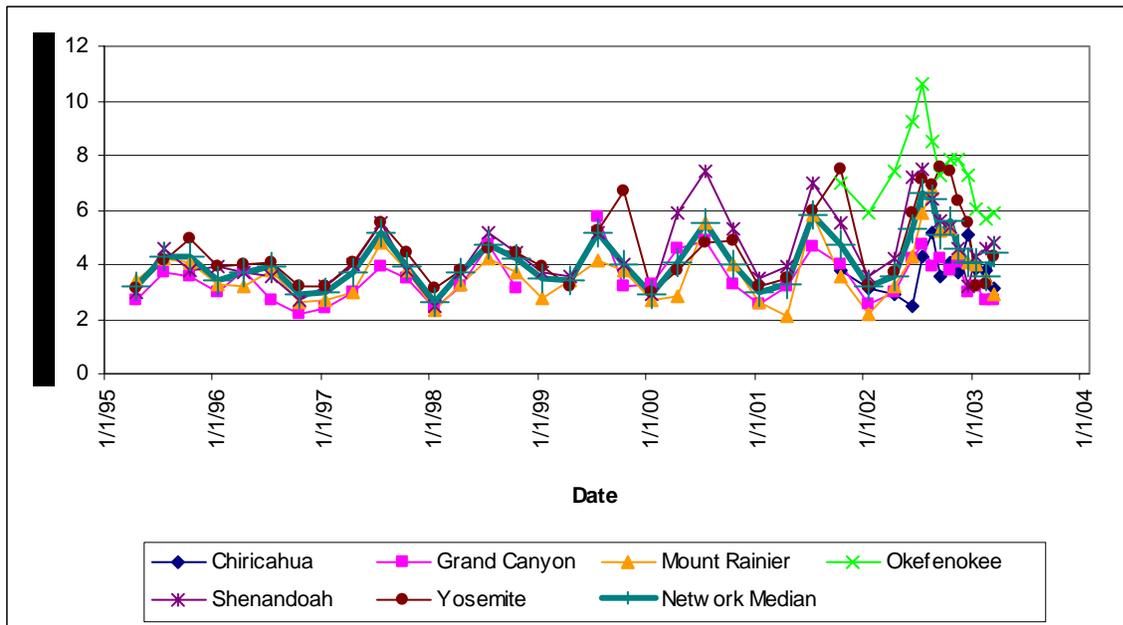


Figure 9. Comparison of the seasonal median artifact concentration for the E2 elemental carbon fraction for each of the six sites. Note that the data for Okefenokee and Chiricahua begin in 2001. The large decrease in 2000 was associated with a change in the filter cassettes.

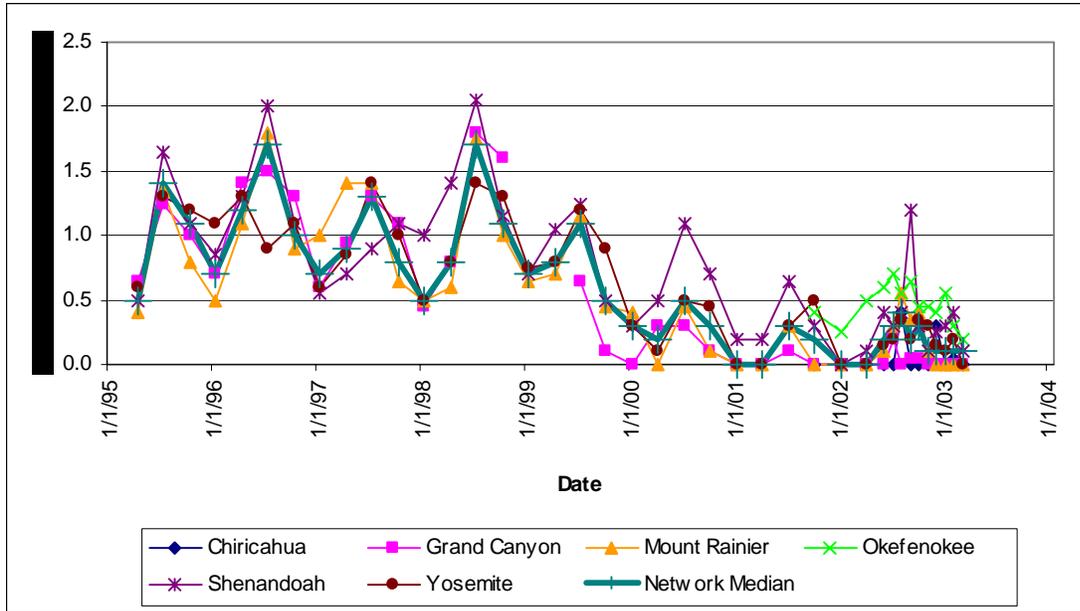
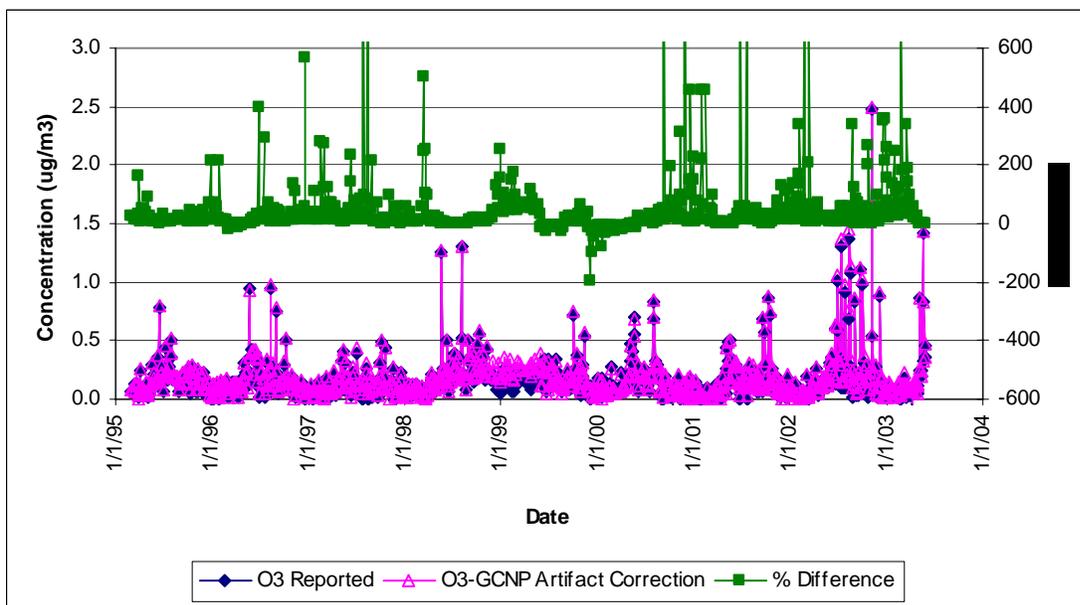


Figure 10. The O3 fraction at Grand Canyon National Park, shown using a network artifact and a site specific artifact.. The blue diamonds show the ambient concentrations using the artifact based on all sites. These are the values in the IMPROVE data base. The pink triangles show the ambient concentrations using the artifact as measured at Grand Canyon only. The green squares show the percent difference between these two values, defined as the new Grand Canyon-adjusted concentration minus the original concentration, divided by the absolute value of the original concentration.



Although the quartz field blanks have not been used for the carbon artifact estimate, they have been routinely analyzed throughout the history of IMPROVE. The comparison of field blanks and afterfilters has provided insight on the nature of the organic carbon artifact for IMPROVE. The organic carbon measured on field blanks and afterfilters have always been similar in magnitude, and much greater than that on blanks that have never been exposed to the atmosphere for any significant time. Laboratory tests were conducted at Davis to determine the origin of this artifact. Quartz filters that were exposed to the atmosphere for a week or more reached the normal organic carbon artifact value, independent of whether they were in a cassette or in an open dish. Those that had contact with the cassette but were not exposed to the atmosphere did not show this normal value. Leaving them exposed for a longer period of time did not increase the measured organic carbon. The hypothesis is that all filters sent to the field, whether field blanks, primary filters, or afterfilters are exposed to the atmosphere for enough time to adsorb ambient organic gases and reach the normal artifact level. The tests indicate that the artifact reaches a saturation limit, at least under the conditions tested at Davis. Note that in the IMPROVE field protocol, primary filters, afterfilters, and field blanks remain in the sampler for one week.

Because afterfilters and field blanks yield comparable concentrations, they are considered to be representations of a positive (gas adsorption) artifact that is independent of the airstream that passes through the filter during sampling. Thus, the afterfilter value is subtracted from the primary filter value. The afterfilter provides no information on any volatilization of organic particles from the primary filter.

CONCLUSIONS

IMPROVE corrects for positive sampling artifacts by subtracting concentrations from nylon filter field blanks and quartz afterfilters from the measured ion and carbon concentrations, respectively. Nylon filter artifacts have been both substantial and variable, with corrections for sulfate up to around 10% of the measured concentration and for nitrate in the range of 10 to 20%. Filters from a new manufacturer, introduced at the beginning of 2004, have substantially lower levels of contamination and promise to reduce the ion sampling artifacts to near zero.

Organic carbon artifacts are determined for each of the components of the organic mass, and can typically represent half of the reported ambient concentration. The afterfilter values are assumed to represent collection of gaseous organic material, and thus are subtracted as a positive artifact. Other studies have suggested that both positive and negative (i.e., particle volatilization) artifacts can compete in the same sample, and it is true that the gas and solid phases exist at equilibrium. However, measured mass and light extinction are reproduced reasonably by the artifact-adjusted IMPROVE chemical components, suggesting that IMPROVE's positive artifact correction is accurate.

Elemental carbon artifacts were substantial through the 1990's, apparently due to contamination from a Viton o-ring in the filter cassettes. Introduction of the Version 2 sampler in 2000 eliminated the o-ring, and the artifacts are now typically less than 10% of the reported ambient concentrations.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge financial support from the National Park Service under Contract C2350990001.

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