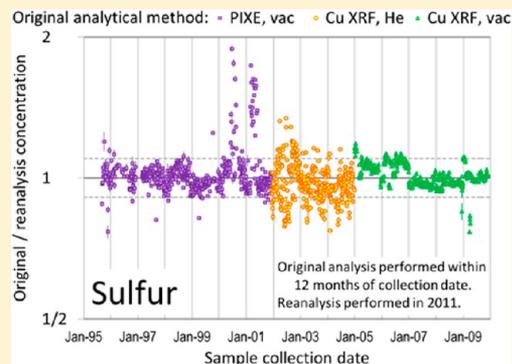


Reanalysis of Archived IMPROVE PM_{2.5} Samples Previously Analyzed over a 15-Year Period

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ABSTRACT: The IMPROVE (Interagency Monitoring of Protected Visual Environments) network has collected airborne particulate matter (PM) samples at locations throughout the United States since 1988. These samples have been analyzed for elemental content using analytical methods that evolved over the years. Changes in analytical methods sometimes introduced shifts in reported concentrations that are evident in the historical record. We sought to illuminate the effects of methodological changes by reanalyzing archived samples with current methods. To test the feasibility of this approach, the 15-year archive of PM samples from Great Smoky Mountains National Park was selected for reanalysis as a single analytical batch using a common protocol and calibration. Comparisons of the reanalyses and original analyses indicate that concentrations of all but one measured element, Br, remained stable on the filters over years of storage. The agreement between the two analyses varied with element and original measurement method. For elements measured well above their contemporary detection limits – S, K, Ca, Fe, and Zn – the reanalysis established that method changes had limited impacts on reported concentrations, generally <10%. For elements originally measured near their detection limits, reanalysis confirmed the presence of discontinuities in the data record, many of which were previously recognized and documented as method-related.



INTRODUCTION

The IMPROVE network (Interagency Monitoring of Protected Visual Environments) is distinguished by the length and stability of its air quality measurement program. IMPROVE is designed to monitor trends in atmospheric visibility, which is largely driven by particulate matter (PM). IMPROVE has collected 24 h samples of PM with diameters less than 2.5 μm (PM_{2.5}) continuously since 1988 at a sustained frequency of twice a week or every third day.^{1,2} The PM_{2.5} samples collected on polytetrafluoroethylene (PTFE) filters are weighed and then analyzed for elements and light absorption (F_{abs}). Collocated samples are collected separately at each site of PM_{2.5} on quartz filters for thermal-optical analysis of carbon, PM_{2.5} on nylon filters for ion chromatography of the major anions, and PM₁₀ on PTFE filters for gravimetric analysis. The network today consists of about 170 sites in mostly rural locations throughout the United States, including 69 sites that have operated continuously at the same locations since 1994. The sampling equipment and techniques have remained fundamentally unchanged throughout IMPROVE's history, and all PTFE filter analyses have been performed by the same laboratory.

However, some significant changes have been made to the elemental and light absorption analysis methods over the years, many of which have been documented on the program Web site, <http://vista.cira.colostate.edu/improve/>. Testing was performed when some of the new methods were introduced to characterize their possible effects on reported data, but method changes are not always immediately obvious in the measured values, especially when the measurements are of inherently fluctuating quantities such as ambient PM_{2.5}

concentrations. Subtle effects sometimes become evident only later as statistical shifts that emerge with large data sets. In addition, some method changes were not deemed significant enough to warrant formal testing. Method changes have the potential to confound trend analyses if their effects are misinterpreted as changes in atmospheric concentration.³ Careful interpretation requires attention to method changes that occurred during the data record.^{4,5} Major method transitions are documented in the public or gray literature, and lesser alterations may be evident as changes in reported data quality parameters such as errors (uncertainties) or detection limits.

The rationale for changing measurement methods is often to reduce overall measurement error. Measurement error is typically characterized by a distribution (such as the normal) with two parameters, the mean (representing bias or systematic error) and standard deviation (representing precision or random error). Changes in measurement method can affect one or both of these parameters and changes in either parameter can affect certain interpretations of the data. In this paper, we will refer to changes in either or both of these parameters generally as shifts in the distribution of measurement error.

Changes in IMPROVE measurement methods have introduced some obvious⁶ and some subtle⁷ shifts in the

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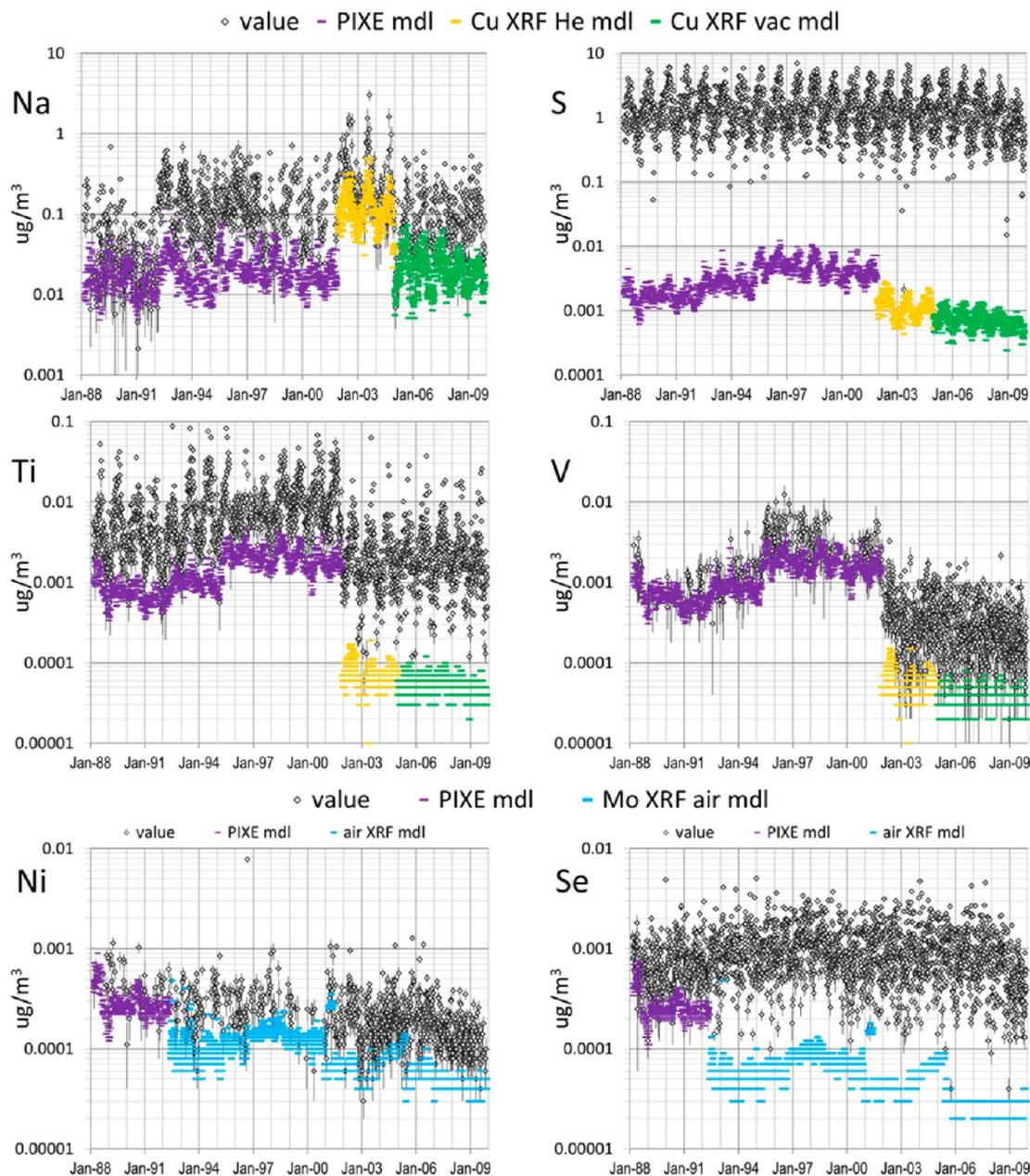


Figure 1. Time-series plots of the original concentration data for Na, S, Ti, V, Ni, and Se at Great Smoky Mountains National Park. Uncertainty bars and detection limits are those reported with the original data. The different analytical methods used over the 15-year period are indicated by different colors for the detection limits (mdl).

concentration time series for many elements. Several of these shifts are evident in the routine IMPROVE data downloaded from the public Web site, <http://views.cira.colostate.edu/web/DataWizard/> (accessed January 2012). Figure 1 shows examples of concentration time-series for six elements measured at Great Smoky Mountains National Park (GRSM1), TN. IMPROVE reports uncertainty and detection limit estimates with each concentration.⁸ Color-coded detection limits (mdl) in Figure 1 indicate the four different analytical methods that were used to measure these elements over the years, as will be described in the Methods section. The mdl shifted with changes in analytical method and sometimes without a documented change in analytical method. The changes in analytical method affected the concentrations to varying degrees. The range of reported Na concentrations

shifted noticeably with the December 2001 and January 2005 changes in analytical method, whereas Ti and V concentrations shifted noticeably only with the December 2001 change in analytical method. Reported S concentrations showed much less effect, following a fairly consistent annual cycle before the economic slow-down that began in 2008–2009.⁹ The reported detection limits for Ni and Se varied over time, as did the observed frequency of Ni detection, even without any fundamental changes in the Mo-XRF instrument. Some of these variations reflect aging and replacement of instrument components or calibration references.

Although the IMPROVE analysis methods changed over the years, the samples themselves may preserve a long-term record of the ambient aerosols. The analytical methods used on the PTFE filters are all nondestructive, and the filters can

potentially be reanalyzed. As a proof of concept, we recovered the 15-year sample archive from one site, GRSM1, and reanalyzed the filters with a single analytical method under the same calibration and measurement techniques. This paper describes the experiment and evaluates the original measurements against the consistent series of elemental and light absorption data generated by the reanalysis.

METHODS

Since sampling began in 1988, IMPROVE has continuously reported measurements of filter light absorption together with concentrations of the elements Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Zr, and Pb. GRSM1 is one of about 30 sites that have operated continuously from the March 1988 beginning of IMPROVE.

The 24-h samples for these analyses have always been collected on 25 mm-diameter stretched PTFE membrane filters drawing ambient air at ~23 lpm through a cyclone with a 50% cut at ~2.5 μm aerodynamic particle diameter.¹⁰ The most significant change in sample collection has been the discontinuation of masks initially used to limit flow to the central portion of the filter; these masks reduced the effective sample deposit area by about 38%, increasing detection sensitivities at the cost of more frequent clogging and other problems. GRSM1 is one of the haziest sites in the network and was accordingly one of the first at which clogging problems prompted the unmasking of PTFE filters; masks were discontinued at GRSM1 in 1995, prior to the archiving of filters. Other changes in field operations include sampler relocations from enclosed to open shelters at some sites and a September 2000 shift from manual twice-weekly to automated every-third-day sample collection at all sites, accompanied by improved flow rate logging and redesigned filter holders. The GRSM1 sampler was moved inside in July 1992 and then moved outside again in March 1997. Any consequences of such sampling changes are likely to affect both the original and reanalysis of the filters, thereby limiting their detectability in comparisons. Our attention herein will accordingly focus on changes in analytical systems and procedures, which we believe to be more consequential for nonvolatile species such as those considered here.

All the light absorption (F_{abs}) and elemental analyses have been performed by Crocker Nuclear Laboratory at the University of California in Davis (UCD) using the analytical systems summarized in Figure 2. Proton Induced X-ray Emission (PIXE) analysis with the Crocker cyclotron was

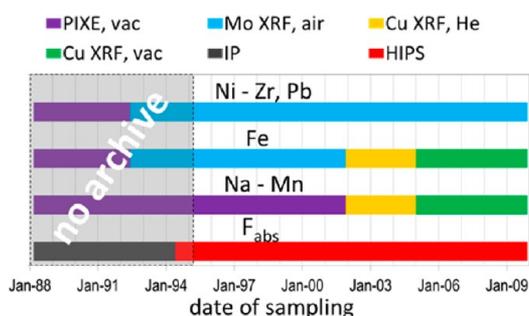


Figure 2. Timeline of analytical methods for IMPROVE PTFE filter samples. The bars show the sequence of methods for light absorption (bottom), elements lighter than iron, iron, and elements heavier than iron (top). Samples were archived beginning in March 1995.

initially used to measure all the elements.¹¹ An energy-dispersive X-ray fluorescence (EDXRF) system with a Mo-anode tube in air (Mo XRF) was introduced in mid-1992 to obtain better sensitivity for the heavier elements, Fe – Pb.¹² A second EDXRF system with a Cu-anode tube replaced PIXE for the lighter elements Na – Fe in December 2001. The sample environment of the initial Cu XRF system was flushed with He to displace atmospheric Ar (Cu XRF, He), but operational difficulties lead to the substitution of a vacuum environment (Cu XRF, vac) for the He flushing at the beginning of 2005. In addition to these changes in the underlying systems, operational factors such as detector performance and calibration procedures have introduced other variations. The same spectral processing software was used for all four instruments, and no documented changes were made to the software.

Filter light absorption (F_{abs}) by the collected sample deposit has been measured at a wavelength of 633 nm since the start of the program. An adaptation of the integrating plate (IP) method to PTFE filters was used before 6/1/94, and a hybrid of integrating plate and integrating sphere (HIPS) has been used since then.¹³ The HIPS system directs a laser at the sample filter and measures the light reflected off the filter and the light transmitted through the filter to determine the light absorption by the deposit. As with the elemental analyses, individual components of the F_{abs} instruments have required occasional maintenance or replacement even when the fundamental measurement principles remained unchanged.

The analytical methods used for all elemental and light absorption determinations have always left the PTFE sample filters intact. After being weighed on their return from the field, the PTFE filters were placed in plastic 35 mm photographic slide mounts to facilitate automation of their subsequent handling. All PTFE filter samples collected since March 1995 have been archived in a storage building at UCD. Samples were stacked in their original slide mounts, wrapped in foil, labeled, and sealed in plastic storage bags for archiving. The archive was not refrigerated or otherwise rigorously climate-controlled and has experienced repeated temperature swings over the years. This unstable environment may increase the potential for composition shifts resulting from long-term chemical and physical aging or biological activity.

The 1995–2009 archived filters for GRSM1 were retrieved and inspected. Retrieval from the IMPROVE archive had not previously been attempted for all filters from a given site. Not unexpectedly, some filters proved impossible to locate in storage. Inspection of the retrieved filters found some to have sustained visible tears, holes, or sample losses in their prior handling and analyses. Reinspection revealed new damage in additional filters after the handling and stress of reanalysis. We retrieved 1514 usable filters from the archive, out of 1626 filters with valid measurements originally reported. Some 1441 of the retrieved filters survived reanalysis, providing valid repeat determinations for 89% of the original measurements. Figure 3 shows a marked improvement in survival rates with the discontinuation of PIXE for samples collected after November 2001. All earlier filters had undergone PIXE in the proton beam and hard vacuum of the cyclotron, which stresses the PTFE filter membranes more than XRF does and leaves them somewhat weakened and brittle.

After retrieval and inspection, the 1995–2009 filters were assembled into a queue for analysis on the same instruments used to process 2010 samples. On each instrument the entire GRSM1 sample archive was reanalyzed within a month. Cu-

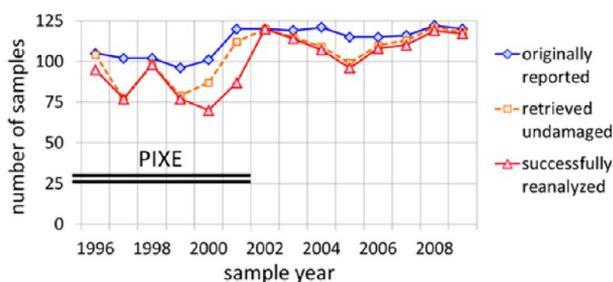


Figure 3. Annual rates of valid original analysis, recovery of undamaged samples from archive, and valid reanalysis for GRSM1. Sample years are plotted from the prior December through the indicated year's November, so PIXE was discontinued at the end of "2001".

anode XRF in vacuum was used for the light elements, Mo-anode XRF in air for the heavier elements, and HIPS for light absorption. The stability of the XRF systems was monitored with weekly calibration checks and by analyzing a designated set of filters before and after the GRSM1 reanalysis batch. The calibration checks require the results to be within 5% of the accepted mean value for each element, except Na and Mg, which are considered qualitative measurements.¹⁴ For HIPS, the system stability is checked with reference filters after every 200 filter analyses and with a designated set of filters that were analyzed twice a day. The reflectance and transmittance measurements were required to be within 5% of the expected values to proceed with analyses. The systems passed all calibration stability checks performed during the GRSM1 reanalysis.

RESULTS AND DISCUSSION

Figure 4 presents a visual summary of the reanalysis results for F_{abs} and many of the elements. The plotted points in each 15-year time series represent individual 24 h samples for which the original analysis result and the reanalysis result were each greater than their mdl. The graphs plot the ratio of the original analysis result to the reanalysis result; because the same sample was the subject of both determinations, the ratio can be calculated directly from analytical output – the dimensionless optical thickness or areal mass density ($\mu\text{g}/\text{cm}^2$). The error bars in Figure 4 accordingly omit nominal uncertainties in sample air volume that are included in the total error bars of Figure 1; the relative uncertainty of the ratio is calculated as the quadratic sum of the relative analytical uncertainties estimated for each determination.

If the original and reanalyses were both unbiased, or shared a common bias, the ratios would be centered at the value one and equally distributed above and below one in Figure 4. Ratios centered on some other value indicate a bias that has shifted between the original analyses and reanalyses. If the reported uncertainties accurately reflected the measurement uncertainty, including bias as well as noise, the uncertainty bars for most ratios would cross the value one.

Changes in the measurement distribution between the three different analytical methods originally used for the lighter elements are evident in most of the ratio series. As shown in Figure 1, reported Ti concentrations fell dramatically with the transition from PIXE to Cu-anode XRF; Figure 4 confirms that this drop results from the analytical method change and not from a real atmospheric change in concentrations. The PIXE Ti measurements are thought to have included stray contributions

from Ti oxide in the slide mounts used to hold the filters in the cyclotron beam.¹⁵ Comparably large drops were also observed in V, Cr, and Mn concentrations (Mn not shown) at this transition. These elements were only marginally detected by PIXE, and their unrealistically high PIXE concentrations are thought to reflect the effects of censoring by the elevated detection limit of a measurement that was noisier than was recognized. This mechanism of bias will be detailed in a separate paper.

The ratios for S and Fe are much more stable than those for other light elements, but when plotted on a finer scale still exhibit changed behaviors at method transitions. The He-flushed XRF system used from December 2001 through December 2004 was characterized by time-varying detector performance that is evident as increased S and Fe variability in the Figure 4 comparison with the reanalysis. The discontinuous shifts in S at the beginning of 2005 and 2007 are not evident in the S concentration time-series plotted in Figure 1 but were previously identified through comparisons with sulfate measurements. They are attributable to known changes in XRF calibration for S and are documented in two data advisories.^{16,17}

The heavier elements and the laser absorption measurements are each plotted in a single symbol type in Figure 4 as these elements were measured by the same method throughout the 15-year period. Even with this consistency, there are some discontinuities in their ratios. The As, Se, and Br ratios display shifts in late 2005 that correspond to an existing data advisory concerning the replacement of Mo-anode XRF calibration standards.¹⁸ These shifts highlighted the weakness of using a one-point calibration for each element. The Br ratio displays unique behavior; it starts out above one and gradually decreases to one over the time period. This behavior may be explained by Br volatilizing from the filters over time. No other measured element displayed this apparent loss in storage. The increased detection frequency for Ni in 2001, noted in the discussion of Figure 1, is also evident in Figure 4 but is not explained by any documented analytical changes.

The F_{abs} measurements are relatively consistent over time (note tighter y-axis scale) with the exception of some significant deviations in the years 2000–2002. These departures are not understood but may have resulted from the redesigned filter support screens introduced in September 2000.

Figure 5 summarizes various element-by-element statistics of agreement between the original and reanalysis data. Each point represents one element measured by one method, the latter being indicated in the legend. Each statistic is plotted relative to the detection frequency (x -axis), which is the percentage of samples with concentrations reported by the original analysis and the reanalysis that were each greater than the reported mdl. The left-hand graph plots relative precision estimates for each element, $\text{precision} = (\text{standard_deviation}([c]_{\text{orig}} - [c]_{\text{rean}})) / (\text{mean}([c]_{\text{rean}}))$. The middle graph plots the relative bias between the reanalysis and the original analysis, $\text{bias} = (\text{mean}([c]_{\text{orig}} - [c]_{\text{rean}})) / (\text{mean}([c]_{\text{rean}}))$. The right-hand graph plots the correlation coefficients between the reanalysis and the original analysis. All original-reanalysis pairs were included in the calculation of the agreement statistics by substituting the value $1/2$ mdl for nondetections.

The agreement between original and reanalyzed concentrations in Figure 5 is best for elements that were consistently well-detected in both determinations. The main exceptions to this pattern – Ti, Si, and Br – are explainable in terms of

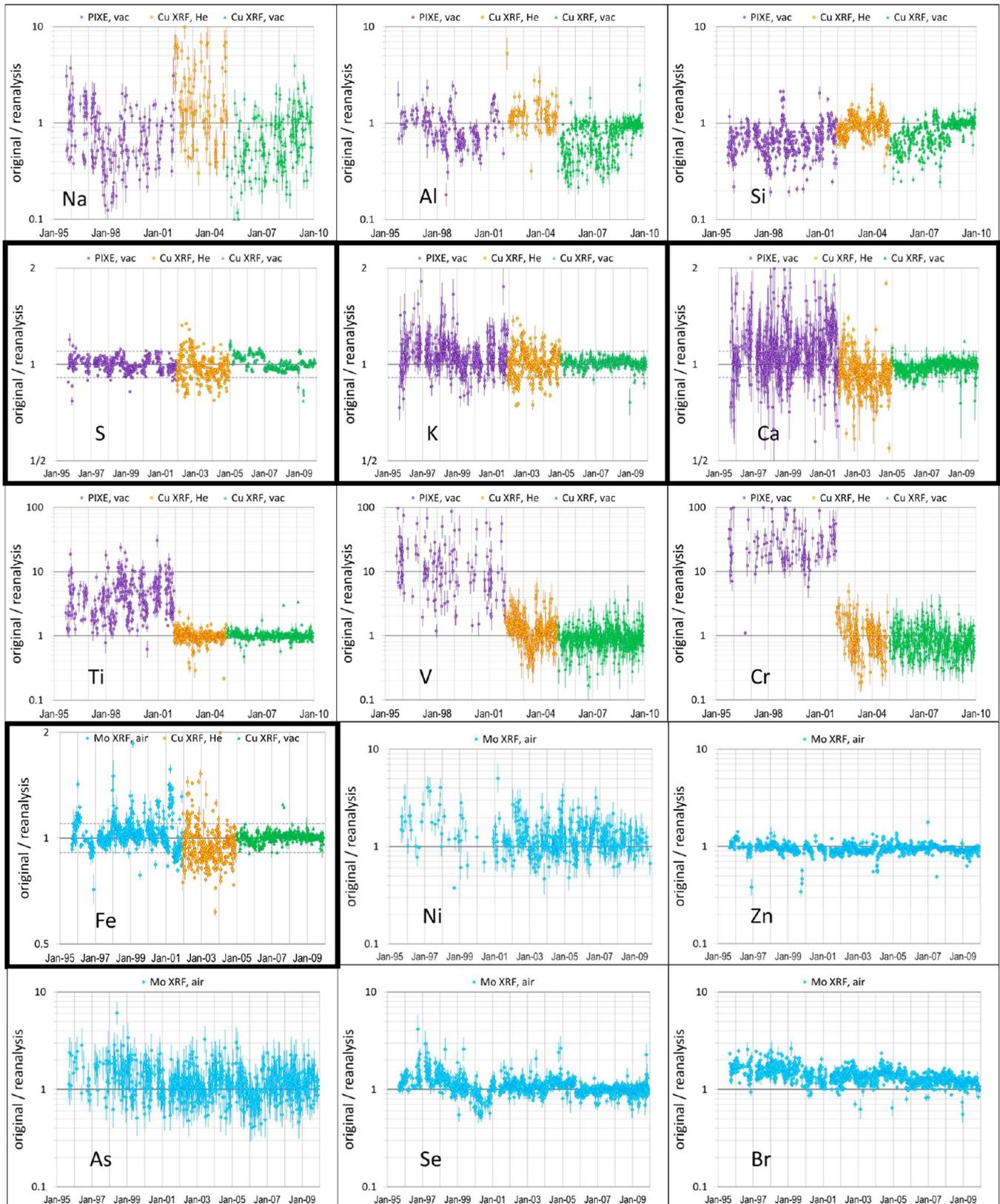


Figure 4. continued

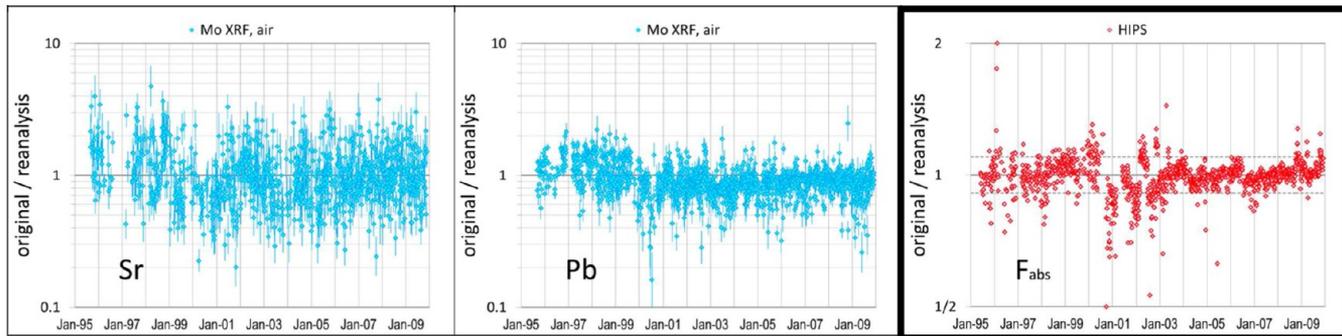


Figure 4. Time-series of the ratio of the original result to the reanalysis result on samples for which both measurements were greater than their detection limits. Different symbols correspond to different original analytical methods. Note the variation in y-axis scales: the plots outlined in bold agree within a factor of 2 and most ratios are within 10%, indicated by dotted lines.

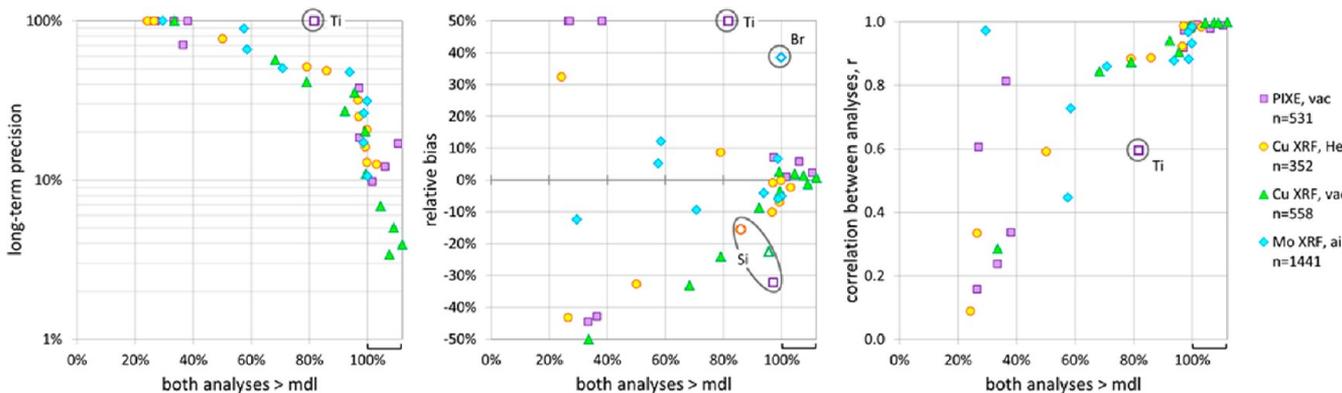


Figure 5. Dependence of reanalysis results on detection frequency. Each point represents one element measured by the method indicated in the legend. Detection frequency (*x*-axis) is the fraction of samples for which both determinations were above their reported mdl. The frequency 100% is exploded (bracket) to resolve the many points at this limit. Results of reanalysis are summarized (*y*-axis) as the standard deviation of original-reanalysis concentration differences divided by the mean concentration of the reanalysis (long-term precision), mean original-reanalysis difference divided by the reanalysis mean (relative bias), and correlation between original and reanalyzed concentrations (*r*).

known measurement issues. The results for Si by all analytical techniques, and for Ti by PIXE, depart from prevailing patterns due to element-specific measurement interferences. Si determinations by XRF are known to be unreliable at high S concentrations, which are common at GRSM1.^{19,20} Ti determinations by PIXE are known to have contained a large and variable positive interference.¹⁵ The unique time-dependence of Br results seen in Figure 4 suggests that losses in storage biased the Br reanalysis as shown in Figure 5. The elements Mg, P, Cl, and Zr were not regularly detected at GRSM1 and are not plotted. In general, detection rate is predictive of precision, relative bias, and correlation between the original and reanalysis data. Tables 1 and 2 list the detection rates for each element and method pair; these tables can be used with Figure 5 to gauge the quality of data for specific elements and measurement eras.

In summary, advances in measurement method may create discontinuities in data quality (e.g., less noise or smaller bias) that impact temporal trends analyses.³ Measurement performance can also vary over time as a result of uncontrollable factors or slight adjustments to the instrumentation or measurement technique: changes in the commercial availability of filters and other consumables, retirement or reassignment of operators, degradation and subsequent replacement of instrument components, changes in mathematical algorithms, and replacement of calibration standards. Shifts are not always obvious in the measured values themselves, particularly when the

Table 1. Detection Rate Summary for the Lighter Elements^a

samples	detection rate; both analyses > mdl		
	531	352	558
era	6/9S - 11/01	12/01 - 12/04	1/05 - 11/09
method	PIXE, vac	Cu XRF, He	Cu-XRF, vac
Na	33%	24%	34%
Mg	2%	2%	8%
Al	36%	26%	68%
Si	97%	86%	96%
P	0%	0%	0%
S	100%	100%	100%
Cl	0%	0%	0%
K	100%	100%	100%
Ca	97%	99%	100%
Ti	82%	97%	99%
V	26%	79%	92%
Cr	27%	50%	79%
Mn	38%	97%	99%
Fe	100%	100%	100%

^aDetection rate is defined as the percent of measurement pairs where both the original and reanalysis measurements were greater than their reported detection limits (mdl).

measurements are of inherently fluctuating quantities such as ambient PM concentrations. Our reanalysis using a consistent protocol revealed method-related shifts in concentrations over

Table 2. Detection Rate Summary for the Heavier Elements

	detection rate; both > mdl
samples	1441
era	6/95 - 11/09
method	Mo XRF, air
Ni	29%
Cu	94%
Zn	100%
As	59%
Se	99%
Br	100%
Rb	57%
Sr	71%
Zr	5%
Pb	99%

time for several elements measured in IMPROVE, many of them outside the reported uncertainties in the concentrations. In addition, this reanalysis demonstrated that the measured elements, with the exception of Br, remained stable on the filters for more than 15 years.

Some elements, notably S, K, Ca, Fe, and Zn, were measured well throughout the 15-year time record. These elements were consistently above the detection limits no matter the measurement method, making them less sensitive to changes. Even for these elements, subtle bias changes are sometimes visible in the concentration time-series, such as the shifts in S concentrations associated with calibrations. Other elements, notably Ti, Cr, V, and Mn, displayed dramatic shifts in detection rates and/or concentration when the measurement methods changed.

These initial results from GRSM1 establish the potential for evolutionary improvements in measurement methods to contribute spurious trends in long time series. A full discussion of these effects requires detailed consideration of the objectives and techniques of various data analyses and would take us well beyond the space available in this 'proof of concept' paper. Quantitative assessments of trend impacts from method changes, and their relationship to detection limits and other reported parameters, will be presented in at least two additional papers. The concentrations based on the reanalysis will be posted for download alongside the originals when documentation and quality assurance have been completed.

Ambient concentration data incorporate sampling errors which are likely to vary from site to site and analytical errors which can affect all samples in the same batch at the central laboratory. To the degree that analytical processes are the dominant source of time-varying bias, a comparison at one site might provide information about the bias at other sites. The success of the reanalysis at GRSM1, motivated us to begin reanalyzing two additional sites: Point Reyes National Seashore and Mount Rainier National Park. These additional sites were selected to highlight different PM compositions.¹ Together, these multisite reanalysis results may inform historical explorations of the irreplaceable IMPROVE data record and reveal trends that have been obscured by measurement issues.

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Notes

The authors declare no competing financial interest.

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