

Posting Type	Informational
Date Submitted	October 22, 2025
Subject	Change in the analytical protocol for XRF analysis
Projects	IMPROVE
Module/Species	A/Manganese (Mn), Iron (Fe), Nickel (Ni), Copper (Cu), Zinc (Zn), Arsenic (As), Selenium (Se), Bromine (Br), Rubidium (Rb), Strontium (Sr), Lead (Pb)
Sites	Entire network
Period	April 2024 to present
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Supporting Information

The element content in IMPROVE samples is quantified by energy-dispersive X-ray fluorescence (XRF) analysis. The XRF instruments, in use since the 2011 sample year, employ a primary X-ray tube to excite a sequence of secondary targets, whose secondary excitation spectra, in turn, irradiate the sample. Different secondary targets produce distinct secondary spectra, which preferentially excite different ranges of elements in the sample. We chose the sequence of secondary targets to optimize the resolution of different sample elements and minimize background interference.

To improve detection of lead (Pb) and other heavy elements, the XRF analytical protocol was slightly modified starting with samples collected in October 2018. As shown in Table 1, the KBr secondary target, previously included for detection of arsenic (As), was dropped to allow more time for other targets in the sequence. Longer target exposure times generally increase the detector signal and improve sensitivity. The effects on data quality were expected to be small and detectable only after a sufficient record was acquired with the new protocol.

After some time operating the new XRF protocol, we realized that As detection rates had decreased, and As was almost always reported as zero. This loss of As detection was more obvious than any increases in detection for other elements (e.g., Pb). Therefore, we decided to revert to the original protocol in 2024. Figures 1 and 2 below show the As and Pb concentrations from 2008 through 2024. The changes in XRF instruments and analysis protocols are indicated by vertical lines on each plot. The 2018 protocol change resulted in decreased As concentrations. When we reverted to the original protocol for April 2024 samples, As concentrations increased, although not back to their former levels and negative As concentrations are regularly reported. The As concentrations did not return to their earlier levels because of another change in data processing. As of October 2018, we started applying a spectral overlap correction to the As concentrations related to an overlapping Pb peak. The negative values suggest that the overlap correction is too large, but further experimentation is necessary to develop a more appropriate correction. The Pb concentration time-series plot does not show discontinuities related to the XRF protocol changes.

Table 1. XRF protocols for IMPROVE samples collected since January 2011.

Sample Element	Secondary Target	Exposure (sec)		
		Samples Collected During the Periods		
		Original Protocol 1/2011 through 9/2018	Modified Protocol 10/2018 thru 3/2024	Original Protocol 4/2024 to present
Na – K	CaF ₂	600	600	600
Ca – Cr	Fe	400	400	400
Mn – Zn	Ge	300	400	300
As	KBr	300	-	300
Se – Br	SrF ₂	300	-	300
As– Br	SrF ₂	-	400	-
Rb – Sr, Pb	Mo	300	400	300
Zr	Al ₂ O ₃	200	200	200

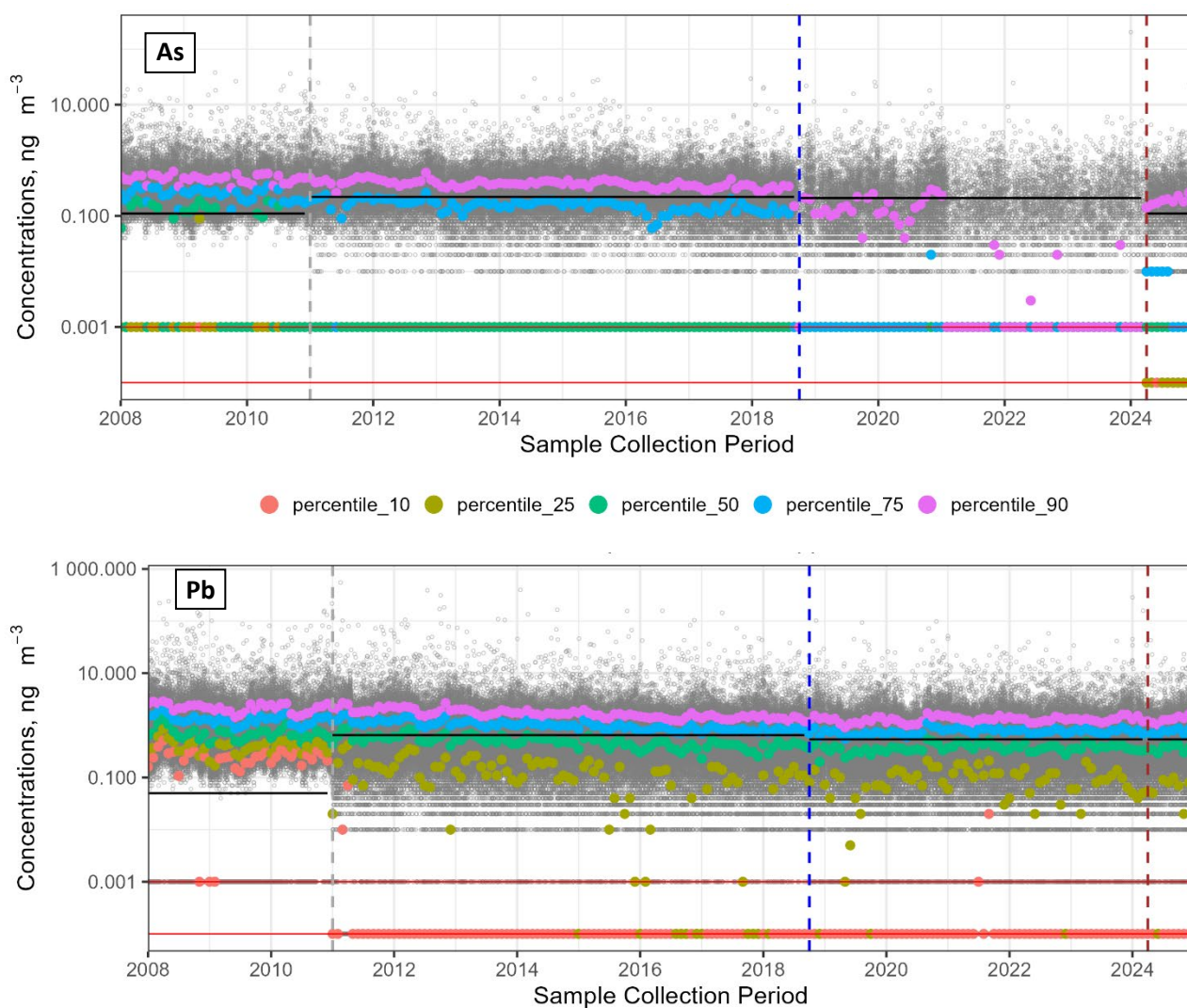


Figure 1. Arsenic (As, top) and Lead (Pb, bottom) concentrations from 67 IMPROVE sites that operated continuously throughout this time period. Gray points are the daily concentrations. The colored points represent different percentiles as detailed in the legend. The dashed vertical lines indicate the ED-XRF changes. Zeros and negatives were substituted with 0.001 and 0.0001, respectively. Black horizontal lines are the median reported detection limit values from different application eras.