Posting type	Advisory
Date Submitted	2025-Feb-26
Subject	Phosphorus (P) underreported by one XRF instrument
Project	IMPROVE
Sites	All sites but not all samples
Sample Period	Jan 2011 through April 2020
Parameters	$PM_{2.5}$ Phosphorus (P) by XRF
Recommendation	Avoid using P data from FED or AQS prior to Feb 2025
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Supporting Information

While reviewing our quality control graphs, we discovered a subtle discontinuity in the phosphorus (P) measurements by X-ray fluorescence (XRF). Upon investigation, we found that one of the five XRF instruments used to analyze IMPROVE samples had been underreporting P concentrations since it was first employed in 2011.

Figure 1 plots the P concentrations measured by each XRF instrument over the years and clearly shows the increase in the P measured by the XRF instrument, referred to as "Froya", in early 2020. The increase in P concentrations coincided with the annual recalibration (identified by the vertical line in the plots), and a review of the laboratory notebooks confirms that the shift was related to a change in the peak fitting parameters. After the change, the P concentrations measured by all XRF instruments agree more closely. Figure 2a plots P summary statistics for the entire IMPROVE network from 2011 to 2024 and illustrates the increase in P mean and median values in early 2020. Figure 2b is the same graph as 2a except that data from Froya is excluded; the concentrations in Figure 2b are more consistent over time than Figure 2a.

The P peak in the XRF spectrum lies on the shoulder of the often-large sulfur peak and can be challenging to resolve. Therefore, little confidence was placed in P measurements in the past. Growing interest in P measurements prompted this historical review, along with the ongoing development of better reference materials to improve future P data quality and consistency.

As of February 2025, the erroneous P data from Froya have been invalidated in the FED and AQS databases; approximately one-third of the P measurements from 2011 through April 2020 are now invalid. Given that the samples are randomly analyzed on a particular XRF instrument, the missing data should not bias future analyses. Unfortunately, any existing quantitative or trends analyses that included this erroneous P data are questionable.

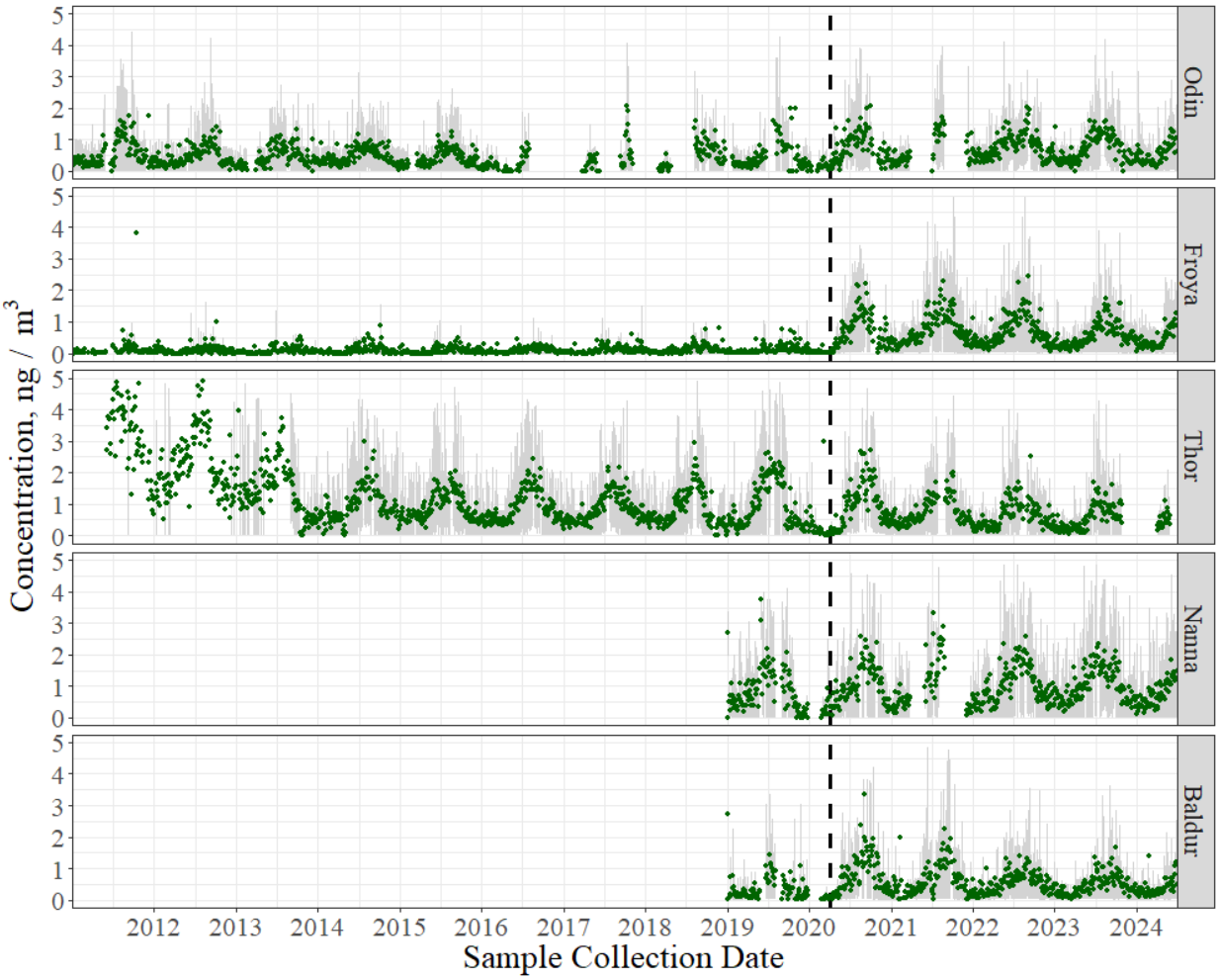

Figure 1. P measurements by each XRF instrument. Gray shading represents the 10th to 90th percentiles, and the green-colored dots represent the means. Three instruments started operating in 2011, while the other two instruments started analyzing IMPROVE samples in 2019. The second graph from the top shows that the Froya measurements were mostly zero until early 2020.

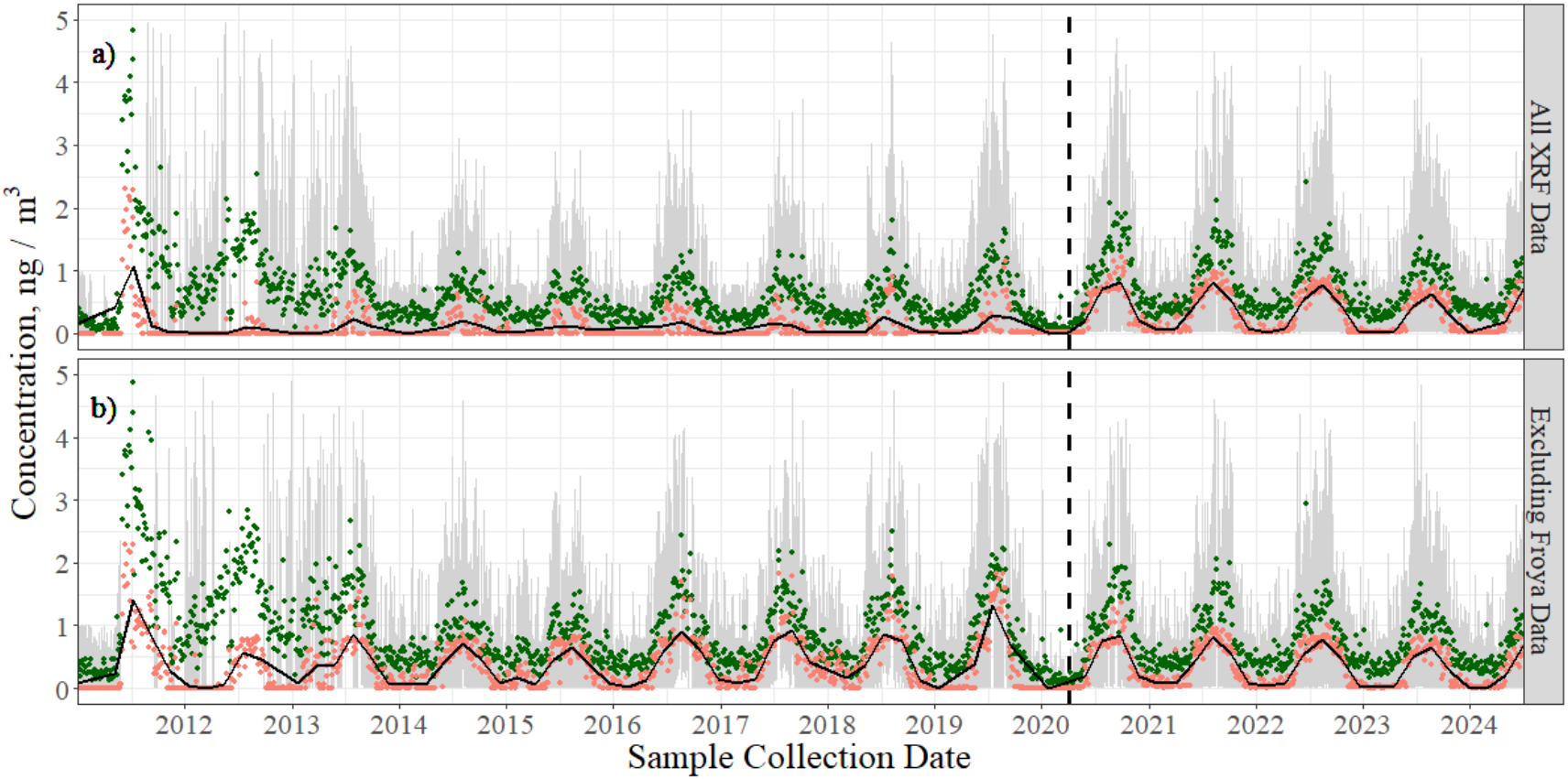

Figure 2. Network-wide P mean (green points), median (salmon points with black smoothed line), 10th, and 90th percentile concentrations (gray bars). The top plot (a) includes P data from all the XRF instruments and shows increases in the metrics, particularly the median and mean P concentrations in early 2020. The bottom plot (b) shows the same P metrics excluding the data from one instrument, referred to as Froya.