

Posting type Advisory update
Subject Inconstant bias in XRF sulfur
Module/Species A/ S
Sites entire network
Period 2003 – 2008
Recommendation Use $\frac{32}{96} [\text{SO}_4^-]$ rather than [S] for trend analyses
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Supporting information

Previous advisories have called attention to observable discontinuities in XRF sulfur data. [Shifts in the sulfur/sulfate ratio during 2003-4](#) were shown to coincide with recalibrations of the XRF system and to correlate with other XRF biases. [A further 15% shift at the start of 2005](#) was explained as the result of a change in the value used for the sulfur calibration foil, from a legacy adjustment to the manufacturer’s quote. Since those advisories further shifts have occurred; Figure 1 updates the series of network sulfur/sulfate ratios to include results from a [new calibration protocol applied to 2007-8 data](#).

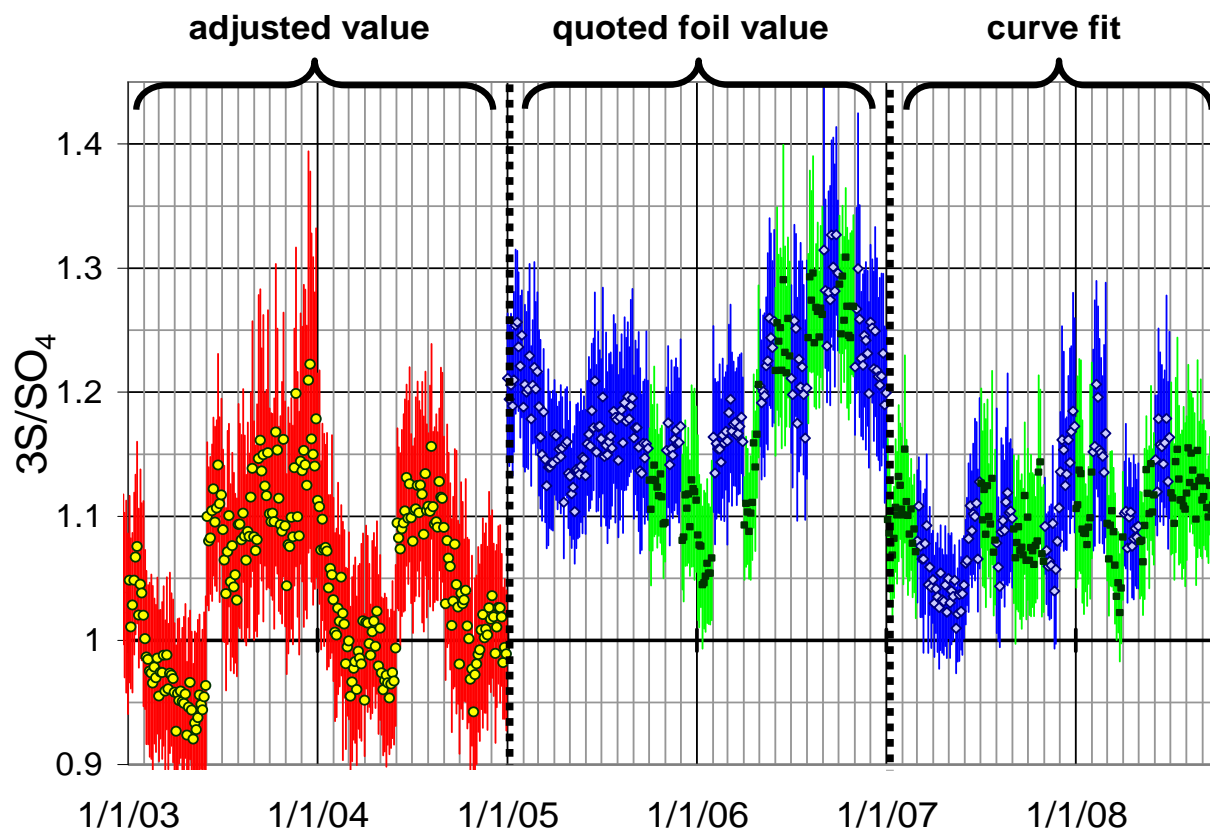


Figure 1. Median and interquartile range of the ratio $3[\text{S}]/[\text{SO}_4^-]$ over all network sample pairs in which both sulfur and sulfate were detected. Sulfur was reported from different copper-anode XRF systems in different months: a helium-flushed system (plotted in red and yellow) before 2005 and two different evacuated systems (plotted in blue or green) from 2005 on. Differing calibration conventions are identified for 2003-4, 2005-6, and 2007-8.

The clearest new (*i.e.* post-1/1/05) discontinuity in Figure 1 is the drop of about 10% in sulfur/sulfate ratios at the start of 2007. Calibrations in 2005-6 were based on the quoted value of a foil for each element. Calibrations in 2007-8 were based on a curve fit to several different elemental foils, and [this fit effectively assigned a value to the sulfur foil different from the manufacturer's quote](#).

The change from helium flushing to vacuum operation at the start of 2005 yielded a somewhat tighter relationship between sulfur and sulfate concentrations. A second vacuum system, designed to be equivalent and calibrated against the same reference foils, was introduced in October 2005 to speed processing. The two systems report concentrations for the single-element foils that agree within prescribed tolerances, but [exhibit some detectable differences for aluminum and silicon in actual samples](#). All IMPROVE samples for a given month are analyzed with the same system, and similar inter-system differences for sulfur may contribute some month-to-month variability to the sulfur/sulfate ratio. Currently observed variations in XRF bias are detectable in comparisons with related measurements (Figure 2a, 2b), but are small relative to the range of concentrations reported across the network (Figure 2c).

Figure 2. Three different comparisons of the same sulfur and sulfate data. Each plot is based on all network observations from two adjacent months for which sulfur was analyzed on different vacuum XRF systems.

