

**Posting type** Advisory

**Subject** Varying bias of XRF sulfur relative to IC sulfate

**Module/Species** A/ S

**Sites** entire network

**Period** 2003 – 2004; may also apply to earlier years

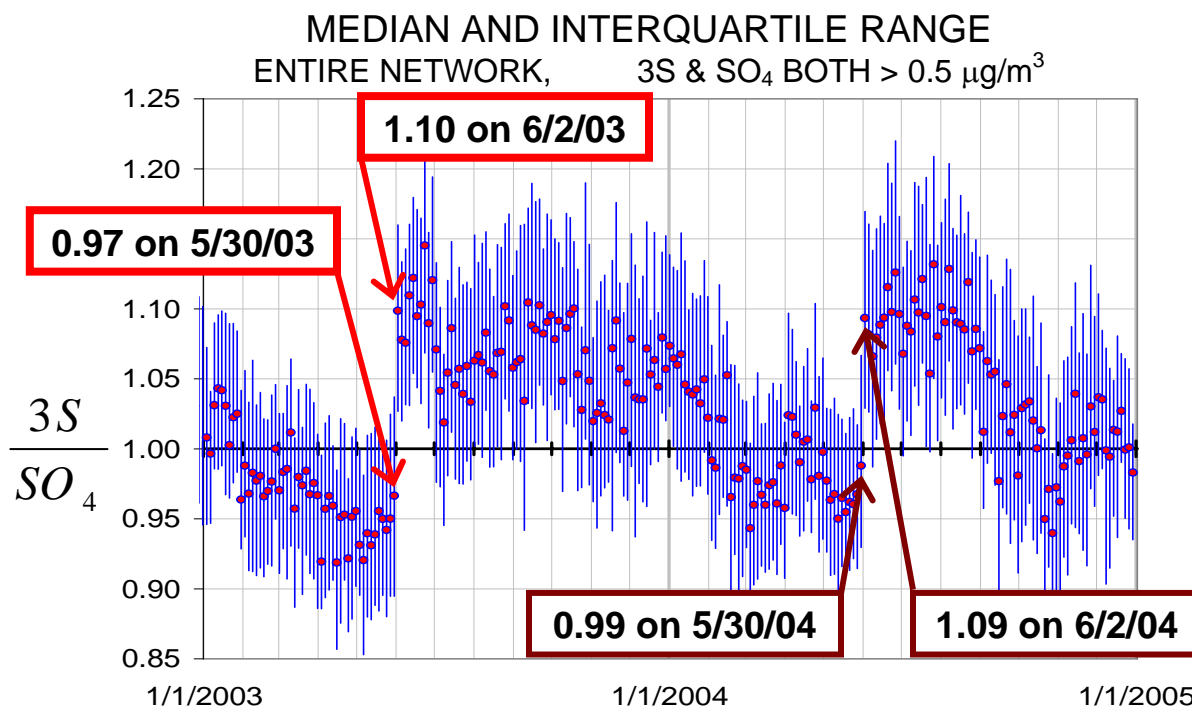
**Recommendation** Use  $\frac{32}{96} [\text{SO}_4^-]$  in preference to [S] for trend analyses

**Submitter** W.H. White, white@crocker.ucdavis.edu

**Supporting information**

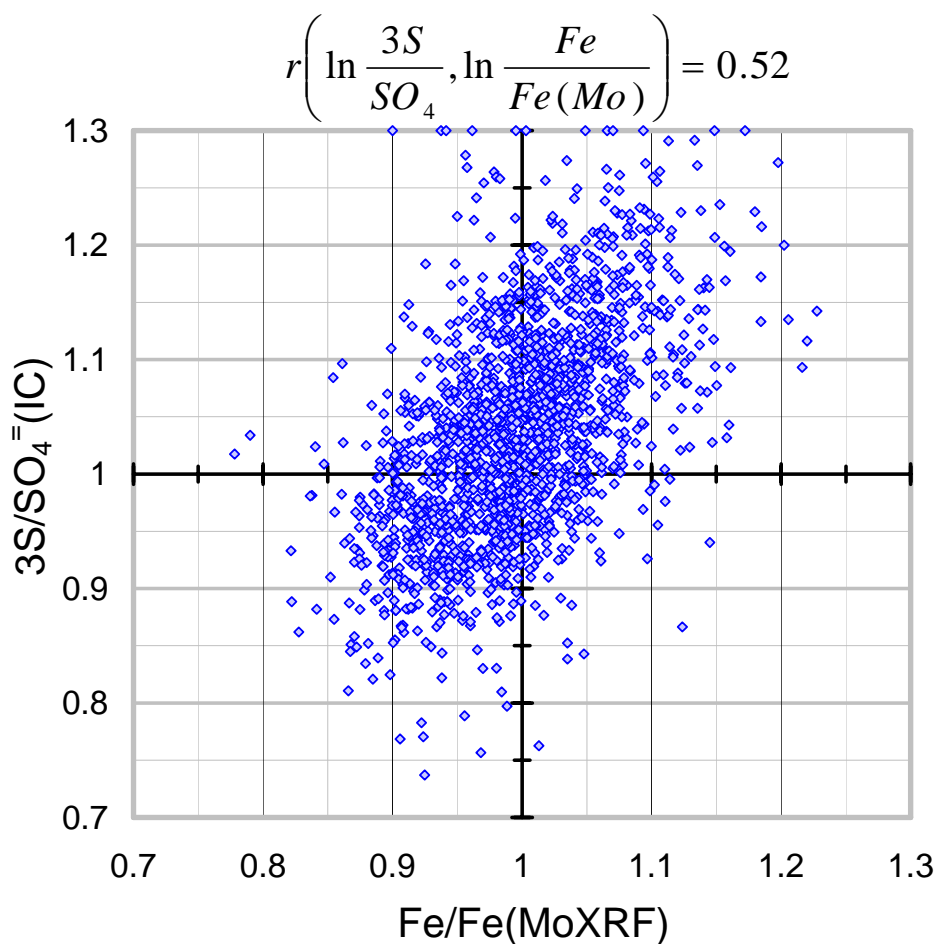
Most fine-particle sulfur is present as sulfate. Measured concentrations are therefore expected to exhibit the ratio  $[S]/[SO_4] \cong 32/(32 + 4 \times 16) = 1/3$ . Reported concentrations often depart from this ratio by more than their reported uncertainties. During the years 2003 and 2004, two independent lines of evidence point to XRF measurement bias as the source of most of the observed variation.

Figure 1 shows that sulfur/sulfate ratios throughout the network exhibited a decreasing trend during 2003 – 2004 that was offset by two abrupt increases, each coming at the start of a new sample month. The XRF analyses, unlike the ion-chromatographic analyses, are quality assured in calendar-month batches, and both of the observed jumps coincided with recalibrations of the Cu-anode system used to determine sulfur. The fact that abrupt changes in the sulfur/sulfate ratio were associated with recalibrations of the XRF system suggests that the gradual changes observed at other times may be due to drift in that system’s calibration.



**Figure 1.** Sulfur/sulfate ratios for all observations with both 3S and SO<sub>4</sub> greater than 0.5 µg/m<sup>3</sup>.

Figure 2 confirms that much of the variation in  $[S]/[SO_4]$  is associated with the sulfur measurement. Since 12/1/01, elemental sulfur and iron have been reported from the Cu-anode XRF system. Iron (but not sulfur) is also reliably determined by the Mo-anode XRF system, from which it was reported before 12/1/01. Clearly, all variations in the ratio  $[Fe](Cu)/[Fe](Mo)$  arise from errors in the two XRF determinations. The fact that  $[S](Cu)/[SO_4]$  correlates with this ratio implies that much of the variation in  $[S](Cu)/[SO_4]$  is also associated with the XRF determination. More specifically, varying biases in the Cu-anode system are estimated to account for a root-mean-square error of about 5% in site-month averages of the sulfur concentration.



**Figure 2.** Comparison of reported XRF data (sulfur and iron from the Cu-anode system) with independent measurements of sulfate by ion chromatography and iron by Mo-anode XRF. Consideration is restricted to precise observations, those with S and  $SO_4^- > 10$  times MDL and spectroscopic uncertainties  $< 2\%$  in both Fe determinations. Each plotted point is the geometric mean from 8 or more such observations at 1 site in 1 month from 2003 – 2004 ( $N = 1772$ ). Values outside the plotting range are plotted at the appropriate boundary.

The variability described in this advisory adds to the [previously identified](#) 15% uncertainty in the sulfur calibration used to report pre-2005 samples, created by the introduction of an ad hoc adjustment at an unknown date. Samples from 2005 are being analyzed with a new and more stable Cu-anode XRF system, and calibrations are now more frequently verified against certified elemental references. These improvements appear to have stabilized the sulfur measurement in samples collected through June 2005, the most recently reported month at this writing.