Posting type Advisory

Subject Bias between masked and unmasked elemental measurements

Module/Species A/ S

Sites entire network

Period evident since 2002

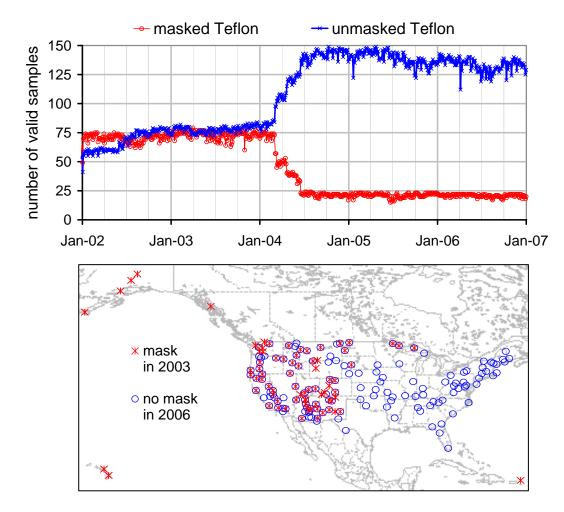
Recommendation Consider masking status when evaluating small differences in time and

space.

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Supporting information

Until recently, masks were used at many sites to reduce the nominal collection area of A-module filters from 3.53 cm² to 2.20 cm². Masking improved XRF sensitivities at low concentrations, but caused occasional clogs at high concentrations. As of 2008, all filters have been unmasked. Figure 1 summarizes the use of masks in 2002-2006.



<u>Figure 1:</u> Daily number of IMPROVE sites with valid observations of both sulfur and sulfate (top) and map of the network in 2006 (bottom).

A relative bias between masked and unmasked elemental measurements can be seen by comparing the <u>sulfur/sulfate ratios</u> measured under both conditions, as sulfate ion concentrations have been measured by the same protocol at all sites since 2001. Unmasked sites have generally reported about 5% more sulfur than masked sites at a given measured sulfate concentration (Figure 2), and the sulfur reported from masked sites has typically risen by about 5% when they have converted to unmasked operation (Figure 3). It is not known whether these differences reflect under-reporting from masked samples or over-reporting from unmasked samples, or contributions from both.

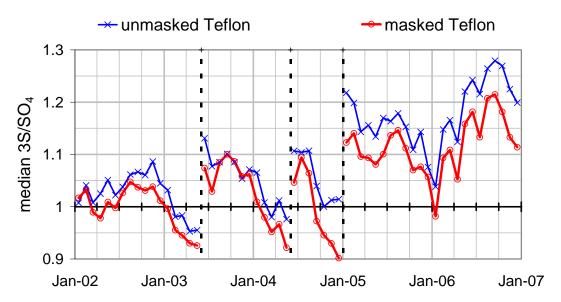


Figure 2. Monthly network medians of 24h sulfur/sulfate ratios from masked and unmasked sites, for all measurements with $[SO_4] > 0.3 \text{ ug/m}^3$. Dashed vertical lines indicate $\frac{XRF}{S}$ system recalibrations in 2003 and 2004 and a sulfur reporting change at the start of 2005.

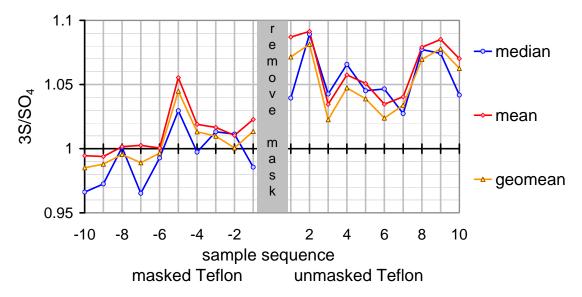


Figure 3. Measured sulfur/sulfate ratios at 55 sites converted from masked to unmasked operation around the beginning of 2004. The 55-site medians, arithmetic means, and geometric means are shown for each of the 10 sampling days immediately preceding and following conversion at each site.