**Supplemental Material**

**Supplemental Material for “The changing face of lower tropospheric sulfur oxides in the United States”**

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The following includes: (a) notes on uncertainties in emissions and measurements that qualify the reporting of trends, (b) a table of sulfur compounds in the troposphere, (c) a table of some historical data on concentrations of SO4, (d) maps of emissions for two time periods, (e) annual average ambient SO2 and SO4 concentrations for two time periods, and (f) maps of annual average SO4 in precipitation for two time periods. These are intended to add detail to the discussion of trends beyond the material in the manuscript.

*Emissions.* Sulfur oxide emissions have been reported for the US from the standard practice of estimation in terms of point and area sources, and transportation. The stationary sources are calculated historically using process characteristic emission factors and input materials, for example, power plant configuration and fuel input. Transportation sources are estimated from fuel use or from emission models initiated in the 1970s. After 1990, large stationary sources, mainly power plants, adopted continuous emission monitoring for direct measurement of emissions. The US national inventory is developed from state inventories currently on a once in three-year basis. The reliability and uncertainty in historical SO2 emission inventories, especially prior to 1980, are indeterminate (e.g. NARSTO, 2005). Post-1990, the inventory for SO2 has become more reliable and uncertainty has been estimated from CEM measurements combined with engineering data for other sources, and has been tested by receptor modeling, for example, chemical mass balance (e.g., Blanchard et al., 2013) and consistency with air quality modeling comparisons with ambient observations (e.g., NARSTO, 2005). We believe that for purposes of discussing SOx in the Anthropocene, the aggregated US and global SO2 emission inventories dating back to the 19th century are adequate to establish historic trends.

*Measurement Methods.* The reconciliation of ambient observational methods for quantitative comparability is beyond the scope of this manuscript. However, we include here some notes on ambiguities that add perspective to the trends documented in the literature. Ambient measurements and precipitation collection have evolved significantly to produce comparable results, especially since the 1980s.

Sampling for gases in long-term monitoring programs involves standardized surface siting of sites and sampling through tubes approximately 10 meters high to instruments located indoors under controlled temperature and humidity conditions. In the case of SO2 concentrations, the standard reference method through the 1970s to the present is the West-Gaeke colorimetric analysis (e.g., Hochheiser, 1964; CFR, 2012; ASTM, 2015). This method is robust for its time, and remains a reference standard. It has a nominal accuracy of 10% and a detection limit of 5-75 ppbv depending on sample time and aqueous absorber volume. This range of detection limits is generally too high for essentially all US conditions after 1980. For continuous SO2 measurements with lower detection limits and relatively fast response times, instruments employing coulometric, flame photometric or pulsed fluorescence principles have been adopted as an alternative for monitoring (e.g., Demerjian, 2000; Hansen et al., 2003; EPA, 2015). Accuracy of these instruments is approximately the same as the standard method, including calibration and reference standards, but detection limits are much lower depending on the use of inlet denuders or pre-filters to minimize interferences. Prior to the 1970s the West-Gaeke method was suitable for urban conditions, but limited for rural monitoring. For data archiving, SO2 data at or below the detection limit are arbitrarily reported at or one-half the detection limit. This in combination with the effect of interferences can potentially introduce a positive bias in reported long-term SO2 trends of an unknown magnitude.

The sampling and analysis for SO4 historically relies on filtration of particles to obtain samples for determination of mass concentration and composition, including SO4. Through the 1970s essentially all of the reported average particle SO4 observations were derived from 24-hour filtration sampling using the high-volume sampler for total suspended particles (TSP), which collected particles nominally < 30-35 µm aerodynamic mass median diameter (AMMD), followed by aqueous extraction and laboratory analysis for SO4 ion. Early studies of SO2 absorption potential on filter media led to constraints on the type of filters used in filter sampling, nominally removing a positive bias in reported SO4 measurements (e.g., Lee and Wagman, 1964; Messerole et al., 1976; Mueller et al., 1983; Appel et al., 1984; Lipfert, 1994; Batterman et al., 1997). For purposes of addressing large variability in particle mass concentrations from fugitive dust, in 1980 the US revised its approach to particle sampling to constrain filter sampling to particles from the TSP sampling to less than 10 µm AMMD. EPA revised its laboratory analytical procedure from a colorimetric analysis to incorporate ion chromatography as a standard method allowing for smaller extracted samples and lower detection limits in sub-microgram range. In the 1990s, the US regulatory requirements focused increasingly on the effect of fine particle exposure on humans. This led in 1999-2000 to further constrain routine particle mass sampling to less than 2.5 µm AMMD.

The combination of constraints of gas absorption in filter media and on size fractionation for SO4 measurements leads to uncertainty and potential bias in long-term annual average trends from the 1960s to present. In the former case, a history of evaluations of filter media and modification of specified sampling protocols after 1960 identifies the ambiguities in reported average SO4 concentration trends. Some examples of tests include a reported positive bias of single 24-hour average samples that could be as high as 40% or more in high SO2 concentration media (e.g., Lee and Wagman, 1964; Messerole et al., 1976); however Frank (1974) asserts that the bias in annual averages is ~ 16%. Lipfert (1994) estimates the sulfate artifact in urban hivol data is ~ 5µg/m3.

A potential bias introduced with constraining filtered particle size varies with location and season. From a 1977 series of short-term tests in six different cities, Stevens et al. (1978) reported a comparison of sulfur measured for the range of <2.5 µm diameter (PM2.5-fine) to >2.5 µm (PM10-2.5 -coarse) diameter using dichotomous samplers. Their results indicated that the fine fraction <2.5 µm ranged from 83-93% of the total fine and coarse fractions. A bias in SO4 concentration of < 10% was reported <2 µm compared with the < 30 µm samples in summer 1970s in southern California (e.g., Whitby and Sverdrup, 1980). A winter study for four sites in Denver area (Heisler et al., 1980) showed a range of 70-98% <PM2.5 sulfate to <30 µm (TSP) sulfate. In the southeastern US, Blanchard et al (2013) report the annual average (1999-2010) PM2.5 SO4 represents about 92-95% of PM10 ­.

Lipfert’s (1994) analysis provides an important comparison between two particle measures, from long term monitoring data using the federally specified TSP alkaline glass-fiber filters and nearly neutral PM10 Teflon filters. For 1989-1990 data from five cities in New York, the average PM10 to TSP SO4 ratio (corrected for 5 µg/m3 bias) was found to be 0.9, range 0.71-1.07. Assuming that this is representative at least of US urban conditions, size and filter bias constraints indicate that historical annual average PM10 and TSP SO4 are comparable. The Blanchard et al (2013) results suggest a similar result for long term average comparisons of PM2.5 and PM10 SO4.

*Precipitation.* The earliest measurements of precipitation relied on capture of rain or snow in open containers or dust fall jars. Some form of these containers date back to the 19th century. They report essentially dry and wet deposition as a bulk value. These approaches involve contamination by debris from blowing vegetation, insects, and from animal or bird droppings, and were poorly designed for leachable container material and the aerodynamics of falling hydrometeors. In the 1960s attempts were made to distinguish between dry deposition and wet deposition. The former use passive samplers with surface orientation, special surfaces and vertical orientation (e.g. face down for gases). Precipitation samplers developed especially after mid-1970 deployed a “bucket” sampler with a lid seal activated by precipitation. These designs are used today by the NADP (2016) in the US and internationally by various investigators. Samples of precipitation are then sent to a central laboratory for SO4 and other chemical analysis using standard procedures. The reliability of pre 1960s precipitation chemistry is uncertain and indeterminate, especially for pre-World War II conditions. Substantial effort to develop a quantitative measurement protocol took place with government and private entities between 1975 and 1985. Most reliable and comparable in terms of well-documented US long-term records are the post mid-1970s observations (NADP, 2016).

Our notes qualify measures of changes in SOx with emissions in the US after approximately 1960. The emission estimates are subject to indeterminate uncertainty until the 1990s, with later improvements in direct CEM SO2 measurements for large emission sources. Measurements of annual average ambient SO2 and SO4 concentrations reported in the literature are subject to uncertainties associated with sampling and analytical methods; SO2 observations are likely to be more consistent in time than particle SO4. Nevertheless, for our purposes of documenting the major decline in US surface level SOx between the sparse measures of the 19th and early 20th centuries and today, the available data seem particularly well-characterized after the 1960s. Likewise, precipitation SO4 in the US shows similar declines with emissions, indicating consistency of the ambient data with emissions.

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