Supplementary Information for

Cosmogenic radiosulfur tracking of solar activity and the strong and long-lasting El Niño events

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Analytical Methods

Submicron aerosol samples (<1 μm) were collected on glass-fiber filter papers (Whatman) by a high-volume air sampler (flow rate: ~1 m³ min⁻¹) on the rooftop of Pacific Hall (~200 m above sea level) at the University of California San Diego (UCSD) (32.7°N, 117.2°W) from March 2014 to November 2016. Most samples were collected for 6 days. During August-November 2015, samples were not collected due to resource limitations.

Measurements of atmospheric ³⁵S were pioneered by Turekian and colleagues at Yale (1), but the early technique (internal SO₂ proportional counting) possesses large uncertainties. Ultra-low-level scintillation counting methods for ³⁵S measurements in both water and aerosol samples have been developed and refined by various groups in the 21st century (2-8). Measurements focusing on water samples are useful for hydrological age-dating (2, 4, 5, 7, 8), but only provide limited atmospheric information. To directly measure ³⁵S in the atmosphere, we developed a series of methods focusing aerosol samples (3, 6), which has been applied in understanding atmospheric sulfur transport and chemistry (9-12). The measurements of ³⁵S in this study followed the method optimized for chemically complex aerosol samples (6).

Soluble ions including sulfate were extracted by soaking filter papers in Milli-Q deionized water (18 MΩ cm) in a 50-mL centrifuge tube under sonication for one hour. Insoluble materials including filter papers were filtered and the filtrate was diluted to 50 mL. An aliquot of sample solution was subject to ion concentration analysis using an ion chromatography (Dionex ICS-2000). A 5 mL of H₂O₂ (30%) was added to another aliquot of samples to remove soluble organic materials, and the solution was dried in a clean oven operated at 80°C. The dried samples were redissolved by deionized water, and quantitatively passed through a poly-vinylpyrrolidone (PVP) column and a Ag cartridge (Dionex OnGuard II) to remove residual impurities (organics and chlorides, respectively) that may influence ³⁵S measurements. The purified sample solution was freeze-dried to solids, and subsequently redissolved by 5 mL of H₂O₂ (12%) and mixed with 10 mL of scintillation cocktail (Insta-Gel Plus) in a 20 mL plastic scintillation vial. Sample-cocktail mixtures were analyzed by an ultra-low-level liquid scintillation counter (Quantulus 1220, PerkinElmer). Each sample was counted for 6-12 cycles (2 hours for each cycle). The average and standard deviation of all counting cycles was calculated. The measured ³⁵S activities were corrected for the counting blank and efficiency, fraction of samples used for counting, and decay time. Standard SO₄ solution with known ³⁵S activities were routinely measured to monitor the possible shift of counting efficiencies, which ranged from 70-80% during the course of this study. SO₄ concentrations at the time when samples were collected are reported in this study at the unit of molecules m⁻³. Errors were propagated in all calculations and reported.

Data Analysis Strategies

Submicron aerosol samples collected during solar minimum (2009-2010) (10) were compiled along with our new measurements to investigate solar cycle influences. These samples were collected at the same campus of UCSD using the same sampling method, but at a different site (Scripps Pier above the Pacific Ocean, ~10 m above sea level), which is ~2 km from the Pacific Hall. Averaged sulfate concentrations measured at Scripps Pier are ~1800 ng m⁻³, notably higher than this study (~450 ng m⁻³). This observation is reasonable because Scripps Pier is directly influenced by sulfate-rich sea-spray aerosols and ship emissions. Nevertheless, sea-spray aerosols and ship-emitted sulfates do not contain ³⁵SO₄ and cannot explain higher ³⁵SO₄ activities during 2009-2010. The only source of ³⁵S is cosmogenic productions via atmospheric ⁴⁰Ar atom spallation reactions. The absolute radiosulfur abundance (³⁵SO₄ concentrations) is therefore directly compared between two datasets as the two sampling sites are in the same region and close to each other (~2 km). The ³⁵S analytical methods for two datasets (see Analytical Methods) are nearly the same, though ³⁵SO₄ concentrations during 2009-2010 may be slightly underestimated due to quenching effects in the early version of our method (3, 6), which cannot explain higher ³⁵SO₄ concentrations during 2009-2010. Consequently, lower ³⁵SO₄ concentrations of samples during 2014-2016 than 2009-2010 cannot be attributed to slight differences in either sampling sites.
or analytical methods and do reflect the inter-annual variation of atmospheric $^{35}$SO$_4$ concentrations in our study region.

The microenvironmental differences in terms of local stable sulfur emission sources between the two sampling sites (Scripps Pier and Pacific Hall) do not allow a direct comparison of $^{35}$SO$_4$ specific activities (the ratio of $^{35}$SO$_4$ to stable sulfate concentrations) between two datasets. Therefore, in Figure 1 where the solar cycle is investigated, a $^{35}$SO$_4$ specific activity time-series is not given. As discussed in the main text, significant differences in rainfall between 2009-2010 and 2014-2016 are not observed. Long-term air quality data in San Diego during 2009-2016 do not display large variabilities in PM$_{2.5}$ concentrations either (https://www.epa.gov/air-trends/air-quality-cities-and-counties). We therefore expect that a solar cycle signal similar to that in $^{35}$SO$_4$ (Figure 1) can be also observed in $^{35}$SO$_4$ specific activities, although such a long-term dataset is not available in this study.

Regarding the El Niño Southern Oscillation (ENSO) influences, both $^{35}$SO$_4$ concentrations and specific activities are studied and discussed (Figures 1b and 2a). Our pilot analysis focusing on $^{35}$S variabilities at multi-year (Figure 1b) and multi-week (Figure 2a) time scales demonstrates a clear solar modulation effect on $^{35}$S and how regional atmospheric circulation changes due to climate events may perturb the signal. We acknowledge that influences of solar activity and ENSO cycles may not be completely separated in this simple way, and their complex structures are responsible for the scattering pattern shown in Figure 1c. For a more quantitative description of the interaction between solar activities and ENSO cycles and its fingerprinting on $^{35}$S, more comprehensive datasets, time-series and climatology analysis are needed, but these efforts are beyond the scope of this brief report. We recommend future studies using signal analysis methods such as wavelet transformation and Empirical Mode Decomposition to extract different components in the time series, especially when more measurements are obtained and available in the future. Indeed, there is an increasing interest in the potential linkage between solar activity and ENSO cycles (13-16) and their separate or combined influences on the climate system (17). The solid physical mechanisms of solar-troposphere interactions and other influences on the Earth surface system remain lacking because most studies are based on simple statistical analysis of meteorology data. Our field-based radionuclide measurements provide a new parameter that may be useful to solve these problems in the future.

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