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Applying New Isotopic Approaches to Differentiate Sulfur Sources in Rainfall

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Transformations of sulfur (S) compounds in Earth's atmosphere influence pollutant levels and the climate system. For example, reduced S emissions by natural ecosystems (e.g., dimethyl sulfide) and anthropogenic activity (e.g., sulfur dioxide) can be oxidized to sulfate, generating high-albedo aerosols and acidifying rainwater. Sulfate's diverse sources and chemical pathways complicate our understanding of the atmospheric S cycle, necessitating additional constraints to interpret the origin of atmospheric sulfate and its environmental consequences.

Houston, Texas presents a unique region to investigate differences in atmospheric S inputs to rainwater, including petrochemical infrastructure, farmlands, and seawater from the Gulf of Mexico. To elucidate their relative contributions to sulfate loading in rainwater, we studied the regional differences in rain chemistry at two sites: Rice University near downtown Houston (new sample collection for 8 months duration) and archived samples from the National Atmospheric Deposition Program (NADP) site (TX10) at the Attwater Prairie Chicken National Wildlife Refuge. Given the more remote, inland location of the NADP site, these samples are expected to have lower contributions of seawater and anthropogenic sources of S than the Rice University site. We found that major solute concentrations and elemental ratios at both sites indicate the presence of sea salt aerosols in precipitation from both areas. However, sea salt aerosols cannot explain total sulfate concentrations, implying the presence of non-sea-salt sulfate (NSS) in the form of anthropogenic and/or biogenic aerosols. Downtown measurements of NSS averaged ~82% of the total sulfate, while the NADP averaged ~86%; furthermore, absolute amounts of both total and NSS sulfate in the urban samples averaged 2.4-fold higher than the rural site. Together, these data suggest a greater influence of both sea-salt and anthropogenic sources on downtown Houston. Ongoing research includes collecting S and O isotopic data using electrospray ionization Orbitrap mass spectrometry, which could improve sulfate source tracing. This method requires roughly 1000 times less sulfate mass than traditional methods, which is important for dilute rain samples that would otherwise preclude isotopic analysis. Ultimately, this study pairs elemental analysis with novel isotopic method development to deconvolve controls on the atmospheric cycling of S.