Assessing pyrite-derived sulfate in the Mississippi River with four years of sulfur and triple-oxygen isotope data

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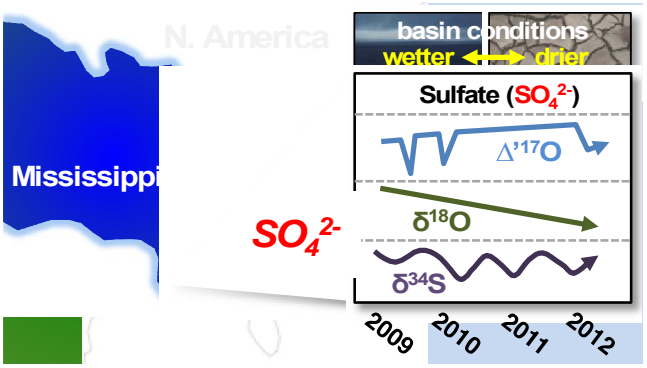
Abstract



Riverine dissolved sulfate (SO_4^{2-}) sulfur and oxygen isotope variations reflect their controls such as SO_4^{2-} reduction and re-oxidation, and source mixing. However, unconstrained temporal variability of riverine SO_4^{2-} isotope compositions due to short sampling durations may lead to mischaracterization of SO_4^{2-} sources, particularly for the pyrite-derived sulfate load. We measured the sulfur and triple-oxygen isotopes ($\delta^{34}S$, $\delta^{18}O$, and $\Delta'^{17}O$) of Mississippi River SO_4^{2-} with biweekly sampling between 2009-2013 to test isotopic variability and constrain sources. Sulfate $\delta^{34}S$ and $\delta^{18}O$ ranged from −6.3‰ to −0.2‰ and −3.6‰ to +8.8‰, respectively. Our sampling period captured the most severe flooding and drought in the Mississippi River basin since 1927 and 1956, respectively, and a first year of sampling that was unrepresentative of long-term average SO_4^{2-}. The $\delta^{34}S_{SO4}$ data indicate pyrite-derived SO_4^{2-} sources are 74 ±10% of the Mississippi River sulfate budget. Furthermore, pyrite oxidation is implicated as the dominant process supplying SO_4^{2-} to the Mississippi River, whereas the $\Delta'^{17}O_{SO4}$ data shows 18 ±9% of oxygen in this sulfate is sourced from air O_2.

Introduction

The characterization of riverine chemical fluxes today is important for establishing natural baselines for understanding the magnitude of human impact on chemical cycles and interpreting the rock record of biogeochemical changes in Earth's past. For the surface sulfur cycle, which is closely linked to the carbon and oxygen cycles over long time scales, its most significant flux is riverine sulfate input to the ocean[1]. Natural variations in the magnitude and isotopic composition of the sulfate flux reflects the exposures and weathering rates of sulfide and sulfate minerals in rocks[2]. Meanwhile, human activities, such as the mining and burning of fossil fuels like coal, can increase riverine sulfate fluxes four-fold and alter sulfate's sulfur isotope composition on a large scale, such as in the Mississippi River[3]. Thus, studies of the continental sulfur cycle have made efforts to constrain riverine SO_4^{2-} fluxes and isotope compositions globally[4-7] and in large[8-10] and small[11-14] rivers. Riverine studies have suggested that global sulfate budgets may underrepresent the pyrite-derived sulfate flux, which is particularly important for sulfur and carbon weathering budgets[9, 15].

An advantage of riverine chemical studies is their integration of spatial and temporal scales. Depending on the research focus, sampling campaigns of different durations can be designed according to the basin size and its assumed variability, to constrain temporal variation with multi-year sampling, or to reveal spatial variations. However, a lack of temporal constraints on SO_4^{2-} isotopes may result in biased conclusions about sulfate sources and processes. For example, the average isotope compositions of inputs are needed to construct stable isotope mixing models to constrain sulfate sources in individual rivers and in models of the global surface sulfur cycle. A low frequency or short duration of sampling may bias model results towards one season or an anomalous year. Only some riverine sulfate isotope studies last a year[8,

[10, 16-18] or longer[19-26], and out of the rivers that were monitored for ≥1 year, just the Yangtze, Indus, Oldman, and Kalix are >5,000 km^2. For these long-term studies, the average ranges for $\delta^{34}S$ and $\delta^{18}O$ are ~5‰ and have no correlation with catchment size. Thus there are insufficient temporal constraints on riverine SO_4^{2-} isotope variability over large, and continental, spatial scales. For example, significant variability was shown within one year of Yangtze River sulfate data where the ranges of $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ were respectively 9.5‰ and 8.9‰[10]. In another example from a highly cited study, 85% ±5% of sulfate flux in the relatively pristine Mackenzie River in Canada was attributed to pyrite oxidation[9]. This assessment was based on stable isotope ($\delta^{34}S$ and $\delta^{18}O$) mixing of sulfate sources for 20 samples taken throughout the basin at one time, with only one sample recovered from the river mouth that could represent the output to the ocean. The respective $\delta^{34}S$ and $\delta^{18}O$ had significant spatial variation of 28.3‰ and 12.6‰, respectively, and the temporal variability was undetermined. While the conclusion appears robust that most of the sulfate in the Mackenzie is pyrite-derived, it remains difficult to know if the estimate of pyrite-derived sulfate flux is applicable to the long term. Regardless, the estimation of pyrite-derived sulfate loads, and its natural and anthropogenic partitioning, is not a trivial task due to large $\delta^{34}S$ and $\delta^{18}O$ ranges and their overlaps with other sulfate sources. High loadings of pyrite-derived sulfate may result in large ranges of $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4,}$ which are commonly used as sulfate source tracers. Regardless, a lack of significant temporal variability, and a coupled response related to sources, are implicitly assumed for $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$.

Figure 1. The Mississippi River basin within the contiguous United States, with the Missouri and Ohio River sub-basins and the sampling location for this study at Baton Rouge, Louisiana identified. Image is modified from the original from NASA/JPL[27].

To test SO_4^{2-} isotopic variability over time and constrain sources, we target the Mississippi River. The Mississippi, Yangtze, and Amazon Rivers are the top three rivers for sulfate flux to the ocean worldwide[28]. The Mississippi River basin (Figure 1) covers ~37% of the contiguous United States[29] and is the largest river system in North America. The Mississippi River basin has been heavily altered by human activities such as agriculture (65% by area[30]), dams and reservoirs in the semi-arid west, and levee systems prevalent in the lower Mississippi River. Bedrock sources of sulfate within the Mississippi River include abundant pyrite-bearing shales in its western reaches, evaporite exposures, and mine drainage from coalbeds within sub-basins in the west (Missouri River) and east (Ohio River). The Mississippi River $\delta^{34}S_{SO4}$ average was previously used in a stable isotope mixing model to characterize sulfate sources[3], whereas the full time series $\delta^{34}S_{SO4}$, $\delta^{18}O_{SO4}$, and $\Delta'^{17}O_{SO4}$ data from 2009-2013 are reported here. In the previous study, it was estimated that human activities account for 75% of the Mississippi River SO_4^{2-} flux and have increased the average Mississippi River $\delta^{34}S_{SO4}$ from −5‰ to −2.7‰, and it

was concluded that the more typical scenario should be the opposite – where most rivers should instead display decreasing $\delta^{34}S_{SO4}$ due to human influence. The distinctly low $\delta^{34}S_{SO4}$ of the Mississippi River was interpreted as the result of a high input of sulfate from the weathering of pyrite. Mississippi River sulfate was partitioned into sources from coalmine drainage (47%), natural and anthropogenic rock weathering (37%), atmospheric sulfur (15%), and fertilizer (1%). In the present study, Mississippi River SO_4^{2-} isotope compositions are compared to ion concentrations, discharge, and temperature from the USGS[31] and discharge from the USACE[32]. While average Mississippi River $\delta^{34}S_{SO4}$ made the previous source partitioning possible, four years of data from 2009-2013 permits us to examine the full variability and controls on $\delta^{34}S_{SO4}$, $\delta^{18}O_{SO4}$, and $\Delta'^{17}O_{SO4}$ and attempt to more finely resolve the pyrite-derived sulfate load here.

Materials and Methods

Mississippi River water was collected biweekly or at greater frequency during the period 03/11/09 to 01/17/13 for $\delta^{34}S_{SO4}$, $\delta^{18}O_{SO4}$, and $\Delta'^{17}O_{SO4}$ measurements. River water samples were collected at the east bank of the Mississippi River at Baton Rouge or St. Francisville, Louisiana, USA and immediately processed or refrigerated for later processing. Our sampling locations near Baton Rouge, Louisiana integrate the main sub-basins of the Mississippi River except for the Red and Ouachita Rivers, and thus here the SO_4^{2-} flux to the ocean for ~37% of the contiguous United States is accounted for.[29] A few additional samples were collected from the sub-basin upper Ohio River at Tell City, Indiana to compare against the main Mississippi River. All samples were treated with the DDARP method, yielding purified $BaSO_4$[33].

The riverine dissolved sulfates were analyzed for their isotope $\delta^{34}S_{SO4}$, $\delta^{18}O_{SO4}$, and $\Delta'^{17}O_{SO4}$ per the methods here with additional details in the supporting information (chapter 1). The classical isotope notation is used here:

$$\delta \equiv R_{sample}/R_{standard} - 1 \qquad (1)$$

Where R is the mole ratio of $^{18}O/^{16}O$, $^{17}O/^{16}O$, or $^{34}O/^{32}O$ and reported in units per mille (× 1000‰) with respect to the international isotope standards VSMOW or VCDT for $\delta^{18}O$ and $\delta^{34}S$, respectively. We note that the linear "capital delta" definition is

$$\Delta^{17}O \equiv \delta^{17}O - C \times \delta^{18}O, \qquad (2)$$

where C is an arbitrary reference slope[34]. Here we use a logarithmic definition,

$$\Delta'^{17}O \equiv \delta'^{17}O - C \times \delta'^{18}O, \text{ where} \qquad (3)$$

$$\delta'^{1x}O = \ln(\delta^{1x}O + 1) = \ln(R_{sample}/R_{standard}). \qquad (4)$$

The ^{1x}O in equation (4) refers to the isotope ^{18}O or ^{17}O, and $\Delta'^{17}O$ is reported in ‰ with respect to the standard VSMOW (Fig. S1). The choice of the reference slope C in equation (3) is 0.5305, which benefits inter-species comparison[34]. All measurements for $\Delta'^{17}O$ were done on samples converted to O_2 and run on a Thermo Finnigan MAT 253 isotope ratio mass spectrometer (IRMS) at Louisiana State University (LSU). The raw average of replicate $\delta^{17}O_{SO4}$ and $\delta^{18}O_{SO4}$ values (in ‰) are available in Tables S1 and S2 for re-normalization to other reference frames of choice. The $\delta^{34}S_{SO4}$, measurements were conducted at the University of Maryland and Indiana University using an Elemental Analyzer coupled to an IRMS. For $\delta^{18}O_{SO4}$, analysis was done at LSU using a high temperature conversion Elemental Analyzer (TCEA) coupled to a Thermo Finnigan MAT 253 IRMS in continuous flow mode. Analytical errors for standards and sample duplicates for $\delta^{34}S_{SO4}$, $\delta^{18}O_{SO4}$, and $\Delta'^{17}O_{SO4}$ are ±0.3‰, ±0.5‰, and ±0.05‰ respectively.

To determine trends and seasonality of sulfate, monthly averages of the isotope data were used for time series decomposition in the software "R"[35] (Figs. S2 and S3), and sulfate fluxes for the main Mississippi River and sub-basins were compared. Additional available data is used from continuously monitored water discharge, ion concentration, temperature, and other parameters at St. Francisville, Louisiana[31], where for that location the main stem water discharge of the Mississippi is represented by the Tarbert Landing, MS and Knox Landing, LA sites monitored by the USACE[32]. Mississippi River sub-basin sulfate concentration and river discharge data is used from the Missouri River at Hermann, MO, Upper Mississippi below Grafton, IL, and Ohio River at Metropolis, IL, which are monitored by the USGS[31].

Sulfate flux estimates for the Mississippi River and its sub-basins use the daily river discharge data with sulfate concentrations reported by the USGS for the respective sites given above. To estimate daily sulfate fluxes for the purposes of matching datasets and making mixing models, sulfate concentrations are interpolated from the approximately once-monthly measurements from the USGS, and matched with daily water discharge reported by the USACE and USGS. Sulfate flux estimates should be considered to have lower resolution than the isotope data due to interpolation from approximate once-monthly concentration measurements.

Results

Mississippi River SO_4^{2-} varies from −6.3 to −0.2‰ and averages −2.7‰ for $\delta^{34}S_{SO4}$, from −3.6 to 8.8‰ and averages 3.4‰ for $\delta^{18}O_{SO4}$, and ranges −0.19 to −0.01‰ with an average of −0.09‰ for $\Delta'^{17}O_{SO4}$ (Figure 2, Table S1). Time series decomposition reveals seasonality in $\delta^{34}S_{SO4}$ with an amplitude of 3‰, with minima in late summer, and a $\delta^{18}O_{SO4}$ decrease of 5‰

159 from 2009 to 2013 (Figure S2), with $\Delta'^{17}O_{SO4}$ exhibiting more secular variation. Histograms of

160 $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ are shown in the supporting information (Fig. S3).

161 Sulfate for the period 01/27/11 to 06/01/11 from the Upper Ohio River sub-basin ranged

162 from −0.3 to 1.6‰ and averaged 0.3‰ for $\delta^{34}S_{SO4}$ and ranged 1.4 to 2.9‰ and averaged 2.1‰

163 for $\delta^{18}O_{SO4}$ (Table S2).

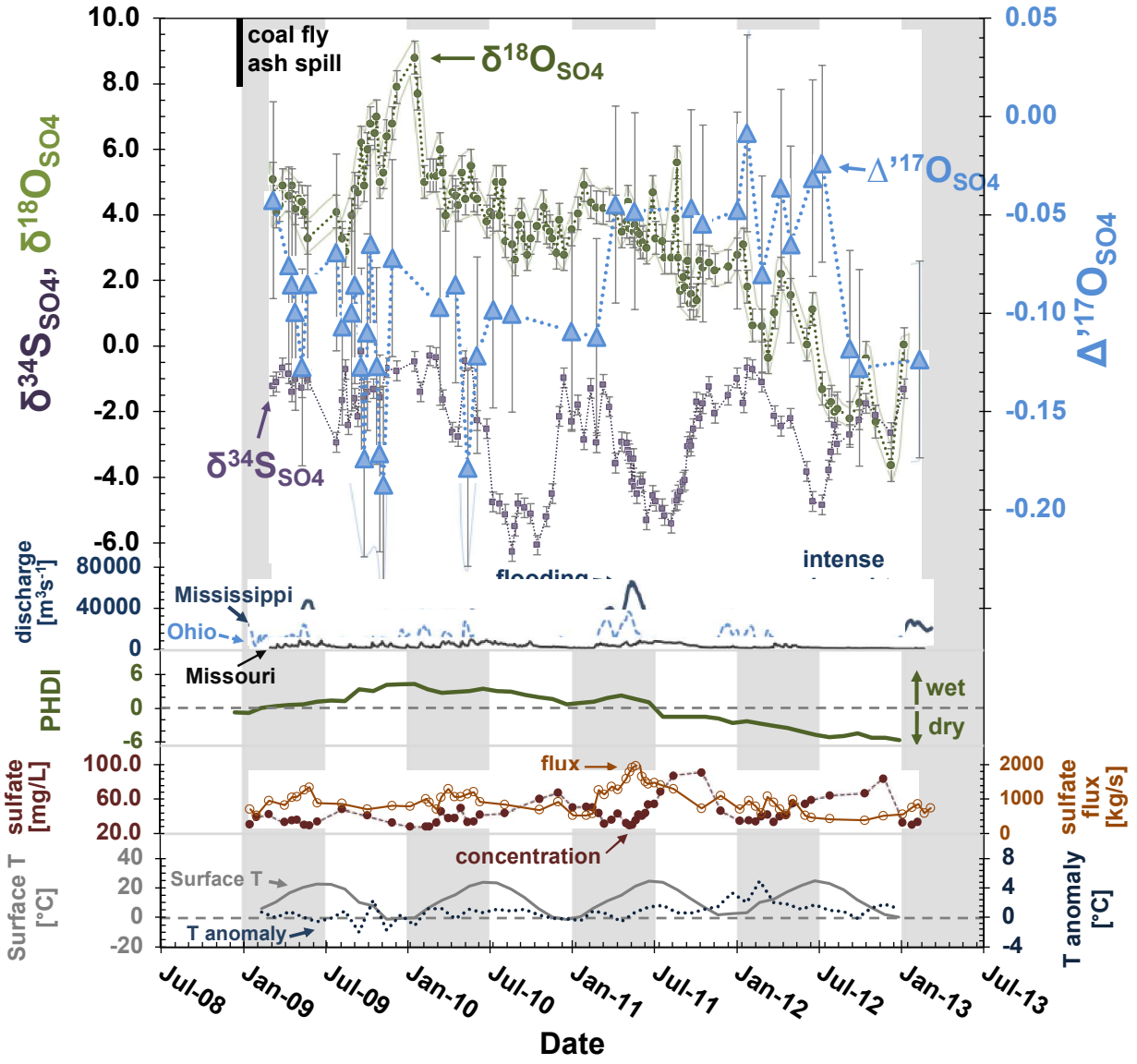


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Figure 2. Mississippi River sulfate isotope $\delta^{34}S_{SO4}$, $\delta^{18}O_{SO4}$, and $\Delta'^{17}O_{SO4}$ data from this study plotted with available data for surface temperature, temperature anomaly (based on monthly averages from 1901-2000), and Palmer Hydrological Drought Index (PHDI) for the contiguous United States[36], river basin discharge data[31, 32], and sulfate concentration[31]. Sulfate flux is calculated from discharge data and sulfate concentration. Analytical errors for isotope data are shown as error bars and envelopes. Significant events are noted: 1) the Kingston Fossil Plant coal fly ash slurry spill on 12/22/08, 2) historical flooding (the most intense since 1927) in the spring of 2011, and 3) historical drought (strongest since 1956) in the summer to fall of 2012.

Discussion

Constraining temporal variability

Mississippi River sulfate had higher average $\delta^{34}S_{SO4}$ and an attenuated seasonality in 2009 that appear unrepresentative of the long term. The year 2009 may be atypical for two reasons: one of the largest coal fly ash spills in United States history occurred in December 2008 where 4.1 million cubic meters of coal ash was released within a tributary of the Mississippi River[37], and the summer of 2009 was wetter than average (see PHDI in Fig. 2). Mississippi River sulfate concentrations did not increase due to the coal ash spill although there were modest increases in the tributary where the spill occurred[37]. The lack of a clear sulfate signal in the Mississippi River from such a spill suggests that widespread coal ash impoundments leaking in the humid southeastern United States[38] may contribute diffuse but large fluxes of sulfate that are difficult to quantify. The mixing model used in the previous study was based on the 4-year Mississippi River $\delta^{34}S_{SO4}$ average of −2.7‰ and gave a solution of −5‰ for the $\delta^{34}S_{SO4}$ of natural (pre-anthropogenic) sulfate[3]. Natural Mississippi River $\delta^{34}S_{SO4}$ would be −0.8‰ from the same model if the 2009 Mississippi River $\delta^{34}S_{SO4}$ average of −1‰ is used. And again, a solution based on the lowest Mississippi River $\delta^{34}S_{SO4}$ of −6.3‰ from 08/26/2010 would imply that natural Mississippi River $\delta^{34}S_{SO4}$ was −14.0‰. This exercise shows how source estimates can

196 significantly differ from the long term when based on an unrepresentative year or a one-time
197 "snapshot".
198
199 **Low $\delta^{34}S$ values of Mississippi River sulfate**
200 The likely source of Mississippi River sulfate with low $\delta^{34}S_{SO4}$ indicated from the
201 Missouri River sub-basin is the weathering of pyrite in rocks deposited during the transgression
202 of a Cretaceous-age epicontinental seaway[3] which are now exposed in western and upper reaches
203 of the Mississippi River basin[39]. The $\delta^{34}S$ of pyrites in Cretaceous shales can span a wide range,
204 with reported values between +16.7‰ to −34.7‰ but mostly negative with a mean at −19.7‰[40].
205 The implication for respectively lower and higher $\delta^{34}S_{SO4}$ of the Missouri River and Ohio River
206 is consistent with the seasonal and spatial patterns in $\delta^{34}S$ from zebra mussels across the
207 Mississippi River basin during 1997-1998[41]. The zebra mussel sulfur is sourced from riverine
208 sulfate but slightly fractionated, for example at Baton Rouge the reported mussel $\delta^{34}S$ was near
209 −4‰ versus the average $\delta^{34}S_{SO4}$ around −3‰ from our study, with their comparison suggesting
210 that Mississippi River sulfate end members have not changed significantly over the past ~20
211 years.
212
213 **Mass balance of pyrite-derived sulfate**
214 Here we provide a more detailed Mississippi River sulfate mass balance that expands on
215 the previous work using the $\delta^{34}S_{SO4}$ average[3]. The $\delta^{34}S$ of sulfate from rock weathering of shale
216 pyrite and evaporite (excluding mine drainage), which here we will call $\delta^{34}S_{RW}$, was previously
217 estimated as −6.5‰, where the sulfate from natural and anthropogenically enhanced rock
218 weathering were assumed to have the same $\delta^{34}S$ value[3]. We adopt $\delta^{34}S$ values of 20‰ for

evaporite[9] and −17‰ for pyrite from marine shales[42], for $\delta^{34}S_E$ and $\delta^{34}S_{Py}$ respectively. Despite a typically wide range in pyrite sulfur isotope compositions, such as a ~50‰ range in Cretaceous pyrite $\delta^{34}S$ data[40], the strong $\delta^{34}S$ difference between average marine evaporite and pyrite is forgiving when using estimated values to partition their mass balance. With the given constraints, the mixing equation becomes:

$$\delta^{34}S_{RW} = f_{Py} * \delta^{34}S_{Py} + (1 - f_{Py}) * \delta^{34}S_E \quad (5)$$

The mass balance of pyrite and evaporite can then be solved for the unknown fraction of pyrite, f_{Py}, which is determined as 0.72 with evaporite being the remainder. Thus, the sulfate load from rock weathering in the Mississippi River is 72% pyrite-derived sulfate and 28% evaporite sulfate, or a respective 26.5% and 11% of the total Mississippi River sulfate budget (Table S3). A scaling of coal production to riverine sulfate load[15] was previously used to estimate the contribution of mine drainage pyrite-derived sulfate. The result was, out of a total flux of 27.8 Tg $SO_4^{2-}yr^{-1}$ from the Mississippi River, sulfate from mine drainage accounted for 47% and its average $\delta^{34}S$ value was estimated as −1.8‰[3]. Thus, the sulfate load from natural and anthropogenically enhanced weathering of shale pyrite and pyrite weathering in mine drainage is 74 ±10%, or 20.6 Tg $SO_4^{2-}yr^{-1}$. Under such heavy loads of pyrite-derived sulfate, the oxygen isotopes of Mississippi River sulfate should strongly reflect variations in the ambient water oxygen source and the pathway of pyrite oxidation.

Seasonal variations

The differences in sulfur isotope compositions of average bedrocks in Mississippi River sub-basins, and the dominance of pyrite-derived sulfate, may explain the $\delta^{34}S_{SO4}$ seasonality as well as the lack of the same in $\delta^{18}O_{SO4}$ (Figs. 2 and 3), all despite a heavy anthropogenic

242 overprint. A global comparison of riverine sulfate reveals smaller ranges of average $\delta^{18}O_{SO4}$ with
243 high contributions from evaporite sulfate and a larger range of average $\delta^{18}O_{SO4}$ in rivers with
244 higher amounts of pyrite-derived sulfate (shale pyrite and mine drainage sources) (Fig. 3a). Also
245 observed in figure 3a, rivers with high pyrite-derived sulfate loads have $\delta^{18}O_{SO4}$ corresponding to
246 local meteoric water differences, whereas sulfate from the North American Mackenzie, Oldman,
247 and Mississippi Rivers plot with respectively lower to higher $\delta^{18}O_{SO4}$ values that reflect the
248 correlation of lower $\delta^{18}O_{water}$ with higher latitudes. The Mississippi River $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$
249 data indicate the strong signature of pyrite-derived sulfate as compared to evaporite sulfate, and
250 mixing of two sources that are significantly different in their $\delta^{34}S_{SO4}$ but not in their $\delta^{18}O_{SO4}$ (Fig.
251 3b). The Ohio and Missouri River sub-basins contribute a respective 33% and 41% of average
252 Mississippi River sulfate flux during the study period. The average Mississippi River $\delta^{34}S_{SO4}$ and
253 $\delta^{18}O_{SO4}$ for the upper ranges of Ohio and Missouri sulfate flux contributions are plotted in figure
254 3b and indicate that the most important source of ^{34}S-depleted sulfate in the Mississippi River
255 comes from the Missouri River sub-basin[3]. Source mixing in the Mississippi River is also
256 apparent in a bimodal distribution of $\delta^{34}S_{SO4}$ data with modes at around −1‰ and −5‰ (Fig.
257 S3). During the periods of seasonally low $\delta^{34}S_{SO4}$ the Missouri River accounts for up to ~80% of
258 total Mississippi River sulfate flux (Fig. S4). Sulfate measurements from 01/27/11 to 06/01/11
259 from the upper Ohio River at Tell City, Indiana (Table S2) show that the Ohio has higher
260 average $\delta^{34}S_{SO4}$ (0.3‰) compared to the Mississippi River (−3.2‰) during the same interval.
261 Meanwhile, from figure 3b we estimate that the difference in $\delta^{18}O_{SO4}$ between Ohio and
262 Missouri river sulfate is less than 1‰.
263

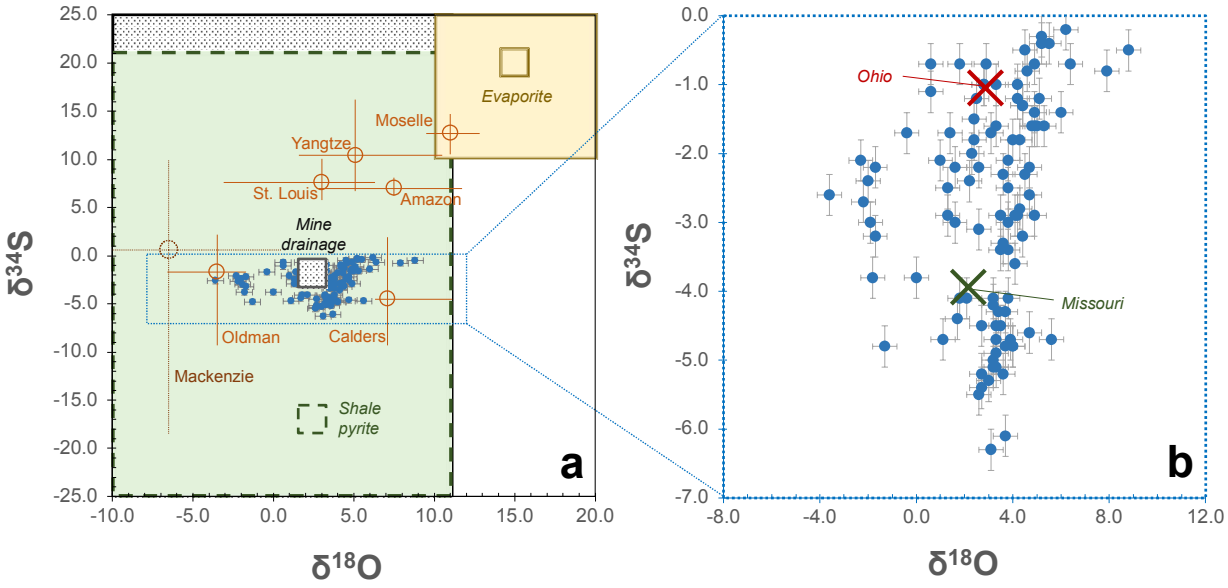


Figure 3. Sulfate $\delta^{34}S$ is plotted against $\delta^{18}O$ for this study, selected rivers, and expected ranges of riverine sulfate sources. In plot (a), sulfate data for the Mississippi River from this study (filled circles) are shown along with previously published river averages and their ranges (open circles and error bars for ranges) [9, 10, 22, 24, 43-45], and the important rock sources of sulfate of evaporites[9], shale pyrite[42], mine drainage[3], with their averages (open squares) and respective ranges (shaded boxes). Note that the Mackenzie River average is from spatial data while all other riverine sulfate averages are from time series. The average $\delta^{18}O_{SO4}$ of sulfate derived from oxidation of pyrite in shales and mine drainage in (a), are estimated from oxygen sources of average Mississippi River water (-6.6‰[46]) and air O_2 (23.5‰[47]), with a typical fractionation between sulfate and water of 9‰[48], and the resulting sulfate oxygen having a source ratio ¾ water and ¼ air O_2[49]. The estimated $\delta^{18}O_{SO4}$ ranges (~−20‰ to 11‰) for sulfate from pyrite oxidation and mine drainage assume that such sulfate can approach a 100% water oxygen end member (~−20‰ at its lowest for US river waters[50]); and on the high end, with US river waters up to ~−2‰[50], sulfate could reach up to 11‰ with the aforementioned sulfate-water fractionation factor and oxygen source ratio. Plot (b) shows an expanded view of the Mississippi River sulfate data and its averages (large symbols) for the upper 25% of flux contributions from the Ohio and Missouri Mississippi River sub-basins with respect to the Mississippi River sulfate total.

Differential response of $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ to sulfate origin

Riverine sulfate oxygen isotope $\delta^{18}O$ has been used previously to help constrain the sources of SO_4^{2-} in river systems[8-10, 51], however the interpretation of $\delta^{18}O_{SO4}$ is not as straightforward as $\delta^{34}S_{SO4}$ because $\delta^{34}S_{SO4}$ is able to more faithfully retain source compositions

288 while $\delta^{18}O_{SO4}$ is prone to variable kinetic isotope effects and replacement of its original oxygen[49, 52]. The oxygen isotopes of SO_4^{2-} reflect a combination of its sources that are mainly water and air O_2 (where $\delta^{18}O_{O2}$ = 23.5‰[47], and US surface waters range ~−20‰ to −2‰ in $\delta^{18}O_{H2O}$[50]), oxygen isotope fractionation factors, the net effect of bacterial sulfate reduction, and the pathways of oxidation from sulfide to sulfate. Sulfate generated from the abiotic or biological oxidation of pyrite have $\delta^{34}S_{SO4}$ compositions that are very similar to their pyrite source and $\delta^{18}O_{SO4}$ compositions linked to the $\delta^{18}O$ of the ambient water source and the oxidation pathway[53, 54]. Similarly, during the mineralization of biomass the re-oxidation of sulfur will affect the resulting $\delta^{18}O_{SO4}$ and leave $\delta^{34}S$ relatively unchanged between its sulfur source and the resulting sulfate. Biological sulfur cycling via bacterial sulfate reduction (BSR) and subsequent re-oxidation of the product sulfide to sulfate (for example, in marine environments 75 to 90% is re-oxidized[7]) is one of the most significant controls on the mix of oxygen sources in SO_4^{2-} in freshwater and marine environments. Due to BSR, the concentration of remaining SO_4^{2-} decreases and becomes more enriched in ^{18}O and ^{34}S[55]. During so-called cryptic sulfur cycling, however, BSR can operate without affecting sulfate concentration or $\delta^{34}S_{SO4}$ but a quantitative re-oxidation of sulfide to sulfate results in replacement of sulfate oxygen and thus an effect on $\delta^{18}O_{SO4}$[56]. The comparison of sulfate concentrations, $\delta^{18}O_{SO4}$, and $\delta^{34}S_{SO4}$ in the Mississippi River, where pyrite-derived sulfate composes 74 ±10% of the budget, may not show conclusive evidence of BSR in the sense of residual sulfate decreasing in concentration and increasing in $\delta^{18}O_{SO4}$ and $\delta^{34}S_{SO4}$. Indeed, the Mississippi River sulfate concentration changes appear related to dilution effects, where spring snowmelt and precipitation result in lower sulfate concentration without a clear signal in $\delta^{18}O_{SO4}$ and $\delta^{34}S_{SO4}$ (Fig. 2).

During 2009-2013, Mississippi River $\delta^{18}O_{SO4}$, in contrast to its $\delta^{34}S_{SO4}$, does not respond seasonally. The $\delta^{18}O_{SO4}$ shows a general decreasing trend concomitant with increasing drought (Figs. 2 and 4) and a strong peak in the beginning of 2010. The $\delta^{18}O_{SO4}$ response appears to be basin-wide behavior across the Mississippi River, as compared to the seasonal control on sub-basin sulfate input reflected in $\delta^{34}S_{SO4}$ variations. First, although it composes just 15% of the Mississippi River sulfate budget[3], the oxygen isotope composition of atmospheric sulfate input is probably replaced, as consistent with results from a 36-year study in Hubbard Brook where internal cycling of atmospheric sulfate occurred during a residence time of 9 years[57, 58]. Furthermore, there are significant variations in the oxygen isotopes of river water between Mississippi River sub-basins[50] and this should register in the Mississippi River that has significant pyrite-derived sulfate that takes most of its oxygen from water. However, water data for the Ohio and Upper Mississippi[59], and Missouri[60] Rivers, indicates respective average $\delta^{18}O_{water}$ for these rivers of −7.5‰, −8.2‰, and −9‰. The average oxygen isotope differences are a maximum of 1.5‰ between Mississippi River sub-basin river waters and this will be reflected in their pyrite-derived sulfate. Thus, while the $\delta^{34}S_{SO4}$ response is strong, the $\delta^{18}O_{SO4}$ responds weakly to the geographic origin of sulfate sources in the Mississippi River (Fig. 3b).

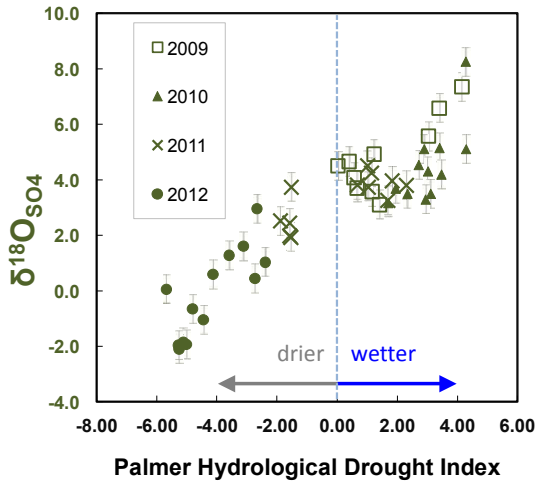


Figure 4. Monthly averages of Mississippi River sulfate $\delta^{18}O$, from this study, cross-plotted against monthly Palmer Hydrological Drought Index (PHDI) for the contiguous United States.[36] Palmer drought indices indicate moisture conditions, with negative and positive values indicating dry and wet anomalies, respectively.[61] In this case, Mississippi River sulfate $\delta^{18}O$ has a positive correlation with the PHDI, where lower and higher $\delta^{18}O_{SO4}$ correspond to increasing drought and wetter conditions, respectively.

Implications of the trend in $\delta^{18}O_{SO4}$

The trend of decreasing Mississippi River $\delta^{18}O_{SO4}$ over 2009-2013 occurs with increasing average drought and surface temperature in the contiguous United States and this suggests possible mechanisms for the $\delta^{18}O_{SO4}$ response. Monthly averages of Mississippi River sulfate $\delta^{18}O$ correlate strongly ($R^2 = 0.82$, linear regression) with the Palmer Hydrological Drought Index (PHDI) (Fig. 4). A "hydrological drought" condition is where surface and ground water availability is lower than average due to meteorological drought, as caused by anomalously low precipitation that can in turn be caused by temperature anomalies[62]. The PHDI can be considered an indicator of environmental response to precipitation input, and as such the PHDI changes more slowly than precipitation[63]. The strong correlation between Mississippi River $\delta^{18}O_{SO4}$ and PHDI, but lack of correlations between $\delta^{18}O_{SO4}$ and changes in sulfate flux between Mississippi River sub-basins or other chemical parameters (e.g., USGS-monitored concentration of redox-sensitive elements such as As and V, water temperature, and dissolved oxygen) suggests that it is a balance between sulfate from more recent surface runoff versus sulfate from groundwater that controls Mississippi River $\delta^{18}O_{SO4}$. It is possible that oxygen source for low $\delta^{18}O_{SO4}$ could be from the northwestern region of the Mississippi River basin, as streamwaters in the upper Missouri River area can range down to a $\delta^{18}O_{H2O}$ of −18‰[50]. However, Mississippi River sulfate should also show the low $\delta^{34}S_{SO4}$ values expected from Missouri River sulfate input if it was more significant during drought but this does not occur (Fig. 2). As reviewed by Van Stempvoort

and Krouse[48], with few exceptions sulfate oxygen isotopes are more ^{18}O-enriched than the ambient water in which the sulfate originates due to fractionation between sulfate and water ($\delta^{18}O \approx +9‰$) and the variably kinetic incorporation of ^{18}O-enriched oxygen from air O_2 ($\delta^{18}O$ = 23.5‰[47]). The ^{18}O-enrichment of sulfate relative to water is due to rapid oxygen exchange between sulfite and water, where sulfite is an intermediate during sulfide oxidation to sulfate, and sulfite is shown to be 9.5 ±0.8‰ ^{18}O-enriched versus water under typical experimental conditions[64]. While there is some correlation between $\delta^{18}O_{SO4}$ and $\delta^{34}S_{SO4}$ during wetter conditions (wet PHDI, Fig. S6), during dry conditions there is no such correlation despite nearly the same range of $\delta^{34}S_{SO4}$ as during wetter conditions in the Mississippi River. Here we suspect a difference in oxidation pathways for pyrite-derived sulfate in surface versus groundwater environments, where more extensive weathering of pyrites in groundwater results in a greater proportion of water oxygen in sulfate as compared to pyrite oxidation in more surficial environments. Thus, a greater proportion of groundwater sulfate sources, attended by lower $\delta^{18}O_{SO4}$, may be represented in the river during drought conditions as compared to normal or high flow periods. As summarized by Taylor and Wheeler, 1993[65], two reactions are typically used to describe pyrite oxidation to sulfate:

$$FeS_2 + 7/2O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (6)$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (7)$$

Where reaction (7) is rate-limited by the oxidation of Fe^{2+} by O_2 in the reaction:

$$Fe^{2+} + 1/4O_2 + H^+ \rightarrow Fe^{3+} + 1/2H_2O \quad (8)$$

In experiments[53], and in natural systems[65], it has been observed that the oxidation of pyrite under submersed and alternating wet/dry conditions results in sulfate with $\delta^{18}O_{SO4}$ that is around 2‰ to 18‰ higher than that of ambient water $\delta^{18}O_{water}$, a scenario that was used to estimate the ranges

of pyrite-derived sulfate for the Mississippi River shown in figure 3a. This $\delta^{18}O$ offset between pyrite-derived sulfate and water can tend towards a more restricted range of about 5‰ to 12‰ in neutral waters and goes towards smaller offsets (down to ~4‰) under submersed, sterile, and anaerobic conditions and larger offsets (up to ~18‰) under wet/dry, with sulfide-oxidizing bacteria present, and aerobic conditions[65]. Mississippi River sulfate during drier PHDI conditions may have an even greater proportion of oxygen from water because it is derived from pyrite preferentially oxidized under reaction (7). Alternatively, changing Mississippi River hydrologic conditions may exert a control on an expression of cryptic sulfur cycling within the basin, and thus characteristically affect $\delta^{18}O_{SO4}$ and not $\delta^{34}S_{SO4}$[56], with $\delta^{18}O_{SO4}$ possibly shifting to lower values in accordance with a changing locus of sulfide oxidation from more to less aerated environments, however the mechanisms behind cryptic sulfur cycling are still poorly understood.

$\Delta'^{17}O_{SO4}$ constraints on sulfate oxygen sources

Variations in $\Delta'^{17}O_{SO4}$ can help to differentiate sources, formation pathways, and processes affecting riverine sulfate. However, $\Delta'^{17}O_{SO4}$ in surface waters is an underdeveloped tracer, with presently only one riverine $\Delta^{17}O_{SO4}$ study available[66]. Here we note that $\Delta^{17}O$ (eq. 2) is used to describe triple oxygen isotopes in general, but we report the logarithmic form $\Delta'^{17}O$ (eq. 3). The difference between $\Delta'^{17}O$ and $\Delta^{17}O$ is very small for measurements not far from the origin, for example within error of each other for the Mississippi River sulfate data (Fig. S1). Generally, sulfate has positive $\Delta^{17}O$ values when originated as secondary atmospheric sulfate, and slightly negative values when formed via oxidation of reduced sulfur[67]. The positive $\Delta^{17}O$ range of atmospheric sulfate, 0.14‰ to 1.43‰ in northern hemisphere precipitation[68, 69], is inherited from ozone and/or hydrogen peroxide[70]. This ^{17}O-enrichment from atmospheric SO_4^{2-}

input, which is ~15% of the Mississippi River sulfate budget[3], is likely lost via replacement with oxygen from ambient water and/or air O_2 during sulfate reduction and sulfide re-oxidation within biologically active surface environments. Likewise, the sulfate generated during oxidative weathering of sulfides, such as pyrite and organic sulfur, will incorporate its oxygen from ambient water ($\Delta'^{17}O$ = −0.03 to +0.11‰ in the Northern Hemisphere[71]) and air O_2 ($\Delta'^{17}O$ = −0.47‰[47]) with effects from associated fractionation factors.

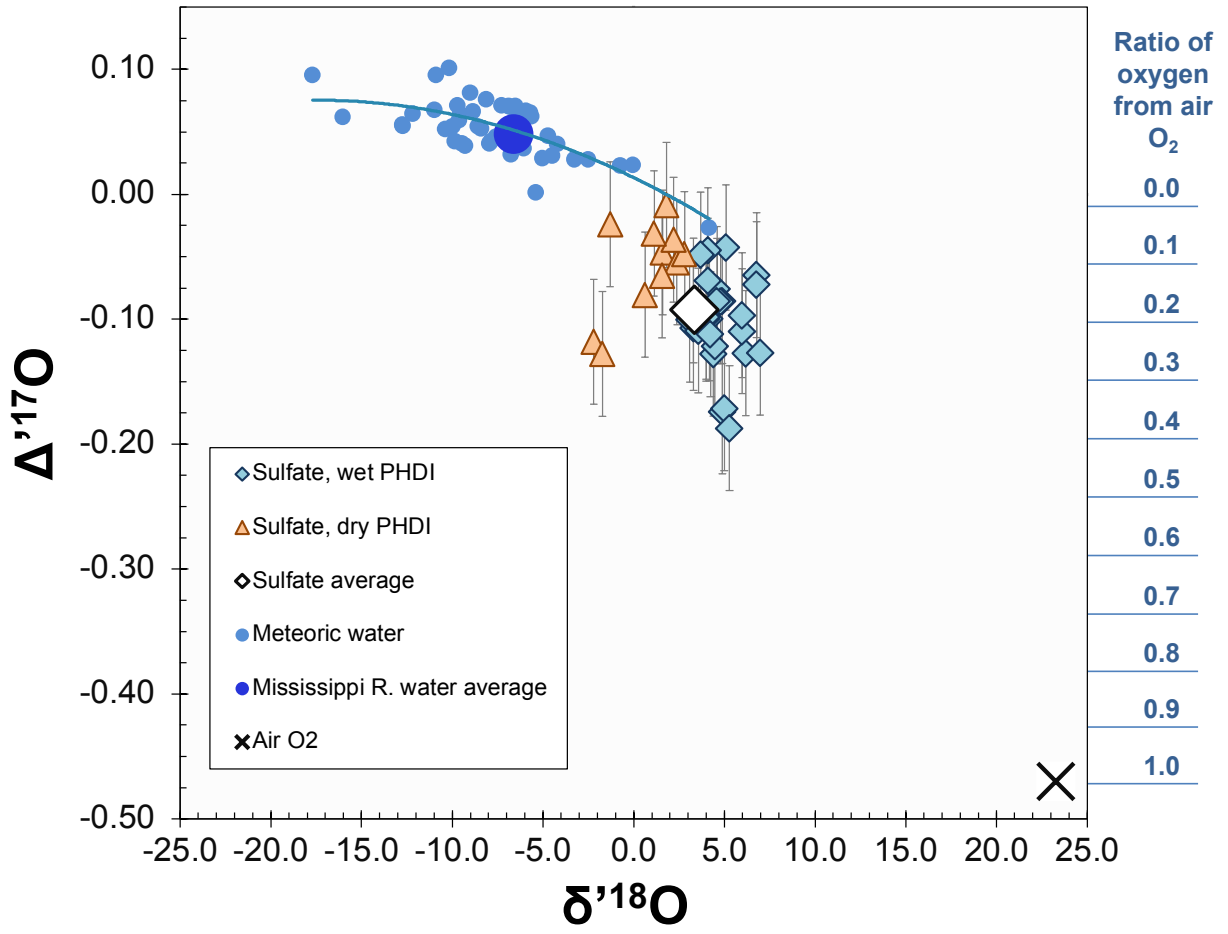


Figure 5. Plot of triple oxygen isotopes reported in ‰ VSMOW. The $\Delta'^{17}O$ uses a 0.5305 reference slope and is cross-plotted against $\delta'^{18}O$. All sulfate data are from the Mississippi River from this study and are shown with values of its potential oxygen sources meteoric water[71] and air O_2[47]. The average Mississippi River $\delta^{18}O_{water}$ is −6.6‰ from the lower Mississippi[59] and here its $\Delta'^{17}O$ is inferred. The sulfate data is divided according to wet or dry conditions in the Mississippi River basin (wet or dry PHDI). The dashed lines schematically represent possible mixing paths between Mississippi River sulfate oxygen end members, average Mississippi River

water and air O_2. The boundaries of this mixing path are based on previous work on $\delta^{18}O$ fractionations between sulfate and water and sulfate and air O_2 during pyrite oxidation[53, 65]. The location and direction of the arrows indicates starting points for mixing between oxygen end members when the fractionation factors between sulfate and water and sulfate and air O_2 are considered.

A very simplified view of the triple oxygen isotope composition of Mississippi River sulfate is linear mixing between average Mississippi River water and air O_2. It is tempting to use the $\delta^{18}O$ difference between sulfate and ambient water to assess the relative contributions of water and air O_2 oxygen to sulfate, but the evidence cautions against this. The oxidation of sulfide to sulfate involves multiple kinetic steps that can result in sulfate with a $\delta^{18}O$ value even lower than that of ambient water[48, 49, 72]. Therefore using $\delta^{18}O$ to estimate water and air O_2 oxygen contributions to sulfate may be unreliable, particularly when the sample populations are small. In the case of $\Delta'^{17}O_{SO4}$, it is less prone to the same kinetic effects observed in $\delta^{18}O_{SO4}$. The use of $\Delta'^{17}O_{SO4}$ to assess air O_2 is relevant for understanding the ancient Earth atmosphere in the geological past via sulfate in rocks[67] and thus characterizing the $\Delta'^{17}O$ tracer in modern riverine sulfates is a necessary calibration step. Under the reference frame we use for $\Delta'^{17}O$ (where the slope C = 0.5305 in eq. 3), sulfate $\Delta'^{17}O$ versus $\delta'^{18}O$ will normally show negative correlation when the oxygen sources are water and air O_2 (Fig. 5). As shown in figure 5, the oxygen isotope offset between pyrite-derived sulfate and water that was observed in $\delta^{18}O_{SO4}$ from submersed (closer to water values) and alternating wet/dry experiments (further from water values)[53] and in natural settings[65] appears to also be expressed in the added triple oxygen isotope dimension of $\Delta'^{17}O$. Previous pyrite oxidation experiments using $\Delta^{17}O$ revealed that a stoichiometric average ¼ of oxygen in pyrite-derived SO_4^{2-} came from air O_2 with the remaining ¾ oxygen coming from ambient water[49]. The triple oxygen isotope compositions of water follow a predictable array due to Rayleigh distillation[71]. We can use this meteoric water array and the relatively large $\Delta'^{17}O$

difference between it and air O_2 to our advantage and estimate if a given sulfate oxygen isotope composition has an almost entirely water oxygen source by simply checking its closeness to meteoric water in triple oxygen isotope space (Fig. 5). We assume that the highest Mississippi River $\Delta'^{17}O_{SO4}$ (−0.01‰, Fig. 5) closely represents the sulfate end member with 100% water oxygen source because its location in triple oxygen isotope space matches well with the sulfate predicted from pyrite oxidation, and its attendant oxygen sulfate-water $\delta^{18}O$ offset, with 100% water oxygen sourced from average Mississippi River water. The 100% air O_2 sulfate end member is represented by the value of modern air O_2, $\Delta'^{17}O = -0.47‰$[47]. With these Mississippi River sulfate oxygen water and air O_2 end members, a mixing equation can be constructed as follows:

$$\Delta'^{17}O_{SO4} = f_{airO2} * \Delta'^{17}O_{airO2} + (1 - f_{airO2}) * \Delta'^{17}O_{water} \quad (9)$$

Between these end members, the fraction of air O_2 in Mississippi River sulfate (f_{airO2}) is 0.18. Thus, with respect to $\Delta'^{17}O$ and including 1 standard deviation error, 18 ±9% of Mississippi River sulfate oxygen is shown to be sourced from air O_2 (Fig. S7). This result is consistent with 74% of Mississippi River sulfate being from pyrite-derived sulfate. With the assumptions that an average of 25% of oxygen from air O_2 is in pyrite-derived sulfate[49], and that all other sulfate sources sum to $\Delta'^{17}O = 0.00‰$, then 0.74*0.25 = 0.19, nearly identical, though perhaps coincidentally so, to the ratio of air O_2 oxygen in Mississippi River sulfate determined via $\Delta'^{17}O$.

Modeling the Mississippi River sulfate $\delta^{34}S$, $\delta^{18}O$, and $\Delta'^{17}O$ time series

Finally, the Mississippi River sulfate isotope time series were modeled with mixing of sulfate fluxes between three sub-basins and an input term for PHDI and respectively assigned isotope values. Twelve inputs are reduced to four variables that are further constrained with our

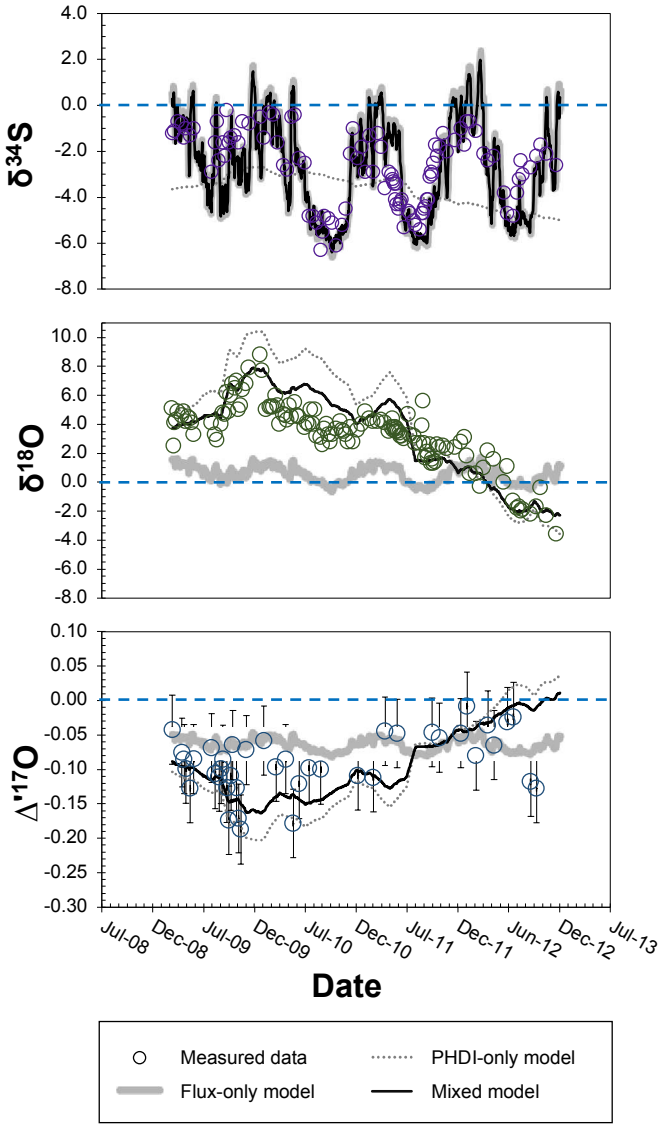
463 sulfate measurements from the Ohio River, published freshwater mussel sulfur isotopes from
464 within the Mississippi River basin, published water oxygen isotope data, and our updated
465 Mississippi River sulfate source partitioning. The mixing model is as follows:

466 $$\delta^{xx}Z_{Model} = f_{Flux}*(f_{MSR}*\delta^{xx}Z_{MSR} + f_{OR}*\delta^{xx}Z_{OR} + f_{UMR}*\delta^{xx}Z_{UMR}) + f_{PHDI}*(f_{Wet}*\delta^{xx}Z_{Wet} +$$

467 $$f_{Dry}*\delta^{xx}Z_{Dry}) \quad (10)$$

468 Here, the $\delta^{xx}Z$ refers to the isotope parameter $\delta^{34}S$, $\delta^{18}O$, or $\Delta'^{17}O$; and $\delta^{xx}Z_{Model}$ is the daily
469 modeled output for Mississippi River $\delta^{34}S_{SO4}$, $\delta^{18}O_{SO4}$, or $\Delta'^{17}O_{SO4}$ during the measured study
470 period (03/11/09 to 01/01/13). The proportion of influence from the mixing of sulfate fluxes
471 from Mississippi River sub-basins versus the continental-scale forcing due to overall
472 hydrological conditions is balanced between f_{Flux} and f_{PHDI}, where $f_{PHDI} = 1 - f_{Flux}$. For the mix of
473 sub-basin sulfate fluxes, f_{MSR}, f_{OR}, and f_{UMR} are the respective sulfate flux ratios and $\delta^{xx}Z_{MSR,}$
474 $\delta^{xx}Z_{OR,}$ and $\delta^{xx}Z_{UMR}$ are the respective isotope values ($\delta^{34}S_{SO4}$, $\delta^{18}O_{SO4}$, or $\Delta'^{17}O_{SO4}$) for the
475 Missouri, Ohio, and Upper Mississippi river sub-basins of the Mississippi River. The sub-basin
476 fluxes were determined by taking daily water discharge data and matching them with sulfate
477 concentrations that were interpolated, from measurements taken approximately monthly, to give
478 daily values. Then, the ratios for sub-basin sulfate fluxes were each sub-basin's sulfate flux
479 versus their combined sum, here using the mix of sulfate flux between three sub-basins to
480 represent the whole Mississippi River. The difference in sulfate flux between the averages
481 determined from the lower Mississippi River and the summed three sub-basins was 6% during
482 the study period, and thus the flux contribution from the middle Mississippi River is neglected in
483 the model. The influence of hydrological conditions represented by the Palmer Hydrological
484 Drought Index is split into "wet" and "dry" components in order to assign different respective
485 "wet" and "dry" isotope values ($\delta^{xx}Z_{Wet}$ and $\delta^{xx}Z_{Dry}$). The PHDI f_{Wet} and f_{Dry} components use

reported monthly PHDI interpolated to give daily PHDI, which is then scaled to make a ratio where maximum dry PHDI during the study period is equal to 1, and wet PHDI is the difference, where $f_{Wet} = 1 - f_{Dry}$. The model input variables are then $\delta^{xx}Z_{MSR,}$ $\delta^{xx}Z_{OR,}$ $\delta^{xx}Z_{UMR}$ and f_{Flux}. The input values are explored for feasible Mississippi River $\delta^{34}S_{SO4}$, $\delta^{18}O_{SO4}$, or $\Delta'^{17}O_{SO4}$ by testing for the average of sum daily modeled outputs against the average of sum measured values, the correlation between daily model outputs and measured values, and good agreement between the curves of measured and modeled time series data. The best-fitting model outputs are shown in figure 6 and the global values for model parameters are in the supporting information (Table S4). The Mississippi River $\delta^{34}S_{SO4}$ time series model is feasible if the Ohio River has higher $\delta^{34}S_{SO4}$ than the Missouri River and it is almost entirely controlled by their balance of sulfate flux input as compared to influence from basinwide wetter or drier conditions, as modeled via PHDI. Mississippi River $\delta^{18}O_{SO4}$ is described well in our model with our estimated contribution of 74% pyrite-derived sulfate dominating sulfate flux and thus resulting in $\delta^{18}O_{SO4}$ that is dominated by a water oxygen source best represented by the average ambient Mississippi River river water $\delta^{18}O$ and a changing oxidation pathway that can be simulated by the PHDI term in the model, whereas only 26% of the Mississippi River $\delta^{18}O_{SO4}$ is due to the balance of sulfate fluxes from the three sub-basins used in the model. The Mississippi River $\Delta'^{17}O_{SO4}$ modeling follows the same forcings as $\delta^{18}O_{SO4}$ but there is an additional transient component in the real data which our model is unable to recreate.



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507 **Figure 6.** Time series of modeled Mississippi River $\delta^{34}S_{SO4}$, $\delta^{18}O_{SO4}$, and $\Delta'^{17}O_{SO4}$ are shown
508 with measured data. Measured data error bars are shown or are smaller than symbols. The flux-
509 only model uses a mix of sulfate flux from three Mississippi River sub-basins, the PHDI-only
510 model simulates forcing from overall hydrological conditions for the contiguous United States,
511 and the mixed model incorporates both flux-only and PHDI-only models with further details and
512 discussion given in the main text.
513
514

515 **Implications for riverine sulfate**

516 Mississippi River $\Delta'^{17}O_{SO4}$, $\delta^{18}O_{SO4}$, and $\delta^{34}S_{SO4}$ each reveal their own different

517 perspectives on the Mississippi River system and its response to seasonal changes or year-to-year

weather patterns. Although our Mississippi River study reveals characteristics of riverine sulfate that might be widespread, each river should be considered as a more-or-less unique case, with its own set of processes and sulfur sources dictated by climate, hydrology, and geology. Moreover, in other rivers, anthropogenic influence on sulfate may be expressed by isotopic shifts in the opposite direction, to lower $\delta^{34}S_{SO4}$ for example, as compared to what is inferred from the Mississippi River. Although not done for this study, measurement of the triple oxygen isotope composition ($\delta^{18}O$ and $\Delta'^{17}O$) of not only the dissolved sulfate, but also the river water from the same sample, could enable high resolution sulfate oxygen isotope mass balance calculations, further assist in tracing river water sources such as runoff versus groundwater, and aid interpretations of the sources of sulfate oxygen and sulfate oxidation pathways. Prime targets for follow-up sulfate sulfur and oxygen isotope studies would be the Missouri and Ohio river sub-basins to characterize the loadings of pyrite-derived sulfate from natural and anthropogenic bedrock weathering and mine drainage. Our results add to the calls for reassessing the contribution of pyrite-derived sulfate to global sulfur budgets[9], especially pyrite-derived sulfate from coal mining[15], and suggest that the important estimates of natural and anthropogenic global riverine sulfate flux[5, 73] are due for an update.

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Supporting Information Available

Supporting Information includes additional details on methods, modeling, oxygen isotope discussion, and tables of sulfate isotope data, an updated Mississippi River sulfate budget, and model inputs.

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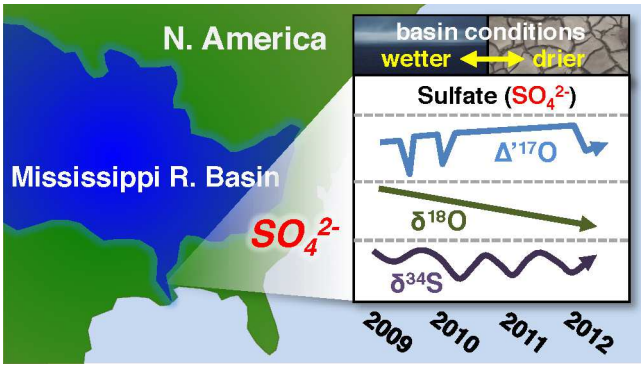
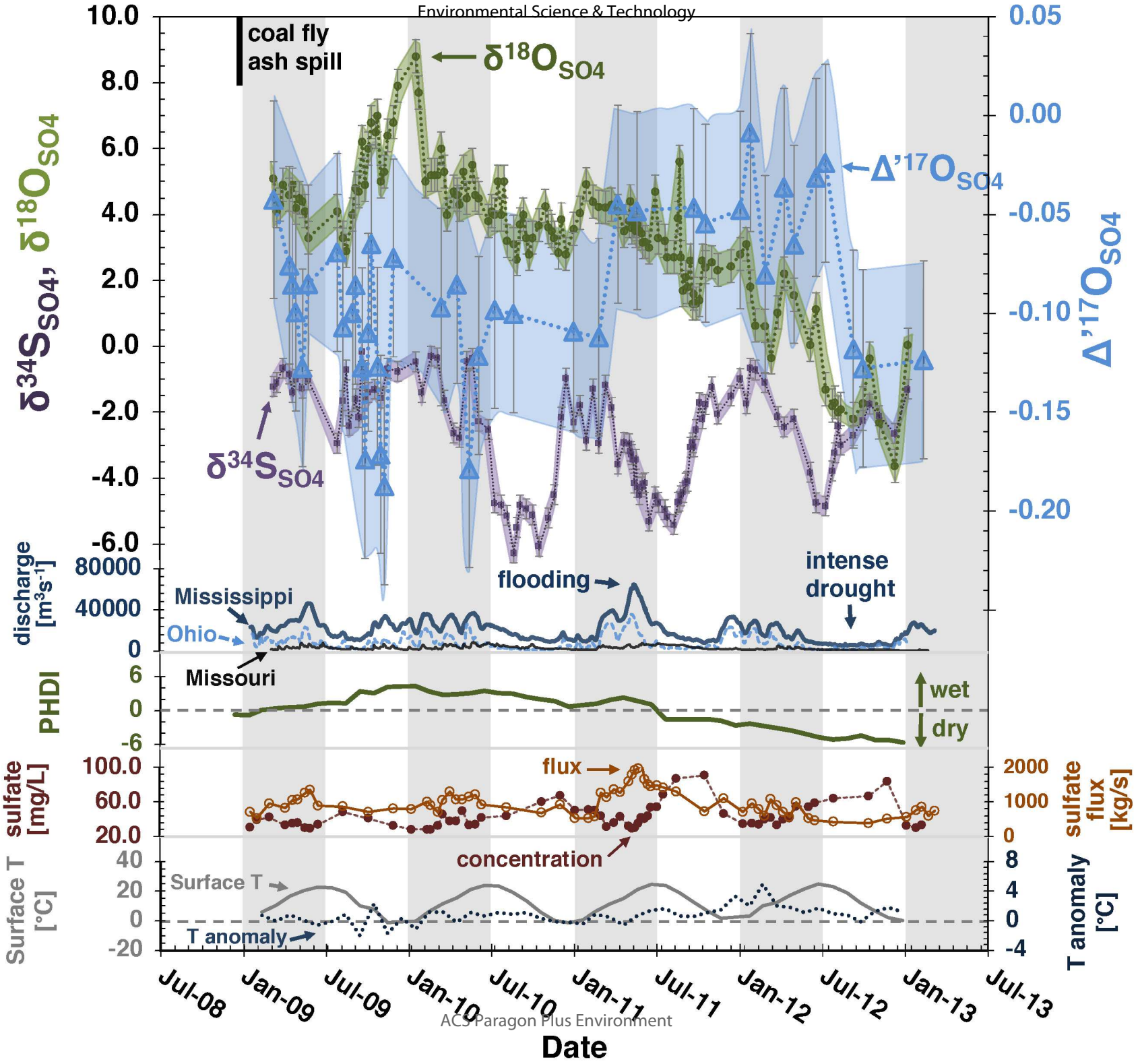
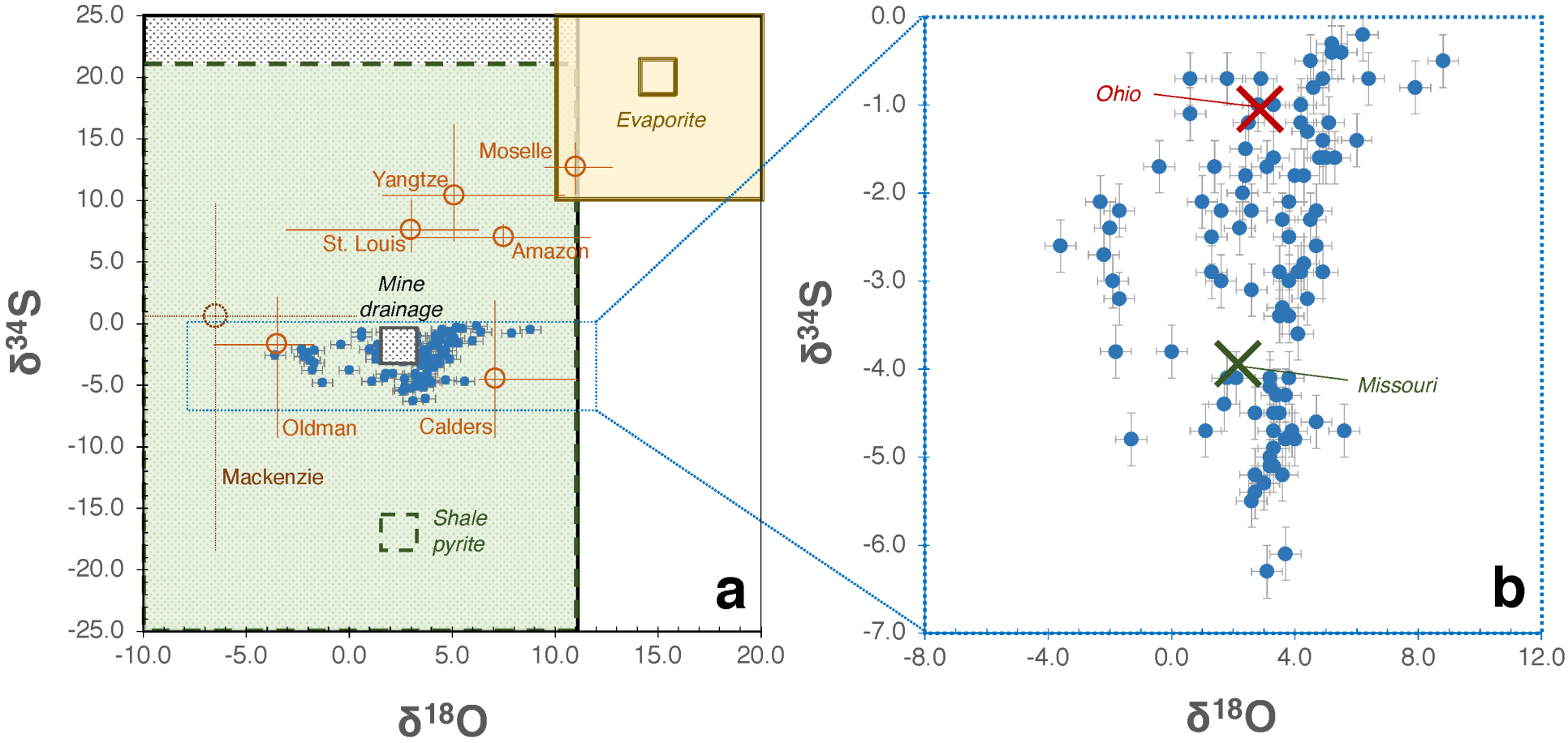
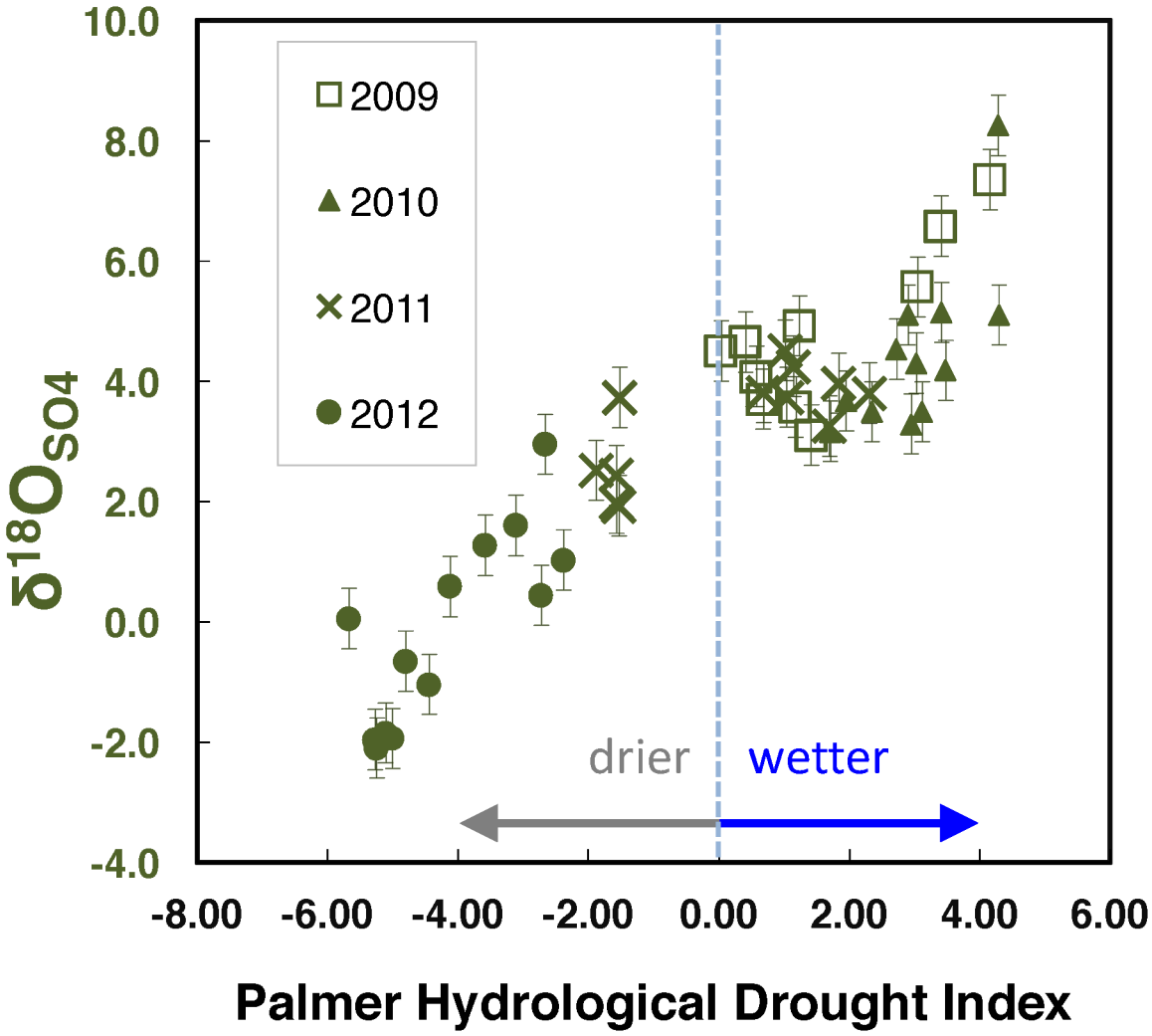
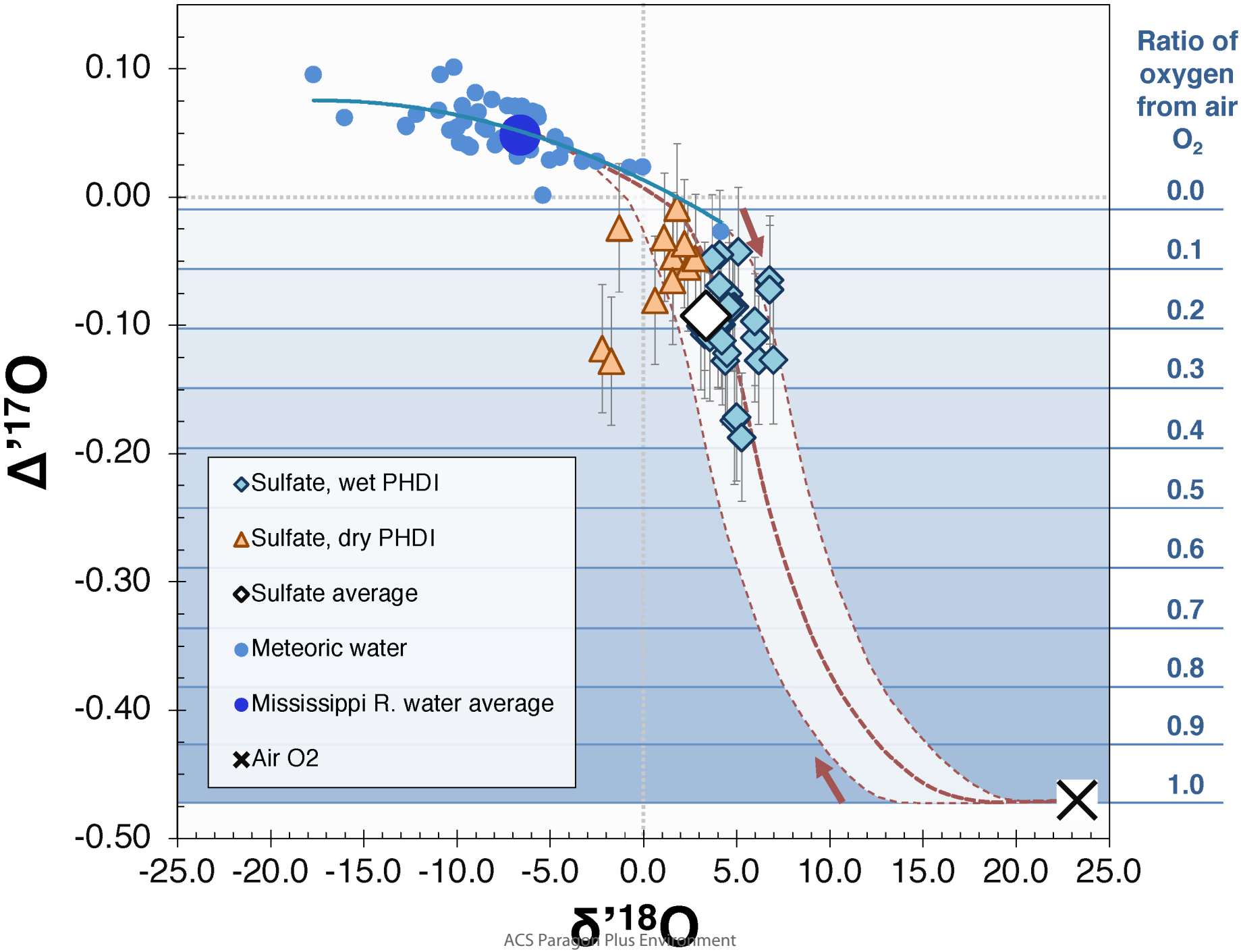

N. America
Mississippi R. Basin
SO_4^{2-}
basin conditions
wetter
drier
Sulfate (SO_4^{2-})
$\Delta'^{17}O$
$\delta^{18}O$
$\delta^{34}S$
2009
2010
2011
2012

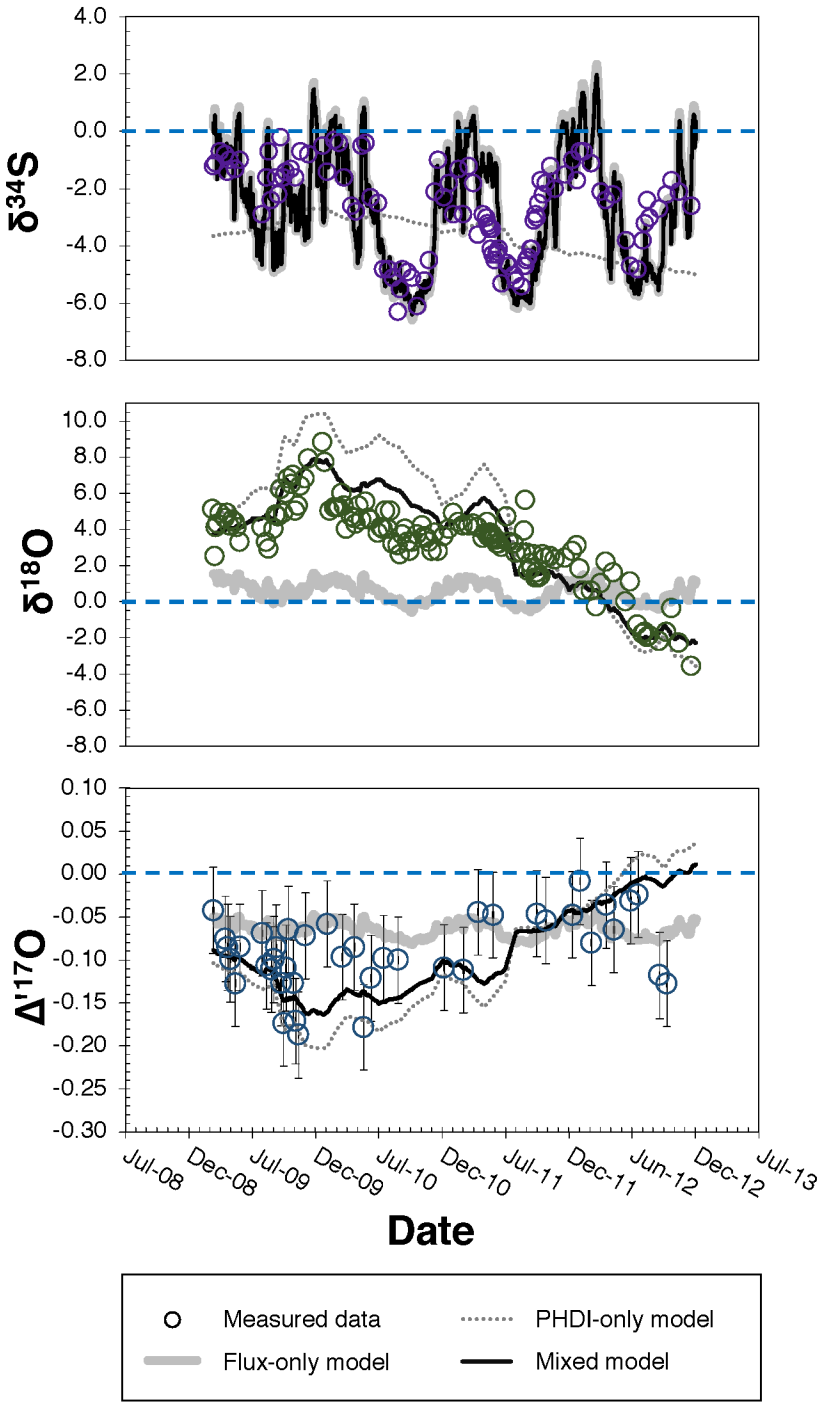

Missouri R.
Upper Mississippi R.
Ohio R.
Baton Rouge


coal fly ash spill
δ18OSO4
Δ'17OSO4
δ34SSO4
δ34SSO4, δ18OSO4
Δ'17OSO4
10.0
8.0
6.0
4.0
2.0
0.0
-2.0
-4.0
-6.0
0.05
0.00
-0.05
-0.10
-0.15
-0.20
discharge [m3s-1]
80000
40000
0
Mississippi
Ohio
Missouri
flooding
intense drought
PHDI
6
0
-6
wet
dry
sulfate [mg/L]
100.0
60.0
20.0
flux
concentration
2000
1000
0
sulfate flux [kg/s]
Surface T [°C]
40
20
0
-20
Surface T
T anomaly
8
4
0
-4
T anomaly [°C]
Jul-08
Jan-09
Jul-09
Jan-10
Jul-10
Jan-11
Jul-11
Jan-12
Jul-12
Jan-13
Jul-13
Date


δ34S
δ18O
25.0
20.0
15.0
10.0
5.0
0.0
-5.0
-10.0
-15.0
-20.0
-25.0
-10.0
-5.0
0.0
5.0
10.0
15.0
20.0
Evaporite
Moselle
Yangtze
St. Louis
Amazon
Mine
drainage
Oldman
Calders
Mackenzie
Shale
pyrite
a
δ34S
δ18O
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-4.0
0.0
4.0
8.0
12.0
Ohio
Missouri
b


10.0
8.0
6.0
4.0
2.0
0.0
-2.0
-4.0
δ18OSO4
2009
2010
2011
2012
drier
wetter
-8.00
-6.00
-4.00
-2.00
0.00
2.00
4.00
6.00
Palmer Hydrological Drought Index


Δ'17O
δ'18O
0.10
0.00
-0.10
-0.20
-0.30
-0.40
-0.50
-25.0
-20.0
-15.0
-10.0
-5.0
0.0
5.0
10.0
15.0
20.0
25.0
Ratio of oxygen from air O2
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
Sulfate, wet PHDI
Sulfate, dry PHDI
Sulfate average
Meteoric water
Mississippi R. water average
Air O2


δ34S
4.0
2.0
0.0
-2.0
-4.0
-6.0
-8.0
δ18O
10.0
8.0
6.0
4.0
2.0
0.0
-2.0
-4.0
-6.0
-8.0
Δ'17O
0.10
0.05
0.00
-0.05
-0.10
-0.15
-0.20
-0.25
-0.30
Jul-08
Dec-08
Jul-09
Dec-09
Jul-10
Dec-10
Jul-11
Dec-11
Jun-12
Dec-12
Jul-13
Date
Measured data
PHDI-only model
Flux-only model
Mixed model