Radiogenic fingerprinting reveals anthropogenic and buffering controls on sediment dynamics of the Mississippi River system

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ABSTRACT
Radiogenic isotopes of strontium (87Sr/86Sr) and neodymium (143Nd/144Nd) are widely used to trace sediment across source-to-sink networks, with samples typically collected from outcrops at basin headwaters and from sediments along the channel margin, floodplain, and/or seafloor. Here, we established the Sr-Nd isotope systematics of recent (in the past 1 k.y.) Mississippi River (USA) basin alluvial sediments, evaluated the sensitivity of these isotope systems to the presence of artificial impoundments that trap sediments behind them, and tested their ability to provenance mixed sedimentary records. Sediment cores collected from floodplain depressions and oxbow lakes along the Mississippi River and its major tributaries, where an extensive lock and dam system was constructed during the mid–twentieth century, show that the isotopic signatures of major tributaries are distinct, and that some of these signatures shift following dam closure. We then used mixing models to demonstrate that, near the confluence of major tributaries, Sr and Nd isotope signatures can be used to ascertain provenance of sediments deposited in floodplain lakes during overbank floods. Further downstream, where sediments are well mixed, the provenance of overbank deposits is more challenging to evaluate using Sr-Nd isotope systematics. Given the global pervasiveness of artificial impoundments on rivers, our findings imply that widely employed sediment fingerprinting techniques based on modern conditions may not be representative of conditions from as recently as a century ago.

INTRODUCTION
Sediment transport from source to sink is a fundamental process that shapes landscapes and the geological record (Allen, 2008). Radiogenic isotopes of strontium and neodymium are widely used as sediment tracers to identify source area and patterns of erosion and deposition within and across drainage networks (e.g., McLennan et al., 1989; Clift et al., 2008; Padoan et al., 2011). Basinwide systematics of Sr and Nd isotopes are typically evaluated by collecting samples from outcrops at basin headwaters (i.e., source rocks), along channel margins, from the floodplain surface, and/or in offshore areas (i.e., mixed sediments). Over the past century, artificial impoundments that trap sediments have been built on many of the world’s major rivers and their tributaries, profoundly altering the downstream delivery of sediments (Syvitski et al., 2005). The potential for these artificial impoundments to influence Sr and Nd isotope systematics has previously been recognized (e.g., Padoan et al., 2011), but, to our knowledge, the magnitude of this influence has yet to be evaluated.

Here, we examined the Sr and Nd isotope systematics for the Mississippi River system, USA (Fig. 1). The Mississippi River is the largest river in North America and one of the world’s most heavily engineered drainage networks (Knox, 2007), where dams constructed primarily during the mid–twentieth century on the Missouri, Upper Mississippi, and Ohio Rivers (Fig. DR1 in the GSA Data Repository1) have reduced average annual sediment fluxes to the Gulf of Mexico by 50%–70% (Horowitz, 2010). We measured isotopes of Sr and Nd on sediment samples collected from the floodplains of the Missouri, Upper Mississippi, and Ohio Rivers to evaluate the isotopic variation among the major tributaries of the Mississippi River system before and after dam closure. Using these data, we constructed Bayesian mixing models (Parnell et al., 2013) to evaluate the provenance of flood deposits preserved in oxbow lakes previously used in paleoflood reconstructions of the Upper Mississippi (Munoz et al., 2015) and Lower Mississippi Rivers (Munoz et al., 2018). Together, our analyses established Sr-Nd isotope systematics for the largest drainage network in North America, tested their ability to establish provenance in mixed sedimentary records, and allowed us to evaluate the sensitivity of these radiogenic tracers to artificial impoundments.

MATERIALS AND METHODS
We collected sediment cores (in October 2016, using a gouge auger) from three infilling depressions in the floodplains of the Missouri River (38.664869°N, 90.702690°W; core length: 97 cm), Upper Mississippi River (39.112535°N, 90.695270°W; core length: 137 cm), and Ohio River (37.166491°N, 89.064583°W; core length: 96 cm) that are periodically inundated by floodwaters and are downstream of most dams (Fig. 1; Fig. DR2). To establish chronological control on these cores, we measured 10Be activity on bulk sediment samples at 5 cm resolution on the upper 60 cm of each core in a Canberra GL2020RS well detector for low-energy germanium radiation (Fig. DR3). We


1GSA Data Repository item 2019097, supplemental data tables (Tables DR1 and DR2) and figures (Figures DR1–DR4), is available online at http://www.geosociety.org/datarepository/2019/, or on request from editing@geosociety.org.

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collected five to seven samples from each core that were stratigraphically >20 cm below the base of 137Cs activity (i.e., A.D. 1954) and above the peak of 137Cs activity (i.e., A.D. 1963) to represent the depositional environment before and after the closing of the majority of artificial impoundments on the Mississippi River system (Fig. DR1). To test the significance of difference between pre- and post-dam samples, we used Welch’s t-test implemented in RStudio v.1.1.423 software (https://www.rstudio.com/products/rstudio/) (t.test function).

To minimize grain-size and hydraulic sorting effects, the <63 µm filtrate was used for grain-size and isotopic analysis. For grain-size analysis, organics were removed by incineration at 360 °C in a muffle furnace, and then the sample was dispersed in water before 5 s of sonication and analysis in a Beckman Coulter LS 13 320 laser diffraction particle-size analyzer. Nd and Sr isotopic analysis was performed with conventional ion chromatography. Strontium was separated and purified from samples using Sr-Spec (Eichrom) resin. Nd chemistry was measured with LN resin (Eichrom) following the method described by Scher and Delaney (2010). Sr and Nd analyses were conducted on a NEPTUNE multicollector–inductively coupled plasma–mass spectrometer (MC-ICP-MS) with internal precision of ~10–20 ppm (2σ). The 143Nd/144Nd and 87Sr/86Sr ratios for unknowns were normalized by the offset between our average measured value of the Nd La Jolla reference standard and the Sr NBS987 standard during the analytical session and the preferred 143Nd/144Nd value of 0.511847 (White and Patchett, 1984) and 87Sr/86Sr value of 0.710240 (Jackson and Hart, 2006), and external precision is estimated to be 15–25 ppm (2σ). The 143Nd/144Nd Nd isotopic composition is expressed further as εNd (DePaolo and Wasserburg, 1976) units relative to (143Nd/144Nd)CHUR = 0.512638 (CHUR—chondritic uniform reservoir). We tested the influence of grain size on Nd and Sr isotopes (McLennan et al., 1989) using regression to find a significant linear relationship between εNd and the mode of grain size in Missouri River and oxbow lake samples (R² = 0.7711, p < 0.001), but not in the other tributaries (Fig. DR4) nor between grain size and 86Sr/88Sr ratios. We thus used linear regression to normalize εNd of Missouri River and oxbow lake samples to the pooled mode of grain-size measurements (Table DR1).

To compare the isotopic composition of the mixed sediments collected as part of this study with that of the source rocks that underlie the Mississippi River basin, we extracted the Sr and Nd isotope measurements within 500 km of the basin (n = 1356) from the GEOROC database (http://georoc.mpch-mainz.gwdg.de/georoc/; Sarbas and Nohl, 2008). To evaluate the potential of Sr-Nd isotopes to provenance sedimentary paleoflood records, we collected two samples from previously dated cores at Horseshoe Lake, Illinois (HRM), ~20 km below the confluence of the Mississippi and Missouri Rivers (Munoz et al., 2015), and four samples from Lake Mary, Missouri (MRY), ~1000 km below the confluence of the Ohio and Mississippi Rivers (Munoz et al., 2018), and performed grain-size and isotope analysis on these samples using the same approach as described above (Fig. 1). Chronologies of these oxbow paleoflood records were developed using a Bayesian age model informed by 137Cs, 210Pb, 14C, optically stimulated luminescence (OSL), and stratigraphic markers; additional details of their age models can be found in their original publications (Munoz et al., 2015, 2018). At HRM, one sample came from a fine-grained deposit dated to A.D. 1160 ± 90 yr (reported as median age ± 2σ confidence interval), interpreted by Munoz et al. (2014) as the suspended load from a large Mississippi River flood event, and one sample came from the same core, dated to A.D. 1450 ± 160 yr, that was not associated with a flood. At MRY, we collected samples of fine-grained sediment immediately overlying prominent flood deposits dated to A.D. 1917 ± 13 yr, 1934 ± 12 yr, 2011 ± 7 yr, and 2014 ± 6 yr, interpreted by Munoz et al. (2018) to represent major historic floods in A.D. 1927, 1937, 2011, and 2016, respectively. To evaluate the provenance of the oxbow lake sediments, we constructed Bayesian mixing models using the simmr package (https:// cran.r-project.org/web/packages/simmr/index.html; Parnell et al., 2013) in RStudio using pre- and post-dam means and standard deviations for each contributing tributary as end members.

RESULTS AND DISCUSSION

**Mississippi River Sr-Nd Isotope Systematics**

Sediment Sr and Nd isotopic compositions from Mississippi River system floodplains exhibit a wide range of values that group into three distinct clusters, where these differences are associated with the major tributaries of the Missouri, Upper Mississippi, and Ohio Rivers (Fig. 2). The εNd values and 86Sr/88Sr ratios of all floodplain sediments range from –14.75 to –11.55 and 0.716688–0.729936, respectively. Floodplain samples from the tributaries are highly differentiated over the 86Sr/88Sr range, with the lowest values for the Missouri River (mean, 3 = 0.717807, standard deviation, σ = 0.000095) and the highest values for the Ohio River (3 = 0.728123, σ = 0.000062) and no overlap among the three tributaries sampled. Over the range of εNd values, samples from the Missouri and Upper Mississippi exhibit high variability (range 1.73 and 1.95, respectively), with less variability in samples from the Ohio River (range of 0.98). All of the floodplain samples fall within the εNd range for the Archean shield and Paleoproterozoic orogens that were incorporated into Paleozoic-age through Cenozoic-age marine and terrestrial sedimentary rocks covering much of the Mississippi basin (Peucker-Ehrenbrink et al., 2010).

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Figure 1. Mississippi River system (North America) and geological provinces of its basin showing locations of tributary floodplain sediment samples collected for this study, oxbow lake sediment samples (Munoz et al., 2015, 2018), and artificial impoundments (dams on Missouri River; lock and dam structures on Upper Mississippi and Ohio Rivers). More detailed maps of floodplain sediment sampling locations are available in Figure DR2 (see footnote 1).

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In contrast to Nd, strong radiogenic Sr enrichment is evident in Mississippi River basin sediments relative to source rocks (Fig. 2A). For the Sr system, older sedimentary cover exhibits higher \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios relative to source rock composition (e.g., Peucker-Ehrenbrink et al., 2010). Incongruent weathering of source rocks is the primary factor leading to this enrichment, because it elevates \(^{87}\text{Sr}/^{86}\text{Sr}\) and favors ingrowth of radiogenic \(^{87}\text{Sr}/^{86}\text{Sr}\) in the resulting sedimentary rocks; this effect is enhanced when sedimentary rocks are recycled multiple times (e.g., Taylor et al., 1983). Sedimentary carbonates are rich in Sr and less radiogenic than siliciclastic rocks, but they are roughly evenly distributed across all three basins examined (King et al., 1974). In comparison to Missouri River sediments, the lower \(\epsilon_{\text{Nd}}\) and enriched \(^{87}\text{Sr}/^{86}\text{Sr}\) values of Upper Mississippi River sediments likely reflect erosion of glacial till and loess originating from the Precambrian Canadian Shield (e.g., Peucker-Ehrenbrink et al., 2010). The lack of radiogenic enrichment for Nd but high \(^{87}\text{Sr}/^{86}\text{Sr}\) ratio for Ohio River sediments suggest instead erosional inputs from old unglaciated sedimentary rocks outcropping in this subbasin (e.g., Oh and Raymond, 2006). In short, the three major tributaries of the Mississippi River system exhibit distinct Sr-Nd isotopic signatures as a result of differences in underlying parent rock material, sedimentary cover, and weathering rates in each basin.

Floodplain sediments deposited prior to and after the closure of artificial impoundments sometimes exhibit significant differences in their isotopic composition (Fig. 2B). On the Missouri and Upper Mississippi Rivers, \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios increase from pre- to post-dam samples, with significant shifts \((p < 0.05; \text{unpaired } t\text{-tests})\) in their means (Table DR2). This enrichment of radiogenic Sr may be related to sorting of the sediment load by dams, which keep lighter radiogenic minerals (e.g., muscovite) suspended but trap the less radiogenic heavier fraction (Garçon et al., 2014). Alternatively, these shifts in the isotopic compositions of Missouri and Upper Mississippi River sediments may be due to trapping of sediments from the upper reaches of their basins behind dams (Meade and Moody, 2010), assuming these regions provide less radiogenic Sr. Sediments from the Ohio River, in contrast, do not exhibit a significant shift in either the \(^{87}\text{Sr}/^{86}\text{Sr}\) ratio or \(\epsilon_{\text{Nd}}\) values \((p > 0.1)\). The insensitivity of Ohio River sediments to the establishment of dams may reflect the placement of the lock and dam system on that tributary relative to the glaciated and unglaciated erodible lithologies. Overall, our data demonstrate that the isotopic composition of sediments transported by the Mississippi River system has shifted markedly over the past century, implying that dams can alter isotope systematics of a continental drainage network.

### Provenance of Mixed Sediments

The isotopic compositions of sediments deposited in floodplain lakes below the confluence of major tributaries reflect both sediment provenance and the degree of mixing (Fig. 3). The Missouri River is the dominant source of suspended sediment to the Lower Mississippi River (Knox, 2007), and this is reflected in the isotopic signatures of sediments in oxbow lakes, which tend to have large contributions from the Missouri River. In sediments from HRM, situated on the Upper Mississippi River, a prehistoric deposit that was interpreted by Munoz et al. (2014) to be the result of an overbank flood is composed primarily of Missouri River sediment \((\bar{x} = 80\%, \sigma = 10\%; \text{Fig. 3A})\). Background sediment deposited in HRM, in contrast, is more similar in composition to material from the Upper Mississippi River \((\bar{x} = 71\%, \sigma = 13\%; \text{Fig. 3B})\), confirming the extralocal provenance of the presumed flood deposit in HRM as hypothesized by Munoz et al. (2014, 2015). Further downstream, sediments in MRY associated with the 1937 and 2011 floods are also

**Figure 2.** \(\text{Sr} \left( ^{87}\text{Sr}/^{86}\text{Sr} \right)\) and Nd \(\left( \epsilon_{\text{Nd}} \right)\) radiogenic isotopes of parent material and sediments of Mississippi River system. A: Envelopes \(\left( \text{"loops" of bag plots} \right)\) of samples from source rocks surrounding Mississippi River basin (Sarbas and Nohl, 2008) and fluvial sediment samples collected in this study. B: Detail of fluvial sediments identifying floodplain samples by tributary and timing \(\left( \text{i.e., pre- or post-dam} \right)\), and oxbow lake samples by site and age. HRM—Horseshoe Lake, Illinois, USA; MRY—Lake Mary, Mississippi, USA.

**Figure 3.** Density plots describing proportion of floodplain lake sample contributed by each tributary derived from Bayesian mixing model \textit{simmr} (Parnell et al., 2013). A: A.D. 1160 flood in Horseshoe Lake, Illinois, USA (HRM). B: A.D. 1450 background in HRM. C: A.D. 1937 flood in Lake Mary, Mississippi, USA (MRY). D: A.D. 2011 flood in MRY.
composed primarily (~60%) of Missouri River sediments, with moderate contributions from the Upper Mississippi (~25%) and Ohio Rivers (~15%), and only minor compositional differences between the two events (Figs. 3C and 3D). The 1937 and 2011 floods rank among the largest historical floods by discharge on the Lower Mississippi River, but these events differed in their hydrometeorological properties. The 2011 flood was triggered by large spring rainstorms over the lowermost part of the basin, while the 1937 event was a winter flood caused by rainfall falling primarily over the Ohio River basin (Smith and Baebaek, 2015). Given the differences in water source between the 1937 and 2011 floods, we expected the 1937 event to have a larger contribution from the Ohio River, but mixing models demonstrate that the sediments deposited by these two events are compositionally indistinguishable (Figs. 3C and 3D). The compositional homogeneity of all Lower Mississippi River sediments (Table DR1) likely reflects buffering (i.e., mixing and reworking of sediments) along the Lower Mississippi alluvial plain constructed with sediment shed from the continental interior during the Cenozoic (Knox, 2007). These findings imply that isotope systems in sediments are most useful to ascertain provenance of fluvial deposits when geological contrasts are not overwhelmed by buffering (e.g., near a tributary with distinctive sediment geochemistry).

CONCLUSIONS
Sediments of the three major tributaries of the Mississippi River system—the Missouri, Upper Mississippi, and Ohio Rivers—exhibit strong contrasts in their Sr-Nd isotopic signatures as a result of their underlying geology. Dam closure can significantly affect this isotopic composition via selective trapping and/or sorting of the sediment load. These isotopes can also establish provenance for recent (in the past 1 k.y.) mixed sediments deposited in floodplain lakes, but they are sensitive to alluvial plain buffering, which increases downstream from confluences of major tributaries. The data and analyses presented in this study will be useful for establishing the dynamics of erosion and sedimentation for the largest river system in North America, and they have implications for similar studies on other large regulated rivers—including the Nile, Yellow, and Indus Rivers—with sharply reduced sediment loads as a result of dams. Our findings imply that dams act as valves that regulate tributary contributions to the main stem, and they can generate measurable shifts in sediment provenance. These findings indicate that widely employed sediment fingerprinting techniques for current conditions may not be representative of past conditions as recently as a century ago.

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