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Key Points:
- Dam reservoirs and oxbow lake cores integrate land use change
- Farming and dams have altered the downstream particle composition
- Organic carbon export is controlled by physical erosion rates

Supporting Information:
- Figure S1

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Paleoreconstruction of organic carbon inputs to an oxbow lake in the Mississippi River watershed: Effects of dam construction and land use change on regional inputs

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Abstract We use a dated sediment core from Lake Whittington (USA) in the lower Mississippi River to reconstruct linkages in the carbon cycling and fluvial sediment dynamics over the past 80 years. Organic carbon (OC) sources were characterized using bulk (δ^{13}C, ramped pyrolysis-oxidation (PyrOx) ^{14}C, δ^{15}N, and TN:OC ratios) and compound-specific (lignin phenols and fatty acids, including δ^{13}C and ^{14}C of the fatty acids) analyses. Damming of the Missouri River in the 1950s, other hydrological modifications to the river, and soil conservation measures resulted in reduced net OC export, in spite of increasing OC concentrations. Decreasing δ^{13}C values coincided with increases in δ^{15}N, TN:OC ratios, long-chain fatty acids, and lignin-phenol concentrations, suggesting increased inputs of soil-derived OC dominated by C_3 vegetation, mainly resulting from changes in farming practices and crop distribution. However, ramped PyrOx ^{14}C showed no discernible differences downcore in thermochemical stability, indicating a limited impact on soil OC turnover.

1. Introduction

Approximately 87% of Earth's land surface is connected to the ocean by rivers [*Ludwig and Probst*, 1998]. The world's 25 largest rivers drain approximately half of the continental surface and transport approximately 50% of the fresh water and 40% of the particulate materials entering the ocean [*Milliman and Meade*, 1983; *Meade*, 1996]. However, the Anthropocene, during which agricultural and industrial revolutions have allowed a greatly increased human population, has resulted in many alterations to these connections between land and sea. For example, there are now over 48,000 registered dams with heights greater than 15 m worldwide; this is an order of magnitude greater than the number in 1950 [*World Commission on Dams*, 2000] and does not include the numerous smaller farm ponds and smaller dams. Dam construction in the past 50 years has increased the volume of water retained within river catchments by about 600 to 700%, which has tripled the basin residence time for a water molecule to be transported down the alluvial valley to the sea [*Vörösmarty et al.*, 2009]. Large dam reservoirs have an estimated sediment trapping efficiency of about 80% [*Syvitski and Milliman*, 2007; *Milliman et al.*, 2008] creating potential records of land use change and carbon biogeochemistry in the catchments behind them.

There have been very few efforts, to our knowledge, that have utilized sediment records in reservoirs to reconstruct past changes in sediment and carbon dynamics as it relates to regional land use and climate change [*Woodbridge et al.*, 2014]. We posit here that both natural (e.g., oxbow lakes) and human-made reservoirs (e.g., hydroelectric) should provide excellent repositories for the paleoreconstruction of how changes to large watersheds have affected the sources and composition of sediments and organic carbon in large river systems in the Anthropocene.

Prior to 1900 the Missouri-Mississippi River system was estimated to have transported ~400 Tg yr^{-1} of sediment from the central U.S to the Gulf coast of Louisiana, decreasing in recent decades to an average of ~145 Tg yr^{-1} [*Meade and Moody*, 2010] or less [*Allison et al.*, 2012]. The largest contributor to this reduction is the extensive damming in the suspended sediment-rich regions of the Missouri and Arkansas Rivers, with the largest dams constructed in the 1940s and 1950s [*Meade*, 2004]. Other land use changes, such as irrigation networks, lock and dam low-flow navigation control (on the Upper Mississippi, Ohio, and Arkansas tributaries), flood control structures, channel-confining jetties, bank stabilization, and soil conservation measures, have most likely contributed to this dramatic reduction of sediment delivery to the Gulf of Mexico [*Meade*, 2004; *Knox*, 2008]. Moreover, efforts of stabilizing channel structures downstream can work in the opposite direction by increasing sediment throughput and speed at which both suspended and large particulate carbon (e.g., bed load) move through the system, in both the Missouri and Mississippi Rivers. These changes have dramatically altered the riparian landscapes, hydrology, and the overall fluvial transport of sediment from the northern Great Plains to the Gulf of Mexico [*Keown et al.*, 1986; *Kesel*, 2003; *Harmar et al.*, 2005].

Here we use a well-dated sediment core from Lake Whittington, an oxbow lake in the Mississippi River watershed (south of the major confluences) to reconstruct past linkages in carbon cycling and fluvial sediment dynamics with regional land use and climate changes. The location of Lake Whittington captures flow and sediment transport from almost all of the Mississippi River basin, including the Missouri and Ohio River basins, and thus represents integrated fluvial sediment chemistry from ~41% of the continental U.S. Our main objectives, using a state-of-the-art multiproxy approach applied to a core with changing sediment loading over time, were to determine the following: (1) if there has been an increase in the amount of C_3 versus C_4 carbon sources over the past 50 to 80 years transported to regions of the Lower Mississippi River basin; (2) if carbon retention in upstream reservoir sediments, soils, and floodplains has increased and delivery of carbon to the ocean decreased associated with a reduction in sediment supply as reflected in reduced core sediment accumulation rates; and (3) whether the chemical and isotopic nature, and the age spectrum, of particulate organic carbon (POC) transported downstream has changed.

2. Methods and Materials

2.1. Site Description, Sample Collection, and Chemical Analyses

Lake Whittington is a large oxbow lake in Mississippi, U.S.A., downstream from where the Arkansas River joins the Mississippi River (Figure 1). This lake was created in 1937, when the U.S. Army Corps of Engineers cut through the neck of this previous Mississippi River meander. Although Lake Whittington is not a reservoir impounding a river behind a dam, it is a long-term depositional site on the middle or Lower Mississippi River that has proven to be an excellent location for paleoreconstruction of basin processes [*Van Metre and Horowitz*, 2012] (see supporting information). We therefore present results herein as indicative of the carbon biogeochemistry of sediments in transported in the Lower Mississippi River basin and as indicative of fluvial sediment in this system stored (trapped) in reservoirs and other off-channel settings.

2.2. Age Dating and Sedimentation Rate

The Lake Whittington core geochronology was determined using four depth-date markers: the initial occurrence (1953) and peak (1964) in ^{137}Cs activity; the transition from sand to fine-grained lacustrine sediment at 237 cm, marking the transition from river to lake (1937); and the top of the core (2005) [*Van Metre and Horowitz*, 2012]. The mass accumulation rates (MAR) between these markers, determined on the basis of dry mass per unit area of the core, decreased over time from 4.8 g cm^{-2} yr^{-1} (1938 to 1953), to 1.9 g cm^{-2} yr^{-1} (1953 to 1964), to 1.0 g cm^{-2} yr^{-1} (1964 to 2005). The decrease in MAR is consistent with an approximate two thirds decrease in suspended sediment discharge in the Lower Mississippi River between the early 1950s and early 1960s caused by construction of seven large reservoirs on the Missouri River, as well as the Arkansas River [*Meade*, 1996] (Figure 2). Support for the use of constant MARs between depth-date markers is provided by the coincidence of the Pb concentration peak in the dated core intervals and Pb emissions in the U.S. in the early 1970s [*Van Metre and Horowitz*, 2012; Figure 5]. The coincidence of MAR in the core and suspended sediment discharge in the river is one line of evidence demonstrating that the lake has been accumulating Mississippi River sediment over time. More detailed analysis of the age model, including data showing the onset of anthropogenic metal contamination in the core, is presented in *Van Metre and Horowitz* [2012].

2.3. Bulk Carbon and Nitrogen Analyses

Total organic carbon (TOC) and total nitrogen (TN) and stable isotopes (^{13}C and ^{15}N) were measured at the University of Florida, Light Stable Isotope Mass Spectrometer Laboratory. Dried sediment samples were decarbonated by vaporization with concentrated HCl [*Harris et al.*, 2001]. Measurements were made using an elemental analyzer (Carlo Erba NA1500 CNS elemental analyzer) interfaced with an isotope-ratio mass

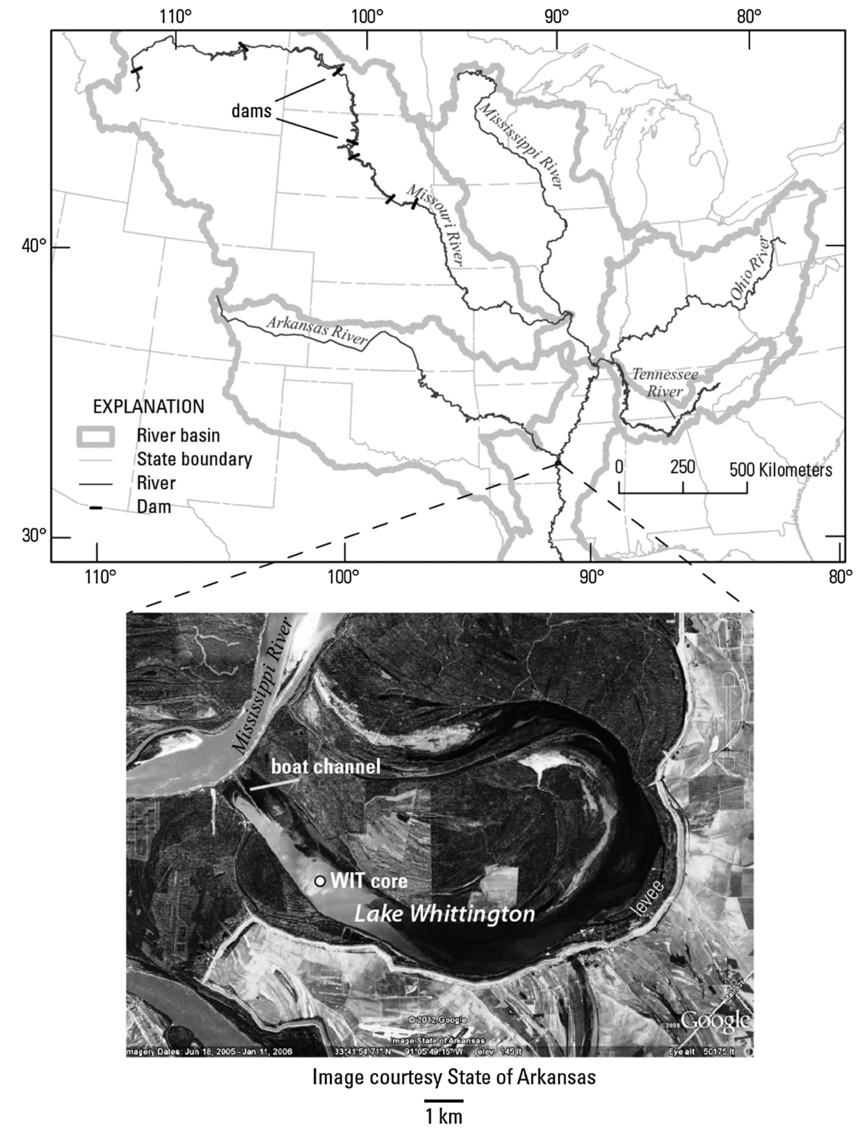

Figure 1. Major subbasins of the Mississippi River contributing to Lake Whittington, Mississippi, and aerial image of the lake showing the Caulk Neck Cutoff, coring sites, and surrounding lands (modified from *Van Metre and Horowitz* [2012]).

spectrometer (Thermo Scientific Delta V Plus). Stable isotope data are reported in $\delta^{13}C$ (‰) notation relative to Vienna Peedee belemnite (VPDB).

2.4. Neodymium (Nd) Isotope Analyses

Samples were digested in concentrated $HF + HNO_3$ mixture in closed precleaned Teflon vials. After digestion the resultant solution was evaporated to dryness. The resultant residue was dissolved in 1N HNO_3 and Nd was extracted with TRU-Spec and LN-Spec resins, following protocol described in *Pin and Zalduegui* [1997]. Nd isotopes were determined on a "Nu-Plasma" multiple collector–inductively coupled plasma–mass spectrometry, following methods described in *Kamenov et al.* [2008]. The reported Nd isotopic compositions are relative to JNdi-1 $^{143}Nd/^{144}Nd = 0.512115$ (±0.000015, 2se).

2.5. Lignin Analyses

Lignin phenols were extracted and analyzed in each sample according to the methods of *Hedges and Ertel* [1982], as modified by *Goñi and Hedges* [1995]. Lignin oxidation products were analyzed on a Thermo Scientific Trace 1310 Gas Chromatograph interfaced to a Thermo Scientific TSQ8000 Triple Quadrupole Mass Spectrometer.

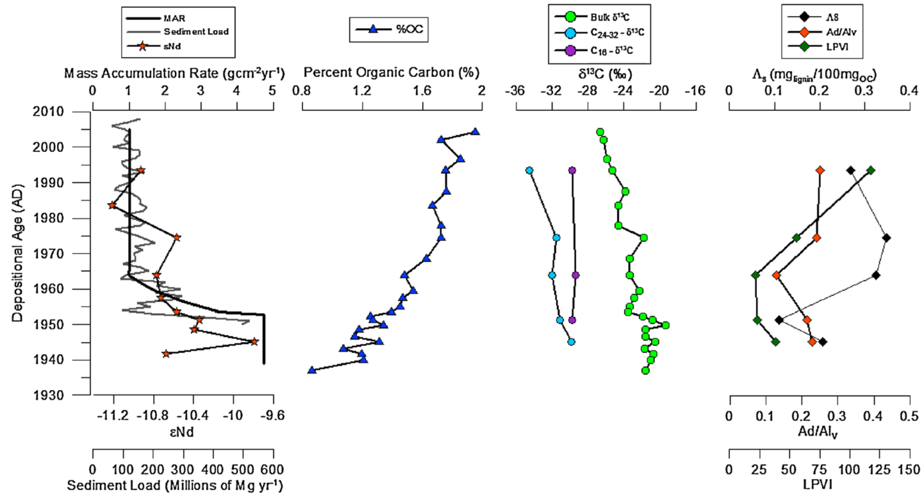

Figure 2. Changes in sediment load (U.S. Geological Survey (USGS) streamflow-gaging station 07295100 Mississippi River at Tarbert Landing, MS [*Van Metre and Horowitz*, 2012]), bulk organic carbon content (%OC), epsilon-neodymium (ε_{Nd}), stable carbon isotopic composition ($\delta^{13}C$), and lignin oxidation products over time in the Lake Whittington core. While sediment discharge records show a pronounced decrease coincident with the construction of seven large reservoirs on the Missouri River in the 1950s, there has been an increase in OC content of Lake Whittington Sediments. The $\delta^{13}C$ values of the C_{24-32} fatty acids correlate significantly with the $\delta^{13}C$ of the total OC ($r = 0.95$, $P < 0.05$), while the C_{16} fatty acid does not. This implies that the trend for the total OC is linked to changing vascular plant inputs. The lignin contribution (Λ_8) shows an increase in Lake Whittington sediments over ~80 years. There is very little decay of lignin over this time based on acid/aldehyde ratios of vanillyl phenols (Ad/Alv), but there was a change in the source of lignin based on lignin phenol vegetation index (LPVI). Eight lignin phenols, vanillin, acetovanillone, syringealdehyde, vanillic acid, acetosyringone, syringic acid, p-hydroxycinnamic acid, and ferulic acid were quantified and normalized to 100 mg OC (Lambda 8, Λ_8). Ratios of vanillic acid to vanillin (Ad/Alv) and syringic acid to syringaldehyde (Ad/Als) were used as indices of lignin decay [*Opsahl and Benner*, 1998]. LPVI = ((Syringyls(Syringyls + 1)/(Vanillyls + 1) + 1) × (Cinnamyls (Cinnamyls + 1)/(Vanillyls + 1) + 1)) was used to infer the source of lignin [*Tareq et al.*, 2004]. Neodymium isotope depletion (ε_{Nd}) downcore. Although the change in eNd values downcore is not significant relative to analytical uncertainty, the trend is toward more depletion after extensive agriculture and damming. This trend is consistent and suggestive of decreased sediment loading from the Missouri River during the accumulation of this core. Mass accumulation rate (MAR) is in units of $gCm^{-2}yr^{-1}$. Although source rock in North America has been characterized for ε_{Nd}, riverine suspended sediments in the major tributaries of the Mississippi River system has not been characterized.

2.6. n-Alkanoic Acid Analyses

Lipids were extracted using an Accelerated Solvent Extractor (Dionex ASE 300) with a 9/1 (vol/vol) mixture of methylene chloride and methanol for four cycles of 5 min at 1500 pounds per square inch, and 100°C. The total lipid extracts were dried down and saponified at 70°C for 2 h using 0.5 M KOH in methanol with 1% Milli-Q H_2O (see supporting information). For quantification, an aliquot was injected on a HP 5890 series II gas chromatograph (GC) equipped with a RTX-1 column (30 m × 0.25 mm i.d., film thickness, 0.25 μm) and a flame ionization detector.

2.7. Compound-Specific ^{13}C Analyses

Stable carbon isotope analysis of *n*-alkanoic acid methyl esters was analyzed at the University of Florida, Light Stable Isotope Mass Spectrometry Laboratory. Previously purified *n*-alkanoic acid methyl esters were injected on an Agilent 6890 Gas Chromatograph interfaced to a Thermo Finnigan GC Combustion III and Thermo Scientific Delta V Plus isotope ratio mass spectrometer. The $\delta^{13}C$ values were normalized using Indiana University *n*-alkanoic acid methyl ester standards. Finally, the stable carbon isotope values were corrected for the C contribution from the added methyl group, using a mass balance equation, and reported relative to VPDB.

2.8. Compound-Specific ^{14}C Analyses

Radiocarbon analyses of individual *n*-alkanoic acid methyl esters were performed at Woods Hole Oceanographic Institution following the method described by *Eglinton et al.* [1996] (see supporting information). Individual *n*-alkanoic acid methyl esters were first separated using a preparative-GC equipped with a RTX-1 column (30 m × 0.53 mm i.d., film thickness, 0.5 μm). ^{14}C measurements were corrected for procedural

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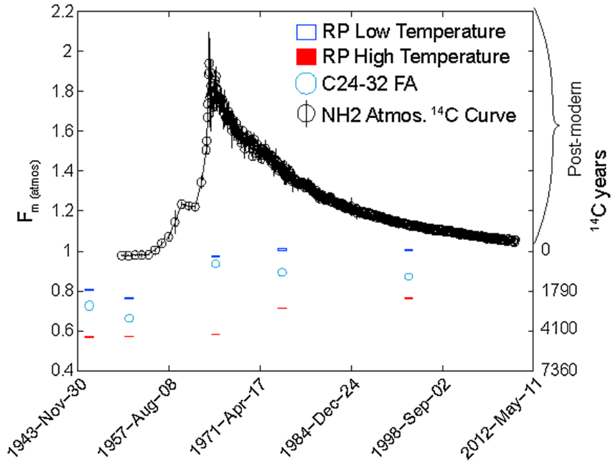

Figure 3. Bomb radiocarbon is evident in C_{24-32} fatty acids and both the low-temperature and high-temperature Ramped PyrOx fractions. The changes appear in all dated carbon pools in the mid 1960s with the exception of the high-temperature Ramped PyrOx fraction. Conversion between fraction modern (F_m, the $^{14}C/^{12}C$ ratio relative to that of 1950 wood) and radiocarbon can be done with the expression $^{14}Cy = -8033\ \ln(F_m)$; however, it is not practical to convert measurements of ^{14}C indicative of bomb carbon levels ($F_m > 1$, postmodern) to radiocarbon years. Values of Fm less than 1 from Ramped PyrOx and fatty acid dating are converted to ^{14}C years (right *y* axis) as they reflect mixtures of atmospheric carbon with older pools that do not contain bomb carbon.

blanks considering the blank contribution determined using the same analytical protocol and equipment [*Santos et al.*, 2010].

2.9. Ramped Pyrolysis (Ramped PyrOx) ^{14}C Analyses

Sediments from the same depths as compound specific ^{14}C analysis treatments were used for Ramped PyrOx analysis after rinsing the acid residue left over from fumigation. Details of the Ramped PyrOx technique can be found in *Rosenheim et al.* [2008] (see supporting information).

3. Results and Discussion

3.1. Change in Sediments, Bulk OC Sources, and Radiocarbon Age

Whereas there has been a significant decrease (twofold to fourfold) in the mass accumulation rate of sediments and sediment discharge in the Mississippi River over the past ~78 years, in sediments of Lake Whittington the bulk %OC has increased from 0.86% to 1.95% (Figure 2). As mentioned earlier, this decrease in MAR and suspended sediment discharge largely occurred between the early 1950s and 1960s coincident with acceleration of dam building on the Missouri River (and Arkansas River) in the 1950s [*Meade*, 1996; *Meade and Moody*, 2010]. This period also coincides with a large decrease in the sediment suspended load (Figure 2) and in the synchronicity of the timing of the reduction observed on the continental shelf of the northern Gulf of Mexico [*Allison et al.*, 2007]. Other land use changes, such as irrigation networks, lock and dam low-flow navigation control, flood control structures, bank stabilization, and soil conservation measures, have most likely contributed to this dramatic reduction of sediment delivery to the coast [*Meade*, 2004; *Knox*, 2008]. Proportionally, this combined decline in MAR and increase in %TOC results in a decrease in carbon accumulation rate (i.e., MAR × %TOC), and presumably, in the carbon delivery rate by the Mississippi River to the Gulf of Mexico, by a factor of ~3 (Figure 2).

Along with the decrease in carbon accumulation, trends in chemical biomarker concentrations, $\delta^{13}C$ values, and ^{14}C ages were also apparent in Lake Whittington sediments over the past ~80 years (Figure 2). For example, based on $\delta^{13}C$ values, there was a change in sources of OC since about 1950, as indicated by the trend toward more depleted ^{13}C values of bulk OC, which changed from −19.4‰ to −26.6‰ since the damming of the Missouri River (Figure 2). Bulk OC radiocarbon ages, derived from the weighted arithmetic mean ages of the ramped PyRox fractions, changed from 3000 ^{14}C year to ~1000 ^{14}C years in sediments deposited between the late 1940s and the 1990s (Figure 3). At least part of this change is influenced by the pulse of ^{14}C-enriched CO_2 resulting from thermonuclear bomb testing in the 1950–1960s. The weighted arithmetic mean radiocarbon ages apparent in the top two horizons of the core (1000–1250 ^{14}C years from 1993 and 1974, respectively) are younger than those observed in suspended sediment POC during both high and low discharge regimes [*Gordon and Goñi*, 2003; *Rosenheim et al.*, 2013a] although the age spectra are similar in magnitude (2000–3000 ^{14}C years). Despite changes in biomarkers and stable carbon isotopes, thermochemical stability of the sediments downcore was constant compared to other depositional environments for which this technique has been used [*Rosenheim et al.*, 2013b; *Williams et al.*, 2014; *Williams and Rosenheim*, 2015] (see supporting information).

Higher discharge in the Mississippi River has been related to older age spectra and radiocarbon geometric mean ages [*Rosenheim et al*., 2013a]. However, despite the presence of sources of old, petrogenic carbon in the vast drainage of the Mississippi River system, even near-record discharges in this system have not produced age spectra as old as those observed during monsoon (high discharge) in a Himalayan tributary to the Ganges River [*Rosenheim and Galy*, 2012]. We posit that the maximum age within the spectra for these sediments is likely limited by the average soil organic carbon turnover time in the Mississippi basin, in concordance with recent conceptual models of passive-margin river systems and the more homogenous carbon they transport through wider floodplains [*Blair and Aller*, 2012].

The Mississippi River drainage basin is composed of different source-rock Nd signatures [*Patchett et al*., 1999]. Any relative change in the proportion of sediments delivered from the Missouri drainage versus the Ohio and Upper Mississippi drainage could be recorded in Nd isotopic signatures of the sediments in Lake Whittington. Whereas we do see only a possible trend in the Nd isotopes that might reflect such changes from the 1940s and 1950s (-9.7 to -10.2) to the 1980s and 1990s (-10.9 to -11.3) (Figure 2), the trend is statistically insignificant relative to the analytical error. One notable factor in understanding the effects of damming the Missouri River is that, even post-1960s, the Missouri supplies more sediment to the Lower Mississippi River than the Upper Mississippi and Ohio Rivers combined, accounting for roughly 50 to 70% of the sediment flux passing Lake Whittington [*Patchett et al*., 1999; *Horowitz*, 2010]; however, we do not fully understand what the ratio was before damming was prominent.

Recent evidence has also shown enhanced bed incision in the main channel of the Missouri River, below the dams, resulting from long profile adjustments and enhanced erosion in lower tributaries below the dam [*Heimann et al*., 2011]. Bed incision in the lower Mississippi has been observed since the late 19th century as this “self-scouring” system continues to evolve with time [*Meade and Moody*, 2010]. Thus, carbon and Nd source inputs from bed incision may also have had an impact on the changing signatures in Lake Whittington sediments since the Missouri is still responsible for the greatest input of sediments to the Mississippi River, despite having the greatest reduction in sediment inputs from damming relative to the Upper Mississippi and Ohio Rivers.

In addition to damming effects, there have likely been significant effects from land use change through agricultural practices. More specifically, it was in ~1880 that croplands in the Northeast and Midwest had reached ~50% of land cover as agriculture [*Hatfield et al*., 2015]. Over the next 100 years, agriculture in the Midwest continued to expand where it peaked at about 80% coverage in the 1980s. During this period there were also changes in agriculture tillage techniques, which increased erosion rates from farmlands [*Olchin et al*., 2008]. *Van Metre and Horowitz* [2012] showed a tripling of Ca concentrations in the Lake Whittington sediments from the 1930s to 2011. This agrees well with the changes that have been reported by *Raymond et al*. [2008], where there have been significant increases in the dissolved inorganic carbon concentrations (associated with carbonate minerals dissolution in watershed soils) in the Mississippi River due to agricultural expansion from ~1900 to the early 2000s. In Lake Whittington sediments, increasing bulk N/C ratios and a 2‰ ^{15}N enrichment over the past 80 years reflect increasing contribution of soil OC over time [*Van Metre and Horowitz*, 2012]. Together, the increase in Ca concentration and change in bulk OC composition (TN/OC, $\delta^{13}C$, and $\delta^{15}N$) of Lake Whittington sediments suggest that land use change during the 19th and 20th centuries impacted the composition of the Mississippi River particulate load in addition to that of the dissolved load as reported by *Raymond et al*. [2008].

3.2. Chemical Biomarker and Compound-Specific Isotopic Signatures

In addition to there being different sources of OC since the damming of the Missouri River, based on more depleted ^{13}C values of bulk OC in Lake Whittington sediments, there was also a greater amount of terrestrial OC loading supported by corresponding increases in the abundance of lignin content (Figure 2). Lignin has been used extensively as a biomarker of vascular plants in aquatic system [see *Bianchi and Canuel*, 2011, and references therein]. Interestingly, there appears to have been little decay of this lignin over time, based on the low values of vanillic acid to vanillin $(Ad/Al)_v$ and the minimal changes in this ratio over time (Figure 2). Increases in the acid/aldehyde ratios of vanillyl phenols (Ad/Al_v) are assumed to reflect diagenetic alteration, as Ad/Al_v values >0.4 are indicative of microbial decay of lignin [*Hedges et al*., 1988; *Goñi et al*., 1993]; thus, little alteration is indicated in the sediments. There also appears to be a corresponding change from non-woody angiosperms to woody angiosperms in Lake Whittington sediments, based on an increase from values of ~22 to ~120 in the lignin phenol vegetation index (LPVI) (Figure 2). These values agree well with associated changes in the LPVI of different vascular plants sources [*Tareq et al*., 2004]. We contend that linking historical changes in the sources, age, and composition of OC in Lake Whittington sediments with dam building in the Missouri River, and other factors that have reduced sediment loading in the Lower Mississippi River, will help to better understand how dams impact the continually changing landscape of large watersheds and their carbon dynamics in the 21st century.

Here we posit that the damming of the Missouri River has resulted in younger, more depleted $\delta^{13}C$, woody OC sources in Lake Whittington sediments due to an increase in the relative importance of OC soil inputs from the Upper Mississippi and Ohio River watersheds. Previous work has shown that bulk particulate organic carbon (POC) derived in the Missouri River is composed of nonwoody angiosperm, relatively ^{13}C-enriched ($\delta^{13}C = -19.4‰$), vascular plants with S/V and C/V ratios of 0.94 and 0.25, respectively, reflective of the large C_4 grassland plains in this region [*Onstad et al*., 2000]. *Kendall et al*. [2001] provided even finer resolution of $\delta^{13}C$ values of POC in Mississippi River watersheds and found that the average $\delta^{13}C$ isotopic signature for the main stem Ohio River ranged between $-26‰$ and $-28‰$ (C_3 plant sources), in comparison to the Missouri River, which had values that ranged from -22 to $-30‰$ (mixed C_3 and C_4 sources), with the most enriched values occurring downstream near the major confluence of the Missouri and Upper Mississippi Rivers [*Kendall et al*., 2001].

Lower $\delta^{13}C$ values of long-chain (C_{24} to C_{32}) fatty acids further support our bulk OC $\delta^{13}C$ data, which suggests an overall change in sources of OC in Lake Whittington sediments over the past ~80 years (Figure 2). The C_{16} fatty acid has been commonly linked with algal, and in some cases, bacterial sources in aquatic systems [see *Bianchi and Canuel*, 2011, and references therein]. Thus, the lack of change in the $\delta^{13}C$ signature of C_{16} fatty acid over time in Lake Whittington sediments indicates that enhanced reduction of bulk OC $\delta^{13}C$ over time was not due to changes in the abundance of algal sources, but more controlled by a change from C_4 to C_3 vascular plant inputs (Figure 2). We believe that this shift from more C_4 input from the Missouri to a mixture of C_3 and C_4 inputs over time, discussed earlier [*Kendall et al*., 2001]. In particular, there was a significant increase in the amount of soybean production in the mid-20th century that could in part have contributed to greater inputs of C_3 plant inputs to the region [*U.S. Department of Agriculture National Agricultural Statistics Service*, 2015]. The radiocarbon content of vascular plant derived $C_{24–32}$ fatty acids changes in response to the atmospheric ^{14}C bomb peak (Figure 3). However, the increase in ^{14}C content of $C_{24–32}$ fatty acids in the mid-1960s is attenuated compared with the atmospheric bomb ^{14}C peak. This suggests that long-chain fatty acids are characterized by a complex age structure, involving at least a "millennial" pool that is relatively insensitive to incorporation of bomb ^{14}C and a "decadal" component that tracks closely the atmospheric bomb spike.

Ramped PyrOx ^{14}C analysis of Lake Whittington sediments shows no discernible difference in thermochemical stability downcore compared to other sedimentary environments [*Rosenheim et al*., 2013b] (see supporting information), but shows changes in radiocarbon ages (Figure 3). The similarity between thermochemical stability can best be interpreted as a constant distribution of bond types through the different levels of discharge management present on the Missouri-Mississippi River system over the time span of the core (1937–2005). This finding differs from what we observe in every proxy except radiocarbon ages—a gradual change through the core. Weight arithmetic mean radiocarbon ages decrease abruptly from ~3000 years to ~1000 years after the atmospheric bomb curve. The low-temperature intervals of the age spectrum respond rapidly to the atmospheric bomb ^{14}C peak, albeit lower amplitude. In contrast, the highest-temperature interval shows a delayed response to the atmospheric bomb ^{14}C spike in addition to overall ^{14}C depletion compared to both low-temperature intervals and long-chain fatty acids (Figure 3). This suggests contributions from an OC pool characterized by intermediate turnover time (e.g., "centennial") that is not readily apparent in the fatty acid age structure. The stable isotope signature of the high-temperature fractions is generally heavier than the lower temperature fractions, indicating that the older components (i.e., centennial and millennial OC) is likely sourced from areas with more C_4 vegetation and rather insensitive to recent changes in relative contributions from C_3 and C_4 plants [*Rosenheim and Galy*, 2012]. Downcore, the proportion of the high-temperature fraction remains constant, suggesting that damming and land use change did not drastically affect the age and reactivity structure of OC exported by the Mississippi River (Figure S1).

4. Implications for OC Cycling in the Mississippi Basin

Overall, the sediment record from Lake Whittington reveals the combined effect of intense damming and land use change on OC cycling in the Mississippi basin over the past 80 years. Because of its unique location in this large river system, Lake Whittington sediments can provide insight into the temporal nature of carbon exports by the Mississippi River to the marine environment. Damming of the Missouri River—the main sediment supplier to the Lower Mississippi River—and other structural and land use changes in the basin have reduced net OC export by a factor of ~3, despite increased OC concentrations [*Van Metre and Horowitz*, 2012]. Overall, our observations are in line with global observations, suggesting that OC export is dominantly controlled by fluvially mediated erosion rates [*Galy et al*., 2015]. This observation suggests that damming large rivers may reduce global OC export (via deltas) to and burial in marine sediments, thereby potentially representing a net increase in C source to the atmosphere on decadal time scales of reservoir life cycles, if the OC retained there remains actively cycling—which would be controlled by a broad suite of physicochemical conditions (e.g., pH, redox, and OC composition). In the meantime, compositional changes—such as increased contribution from C_3 plants and soils—appear to mostly reflect land use change. The lack of significant change in thermochemical stability, though, suggests that land use change itself has a limited impact on OC stability of basin soils and sediments reflected in Mississippi River POC. In some cases, offshore sediments have been used to document changes in riverine OC inputs to the shelf; in these cases, it is critical to account for possible recent (decadal) changes riverine OC composition. For example, the composition of sediments from the Mississippi River shelf [*Gordon and Goni*, 2004] resembles that of early-mid-19th century Mississippi River sediments. This actually suggests limited alteration of riverine POC and the dominance of sediment and OC pre-dating widespread damming, in line with the postdamming threefold reduction of POC delivery inferred from the Lake Whittington record. So the large reduction in POC flux to the Gulf caused by damming and retention on the continent might help explain the apparent dominance of predamming sediment on the shelf.

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