


The C-biogeochemistry of a Midwestern USA agricultural impoundment in context: Lake Decatur in the intensively managed landscape critical zone observatory

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Abstract The damming of rivers has created hotspots for organic carbon sequestration and methane production on a global scale as the reservoirs intercept fluvial suspended and dissolved loads. To better understand how the C-biogeochemistry of a reservoir responds to watershed processes and evolves over time, Lake Decatur, located in the Intensively Managed Landscape Critical Zone Observatory (IML-CZO) was studied. Solid phase analyses (% organic C, C/N, $\delta^{13}\text{C}$, $\delta^{15}\text{N}$) of soils and sediments sampled from stream bank exposures, river suspensions, and the lake bottom were

conducted to characterize organic C (OC) sources throughout the sedimentary system. Agriculturally-driven soil erosion rapidly altered lake bathymetry causing an evolution of sedimentary and OC deposition patterns, which in turn shaped where and when methane production occurred. A positive correlation between OC accumulation rate and porewater dissolved inorganic C (DIC) $\delta^{13}\text{C}$ profiles indicates that methane generation is strongly influenced by OC burial rate. The sources of the lake bed particulate organic C (POC) have also evolved over time. Drowned vegetation and/or shoreline inputs were dominant initially in areas adjacent to the original river channel but were rapidly

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overwhelmed by the deposition of sediments derived from eroded agricultural soils. Eutrophication of the lake followed with the onset of heavy fertilizer application post-1960. This succession of sources is expected to be commonplace for reservoirs greater than ~ 50–60 years old in agricultural settings because of the relative timing of tillage and fertilizer practices. The $^{13}\text{C}/^{12}\text{C}$ ratios of methane from Lake Decatur were more depleted in ^{13}C than what is commonly expected for freshwater sedimentary environments. The ^{13}C -depletion suggests that CO_2 -reduction is the dominant methanogenic pathway rather than the anticipated acetate dissimilation process. The isotopic observations reveal that commonly held assumptions about methane production and its C-isotopic signature in freshwater systems are over-simplified and not strictly applicable to this system.

Keywords Reservoirs · C-cycle · Methane · Carbon sequestration

Introduction

The interception of riverine flow and its dissolved and sediment loads by reservoirs or impoundments has the potential to alter biogeochemical cycles on a global scale because of their fragmentation of nearly half of the world river volume (Grill et al. 2015; Maavara et al. 2017). There are an estimated 16.7 million reservoirs larger than 0.0001 km^2 globally with a collective surface area of ~ $305,000 \text{ km}^2$ (Lehner et al. 2011). Large dams contribute to 12–16% of global food production (Lehner et al. 2011; WCD 2000). Hydropower represents ~ 19% of the world's electricity generation (WCD 2000). Flood control and potable water management are other uses of reservoirs (Lehner et al. 2011; WCD 2000).

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Even though reservoirs serve their intended application of water management and energy production well, the unintended consequences of their use are emerging and becoming significant in scale. The potential impact on the global C-cycle is one area of concern yet it is challenging to quantify because of the diversity of reservoir characteristics (Maavara et al. 2017; Mendonça et al. 2017). Small reservoirs ($\leq 10 \text{ km}^2$) are not well represented in C-burial budgets even though they constitute ~ 99% of all impoundments (Lehner et al. 2011; Maavara et al. 2017). The evolving nature of these reservoirs with age is another contributing uncertainty. Conceptual models describing the evolution of the C-biogeochemistry in small reservoirs are needed.

Despite a nearly 3.5-fold increase in landscape erosion driven by agriculture (Wilkinson and McElroy 2007), the export of sediment to the ocean is comparable to pre-anthropogenic conditions due to the trapping of sediment by reservoirs (Syvitski et al. 2005). Sediment accumulation in reservoirs is between 4000 and 10,000 Tg/year (Beusen et al. 2005; Syvitski et al. 2005; Vorosmarty et al. 2003; Walling 2006). In comparison, the best estimate for sediment exported to the ocean is 13,000–20,000 Tg/year compared to ~ 14,000 Tg/year before the Anthropocene (Beusen et al. 2005; Syvitski et al. 2005; Vorosmarty et al. 2003; Walling 2006). Export of sediment from some rivers has been sufficiently curtailed leading to the starvation and ultimate net erosion of deltas and shorelines (Syvitski et al. 2005, 2009).

The delivery of sediment and nutrients to reservoirs drives the sequestration of OC from both allochthonous fluvial sources and autochthonous (in situ) primary production. Approximately 38–153 Tg C are delivered to reservoirs per annum by rivers (Table 1). The total (allochthonous plus autochthonous) burial flux of OC is 26–300 Tg C/year. Oceans, with an area over 1000-times greater than reservoirs, bury ~ 300 Tg C/year (Table 1; Burdige 2005, 2007). Reservoirs have thus displaced the locus of a substantial portion of global C burial for the short-term (the lifetime of the reservoir) and by doing so have become biogeochemical hot spots. In the marine environment, OC oxidative processes are dominated by the aerobic respiration and sulfate reduction in which CO_2 is the primary C-product. By shifting OC deposition to the freshwater and sulfate-poor sediments of reservoirs,

Table 1 Estimates of global OC fluxes

Flux (Tg C/year)	Ocean	Reservoirs
Riverine flux of terrestrial OC to ...	170–200 ^{a,f}	38–153 ^b
Biospheric (potentially reactive) C	127–173 ^c	16–137 ^d
Fossil (unreactive) C	27–43 ^c	16–22 ^e
Burial flux of terrestrial OC	40–75 ^f	
Burial flux of terrestrial plus aquatic OC	309 ^f	26–300 ^g
Methane emissions	4–25 ^h	2–70 ⁱ
Area (km ²)	361,383,969 ^j	305,000 ^k

^aBeusen et al. (2005), Ludwig et al. (1996) and Schlünz and Schneider (2000)

^b Assumes 3.8–5.1 Pg sediment trapped by reservoirs with 1–3% OC by weight (Syvitski et al. 2005)

^cBlair and Aller (2012) and Galy et al. (2015)

^dBiospheric flux = total—fossil (see e)

^e Sum of high mountain to upland trapped sources $\times 0.0044 \pm 0.0001$ (Blair and Aller 2012; Syvitski et al. 2005)

^fBurdige (2005) and Burdige (2007)

^g Downing et al. (2008), Maavara et al. (2017), Mendonça et al. (2017), Mulholland and Elwood (1982), Ritchie (1989) and Stallard (1998)

^hDlugokencky et al. (2011)

ⁱDeemer et al. (2016), Lima et al. (2008), Maeck et al. (2013), St Louis et al. (2000) and Varis et al. (2012)

^jCostello et al. (2010)

^kLehner et al. (2011)

methanogenesis rises in importance. The global atmospheric flux of methane from reservoirs, approximately 2–70 Tg C/year with a best estimate 8.9–22.2 Tg C/year (Deemer et al. 2016), is equivalent to or exceeds that from the global ocean (Table 1) and is responsible for 2–5% of the global budget (Deemer et al. 2016; Lima et al. 2008; Maeck et al. 2013; Saunio et al. 2016; St Louis et al. 2000). Reservoirs are also a source of N₂O to the troposphere thus their contribution (0.03 Tg N/year) to greenhouse gas emissions merit inclusion in global inventories (Deemer et al. 2016; St Louis et al. 2000).

Methane production within reservoirs is an evolving process in terms of sources and rates. The burial flux of fermentable OC is hypothesized to be the master variable for methane production, just as it is in marine sediments (Blair 1998; Martens et al. 1998). The source and composition of the OC buried will therefore be a significant factor in addition to the

burial rate. OC sources are expected to change with reservoir age. Drowned vegetation and soils fuel methanogenesis from the outset after dam emplacement and subsequent burial (Barros et al. 2011). The lifetime of the drowned source is uncertain, but likely persists over timescales of decades because of the volume of material and the low reactivity of lignocellulosic components from woody plants in anoxic sediments (Blair and Aller 2012; Deemer et al. 2016). Fluvial inputs are the dominant source of OC delivered to reservoirs globally (Table 1; Maavara et al. 2017). Having survived diagenetic processes within soils and the transport to the reservoir, the fluvial OC is hypothesized to be at best modestly reactive (Blair and Aller 2012). As such, it is expected to dominate the buried OC pool.

In contrast, autochthonous primary production driven by the influx of nutrients from the surrounding watershed may overshadow allochthonous sources of OC in terms of fueling lake bed diagenetic processes such as methanogenesis because of its greater reactivity (Deemer et al. 2016; West et al. 2016). Autochthonous sources are especially important in agricultural settings where eutrophication is common (Clow et al. 2015; Dietz et al. 2015; Downing et al. 2008; West et al. 2016). The temporal evolution of the OC sources, while dependent on the individual characteristics of a reservoir and its surrounding watershed, should also reflect globally more universal patterns in agricultural practices over time (Dietz et al. 2015).

Reservoirs continue to be built and are predicted to fragment 90% of the world river volume by 2030 (Grill et al. 2015). Models are required to project the impacts of the fragmentation on the global C-cycle (Maavara et al. 2017). The large number of reservoirs and their diversity makes the development of models and their supporting databases challenging. Conceptual models, or rubrics that link processes across the variety of environments, are needed as part of the predictive toolbox.

Because both allochthonous and autochthonous sources of OC are expected to be highly dependent on watershed land use practices (Dietz et al. 2015), a catchment-wide perspective is necessary to understand the cycling of C within reservoirs. In this study, the sedimentary biogeochemistry of a reservoir situated in an intensive agricultural setting was investigated within the context of an interdisciplinary

watershed-scale project, the US. NSF-supported Intensively Managed Landscape Critical Zone Observatory (IML-CZO). The fundamental goal of the IML-CZO is to better understand the consequences of landscape, hydrologic and ecosystem engineering on environmental sustainability. One of the study sites is in the watershed of the Upper Sangamon River in Illinois (Fig. 1) where Lake Decatur serves as a sediment-trapping terminus.

The objective of this project was to evaluate how a reservoir evolves with age in terms of the OC sources and fates. Sediment and OC depositional patterns in the lake were determined, as were the sources of the OC and how they changed over time. Lakebed concentrations and C-isotopic compositions of dissolved inorganic C (DIC) and methane were used to constrain the pathways of OC remineralization. This information was linked to land use history to identify both watershed and in-reservoir processes that influence reservoir biogeochemistry.

Approach and methods

Field site

Lake Decatur has evolved as an impoundment of the Sangamon River via a succession of dams emplaced in 1878, 1910 and 1922 (Fig. 1; Fitzpatrick et al. 1987). The 1922 dam was the largest and it accomplished the most significant flooding of the Sangamon River floodplain. The addition of bascule spillway gates to the top of the dam in 1956 raised the water level over a meter, widened the lake, and temporarily increased sediment trapping efficiency (Fitzpatrick et al. 1987). The watershed area upstream of the dam is approximately 2400 km² (Borah et al. 2002). Land use is dominated by row crop cultivation, principally for corn and soybeans with historical records extending back to at least 1925 (Fig. 1; Fitzpatrick et al. 1987). As the result of intensive agriculture, the approximately 12 km² lake filled with sediment more rapidly than expected, thus prompting multiple analyses of sedimentation patterns and inventories since the 1930s (Bogner 2002; Fitzpatrick et al. 1987). Concerns about deteriorating water quality as a result of agriculturally-derived N-inputs initiated water column monitoring in 1967 (Borah et al. 2002). The end result is that Lake Decatur has the potential to provide a well-constrained

sedimentary record of the changes in biogeochemical fluxes within the upstream watershed through periods of dramatic climate change (e.g., major droughts) and expansion of agriculture. The lake has a history of dredging; however, the lower half of the system where samples for this study were collected was undisturbed prior to our investigation.

Sample collection

Our sampling strategy followed a Source-to-Sink approach in which samples were collected from representative sediment sources in watershed's upland and lowland regions, river suspended load and depositional sinks to identify how the particulate organic C changes as it moves through the system (Blair et al. 2004; Leithold et al. 2016). River bank samples were collected from sites that were previously characterized (Grimley et al. 2017). These alluvial deposits provided both spatial (upland vs. lowland) and temporal OC source information. The biogeochemical signatures (%C, C/N, $\delta^{13}\text{C}$, $\delta^{15}\text{N}$) of the alluvium and their soils were compared to the suspended load in the Sangamon River during a summer storm event to better understand the sources of C and N transported downstream and imported to Lake Decatur. Coring in the lake itself proceeded along and cross-channel so as to sample a range of sediment accumulation rates. Accumulation rates are hypothesized to be the master variable controlling OC burial and methane production.

Soil samples SB8-11 and SayFor were collected in the Saybrook upland area (Fig. 1). Additional samples were obtained from the lowland floodplain portion of the watershed (Allerton Park, AP). The SB8-11 and AP samples were from exposed banks that were scraped to remove approximately 1 cm of surface material in an effort to access fresh material. Samples were collected from just below the litter layer down almost to stream level. The alluvial bank soils have been classified as a Sawmill silty clay loam (Cumulic Endoaquolls). SB11 was from the same location as cores FA-4a,b in Grimley et al. (2017). Holocene alluvium represents 91–97 cm of deposition at that site, of which the upper 40–42 cm was characterized as post-European settlement (post-1850). The AP samples were collected near the FA-5 core, in which Holocene deposition was estimated to be 550 cm and the post-settlement alluvium was 70 cm (Grimley et al. 2017).

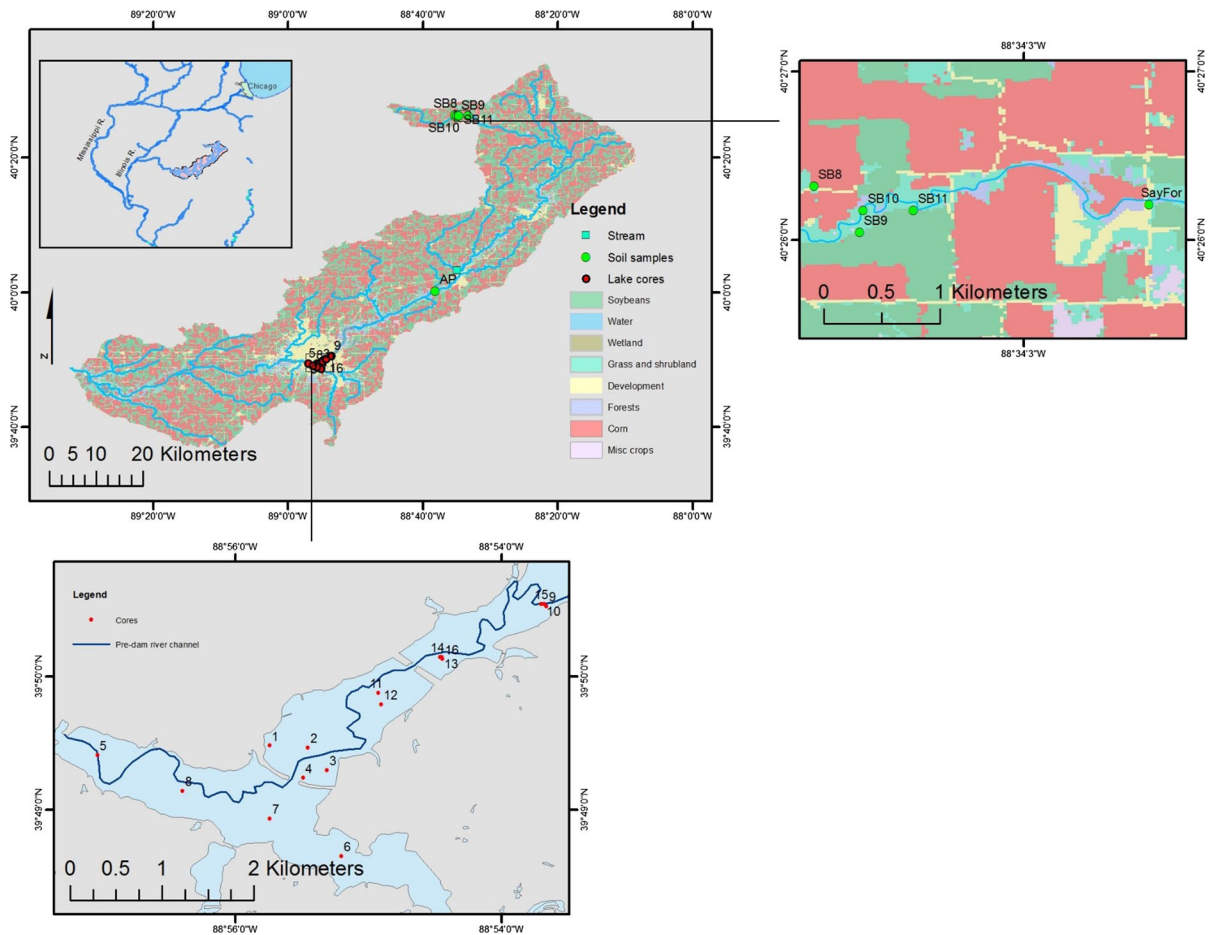


Fig. 1 Maps of Lake Decatur and the Upper Sangamon watershed. Land use is color coded. Sample locations are shown as green circles for soils and red circles for lake

The SayFor surface soil (0–5 cm) was collected from a forested area within a transition zone between the Sawmill and Lawson Aquic Cumulic Hapludolls soil types. “SB11 corn” was a surface sample (0–5 cm) from a field planted in corn at the time of sampling at the border of the Sawmill and the Warsaw loam (Mollisol, Typic Endoaquolls). All soils were stored frozen until analysis.

Stream suspended load was collected before, during and after a storm event on June 26–27, 2015 using an ISCOTM autosampler equipped with 1 L bottles. A nearby USGS gauging at Monticello provided water discharge data for the event. The water samples were stored frozen in the ISCO bottles after collection.

Lake bed sediments were collected using a gravity corer in May 2014 and a vibracorer in June 2015, both

sediments. The line in the center of the lake traces the original river channel prior to dam emplacement (adapted from Fig. 2 in Fitzpatrick et al. 1987). (Color figure online)

equipped with polycarbonate tubing. Station locations and ID numbers are shown in Fig. 1. The cores were extruded and subsampled in 5 cm intervals with 12 mL cut-off plastic syringes that were used as mini-piston corers to minimize gas loss. The extruded mud from each depth interval was split between two containers. Two cut-off syringes were used to fill 15 mL centrifuge tubes leaving no headspace to be used for porewater dissolved inorganic C (DIC) analyses (Thomas et al. 2002). Four syringes were used to deliver ~ 48 mL mud to 4 oz MasonTM canning jars containing 5 mL of 1 N NaOH for methane analyses. The jars were sealed with the normal MasonTM jar lids (Blair and Aller 1995). The porewater samples were kept refrigerated (< 24 h) until the porewater could be isolated by centrifugation

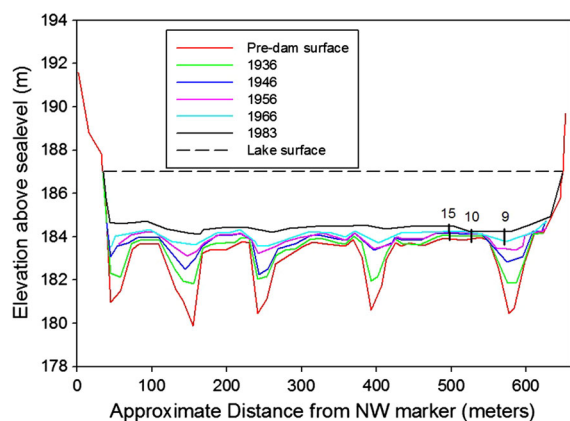


Fig. 2 Bathymetry of Lake Decatur as a function of time (adapted from Fitzpatrick et al. 1987). The transect (R15–16 in Fitzpatrick et al. 1987) intercepted meandering channels. Approximate core locations are shown for station 9, 10, 15. The NW marker referenced on the figure was a georeferenced location on the western shoreline

(4000 rpm for 30 min). The porewater was then forced through a 0.2 μm GHP AcrodiscTM filter with a syringe and sealed in 3 mL crimped-topped WheatonTM bottle containing several grains of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ as a preservative and sulfide trap (Thomas et al. 2002). All other samples, including the sediment recovered from the centrifugation, were archived frozen until further processing and analysis.

Analyses

Soil and lake sediment samples were lyophilized and ground to a fine powder. Stream water samples collected with the ISCO autosampler were filtered using pre-weighed, roasted 47 mm o.d. glass fiber filters (0.7 micron nominal pore size, MilliporeTM). Filters were roasted at 500 °C overnight before use to remove trace organic matter. Filters and sediment were lyophilized and then weighed to determine sediment load.

Soil and filtered sediment samples to be analyzed for OC were fumigated with gaseous HCL for up to 4 days to remove carbonate C. Similarly, the lake sediments were treated with aqueous 2 N HCL for 1–2 days and then dried *in vacuo* (Brackley et al. 2010). Carbonate removal was verified via trans-reflectance FTIR (Cui et al. 2016) using a Bruker Tensor 37 FTIR [NIR/MIR] equipped with a Hyperion microscope and MCT detectors by monitoring an

absorbance peak at 2513 cm^{-1} . Sediment was either analyzed directly on the glass fiber filters, or a small aliquot of the powdered sediment was spread on Al weighing boats.

MasonTM jar samples were thawed shortly before analysis and shaken vigorously to equilibrate the methane in the sediment with the headspace in the jar. An aliquot of the headspace was recovered using a septa-sealed lid piercing device and was analyzed for methane content using a Shimadzu Mini-2 GC equipped with a custom-made molecular sieve 5A column (0.9 m \times 1.4 mm) and a flame ionization detector. Headspace concentrations were then used to calculate original sedimentary contents. A second aliquot of headspace gas was analyzed isotopically as described below (Blair and Aller 1995).

Decarbonated soils and sediment samples were analyzed for particulate organic C (POC) and particulate total N contents and stable isotopic compositions using a Costech Elemental Analyzer-Conflo IV interface-Thermo Delta V Plus isotope ratio mass spectrometer (IRMS) combination. Aliquots of porewater were acidified with H_3PO_4 and analyzed for dissolved inorganic C (DIC) concentrations and $^{13}\text{C}/^{12}\text{C}$ ratios using a Thermo Gasbench-Delta V Plus IRMS. Methane $\delta^{13}\text{C}$ values were measured on a Thermo Trace GC-combustion-Delta V IRMS equipped with a Varian 25 m \times 0.3 mm Porapak Q GC column. Isotopic compositions were related to international standards (VPDB, air) through calibrated laboratory reference materials (Leithold et al. 2013).

Lake sediment samples used for radioisotope measurements to determine lakebed chronologies were dried in a convection oven at 60° C and then ground to a fine powder. The powders were sealed in a standardized geometry and set aside for 18 days to allow secular equilibrium ingrowth of gaseous ^{222}Rn from the decay of its ^{226}Ra parent. The activity of supported ^{210}Pb was determined from the activity of the ^{214}Bi parent (Wilson et al. 2005; Wren et al. 2007).

Gamma spectroscopy was used to determine the activities of ^{137}Cs and ^{210}Pb . Samples were counted for at least 82,800s on an EG&G Ortec[®] HPGe detector. Counting efficiencies were established using two mixed radionuclide solutions. Quality assurance was established through an inter-laboratory comparison with the radionuclide facility at the USDA-ARS National Sedimentation Laboratory (Wilson et al. 2005; Wren et al. 2007).

Riparian buffer vegetation analyses

The use of riparian buffers to ameliorate the impacts of agriculture on waterways may influence reservoir biogeochemistry. The change in area of riparian buffers over time in the Sangamon watershed was determined in the following manner. Historical aerial photographs obtained in 1940 and 1941 for the Upper Sangamon River watershed were downloaded from the Illinois State Geological Survey (ISGS) Geospatial Data Clearinghouse website (<https://clearinghouse.isgs.illinois.edu/>) and georeferenced (Rhoads et al. 2016). Channel centerlines were digitized for the Sangamon River and its major tributaries from the photos. A supervised land cover classification was used to estimate the percentage forest cover within 100 meters of the channels using ArcGIS version 10.1.

One meter resolution digital imagery was acquired through the National Agricultural Imagery Program (NAIP) of the US Department of Agriculture (USDA) during leaf-off conditions. The Sangamon River and major tributary centerlines were manually digitized. Current land cover information was derived from a 2007 Cropland Data Layer (CDL) derived from the USDA National Agricultural Statistics Service (NASS) and downloaded from the Illinois State Geological Survey Geospatial Data Clearinghouse website. Forested land was composed of National Land Cover Database code 141—Deciduous forest (the revised 2007 CDL incorporates 143—Mixed Forest with 63—Woodland) and code 190—woody wetlands. The area of these land covers was divided by the total riparian buffer area to obtain the 2007 forest cover percentage.

Regressions and statistical analyses

Isotopic mixing models were analyzed with SigmaPlot v 10.0 (Systat Software, Inc). Linear regressions were used to determine slopes and their standard errors, as well as goodness of fit correlation coefficients (r^2) and Pearson p values.

Results and discussion

Sediment accumulation and POC burial

Sediment accumulation rates and lakebed age models were estimated so that the POC burial history could be

Table 2 Lake Decatur sediment accumulation rates

Wet sediment accumulation rates (cm/year)				
Station	Pre-dam surface (1922)	$^{137}\text{Cs}^b$	$^{210}\text{Pb}^b$	Nearest sediment inventory
6				2
8				1
9		≥ 1.5		2.1
10	0.73			0.82
11		0.34	0.35	1.1
12	0.94			1.1
13	0.67 (0.48 ^a)	0.83	0.92	
14		0.64	0.71	
15	0.92			0.93
16	0.77			

^aAccumulation rate between 1922 and 1964

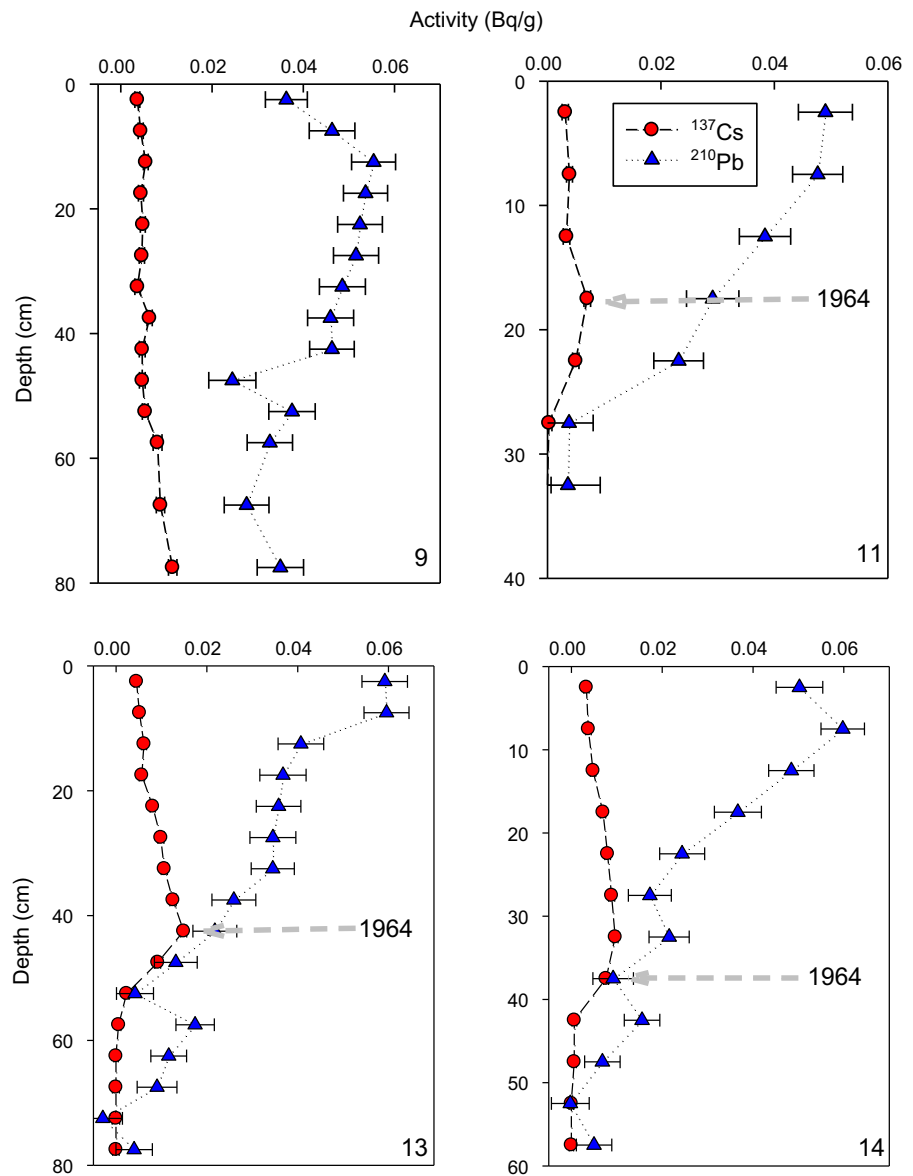
^bStandard deviation = 0.05 cm/year

determined. The average sediment accumulation rate within the lake for the period 1922–1983 was 1.5 cm/year (Fitzpatrick et al. 1987). To best constrain the chronologies within core samples and to evaluate the post-1983 period, station-specific sediment accumulation rates were estimated using multiple approaches described below. Lakebed cross sections developed as part of the sediment inventories by the City of Decatur (Bogner 2001, 2002; Bogner et al. 1984; Fitzpatrick et al. 1987) were used to estimate accumulation rates near the coring stations in this study (Fig. 2). Sediment accumulation was spatially variable in that the original river channel filled most rapidly initially and, as the lakebed levelled, rates became similar between the channel and original floodplain locations. Average accumulation rates of 0.8–2 cm/year were obtained for seven stations using the historical lakebed surveys (Table 2).

Five of the cores collected in 2015 (stations 10, 12, 13, 15, 16) penetrated a sand-rich layer topped by a sand-to-mud transition. The sandy horizon has been interpreted to be a pre-dam surface of the floodplain (Fitzpatrick et al. 1987). Using it as a marker for the year 1922, accumulation rates were ~ 0.7 – 0.9 cm/year (Table 2). Comparisons between this method and the bathymetric survey approach revealed good agreement on a station by station basis.

Radionuclide (^{210}Pb , ^{137}Cs) analyses further constrained accumulation rates in the 2015 cores (Fig. 3).

Fig. 3 ^{137}Cs and ^{210}Pb activities as a function of depth into Lake Decatur sediments. The peak in ^{137}Cs was attributed to atmospheric testing of nuclear weapons that crested in 1964. The best fit linear slope of the ^{210}Pb activities was used to produce an additional estimate of sediment accumulation rate. Station numbers are noted in the bottom right corner of each graph



Peak ^{137}Cs activities are attributed to the atmospheric testing of nuclear weapons with the highest activity pegged to 1963–1964 (Grimley et al. 2017; Robbins and Edgington 1975). Three of the cores (11, 13, and 14) exhibited distinct peaks at depths of 15–45 cm below the lake bed surface. ^{210}Pb decay ($t_{1/2} = 22.2$ years) provides a multi-decade to ~ 100 year integrated accumulation rate (Robbins and Edgington 1975). The radiochemical estimates of sediment accumulation (0.4 to ≥ 1.5 cm/year) were consistent with each other and generally paralleled those obtained by previous methods (Table 2). The rather

large difference between the radiochemical and bathymetric survey estimates for station 11 likely reflects spatial variability in accumulation between the core station and the nearest bathymetric survey transect.

Sufficient information was available to develop relationships between the depth within the lakebed and the approximate time of deposition for many of the stations (9, 11, 13 and 14 are shown in Fig. 4). Average whole core accumulation rates were used for 9, 11 and 14 to generate single-slope linear age models. The presence of both the pre-dam (1922)

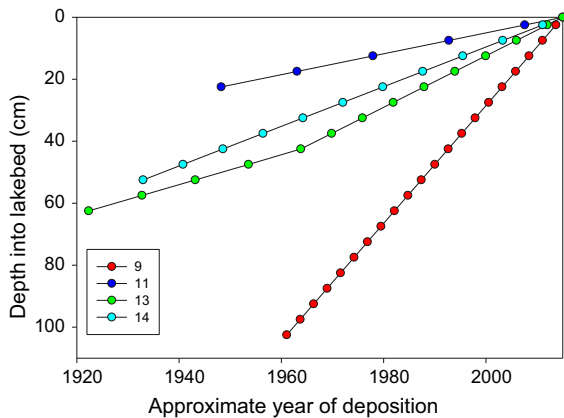


Fig. 4 Age models (depth versus time) for cores used for geochemical measurements. Preferential weight was given to ^{137}Cs data and the presence of a pre-dam surface if intercepted by the core. ^{210}Pb data and local bathymetric surveys typically validated estimates of sediment accumulation rates. Core 13 had both ^{137}Cs and pre-dam surface markers, thus a two-slope model could be constructed

surface and the ^{137}Cs peak allowed a bi-slope linear age model for 13. Age models for other stations with measured accumulation rates (Table 2) are not shown in Fig. 4 because geochemical analyses were not performed on their cores.

Lakebed sediment OC measurements provide a historical perspective on how OC inputs and burial have varied over the lifetime of the reservoir. With two exceptions (stations 1 and 11), OC concentrations were between 2 and 3 percent dry weight (Fig. 5) in surface sediments, which are within the range observed in numerous other reservoirs (Clow et al. 2015; Knoll et al. 2014). Generally, concentrations decreased with depth below the surface of the lakebed (Fig. 5). The largest change in %C with depth occurred in cores that captured the grain-size transition between the pre-dam surface and ~1960s deposition (Fig. 6). This change in carbon content is a grain-size effect whereby high OC contents are associated with fine-grained particles possessing large surface areas per unit volume (Hedges and Keil 1995).

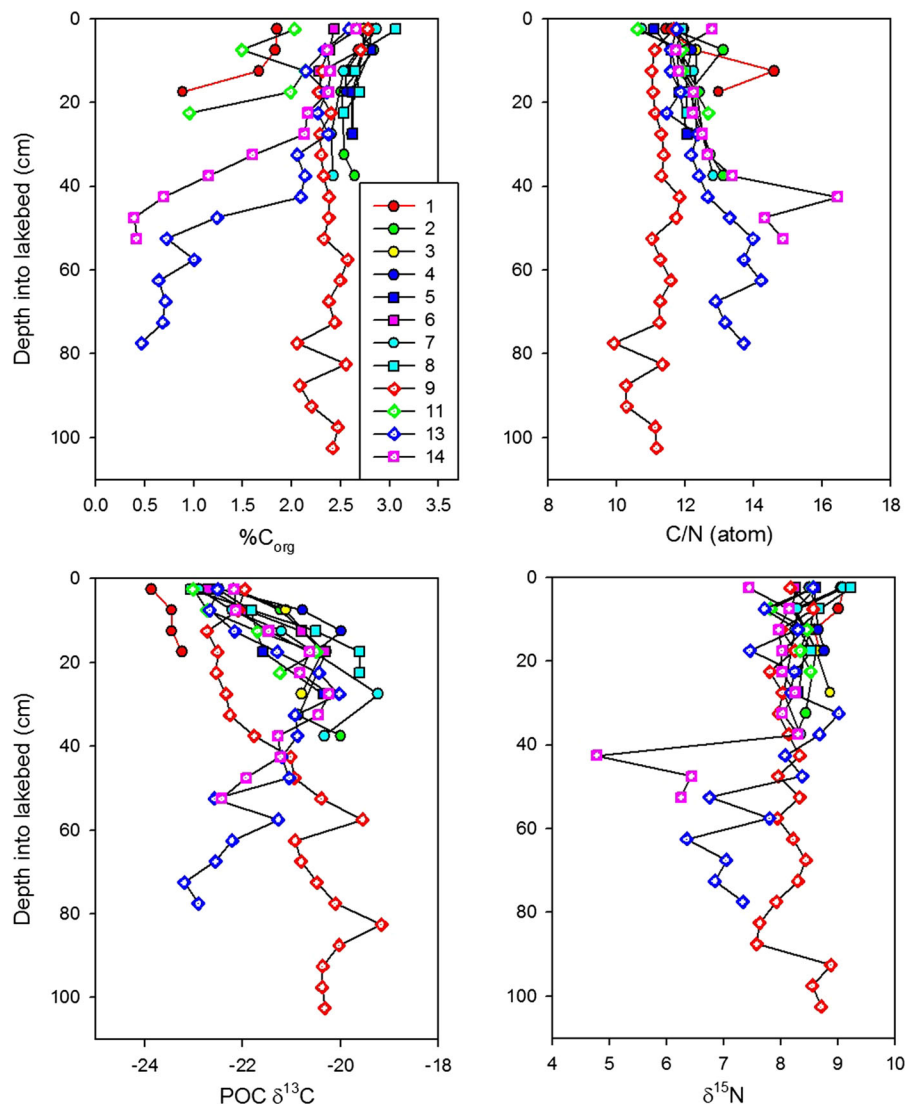
After the transition to mud deposition circa 1960, porosity (as a proxy for grain-size) and %C abruptly stabilized (Fig. 6). The change in sediment caliber corresponded in time with the raising of the water level by the 1956 addition of the spillway gates to the top of the dam. We hypothesize that prior to the addition of the gates, the lakebed at the coring locations was

sufficiently shallow (< 2 m) that it experienced frequent storm-induced resuspension thereby mixing the underlying pre-dam sands with incoming muds. A severe drought in the 1950s further lowered lake levels for several years (Fitzpatrick et al. 1987), which could have exacerbated sediment resuspension and enhanced the potential for winnowing. When the water level was raised, the lakebed fell below the normal wave base, attenuating mixing. Thereafter, accumulation of mud became the dominant sedimentary process. More subtle changes in %C within the muddy post-1960s interval reflect a combination of historical shifts in OC inputs and diagenetic effects associated with the remineralization of the organic matter (Hedges and Keil 1995).

Sediment resuspension is prevalent in shallow reservoirs (Hamilton and Mitchell 1996) and it can have counteracting influences on POC behavior. It both re-oxygenates sediments thereby lowering the efficiency of OC burial (Blair and Aller 2012), and it feeds the transport of sediment and POC to greater depths which could facilitate OC burial. The latter scenario was evident before the Decatur dam was raised in 1956 when shallow water fine sediments were moved to the submerged river channel. Wind speed, fetch and water depth will influence resuspension (Hamilton and Mitchell 1996). Because of the roughly N-S orientation of this narrow waterbody, winds along that axis would have been most effective at sediment resuspension. We can speculate that Lake Decatur was heading to a sedimentary state dominated by resuspension as it filled with sediment over its first three decades. However, the raising of the dam curtailed that trend sending portions of the lake and its C-cycle down a different trajectory as described in subsequent sections.

The evolution of the Lake Decatur bathymetry parallels that seen in many reservoirs (Juracek 2015) and as a result, has implications for how we reconstruct the generic reservoir C-cycle of the past, or predict what may happen in the future with new dam construction. The focusing of OC burial into a significantly narrower area than defined by the whole lake contours during the early life of the reservoir is expected to be a general occurrence. Estimates of C burial, or models that use a C-burial term to drive other processes, that are based on reservoir area will not capture the early behavior of the C-cycle well.

Fig. 5 Biogeochemical parameters ($\%C_{org}$, C/N, POC $\delta^{13}C$, $\delta^{15}N$) as a function of depth from surface in Lake Decatur sediments. The $\%C$ parameter represents the percentage of organic C on a dry weight basis in the soils. C/N ratios are given on an atomic basis. The $\delta^{13}C$ values are for organic C and the $\delta^{15}N$ are for total N. Cores 1–8 were collected in 2014, 9–14 in 2015



The spatial and temporal evolution of particulate organic carbon from soil source-to-reservoir

A watershed and its sedimentary system can be viewed as an integrated network of biogeochemical reactors (e.g., soils and sediments) that mix, process, and export organic matter (Blair et al. 2004). Exported material will have characteristics derived from the sources feeding a particular reactor, the products of reactions within a reactor, and the residence time in the reactor. One consequence of the reactor network model is that lowland-derived material will be more complex in terms of sources of C because it is in part a product of upland sources processed through lowland

reactors (Abban et al. 2016). Alluvium will carry the history of the source sediment overprinted by local conditions. Lake sediments will be overprinted and modified further. Despite the array of contributing sources, downstream materials may appear relatively homogeneous as a result of heterotrophic and physical blending (Blair et al. 2004, 2010).

With this network model in mind, alluvial soils were studied from the dual perspective of being reactors that have captured a history of local and upstream OC sources, and as potential sources of material to downstream sinks. Stream banks were analyzed in an upland region (Saybrook, SB) and in the lower floodplain (Allerton Park, AP). As is

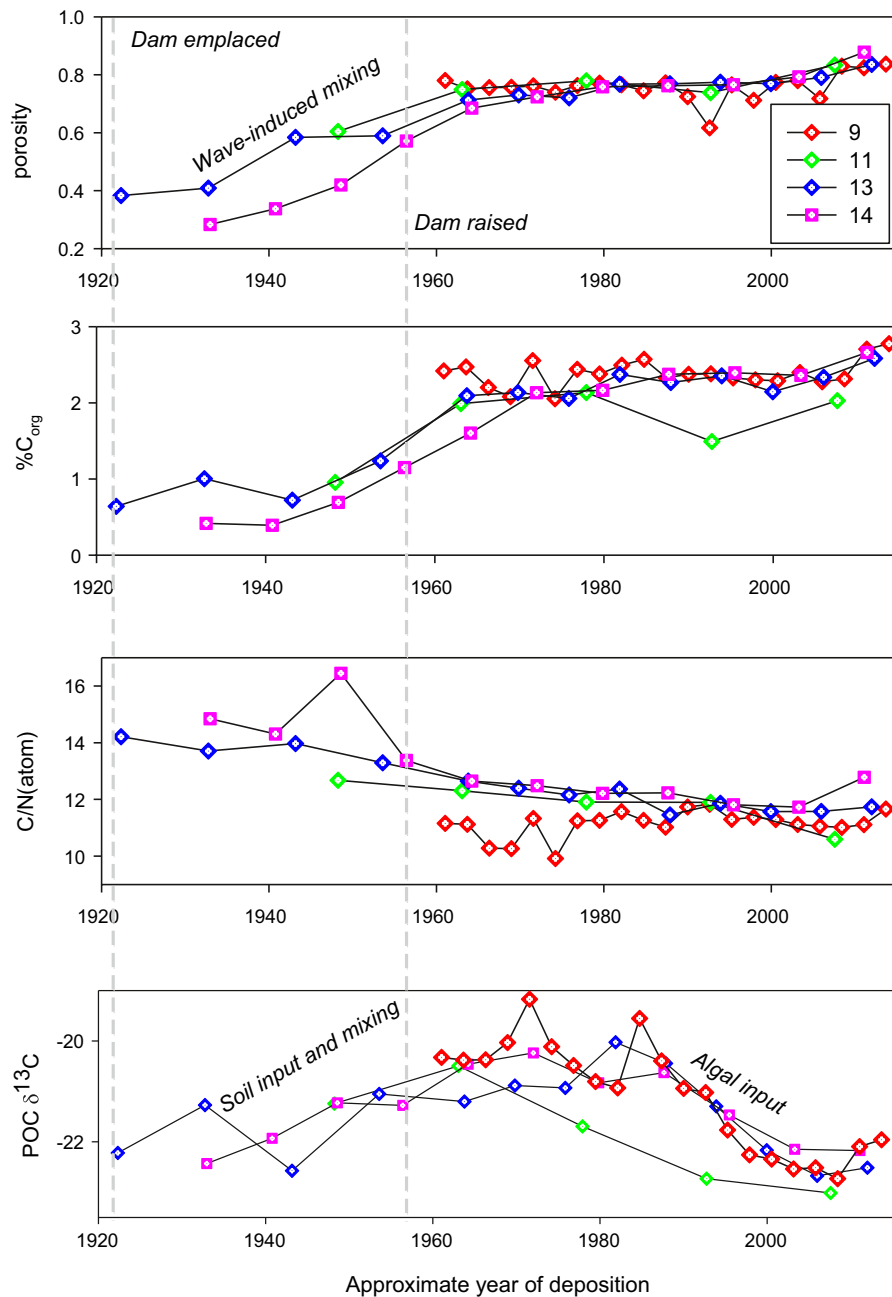
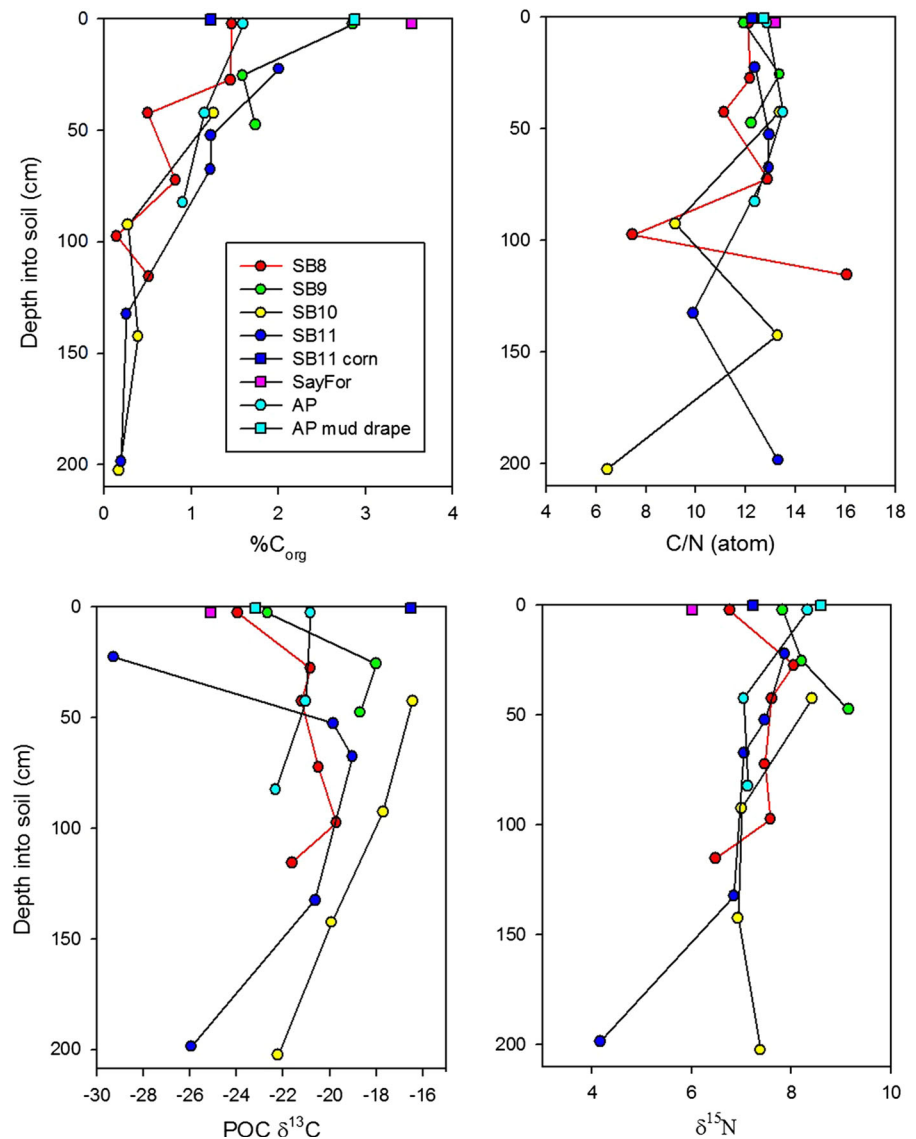


Fig. 6 Sedimentary characteristics (porosity, %C_{org}, C/N, POC $\delta^{13}\text{C}$) as a function of approximate time of deposition. Data from Fig. 5 (plus porosity depth profiles) were transformed to time-dependent profiles using age-models (Fig. 4)

typically seen in soils, organic C contents (%C) decrease with depth from the surface as a result of surface vegetation inputs followed by below-surface degradation (Hedges and Oades 1997; Fig. 7). The organic matter associated with the original alluvial material is masked near the surface by the more

abundant vegetative input. The parent material OC is expected to become more resolvable with depth as one moves further away (down) from the more reactive surficial plant inputs. The biogeochemical profiles thus should be interpreted in part as mixing curves between original OC associated with sediments

Fig. 7 Biogeochemical parameters ($\%C_{org}$, C/N, POC $\delta^{13}C$, $\delta^{15}N$) as a function of depth from surface in exposed stream bank soils. The SB11 corn sample was stover collected from the soil surface in a field. The AP mud drape was a sample of recent undisturbed deposition on floodplain surfaces in the Allerton Park area



arriving at the site and more recently produced OC introduced at the surface during soil development (O'Brien and Stout 1978; Trumbore 2009).

Changes in OC source were evident from the $\delta^{13}C$ values (Fig. 7), which spanned the range for C3 (~ -25 to -35%) and C4 (~ -10 to -13%) plant sources (Farquhar 1983; Farquhar et al. 1989; O'Leary 1981). Whereas most plants utilize C3 pathways, notable C4 plants in this region are corn and some prairie grasses (e.g., Big Bluestem; Teeri and Stowe 1976). In several locations (SB 9–11), $^{13}C/^{12}C$ ratios increased ($\delta^{13}C$ values became more positive) down-profile towards a more C4 plant

signature and then reversed. This signals a transition from a predominantly C3 plant source to a C4 and then back again. The change in the upper 25–100 cm signals a shift from an earlier C4 source to more recent C3 plant inputs. The sites sampled are currently either forested or pastured, thus the changes in soil $\delta^{13}C$ likely indicate a transition in land use. This change from C4 vegetation near the river channel may be reflect the broader practice of incorporating uncultivated buffers between cultivated fields and stream and river channels. Aerial surveys of the Sangamon watershed indicate forested riparian buffers within 100 m of the river and tributary channels increased

from 29% of the area in the 1940s to 43% in 2007 as an example.

The deeper transition appears to predate the post-settlement alluvial deposition (Grimley et al. 2017), thus it may represent a shift first to a C4 grass prairie that was followed by corn cultivation in the middle to late 19th century. Alternatively, corn-derived OC may have leached or mixed to greater depths, thus producing the isotopic gradient (O'Brien and Stout 1978; Trumbore 2009).

In contrast, the downstream Allerton Park site lies within relatively undisturbed forested bottomland that has been designated a U.S. National Natural Landmark (<http://allerton.illinois.edu/>). The modest $\delta^{13}\text{C}$ change with depth into the alluvium ($\sim 1.5\text{‰}$) indicates there have not been major changes in the C3–C4 balance of inputs, which is consistent with the undisturbed nature of this site. The local stream ecosystem is dominated by C3 plants, namely trees as there are no prairie grasses or corn. Even so, the average $\delta^{13}\text{C}$ value of $-21.4 \pm 0.8\text{‰}$ for the AP bank samples signals the presence of a C4 source. This material must have been delivered from upstream and deposited during overbank flooding (Robertson et al. 1999).

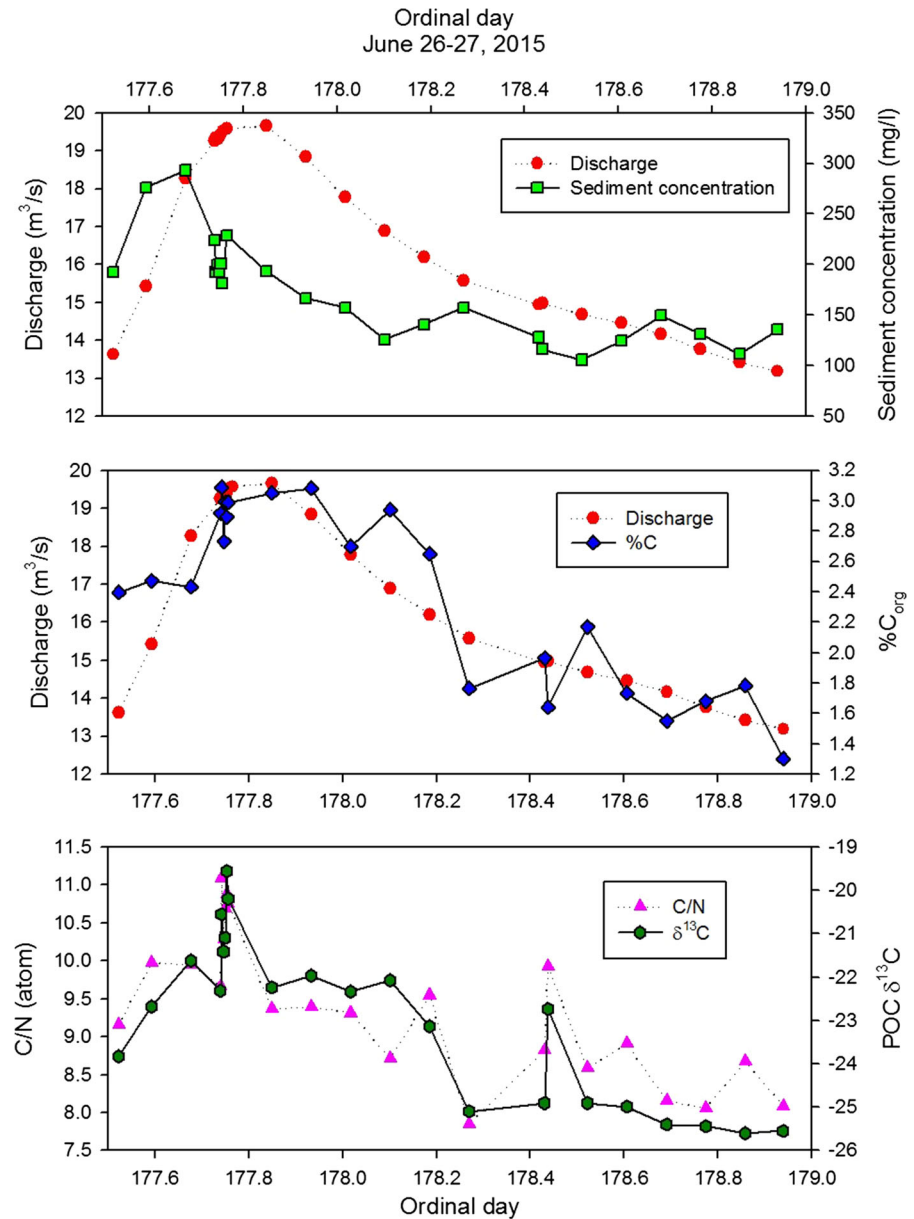
Homogenization of source biogeochemical signatures (e.g. $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, C/N) is a characteristic of watersheds as sediment is deposited, stored and reacted, and then remobilized repeatedly (Blair et al. 2004). While this capability has been appreciated for large river systems, it is poorly documented for POC in small watersheds (Blair et al. 2004, 2010; Olley 2002). With the caveat that our sampling of the downstream region of the Sangamon is extremely limited, the relatively constant $\delta^{13}\text{C}$ values of the AP samples hint that portions of the watershed have a capacity to buffer variability in C-isotopic signatures. Homogenization is indicated also by the C/N ratios and $\delta^{15}\text{N}$ values of both the Saybrook and Allerton Park soils. Both fall within typical soil ranges, but show no obvious systematic change with depth in soil profiles (Fig. 7; Hedges and Oades 1997; Peterson and Fry 1987). Whereas vascular plants display C/N ratios > 20 because of their high lignocellulose content, other sources of OC, including non-vascular plants and microbes, have values in the range of 6–12 (Tremblay and Benner 2006). Soil surface litter thus resembles the plant input and subsurface mineral horizons reflect the heterotrophic processing of the original plant OC.

$^{15}\text{N}/^{14}\text{N}$ ratios are the product of source signatures and the isotope effects associated with N-cycling processes (Amundson et al. 2003; Fox and Papanicolaou 2008). Homogenization of $\delta^{15}\text{N}$ values in soils and sediments results from the continual cycling of N that can ultimately replace source signatures with that of the diagenetic processes, such as denitrification, given sufficient time (Amundson et al. 2003). The implication for Lake Decatur and reservoirs in general is that range of values for potential biogeochemical signals of fluvial inputs is substantially narrowed by watershed processing.

Riverine sediments are an integrated product of catchment-wide erosional, depositional and transport processes that can vary with time and discharge (Gellis 2013). There has been substantial study of the behavior of fluvial sediments in response to rapid changes in discharge associated with storms (Gellis 2013 and references within), but the moderate to high-frequency behavior of POC has been investigated only in steep-sloped, mountainous terrains (Jeong et al. 2012; Jung et al. 2012). Suspended sediments were collected from the Upper Sangamon through a storm event in June 2015 with the goal of evaluating the sources and behavior of the POC exported to the lake in what is a low-gradient landscape. Even though the specifics of the observations are anticipated to vary between events and locations in the Sangamon, the information gleaned from this one event does provide insight into the behavior of exported OC.

The concentration and composition of particulate OC were sensitive to the hydrograph. Suspended sediment concentrations peak just prior to maximum discharge (Fig. 8). Similar early flushes of sediment have been observed in other systems and are thought to be derived from in-channel sources (Gellis 2013). Particulate OC concentrations (as %C dry weight of the sediment) crest at or slightly after peak discharge thus the early flush sediment is OC-poor in comparison. The OC-poor sediment is hypothesized to originate from material derived from the channel banks (Fig. 7). Saturated banks may fail upon the loss of retaining pressure during the falling limb of a storm event (Simon et al. 2000) thus providing a source of early flush sediment for a subsequent event. This same material may be the origin of non-surface-derived sediment detected in other Midwestern river and stream beds using ^7Be and ^{210}Pb distributions (Gellis et al. 2017).

Fig. 8 Suspended load characteristics as a function of time through a storm event. Samples were collected at stream location noted in Fig. 1. Sediment concentration peaks before discharge as stored sediment is flushed out of the system. $\%C_{org}$, C/N and POC $\delta^{13}C$ more closely track discharge, reflecting an evolution of sediment sources. The correlation of C/N and $\delta^{13}C$ indicate pulses of C4 plant (corn) debris into the stream, which provides a tracer for surface erosion



At peak discharge, overland flow transporting more OC-rich material from surface soils increased in importance. An increase in both $\%C$ and C/N ratio during peak discharge reflected an influx of material richer in plant debris (Fig. 8). The $\delta^{13}C$ values became more positive with higher C/N ratios, which suggests the plant debris has a corn-derived component. A small increase in POC $\delta^{13}C$ with discharge was noted in weekly measurements in the Schwabach River,

Germany, which was attributed to corn cultivation as well (Lee et al. 2017).

We conclude that at least two different sources of OC are observed that become time-resolved within the event. One is derived from surface soils containing variable amounts of corn-derived C (high $\%C$, C/N, $\delta^{13}C$) and the other contains more degraded OC bound to subsurface soil particles (low $\%C$, C/N). This second source is consistent with material from bank alluvium. Other studies, in both low- and high-

gradient environments, have identified the same two general sources with the surface material containing fresher (younger) organic matter and requiring a higher threshold for erosion as seen here (Gellis et al. 2017; Jeong et al. 2012; Jung et al. 2012; Rowland et al. 2017). For this one storm event, the flux-weighted $\delta^{13}\text{C}$ of the POC exported as suspended load past the sampling site was $\sim -22\text{‰}$. This value is not substantially different from the AP alluvial deposits (Fig. 7) thus we conclude that it is representative of what is transported through the lower reaches of the Upper Sangamon even though some variability is expected among events.

Our conclusions about the sources of OC differ somewhat from those reached concerning the bulk suspended sediment in the Sangamon River (Neal and Anders 2015; Yu and Rhoads, in press). Multi-tracer fingerprinting suggests that the suspended load is derived from sources near the channel such as floodplain pasture surfaces and channel banks. This does not contradict the OC story in which the surface source has a corn-derived component however and in fact illustrates a potential danger in relying heavily on OC characteristics as a quantitative sediment tracer. OC concentrations vary by over an order of magnitude among sources as seen in the bank profiles (Fig. 7). This means that OC measurements of suspended load sediments can be biased towards OC-rich sources, such as soil surface litter, and insensitive to OC-poor materials such as subsurface bank deposits. Plant debris with its lower density ($d < 1.8 \text{ g cm}^{-3}$) and settling velocity (Leithold et al. 2005) has the potential to be transported further than bulk inorganic sediments ($d \sim 2.5 \text{ g/cm}^3$). The OC and bulk sediment observations can be reconciled simply if plant litter and/or OC-rich soil aggregates are transported to the channel from a greater distance than the bulk sediment yet comprise a relatively small proportion of the total sediment. It can also be reconciled by the observation that not all agricultural fields in the watershed possess riparian buffers and instead directly border waterways.

Lake Decatur sedimentary OC $\delta^{13}\text{C}$ values fell between ~ -19 and -23‰ with some discernable trends with depth into the lake bed (Fig. 5). The $\delta^{13}\text{C}$ values bracket the expected isotopic composition of the riverine OC thus suggesting that the fluvial source has dominated POC inputs for much of the lake history. Based on first principles, the observed $\delta^{13}\text{C}$ variations could be driven by some combination of

variability in riverine signature, OC sources within the lake, and lake bed processes. The most pronounced gradient in $\delta^{13}\text{C}$ value occurred prior to circa 1960 which raises the possibility that it is associated with the changing sedimentation patterns over that time period. We hypothesize that the isotopic gradient is a mixing profile of OC sources derived from local coarse-grained materials (C3 plant debris) and incoming soil-derived suspended load (Figs. 5, 6). The C3 POC is inferred to have been plant debris from the shore and/or material that was submerged when the river valley was flooded. The relatively shallow conditions for parts of the lakebed that prevailed between the 1920s to approximately 1960 allowed wave-driven mixing of the lakebed sediments via resuspension-deposition cycles that in turn drove the mixing of POC sources.

The raising of the dam in 1956 effectively slowed down the mixing process at the sample stations and the lakebed settled into an accumulation-dominated mode. Lake sediment POC $\delta^{13}\text{C}$ reversed its temporal trend and moved towards more negative values between ~ 1970 and present (Fig. 6). This behavior does not track watershed-wide changes in crop cultivation when corn acreage and % corn cultivated increased (not shown; Keefer and Bauer 2011). An expected contributor of POC was eutrophication from fertilizer run-off (Borah et al. 2002). Fertilizer application rates increased rapidly in Illinois and presumably within the watershed between 1960 and 1980 and thereafter have remained at high levels (Fig. 9; Keefer and Bauer 2011). Lacustrine planktonic OC $\delta^{13}\text{C}$ values are highly variable in general (e.g., -23 to

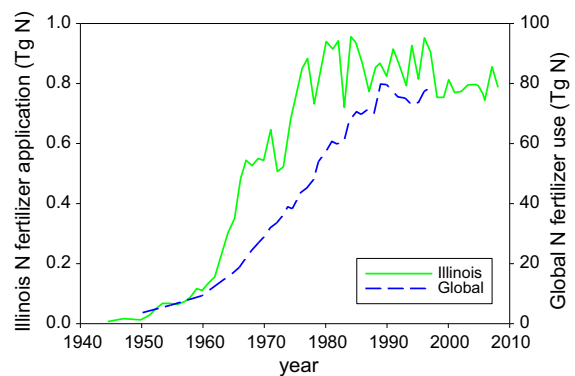


Fig. 9 Industrial N-Fertilizer application in Illinois and globally as a function of year (adapted from Keefer and Bauer 2011; Galloway 1998)

– 36; Francis et al. 2011) but are typically reflective of C3 photosynthetic sources (Peterson and Fry 1987). The carbon isotopic shift thus likely captured the eutrophication of the lake. In addition, the growth of forested riparian buffer area between 1940 and 2007 was predicted to have contributed to the isotopic shift by filtering surface soil erosion from agricultural fields. This would have reduced the surface soil source to the river and diluted its C4 C-isotopic signature with a C3 plant component. The AP site C-isotope record indicates that this effect is small however. Insofar as the riparian buffers are concentrated along the lower gradient portions of the river and not in the uplands where much of the corn is planted, it appears they are ill-placed to intercept the C4 signal.

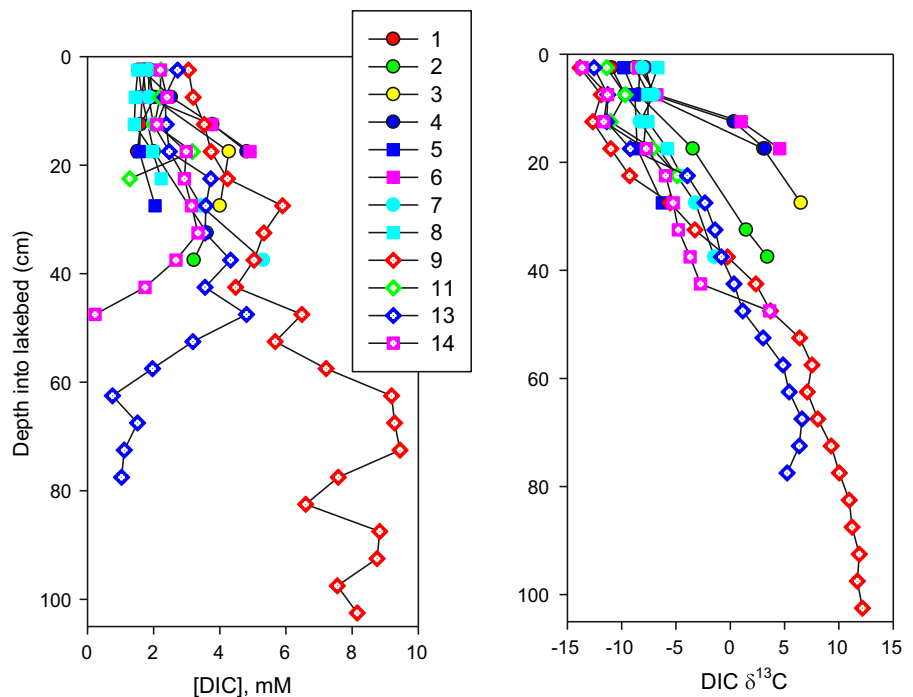
The succession of anticipated POC sources (drowned plus local, fluvial, and autochthonous primary production) has been seen in other reservoirs within agriculturally impacted watersheds (Dietz et al. 2015). World-wide industrial N-fertilizer application has paralleled that in the Upper Sangamon with a rapid increase post-1950s (Fig. 9; Galloway 1998). Rapid soil erosion was initiated almost a century earlier in the Midwest (Dietz et al. 2015; Grimley et al. 2017) and far earlier elsewhere in the world. This means that the sequence of eroded soil inputs followed by eutrophication should be ubiquitous for those reservoirs within impacted watersheds created prior to the ~ 1960s. Using indices for either river fragmentation (RFI) or flow regulation (RRI; Grill et al. 2015), one estimates that approximately one third to a half of reservoirs world-wide are of the appropriate age to have captured the OC source succession.

The succession of OC sources has implications for global C budgets. Erosional loss of soil C has been argued to be either a source of CO₂ to the atmosphere (Lal 2003) or a sink (Berhe et al. 2007; Smith et al. 2005; Wang et al. 2017). Whereas the disturbance of surface soils by cultivation disrupts organic C protective mechanisms, such as particle aggregation, and thereby leads to remineralization of organic matter to CO₂; loading of newly exposed C-poor subsurface soils with organic C is a removal mechanism for CO₂ (Harden et al. 1999). The Lake Decatur results and those from other reservoirs (Clow et al. 2015; Downing et al. 2008; Maavara et al. 2017; Mendonça et al. 2017; Smith et al. 2005) indicate that some of this loading can occur in reservoirs as a result of eutrophication. Reservoir sedimentation is a significant sink

for eroded soils and organic C (Syvitski et al. 2005), especially in lakes where trapping efficiencies can approach 100% (Brune 1953). Lake Decatur's trapping efficiency was 74–80% for the period 1922–1983 (Fitzpatrick et al. 1987) and its current ability to retain sediment is not expected to differ appreciably. Lake Decatur's contribution to the Sangamon watershed's net C-budget is thus potentially high. OC depositional rates range between 30 and 180 g C/m²/year based on surface (0–5 cm) OC contents and respective sediment accumulation rates. Lake Decatur falls well within the range of the most recent estimates of global reservoir OC accumulation rates, 63–239 g C/m²/year (Mendonça et al. 2017) but is on the low side of estimates for eutrophic reservoirs (148–17,392; Downing et al. 2008). The studies employed a variety of empirical and modeling approaches to determine the OC accumulation rates and they emphasized different groups of reservoirs thus the difference in range is methodological in origin. The extremely high C-accumulation rates are associated with the small agricultural lakes and ponds and these are not typically included in global budgets (Downing et al. 2006).

Using the mean whole lake sediment accumulation rate (1.5 cm/year) and the mean OC concentration (2.6%), approximately 1.9×10^6 kg C are delivered to the lakebed per year. This amount includes both watershed-derived material and in-lake production. These estimates do not include inputs that are rapidly remineralized at the lakebed surface and thus are not detected by the OC measurements. More comprehensive C-inventories of the soils, sediments and river are required throughout the watershed before a quantitative conclusion can be reached concerning whether the whole system is a net source or sink of CO₂ to the atmosphere. For instance, large burial fluxes of C-poor or C-rich sediments in post-settlement alluvial deposits or lakes could tip the system into either source or sink mode. However, the available evidence suggests that the Sangamon watershed is a net sink given the sediment trapping efficiency of Lake Decatur and the organic C content of the buried sediments. This serves as an example that continued eutrophication of reservoirs has the potential to tip the world's eroding landscapes to being net C-sinks (Downing et al. 2008; Maavara et al. 2017; Smith et al. 2005).

Fig. 10 Porewater concentrations and $\delta^{13}\text{C}$ of dissolved inorganic carbon (DIC) as a function of depth in Lake Decatur sediments. Concentrations typically increase with depth as microbially respired DIC is added to the porewater pool during burial. The exception is when the pre-dam surface is approached in which case the decrease in concentration with depth may reflect losses that occurred during resuspension events. $\delta^{13}\text{C}$ values initially become more negative with the addition of the respired DIC, then become more positive as a result of methanogenesis



The remineralization of POC to DIC and CH_4

A portion of the organic matter delivered to the lakebed was oxidized to DIC that in turn accumulated to concentrations approaching 10 mM as sediment parcels were buried (Fig. 10). The brownish coloration of sediments and the presence of animal burrows in the upper ~ 5 cm indicated an oxic-suboxic state of the surface sediments. The presence of black mottling as shallow as 3–4 cm in some cores were evidence of iron and sulfate reduction. Methane was ubiquitous below 5–10 cm as observed by the presence of bubbles and subsequently confirmed and quantified by gas chromatography (Fig. 11). The downcore transition to pre-dam surfaces that lacked abundant organic C led to a large drop in DIC concentration at depth in cores 11, 13, 14.

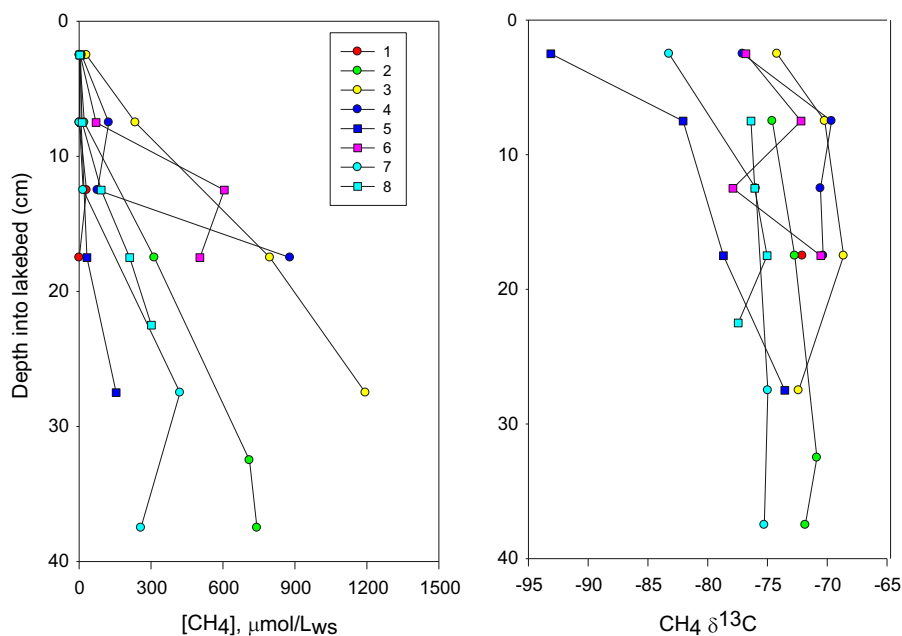
Methane bubble formation smeared its concentration and $\delta^{13}\text{C}$ profiles (Fig. 11), thus obscuring zones of production. Porewater DIC $\delta^{13}\text{C}$ profiles were less impacted by bubble formation and thereby provide more information on remineralization processes as a function of depth into the lakebed. CO_2 generated via non-methanogenic processes tends to have $^{13}\text{C}/^{12}\text{C}$ ratios similar to the source organic C (Blair et al. 1985; Boehme et al. 1996). Methanogenesis in contrast

exhibits a large carbon isotope effect such that ^{12}C -enriched material enters the methane stream. The residual ^{12}C -poor carbon flows to the DIC pool. As a result, pronounced ^{13}C -enrichment (more positive $\delta^{13}\text{C}$) of the DIC was evident below 10 cm depth in some cores (e.g., 3, 4, 5). In others, the increase in $\delta^{13}\text{C}$ was more gradual. The differences in isotopic gradient reflect the contribution of methanogenesis to DIC production relative to other processes that influence the DIC pool. A C-isotope mass balance model can be used to estimate the relative flow of remineralized C to either methane or DIC (Blair 1998; Vinson et al. 2017). The mass balance constraint is:

$$\delta^{13}\text{C}(\text{remineralized C}) = f_{\text{CH}_4}\delta^{13}\text{C}(\text{CH}_4) + (1 - f_{\text{CH}_4})\delta^{13}\text{C}(\text{DIC}) \quad (1)$$

where f_{CH_4} is the fraction of C that goes to methane. For the purpose of these calculations, the $\delta^{13}\text{C}$ of the remineralized C was assumed initially to be similar to the bulk POC fraction. The mean of sedimentary POC values, $-21.4 \pm 1.1\text{‰}$, was used. The $\delta^{13}\text{C}$ of methane was obtained from the sedimentary profiles. Methane bubbles homogenized the gas at depths below 5 cm, thereby making it easier to obtain an average $\delta^{13}\text{C}$ value of the methanogenic zone. The

Fig. 11 Methane concentrations and $\delta^{13}\text{C}$ values as a function of depth in the lakebed. Concentrations increase as a result of methanogenesis. $\delta^{13}\text{C}$ values are largely homogenized below 10 cm depth by bubble formation and release



average methane $\delta^{13}\text{C}$ value from below 5 cm depth was $-73.4 \pm 2.8\text{‰}$ (Fig. 11). To determine the $\delta^{13}\text{C}$ of the DIC produced in the lakebed below 5 cm, a mixing model was used:

$$c_{\text{tot}}\delta^{13}\text{C}(\text{total DIC}) = c_{\text{prod}}\delta^{13}\text{C}_{\text{prod}} + c_{\text{bkgrd}}\delta^{13}\text{C}_{\text{bkgrd}} \quad (2)$$

and

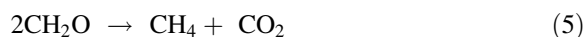
$$c_{\text{tot}} = c_{\text{prod}} + c_{\text{bkgrd}} \quad (3)$$

The DIC concentrations for the observed total pool (c_{tot}) were assumed to be a mixture of the DIC produced in the lakebed below 5 cm (c_{prod}) and a background component inherited from the overlying sediments (c_{bkgrd}). The corresponding $\delta^{13}\text{C}$ values were similarly identified. Eqs (2) and (3) were rearranged to provide

$$c_{\text{tot}}\delta^{13}\text{C}_{\text{tot}} = c_{\text{tot}}\delta^{13}\text{C}_{\text{prod}} + c_{\text{prod}}(\delta^{13}\text{C}_{\text{prod}} - \delta^{13}\text{C}_{\text{bkgrd}}) \quad (4)$$

The slope of the linear regression relation between c_{tot} and $c_{\text{tot}}\delta^{13}\text{C}_{\text{tot}}$ is equivalent to $\delta^{13}\text{C}_{\text{prod}}$ (Blair et al. 2010). Using data for depths below 5 cm, and above the basal sandy transitions (core 1 was excluded), an average value of $\delta^{13}\text{C}_{\text{prod}} = +14.7 \pm 1.2\text{‰}$ ($r^2 = 0.72$, $p < 0.0001$) was obtained. Using this

value in Eq. (1), f_{CH_4} was 0.41 ± 0.03 . Given that the average stoichiometry of the methanogenic process is



methanogenesis was responsible for $82 \pm 6\%$ of the OC remineralization below 5 cm. This is consistent with the observation that methanogenesis dominates OC remineralization in lakes (Gruca-Rokosz and Tomaszek 2015; Murase and Sugimoto 2001). The effect of the assumption that the $\delta^{13}\text{C}$ of the remineralized C was similar to that of the bulk C was tested by substituting a mid-range value for lacustrine phytoplankton (-29‰) for that term. This is a plausible scenario because the algal C pool may be preferentially reacted. In doing so, one estimates that methanogenesis was responsible for 98% of the POC degradation below depths of 5 cm, thus the conclusion that OC degradation was facilitated primarily via methanogenesis is unchanged.

Establishing a relationship between methane production rate and environmental parameters, such as OC burial flux, is difficult to do using methane concentrations because of low solubility of methane and its facile formation of bubbles. These promote rapid loss of gas from the sediments by ebullition (Maeck et al. 2013). Porewater methane concentrations correlated strongly with DIC $\delta^{13}\text{C}$ (Fig. 12)

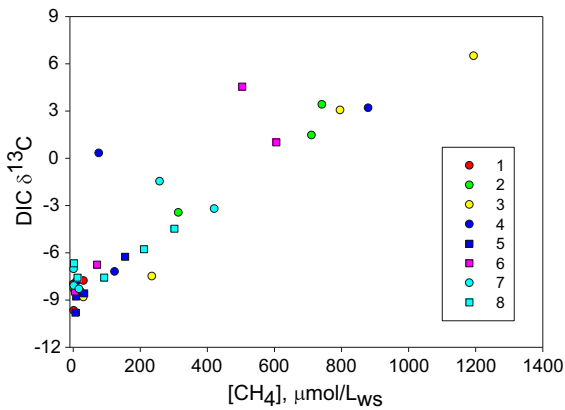


Fig. 12 Porewater DIC $\delta^{13}\text{C}$ values versus methane concentrations. As expected, the more methane produced in the lakebed, the greater the ^{13}C -enrichment in the DIC. Deviations in the relationship are most consistent with methane loss via ebullition, either natural or during core recovery and subsampling

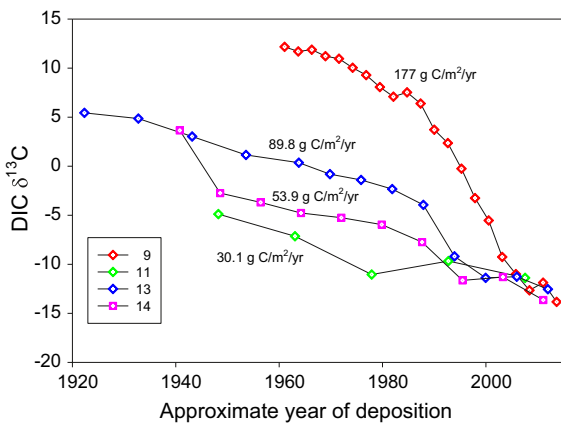


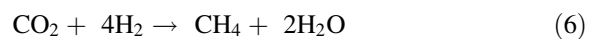
Fig. 13 Porewater DIC $\delta^{13}\text{C}$ values as a function of approximate deposition time of the sediment. The numbers by each set of core results are OC accumulation rates in $\text{g C/m}^2/\text{year}$. Greater DIC ^{13}C -enrichment occurs under conditions of more rapid OC burial because the delivery of OC drives methanogenesis

because of the linkage between methane production and ^{13}C -enrichment of the DIC. The outlier data have lower methane concentrations than expected for the corresponding DIC $\delta^{13}\text{C}$, which is expected with the periodic ebullitive loss of gas. DIC $\delta^{13}\text{C}$ values thus appear to be a more stable proxy for time-integrated methane production. Combining the DIC $\delta^{13}\text{C}$ depth profiles with the sediment column age models, one can visualize differences in apparent methanogenic rate between stations (Fig. 13). Net ^{13}C -enrichment over

time ($\Delta\delta^{13}\text{C}/\Delta t$) increases with OC accumulation rate as would be predicted if OC burial drives methanogenesis. Methane ebullition has been correlated with sediment accumulation rate (Maeck et al. 2013) further establishing the link between OC burial and methane production and emissions in reservoirs (Sobek et al. 2012).

Just as sedimentation and OC deposition have evolved over the lifetime of Lake Decatur, so must have methanogenesis. The highest rates of methanogenesis was focused in portions of the lake where sediment accumulated rapidly, such as locations within the original river channel (station 9) and at the mouth of an inflowing creek (station 6). Diagenesis in these locations can be viewed as a quasi-steady state conveyor-belt like process where sediment parcels accumulate methane and DIC as they are buried. In contrast, methanogenesis would have been inhibited and/or interrupted by periodic resuspension events in shallow water ($< 2\text{ m}$) flanking areas during the early decades of reservoir life. Approximately 56% of the lakebed was at water depths $> 2\text{ m}$ prior to 1956 (Fitzpatrick et al. 1987) and thus able to sustain methane production. Once the water level was raised by approximately 1 meter in 1956, mixing became less pronounced and the lakebed in some areas settled into an accumulation-dominated mode. This condition would have allowed steady methane production to spread to about 67% of the lakebed area. The observation that methanogenesis is focused towards the in-filled river channel, especially at the stage when allochthonous inputs dominate, is predicted to be a general feature of many reservoirs.

The average $\delta^{13}\text{C}$ of the sedimentary methane, $-73 \pm 3\text{‰}$, was more negative than what has been frequently seen in lakes (Conrad et al. 2009; Gruca-Rokosz and Tomaszek 2015; Itoh et al. 2017; Rinta et al. 2015), though similar to the oligotrophic Lake Biwa (Murase and Sugimoto 2001). The isotopic composition of methane is dependent on the pathway of production (Whiticar et al. 1986). Methane is produced via two dominant biochemical pathways in most sedimentary systems, CO_2 -reduction (Eq. 6) and acetate dissimilation (Eq. 7):





The asterisked methyl group in acetate is preferentially converted to methane (Buswell and Sollo 1948; Zeikus 1983). CO₂-reduction expresses a larger isotope effect (i.e., the methane is more depleted in ¹³C relative to the methanogenic substrate) as a result of a larger fractionation factor (α or ¹²k/¹³k) and much larger substrate (CO₂ or acetate) pool size that attenuates the closed system effect (Blair et al. 1993). Consequently, methane $\delta^{13}C$ values are often used to identify the dominant pathways of production (Conrad et al. 2009; Gruca-Rokosz and Tomaszek 2015; Murase and Sugimoto 2001; Whiticar et al. 1986). The isotopic mass balance model can be expressed as:

$$\delta^{13}C \text{ (methane)} = \delta^{13}C \text{ (substrate)} - (1 - f_{CH_4})(\alpha_{CH_4} - \alpha_x)1000 \quad (8)$$

where α_{CH_4} is the fractionation factor for methanogenesis, and α_x is the fractionation factor for processes competing for the methanogenic substrate, which could include oxidation and transport away from the reaction zone. The simple formulation offered by Eq. 8 requires a steady state assumption (Blair et al. 1985; Hayes 1993).

The fractionation factor, α_{CH_4} , provides a constraint on the dominant methanogenic pathway. The CO₂-reduction pathway typically exhibits a significantly larger α_{CH_4} (1.05–1.07) than acetate dissimilation (1.01–1.03; Blair et al. 1993; Blair and Carter 1992; Conrad et al. 2012). Using values from Lake Decatur ($\delta^{13}C$ (methane) = −73.4, $\delta^{13}C$ (substrate) = −21.4, and f_{CH_4} = 0.41) in Eq. 8, ($\alpha_{CH_4} - \alpha_x$) is found to be 0.088. Adjusting the values for the assumption that the remineralized OC is algal-derived (−29%, f_{CH_4} = 0.46), one obtains 0.084. Assuming α_x = 1.00, a minimum value for α_{CH_4} must be 1.088 (or 1.084), which is most consistent with CO₂-reduction. This seemingly contradicts the often-held assumption that acetate dissimilation is the dominant process in freshwater systems (Whiticar et al. 1986). That assumption may be overgeneralized however (Avery and Martens 1999) or some aspect of the isotopic model may be in error (Vinson et al. 2017). As an example, the biosynthesis of ¹³C-depleted acetate via homoacetogens employing the pathway



which has its own a kinetic isotope effect (Gelwicks et al. 1989) could reconcile the apparent contradiction. The use of ¹³C-depleted acetate in acetate dissimilation (Eq. 7) would contribute to the large ¹³C-depletion of the methane. This scenario requires the acetogens to compete successfully for H₂ within the methanogenic zone. Elevated H₂ levels appear to favor acetogens (Fu et al. 2018; Heuer et al. 2010). The warming of sediments during spring and early summer, which is when our samples were collected, increases fermentation rates. This situation can create a favorable environment for acetogens, albeit temporarily, if H₂ consumption by CO₂-reducing methanogens initially lags H₂ production (Alperin et al. 1992; Fu et al. 2018; Heuer et al. 2010; Hoehler et al. 1999). The anomalous methane $\delta^{13}C$ thus may be a seasonally ephemeral phenomenon signaling an adaptation by the microbial ecosystem to non-steady conditions as has been hypothesized for the methanogenic marine setting, Cape Lookout Bight, NC (Alperin et al. 1992; Martens et al. 1986). Regardless of actual reason, the methane $\delta^{13}C$ values indicate that the classic assumptions about the anaerobic biogeochemical pathways and their isotope effects are not adequate for this and perhaps other freshwater systems.

Conclusions

The damming of streams and rivers has impacted the C-cycle on a global scale because millions of human-constructed reservoirs act as hotspots for OC burial and methane production. Estimating the respective fluxes, as well as projecting the responses of the reservoir C-cycle to future land use and climate change, will require models to extrapolate the observations from a small number of systems to a global scale. Process-driven models are required because reservoirs evolve as a function of age. The results from this study illustrate the interrelationships of watershed and reservoir processes on lacustrine C-biogeochemistry and can be used to enlighten the process-driven models.

Land use that promotes rapid soil erosion will substantially alter small reservoir bathymetry by rapidly supplying in-fill sediment. The original river

channel serves as the depocenter for sediment and organic C initially. Over time as the channel is filled, net deposition spreads over a wider area of the lake floor. Methanogenesis follows OC burial patterns in general, i.e., high OC burial rates promote greater methane production. However, water depth can also be a factor controlling methane formation. Shallow lake bed areas that reside at depths less than the storm-induced wave base will see inhibited or interrupted methane production. Reservoir management practices that raise or lower water levels are expected to influence methane production and release (Deemer et al. 2016).

Flooded vegetation and organic debris are among the first sources of OC in a new reservoir (Barros et al. 2011; Deemer et al. 2016). For locations where the pre-dam surface was sampled in Lake Decatur, the original OC contribution was modest compared to subsequent inputs. This material was detrital in nature and derived from C3 plants. Flooded OC was likely to be more important close to shorelines where vegetation is encountered.

Corn cultivation provided a clear tracer and proxy for watershed-derived OC because of its distinctive C4-plant $^{13}\text{C}/^{12}\text{C}$ ratio. The corn isotopic signature was attenuated as particulates move through the system because of mixing with, or replacement by, other sources of OC. Even so, the delivery of sediment to Lake Decatur by soil erosion was evident from the biogeochemical data. Soil-associated organic matter dominated the organic C buried in the lake bed for approximately the first 50 years of reservoir life.

Fertilizer applications to agricultural landscapes soared post-1960s in the Sangamon and worldwide (Galloway 1998). The resulting eutrophication thus provided a third source of OC to sediments. The sequence of soil OC followed by algal input should be ubiquitous for reservoirs older than ~ 50 –60 years in agricultural watersheds. This has several implications for the global C-cycle. The eutrophication of reservoirs, with the subsequent loading of algal C on sediments derived from soil erosion, may have tipped agricultural landscapes into being a net sink of C from the atmosphere even though there is loss of C from surface soils. Eutrophication also is hypothesized to preferentially drive methane production because of the anticipated greater reactivity of locally produced algal OC (Blair and Aller 2012; Deemer et al. 2016; West et al. 2015). Regulating the relative and absolute rates

of allochthonous and autochthonous inputs should influence the production and release of the greenhouse gas. The regulation would start in the watershed with nutrient management and erosion controls (Borah et al. 2002).

DIC and methane are the terminal products of OC remineralization. The large kinetic C-isotope effect associated with methanogenesis leaves an unambiguous imprint on the porewater DIC $\delta^{13}\text{C}$ value making it a sensitive proxy for biogenic methane formation. The upper 5 cm of the lakebed appears to be dominated by non-methanogenic processes based on porewater DIC $\delta^{13}\text{C}$ values and visual observations. Methanogenesis is the primary process below 5 cm. The magnitude of the C-isotope effect is most consistent with the CO_2 -reduction pathway of methanogenesis. This contradicts the common assumption that acetate dissimilation is the dominant pathway in freshwater environments (Whiticar et al. 1986). One hypothesis is that the shift in pathway is a seasonal phenomenon similar to what has been seen in a marine setting (Alperin et al. 1992, 1993). Time-series monitoring across seasons would be needed to test the hypothesis. The isotopic observations illustrate that reservoir methanogenic processes cannot be assumed to follow what may be an over-simplified freshwater paradigm.

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Compliance with ethical standards

Conflict of interest The authors declare they have no conflict of interest.

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