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Dynamics in Intensively Managed Landscapes: Water, Sediment, Nutrient, Carbon, and Ecohydrology

Key Points:

- Nutrients in lakebed sediments increased longitudinally along an agricultural reservoir due to higher clay and organic matter deposition downstream
- Reservoir sediments in intensively managed landscapes act as overall sinks for excess N inputs over both annual and decadal timescales
- Sediments in agricultural reservoirs are short-term sinks and long-term sources for P contamination

Supporting Information:

- Supporting Information S1

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Sediments in Agricultural Reservoirs Act as Sinks and Sources for Nutrients over Various Timescales

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Abstract Reservoirs along rivers have the potential to act as nutrient sinks (e.g., denitrification and sedimentation) or sources (e.g., decomposition and redox changes), potentially reducing or enhancing nutrient loads downstream. This study investigated the spatial and temporal variability of water and lakebed sediment chemistry for an agricultural reservoir, Carlyle Lake (Illinois, U.S.), to assess the role of sediments as nutrient sinks or sources. Samples were collected across the reservoir over a 2-year period. We measured N- and P-species in water at the sediment-water interface, in sediment porewaters, and loosely bound to sediment exchange sites. Total N, total P, total C, organic matter, Fe, Mn, and grain size were measured in bulk sediments. We observed a strong gradient in sedimentary total N, total P, total C, organic matter, and metals along the reservoir, with the lowest concentrations at the river mouth and the highest concentrations near the dam. Additionally, we did a long-term nutrient mass balance using historical water quality data for streams entering and exiting the reservoir and the reservoir itself. Mass balance calculations showed that Carlyle Lake, on average, removed 2,738 Mg N/year and released 121 Mg P/year over the multidecadal observation period. While N was consistently removed from the system over time, P was initially stored in, but later released from, the reservoir. The subsequent release of legacy P from the reservoir led to higher outgoing, compared with incoming, P loads. Thus, reservoirs in intensively managed landscapes can act as sinks for N but sources for P over decadal timescales.

1. Introduction

The availability of nutrients, such as N and P, typically limits algal growth in aquatic ecosystems. Excess inputs of nutrients from chemical fertilizers, manures, and wastewaters that enter aquatic environments can trigger algal blooms, which can have severe impacts on humans and ecosystems. Cyanobacterial blooms can produce toxins, such as microcystin and anabaenopeptin, which adversely affect human health (Falconer, 1999; Lambert et al., 1994; Murakami et al., 1997). In addition to production of toxins, algal blooms can cause hypoxia (Azanza et al., 2005; Boesch et al., 2001; Granéli & Turner, 2006), leading to ecosystem degradation. For example, the number of dead zones across the globe approximately doubled every decade from 1960 to 2007 (Diaz & Rosenberg, 2008), and the Gulf of Mexico Dead Zone measured up to nearly 23,000 km² in 2017 (U.S. Environmental Protection Agency (USEPA), 2019). Algal blooms are predicted to increase in magnitude and frequency with changing land use and climate (Paerl et al., 2011; Paerl & Paul, 2012).

Successful management of nuisance and harmful algal blooms requires an understanding of nutrient dynamics in aquatic systems like rivers, which deliver these excess nutrients to the ocean or inland bodies of water (Conley et al., 2009). Years of fertilizer application can cause N and P loading in streams but may also lead to accumulation of these nutrients in soils, which can subsequently be eroded and transported into lakes and reservoirs (Bennett et al., 2001). Of particular interest are the reservoirs along river systems in intensively managed landscapes because they often provide local communities with drinking and irrigation water, flood control, and recreation, modify water and solute residence times (e.g., Musolff et al., 2017), and feature high N and P inputs from fertilizer application in nearby agricultural areas.

Lakebed sediments in reservoir systems can sequester excess nutrients loaded by rivers through biotic and abiotic sedimentation as well as bioavailable N losses through denitrification (David et al., 2006; Saunders & Kalff, 2001). Scavenging of P from the water column is also possible via coprecipitation with redox-sensitive metals like Fe and Mn (Mayer et al., 1982; Pearce et al., 2017). Due to these mechanisms, at both

basin- and global-level scales, agricultural reservoirs have largely been assumed to be overall sinks for N and P, consequently decreasing downstream nutrient loads (Bosch & Allan, 2008; Brown et al., 2011; David et al., 2006; Harrison et al., 2009; Powers et al., 2014; Powers et al., 2015; Robertson & Saad, 2011; Smith et al., 1997; Wollheim et al., 2008). For example, in the Missouri River basin, reservoirs have reduced N and P loads to the Mississippi River by 16% and 33%, respectively (Brown et al., 2011), impacting nutrient loads during both low- and high-flow conditions (Morris et al., 2014). Another model estimated that reservoirs retain a third of all N removed by lentic systems, despite representing only 6% of the global lentic surface area (Harrison et al., 2009). David et al. (2006) found that denitrification in an agricultural reservoir in the midwestern U.S. Corn Belt could remove 60,900 Mg N/year, while Havens and James (2005) found that an average of 297 Mg P/year was retained in an agricultural lake in Florida. Although reservoirs can sequester large amounts of N and P in lakebed sediments, retention in sediments can be highly variable with total N (TN) concentrations ranging from <500 to 12,000 mg/kg and total P (TP) concentrations ranging from <200 to 2,000 mg/kg (Pearce et al., 2017; Pulatsü et al., 2008; Xu et al., 2003; Zhang et al., 2008). Despite this variability in nutrient retention efficiency, reservoirs and lakes decrease the overall magnitude and interannual variability of river mass exports (Powers et al., 2014; Powers et al., 2015).

However, lentic nutrient retention does not always occur, particularly in forested and smaller agricultural systems (Huang et al., 2015; Powers et al., 2014; Powers et al., 2015). Even after external sources of nutrients are reduced to a reservoir, N and P stored in lakebed sediments can internally load the water column, preventing any improvement in water quality and potentially triggering algal blooms (Granéli, 1999; Scharf, 1999). Internal nutrient loading from lakebed sediments is controlled by many factors including water residence times, loading history, and the chemical characteristics of the sediments (Søndergaard et al., 2003, and references therein). There are several biotic and abiotic mechanisms that may release nutrients from sediments into the water column including decomposition, diffusion, advection (i.e., the resuspension of sediments), changes in redox conditions at the sediment-water interface, photosynthetically induced high pH, and macrophyte senescence in the summer (Bonanni et al., 1992; Callender & Hammond, 1982; Newman & Reddy, 1992; Pearce et al., 2017; Søndergaard et al., 2003; Welch & Cooke, 1995). For example, longer data sets (~25 years) for nutrients in Finnish rivers and lakes showed that large lakes effectively retained >80% of the N and P load from incoming streams (Ekholm et al., 1997; Räike et al., 2003). Smaller, agricultural lakes, however, could experience internal N and P loading as these nutrients were released from lakebed sediments (Ekholm & Mitikka, 2006; Räike et al., 2003), especially in the summer months (Ekholm et al., 1997). The lack of nutrient retention in some systems is thought to be largely due to decomposition or desorption of internal N and P pools in lakes (Powers et al., 2013) or rivers (Jarvie et al., 2012) or exhaustion of storage sites in smaller systems as sedimentation proceeds and/or nutrients accumulate.

Larger agricultural reservoirs have nevertheless demonstrated only limited internal nutrient loading over decadal timescales (Lafrancois et al., 2009). Thus, the long-term effectiveness of large reservoirs at mitigating downstream N and P loads, particularly in heavy agricultural areas like the midwestern U.S., is unclear (Basu et al., 2011). This is because most previous studies of nutrient retention in lentic environments have (1) focused on systems that are not in intensively managed landscapes, (2) examined nutrient behaviors on short (<1 year) time frames, (3) not linked short- and long-term nutrient behavior, (4) concentrated on only one element (either N or P), and (5) centered on internal lake processes rather than potential transport to downstream sites. With >90,000 registered dams in the U.S. alone (U.S. Army Corps of Engineers (USACE), 2018a), many of which occur in agricultural landscapes, and the potential for extreme hydrologic events due to a changing climate, reservoirs now clearly play an important role in the global cycling of N and P. Hence, understanding how nutrients flux through these systems is critical.

This study therefore investigated the distribution of nutrients across a large, agricultural reservoir in Illinois, U.S., over both short and long timescales to determine the effectiveness of these systems at retaining nutrients as loading from agricultural land use continues. We compared 2 years of high spatial and temporal resolution data for the water column, sediment porewaters, sediment exchange sites, and bulk sediments with 39 and 47 years of water quality data for the streams entering and exiting the reservoir and the reservoir itself, respectively, to understand whether the reservoir sediments act as long-term sinks or sources for N and P. We found that the reservoir remained a continuous sink for N over both short and long timescales, which is consistent with previous results. However, we observed that the reservoir switched from P storage to

release on decadal timescales. This demonstrates that large, agricultural reservoirs have a limited capacity to mitigate high P loads before releasing internal legacy P, thereby becoming a source for downstream P contamination. Our findings could help inform nutrient mitigation and reservoir management strategies, particularly in intensively managed landscapes where nutrient load reduction efforts are most critical.

2. Methods

2.1. Site Description

We studied Carlyle Lake, a large (area = 105 km²) and shallow (mean depth = 3.4 m) reservoir on the Kaskaskia River in central Illinois, U.S. (Illinois Department of Natural Resources, 2016; Figure 1). The reservoir lies downstream of another impoundment on the Kaskaskia River (Lake Shelbyville), is generally aligned northeast to southwest, and is split into upper and lower basin segments by a railroad trestle (Figure 1). The portion of the Kaskaskia River watershed that drains to the reservoir is predominantly agricultural land use (73%; U.S. Department of Agriculture (USDA), 2017), featuring areas with tile drainage that can quickly transmit nutrient-rich runoff from agricultural fields to surface waterbodies (Chiang et al., 2014). The reservoir is currently managed by the U.S. Army Corps of Engineers (USACE; Singh et al., 1975) and was developed for the purpose of flood control. However, it is also used for recreation and water supply. Water in the reservoir is allocated for public water supply systems, power plants, and golf courses. Maximum withdrawal allocations to all users represent <1% of the total volume of the reservoir at average stage, but actual water usage rates are much lower at <0.01% of the normal volume (Kaskaskia Basin Water Supply Planning Committee, 2012; Knapp, 2017; Knapp et al., 2012).

The intensive land management in the basin has led to eutrophic conditions in Carlyle Lake. Indeed, USACE (2006) and Pearce et al. (2017) observed high concentrations of P in the water column that were above the regional water quality standards of 0.05 mg/L for total dissolved P in lakes (Illinois Environmental Protection Agency (ILEPA), 2018a). Elevated N concentrations of up to ~3.0 mg/L for dissolved NO₃⁻-N and up to ~0.5 mg/L for dissolved NH₃-N have also been observed (Pearce et al., 2017). High nutrient concentrations, coupled with anecdotal observations of algal blooms and fish kills, make Carlyle Lake an ideal location for studying the influence of lakebed sediments on short- and long-term nutrient dynamics in reservoirs.

2.2. Field Sampling

To understand the spatial and temporal variations in lakebed sediment chemistry and the potential influence of sediment chemistry on water quality, we collected a suite of water and sediment samples at 10 different locations across Carlyle Lake on six separate occasions from 2016 to 2017 (i.e., 6 June 2016, 23 June 2016, 8 July 2016, 28 October 2016, 21 May 2017, and 31 October 2017). On all of the sampling dates, except for 21 May 2017, the reservoir featured near-average stage (depth at the river mouth = ~0.3 m and depth at the dam = ~5.2 m). Record high stage was observed during the 21 May 2017 sampling date (depth at the river mouth = 2.4 m and depth at the dam = 7.9 m).

Water samples were collected near the sediment-water interface (i.e., ~0.3 m above the sediment surface) at each site on each sampling date using a Van Dorn water sampler. Water quality parameters (e.g., turbidity, dissolved oxygen (DO), fluorescent dissolved organic matter (fDOM), chlorophyll-a, and blue-green algae) were measured in situ at the sediment-water interface using a YSI EXO2 Multiparameter Sonde. All water samples were placed on ice for transport to the lab, filtered in the lab using 0.45- μ m filters, refrigerated at 4°C until analysis, and analyzed for nutrients, total suspended solids (TSS), and chlorophyll-a within 48 hr. In addition to water samples, for each sampling date, sediment samples were collected using a Petite Ponar grab sampler. These sediment samples represent the top 5 cm of the lakebed. We also collected three replicate, intact sediment cores to depths of 10 cm from one site in the reservoir (Figure 1; see star) on both 21 May 2017 and 31 October 2017 for high-resolution analysis of the sediment depth profile. All sediment samples were placed on ice for transport to the lab and refrigerated at 4°C until analysis. Subsamples for wet sediment extractions were analyzed within 48 hr. Other subsamples for bulk digestions and metal content analysis were stabilized within 24 hr by drying and subsequently analyzed within 14 days.

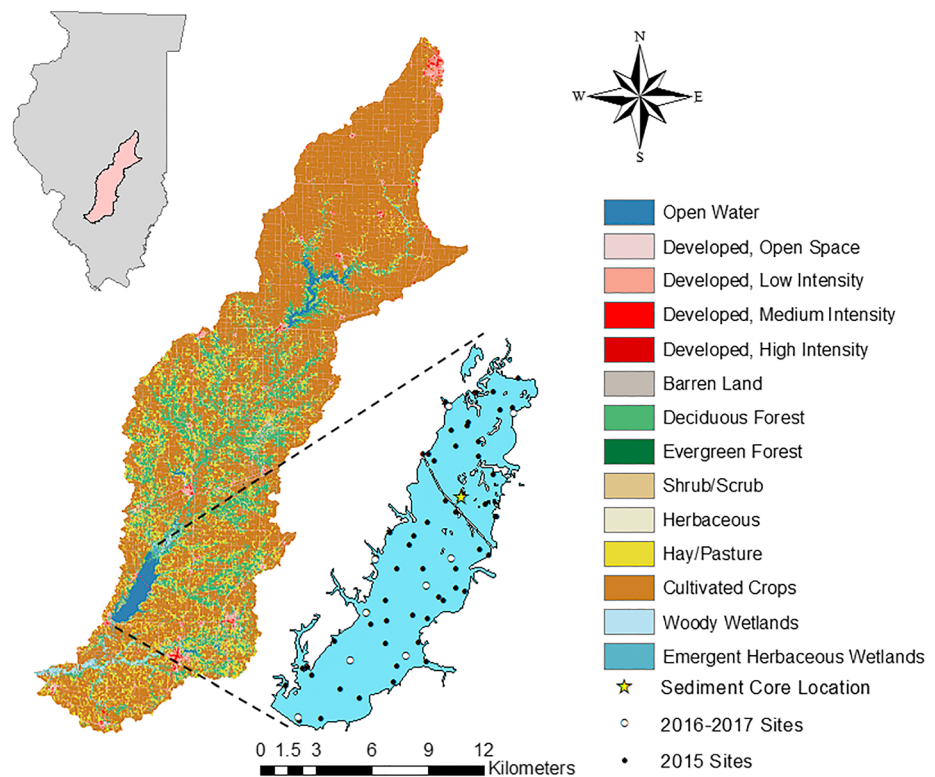


Figure 1. The land use/land cover map for the Kaskaskia River watershed, which is predominately agriculture (U.S. Department of Agriculture (USDA), 2017). Note that there is another impoundment on the Kaskaskia River (Lake Shelbyville) upstream of Carlyle Lake. The inset shows Carlyle Lake in detail with circles indicating our sampling sites. The sites that we monitored for temporal changes in sediment chemistry from June 2016 to October 2017 are shown in white. We also analyzed an archive of samples from other sites at the reservoir (black) collected in 2015 by Pearce et al. (2017).

2.3. Physiochemical Analyses of Water and Sediment Samples

The water samples collected near the sediment-water interface were analyzed using U.S. Environmental Protection Agency (USEPA) methods for NO_3^- -N (USEPA Method 353.2; USEPA, 1993a), NH_3 -N (USEPA Method 350.1; USEPA, 1993b), and PO_4^{3-} -P (USEPA Method 365.1; USEPA, 1993c) with a Westco SmartChem 170 discrete analyzer. The TSS samples were analyzed following USEPA method 160.2 (USEPA, 1971). Chlorophyll-a values measured by the YSI EXO2 Multiparameter Sonde were verified using USEPA method 445.0 (Arar & Collins, 1997).

We performed wet sediment extractions on untreated sediments to determine nutrient concentrations in porewaters and loosely bound to mineral or organic surfaces. For the porewater extractions, 20 ml of 18.2 M Ω cm distilled deionized water (DDI) was mixed with 20 g of wet sediment. To ensure the sample was fully mixed, the slurry was continually agitated on a New Brunswick Scientific Excella E25 shaker table at 120 rpm for 1 hr. The mixtures were then transferred into two 15-ml centrifuge tubes and centrifuged for 2 min at 3,400 rpm to separate the sediment and fluid. The supernatant was passed through a Whatman No. 1 filter and frozen until analysis. For the loosely bound nutrient extractions, 11 g of wet sediment and 100 ml of 2.0 M KCl were added to a specimen cup. The slurry was continually agitated in the same manner as the DDI extraction, filtered into a 125-ml Nalgene bottle, and frozen until analysis. Sediment DDI extracts were analyzed for NO_3^- -N, NH_3 -N, and PO_4^{3-} -P, while 2.0 M KCl extracts were analyzed for only NO_3^- -N and NH_3 -N (due to interferences with the PO_4^{3-} -P method) using the discrete analyzer described earlier.

Bulk sediments were digested following Andersen (1976) to determine sedimentary TP concentrations. In short, dried, ground (<0.42 mm) sediments were first ashed at 550°C for 3 hr to volatilize the organic matter (OM). This step also yielded OM content for each sample by measuring loss on ignition. The sediments were

then boiled in 6.0 M HCl to solubilize P. Aliquots of the digests were separated for P analysis using the discrete analyzer, which measured the P as $\text{PO}_4^{3-}\text{-P}$. The dried, ground bulk sediments were also used to determine TN and total C (TC) using an Elementar vario MAX cube elemental analyzer.

Additionally, we used the ground, dried sediments to determine the metal content (e.g., Fe and Mn) for each sediment sample using an Olympus model DPO-4050-C portable X-ray fluorescence (pXRF) analyzer (beam 1: 50 kV, 30 s; beam 2: 40 kV, 30s; and beam 3: 15 kV, 30 s). Each sample was run in triplicate. We also ran a subset of the TP digests on a Perkin Elmer Optima 8300 inductively coupled plasma optical emission spectrometer (ICP-OES) to verify Fe and Mn results from the pXRF. Results from the pXRF and ICP-OES were comparable, but the pXRF values were, on average, 10.6% and 5.8% higher than the ICP-OES results for Fe and Mn, respectively. In addition, we performed pXRF and ICP-OES metal analyses for archived lakebed sediment samples collected at high spatial resolution by Pearce et al. (2017) in 2015 (4-6 May 2015 and 9 June 2015), which had not been previously analyzed for metal content.

Particle size distributions for a subset of sediment samples (from 23 June 2016, 28 October 2016, and 21 May 2017) were determined using a Beckman LS 13 320 laser diffraction particle size analyzer. Dried, unground sediments were rehydrated with DDI water and then deflocculated with 10-15 ml of 2,000 mg/L sodium hexametaphosphate before analysis. The samples were then wet-sieved using a 2-mm sieve to remove particle sizes too large for the analyzer; however, the samples did not contain any particles >2 mm. Immediately before analysis, the sediments were thoroughly mixed with a vortex mixer and then quickly pipetted into the instrument to avoid settling of larger grain sizes. The samples were then sonicated and run four consecutive times for 60 s, which is similar to the method outlined in Eshel et al. (2004).

2.4. Long-Term Nutrient Mass Balance

We did mass balance calculations to investigate nutrient fluxes through Carlyle Lake over a 39-year period. Water quality and discharge data for incoming and outgoing streams were downloaded from the Water Quality Portal. Data for 1977-1997 were from the U.S. Geological Survey (USGS; see USGS, 2018) and data for 2003-2016 were from the Illinois Environmental Protection Agency (ILEPA; see ILEPA, 2018b) and the National Water Information System. We accessed data via the dataRetrieval R package (Hirsch & De Cicco, 2015). Water quality data for 1999-2003 were received directly from the ILEPA (ILEPA, 2018c). The USGS and ILEPA monitoring sites were collocated. Additionally, 47 years (i.e., 1971-2018) of data for nutrient concentrations in the reservoir itself were collected by the USACE (USACE, 2018b).

The incoming streams for which there was both discharge and water quality data included the Kaskaskia River (USGS 05592500 and ILEPA O-08; 71.3% of the watershed), Hurricane Creek (USGS 05592800 and ILEPA OL-02; 5.6% of the watershed), and East Fork Kaskaskia River (USGS 05592900 and ILEPA OK-01; 4.2% of the watershed). These streams collectively represented a total of 81.1% of the area draining to Carlyle Lake. To compensate for the missing 18.9% of the reservoir drainage area that was not monitored for discharge or water quality, we assumed that the unaccounted area represented a proportional load of each constituent of interest (i.e., $\text{NO}_3^- \text{-N}$, $\text{NH}_3 \text{-N}$, $\text{PO}_4^{3-}\text{-P}$, Fe, Mn, and TSS). In other words, we estimated the water quality parameter inputs for the missing watershed area using the weighted average of the three monitored streams. The outlet site was located just below the reservoir dam on the Kaskaskia River (USGS 05593010 and ILEPA O-07).

Yearly, flow-weighted concentrations were calculated for each water quality constituent using an equation modified after Moatar et al. (2013):

$$C^* = \frac{\sum_{i=1}^n C_i q_i}{\sum_{i=1}^n q_i} \quad (1)$$

where C^* is the flow-weighted concentration, C is the average, annual concentration, and q is the average, annual discharge for the input, i (i.e., the Kaskaskia River, Hurricane Creek, or East Fork Kaskaskia River), to Carlyle Lake. Yearly, average loads were calculated as a product of C^* and $\sum_{i=1}^n q_i$. We also included discharge estimates for the 18.9% of the drainage area that was not monitored. We did not consider water supply withdrawals from the reservoir in our mass balance calculations because these volumes were negligible (i.e., <0.01% of the normal reservoir volume). Yearly averages of discharge and the water

quality constituents were utilized to account for changes in storage for the reservoir and the periodic sampling regime of the archived data.

2.5. Spatial Data and Statistical Analyses

ArcMap 10.4.1 was used to determine land use/land cover for the Kaskaskia River and Carlyle Lake watersheds (USDA, 2017; USDA Natural Resources Conservation Services, 2000). We also used ArcMap 10.4.1 to interpolate physiochemical data for waters and sediments using inverse distance weighting interpolation. Inverse distance weighting is a technique to estimate unknown values based on their distances from known values. Statistical analyses were performed in R using a significance level of $\alpha = 0.05$.

3. Results

3.1. Spatial Distributions of Nutrients and Metals Across the Reservoir

3.1.1. Water Column

An unpaired t test showed that turbidity and TSS at the sediment-water interface were significantly ($p \leq 0.03$) higher above the railroad trestle near the river mouth (average = 54.2 FNU and 74.7 mg/L, respectively) compared with the portion of the reservoir below the trestle near the outlet of the reservoir (average = 27.5 FNU and 28.2 mg/L, respectively). The DO concentrations ranged from 0.3 to 9.7 mg/L (average = 7.0 mg/L) and were lowest in the deepest portion of the reservoir near the dam wall. Sites upstream of the dam had higher DO concentrations, with 93% of the measurements above the USEPA aquatic life criterion of 5.0 mg/L (e.g., the 1-day minimum DO concentration; see USEPA, 1986, and USEPA, 2019). The fDOM values ranged from 18.2 to 83.8 QSU, chlorophyll-a ranged from 3.3 to 65.5 $\mu\text{g/L}$, and blue-green algae ranged from 0.23 to 5.51 $\mu\text{g/L}$. The fDOM, chlorophyll-a, and blue-green algae distributions across the reservoir were either uniform (with no significant ($p > 0.05$) differences among sites) or exhibited seemingly random “hot spots” (where an individual sample site had a much higher concentration than the rest of the sites; these hot spots could vary in location across time). We added NO_3^- -N and NH_3 -N together to understand the dynamics of N in the reservoir, regardless of speciation, and found that NO_3^- -N + NH_3 -N ranged from 0.04 to 3.10 mg/L (Table 1). The PO_4^{3-} -P concentrations ranged from below detection (i.e., 0.02 mg/L) to 0.32 mg/L (Table 1). Water column PO_4^{3-} -P concentrations were consistently higher than the ILEPA regulatory limit of 0.05 mg/L (ILEPA, 2018a) for nearly all of the sampling dates. The nutrient distributions were uniform across the reservoir at the sediment-water interface (i.e., there were not significant differences in concentrations among the sites).

3.1.2. Sediment Extractions

For sediment porewaters, N-species (NO_3^- -N + NH_3 -N) ranged from 0.75 to 4.71 mg/L and PO_4^{3-} -P ranged from below detection (i.e., 0.02 mg/L) to 0.23 mg/L (Table 1). The N-species were higher, while the P-species were lower, in the porewater compared with the water column ($p \ll 0.01$). The exchangeable (i.e., 2.0 M KCl extract) N-species concentrations ranged from 4.21 to 41.11 mg/kg and were significantly ($p \ll 0.01$) higher than porewater N values (Table 1). We observed uniform or random distributions of nutrients in porewaters and on exchange sites across the reservoir.

3.1.3. Bulk Sediments

We observed strong TP, TN, TC, and OM concentration gradients for bulk sediments collected to 5-cm depth across the reservoir. The lowest values for these parameters were observed near the mouth of the Kaskaskia River in the upper portion of the reservoir, and the highest parameter values were observed near the outlet at the reservoir dam (Figure 2). The TP concentrations were highly variable and ranged from 138 to 1,720 mg/kg with an average value of 840 mg/kg. The TN ranged from 180 to 3,680 mg/kg, the TC ranged from 450 to 30,570 mg/kg, and OM ranged from 1.7 to 18.1% (Figure 3).

The average TC:TN ratio (\pm standard deviation) in the sediments was 11.9 ± 4.3 (range = 7.9–30.1), excluding six anomalous samples in the upper portion of the reservoir near the mouth of the East Fork Kaskaskia River tributary whose TC:TN ratios were 0.1–3.2. We excluded these low TC:TN values from the data set because the sample mean is significantly ($p \ll 0.01$) lower than all other samples for the reservoir and these values do not fall in the expected range for lake sedimentary OM, where algae-derived OM ranges from 4 to 10 and terrestrially-derived OM is > 20 (Meyers, 1994). Excluding the anomalous points from the regression, we observed significant ($p \ll 0.01$), positive relationships between TN and OM ($R^2 = 0.59$; Figure 3a) and TC and OM ($R^2 = 0.56$; Figure 3a). The TC:TN ratios were generally higher near the inlets of the

Table 1

N- and P-Species Concentrations for Water at the Sediment-Water Interface (SWI), in Sediment Porewater, and Loosely Bound to Sediments or Organics (Exchangeable) for Each Sampling Date

Date	Sample	NH ₃ -N + NO ₃ ⁻ -N (mg/L)			PO ₄ ³⁻ -P (mg/L)		
		Average	Minimum	Maximum	Average	Minimum	Maximum
6 June 2016	SWI	1.23	0.72	3.10	0.03	BDL	0.09
	Porewater	1.37	0.92	2.57	0.05	BDL	0.12
	Exchangeable	9.02	4.76	12.94	NA	NA	NA
23 June 2016	SWI	0.74	0.04	2.60	0.14	0.11	0.18
	Porewater	1.84	1.08	2.97	0.07	0.03	0.23
	Exchangeable	17.05	9.16	20.40	NA	NA	NA
8 July 2016	SWI	1.04	0.44	2.61	0.24	0.09	0.32
	Porewater	2.47	1.52	4.21	0.07	0.02	0.15
	Exchangeable	16.44	9.01	19.14	NA	NA	NA
28 October 2016	SWI	0.51	0.26	1.01	0.13	0.09	0.17
	Porewater	2.11	1.46	3.32	0.03	BDL	0.06
	Exchangeable	19.19	10.13	28.31	NA	NA	NA
21 May 2017	SWI	1.05	0.93	1.74	0.16	0.08	0.2
	Porewater	1.89	0.80	4.71	0.02	BDL	0.06
	Exchangeable	19.36	7.29	32.13	NA	NA	NA
31 October 2017	SWI	0.10	0.07	0.15	0.12	0.12	0.12
	Porewater	2.88	0.75	3.93	0.02	BDL	0.09
	Exchangeable	25.28	4.21	41.11	NA	NA	NA

Abbreviations: BDL, below the detection limit for the method; NA, not applicable because of interferences between the 2.0 M KCl and the detection method.

Kaskaskia River and Hurricane Creek compared with the deeper, downstream portions of the reservoir. This TC:TN ratio distribution across the reservoir implies relatively higher terrestrial vegetation contributions near the inlet and higher algal contributions downstream. We also observed a significant ($p < 0.01$), positive correlation between TP and OM, but the R^2 value was lower ($R^2 = 0.20$; Figure 3b).

Similar to the sedimentary nutrient and OM patterns, redox-sensitive metal (Fe and Mn) and clay content in the lakebed sediments increased in concentration from the river mouth to the outlet of the reservoir (Figure 4). Concentrations of Fe ranged from 6,270 to 51,000 mg/kg, while concentrations of Mn ranged from 215 to 2,490 mg/kg. However, we note that a subset of samples that were run using both a pXRF

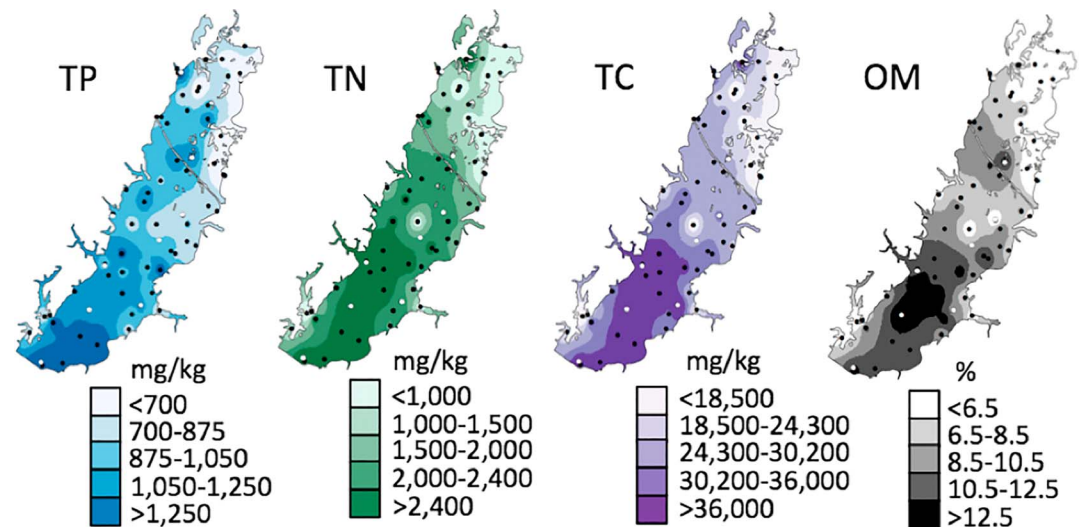


Figure 2. Maps showing the distributions of sedimentary total P (TP), total N (TN), total C (TC), and organic matter (OM) across Carlyle Lake. The maps combine data from this study (white circles) with data from Pearce et al. (2017; black circles) to show the average concentrations from all sampling dates.

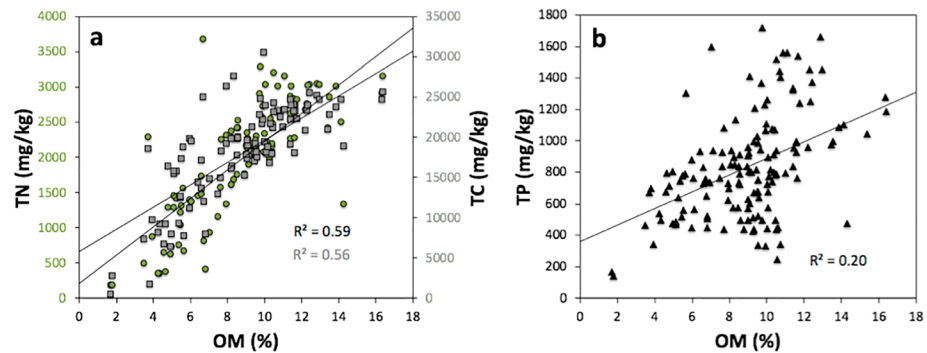


Figure 3. Plots showing the relationships between (a) total N (TN; green circles) or total C (TC; gray squares) and organic matter (OM) as well as (b) total P (TP; black triangles) and OM.

and ICP-OES showed that our pXRF results were an average of 10.6% and 5.8% higher than our ICP-OES results for Fe and Mn, respectively. Nevertheless, our Fe values were consistent with the observations of Pearce et al. (2017) who measured Fe concentrations of ~14,000 mg/kg with an ICP-OES for a single site in the middle portion of Carlyle Lake at a tributary inlet. Clay content in the sediments ranged from 3.2 to 16.5%. There was significantly ($p < 0.05$) lower clay and higher sand content in samples from the upper reservoir near the mouth of the Kaskaskia River compared with samples collected closer to the dam ($R^2 \geq 0.53$; Figure S1). Additionally, we observed strong, positive correlations between clay-sized particles and Fe ($R^2 = 0.91$; Figure S2) as well as Mn ($R^2 = 0.70$; Figure S2).

Our intact core samples were used to resolve nutrient and metal variations in the sediments as a function of depth. While the cores were collected from only one site, the selected site was located in the center of the lateral cross section of the reservoir and featured intermediate values for sedimentary nutrients, OM, metals, and grain sizes compared with the ranges for these parameters over the entire reservoir (Figures 1, 2, 4, and 5). We observed that TP, OM, Fe, and Mn generally decreased with depth in the sediment profile (Figure 5). The TP, OM, and Fe values were significantly different between the two sampling dates, with the highest TP and Fe values observed on 31 October 2017 and the highest OM values observed on 21 May 2017. There was no significant difference in Mn with depth between the two sampling dates.

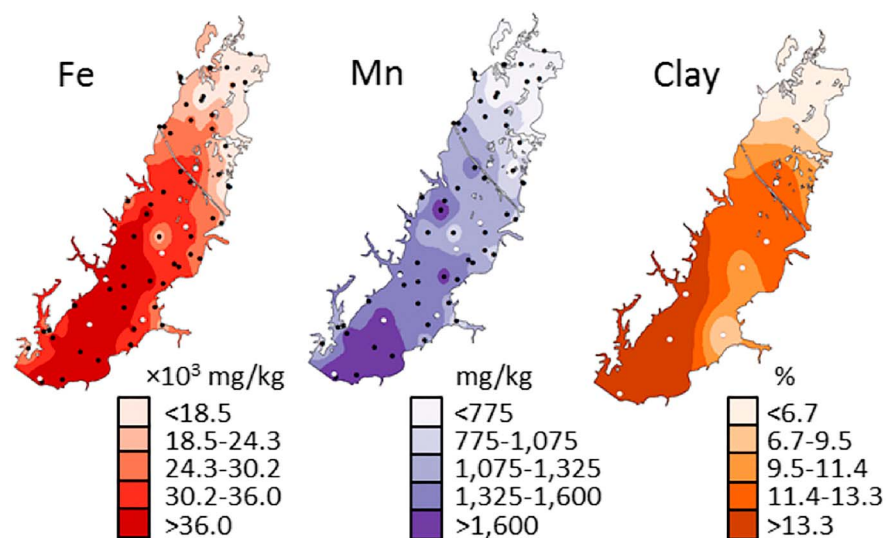


Figure 4. Maps showing the distributions of sedimentary Fe, Mn, and clay across Carlyle Lake. The Fe and Mn concentrations were measured in this study using archived samples collected in 2015 (Pearce et al., 2017; black circles) and new samples collected in 2016-2017 for this study (white circles). Particle size samples were only analyzed for samples collected in this study.

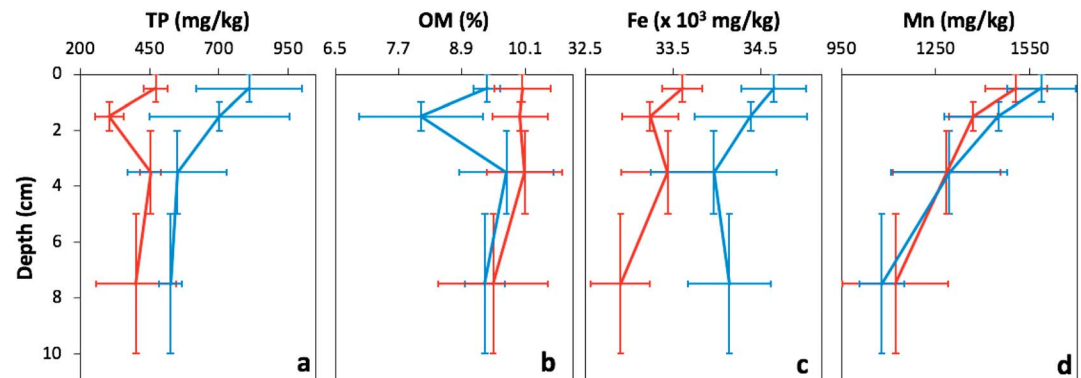


Figure 5. Plots of the sedimentary (a) total P (TP), (b) organic matter (OM), (c) Fe, and (d) Mn content as a function of depth in intact sediment cores collected from one site in Carlyle Lake (see star in Figure 1) on 21 May 2017 (red lines) and 31 October 2017 (blue lines). Cores were split into the following depth increments: 0–1 cm, 1–2 cm, 2–5 cm, and 5–10 cm; these depth ranges are denoted by the vertical bars. The standard deviation among replicate cores is denoted by horizontal bars.

3.2. Temporal Variations in Water and Sediment Chemistry

Water collected at the sediment-water interface showed significant ($p < 0.01$) variability in nutrient content among the sampling dates, with N-species (i.e., $\text{NH}_3\text{-N} + \text{NO}_3\text{-N}$) and $\text{PO}_4^{3-}\text{-P}$ varying as much as 85.0% and 87.3%, respectively (Table 1). The N-species varied seasonally at the sediment-water interface and were significantly ($p < 0.01$) higher during warmer weather sampling dates (i.e., June to August) than during the cooler weather sampling dates (i.e., October). There was, however, no significant ($p > 0.05$) change in the $\text{PO}_4^{3-}\text{-P}$ concentrations at the sediment-water interface across seasons. Porewater and exchangeable nutrients also varied significantly ($p < 0.05$) among sampling dates (Table 1). Porewater (DDI extracts) N-species and $\text{PO}_4^{3-}\text{-P}$ varied as much as 42.0% and 65.0%, respectively, while exchangeable (2.0 M KCl extracts) N-species varied as much as 64.0%. There was not, however, any significant ($p > 0.05$) difference in porewater and exchangeable nutrient concentrations between seasons. The bulk nutrient content of the sediments did not change significantly ($p \geq 0.35$) over the 2-year study period, with TP, TN, and TC varying no more than 11.0% across sampling dates.

3.3. Long-Term Water Quality Mass Balance

Mass balance calculations from 1977 to 2016 for water quality parameters were conducted for streams entering and exiting the reservoir (Figures 6 and 7). Our results showed that, on average, 50.7% of the total load of $\text{NO}_3\text{-N}$ entering Carlyle Lake was retained (Figure 6a). Additionally, our yearly mass balance showed that, on average, 363.1% and 229.5% of the total loads of $\text{NH}_3\text{-N}$ (Figure 6b) and $\text{PO}_4^{3-}\text{-P}$ (Figures 6c and 7) entering the reservoir were released at the outlet over the last 39 years. When both $\text{NO}_3\text{-N}$ and $\text{NH}_3\text{-N}$ were combined, we observed that the reservoir acted as a net sink for N-species. Additionally, there was no significant change in N-species entering or leaving the reservoir as a function of time ($p \geq 0.50$). In other words, the rate of N retention in Carlyle Lake did not change over the observation period. Metal mass balance calculations showed that 38.3% and 15.0% of the Fe and Mn loads, respectively, were retained by the reservoir (Figure 6d and 6e). Suspended sediments were also retained by the Carlyle Lake (Figure 6f), and we therefore observed a strong positive correlation between the Fe and TSS loads over the long-term data set ($R^2 = 0.85$, $p < 0.01$; Figure S3).

We did not observe a significant change in the amount of either total (dissolved and particulate) or dissolved P entering the reservoir ($R^2 < 0.01$, $p \geq 0.63$; Figure 7a) over the 39-year observation period. Both the total and dissolved P concentrations within the reservoir changed significantly over 47 years ($R^2 \geq 0.18$, $p < 0.01$; Figure 7b), however. On average, the $\text{PO}_4^{3-}\text{-P}$ concentrations were below the regional water quality standard for dissolved P in lakes (i.e., 0.05 mg/L; ILEPA, 2018a) between 1971 and 1985, but exceeded this standard from 1986 to 2018, with recent years averaging as much as 0.25 mg/L (Figure 7b). Likewise, there was also a significant increase over time in total and dissolved P loads for the Kaskaskia River below the

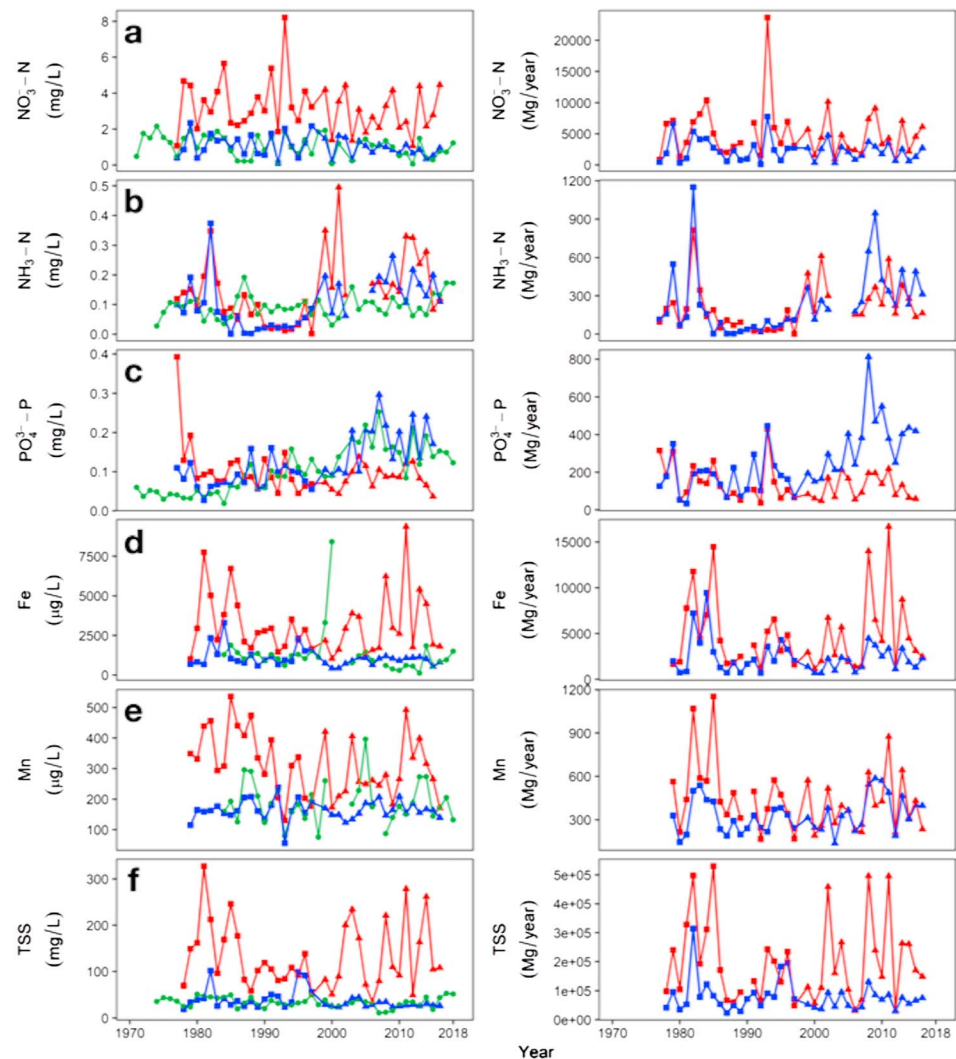


Figure 6. Plots showing concentrations (left) and loads (right) for (a) NO₃⁻-N, (b) NH₃-N, (c) PO₄³⁻-P, (d) Fe, (e) Mn, and (f) total suspended solids (TSS) in the incoming streams (red; values are flow-weighted), reservoir (green), and outgoing Kaskaskia River below the reservoir dam (blue). Data from the U.S. Geological Survey (USGS; squares), U.S. Army Corps of Engineers (USACE; circles), and Illinois Environmental Protection Agency (ILEPA; triangles) are indicated.

reservoir ($R^2 \geq 0.41$, $p \ll 0.01$; Figure 7c), indicating decreased reservoir retention of the incoming P over time ($R^2 \geq 0.28$, $p \ll 0.01$; Figure 7d).

4. Discussion

4.1. Controls on the Spatial Distributions of Lakebed Sedimentary Physiochemical Properties

We observed a gradient of sediment grain sizes across Carlyle Lake, with the largest proportion of clay-sized particles deposited near the dam wall and the highest proportion of sand-sized particles deposited near the river mouth. As suspended sediments moved across the reservoir, larger sediments were deposited first, leaving mostly clays and silts in the water column by the time the water reached the dam. The turbidity and TSS data support this mechanism of sediment transport, demonstrating that there was more sediment suspended in the water column in the upper portions of the reservoir. There was also a significant, positive correlation between redox-sensitive metals and clay-sized particles in the lakebed sediments (Figures 4 and S2). Given that clay minerals are generally found only in the clay-sized particle fraction, this correlation implies that Fe and Mn may either be part of clays or adsorbed on surface exchange sites. Redox-sensitive metals are known

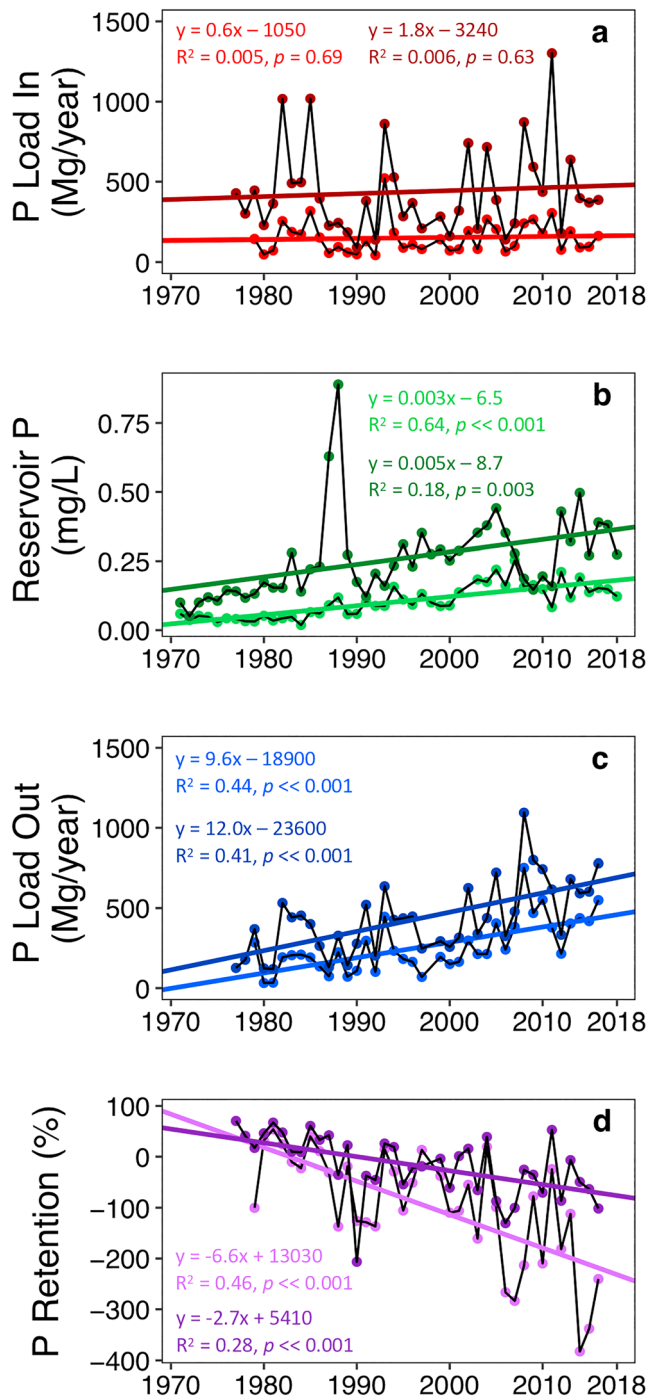


Figure 7. The $\text{PO}_4^{3-}\text{-P}$ loads for the (a) incoming streams (red; values are flow-weighted), (b) reservoir (green), and (c) outgoing Kaskaskia River below the reservoir dam (blue). The percent P retention in the reservoir (purple) is shown over time (d). In all cases, the darker colors represent the total (i.e., dissolved plus particulate) concentrations and the lighter colors represent the dissolved concentrations.

was reduced by an average of 50.7%. We found that more $\text{NH}_3\text{-N}$ leaves Carlyle Lake than enters it, but $\text{NH}_3\text{-N}$ makes up <5% of the combined N-species signature for the reservoir system. When the $\text{NO}_3\text{-N}$ and $\text{NH}_3\text{-N}$ loads are combined, 47.3% of the total N signature is removed from the incoming streams by the reservoir. We found that the rate of N retention in the reservoir did not change over the ~40-year

to bind TP (Mortimer, 1941; Søndergaard et al., 2003), and correspondingly, we observed a significant, positive correlation between TP and Fe as well as TP and Mn. Like clay content, sedimentary OM increased downstream along the reservoir. The significant and positive correlations of TP, TN, and TC with OM suggest that OM deposition across the reservoir could control the concentrations of these elements in the lakebed sediments.

We contend that these abiotic and biotic depositional processes largely control the distribution of nutrients in this reservoir that drains intensively managed landscapes in Illinois. High sand content where the Kaskaskia River enters Carlyle Lake implies that sediments were dropped from the water column as they transitioned from a lotic to lentic environment. Indeed, Carlyle Lake receives large volumes of sediment from the Kaskaskia River ($3.11 \times 10^5 \text{ m}^3/\text{year}$), which has contributed to a 3.5% reduction in the holding capacity of the reservoir since its inception up to 1999 (Knapp, 2017). These high deposition rates near the mouth of the Kaskaskia River likely bury OM rapidly, thereby “diluting” its signature in the upper portion of Carlyle Lake. Suspended sediment concentrations decrease as the water travels through the reservoir as shown by decreasing turbidity and TSS in the water column and higher clay content, but lower sand content, in the sediments. Thus, OM deposited near the dam is more concentrated due to lower deposition rates of inorganic material. We also observed a shift from high to low TC:TN ratios across the reservoir that imply relatively higher terrestrial vegetation contributions to the OM signature near the inlet and higher algal contributions to the OM signature downstream (Meyers, 1994). This observation indicates that algae become increasingly important for OM deposition toward the outlet of the reservoir.

The positive correlation between TP and Fe is likely a result of how sediments disperse and settle throughout the reservoir in terms of both OM burial and P bound to Fe-bearing minerals. We also observed an apparent correlation between TN and Fe. This relationship may simply be due to the association between OM (which contains N) and clay-sized particles (which likely contain Fe-bearing clay minerals), whose distributions are driven by the aforementioned sedimentation processes. Though N is not known to bind to Fe directly, OM can bind to Fe-bearing clays and oxides. This process may result in correlations between not only Fe and OM, but also Fe and the nutrients contained in the OM (Tipping, 1986). This reinforces the assertion that sediment depositional patterns largely influence lakebed OM distributions in agricultural reservoirs. However, overlapping abiotic and biotic sedimentation processes make delineating inorganic and organic nutrient pools and determining how these nutrient pools contribute to the high fDOM and chlorophyll-a signatures at Carlyle Lake difficult.

4.2. Lakebed Sediments as Both Sinks and Sources for Nutrients From Intensively Managed Landscapes

Our mass balance calculations indicated that over a 39-year period, Carlyle Lake has acted as a net sink for N. In detail, the load of $\text{NO}_3\text{-N}$ was reduced by an average of 50.7%. We found that more $\text{NH}_3\text{-N}$ leaves Carlyle Lake than enters it, but $\text{NH}_3\text{-N}$ makes up <5% of the combined N-species signature for the reservoir system. When the $\text{NO}_3\text{-N}$ and $\text{NH}_3\text{-N}$ loads are combined, 47.3% of the total N signature is removed from the incoming streams by the reservoir. We found that the rate of N retention in the reservoir did not change over the ~40-year

study period. Some of this N is lost to sediments, as demonstrated by high TN concentrations across the reservoir, particularly by the dam. David et al. (2006), who assessed N loads in Lake Shelbyville, another reservoir on the Kaskaskia River upstream of Carlyle Lake, attributed the majority of N loss to denitrification.

Although there is a net retention of N in Carlyle Lake, the reservoir has changed from a P sink to source, with an average of 228.5% more P leaving the reservoir than entering it. Loading of P to the reservoir occurred as nutrient-rich runoff and sediments with sorbed P (Meybeck, 1982) entered the system. Our results suggest that there is a limit to the amount of P that reservoir sediments can retain. Up to 1987, the P loads entering Carlyle Lake were higher than those exiting the reservoir. However, since the late 1980s, there has been a significant increase in the amount of P released from the reservoir (Figure 7c), which is almost certainly due to internal loading from legacy P in sediments. There is no long-term data for the sediment chemistry in Carlyle Lake, but sediments represent an important pool of P that is probably the source of the excess P loads to the water column. This is demonstrated by both the increasing reservoir P concentrations and the increasing P loads out of the reservoir—despite no significant change in the incoming P loads (Figure 7).

As sediments rich in P and Fe enter the reservoir, they are deposited and quickly buried due to the high sedimentation rates within Carlyle Lake (i.e., $3.11 \times 10^5 \text{ m}^3/\text{year}$ from the Kaskaskia River). Buried Fe can be reduced in the anoxic conditions beneath the sediment-water interface, changing from insoluble Fe^{3+} to soluble Fe^{2+} , thereby releasing sorbed P. We found that the overlying water column at Carlyle Lake was typically oxic and homogenous across the shallow reservoir, with the exception of the deeper areas of the reservoir by the dam. Nonetheless, Revsbech et al. (1980) described that marine sediments are only oxic in the top 1 cm and quickly become reducing by 3-cm depth. Thus, sediments below the shallow oxic layer can solubilize Fe, releasing P to the water column at Carlyle Lake. Alternatively, OM decomposition can also release bound P to the water column, as 40% of particulate P is OM-bound (Meybeck, 1982). Our sediment cores generally showed a decrease in TP and OM with depth (Figure 5), which could be a result of decomposition. In addition, lab diffusion experiments, conducted with sediment cores from Carlyle Lake, showed net P release from sediments to an overlying water column via diffusion gradients (Pearce et al., 2017). Sedimentary P concentrations are much higher than the overlying water column, and, at some point in the late 1980s, the sediments surpassed their capacity to retain P. This resulted in P diffusion out of the sediments and a net release of P out of Carlyle Lake.

We did not observe significant changes in the TP and Fe concentrations of the sediment on shorter timescales (i.e., during our 2-year study). Still, even small changes in the bulk sediment composition can significantly alter the chemistry of the overlying water column. With an average net release of 119.6 Mg P/year from Carlyle Lake, TP in the sediment would only need to be reduced by an average of 22.3 mg/kg each year. This represents a 2.7% reduction in the average sedimentary TP concentration that, on short timescales, would be masked by the variability among our sites. While this change is insignificant from year to year, it becomes important over decadal timescales. Indeed, if we assume that (1) all influxes of P to the reservoir stop, (2) the total net P release is solely derived from sediments, (3) the release rate does not change over time, and (4) only the top 5 cm of sediment is reactive (across the 105-km² reservoir area, where the average sediment TP concentration and bulk density are 840 mg/kg and 0.6 g/cm³, respectively), then Carlyle Lake sediments could sustain an output of 119.6 Mg P/year for 22 years. Our estimate represents a minimum release timeline as P will continue to be loaded into the reservoir, the release rate would likely change over time if P loading were to cease, and P can be released from as deep as 25 cm in the sediments (Søndergaard et al., 1999).

4.3. The Role of Reservoirs in Nutrient Cycling

Carlyle Lake has been a N sink for at least ~40 years but has been releasing P for >30 years. We estimate that it could continue to release P for at least another two decades if all P loading were to stop. Indeed, eutrophic, unstratified lakes, like Carlyle Lake, have been shown to respond slowly to external nutrient load reduction. Welch and Cooke (1995) estimated that internal loading in shallow lakes can persist for 5-10 years after external loading is reduced because sediments can release nutrients (particularly P) to the water column. The transmission of nutrients from the sediments to the water column is especially enhanced during the growing season due to higher decomposition rates, higher pH due to photosynthetic activities, and low

DO near the sediment-water interface that can change redox conditions so that reduced Fe might liberate P. However, during our short-term study of the sediment properties, we did not observe any significant differences in nutrients found in porewaters, loosely bound to sediments, or bulk sediments between the warmer and cooler months.

Haygarth et al. (2014) theorized that catchment-scale nutrient balance can be in one of the following states at any given time: (1) an equilibrium, when inputs balance outputs, (2) an accumulation phase, when inputs are larger than outputs (i.e., storage in the system), or (3) a depletion phase, when inputs are smaller than outputs (i.e., loss of legacy nutrients from the system). Accumulation of N over the past 140 years, particularly from agricultural loading since the late 1940s, has been noted in the River Thames basin (Howden et al., 2011). Howden et al. (2011) attributed some of this N storage in the catchment to retention in groundwaters. In contrast, a N depletion phase was observed in a Canadian river system due to legacy N and the subsequent lag time between N load reduction and water quality improvement (van Meter & Basu, 2017). An accumulation phase for P has been demonstrated to occur in large river systems like the Maumee River, River Thames, and Yangtze River, but the rural Maumee River and mixed agricultural-urban River Thames basins have switched from net P accumulation to depletion in the past 20 years (Powers et al., 2016).

We now show that reservoirs along river systems also undergo accumulation phases for N and P. However, we found that reservoir P storage is eventually exhausted on decadal timescales in agricultural landscapes where there have not been meaningful reductions in P loads. This inflection point, where systems switch from net P storage to the net mobilization of the internal P pool accumulated in earlier decades, could serve as an indicator of the timescales over which reservoirs can effectively mitigate high P loads from agricultural land use. Once the P storage pools in reservoirs are exhausted, they can become sources for downstream nutrient contamination that may lead to eutrophication that impacts other aspects of water quality (e.g., low DO or increased particulate organic C; Minaudo et al., 2016). Understanding the nutrient retention and release behaviors of freshwater systems like reservoirs will become increasingly important as land use and climate change (Heathwaite, 2010).

5. Conclusions

Surface waterbodies in intensively managed landscapes are at a high risk of algal blooms and hypoxia due to inputs of typically limiting nutrients, such as N and P, from fertilizers. Understanding how nutrients are stored in these systems is pivotal to developing remediation and mitigation strategies. We found that the spatial distributions of lakebed nutrients were predominantly controlled by sediment depositional patterns in an agricultural reservoir. In detail, there were significantly higher proportions of sand-sized particles in lakebed sediments and higher turbidity and TSS concentrations in the water column at the upper portions of Carlyle Lake compared with downstream sections by the dam. The higher inorganic sediment deposition rates and larger particle sizes “diluted” the OM signature in the upper reaches of the reservoir. Additionally, clay-sized particles rich in P and Fe traveled farther through the reservoir and accumulated near the dam wall. Our long-term mass balance showed that Carlyle Lake removed a large proportion of the N load (47.3%), probably mainly via denitrification, but also by OM deposition. However, a large quantity of P (229.5%) has been released from the reservoir, likely via metal reduction and/or OM decomposition. Our mass balance indicated that the reservoir initially retained a portion of the P entering the system. Over the last ~30 years, however, Carlyle Lake has changed from a sink to a source for P, contradicting the paradigm that large reservoir systems are nutrient sinks. Our study showed that agricultural reservoirs can become important sources for nutrient contamination in the future.

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