

Retention and transport of nutrients in a mature agricultural impoundment

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[1] Small impoundments intended for irrigation, livestock watering, and hydropower are numerous in agricultural regions of the world. Many of these artificial water bodies are well positioned to intercept fertilizer runoff and pollutants but could be vulnerable to long-term sedimentation, management intervention, or failure. We examined solute retention in a mature, sediment-filled, run-of-river impoundment created by a small, >100 year old dam in agricultural Wisconsin, United States. To do so, we measured instantaneous net fluxes of inorganic and organic solutes through the system, which contained wetlands. The impoundment was a persistent net sink for sulfate and, during the warm season only, a net sink for nitrate, ammonium, and soluble reactive phosphorus. There was also a negative relationship between nitrate and sulfate retention, suggestive of nitrate-stimulated sulfate production. Impoundment hydraulics were then altered by a management manipulation (dam removal) that caused mean water travel time to decrease by approximately 40%. Following manipulation, autoregressive modeling of solute time series indicated a decrease in mean net retention of nitrate, sulfate, ammonium, and soluble reactive phosphorus. There was also a decrease in the variability (coefficient of variation) of instantaneous net exports of dissolved organic nitrogen and dissolved organic phosphorus. These biogeochemical changes were consistent with predictions based on hydraulics (reduced water travel time), with the exception of ammonium release immediately following reservoir dewatering. Our results emphasize the biogeochemical importance of reservoir-wetland ecosystems, which are expanding with impoundment sedimentation but are threatened by infrastructure aging. We suggest that reservoir wetlands be considered in the management of dams and surface water pollution.

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1. Introduction

[2] In recent years, it has become clear that a remarkable number of small, artificial water bodies occur in agricultural landscapes. Between 3.5 and 8 million water bodies exist in the United States alone [Doyle and Havlick, 2009; McDonald et al., 2012; Renwick et al., 2005b]. For some regions, the number of very small water bodies (<0.001 km²) is comparable with the number of lakes >0.001 km² [McDonald

et al., 2012]. These systems intercept a large quantity of runoff and material exported from upslope terrestrial and aquatic systems. For example, small impoundments have been implicated as sites of major long-term storage of sediment in North America [Renwick et al., 2005b]. Because high impoundment densities occur in agricultural areas such as the Midwestern grain belt [Downing et al., 2006; Smith et al., 2002] many impoundments are well positioned to influence riverine transport of fertilizing nutrients and pollutants that dictate surface water quality.

[3] To date, most biogeochemical studies of impoundments have focused on large, long-lived systems [e.g., Kelly, 2001; O’Keefe et al., 1990]. But relative to large systems, small impoundments are far more numerous, have a comparable total (global) surface area [Downing et al., 2006], and are more vulnerable to dam failure [Evans et al., 2000] or management interventions such as dam removal [Ahearn and Dahlgren, 2005; Doyle et al., 2005; Stanley and Doyle, 2003]. Meanwhile, of the modest number of studies involving small impoundment biogeochemistry [e.g., Fairchild and Velinsky, 2006; Mander and Järvet, 1998; McIntyre, 1993; Nowlin et al., 2005], few have targeted mature, sediment-filled impoundments (but see Gill et al. [1976]). Further

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studies of mature impoundments are needed because these systems (1) potentially have a different biogeochemical role than larger, deeper lakes and reservoirs and (2) could foreshadow the future status of numerous younger impoundments as they age and fill with sediment.

[4] During impoundment maturation, sedimentation sometimes progresses rapidly [Graf *et al.*, 2010; Renwick *et al.*, 2005a] and is a major concern for reservoir management. For example, Downing *et al.* [2008] reported water storage losses of 0.4–11.0% annually for small impoundments (<1 km²) of Iowa, United States. Others have observed similarly rapid rates of water storage loss [Dendy, 1968; McHenry, 1974], which has led to major losses of water storage capacity in some systems [Hargrove *et al.*, 2010; Minear and Kondolf, 2009]. The initial effects of sedimentation are usually most apparent near inlets, where shallow depth promotes the establishment of wetlands, especially in regions of modest relief [Kalff, 2002] such as the midwestern United States. Thus, the process of impoundment sedimentation produces hybrid ecosystems with wetland characteristics that expand over time. We refer to such ecosystems as reservoir wetlands. Reservoir wetlands share design features of treatment wetlands including shallow depth, stores of accumulated particulate organic matter, and abundant emergent vegetation or biofilms [Kadlec *et al.*, 2005] and so too could be important sites of biological uptake and transformation of fertilizers and pollutants. Many reservoir wetlands also differ from isolated wetlands and drainage wetlands in that they intercept substantial inputs of water and solutes that would otherwise be delivered to downstream aquatic ecosystems. Barring intervention, the contribution to global wetland coverage by impoundments will increase as they age and fill with sediment, and this could be an important consideration for the future management of dams, wetlands, and water resources.

[5] Here, we focus on a 6 year period of record for net fluxes of inorganic and organic solutes through a mature (>100 year old) run-of-river impoundment in agricultural Wisconsin. At the onset of the study, the system was a reservoir wetland ecosystem with approximately balanced annual inputs and outputs of sediment. We then used a management manipulation—incremental dewatering and removal of a small dam (resulting in hydrogeomorphic alteration)—to evaluate changes in solute retention. Hydraulic characteristics such as mean water residence time can greatly influence whole ecosystem solute retention in impoundments and wetlands [Jenkins and Greenway, 2005; Martinez and Wise, 2003; Persson *et al.*, 1999]. We posited that if hydraulics strongly dictates impoundment solute fluxes, then a reduction in mean water residence time should increase the similarity between input and output solute time series; this would (1) shift mean retention/export toward balanced mass (conservative transport) and (2) reduce the temporal variability of instantaneous retention/export. Alternatively, many factors other than (or in addition to) hydraulics, such as changed benthic productivity or mobilization of novel solute sources, must be important if any other type of change in retention/export occurs (increase in magnitude, sign reversal, increase in temporal variability). We suggest that hydraulic dominance of solute fluxes could provide a convenient basis for examining the functionality of numerous small impoundments.

2. Methods

2.1. Site Description

[6] Site selection was prompted by a planned removal of the 100+ year old, 5.4 m tall Big Spring dam (hydraulic height = 3.4 m) on Big Spring Creek, WI (43°40′10.92″N, 89°38′53.88″W) by resource managers. We used a 1.4 km study reach that bounded the entire impoundment (Figure 1), which was approximately 1.0 km long (surface area of 0.018 km², drainage area of 20 km²). Prior to dam removal, the impoundment was a mature, flow-through reservoir wetland, which at the dam had accumulated 2.5 m of benthic sediment and organic matter. The sediment budget was variable but approximately balanced during the pre-manipulation phase (mean instantaneous net retention of total suspended sediment (TSS) = 0.008 ± 0.49 standard deviation (SD), as a proportion of inputs; n = 28 observations collected at 4–8 week intervals). The catchment consists mainly of corn crop and pastureland, and has abundant springs, sandy soils, and low relief. One large perennial spring contributes the majority of surface water inputs to the study reach and stabilizes the flow regime. As a consequence, base flows supply most of the annual water yield, and runoff periods are abbreviated. Inflowing stream dissolved inorganic nitrogen is high (background NO₃-N = 2–3 mg L⁻¹, Table 1), and average discharge (*Q*) entering through the main stem of the study reach is 0.27 m³ s⁻¹. The study reach also lacked canopy cover over the majority of its length [Julian *et al.*, 2011].

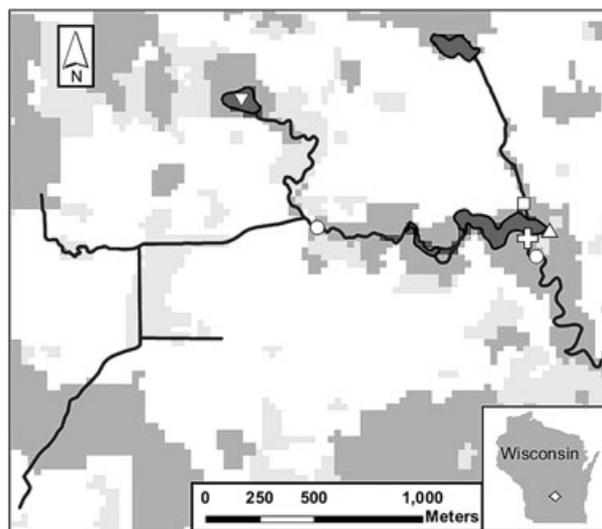


Figure 1. Big Spring Creek prior to manipulation and surrounding catchment. The study reach (43°40′10.92″N, 89°38′53.88″W) is bounded by white circles. Flow direction is left to right. Dark gray = wetlands or ponds; black lines = streams; cross = dam site; leftmost circle = main input sampling station (*I*); rightmost circle = output sampling station (*O*); square = tributary (Buckley Creek) sampling station (*T*); up triangle = groundwater sampling station (*G*); down triangle = large headwater spring; white = agricultural land (cultivated and pasture); light gray = grassland or shrub; medium gray = mixed forest.

Table 1. Baseflow Chemistry and Hydrology of the Big Spring Creek Study Reach^a

Category	Variable	Range
Chemistry	Nitrate-N (mg L ⁻¹)	2–3
	Ammonium-N (mg L ⁻¹)	0–0.05
	Total dissolved N (mg L ⁻¹)	2–3
	Total N (mg L ⁻¹)	2–3
	Dissolved organic N (mg L ⁻¹)	0–0.25
	Soluble reactive P (mg L ⁻¹)	0–0.04
	Total dissolved P (mg L ⁻¹)	0.01–0.05
	Total P (mg L ⁻¹)	0.02–0.1
	Dissolved organic P (mg L ⁻¹)	0.00–0.01
	Chloride (mg L ⁻¹)	1–1.5
	Dissolved organic carbon (mg L ⁻¹)	2–3
	Sulfate (mg L ⁻¹)	7–9
	DIN:SRP (atomic ratio)	30–50
	pH	7.5–8.0
	Water temperature	12–18
	Dissolved oxygen (mg L ⁻¹)	8–12
	Dissolved oxygen (% saturation)	80–100
	Total suspended sediment (mg L ⁻¹)	1–4
	Organic matter in suspended sediment (%)	10–30
Hydrology	Inflow discharge Q_I (m ³ s ⁻¹)	0.18–0.27
	Outflow discharge Q_O (m ³ s ⁻¹)	0.31–0.49
	Discharge gain (%)	25–45

^aChemistry is from the main input (I) station.

2.2. Study Design

[7] We evaluated solute transport through the study reach over a 6 year period of record, including 3+ year prior to manipulation (reservoir wetland state). To do so, we took repeated measures of inorganic solutes (chloride; nitrate; ammonium; sulfate; soluble reactive phosphorus, SRP) and organic solutes (dissolved organic N (DON) and dissolved organic P (DOP)). Water samples were collected at multiple stations including one primary output station located 100 m downstream of the dam site, one primary upstream/input station located 1.3 km upstream of dam site (near the original reservoir inlet), and three additional stations used for characterization of minor tributary or spring inputs. For the transitional period of 2008, which involved phased management interventions, we sampled during periods of quasi-equilibrium only (>7 days following each management intervention).

[8] To examine possible changes in solute retention of the study reach following manipulation, we used intervention analysis of input/output time series for solute concentration. We then estimated instantaneous solute fluxes (net) and retention metrics based on supporting hydraulic measures. To examine the possibility of linked biogeochemical processes, we also tested for statistical relationships between solute forms. The very stable flow regime, caused by the large perennial spring upstream of the study reach, facilitated accurate flux estimation throughout the study.

2.3. Manipulation Sequence

[9] The Big Spring management manipulation involved incremental dewatering in 5 phases during summer 2008, which caused a gradual channelization of the study reach. This began with the removal of a 0.3 m tall flashboard in July 2008, and proceeded with subsequent notching of dam concrete at approximately two week intervals between July 2008 and September 2008. All remaining dam

infrastructure was removed by September 2008. Between fall 2008 and spring 2009, two sections of the study reach (each <100 m) were rerouted into restored channel meanders, which lengthened the study reach from 1400 to 1580 m. Planning information associated with the dam removal may be obtained from the Wisconsin Office of Dam Safety, the Wisconsin River Alliance, or Inter-fluve Inc.

2.4. Analysis of Solute Concentration Time Series

[10] We used intervention analysis [Box and Tiao, 1975] to test for changes in solute concentration due to manipulation. Detailed modeling methods, as well as model diagnostics, are contained in Appendix A. Our response variable (Y , mg L⁻¹) was

$$Y = C_O - C_I \tag{1}$$

where C_O is a time series of solute concentration at the primary output or “treatment” station, and C_I is the time series of solute concentration at the primary input or “reference” station. A similar statistical approach has been used in previous whole ecosystem manipulation experiments, in which time series from the manipulated system are compared to corresponding time series from a reference (not manipulated) system [Carpenter et al., 1989]. Y was consistently autocorrelated at lag 1, but not at higher lags by the Durbin-Watson test. A time series with lag 1 autoregressive structure, along with experimental effects, may be expressed in the general form

$$Y = B_0 + \varphi Y_{t-1} + \sum_i^n M_i D_i + e_t \tag{2}$$

where B_0 is the intercept parameter, Y is the time series from equation (1), φ is an autoregressive parameter, M_i is a vector of model coefficients employed by dummy variables D_i (zeros indicate the premanipulation phase, ones indicate one or more postmanipulation phases), and e_t is a time series of independent, normally distributed residuals. For a minority of sampling dates, samples were not available for every solute form. Therefore the sample size for Y varied slightly among solutes. DON had the smallest sample size ($n=49$), and 26 of these observations took place prior to manipulation. SRP had the highest sample size ($n=64$), and 36 of these observations took place prior to manipulation.

[11] For each solute form, we selected the most parsimonious stationary model using AIC_c [Burnham and Anderson, 2002]) from four different candidate models (Table 2): (1) null, no change following manipulation (intercept parameter B_0 only), (2) simple effect, one-step change following

Table 2. Candidate Models for Solute Dynamics Following Manipulation^a

Candidate Model	Parameters	k
Null (no change following manipulation)	B_0	1
Simple effect	B_0, M_{simple}	2
Seasonal effect	B_0, M_{warm}, M_{cool}	3
Annual effect	$B_0, M_{year1}, M_{year2}$	3

^aThe response variable for all models is $Y = C_O - C_I$, where C_O is the time series of solute concentration at the output station, and C_I is the time series of solute concentration at the main input station.

manipulation (intercept parameter B_0 , plus parameter M_{simple} for changes incurred following manipulation), (3) seasonal effect, season-specific change following manipulation (intercept parameter B_0 , plus parameter M_{warm} for postmanipulation changes incurred during the warm season defined as 15 May to 15 September, and M_{cool} for postmanipulation changes incurred during the remainder of the year), and (4) annual effect, year-specific change following manipulation (intercept parameter B_0 , plus parameter M_{year1} for postmanipulation changes incurred up to the end of 2009, and M_{year2} for postmanipulation changes incurred in 2010).

[12] Parameter values, standard errors, and p values were estimated for the best model of each solute form. M_i units are mg L^{-1} , such that $M_i = 1.0$ and $M_i = -1.0$ directly correspond to postmanipulation changes in Y of $+1.0$ and -1.0 mg L^{-1} , respectively. Time series of predicted upstream-downstream differences (Y_{pred}) were calculated for each solute form using the null model and the best model (if different).

[13] The coefficient of variation (CV) of Y was calculated for premanipulation and postmanipulation phases for each solute form. On the basis of hydraulics only (reduced water residence time), CV (Y) would be expected to decrease due to enhanced synchrony between input and output time series (a reflection of reduced temporal variability for instantaneous retention/export). Finally we examined evidence for coupled cycling of solute pairs (e.g., $Y_{sulfate}$ and $Y_{nitrate}$), grouped by premanipulation and postmanipulation phases, using ANCOVA.

2.5. Hydraulics

[14] Hydraulic measures were determined premanipulation and postmanipulation. We used 6 pulse releases of NaCl (3 prior to manipulation), in situ specific conductivity meters, and chloride water sampling [Gooseff and McGlynn, 2005] to identify time of peak concentration at input/output stations. Mean water residence time (τ , t) was estimated as the difference in peak times, and mean water velocity ($u = \text{length}/\tau$) was calculated. Point measurements of thalweg water velocity were taken in accessible sections of the main (lower) impoundment body.

2.6. Water and Solute Balance

[15] Time series of instantaneous net solute fluxes across the manipulated reach were used to evaluate biogeochemical functioning of the Big Spring ecosystem. Along with solute concentration measurements, discharge (Q) was measured at both input and output stations (same as reference and treatment stations in the autoregressive analysis) using a velocity \times area technique for calculation of loads ($C \times Q$). Solute mass outputs (O) were estimated as the product of discharge and solute concentration at the stream output station ($Q_O \times C_O$). Total solute mass inputs (I_{TOT}) were estimated from the sum of three component (input) stations ($I_{TOT} = I + T + G$) where I is mass input from the primary input station ($Q_I \times C_I$), T is mass input from one minor surface water tributary within the study reach (Buckley Creek, with discharge term Q_T), and G is mass input from groundwater (with discharge term Q_G). Q_T and Q_G required for calculation of T and G were estimated from

$$Q_T = b \times Q_I \quad (3)$$

$$Q_O = Q_I + Q_T + Q_G - Q_S - Q_E \quad (4)$$

where b is an empirically determined coefficient driven by hydrologic coherence of the two tributaries (mean $b = 0.14$; 1 SD = 0.03; $n = 9$), and equation (4) is the water balance with Q_S as seepage (into groundwater) and Q_E as evapotranspiration. Given consistent hydrologic gains over the study reach ($Q_O \sim 1.25 \times [Q_I + Q_T]$), and a low stream gradient (0.15 %), we assumed $Q_S = 0$. We also assumed $Q_E = 0$ because evapotranspiration likely represented a small part of the water balance in this system. To illustrate, over an impoundment area of 0.018 km^2 , using a liberal estimate of evapotranspiration rate, 20 mm d^{-1} [see Wetzel, 2001], water is displaced at a rate of $0.004 \text{ m}^3 \text{ s}^{-1}$, which represents only 1.07 % of mean output discharge ($0.39 \text{ m}^3 \text{ s}^{-1}$). T was estimated as $T = Q_T(t) \times \bar{C}_T$, where $\bar{C}_T = \text{mean } C_T$, and G was estimated as $G = Q_G(t) \times \bar{C}_G$, where \bar{C}_G is mean C_G . Water samples from a surface spring near the primary region of groundwater discharge (lower end of study reach) were used to represent C_G . This spring was sampled at a lower frequency than C_I and C_O under the expectation of a relatively static groundwater solute pool. Alternative approaches to estimating C and G based on linear trends for C_T or C_G within years, among years, and with discharge (Q_T and Q_G) were tested. However, such predictive relationships were either absent or questionably significant, which presumably reflects the stability of solute concentrations in this groundwater-dominated system. Observed spring chloride (C_G) was compared to expected spring chloride under conservative transport ($E = [O - I - T]/Q_G$) to evaluate the assumption that spring water was representative of groundwater chemistry.

[16] Net instantaneous solute flux through the study reach was calculated as a percentage of mass input ($F_{net} = 100 \times [O/I_{TOT} - 1]$), such that negative values indicate net retention and positive values indicate net export. Predicted net solute fluxes were calculated from the null model and best model of each solute form (if different) by replacing O in the immediately previous equation with the predicted solute outputs ($O_{pred} = [Y_{pred} + C_I] \times Q_O$). Because these predicted solute fluxes are based on simple models, they are representative of aggregate trends but do not always capture outliers/extremes.

[17] Mass solute retention as a proportion of inputs ($R = 1 - O/I_{TOT}$) for water bodies may be expressed in biological and hydraulic terms using

$$R = 1 - \exp \frac{-v_f}{H_L} \quad (5)$$

where H_L is hydraulic loading (depth/ τ) and v_f is uptake velocity ($\text{L } \tau^{-1}$) [Harrison et al., 2009; Wollheim et al., 2008]. Reservoir wetland nutrient uptake metrics were then calculated using equation (5) and mean instantaneous solute fluxes from warm season and annual time frames. For H_L , we used mean τ from solute releases, and obtained depth values from $Q/(u \times \text{width})$ where width was the average of 20 evenly spaced channel cross sections. H_L may be equivalently calculated as Q/A , where A_{sw} is water body surface area. v_f was then calculated following rearrangement of equation (5) ($v_f = -H_L \times \ln(1 - R)$). Decay constants

($K_c = v_f/\text{depth}$, τ^{-1}) and areal uptake ($U = v_f \times C$, $\text{ML}^{-2}\tau^{-1}$) were also calculated.

2.7. Laboratory Methods

[18] Several solute forms were measured. Nitrate (operationally, nitrate + nitrite; $\text{NO}_3\text{-N}$), ammonium ($\text{NH}_4\text{-N}$), total dissolved N (TDN), and total dissolved phosphorus (TDP) were determined by flow injection analysis on an Astoria Pacific Instruments autoanalyzer (APIA). NaOH-persulfate digestion was used for determination of TDN and TDP, as well as for total N (TN) and total P (TP). Chloride (Cl^-) and sulfate (SO_4^{2-}) were determined by ion chromatography on a Dionex DX-500. Soluble reactive P (SRP) was determined colorimetrically using the molybdate blue method [American Public Health Association, 1995] and a Beckman DU-640 UV/Vis spectrophotometer. DON and DOP were estimated by difference (DON = TDN - DIN, where DIN = nitrate + nitrite + ammonium; DOP = TDP - SRP). DOC was determined using a Shimadzu carbon analyzer.

[19] Additional variables were measured for site characterization. Total suspended sediment (TSS) and percent volatile organic matter in suspended sediment (OM as percentage ash-free dry weight) were measured by standard methods [American Public Health Association, 1995]. Water temperature was logged at output and main input stations. Dissolved oxygen and pH were measured near the beginning of the study.

3. Results

3.1. Hydrology, Hydraulics, and Channel Form

[20] Main stem input discharge (Q_I) was the largest input of the water balance (Table 3). Groundwater discharge (Q_G) of the study reach was always positive (range from 14 to 30 % of main stem input discharge (Q_O), or a gain of 25 to 40% over the study reach), indicating a persistent net gain throughout the study period. Prior to manipulation, mean water velocity for the whole 1400 m study reach, which included short stream subreaches near the impoundment inlet and outlet, was $0.12 \pm 0.003 \text{ m s}^{-1}$ (mean ± 1 SD, $n=4$); this corresponded to a mean water travel time of 3.24 h. Mean water velocity over the impoundment (1000 m) was approximately 0.09 m s^{-1} and mean water travel time was 3.09 h. Point velocity measurements varied substantially due to discontinuous ponding, including thalweg values as low as 0.06 m s^{-1} . Mean wetted width was 18.1 m, and ranged from 5 m in free-flowing subreaches to 40 m in ponded sections.

[21] Hydrogeomorphology of the study reach was altered incrementally in 2008 by the management manipulation (Figure 2). Ultimately, following complete removal of

dam infrastructure, mean water velocity for the study reach increased from the premanipulation value of 0.12 to $0.19 \pm 0.02 \text{ m s}^{-1}$ ($n=5$), which corresponded to mean water travel time of 2.05 h, while wetted width decreased from 18.1 to 8.3 m. Manipulation was also associated with short-term erosion of sediment and organic matter from the study reach, which abated following 2008. Mean observed chloride concentration of spring water (± 1 SD) was $1.7 \pm 0.16 \text{ mg L}^{-1}$ ($n=12$) and similar to expected spring chloride concentration under conservative transport ($E = 1.9 \pm 1.1 \text{ mg L}^{-1}$). The considerable variability for E is largely attributable to error propagation from the multiple terms required to estimate this value.

3.2. Premanipulation Solute Transport

[22] Main stem surface water input (I) represented the majority of total input (I_{TOT}) for all solute forms, except in the case of DON. On average, chloride transport was approximately conservative prior to manipulation (mean $F_{net} = -1.1 \pm 4.4$, $n=19$; Figure 3) with variability that is most likely within the bounds of discharge and analytical errors. Sulfate was consistently retained within the study reach (mean $F_{net} = -3.9 \pm 2.3$; Figure 4) with no observations of $F_{net} > 0.0$. Other solute forms were more seasonally variable. During the warm season, instantaneous solute fluxes (Table 4) showed substantial net retention of nitrate (mean $F_{net} = -4.4 \pm 6.9$; $F_{net} < -10.0$ in seven instances), ammonium (mean $F_{net} = -33.6 \pm 42.1$), and to a lesser degree, SRP (mean $F_{net} = -3.4 \pm 32.7$). Warm season fluxes for dissolved organic solutes were positive, indicating net release/export, but highly variable (for DON, mean $F_{net} = 27.7 \pm 161.0$; for DOP, $F_{net} = 21.6 \pm 107.4$); note that organic solutes had low absolute concentration. Nutrient uptake metrics (net, Table 5) revealed rapid uptake of ammonium (7.2 d^{-1} , or 0.3 h^{-1}) comparable to that reported by O'Brien et al., 2011, although maximum ammonium uptake rates could not be effectively estimated due to negligible outflowing ammonium concentration for some observations (infinite uptake). There was also a significant negative relationship between the upstream-downstream difference in sulfate ($Y_{sulfate}$) and the upstream-downstream difference in nitrate (slope = -1.61 ± 0.44 standard error (SE), $p=0.001$, adjusted $r^2=0.31$; intercept = -0.81 ± 0.19 SE, $p=0.0002$). No other solute pair had any significant relationship during the premanipulation phase.

3.3. Postmanipulation Solute Transport

[23] Parameter estimates from best models of upstream/downstream concentration differences ($Y = C_O - C_I$) are reported in Table 6. Chloride continued to be transported approximately conservatively following manipulation (mean

Table 3. Hydraulics and Hydrology of the Big Spring Creek Study Reach^a

Phase	Mean Water Velocity (m s^{-1})	Mean Water Residence Time (h)	Output Discharge Q_O ($\text{m}^3 \text{ s}^{-1}$)	Water Inputs (% of Q_O)		
				Q_I	Q_T	Q_G
Premanipulation	0.12	3.24	0.39 (0.31–0.49)	68 (54–79)	11 (7.4–16)	21 (14–30)
Postmanipulation	0.19	2.05	0.39 (0.35–0.44)	72 (53–79)	9.7 (7.3–16)	18 (14–30)

^aValues are means (range). Q_O is main stem stream output ($n=56$), Q_I is main stem stream input, Q_T is tributary stream input, and Q_G is groundwater input.



Figure 2. The Big Spring Creek study reach, premanipulation (reservoir wetland state) and postmanipulation. Photos are from July 2008 (immediately prior to initial dewatering) and July 2010. Mean wetted width (w) of the study reach decreased from 18.1 to 8.3 m.

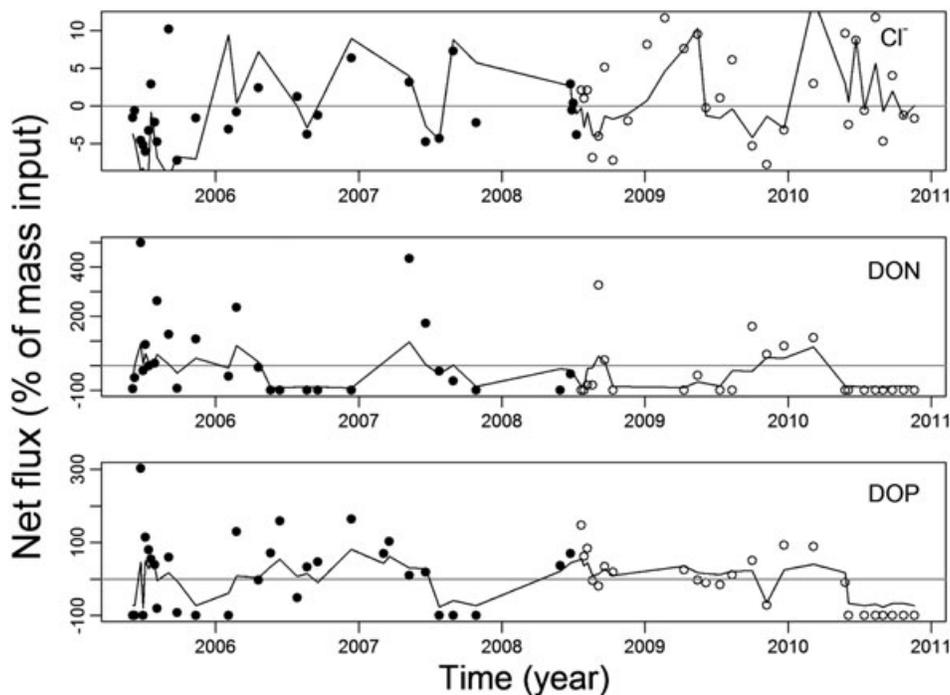


Figure 3. Instantaneous net fluxes of chloride (Cl^-) and organic solutes (dissolved organic nitrogen (DON) and dissolved organic phosphorus (DOP)) through the Big Spring study reach. For these solute forms, postmanipulation changes in Y were not supported (null model selected). Negative values indicate net retention, and positive values indicate net export. Black dots are premanipulation. White dots are postmanipulation. Solid lines are predictions from the best model (no change).

$F_{net} = 1.6 \pm 5.9$), and showed no change in Y (null model selected). For every other solute form, there was either an increase in Y of some type (corresponding to reduced net retention), or a decrease in $\text{CV}(Y)$. Y increased in the cases of ammonium, nitrate, sulfate, and SRP, but the type and magnitude of increase varied. For both sulfate and nitrate, the simple effect model had the lowest AIC_c , but was separated by only 1.9 AIC_c units from a more complex model (annual effect model in the case of nitrate, seasonal effect model in the case of sulfate); both models nonetheless yielded similar predictions for the postmanipulation phase (increase in Y). The best model for ammonium was the annual effect model, with higher Y occurring in the first year following dam removal ($B_4 = 0.021 \text{ mg L}^{-1}$) compared to the second year ($B_5 = 0.0054 \text{ mg L}^{-1}$). The increase in Y for ammonium was

sufficient to shift the study reach from a net sink to a net source during the warm season (mean $F_{net} = 49$). Sulfate shifted toward conservative transport, and was somewhat variable (mean $F_{net} = 0.1$, range = -4.9 to 5.6). For nitrate, the study reach also shifted from a net sink to a net source during the warm season (mean $F_{net} = 4.6$), which due to high background nitrate results in a substantial change in N mass delivered downstream. Postmanipulation, there were no instances in which net retention of nitrate exceeded 10% of inputs.

[24] For DON and DOP, like chloride, solute concentration changes in relation to manipulation were not detected (null model selected). Nonetheless, $\text{CV}(Y)$ was lower for both forms following manipulation (for DON, postmanipulation $\text{CV} = 13.4$, premanipulation $\text{CV} = 16.6$; for DOP,

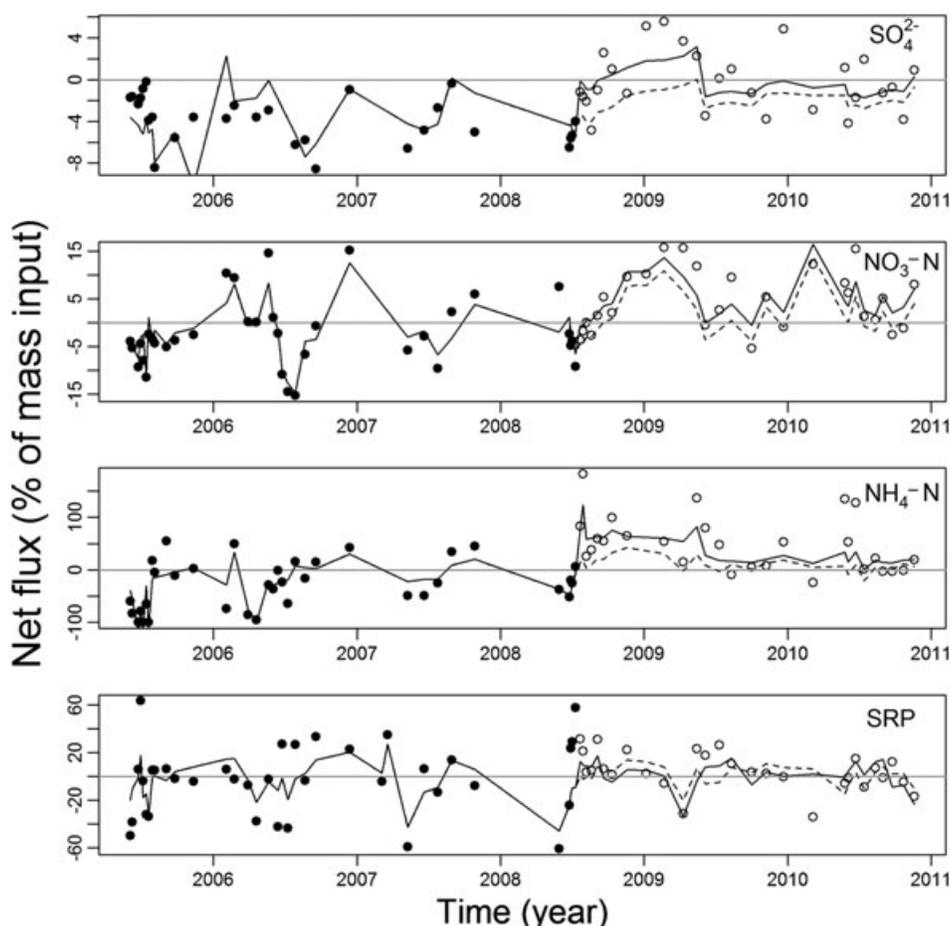


Figure 4. Instantaneous net fluxes of sulfate (SO_4^{2-}), nitrate ($\text{NO}_3\text{-N}$), ammonium ($\text{NH}_4\text{-N}$), and soluble reactive phosphorus (SRP) for the Big Spring study reach. For these solute forms, postmanipulation changes in Y were supported. Negative values indicate net retention, and positive values indicate net export. Black dots are premanipulation (reservoir wetland state). White dots are postmanipulation. Solid lines are predictions from the best model (Table 6), and dashed lines are predictions from the no-change model.

postmanipulation $\text{CV} = 7.3$, premanipulation $\text{CV} = 9.6$). This reflects the absence of higher values postmanipulation, and potentially, loss of transient DON and DOP sources within the study reach. A similar phenomenon was more pronounced for SRP (postmanipulation $\text{CV} = 13.2$, premanipulation $\text{CV} = 20.9$). Model coefficients reported in Table 6 were significant at the $\alpha = 0.05$ level, except for SRP (no significant coefficients), $M_{\text{year}2}$ in the cases of ammonium ($p = 0.067$), and B_0 in the cases of DON and DOP. In contrast to the premanipulation phase, when there was a linear relationship between Y_{sulfate} and Y_{nitrate} , no solute pair had any significant relationship postmanipulation.

4. Discussion

[25] Several recent works have emphasized the broadscale role of lakes and reservoirs in global biogeochemical cycles [e.g., Downing et al., 2006; Harrison et al., 2009; Wollheim et al., 2008]. But research is still needed to understand the biogeochemical role of small impoundments, which are distinct from other water body types due to shallow depth and close proximity to agricultural inputs.

Small impoundments are also abundant within agricultural river networks, so in aggregate may substantially influence downstream deliveries of fertilizing nutrients and pollutants. Here we focused on the influence of a mature impoundment on solute transport. Mature impoundments such as the former Big Spring reservoir wetland foreshadow the trajectory for numerous aging and neglected dams, whose biogeochemical role will likely shift with ongoing sedimentation, management intervention, or infrastructure decline/failure. Ultimately, impoundment aging could serve as a widespread mechanism of wetland creation, depending on management decisions.

[26] Prior to manipulation, the biogeochemical functioning of the Big Spring reservoir wetland was influenced by >100 years of accumulated agricultural sediment and organic matter behind a small dam. Other noteworthy factors included an open canopy and a stable, spring-dominated flow regime. All of these features were associated with prolific benthic algae and macrophytes during the warm season [Julian et al., 2011]. In turn, the annual periodicity of solute retention for nitrate and ammonium prior to manipulation clearly coincided with seasonal cycles of

Table 4. Mean Solute Inputs and Outputs for the Big Spring Creek Study Reach Prior to Manipulation^a

Solute Category	Solute Form	Phase	Total Input Mass I_{TOT} (kg d ⁻¹)	Input components (% of I_{TOT})			Output (% of I_{TOT})	
				I	T	G	O	O_{warm}
Inorganic Solute	Cl ⁻	pre	99	71	17	12	99	99
	Cl ⁻	post	103	76	14	10	102	102
	NH ₄ -N	pre	1	56	35	9	71	66
	NH ₄ -N	post	1	74	20	6	149	160
	NO ₃ -N	pre	77	79	10	11	98	95
	NO ₃ -N	post	83	83	8	9	105	103
	SO ₄ ²⁻	pre	282	66	15	19	96	96
	SO ₄ ²⁻	post	278	70	13	17	100	99
	SRP	pre	1	65	9	26	97	97
	SRP	post	1	72	7	21	105	111
Organic Solute	DON	pre	3	43	46	11	131	128
	DON	post	2	25	61	14	63	94
	DOP	pre	0	51	49	0	118	122
	DOP	post	0	55	45	0	91	88

^aFlux components are expressed as a percentage of total inputs (I_{TOT}). I is percentage main stem stream input, T is percentage tributary stream input, G is percentage groundwater input, and O is percentage output. O_{warm} is percentage output during warm season (15 May to 15 September) relative to I_{TOT} during warm season. Pre is premanipulation and post is postmanipulation.

algal growth and senescence within the study reach. Sulfate retention, however, was more persistent throughout the year and could be attributable to sulfate-reducing bacteria, leading to production of hydrogen sulfide (supported by the observation that sediments emitted the sulfide odor). For DON and DOP, net fluxes (as a fraction of inputs) were more variable than other solute forms, and concentrations were low relative to other systems such as peat-rich wetlands. Still, the reservoir wetland was a net source for these organic solutes during most days of observation, and this is consistent with the expectation of high dissolved organic matter export from wetlands [Mulholland, 2003]. More generally, we suspect the aggregate export of dissolved organic solutes from small agricultural impoundments could be substantial, as suggested by [Fairchild and Velinsky, 2006], due to large inputs of allochthonous organic matter (particulate) combined with high autochthonous (benthic) production. In contrast, F_{net} for chloride trended toward 0.0, consistent with the conservative transport expectation for this solute. Note that in a small number of

instances, chloride net flux exceeded 10% of I , which is probably outside the bounds of discharge observation errors and could indicate modest misrepresentation of inputs for chloride or other solutes.

[27] There was also evidence of coupled biogeochemical processes within the reservoir wetland. Recent studies have emphasized a linkage between N and S cycling in aquatic ecosystems [Burgin and Hamilton, 2008; Whitmire and Hamilton, 2005] and we observed this pairing in the form of a negative relationship between $Y_{sulfate}$ and $Y_{nitrate}$ (each a relative measure of net flux, Figure 5) prior to manipulation. This negative relationship is consistent with the suggestion by Burgin and Hamilton [2008] that chemolithoautotrophic bacterial metabolism of excess nitrate stimulates sulfate production. Two associated hypotheses include (1) linkages between N and S cycling are stronger in wetlands relative to streams and (2) benthic disturbance severs the aquatic N-S linkage (potentially through corelease of nitrate and sulfate, which was observed in the period shortly after manipulation in 2008). Similarly, while the relationship between $Y_{ammonium}$ and $Y_{nitrate}$ was not statistically significant premanipulation or postmanipulation, coupling between nitrification and denitrification has been observed in aquatic systems [Seitzinger et al., 2006], and we believe this aids interpretation of our results. Prior to manipulation, reservoir sediments were likely ammonium-rich (note the release of ammonium upon manipulation). The presence of a substantial benthic ammonium pool that was subjected to infiltration by abundant spring water (oxygenated), combined with high warm season ammonium uptake efficiency (Table 5), points to a potentially active population of nitrifying bacteria, which would in turn generate a novel (biological) input of nitrate from within the study reach. If true, the near balance of annual nitrate inputs and outputs during the reservoir wetland state ($O=0.98 \times I$, Table 4) may actually be interpreted as reasonable evidence of aquatic denitrification [Deemer et al., 2011] because annual retention of nitrate cannot be explained by algal uptake alone. Coupling between nitrification and denitrification along subsurface spring flow paths could also provide one explanation for an apparent lag in the seasonal peak for net nitrate retention (plotted minima in Figure 4) behind that of ammonium, which was most evident in the year 2006.

[28] After manipulation, channel narrowing and increased water velocity were evident from both visual observations and measurements, ultimately producing a stream state. Seasonal net sinks for nitrate and ammonium within the reservoir wetland were in turn reduced by a shift toward export, most easily discerned from the higher warm season values in Figure 4 following manipulation. An annual net sink for sulfate was also eliminated. Models did not detect statistical changes in mean DON or DOP, in part due to low concentrations, but the lower CV following manipulation suggests that the propensity for releases of organic solutes may have been reduced. Note that the loss of mean water residence time within the study reach was buffered slightly by the installation of channel meanders following dam removal. These meanders caused a gross increase in mean water residence time of approximately 0.15 h (small compared to the net decrease in mean water residence time of 1.19 h), which may have contributed to

Table 5. Net Nutrient Uptake Metrics for Big Spring Reservoir Wetland Prior to Manipulation

Time Frame	Solute Form	Proportion Removed	K_c (d ⁻¹)	v_f (m d ⁻¹)	U (g m ⁻² d ⁻¹)
Warm Season	NH ₄ -N	0.50–1.0	7.2 to ∞	1.3 to ∞	0.028 to ∞
	NO ₃ -N	0.05–0.15	0.53–1.7	0.095–0.30	0.20–0.64
	SRP	0–0.6	0–9.5	0–1.7	0–0.026
	SO ₄ ²⁻	0.02–0.08	0.21–0.87	0.038–0.16	0.29–1.2
Annual	NH ₄ -N	0.29	3.6	0.64	0.014
	NO ₃ -N	0.02	0.21	0.038	0.083
	SRP	0.03	3.6	0.63	0.010
	SO ₄ ²⁻	0.04	0.42	0.076	0.61

Table 6. Best Models for Solute Dynamics Following Manipulation^a

Solute Form	Best Model	Improvement Over Null Model ($\Delta AICc$)	k	Parameter Estimates (± 1 standard error)	Interpreted Response of Y to Manipulation
Cl ⁻	null		1	$B_0 = -0.18 \pm 0.029$	no change
DON	null		1	$B_0 = 0.0045 \pm 0.0092$	no change
DOP	null		1	$B_0 = 0.00030 \pm 0.00037$	no change
SO ₄ ²⁻	simple effect	4.8	2	$B_0 = -0.14 \pm 0.064$, $M_{simple} = 0.22 \pm 0.091$	+0.22 mg L ⁻¹
SO ₄ ²⁻	annual effect	6.7	3	$B_0 = -0.14 \pm 0.059$, $M_{year1} = 0.35 \pm 0.11$, $M_{year2} = 0.12 \pm 0.099$	+0.35 mg L ⁻¹ in year 1, +0.12 in year 2
NO ₃ -N	simple effect	12.1	2	$B_0 = -0.41 \pm 0.022$, $M_{simple} = 0.11 \pm 0.033$	+0.11 mg L ⁻¹
NO ₃ -N	annual effect	10.4	3	$B_0 = -0.41 \pm 0.022$, $M_{year1} = 0.13 \pm 0.043$, $M_{year2} = 0.097 \pm 0.039$	+0.13 mg L ⁻¹ in year 1, +0.097 in year 2
NH ₄ -N	annual effect	23.0	3	$B_0 = -0.0020 \pm 0.0016$, $M_{year1} = 0.021 \pm 0.0034$, $M_{year2} = 0.0054 \pm 0.0029$	+0.021 mg L ⁻¹ in year 1, +0.0054 in year 2
SRP	seasonal effect	2.7	3	$B_0 = -0.00019 \pm 0.00077$, $M_{warm} = 0.0019 \pm 0.0014$, $M_{cool} = -0.0023 \pm 0.0014$	+0.019 mg L ⁻¹ in warm season, -0.0023 mg L ⁻¹ in cool season

^aTime series of the downstream-upstream difference in solute concentration ($Y = C_O - C_I$) were evaluated for a change in response to manipulation. Four different models were compared: (1) null (no change, intercept parameter B_0 only), (2) simple one-step change (B_0 plus parameter M_{simple}), (3) season-specific change (B_0 plus parameters M_{warm} and M_{cool} for postmanipulation changes incurred during the warm season and cool season), and (4) year-specific change (B_0 plus parameters M_{year1} and M_{year2} for postmanipulation changes incurred during years 1 and 2).

the postmanipulation solute balance by restoring a small capacity for solute retention. It is also important to recognize that our simple models (equation (2) and Table 6) are appropriate for detecting changes in aggregate biogeochemical functionality, but are generally poor predictors of certain process details such as the range (maxima/minima) of net retention within each season.

[29] We have focused our effort on quantifying the net solute retention of a small impoundment, and examining changes in that role following a shift from reservoir wetland

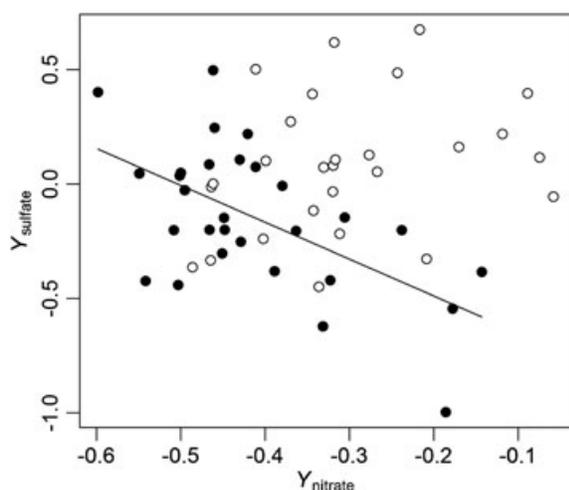


Figure 5. Change in the relationship between sulfate and nitrate following manipulation. Axes are plotted as the difference between output concentration and main input concentration ($Y = C_O - C_I$). Black dots are premanipulation (reservoir wetland state). White dots are postmanipulation. The line is the linear regression of premanipulation data (slope = -1.61 ± 0.44 SE, $p = 0.001$, adjusted $r^2 = 0.31$; intercept = -0.81 ± 0.19 SE, $p = 0.0002$).

state to stream state. But why should solute fluxes change in response to the manipulation? The change in hydraulics (water residence time) provides, at minimum, a partial explanation. At the ecosystem level, possible responses of the solute balance (as expressed by either F_{net} or Y) to a decrease in water residence time, if all other things remain the same, include (1) shift in the mean toward zero (with sign conserved) and (2) reduced temporal variability of instantaneous values. While many other factors could potentially explain altered solute fluxes in relation to the manipulation, we prefer the hydraulic explanation on the basis of its consistency; for every solute form except chloride, either mean Y shifted toward zero, or $CV(Y)$ was reduced. Note that we have assumed changes in land use or climate, which could be important to solute fluxes over the long term, are lacking over the time frame of our study. Because bathymetry and morphometry are closely related to hydraulics, this may offer a convenient basis for predicting individual or aggregate (basin-level) impoundment functioning currently, or as impoundment structure changes with age, intervention, or new dam construction. We return to that idea shortly.

[30] Nonetheless, some aspects of biogeochemical change in the Big Spring study reach following manipulation are not explainable from hydraulics alone. These “nonhydraulic” processes include mobilization of preexisting solute pools associated with sediments, particulate organic matter, or pore waters; creation or elimination of preexisting gross sources or gross sinks of solute; and/or alteration of hydrologic connections, which can shift the relative influence of solute sources or sinks. In particular, reservoir drawdown can promote rapid release of ammonium from newly exposed sediments [Perrin et al., 2000]. This probably explains why some of the highest observations of ammonium concentration in our study occurred at the output sampling station during the initial phase of manipulation (prior to major changes in hydrogeomorphology). There is also statistical support for such mobilization of ammonium, due to selection

of the annual effect model (note $M_{year1} > M_{year2}$) which is not explainable on the basis of hydraulic changes alone. This points to legacy effects of impoundment, which could persist through drying and mineralization of recently exposed benthic detritus [Qiu and McComb, 1996] or leaching from sediments, potentially for several years. Thus, the biogeochemical functioning of previously impounded waters is best interpreted with knowledge of earlier ecosystem states.

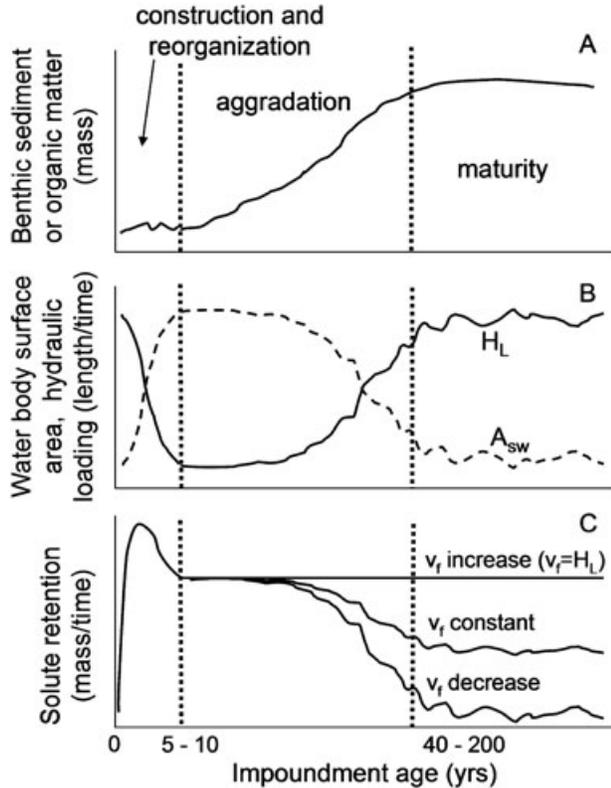


Figure 6. Proposed successional patterns for benthic, hydraulic, and biogeochemical characteristics during the maturation of a small impoundment. Discharge (Q) and mass solute input from the contributing drainage are assumed constant. (a) The standing stock of benthic sediment and organic matter increases with age during aggradation, then saturates at maximum capacity (maturity). (b) Loss of water surface area (A_{sw}) with age produces a corresponding increase in hydraulic loading (H_L). Note that A_{sw} may remain constant during early aggradation if sedimentation first occurs at depth (as shown), in which case decreasing mean depth is associated with equivalently decreasing hydraulic residence time (τ) such that H_L remains constant. (c) Mass solute retention declines with impoundment age under two different assumptions for uptake velocity (v_f remaining constant with aging and v_f decreasing with aging). In order for mass solute retention to remain constant, v_f must increase directly in proportion to H_L (v_f increasing with age, such that $v_f=H_L$) as depicted by equation (5). If large impoundments (which generally have much longer lifespans) are to be considered, these patterns shift to a time frame of hundreds or thousands of years [Graf et al., 2010]. The first phase (construction and reorganization) includes a response following wetting that is known as the trophic upsurge [Kalff, 2002].

4.1. Biogeochemical Implications of Impoundment Succession

[31] Relative to succession in natural lakes [Lindeman, 1942; Wetzel, 2001] or pristine forested streams [Valett et al., 2002] which proceed slowly over centuries, succession in artificial impoundments is often accelerated by major inputs of sediment and nutrients from agricultural or urban landscapes. Changes in hydraulic loading (H_L in equation (5)) as a direct consequence of sedimentation can also produce substantial changes in solute retention over the lifespan of an impoundment. In Figure 6, we present trajectories for impoundment solute retention in response to steady sedimentation, and changes in H_L , that may occur during impoundment maturation. Our proposed patterns in solute retention are conceptual, but explainable from underlying equations, and remain to be tested in relation to interacting factors such as land use change or reservoir management. Given the inverse relation between H_L and water body surface area ($H_L=Q/A_{sw}$), a 50% reduction in A_{sw} corresponds to a doubling of H_L (under the assumption of constant Q). Further, due to reciprocal positioning of v_f and H_L terms in equation (5), v_f must increase over time at an equal rate as H_L in order for the impoundment to retain the same solute mass throughout its lifespan. It is possible that biological process rates of maturing impoundments could compensate for hydraulic changes in this fashion, on the basis of increasing sediment-water contact with loss of water depth [Alexander et al., 2000]. However, Wollheim et al. [2006] showed the relationship between v_f and depth in streams, for three of four models, varied between uniform and strongly positive (depending on model assumptions and data aggregation choices) for a depth range of 0.1 to 10 m. If either uniform or positive v_f -depth relationships apply during impoundment succession, then a substantial decline in mass solute retention should occur; this would still leave open the question of solute fate. Alternatively, more biologically based hypotheses could be useful for shallow (<1 m deep) impoundments, because shallow aquatic ecosystems are notoriously diverse as well as dynamic in biological properties [Wetzel, 2001].

5. Conclusion

[32] Small impoundments are abundant in agricultural landscapes, and solute retention in such systems is vulnerable to sedimentation. In this paper we examined solute retention in a small, mature (>100 year old) impoundment, which had accumulated substantial sediment and organic matter over its lifespan, and was subjected to wetland encroachment. Similar processes are occurring in other agricultural impoundments, and changes in the biogeochemical role of these systems may be partly explained by changes in hydraulics.

[33] Within the United States, numerous small dams have exceeded or are approaching the end of their design lives but lack coordinated management [Doyle and Havlick, 2009], and history provides a warning on this subject. Abandonment and breaching of tens of thousands of small mill dams in the northeastern United States during the 17th to 19th centuries resulted in major wetland losses, channel alterations that are resistant to restoration, and legacy sources of fluvial sediment [Hamilton, 2012; Schenk and Hupp, 2009; Walter and Merritts, 2008]. In the next few decades, barring intervention, some impoundments will have substantially

shallower depth and altered morphometry due to sedimentation. Reservoir sedimentation could in turn feedback either positively or negatively on regional surface water quality, or perhaps greenhouse gas emissions, although our current ability to predict these outcomes is hindered by a lack of information about small impoundment functioning. We are addressing this need. Still, impoundment density continues to increase in many nations, especially within regions of expanding agricultural extent. For example, in the United States, the total surface area of small freshwater ponds increased more than 11% between 1998 and 2004 [Dahl, 2006]. During the early 2000s, impoundment density was also increasing at 1–2% per year in agricultural areas of

the United States and 60% per year in dry agricultural regions of India [Downing *et al.*, 2006]. These widespread alterations to the routing of polluted continental water are major concerns for the management of dams and surface water pollution.

Appendix A: Expanded Methods for Solute Time Series Modeling

[34] We tested for changes in solute concentration due to manipulation using intervention analysis [Box and Tiao, 1975] and autoregressive time series modeling. Our goal was to evaluate simple alternative responses of solute to

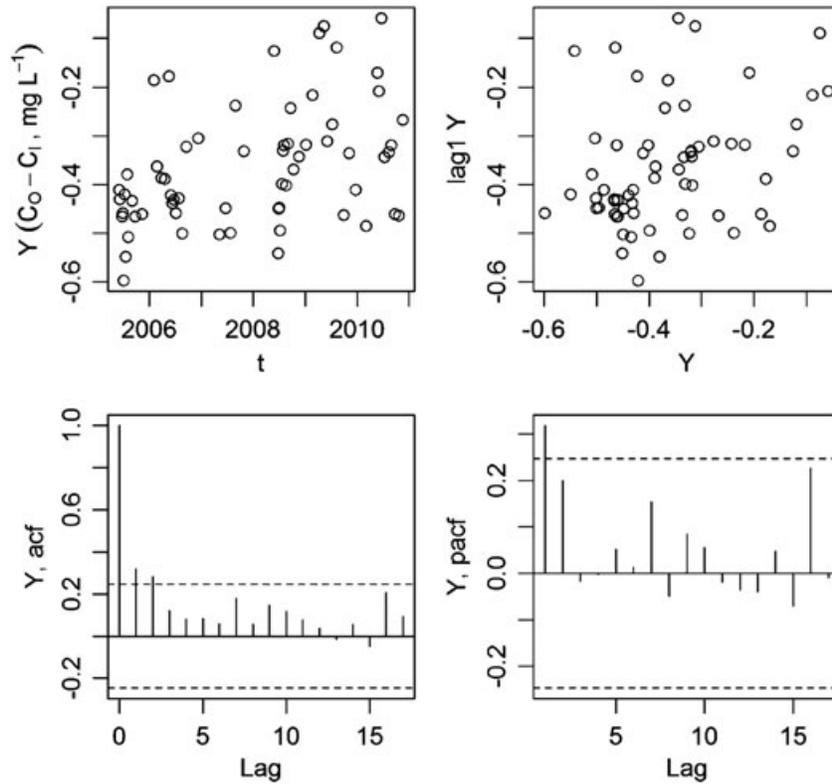


Figure A1. Diagnostic plots of the intervention analysis response variable ($Y = C_0 - C_1$), using the nitrate data. Autocorrelation at lag 1 is apparent. t is time in decimal years. Bars extending beyond the dashed line are significant.

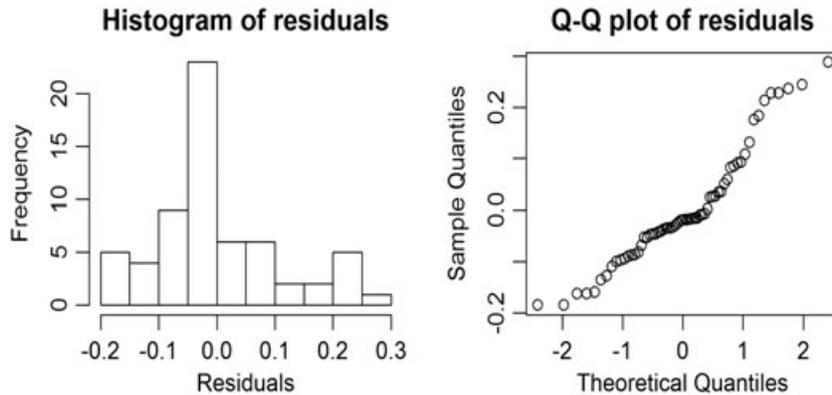


Figure A2. Histogram and Q-Q plot of model residuals for the nitrate data, indicating the distribution is approximately normal.

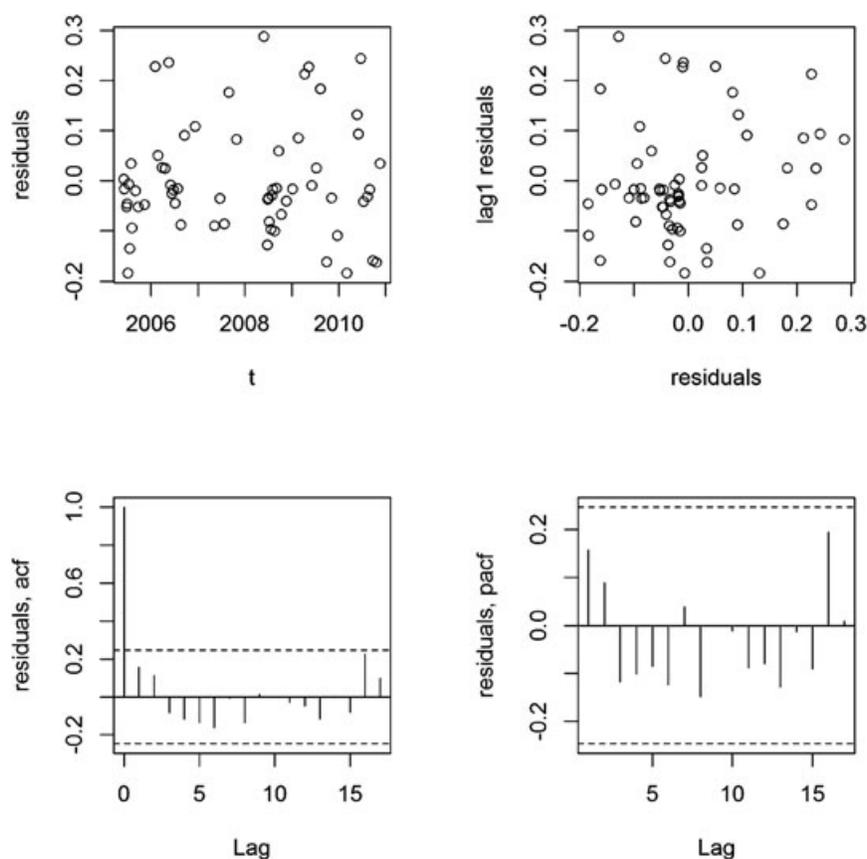


Figure A3. Diagnostic plots for intervention analysis model residuals of the nitrate data. The residuals are not significantly autocorrelated, suggesting model stationarity. t is time in decimal years. Bars extending beyond the dashed line are significant.

manipulation. Modeling was conducted independently for each solute form. A detailed modeling example using the nitrate data is provided below.

[35] In the case of nitrate, autocorrelation for Y (the time series of output concentration minus input concentration, $C_O - C_I$) was evident in preliminary analysis, indicating the likely need for an autoregressive model structure. More specifically, the Durbin-Watson test indicated statistically significant spikes in the autocorrelation function (ACF) and partial autocorrelation function (PACF) at lag1, but not at higher lags (Figure A1). Lag 1 autocorrelation of nitrate Y may be alternatively observed in the slightly positive slope for the scatter plot of Y_{t-1} and Y_t . We postulated that equation (2) from the manuscript body might provide a stationary model structure, which if true should yield (1) an unbiased, normal distribution of model residuals and (2) a time series of residuals that is not autocorrelated. Figure A2 shows that equation (2) (simple effect model) does indeed yield approximately normal residuals. Figure A3 shows the associated time series of residuals is also not autocorrelated. Diagnostic plots for other candidate models of nitrate Y (null model, seasonal effect, annual effect) also lacked residual patterns. Identical procedures to those above were followed for the other solute forms, which yielded similarly robust model diagnostics.

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