

# Whole-Catchment Manipulations of Internal and External Loading Reveal the Sensitivity of a Century-Old Reservoir to Hypoxia

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## ABSTRACT

Climate change is predicted to have widespread impacts on freshwater lake and reservoir nutrient budgets by altering both hypolimnetic hypoxia and runoff, which will in turn alter the magnitude of internal and external nutrient loads. To examine the effects of these potential climate scenarios on nitrogen (N) and phosphorus (P) budgets, we conducted a whole-catchment manipulation of hypolimnetic oxygen conditions and external loads to Falling Creek Reservoir (FCR), an old, eutrophic reservoir in a reforested catchment with a history of agricultural land use. Throughout 2 years

of monitoring, internal N and P loading during hypoxic conditions dominated the hypolimnetic mass of nutrients in FCR, regardless of changes in external loading. FCR commonly functioned as a net sink of N and P, except during hypoxic conditions, when the reservoir was a net source of ammonium ( $\text{NH}_4^+$ ) to downstream. We observed extremely high nitrate–nitrite ( $\text{NO}_3^- - \text{NO}_2^-$ ), soluble reactive P (SRP), total nitrogen (TN), and total phosphorus (TP) retention rates, indicating that the reservoir served as a sink for greater than 70% of  $\text{NO}_3^- - \text{NO}_2^-$  inputs and greater than 30% of SRP, TN, and TP inputs, on average. Our study is notable in the length of time since reforestation (>80 years) that a reservoir is still exhibiting high N and P internal loading during hypoxia, potentially as a result of the considerable store of accumulated nutrients in its sediment from historical agricultural runoff. Our whole-catchment manipulations highlight the importance of understanding how multiple aspects of global change, waterbody and catchment characteristics, and land use history will interact to alter nutrient budgets in the future.

**Key words:** ammonium; nitrate; nutrient budget; nutrient retention; oxygenation; phosphorus; reforestation.

Received 1 August 2015; accepted 23 October 2015;  
published online 4 January 2016

**Electronic supplementary material:** The online version of this article (doi:10.1007/s10021-015-9951-0) contains supplementary material, which is available to authorized users.

**Author contributions** ABG, PAG, JCL, CCC designed the study; ABG, ZWM, JPD, KDH, PAG, CCC performed research; ABG, ZWM, CCC analyzed data; ABG, PAG, JCL, CCC contributed methods; ABG, CCC wrote the paper.

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## INTRODUCTION

Climate change is predicted to have many diverse effects on freshwater lake and reservoir water quality and ecosystem functioning worldwide (for example, Adrian and others 2009; Williamson and others 2009). For example, in many regions, it is expected that warmer air temperatures will increase water temperatures, resulting in stronger thermal stratification and decreased hypolimnetic oxygen concentrations (reviewed by Jiménez Cisneros and others 2014). Hypolimnetic hypoxia (defined here as dissolved oxygen (DO) concentrations  $<2$  mg/l in the bottom stratum of a waterbody) alters many biological and chemical processes, including increased loading of nutrients from the sediments into the water column (that is, internal loading; Boström and others 1988; Mortimer 1941; Søndergaard and others 2003), and thus is of much interest to managers.

In concert with predictions of increased thermal stratification and hypolimnetic hypoxia, many lakes and reservoirs are also predicted to experience increased storm frequency and intensity (Bindoff and others 2013; Easterling and others 2000; Min and others 2011). Storms mobilize nutrients and sediments from the catchment and result in increased nutrient runoff into water bodies (that is, external loading; Beaulac and Reckhow 1982). In comparison to the number of analyses conducted on warming water temperatures (reviewed by Adrian and others 2009; Jiménez Cisneros and others 2014; Williamson and others 2009), there have been fewer studies that have explored the impacts of increased storm frequency and intensity on nutrient loading to lakes and reservoirs. The studies that have investigated this aspect of climate change found that storms substantially increase external loading of nitrogen (N) and phosphorus (P) to waterbodies (for example, Jeppesen and others 2009, 2011). However, it is not clear if the nutrients from the higher external loads remain in those ecosystems, or if they are exported downstream.

Through increasing hypolimnetic hypoxia and runoff, climate change may have cascading impacts on freshwater ecosystems because waterbodies in many regions will experience both stressors simultaneously (Bindoff and others 2013; Palmer and others 2014; Sahoo and others 2010). As a result, determining the relative importance of increased hypoxia and runoff and how they will interact to alter nutrient budgets is critically important because they will likely have substantial effects on water quality and nutrient cycling in lakes and reservoirs. In particular, increased inter-

nal and external loads of N and P can promote the formation of phytoplankton blooms and trigger a shift in trophic state (Conley and others 2009; Schindler and others 2008).

Examining these interactions in freshwater reservoirs is especially important because of the ubiquity of reservoirs and the critical role they play in global nutrient cycles. Reservoirs are abundant worldwide and are increasingly being built for water supply, hydropower, and irrigation (Downing and others 2006; Rosenberg and others 2000; Smith and others 2002). Over 10,000 km<sup>3</sup> of water has been impounded into reservoirs since the 1950s globally (Rosenberg and others 2000), with more than 2 million small reservoirs currently present across the U.S. (Smith and others 2002). Recent studies have indicated that reservoirs retain a substantial amount of N and P globally (Harrison and others 2009; Wollheim and others 2008) and generally function as N and P sinks, thereby reducing nutrient export to downstream (Nowlin and others 2005; Powers and others 2015; Teodoru and Wehrli 2005). However, if external nutrient loads increase (for example, due to increased storms), reservoir nutrient retention may decrease (Kõiv and others 2011; Powers and others 2015; Shostell and Bukaveckas 2004). Similarly, if hypoxia increases internal loads, the nutrients accumulated over time in the sediments may be remineralized and released downstream, further decreasing nutrient retention.

The hypolimnetic oxygen concentration of a reservoir is a key determinant of its nutrient budget because of the different biogeochemical processes that alter dissolved N and P cycles in hypoxic versus oxic conditions at the sediments, which hold the biggest store of N and P in a reservoir. For example, under hypoxic conditions in the hypolimnion,  $\text{NH}_4^+$  is released from the sediments into the water column while  $\text{NO}_3^-$  and  $\text{NO}_2^-$  are denitrified to dinitrogen ( $\text{N}_2$ ) (Knowles 1982; Stumm and Morgan 1996). Similarly, decreased redox potential at the sediment–water interface during hypoxia promotes the reduction of Fe(III) to Fe(II) in the sediments, leading to the release of SRP into the water column (Einsele 1936; Mortimer 1941). Under oxic conditions, by comparison,  $\text{NH}_4^+$  concentrations are generally low as a result of nitrification (Canfield and others 2010; Stumm and Morgan 1996) and an oxidized microzone at the sediment–water interface prevents the upward diffusion of SRP into the water column (Einsele 1936; Mortimer 1941).

The sensitivity of a reservoir to hypoxia and increased runoff may also depend on land use in the catchment. Although several studies have quanti-

fied nutrient budgets in reservoirs located in catchments with current agricultural land use (for example, Downing and others 2006; Renwick and others 2005; Smith and others 2002), less is known about the effects of historical agriculture on N and P dynamics in reforested catchments. Because agriculture can substantially increase nutrient export from the landscape via runoff (Powers and others 2013; Turner and Rabalais 2003), even after reforestation (Foster and others 2003; Harding and others 1998), it is possible that historical agriculture could continue to influence reservoir nutrient budgets in completely reforested catchments. In dimictic reservoirs, these nutrients will be reabsorbed into the sediments over the winter, with some fraction remineralizing back into the hypolimnion in the subsequent summer (Rydin 2000). If reservoir outflows do not discharge water from the hypolimnion, the effects of historical agricultural land use may be particularly long-lasting for hypolimnetic nutrient budgets because a large proportion of the hypolimnetic nutrient mass would continue to cycle between the water column and sediments, sustained by prolonged high external loads.

Here, we conducted whole-catchment manipulations of an old, eutrophic, dimictic reservoir in a reforested catchment to measure the effects of the potential climate change scenarios of increased hypoxia and increased runoff on reservoir N and P budgets. We manipulated hypolimnetic oxygen conditions and external nutrient loads by operating a hypolimnetic oxygenation system and controlling the volume of inflow water to the reservoir from an upstream tributary over a 2-year monitoring period. For each of the four treatments, we calculated whether the reservoir was a net nutrient sink or source of nutrients to downstream. We identified the four whole-catchment treatments as “Oxic-Low Inflow” (the reference treatment), “Oxic-High Inflow,” “Hypoxic-Low Inflow,” and “Hypoxic-High Inflow.” We predicted that the Hypoxic-High Inflow treatment would have the highest hypolimnetic mass of N and P and export more N and P downstream than any other treatment, in contrast to the Oxic-Low Inflow treatment, which would have the lowest hypolimnetic N and P mass and greatest nutrient retention. For a reforested reservoir with historical agricultural land use in its catchment, we expected that the Hypoxic-Low Inflow treatment would have higher hypolimnetic masses of N and P than the Oxic-High Inflow treatment due to the legacy of accumulated nutrients in the sediments.

## METHODS

### Study Site

We conducted whole-catchment manipulations in Falling Creek Reservoir (FCR), which is located in Vinton, Virginia, USA (37°18'12"N, 79°50'14"W) and is managed by the Western Virginia Water Authority (WVWA) as a drinking water source. FCR is eutrophic, has a maximum depth of 9.3 m, and has a volume of  $3.1 \times 10^5 \text{ m}^3$  (Figure 1; Gerling and others 2014). The reservoir receives water primarily from one upstream tributary that flows from Beaverdam Reservoir (BVR; Figure 2). A comprehensive water budget of FCR indicates that more than 95% of the reservoir water inputs come from the BVR inflow (WVWA, unpubl. data). When FCR was constructed in 1898, over 80% its catchment area was cropland or pasture (WVWA, unpubl. data). By the end of the 1930s, all of the farmland in FCR's catchment was abandoned, resulting in a forested catchment today (Figure 2; WVWA, unpubl. data).

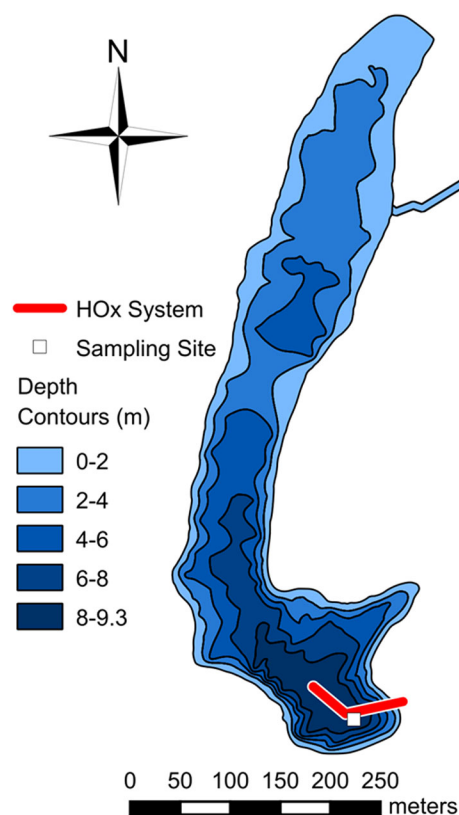
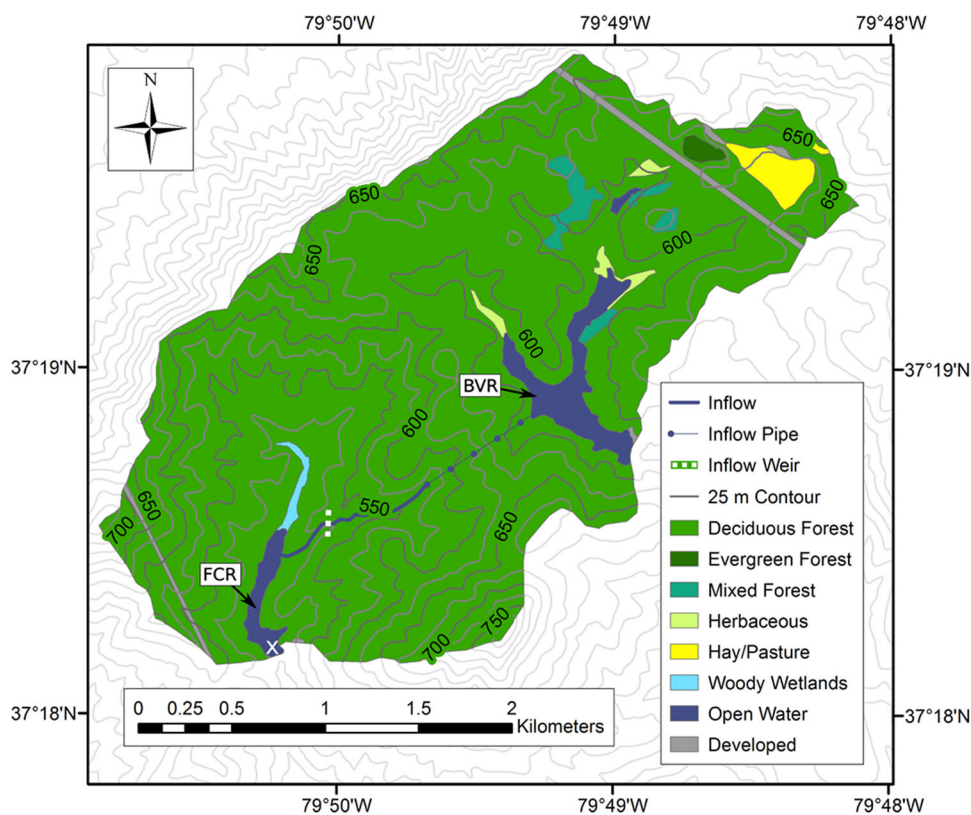


Fig. 1. Bathymetric map of Falling Creek Reservoir (FCR), located in Vinton, Virginia, USA. The white dot represents our sample site and the red line represents the location of hypolimnetic oxygenation (HOx) system (Color figure online).



**Figure 2.** Falling Creek Reservoir (FCR) and Beaverdam Reservoir (BVR) catchments located in Vinton, Virginia, USA. Water samples were collected from the deepest site of FCR (denoted by the “X”) and at the gauged weir (denoted by the *three white squares*) (Color figure online).

To increase oxygen concentrations in FCR’s hypolimnion, the WWA installed a hypolimnetic oxygenation (HOx) system in the reservoir in 2012 (see Gerling and others 2014). The HOx system withdrew hypolimnetic water from 8.5 m depth by a pump into piping that transported the water into an oxygen contact chamber on shore. In the chamber, 95% pure oxygen gas was dissolved in the water, resulting in supersaturated oxygen concentrations relative to the hypolimnion. The oxygenated water was piped from the oxygen contact chamber back into the hypolimnion at the same depth and temperature through nozzles. Although the nozzles were located at the deepest site of the reservoir near the dam (Figure 2), the HOx system increased oxygen concentrations in the majority of the hypolimnion (Gerling and others 2014).

### Manipulations of Hypolimnetic Oxygen and Inflow Volumes

We manipulated the hypolimnetic oxygen concentrations in the reservoir during our treatments by turning the HOx system sequentially on and off for about 4–6 week periods. We activated the HOx system twice in 2013 and three times in 2014 (see Table 1 for dates of HOx activation). During the

two activation periods in 2013 and the last activation period in 2014, the HOx system was operated to add oxygen to the hypolimnion at a rate of  $25 \text{ kg day}^{-1}$ ; in the first two activation periods in 2014, it added oxygen at  $20 \text{ kg day}^{-1}$  (see Table 1). Regardless of oxygenation rate, mixing induced by HOx operation circulated the hypolimnetic volume approximately every 26 days. Because of this induced mixing in the hypolimnion, our treatments were determined based on HOx activation (Oxic-Low Inflow, Oxic-High Inflow) or deactivation (Hypoxic-Low Inflow, Hypoxic-High Inflow) rather than observed hypolimnetic conditions for consistency across treatments and years.

We manipulated external loading to FCR by controlling the amount of water released from BVR into FCR (Figure 2). In 2013, for the two Low Inflow treatments, the inflow pipe from BVR into the FCR tributary was closed, so the only water entering FCR was other runoff from the catchment. On 28 April 2014, we opened the inflow pipe at BVR to recreate the peak amount of inflow that occurred during very large precipitation events in July 2013, as measured at the gauged weir (Figure 2). The inflow pipe originates in the epilimnion of BVR and is underground for about 750 m until it flows into a stream for about 950 m before entering FCR. The inflow pipe remained continuously open

**Table 1.** Hypolimnetic Oxygenation (HOx) System Activation Periods and Oxygen Addition Rates to the Bulk Hypolimnion in 2013 and 2014

Year	Dates of HOx activation	Oxygen addition rate (kg/day)
2013	14 May–20 June	25
2013	1 August–25 September	25
2014	6 May–3 June	20
2014	29 June–22 July	20
2014	18 August–29 September	25

*We activated the HOx system for two periods in 2013 and three periods in 2014.*

for the remainder of 2014 as part of the High Inflow treatments. As a result of the HOx and inflow volume manipulations and sampling limitations, the two Low Inflow treatments were composed of only one period in 2013 whereas the Oxidic-High Inflow treatment had three periods and the Hypoxic-High Inflow treatment consisted of two periods in 2014.

## Field Data Collection

We monitored the temperature and dissolved oxygen concentrations of FCR following the protocols described in Gerling and others (2014) a minimum of once to three times per week from June to September 2013 and May to September 2014, when the reservoir was thermally stratified (see Appendix 1 in Electronic supplementary material). We collected water samples to measure N and P concentrations in the upstream tributary from BVR about 150 m before it entered FCR at the weir and throughout the water column at the deepest site of FCR (Figures 1, 2). The water samples were collected at the reservoir's deepest site (Figure 1) to integrate hypolimnetic conditions in the reservoir. The samples were collected with a 1.2 l Kemmerer bottle or 4 l Van Dorn bottle (Wildlife Supply Company, Yulee, Florida) on a depth profile of the eight discharge depths of the reservoir: 0.1, 0.8, 1.6, 2.8, 3.8, 5.0, 6.2, and 8.0 m; 9.0 m was added in 2014. It is possible that there may have been slight variation in sampling depths from the Kemmerer or Van Dorn sampling bottles. In both years, 120 ml from each depth was syringe-filtered through 0.7  $\mu\text{m}$  Whatman GF/F filters in the field and poured into acid-washed plastic bottles. We analyzed the filtered samples for  $\text{NH}_4^+$ , SRP, and  $\text{NO}_3^- - \text{NO}_2^-$  on a Lachat (Lachat Instruments, Loveland, Colorado) following the Quik-Chem Method 10-115-10-1-B. We did not collect total nutrient data during 2013. However, water samples for total nitrogen (TN) and total phosphorus (TP) were collected from the nine discharge depths in 2014. The water was poured directly from the Van Dorn bottle into 120 ml acid-washed plastic bottles. We analyzed

the samples for TN and TP on a Lachat following USGS method I-4650-03. During the 2 years of monitoring, the mean ( $\pm 1$  SD) method detection limits were  $3.3 \pm 2.2 \mu\text{g l}^{-1}$  for  $\text{NH}_4^+$ ,  $2.0 \pm 0.8 \mu\text{g l}^{-1}$  for SRP,  $0.9 \pm 0.6 \mu\text{g l}^{-1}$  for  $\text{NO}_3^- - \text{NO}_2^-$ ,  $10.9 \pm 8.1 \mu\text{g l}^{-1}$  for TN, and  $2.9 \pm 1.2 \mu\text{g l}^{-1}$  for TP.

We measured the flow from the BVR tributary into FCR through the weir every 15 min with an INW Aquistar PT2X pressure sensor (INW, Kirkland, Washington), which recorded the temperature and water level above the weir notch. We used the water level data to calculate the mean daily flow rate of the stream into the reservoir, as described by Gerling and others (2014). We calculated the reservoir's hydraulic residence time using the flow rate of the upstream tributary and assuming that the reservoir was at full pond, which corresponded well to observations (WVWA, unpubl. data).

## Data Analysis

We used the nutrient concentrations measured in the reservoir's deepest site and at the weir to calculate the internal and external contributions of the masses of  $\text{NH}_4^+$ , SRP, and  $\text{NO}_3^- - \text{NO}_2^-$  in 2013 and 2014 and TN and TP in 2014 in the hypolimnion during our treatments. We focused on the hypolimnion and not the entire water column because the reservoir was thermally stratified throughout the entirety of our monitoring period and diffusion of N and P across the thermocline boundary was minimal. First, by analyzing temperature profiles, we identified the thermocline depth for each day as the depth that exhibited the maximum rate of change in temperature (Wetzel 2001), separating the epilimnion from hypolimnion. Regardless of inflow rate, the inflow water from BVR was consistently colder than the FCR water, resulting in underflow throughout both years. Thus, we assumed that all inflow water entering FCR went into the bottom of the hypolimnion. Throughout both years, water was only extracted for drinking water from the upper

epilimnion (WVWA, unpubl. data), and thus the hypolimnion did not have any other outflows except for water in the upper hypolimnion, which was entrained into the epilimnion to maintain the hypolimnetic volume.

In both years, the thermocline depth during the stratified summer period (June–September in 2013, May–September in 2014) was consistently observed between 3.8 and 5.0 m. Because our sampling depth profile was determined by the reservoir discharge depths, it did not include any coverage between 3.8 and 5.0 m at the thermocline boundary. We therefore designated depth samples collected at 0.1, 0.8, 1.6, 2.8, and 3.8 m as part of the epilimnion and 5.0, 6.2, and 8.0 m as part of the hypolimnion throughout our monitoring periods. We excluded the 2014 water samples collected from 9.0 m depth in this analysis for consistency between years.

To calculate the external loads from the inflow tributary, we first linearly interpolated the observed nutrient concentrations at the tributary weir between samplings to the daily scale. Next, we multiplied the observed mean flow rate on each day by the daily concentrations of each fraction of N and P to calculate the external load entering FCR in kg. We determined the hypolimnetic masses of each fraction of N and P by using our three sampling depths (5.0, 6.2, and 8.0 m) to partition the hypolimnetic volume of FCR into corresponding layers encompassing each sampling depth. We linearly interpolated the observed hypolimnetic concentrations between sample days and then multiplied the N and P concentrations observed at 5.0, 6.2, and 8.0 m by the respective water volume for each layer. Because the hypolimnetic volume did not substantially change through the stratified period, yet water was entering the bottom of the hypolimnion from the inflow tributary, we accounted for water being entrained from the top of the hypolimnion to the epilimnion (see Electronic supplementary material 2). We assumed that groundwater sources of N and P were negligible. Finally, we subtracted the observed external load from the hypolimnetic mass for each day and attributed the remainder of nutrient loading to internal sources.

To determine if FCR was a net nutrient sink or source of nutrients to downstream, we calculated the net fluxes of each fraction of N and P for each treatment. The nutrient inputs to FCR were defined as the external loads from BVR, as described above. To determine the nutrient outputs, we assumed that the inflow volume was equivalent to the outflow volume downstream, which left FCR at 0.1 m depth. Similar to the external loads, we first linearly interpolated the observed nutrient con-

centrations at 0.1 m depth between samplings to the daily scale. Next, we multiplied the observed mean inflow rate each day by the daily concentrations of each fraction of N and P to calculate the output of nutrients leaving FCR in kg. Finally, following Powers and others (2015), we estimated the net reservoir fluxes of each fraction of N and P as a percentage of the inputs using the equation:

$$[F_{\text{net}} = 100 \times (\text{Outputs} - \text{Inputs})/\text{Inputs}], \quad (1)$$

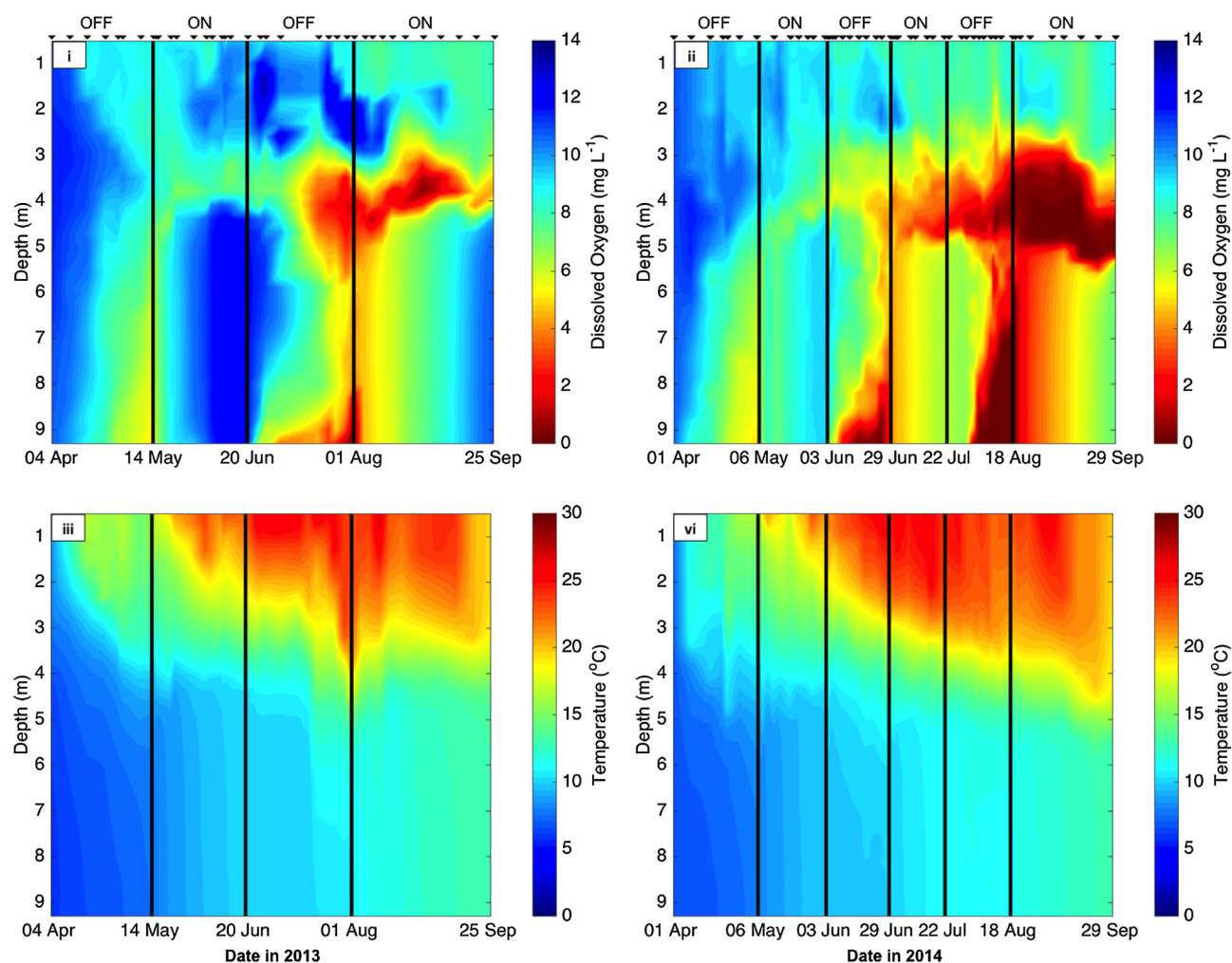
where  $F_{\text{net}}$  is defined as the net flux of nutrients. Negative values indicated that the reservoir exhibited net nutrient retention as a nutrient sink, and positive values represented net nutrient export to downstream.

Because we did not have a reference reservoir as part of our experimental design, the four treatments occurred sequentially, potentially confounding the comparison of nutrient budgets among treatments when the reservoir did not fully flush all water between treatment periods. Given this limitation, we standardized the hypolimnetic mass of each nutrient by subtracting the hypolimnetic mass observed on the last day of the previous treatment, corrected for the daily residence time of the reservoir to account for nutrient loss over time, from the hypolimnetic mass observed every day of the subsequent treatment. Thus, we were able to account for any remaining nutrients in the hypolimnion that accumulated during the previous treatment, as those nutrients were flushed from the reservoir over time. This standardization allowed us to compare nutrient dynamics among the treatments over the two monitoring years.

## RESULTS

We successfully manipulated hypolimnetic oxygen conditions and inflow volumes to FCR through our four treatments (Figures 3, 4). In both 2013 and 2014, HOx activation successfully increased hypolimnetic DO concentrations during the Oxidation treatments, producing a well-mixed hypolimnion with uniform DO concentrations from the thermocline to the sediments (Figure 3). Regardless of oxygen addition rate, the HOx operation increased DO concentrations in the bulk hypolimnion by approximately  $1 \text{ mg l}^{-1} \text{ week}^{-1}$ . A metalimnetic oxygen minimum developed at the thermocline in 2014, likely due to detritus accumulating as it settled more slowly at the cooler thermocline (Figure 3).

HOx deactivation to establish the Hypoxic treatments in 2013 and 2014 resulted in an immediate decline in hypolimnetic DO concentrations (Figure 3). Excluding the first monitoring periods in spring 2013 and 2014 when thermal stratification



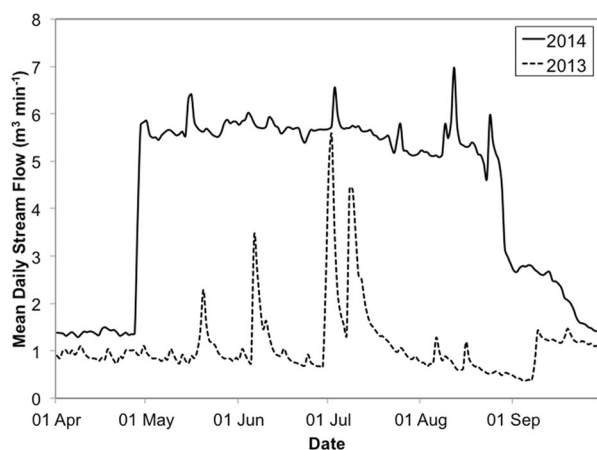
**Figure 3.** Dissolved oxygen concentrations (**i**, **ii**) and temperature (**iii**, **iv**) in FCR from April 04 to September 25, 2013 and April 01 to September 29, 2014. The hypolimnetic oxygenation system was activated for two periods in 2013 and three periods in 2014 as denoted by the “ON”; deactivation periods are denoted by the “OFF.” Sampling days are indicated by inverted black triangles; data were interpolated between sample days for the figure.

was weaker, hypoxic conditions at the sediments were consistently observed within 7 days of HOx deactivation in the Hypoxic treatments. Depending on the extent of hypoxia in the prior treatment, there were up to 3 days of hypoxic conditions in the Oxidic treatments after HOx reactivation until oxidic conditions were observed.

As a result of opening the inflow pipe at BVR, mean base flow in the tributary entering FCR from BVR during the High Inflow treatments ( $4.9 \pm 1.4 \text{ m}^3 \text{ min}^{-1}$ ; 1 SD) was approximately four times higher than in the Low Inflow treatments ( $1.2 \pm 0.9 \text{ m}^3 \text{ min}^{-1}$ ; Figure 4). Throughout bi-weekly sampling of BVR in summer 2014, we observed median ( $\pm 1$  SD) epilimnetic  $\text{NH}_4^+$ , SRP,  $\text{NO}_3^- - \text{NO}_2^-$ , TN, and TP concentrations of  $6.4 \pm 10$ ,  $4.1 \pm 24$ ,  $8 \pm 1.8$ ,  $205 \pm 49$ , and  $10 \pm 3.5 \text{ } \mu\text{g L}^{-1}$

respectively; in 2013, BVR was not monitored. The mean hydraulic residence time in FCR in 2013 during the Low Inflow treatments was  $247 \pm 118$  days and decreased to  $67 \pm 45$  days in 2014 during the High Inflow treatments. The reservoir experienced more large precipitation events in 2013 compared to 2014; a maximum flow rate of  $21.4 \text{ m}^3 \text{ min}^{-1}$  on July 10, 2013 was observed in the tributary after 10 cm of rain in the preceding 24 h (Figure 5).

Across all four treatments, epilimnetic  $\text{NH}_4^+$ , SRP, and  $\text{NO}_3^- - \text{NO}_2^-$  concentrations were consistently lower than observed in the hypolimnion (Figure 4i–vi), especially during hypoxic conditions, when  $\text{NH}_4^+$  and SRP concentrations peaked at the sediment–water interface (Figure 6i–iv). In 2014, the epilimnetic TN and TP concentrations were also lower than



**Figure 4.** Stream flow data calculated from the weir located on Falling Creek Reservoir (FCR)'s upstream tributary from April to September 2013 and 2014. In 2013, the inflow pipe from Beaverdam Reservoir into the tributary was closed, so the only water entering FCR through the tributary was runoff from the catchment. In April 2014, we increased the volume of water entering FCR by opening the inflow pipe at the upper Beaverdam Reservoir.

observed in the hypolimnion, with the highest concentrations measured just above the sediments during hypoxic conditions (Appendix 3 in Electronic supplementary material). In contrast to  $\text{NH}_4^+$ , SRP, TN, and TP, the maximum  $\text{NO}_3^- - \text{NO}_2^-$  concentrations were observed during oxic conditions and decreased substantially as hypoxia intensified (Figure 6v–vi). Below, we report the N and P budgets calculated for each of the four treatments.

### Oxic–Low Inflow Treatment

As expected,  $\text{NH}_4^+$ , SRP, and  $\text{NO}_3^- - \text{NO}_2^-$  standardized hypolimnetic masses exhibited some of their lowest levels in the 2 years of monitoring during the Oxic–Low Inflow reference treatment (Figure 7). On every day in this treatment, the external loading rates for  $\text{NH}_4^+$ , SRP, and  $\text{NO}_3^- - \text{NO}_2^-$  (all  $< 0.12 \text{ kg day}^{-1}$ ) were much lower than internal loading rates. As a result, internal sources were the largest contributor to the dynamics of the nutrient hypolimnetic masses (Figure 8i, iii, v), despite oxic conditions. On all days, internal loading contributed  $> 99\%$  of the observed  $\text{NH}_4^+$  mass. Similarly, internal sources contributed the majority (54 and 67%) of the hypolimnetic masses of SRP and  $\text{NO}_3^- - \text{NO}_2^-$ , respectively. FCR consistently functioned as a net nutrient sink, retaining a mean of  $25 \pm 37\%$  of  $\text{NH}_4^+$  inputs,  $76 \pm 8\%$  of SRP inputs, and  $90 \pm 6\%$  of  $\text{NO}_3^- - \text{NO}_2^-$  inputs (Figure 9).

### Hypoxic–Low Inflow Treatment

The hypolimnetic masses of  $\text{NH}_4^+$ , SRP, and  $\text{NO}_3^- - \text{NO}_2^-$  were much larger during the Hypoxic–Low Inflow treatment than the Oxic–Low Inflow reference treatment (Figure 7). Similar to the reference treatment, the largest contribution to the hypolimnetic masses of  $\text{NH}_4^+$ , SRP, and  $\text{NO}_3^- - \text{NO}_2^-$  throughout the Hypoxic–Low Inflow treatment was from internal sources (Figure 8i, iii, v), though much higher: for example, internal loading rates of  $\text{NH}_4^+$  were on average 130% higher than in the reference treatment. On all days, internal sources contributed 95–100% of the  $\text{NH}_4^+$  mass. With such high internal loading, FCR was a net source of  $\text{NH}_4^+$  downstream (exporting up to 300% of inputs, or three times the level of external loads) in this treatment (Figure 9). SRP and  $\text{NO}_3^- - \text{NO}_2^-$  were also primarily driven by internal sources, which contributed 70 and 65% of the mass of each nutrient in the hypolimnion, respectively. Unlike  $\text{NH}_4^+$ , however, FCR functioned as a net sink for  $\text{NO}_3^- - \text{NO}_2^-$  and SRP, retaining at least 68% of both nutrients' external loads (Figure 9), likely due to  $\text{NO}_3^- - \text{NO}_2^-$  removal via denitrification. External loads on eight days in this treatment were slightly larger than the reference due to storms (Figure 4); however, the external loads on all other days throughout the Hypoxic–Low Inflow treatment were still much smaller than observed in either High Inflow treatment. Regardless of the storms, internal loading was still the largest contributor to the nutrient dynamics in this treatment.

### Oxic–High Inflow Treatment

Following our predictions for a reforested reservoir with a history of agricultural land use in the catchment, the hypolimnetic nutrient masses in the Oxic–High Inflow treatment were consistently smaller than in the Hypoxic–Low Inflow treatment (Figure 7). All three periods within the Oxic–High Inflow treatment exhibited similar internal and external loads. Despite much higher inflow volumes into FCR from BVR and largely oxic hypolimnetic conditions, internal sources still primarily dominated the nutrient budget of  $\text{NH}_4^+$  in this treatment, though the internal  $\text{NH}_4^+$  loading rates were one to three orders of magnitude lower than observed in the Hypoxic–Low Inflow treatment (Figure 8i, ii). During the three periods that composed the Oxic–High Inflow treatment, internal loading contributed 50, 73, and 87%, respectively, of the observed hypolimnetic  $\text{NH}_4^+$  masses (Figure 8ii). For all three periods, FCR was consistently



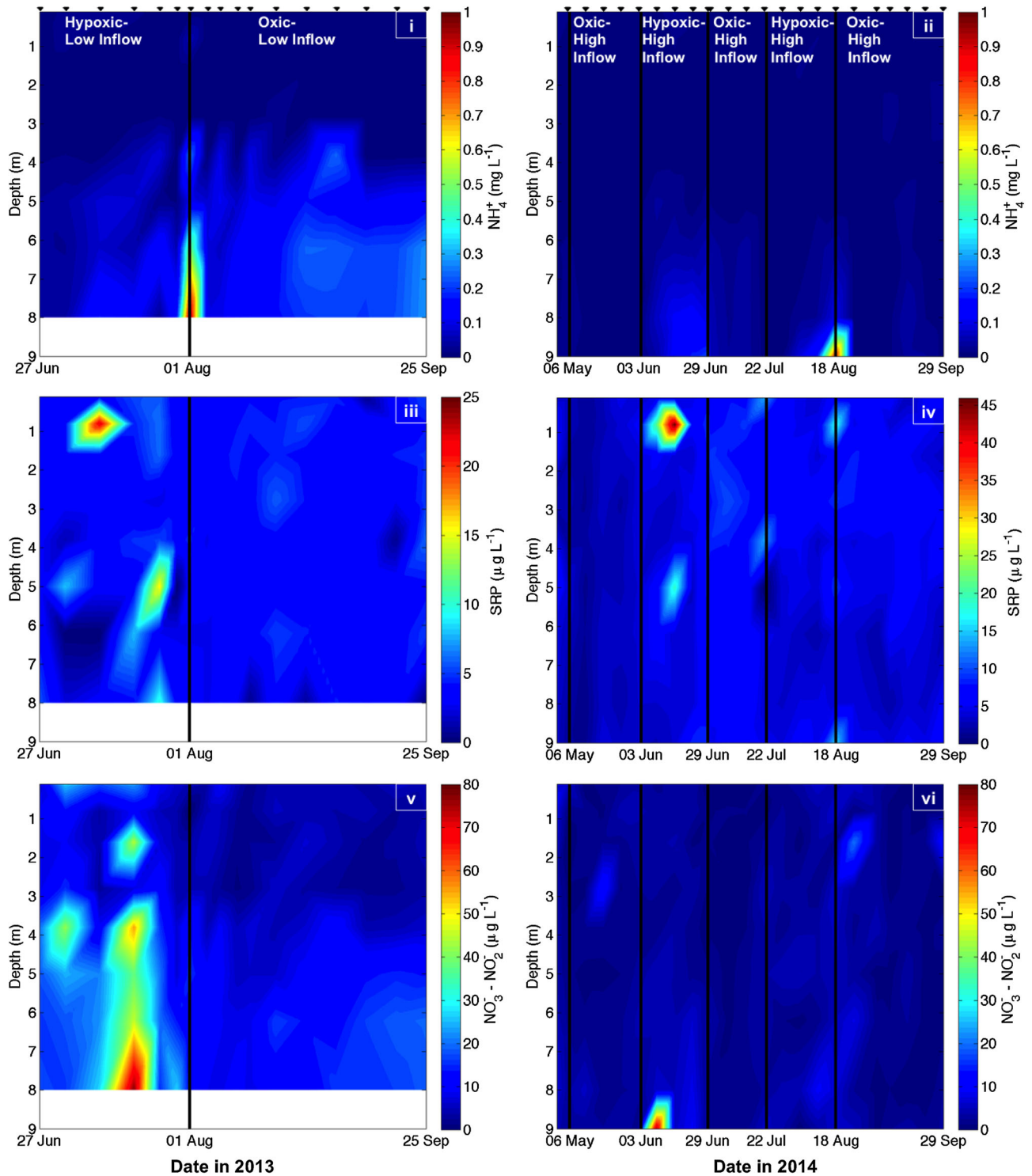


Figure 5. Water column  $\text{NH}_4^+$  (i, ii), SRP (iii, iv), and  $\text{NO}_3^- - \text{NO}_2^-$  (v, vi) concentrations in 2013 and 2014, respectively.  $\text{NH}_4^+$  concentrations are given in  $\text{mg L}^{-1}$  and SRP and  $\text{NO}_3^- - \text{NO}_2^-$  concentrations are given in  $\mu\text{g L}^{-1}$ ; note the difference in color scales among panels. All measurements were collected at the deepest site of Falling Creek Reservoir from June 27 to September 25, 2013 and May 01 to September 29, 2014. All sample days are denoted by *inverted black triangles* and data were interpolated between sample days for the figure. The *black lines* represent transitions between treatments labeled in *white font* (Color figure online).

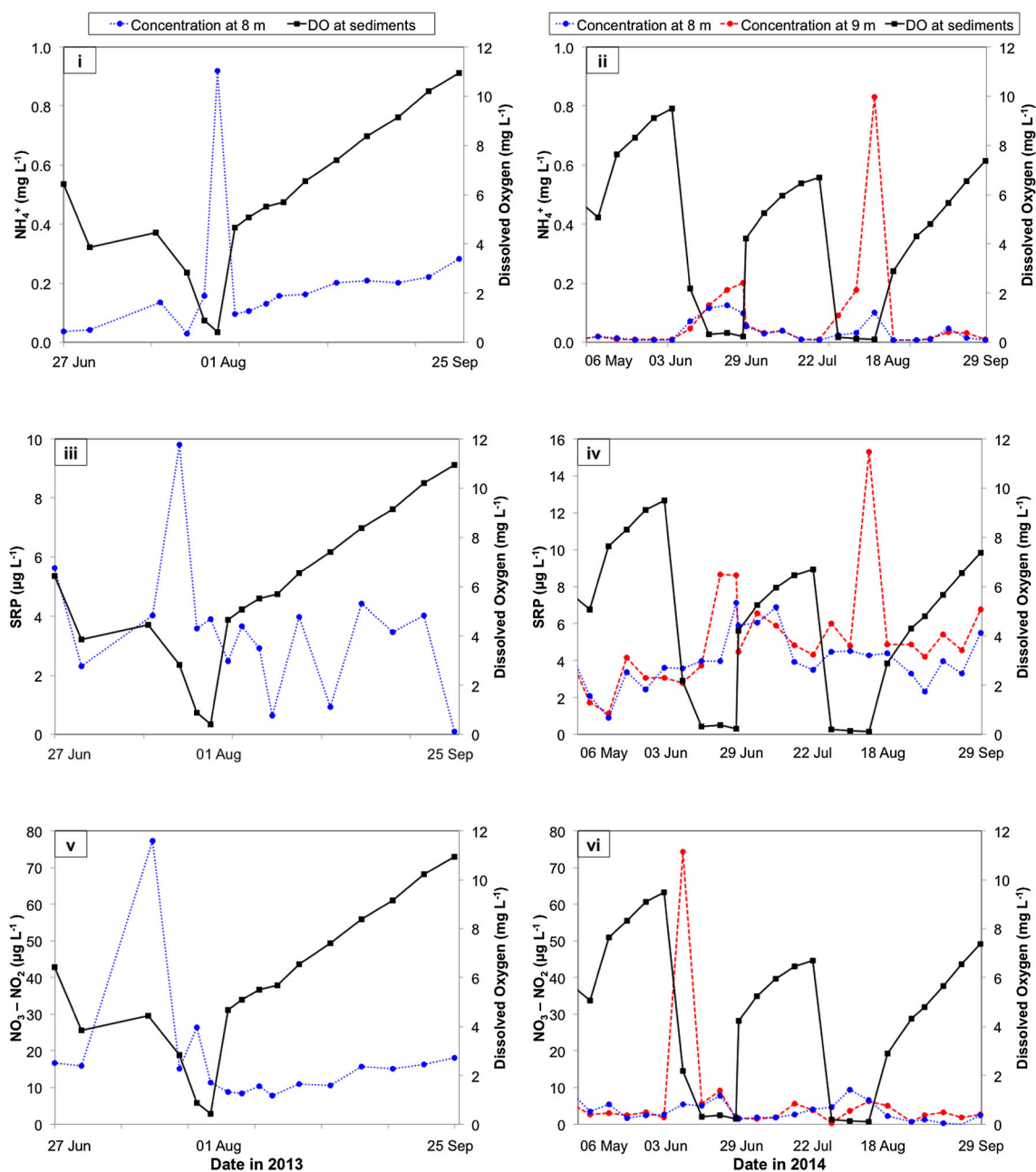
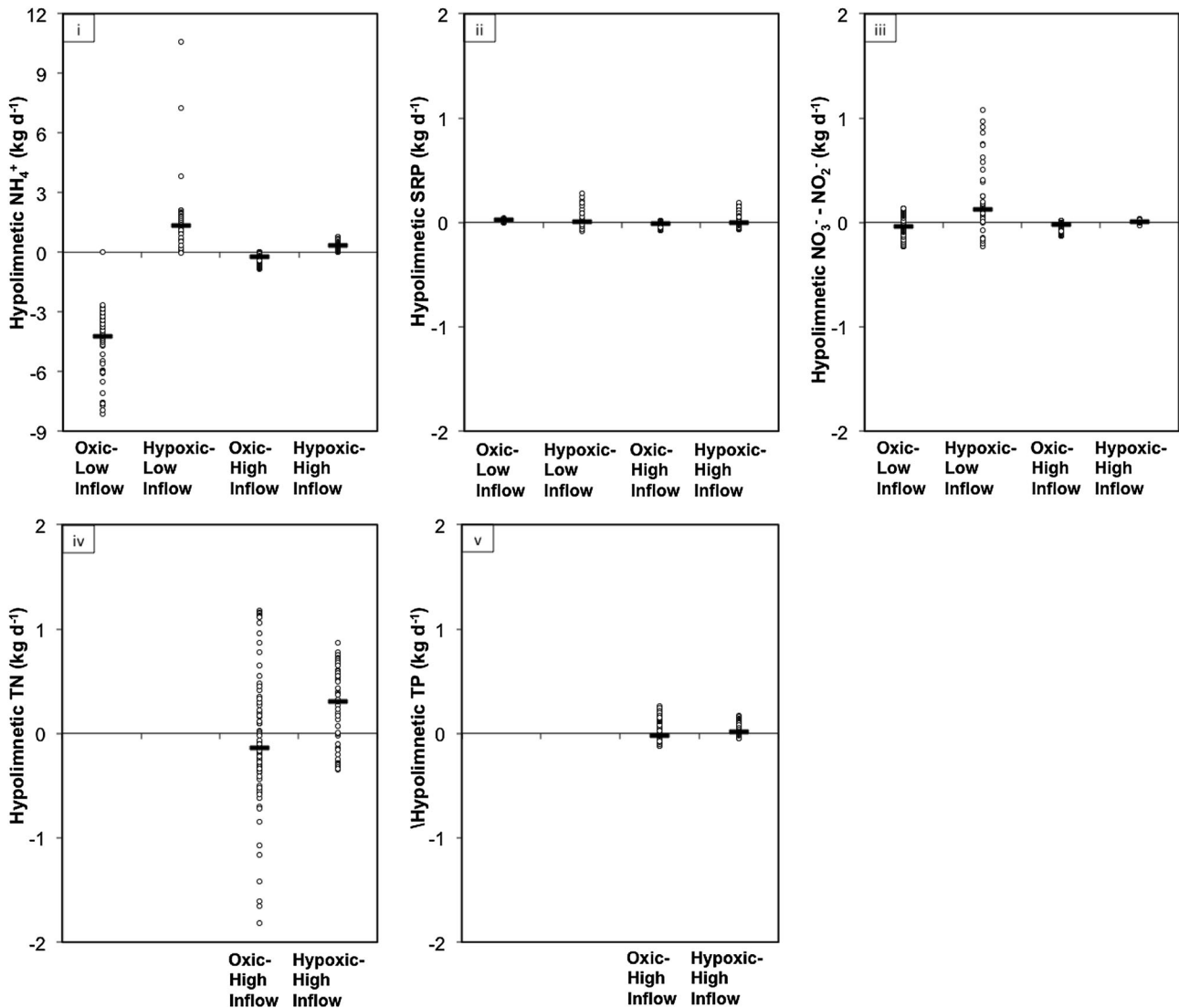


Figure 6.  $\text{NH}_4^+$  (i, ii), SRP (iii, iv), and  $\text{NO}_3^- - \text{NO}_2^-$  (v, vi) concentrations measured at 8 m depth in 2013, 8 and 9 m depths in 2014, and dissolved oxygen (DO) concentrations at the sediments. DO and  $\text{NH}_4^+$  concentrations are given in  $\text{mg l}^{-1}$  and SRP and  $\text{NO}_3^- - \text{NO}_2^-$  concentrations are given in  $\mu\text{g l}^{-1}$ . All measurements were collected at the deepest site of Falling Creek Reservoir from June 27 to September 25, 2013 and May 01 to September 29, 2014.

a sink of  $\text{NH}_4^+$  and retained at least 58% of  $\text{NH}_4^+$  inputs (Figure 9).

In contrast to  $\text{NH}_4^+$ , the majority of the hypolimnetic SRP,  $\text{NO}_3^- - \text{NO}_2^-$ , TN, and TP masses were contributed by external loads during the three periods of the Oxidic-High Inflow treatment, as a result of increased inflow volume (Figure 8iv). Aggregated across the three periods, external

loading contributed 52–88% of the hypolimnetic SRP mass, 73–89% of the  $\text{NO}_3^- - \text{NO}_2^-$  mass (Figure 8). During the first two periods, external loading contributed 79–92% of the TN mass, and 72–87% of the TP mass (Appendix 3 in Electronic supplementary material). However, during the last period of the treatment, internal sources contributed the majority of TN and TP hypolimnetic



**Figure 7.** The standardized hypolimnetic masses of  $\text{NH}_4^+$  (**i**), SRP (**ii**),  $\text{NO}_3^- - \text{NO}_2^-$  (**iii**), TN (**iv**), and TP (**v**) displayed for all days within a treatment in  $\text{kg day}^{-1}$ . The *black dash* represents the median of each treatment. The two Low Inflow treatments were composed of one period, the Oxidic-High Inflow treatment had three periods, and the Hypoxic-High Inflow treatment had two periods. Data in this figure for the two High Inflow treatments were aggregated across periods.

masses (57 and 63%, respectively; Appendix 3 in Electronic supplementary material). Similar to  $\text{NH}_4^+$ , the mean internal SRP and  $\text{NO}_3^- - \text{NO}_2^-$  loads during the three periods were two orders of magnitude smaller than observed in the Hypoxic-Low Inflow treatment (Figure 8iii, iv). FCR was a sink for all four nutrients during the three periods, especially for  $\text{NO}_3^- - \text{NO}_2^-$ , retaining 19–47% of SRP, 91–98% of  $\text{NO}_3^- - \text{NO}_2^-$ , 21–50% of TN, and 35–63% of TP inputs (Figure 9).

### Hypoxic-High Inflow Treatment

The Hypoxic-High Inflow treatment did not exhibit the largest hypolimnetic masses for every nutrient,

contrary to our predictions: this treatment's hypolimnetic nutrient masses were consistently at the level of, or slightly below, the masses observed in the Hypoxic-Low Inflow treatment (Figure 7). Both periods of the Hypoxic-Low Inflow treatment exhibited similar nutrient dynamics, except that SRP and TP internal loads were higher in the first period.

Internal sources largely dominated the nutrient budgets of  $\text{NH}_4^+$  during hypoxic and high inflow conditions, contributing 72–87% of the hypolimnetic mass of  $\text{NH}_4^+$ . Despite a lower contribution of SRP from internal sources throughout the two periods (31–54%), FCR functioned as a nutrient sink for both nutrients, retaining a mean of 1–59%

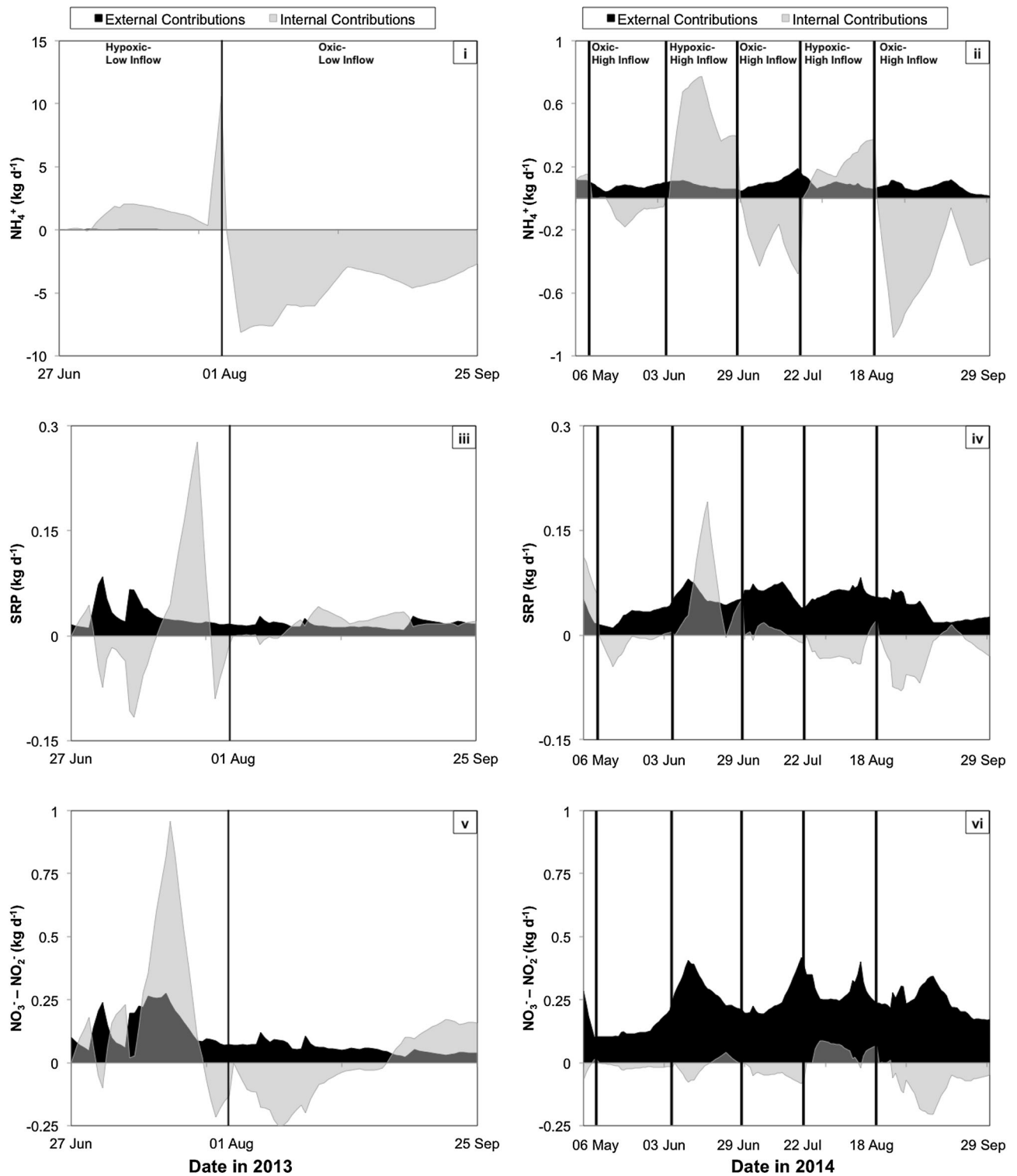


Figure 8. The internal (gray area) and external (black area) contributions of hypolimnetic  $\text{NH}_4^+$  (i, ii), SRP (iii, iv), and  $\text{NO}_3^- - \text{NO}_2^-$  (v, vi) in 2013 and 2014, respectively. All loads are given in  $\text{kg day}^{-1}$ . The black lines represent transitions between treatments. Note that the scales on the y-axes for  $\text{NH}_4^+$  differ between 2013 and 2014 but are the same for SRP and  $\text{NO}_3^- - \text{NO}_2^-$ .

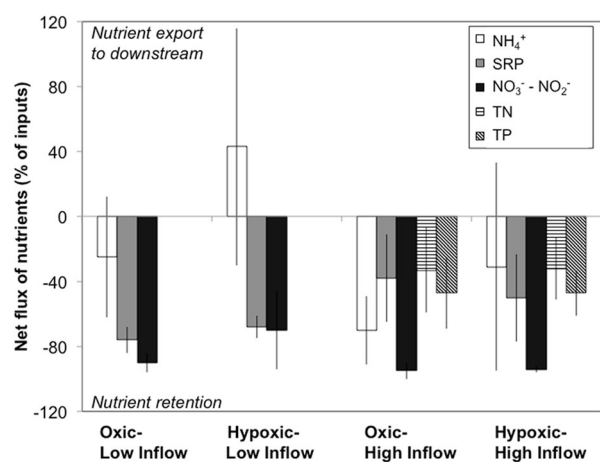


Figure 9. The net fluxes (mean  $\pm$  SD) of  $\text{NH}_4^+$ , SRP,  $\text{NO}_3^- - \text{NO}_2^-$ , TN, and TP as a percentage of the nutrient inputs for each treatment. *Negative values* represent net nutrient retention/loss and *positive values* represent net nutrient export to downstream.

of  $\text{NH}_4^+$  inputs and 48–54% of SRP inputs; Figure 9). During both periods, the mean internal loading rate of  $\text{NH}_4^+$ ,  $0.4 \pm 0.2 \text{ kg day}^{-1}$ , was considerably smaller than the mean internal loading rate of  $\text{NH}_4^+$  in the Hypoxic-Low Inflow treatment,  $1.6 \pm 2.0 \text{ kg day}^{-1}$ . However, the mean internal loading rates of SRP in the two treatments were very similar,  $0.02 \pm 0.1$  and  $0.02 \pm 0.06 \text{ kg day}^{-1}$ , respectively.

In comparison to  $\text{NH}_4^+$  and SRP, external loading contributed a much higher proportion of the hypolimnetic masses of  $\text{NO}_3^- - \text{NO}_2^-$ , TN, and TP. External sources contributed more than 68% of the masses of  $\text{NO}_3^- - \text{NO}_2^-$ , TN, and TP present in the hypolimnion during both periods. In the hypoxic conditions of this treatment, FCR was a major  $\text{NO}_3^- - \text{NO}_2^-$  sink during both periods, removing a mean of  $95 \pm 2$  and  $94 \pm 1\%$ , respectively, of  $\text{NO}_3^- - \text{NO}_2^-$  inputs (Figure 9). FCR was also a sink for TN and TP during both periods, removing a mean of  $32 \pm 19$  and  $47 \pm 14\%$  of TN and TP inputs, respectively.

## DISCUSSION

The hypolimnetic nutrient dynamics in FCR were substantially affected by our manipulation of hypolimnetic oxygen conditions and inflow volumes to the reservoir. Below, we discuss the observed nutrient budgets in the reservoir, and the implications of our findings for reservoir biogeochemical cycles in the face of global change.

## Internal Loads Dominated FCR's Nutrient Budgets

Our results provide substantial evidence that internal N and P loads greatly influence the hypolimnetic nutrient dynamics in FCR (Figure 8). Internal loads largely controlled the hypolimnetic masses of  $\text{NH}_4^+$  and SRP, even when external volumes were experimentally increased by approximately 400% from 2013 to 2014 and the reservoir had an oxic hypolimnion. Furthermore, the reservoir responded quite predictably to the multiple HOx activation and deactivation transitions across the 2 years: internal loads of  $\text{NH}_4^+$ , SRP, TN, and TP peaked in the Hypoxic treatments. These increases in internal loading during hypoxia were likely due to the diffusion of  $\text{NH}_4^+$  and TN from the sediment pore water into the water column and redox-mediated SRP and TP release from the sediments (Boström and others 1988; Mortimer 1941; Stumm and Morgan 1996).

The hypolimnetic masses of  $\text{NH}_4^+$ , SRP, TN, and TP were particularly sensitive to oxygen conditions at the sediments, even during the treatments with higher external loads from BVR (Figure 8ii, iv). From 2013 to 2014, we calculated that the  $\text{NH}_4^+$  and SRP external loading rates would have needed to additionally increase by about 1000% and about 350%, respectively, to have equaled the mass of nutrients contributed by internal loads in the Hypoxic-High Inflow treatment. The largest release of  $\text{NH}_4^+$  and SRP from the sediments occurred during the first period of the Hypoxic-High Inflow treatment (Figure 6ii, iv; Figure 8ii, iv), which has also been observed in several other lakes that experience hypolimnetic hypoxia (for example, Rydin 2000), potentially because there are less nutrients remaining in the surface sediment that could be released into the water column as the hypoxia continues. As a result, during the second Hypoxic-High Inflow period, the external contribution of the hypolimnetic mass of SRP was more prominent (Figure 8iv). During all periods of the Hypoxic treatments, we observed more variability in the internal nutrient loads and hypolimnetic masses than in the periods of Oxic treatments (Figures 7, 8). This variation may be an effect of the longer time it took for hypoxic conditions to be achieved in the Hypoxic periods than oxic conditions in the Oxic periods, resulting in more variability in the internal loads over time within the Hypoxic treatment.

In contrast to  $\text{NH}_4^+$  and SRP, external loading of  $\text{NO}_3^- - \text{NO}_2^-$  dominated nutrient budgets in the High

Inflow treatments. The relative proportion of  $\text{NO}_3^- - \text{NO}_2^-$  contributed from internal sources was low throughout our monitoring period in 2014, suggesting accelerated rates of N removal during the High Inflow treatments, presumably through denitrification (Figure 8vi) (Koop-Jakobsen and Giblin 2010). In both years, the internal loading rates of  $\text{NO}_3^- - \text{NO}_2^-$  decreased considerably in the Hypoxic treatments, also likely due to denitrification (Figure 6v, vi). As a result, the reservoir served as a large sink of  $\text{NO}_3^- - \text{NO}_2^-$ , as discussed below.

Our experimental design during the 2-year monitoring period presented some limitations. For example, it was difficult to compare the magnitude of the treatments between years. However, the comparison of oxic and hypoxic hypolimnetic conditions within the same year (that is, the Hypoxic-Low Inflow and Oxic-Low Inflow treatments in 2013 and the Hypoxic-High Inflow and Oxic-Low Inflow treatments in 2014) demonstrated that the hypolimnetic masses were strongly driven by internal loads under hypoxic conditions in the reservoir, despite autocorrelation between sequential treatments and interannual variability. Although we did not have a reference ecosystem to monitor for comparison, standardization of the hypolimnetic masses allowed us to segregate the effects of nutrient dynamics between treatments. Even without standardization among the treatments, we found that internal loads still primarily dominated the hypolimnetic masses of nutrients in FCR.

### FCR as a Net Nutrient Sink

Nutrient retention or removal in reservoirs is broadly affected by interacting internal and external dynamics, including residence time and loading from the catchment via runoff (Essington and Carpenter 2000; Kõiv and others 2011; Powers and others 2015). During our 2-year monitoring period, FCR commonly functioned as net nutrient sink, though there was variation in the magnitude of nutrient losses among treatments (Figure 9). Nutrients were retained presumably by sedimentation, nutrient burial, and biological uptake, as well as N removal via denitrification and other N removal processes (Burgin and Hamilton 2007; David and others 2006; Essington and Carpenter 2000; Molot and Dillon 1993; Vanni and others 2011). The only time FCR served as a net nutrient source to downstream (that is, positive net flux) was for  $\text{NH}_4^+$  during the Hypoxic-Low Inflow, due to very large internal  $\text{NH}_4^+$  loads during hypoxia, some of which were likely entrained into the

epilimnion and exported downstream through the reservoir outflow.

The magnitude of net fluxes varied among nutrients (Figure 9). Throughout all four treatments, FCR retained a mean of 38–76% of SRP inputs, which corresponded closely to a mean of 47% of TP inputs. SRP retention was lower in the High Inflow treatments than in the Low Inflow treatments, presumably due to their higher external loads and shorter residence time (Figure 9). By comparison, FCR was a sink for a remarkably large proportion of  $\text{NO}_3^- - \text{NO}_2^-$  inputs (a mean of 70–95% across treatments), with the highest retention rates observed in the High Inflow treatments. After increasing the inflow volume from BVR, external  $\text{NO}_3^- - \text{NO}_2^-$  loads to FCR increased by 240%. It is possible that these higher external loading rates may have accelerated the rate of denitrification during 2014, as also observed by Koop-Jakobsen and Giblin (2010), resulting in the reservoir serving as a much greater  $\text{NO}_3^- - \text{NO}_2^-$  sink that year. The site of the reservoir where the inflow enters FCR (Figure 3) is only about 3.5 m depth, yet still experiences thermal stratification and hypoxia (Gerling and others 2014). These warm, shallow, littoral sediments with high organic material deposits are likely a biogeochemical hotspot for N removal via denitrification (Bruesewitz and others 2012), with much higher denitrification rates in years with increased  $\text{NO}_3^- - \text{NO}_2^-$  loads.

In comparison to SRP and  $\text{NO}_3^- - \text{NO}_2^-$ , FCR served as both a sink and source of  $\text{NH}_4^+$  downstream, which was largely controlled by the magnitude of internal loading rates. During the Hypoxic-Low Inflow treatment, the reservoir exported up to 300% of  $\text{NH}_4^+$  inputs downstream. These high export rates are due to the extremely high internal loading rates of  $\text{NH}_4^+$  during the 2-year monitoring period, up to  $11 \text{ kg day}^{-1}$ . Throughout the other treatments, dissolved N retention in FCR was higher in High Inflow treatments than Low Inflow treatments (Figure 9), again suggesting that higher rates of sedimentation, nutrient burial, and uptake occurred in the reservoir in 2014 compared to 2013 (David and others 2006; Koop-Jakobsen and Giblin 2010). The TN dynamics in 2014 integrated the dissolved fractions of N, largely reflecting the combined pattern of  $\text{NH}_4^+$  and  $\text{NO}_3^- - \text{NO}_2^-$ .

Previous studies (for example, Harrison and others 2009; Powers and others 2015; Smith and others 1997) have also reported net N and P retention in reservoirs. For example, Powers and others (2015) found many reservoirs in currently agricultural catchments across the Midwestern U.S.

retain more than 20% of N and P inputs. Additionally, reservoirs along large rivers across the United States retained 34% of P inputs whereas reservoir N retention represented 0–32% of inputs to 17 temperate reservoirs (Harrison and others 2009). These reservoirs varied considerably in age, trophic status, size, catchment history, residence time, and magnitude of nutrient loads, but most were much larger in size than FCR. FCR exhibited much higher nutrient retention rates than those measured in previous studies, likely due to both its small size and shallow depth (Powers and others 2013; Renwick and others 2005), which promotes high settling velocities of nutrients and sediments (Harrison and others 2009), and its management. Because water for drinking is only extracted from the epilimnion and the cold inflow water bringing in external nutrient loads enters the bottom of the reservoir, the external loads are able to accumulate in the hypolimnion with minimal flushing downstream. As a result, the  $\text{NH}_4^+$ , SRP, and  $\text{NO}_3^- - \text{NO}_2^-$  retention rates measured in this study for FCR are among the highest rates observed for reservoir ecosystems (Harrison and others 2009; Kelly 2001; Leavitt and others 2006; Patoine and others 2006; Salas and Martino 1991).

Aging reservoirs such as FCR play an important role in the landscape as sites for nutrient retention, thereby reducing the magnitude of nutrient export to downstream aquatic ecosystems (Powers and others 2013). For the case of FCR, our results suggest that the reservoir has resilience to increased external nutrient loads expected with more frequent and powerful storm events. This observation is particularly relevant for  $\text{NO}_3^- - \text{NO}_2^-$ , which was demonstrated by FCR's increased retention rates in response to increased external loads in the High Inflow treatments. However, hypolimnetic hypoxia may mediate the role of reservoirs as nutrient sinks or sources, as we observed for  $\text{NH}_4^+$ . Future increases in N and P internal loads will undoubtedly modify nutrient delivery downstream and the ability of the reservoir to serve as a sink or source of N and P.

### Long-Term Effects of FCR's Catchment Land Use

As a result of its agricultural legacy and epilimnetic water extraction, FCR has accumulated a substantial amount of nutrients in its sediments, despite little human activity in the catchment for the past approximately 80 years. Because the hypolimnion of FCR becomes hypoxic during the summer stratified period in the absence of human intervention, it is possible that some fraction of the nutrients that en-

tered the reservoir prior to reforestation have been continually recycled into the water column in the summer and then redeposited onto the sediments each year. This nutrient cycling was likely also subsidized by elevated nutrient export from the catchment post-reforestation. Consequently, historical high external loading may be responsible for high internal loading in hypoxic conditions in the present (for example, "the ghost of loadings past"; Harding and others 1998). It is possible that other nutrient sources may have also contributed to the high internal loads observed in FCR, such as weathering bedrock. Regardless of nutrient source, FCR is notable in the length of time since catchment reforestation (> 80 years) that a reservoir with a relatively short residence time (< 1 year) is still exhibiting high internal loading rates during hypoxia. Consequently, our results suggest that it is critical to consider reservoir catchment history and waterbody characteristics, such as size and management, when predicting the effects of hypolimnetic hypoxia and increased storms on reservoir nutrient budgets.

### Looking Ahead: The Power of the Whole-Catchment Experiment Approach

Although it is not always feasible, whole-catchment and whole-ecosystem experiments offer invaluable insight to biogeochemical processes that are crucial for understanding how to adaptively manage for climate change (Carpenter 1996; Carpenter and others 1995). Given that FCR's region is predicted to experience both rising air temperatures and increased storm frequency and intensity in the future (Bindoff and others 2013; Easterling and others 2000; Min and others 2011), the whole-catchment manipulations provided a powerful approach for determining the sensitivity of the reservoir to potential future climate changes. Our manipulations demonstrated that the greatest climate change risk to FCR's water quality may be increased internal loads stimulated by hypoxic conditions in the hypolimnion, as expected under future scenarios of longer and more intense thermal stratification. As the construction of reservoirs increases globally (Downing and others 2006; Rosenberg and others 2000; Smith and others 2002), their responses to future climate will have substantial implications for biogeochemical processes in the landscape over decades to centuries.

### ACKNOWLEDGEMENTS

We thank the staff at the Western Virginia Water Authority, especially C. Brewer, J. Morris, J. Booth,

G. Belcher, B. Benninger, P. Martin, and G. Robertson for their long-term support. K. Bierlein, R. Browne, M. Flood, Z. Gajewski, M. Haberman, B. Niederlehner, and C. Urbanczyk provided critical help in the field and laboratory. This work was supported by the Virginia Tech Dept. of Biological Sciences, the Institute for Critical Technology and Applied Science, Fralin Institute of Life Sciences, National Fish & Wildlife Foundation Grant 13014.042027, and a Virginia Tech Organismal Biology and Ecology grant to C.C.C.

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