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Reservoirs are hotspots of nitrogen cycling in peatland catchments

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Abstract

This study presents input-output budgets of total dissolved nitrogen (TDN), dissolved organic N (DON) and dissolved inorganic N (DIN) for a reservoir in a peatland catchment in the south Pennines (UK). This site receives high levels of atmospheric inorganic N deposition, in the range of $26 \text{ kg N ha}^{-1} \text{ yr}^{-1}$. The results show that the reservoir retains ~21 to 31% of the annual TDN input ($8806 \pm 741 \text{ kg N}$). Approximately 39 to 55% of DON ($3782 \pm 653 \text{ kg N}$) and 6 to 13% of DIN ($5024 \pm 349 \text{ kg N}$) was retained/processed. A long water retention time (104 days), average annual pH of 6.5, high concentrations of DIN in the reservoir water and a deep water column suggests that denitrification is potentially a key mechanism of N retention/removal. The results also demonstrate that DON is potentially photodegraded and utilised within the reservoir, particularly during the summer season when 58 to 80% of DON input ($682 \pm 241 \text{ kg N}$) was retained, and a net export of DIN ($\sim 34 \text{ kg N}$) was observed. The findings therefore suggest that DON may play a more crucial role in the biogeochemistry of peat-dominated acid sensitive upland freshwater systems than previously thought. Reservoirs, impoundments, and large lakes in peatland catchments may be important sites in mediating downstream N transport and speciation.

Keywords: Nitrogen; Reservoir; Nutrient budget; Peat; DON; south Pennines

1. Introduction

The use of nutrient input-output budgets as a method for evaluating the impacts of anthropogenic activities on the fluvial environment has long been recognised (Vogt et al., 2013; Rothwell et al., 2008; Cooper, 2005; Winter et al., 2002; Crisp, 1966). Freshwater acidification from high atmospheric sulphur (S) and inorganic nitrogen (N) deposition is a major water quality problem in many upland environments in the Northern Hemisphere (Aherne et al., 2003; Skjelkvale et al., 2003; Curtis et al., 2000; Evans et al., 2000; Stoddard et al., 1999). Although a significant decline in S deposition has been observed (Futter et al., 2014; Curtis et al., 2005; Cooper and Jenkins, 2003; Dillon et al., 2003), N deposition has remained high in some upland regions (Helliwell et al., 2007; Evans et al., 2000; Goodale et al., 2000; Aber et al., 2003). Elevated N deposition alters biogeochemical cycling in lakes and freshwater systems (Elser et al., 2009, 2007; Wolfe et al., 2001), potentially resulting in deleterious ecological consequences (Lepori and Keck, 2012; Baron et al., 2011). In areas of high N input, reservoirs or lakes with their large surface area for nutrient exchange and turnover (Durand et al., 2011; Shotbolt et al., 2005; Thornton et al., 1990) can be effective traps of N, thus mediating the downstream effects of excess N loading (Jansson et al., 1994).

Reservoirs contain a significant array of biological assemblages that directly utilise dissolved nutrients (Kelly, 2001), with the stream–reservoir–stream fluvial system offering a unique environment for understanding the changes of dissolved N at a range of temporal scales. The interaction between the chemistry of inflowing water and the processes occurring within reservoirs influences the downstream transport of nutrients (Thornton et al., 1990), and gives extra significance to reservoir outlets (Toetz, 1973). Reservoirs play important roles in the global carbon (C) cycle; acting as recipients of dissolved organic, inorganic, and particulate organic C (DOC, DIC and POC, respectively), as well as producers of greenhouse gases,

including carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O) (Battin et al., 2009; Tranvik et al., 2009). Large amounts of C and N are stored by reservoirs and lakes through sedimentation (Kunz et al., 2011; Tranvik et al., 2009; David et al., 2006; Jansson et al., 1994). The global annual burial rate of organic C (OC) by sediments of reservoirs is estimated to be 160 Tg yr⁻¹; ~ 3.8 times higher than in lake sediments (Dean and Gorham, 1998). Although the growing demand for water due to the increasing needs of a rising human population may increase the propagation of impoundments across the globe (Downing et al., 2006), alongside the associated impacts of such landscape modifications (Tranvik et al., 2009), recent studies have suggested that the number of large dam construction projects has levelled off in the last 10-15 years (Steffen et al., 2015).

The extensive Pennine uplands of the UK contain a remarkable number of reservoirs that provide a vital source of drinking water to the surrounding urban population (Evans et al., 2000; Shotbolt et al., 2000). A significant proportion of this peatland environment is heavily eroded and extensively gullied (Tallis, 1997), with organic sediment yields of ~200 t km⁻² a⁻¹ (Evans et al., 2006). As a consequence, water supply reservoir catchments in these uplands are generally managed (stabilisation of soils, moorland restoration and protection of watercourses) to ensure the provision of good water quality (United Utilities, 2011), with major focus on DOC removal; the most significant cost to water treatment in the UK (Worrall et al., 2004). Whilst soil erosion and sediment transport of particulate nutrients to reservoirs and impoundments constitute redistribution or translocation of nutrient sinks within catchments (Battin et al., 2009; Downing et al., 2008; Ittekkot and Zhang, 1989), the focus of our study was on the biologically active component of N – dissolved N; one of the most common chemical metrics used to evaluate freshwater ecosystem health (Roley et al., 2014). At present, there is a significant deficiency in current understanding of the role of reservoirs

as mechanisms of N retention, cycling and removal in peat-dominated catchments where high atmospheric N deposition coincides with a high density of reservoir impoundments supplying major urban areas, for example in northern England. The main objective of this study was to produce a total dissolved N (TDN), dissolved inorganic N (DIN) and dissolved organic N (DON) budget for a reservoir in an acid-sensitive peatland catchment in the south Pennines. Consideration of DON budgets in this context is novel and central to providing insight into biogeochemical cycling of N in a peatland context. This data will quantify the role of the reservoir as a sink or source of N. This will provide a better understanding of N dynamics in one of the most acidified upland regions of the UK, and will assist in constraining estimates of N fluxes downstream of stream-reservoir systems.

2. Study site

This study was conducted in the Kinder Reservoir catchment in the Dark Peak, south Pennines, UK (Figure 1). Rainfall for the catchment is ~1157 mm, whilst average air temperature is 8.5 °C (Dec 2012 – Nov 2013 data). The Kinder Reservoir is fed by three main sub-catchments or inlets: William Clough (WC), Kinder River (KR) and Broad Clough (BC). Water is abstracted from the reservoir at an engineered channel with a known stage-discharge relationship in the bottom valve house (VH), whilst the specific volume of water or extra draw-off are occasionally released to the stream to fulfil legal obligations. This released water plus any overflow (spillway) over the dam (which mainly occurs in the winter months) represents the reservoir overflow (KRO). A combination of VH and KRO constitute the reservoir outlet. The morphometric details of the Kinder Reservoir and its main tributaries are given in Table 1.

Table 1: Morphometry of Kinder Reservoir and its main tributaries

Kinder Scout, overlain by blanket peat deposits of 2-4 m thick, marks the highest point (633 m) of the catchment. The geology of the catchment is dominated by grit and coarse sandstones. Approximately 2.6 km² of the catchment is blanket peat, with very acid loamy soils occurring mostly in the WC and BC sub-catchments. The vegetation cover of the catchment is mainly blanket bog, acid grassland, heather and shrub heathland, with small plots of improved grassland. Dense patches of bracken are also present on the hillsides, with sparse alder and birch tree cover scattered across the lower catchment valleys. There is low-intensity sheep grazing within the catchment. To ensure high water quality provision, the catchment is generally managed to limit organic, particulate and nutrient losses from the terrestrial environment to the watercourses (United Utilities, 2011). A small part of the KR headwater has undergone some form of peatland restoration (Edokpa et al., 2015).

Figure 1: Study site location

3. Materials and Methods

3.1. Water sampling and analyses

High resolution stormflow monitoring (15 min to 1 h interval) and fortnightly samples were collected between December 2012 and November 2013 from the reservoir inlets (WC, KR and BC). Fortnightly sampling was also conducted at VH and KRO. A total of 240 high resolution and 75 fortnightly samples were collected at the reservoir inlets. A combined total of 49 fortnightly samples were collected at the VH and KRO. Twenty-five (25) fortnightly water samples were also collected at the west side of the reservoir (R), where mixing of waters from the three inlets was assumed to be readily captured. Details of sample collection are shown in Table 2. Samples were syringe filtered through 0.45 µm Whatman G/F

membrane filter into sterile plastic vials. All samples for chemical analysis were stored at 4 °C prior to analysis, except samples for ammonium (NH_4^+) determination, which were frozen to significantly reduce biological degradation (Cape et al., 2001). Laboratory analysis was carried out within a few days of sample collection. TDN was analysed using a Shimadzu TOC-V CPN ASI-V analyzer with a TNM-1 unit. DON was determined as TDN minus DIN; where DIN is the sum of NO_3^- , NO_2^- and NH_4^+ . Nitrate (NO_3^-) nitrite (NO_2^-) and NH_4^+ were analysed using a Metrohm 882 COMPACT IC PLUS ion chromatograph.

Table 2: Sampling details

3.2. Rainfall data and stream hydrological monitoring

Rainfall for the catchment was obtained from a rain gauge station established at close proximity to the Kinder Reservoir outlet and assumed to be representative of the entire catchment. Rainwater chemistry samples were collected at the reservoir inlets using polythene filter funnels which drained into Nalgene bottles pre-rinsed with deionised water. Daily discharge at the reservoir outlet was recorded at a calibrated engineered channel with a known stage-discharge relationship. The reservoir inlets were ungauged, thus stage-discharge relationships for the individual sites were established from a series of flow measurements using an electromagnetic flow meter (SENSA RC2) under a range of flow conditions. Stage and air temperature were continuously recorded at 15 min interval on the rated sections of the reservoir inlets using TruTrack WT-HR 64K capacitance probes with internal data logger. The probes were embedded in hard plastic PVC tubes and attached to river banks. Calibrated measuring boards were attached to the PVC tubes and manually read off at the time of sampling. This provided an independent check on the performance of the logger(s) and was

used to correct for logger drift. Recorded stage values for the inlets were inputted into the respective rating curves and used to calculate discharge.

3.3. Water balance calculation

For this type of study, it is important to derive an input-output water-balanced budget, before calculating the input-output fluxes of nutrients (Crisp, 1966) to reduce the uncertainty or error in flux estimation (Adams et al., 2013). This makes water balance closure a crucial component in catchment-scale hydrological processes (Beven, 2006). We adopted a simple in-out water balance model which was based on inlet and outlet discharge data, including direct rainfall and evaporation. The main assumption in our water balance calculation was that the uncertainty associated with the discharge data recorded at the calibrated engineered channel at the reservoir outlet was negligible, and could therefore be ignored. Groundwater exchanges were also considered and assumed to be negligible on the basis of the distribution in the positive residuals of the water balance, and consultation with the reservoir manager. Therefore, it was assumed that error in the water balance was associated with measurement of inlet discharges. To create a closed water balance, the inlet discharges derived from the rating curves were corrected with data from the reservoir outlet. The difference between the sum of all inlet and outlet discharges (after accounting for evaporation and reservoir drawdown) was added to (or subtracted from, depending on reservoir filling/emptying) the sum of outlet discharge to obtain the target inlet discharge (T_{in}). The discharge from the individual inlet site was then ratio-corrected to arrive at a balanced in-out water budget using the following equation:

$$RCQ = I_sQ / T_iQ * T_{in}$$

Where, RCQ = ratio corrected discharge, I_sQ = individual inlet site discharge, T_iQ = total inlet discharge, and T_{in} = target inlet discharge.

The recorded 15 min discharge data from the logger(s) were then multiplied by the percentage change between the sum of the uncorrected inlet discharge and the ratio-corrected discharge, from which fluvial N fluxes were derived. The uncorrected and corrected discharge hydrographs for the inlet sites are shown in Figure 2. Reservoir drawdown data was provided by United Utilities, and evaporation was calculated using the simplified Penman evaporation formula (Linacre, 1977), given as:

$$E_0 = \frac{700 T_m / (100 - A) + 15 (T - T_d)}{(80 - T)} \text{ (mm day}^{-1}\text{)}$$

Where;

$$T_m = T + 0.006h,$$

h = elevation (metres)

T = mean temperature

A = latitude (degrees)

T_d = mean dew-point

$(T - T_d) = 0.0023h + 0.37 T + 0.53 R + 0.35 R_{\text{ann}} - 10.9^\circ\text{C}$ (provided precipitation is at least 5 mm a month and $T - T_d$ is at least 4°C), where R = mean daily range of temperature and R_{ann} is the difference between the mean temperature of the hottest and coldest month.

Figure 2: Corrected and uncorrected discharge (Q) hydrographs for (a) William Clough (WC), (b) Kinder River (KR), and (c) Broad Clough (BC) Kinder Reservoir inlet sites.

3.4. Fluvial nitrogen load estimation

To obtain fluvial N (DON, DIN) input from the inlets and output from the reservoir, measured concentrations were multiplied by discharge. The fluxes from the individual inlets (WC+KR+BC) were summed and represent the total fluvial N input to the reservoir, whilst fluxes from VH and KRO were summed to give reservoir N output. The regression

(extrapolation) method (Haggard et al., 2003) was used to estimate input fluxes of N when good relationships were found between discharge and concentration (Table 3).

Table 3: Linear regression models and flux estimation method for the Kinder Reservoir inlets

Rating curves were created using log-transformed concentration and discharge data from both fortnightly and high resolution sampling. The Duan (1983) smearing estimator was used to correct for back transformation error whilst, the standard error of the regression line was used to calculate the error in the estimated flux. In cases where there was a poor relationship ($R^2 < 0.20$ and $p > 0.05$) between discharge and concentration, the Walling and Webb (1985) ‘Method 5’ (interpolation) approach was used to estimate N fluxes using only fortnightly concentration data (Table 3). Annual and seasonal reservoir output fluxes of N were also estimated using Walling and Webb (1985) ‘Method 5’, as discharge was relatively constant at the reservoir outlet. The Walling and Webb (1985) ‘Method 5’ takes the following form:

$$\text{Total Load} = \frac{K \sum_{i=1}^n (C_i Q_i)}{\sum_{i=1}^n Q_i} \overline{Q_r}$$

Where;

K = a conversion factor to take into account the period of monitoring

C_i = the concentration associated with each sample point

Q_i = the discharge at time of sampling

$\overline{Q_r}$ = mean discharge over the monitoring period

n = the number of samples

3.5. Nitrogen deposition

Total (wet + dry) atmospheric inorganic N deposition values modelled by the Centre for Ecology and Hydrology (CEH) using the FRAME (Fine Resolution Atmospheric Multi-pollutant Exchange) model were downloaded from the Defra website (<http://pollutantdeposition.defra.gov.uk/data>) and available on a 5 km grid square resolution. Average modelled value (2010-2012) was derived for the catchment by digitally overlaying the catchment area on the 5 km grid square resolution deposition data covering the catchment in ESRI ArcGIS. Deposition data were available for total N, oxidised (NO_x) and reduced (NH_x) N, but not for organic N. Wet atmospheric N deposition was derived for the reservoir by multiplying measured average rainwater N concentration by rainfall over the reservoir surface area.

3.6. Nitrogen budget

Annual and seasonal input-output budgets were calculated for TDN, DIN and DON (TDN minus DIN). Net gain or loss by the reservoir was derived by subtracting N input from reservoir output. A negative N balance indicates that the reservoir is acting as a sink of N, whilst positive N balance is an indication that the reservoir is acting as a source of N.

4. Results

4.1. Nitrogen concentration

Average monthly dissolved N concentrations for the sites are shown in Figure 3. Of all the three inlets, WC had the lowest concentration of dissolved N, averaging 27–51 $\mu\text{mol l}^{-1}$ in all months, except January and April, when average TDN concentrations were $\sim 66 \mu\text{mol l}^{-1}$ (Figure 3a). In the KR and BC inlets, average concentrations of TDN were $\sim 80\text{--}110 \mu\text{mol l}^{-1}$ in January through April, but declined to $\sim 40\text{--}60 \mu\text{mol l}^{-1}$ for the rest of the study (Figure 3a). Average TDN concentrations at the VH and KRO were $\sim 67\text{--}99 \mu\text{mol l}^{-1}$ in January

through May, but declined to $< 60 \mu\text{mol l}^{-1}$ in the subsequent months of the study year (Figure 3a). In mid-winter (January), average concentrations of DIN reached $70 \mu\text{mol l}^{-1}$ in KR, and $77 \mu\text{mol l}^{-1}$ in BC (Figure 3b). During the study year, average concentrations of DON in the reservoir inlets reached a peak of $\sim 67 \mu\text{mol l}^{-1}$ in KR in early summer, but were as low as $\sim 1\text{--}8 \mu\text{mol l}^{-1}$ in the reservoir outlet (Figure 3c).

Figure 3: Average monthly concentration of (a) TDN (b) DIN and (c) DON for the Kinder Reservoir inlet (WC, KR and BC) and outlet (VH and KRO) sites.

The combined monthly average concentrations of dissolved N in the reservoir inlet and outlet, and the reservoir water residence time (WRT) are shown in Figure 4. The WRT for the study year was ~ 104 days (Table 1), but varied from 52 days in December, to 108 days in May (Figure 4). Average monthly concentrations of TDN in the reservoir inlet and outlet were approximately equal in December through February when WRT was ≤ 80 days (Figure 4a). In comparison to the reservoir inlet, average concentrations of TDN declined in the outlet between March and June, coinciding with the months when the WRT was > 100 days (Figure 4a). Variation in average concentrations of DIN between the reservoir inlet and outlet was low during the study period, except in January and November when DIN concentrations in the outlet were higher than inlet DIN concentrations (Figure 4b). In January, and March through June, average concentrations of DON were lower in the reservoir outlet in comparison to the inlet (Figure 4c). Average concentrations of DIN in the reservoir were $\sim 26\text{--}45 \mu\text{mol l}^{-1}$ during the study year, except in January when it reached $55 \pm 4 \mu\text{mol l}^{-1}$ (Figure 4d). Monthly average concentrations of DON in the reservoir varied widely, reaching $53 \pm 1 \mu\text{mol l}^{-1}$ in April and declining to $16 \mu\text{mol l}^{-1}$ in May (Figure 4d).

Figure 4: Monthly average inlet and outlet concentrations of (a) TDN (b) DIN (c) DON, and (d) DIN and DON concentrations in the Kinder Reservoir. Error bars represent the standard error of the mean. Water residence time (estimated as reservoir volume divided by total discharge from its outlet) is plotted on the TDN, DIN and DON graphs.

There were no marked changes between average annual and seasonal concentrations of TDN in the reservoir inlet and outlet, except in summer (Figure 5a) when there was a $45\pm 2\%$ decrease in concentration of TDN in the outlet in comparison with inputs (Figure 6a). The summer decrease in outlet TDN was linked to the decrease in summer DON (Figure 4c). The highest percentage decrease ($78\pm 2\%$) in DON concentration in the reservoir outlet relative to its inlet was observed in early summer (June) when WRT was ~ 105 days (Figure 6a and b). Average annual DIN and DON concentration for the combined reservoir inlets was $37 \mu\text{mol l}^{-1}$ and $31 \mu\text{mol l}^{-1}$, respectively (Figure 5b and c). Relative to inputs from inlet streams, there was a $13\pm 2\%$ decrease in DIN concentration in the reservoir outlet in summer (Figure 6a). Average seasonal concentrations of DIN in the Kinder Reservoir were higher in the winter ($45\pm 5 \mu\text{mol l}^{-1}$) and spring ($44\pm 1 \mu\text{mol l}^{-1}$) seasons, compared to the summer and autumn seasons (Figure 5b).

Figure 5: Average annual and seasonal concentrations of (a) TDN (b) DIN, and (c) DON for the three inlets, Kinder Reservoir and its outlet. Error bars represent the standard error of the mean.

Figure 6: Change (as a percentage of fluvial input concentration) in average (a) annual, seasonal, and (b) monthly dissolved N concentration between fluvial input of N from the combined inlets and outlet. Error bars represent % standard error of the mean.

4.2. Water balance

Rainfall and stream discharge from the reservoir inlets and outlet for the study year are shown in Table 4. Stream discharge to the reservoir was 8.11 million m³, whilst direct rainfall over the reservoir free surface was 0.21 million m³. Total water input (stream flow plus direct rainfall over the reservoir surface) to the reservoir was 8.32 million m³ and water output from the reservoir was 8.25 million m³, with reservoir evaporation accounting for the ~1% imbalance (0.07 million m³) in the water budget. Drawdown for the study period equates to zero, but varied monthly depending on the volume of water in the reservoir. A negative drawdown indicates that the reservoir is emptying whilst a positive drawdown value indicates reservoir filling.

Table 4: Water balance for Kinder reservoir (Dec 2012- Nov 2013). Note: units are million m³

To demonstrate that the input fluxes and N balance results derived using the ratio-corrected (water-balanced) discharge are significant, we examined the sensitivity of the fluvial input of N by separately deducting the sum of the error (excess water) in the inlet discharge from each of the inflow (KR, BC and WC) measurement. This produced three different flux and N balance scenarios, in addition to N fluxes derived using ratio-corrected discharge. For simplicity, fluxes were calculated by multiplying average annual TDN concentration by total annual discharge. In the first scenario (when the total error in the inlet discharge was deducted from only the KR inflow measurement), total fluvial input of N to the reservoir was 7491 kg

N, with a retention of 14% (1062 kg N). In the second scenario (when the total error in the inlet discharge was deducted from only the BC inflow measurement), total fluvial input of N to the reservoir was 8059 kg N, with a retention of 20% (1630 kg N). For the third scenario (when the total error in the inlet discharge was deducted from only the WC inflow measurement), total fluvial input of N to the reservoir was 8470 kg N, with a retention of 24% (2041 kg N). The fluvial input of N to the reservoir calculated using the ratio-corrected discharge produced a flux of 7893 kg N, with a retention of 19% (1464 kg N); about the average percentage retention of the other three scenarios. These results suggest that variability resulting from the spatial lumping of discharge correction to any of the separate inflows does not substantially alter the conclusions of the N mass balance calculated using the ratio-corrected inlet discharge method.

4.3. Fluxes of nitrogen

The Kinder Reservoir catchment received 25.6 kg N ha⁻¹ yr⁻¹ of atmospheric inorganic N deposition (2010-2012 CEH modelled average). Measured wet atmospheric N input to the free reservoir surface area was 7.44±1.05 kg N ha⁻¹ yr⁻¹. There was marked winter-summer variation in the fluxes of TDN, DIN and DON to the Kinder Reservoir from its sub-catchments (WC, KR and BC), with winter high and summer low (Table 5) reflecting the pattern of discharge (Table 4) and biological demand. Relative to DON, fluxes of DIN made up a higher proportion of the TDN flux to the reservoir in all seasons except in the very peaty KR sub-catchment where DON was dominant in all but the spring season (Table 5). Annual flux of TDN from the Kinder Reservoir catchment was 7.45±0.11 kg N ha⁻¹ yr⁻¹, with DIN making up ~ 70% of the flux (Table 5). Fluxes of TDN from the reservoir catchment were highest in winter (3.08±0.09 kg N ha⁻¹ season) and lowest in summer (1.07±0.003 kg N ha⁻¹

season). DON constituted ~ 20% of the TDN flux from the reservoir catchment in summer, and between 30-33% in the other seasons (Table 5).

Table 5: Seasonal and annual fluxes per unit area (kg N ha^{-1}) calculated using the surface areas shown in Table 1.

4.4. Kinder Reservoir nitrogen mass balance

The N mass balance we constructed for the Kinder Reservoir for December 2012 through November 2013 is shown in Figure 7 and Table 6. Riverine N input to the reservoir was dominated by DIN ($4946 \pm 349 \text{ kg N}$), and represented $57 \pm 4\%$ of the annual fluvial N input (Table 6). Fluvial input of DON to the reservoir ranged between 3074 and 4380 kg N (Table 6). Measured wet atmospheric deposition ($133 \pm 19 \text{ kg N}$) was a minor contributor to total N input (Figure 7). The net loss of dissolved N to the Kinder Reservoir during the study year was $2309 \pm 747 \text{ kg N}$. Approximately $90 \pm 3\%$ ($4539 \pm 132 \text{ kg N}$) of annual DIN input was exported from the reservoir, implying a percentage retention of $10 \pm 3\%$ (Figure 7).

Table 6: Seasonal and annual mass balance of fluvial N (kg N) for Kinder Reservoir (Dec 2012-Nov 2013). Percentage retention was calculated as the difference between output minus input of N as a percentage of input. A negative N balance indicates that the reservoir is acting as a sink of N, whilst positive N balance is an indication that the reservoir is acting as a source of N.

The retention of DON as a percentage of N inputs to the reservoir ranged between 39-55% ($1216 - 2432 \text{ kg N}$) during the study (Figure 7). The status of the reservoir as a sink or source of N species varied between seasons (Table 6). In spring, the Kinder Reservoir was a source

of DIN (225 – 248 kg N), and a sink or source of DON when considered within the margin of error (Table 6). In the vegetative season (summer), 58 to ~ 80% (225 – 730 kg N) of DON was retained by the reservoir, whilst there was between a 1% (5 kg N) retention or an 11% (74 kg N) net increase in DIN export from the Kinder Reservoir (Table 6).

Figure 7: Schematic of dissolved N mass balance for the Kinder Reservoir (December 2012 to November 2013). Fluxes are proportional to thickness of the arrows in the diagram.

5. Discussion

Consistent with other mass-balance studies (e.g. David et al., 2006; Kelly, 2001; Garnier et al., 1999), this study demonstrates the capacity of reservoirs to remove/retain more than 30% of N inputs. Most of these studies have been focused on DIN, thus limiting our understanding of DON cycling in stream-reservoir systems. Garnier et al. (1999) estimated a 40% retention of NO_3^- inputs in three reservoirs of the Seine Basin, whilst 29% of NO_3^- input (March 2002 through March 2013) to Lake Shelbyville reservoir was retained/removed (David et al., 2006). Our mass balance for the Kinder Reservoir shows an annual net retention of ~ 26% for TDN, ~ 10% for DIN and ~ 48% for DON (Figure 7). The low retention of DIN is not surprising, considering that the catchment has been exposed to decades of atmospheric inorganic N deposition (Edokpa et al., 2015; Helliwell et al., 2007). At the whole catchment scale, atmospheric inorganic N deposition was $25.6 \text{ kg N ha}^{-1} \text{ yr}^{-1}$, whilst the flux of DIN from the Kinder Reservoir catchment was $5.21 \pm 0.15 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ (Table 5), suggesting that ~20% of DIN input was leached from the catchment. At the sub-catchment scale, $11.1 \pm 1.08 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ of DIN was leached from BC; $5.26 \pm 0.69 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ from KR, and $3.49 \pm 0.17 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ from WC (Table 5) during the study. This is reminiscent of catchments at advanced stage of N leaching, characterised by accelerated nitrification and reduced biological demand (Aber

et al., 1995; Stoddard, 1994). In addition to atmospheric inorganic N deposition, the rapid mineralisation of organic N stored in the peat soils of the catchment may also encourage DIN leaching to the surface waters (Daniels et al., 2012).

The Kinder Reservoir switched from being a sink of TDN in the biologically dormant winter season, to being a source of N in the spring season, with ~ 237 kg N of DIN exported in excess of fluvial DIN input (Table 6). Although immobilisation of DIN was slightly higher than mineralisation in winter, in spring, mineralisation is as much or greater than immobilisation, thus allowing for the direct export of DIN from the catchment (Lin et al., 2015). Whilst a $42\pm 5\%$ decrease in the annual average DON concentration was observed in the reservoir outlet, relative to fluvial inputs (Figure 6), there was little or no difference between the average annual concentrations of DIN in the Kinder Reservoir, and its inlet and outlet (Figure 5b). This may suggest the mineralisation of DON into DIN in the reservoir, or the direct utilisation of atmospherically deposited inorganic N by the biological assemblage of the reservoir, such that, there is an accumulation of DIN derived from other sources e.g. mineralisation. Yesmin et al (1995) suggest that the high retention of NO_3^- and NH_4^+ at their most polluted sites may be due to the preponderance of direct biomass utilisation of inorganic N in precipitation, as opposed to DIN derived from mineralisation/nitrification. However, recent isotope studies suggest that most NO_3^- in upland waters have been biologically produced (Curtis et al., 2012).

Interestingly, in the vegetative season (summer), DIN export from the Kinder Reservoir was greater than or approximately equal to its input, whilst 58 to $\sim 80\%$ of DON was retained by the reservoir (Table 6). Two candidate mechanisms are potentially responsible for the large amount of DON retained by the reservoir in summer. The first mechanism involves the preferential sorption of total hydrolysable and N-rich amino acids to fine-grained minerogenic

particles (Hedges and Keil, 1999; 1995) in the reservoir. The second mechanism involves mineralisation via photochemical degradation of DON/dissolved organic matter (DOM) (Vahatalo and Zepp, 2005; Kohler et al., 2002; Bertilsson and Tranvik, 2000) and/or the rapid consumption of the resultant bioavailable low molecular weight (LMW) DON photoproducts (e.g. dissolved primary amines) by the microbial assemblage (Jorgensen et al., 1998; Fuhrman, 1990) of the reservoir. Based on the seasonal behaviour of DON in this study (Figure 4, 5 and 6), and findings from elsewhere (Kaushal and Lewis, 2005; Kohler et al., 2002; Bertilsson and Tranvik, 2000; Jorgensen et al., 1998; Seitzinger and Sanders, 1997), we suggest the latter mechanism as the most likely explanation for the marked reservoir retention of DON in summer (Table 6). Solar radiation can transform photoreactive but biologically recalcitrant DON/DOM into NH_4^+ (Vahatalo and Zepp, 2005; Moran and Zepp, 1997), thereby decreasing DON, and increasing the DIN pool in the reservoir. This may help explain the high export of DIN from the Kinder Reservoir relative to input in summer (Table 6). Whilst some retention/export of dissolved N may be due to precipitation of particulate N, the overall seasonal dynamics of fluvial N strongly suggest that biological processes (possibly complemented by abiotic processes) is the dominant control of N in this peatland system.

The other mechanisms of N retention/removal in freshwater systems include uptake of N by aquatic plants, denitrification and sedimentation (David et al., 2006; Saunders and Kalff, 2001; Noges et al., 1998). As a primary mechanism of N retention, uptake of N by aquatic plants is often viewed as a temporary sink of N, and the least effective mechanism of N retention in freshwaters (Saunders and Kalff, 2001; Jansson et al., 1994), due to re-mineralisation into the water column when the plants die (Ensign and Doyle, 2006; Jansson et al., 1994).

Denitrification, as an important pathway of N removal in aquatic systems (Saunders and Kalff, 2001; Jansson et al., 1994), has both geochemical and ecological significance, including the control of eutrophication in freshwaters receiving high N deposition (Seitzinger, 1988). Similar to denitrification is the process of dissimilatory nitrate reduction to ammonia (DNRA), wherein heterotrophic bacteria utilise NO_3^- as a terminal electron acceptor in respiration to reduce NO_3^- to gaseous N compounds (NO , N_2O and N_2) or NH_4^+ (Rutting et al., 2011; Katterer et al., 2011; Scott et al., 2008). Although denitrification and DNRA occur under low oxygen condition, C/NO_3^- has been identified as a key factor regulating the partitioning of both processes (Fazzolari et al., 1998; Yin et al., 1998). The Kinder Reservoir catchment is exposed to high atmospheric NO_3^- deposition, and average C/NO_3^- for the reservoir during the study year was <5 (C/NO_3^- data not presented here). Also, some parts of the reservoir reach depths of >11 m, and depending on mixing, anoxia occurs at lake depths of ≥ 9 m (Chapman et al., 1998). Although denitrification rate was not directly measured in this study, the observed low C/NO_3^- (<5) inhibits DNRA, but increases denitrification under anoxic conditions (Fazzolari et al., 1998); thus making denitrification a potential pathway of N loss from the Kinder Reservoir water column. Whilst oxygen is the main regulator of denitrification, pH has been identified as a major controlling factor of denitrification rates (Sun et al., 2012). Average pH for water in the Kinder Reservoir was ~ 6.5 during the study year, and was as high as 7.1 in the summer month of June (Figure 8) when the most marked decrease in fluvial TDN output, relative to input was observed (Figure 6b). Although most studies have shown that denitrification is positively related to pH, with an optimum range of 7 – 8 (Wang et al., 1995; Weier and Gilliam, 1986; Knowles, 1982), there is evidence to suggest that denitrifying activity is significant at a pH range of 6 – 7 (Bradley et al., 1992; Klemetsson et al., 1977). The C-rich (peat) soils of the reservoir catchment ensures that denitrifiers have access to a large supply of OC, which serves as an energy source and

electron donor in the denitrification process (Brodrick et al., 1988; Knowles, 1982). In addition, average concentrations of DIN in the reservoir were fairly high in spring through early summer (Figure 4d and 3b) when denitrification rates were found to be highest (e.g. David et al., 2006).

Figure 8: Monthly average pH of Kinder Reservoir water (December 2012 to November 2013)

Sedimentation of dead plankton or organic material may be another pathway of N loss/retention in the Kinder Reservoir. Sorption to settling and sedimenting particles in reservoirs/lakes (Kunz et al., 2011; David et al., 2006; Tang and Xie, 2000) is influenced by the DIN concentration of overlying water (Gruca-Rokosz et al., 2009), the sediment composition and associated structure of organic compounds (Henrichs and Sugai, 1993), and the population of pelagic and benthic organisms (Durand et al., 2011). Active erosion of peat soils which may transport organic particles as suspended sediments to the reservoir has previously been reported in the headwaters of the Kinder Plateau (Allott et al., 2009; Rothwell et al., 2008; Evans et al., 2006). A recent study (Shuttleworth et al., 2015) found that the ongoing restoration of these headwater systems by Moors for the Future Partnership have reduced sediment fluxes by two orders of magnitude compared to eroding sites. However, Kinder Reservoir sedimentation rate was not measured in this present study. Further research on benthic sediment composition, denitrification rates, and DON characterisation is needed to provide complete ecosystem analysis and conclusive evidence of the prevailing mechanism of N retention/removal in this acid sensitive fluvial system.

6. Conclusion

The N mass balance results show a ~21 to 31% (1665 – 2953 kg N) retention of TDN input to the Kinder Reservoir during the study year. With regards to the species of TDN, ~6 to 13% of DIN, and 39 to 55% of DON fluxes were retained or cycled by the reservoir. The long WRT (~104 days), average pH of 6.5 and high average concentrations of DIN, particularly in spring and early summer in the reservoir suggests that denitrification is potentially a key mechanism of N retention/removal. This study also demonstrates the importance of DON in the N cycling and biogeochemistry of upland freshwater systems. Whilst the Kinder Reservoir was a source of DIN in the vegetative season (summer), 58 to ~ 80% (255 – 730 kg N) of DON was retained. This may suggest that DON/DOM is either being photodegraded into DIN in the reservoir or there is rapid utilisation of DON and its photoproducts (e.g. dissolved primary amines) by the microbial community of the reservoir. This has implications for N limitation in upland freshwater systems where transformation in the availability of bioavailable N could increase the eutrophic burden of these sensitive fluvial environments.

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