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Interannual variations in atmospheric forcing determine trajectories of hypolimnetic soluble reactive phosphorus supply in a eutrophic lake

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Running header: Variation in timing of hypolimnetic SRP load

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Summary

- We tested the hypotheses that variability in soluble reactive phosphorus (SRP) loading from the hypolimnion to the epilimnion of a small, eutrophic, temperate zone lake is significant at both interannual and subannual scales, and that this variability is influenced by changes in lake thermal structure. We calculated weekly hypolimnetic fluxes of SRP, during the stratified periods of 2008 and 2009 in Esthwaite Water, UK and compared them with the SRP fluxes from external sources.
- 2. As a result of variations in the supply from the hypolimnion which differed by ~80%, we found a 30% difference in overall SRP loading between the two years. Despite similarities in average summer meteorological conditions, relatively subtle differences in weather conditions during the mid-summer of only 0.7 m s⁻¹ in wind speed and 8 W m⁻² in solar radiation between the two years resulted in two diverging trajectories of hypolimnetic SRP loading.
- 3. In the first year, there was a high thermal lake stability of 102 J m⁻² on average, and a relatively shallow epilimnion depth until the late-summer, giving rise to prolonged deep water anoxia and a large accumulation of SRP that was mixed into the surface waters at the end of the summer. In contrast, 30% lower thermal stability and 20% deeper epilimnetic mixing in the second year resulted in the arrest and early decline of deep water anoxia and SRP accumulation, leading to lower SRP fluxes to the epilimnion.
- 4. Understanding this meteorologically driven variability in SRP supply is crucial for predicting nutrient loading in lakes. It is likely to become especially relevant to lakes around the globe for which the importance of internal loading is predicted to increase due to the effects of climate change.

Introduction

The enrichment of phosphorus, which can cause hypertrophication and trigger algal blooms, is a major concern in the management of lakes, reservoirs and other standing waterbodies. While the reduction in external loads from catchments has, in some cases, resulted in concomitant reductions in in-lake concentrations of phosphorus and phytoplankton biomass (Sommer, Gaedke & Schweizer, 1993; Evans, Fahnenstiel & Scavia, 2011), in many waterbodies it has not, at least over the short-term (Marsden, 1989; Anderson, Jeppesen & Søndergaard, 2005). This is primarily because of internal loading of phosphorus from nutrient-rich bed sediments within lakes, which has been found to prolong eutrophic conditions for several years (Jeppesen *et al.*, 2005). Internal nutrient loading can form a significant fraction of the overall phosphorus budget in standing waterbodies, particularly those which are eutrophic or hypereutrophic (Larsen, Schults & Malueg, 1981; Søndergaard, Kristensen & Jeppesen, 1993).

Internal phosphorus supply often occurs in a highly bioavailable form as soluble reactive phosphorus (Boström, 1984; Nürnberg, 1988) and is therefore of particular importance. In addition, internal loading has a seasonal cycle and is greatest during the growing season for phytoplankton, making these inputs important from a management perspective. Despite the importance of this internal load, its quantification has been often neglected (Nürnberg, 2009) or calculated only as a residual of the external input-output nutrient budget (Vollenweider & Kerekes, 1980; Welch & Jacoby, 2001). Understanding the temporal variability of the soluble reactive portion of the internal phosphorus load is essential when assessing the value of mitigation measures aimed at reducing algal biomass.

The internal supply of SRP to the main primary producers in most lakes – epilimnetic, pelagic phytoplankton – requires the liberation of SRP from sediment or the transformation of other phosphorus forms to SRP in the water column, followed by its physical transfer to the epilimnion. In the hypolimnion, the pool of SRP in the water builds up from these

sediment or water column sources when hypolimnetic dissolved oxygen concentrations are depleted and reducing conditions pertain (Mortimer, 1941; Nürnberg, 1984). While many studies that consider this internal supply, focus on the sediment release processes (e.g. Penn *et al.*, 2000; Nowlin, Evarts & Vanni, 2005), few have focussed on the method of transfer of SRP to epilimnion. Here we specifically target this physical transfer process, both of the downward movement of oxygen, which influences the sediment release rate and the solubility of SRP in the hypolimnion and the upward transport of SRP to the epilimnion.

In the presence of water column stratification, SRP released into the hypolimnion is isolated from the epilimnetic phytoplankton by the thermocline. Mechanistically, SRP can be transferred to the epilimnion by either vertical diffusion across an approximately static thermocline or the entrainment of hypolimnetic waters into the epilimnion, when the epilimnion deepens (Wodka *et al.*, 1983; Soranno, Carpenter & Lathrop, 1997; MacIntyre *et al.*, 1999). The relative importance of these mechanisms for internal 'hypolimnetic loading' is dependent on the strength and timing of mixing, and on the pool of SRP in the hypolimnetic SRP pool through both transportation of SRP and replenishment of hypolimnetic dissolved oxygen (Lam, Schertzer & Fraser, 1987). It is therefore important to understand the influence of physical forcing on lakes and how the position and movement of the thermocline can affect the accumulation and transfer of hypolimnetic SRP to the epilimnion.

Atmospheric forcing is closely linked to the intensity of cross thermocline mixing, determining the strength of vertical diffusion and the extent of hypolimnetic entrainment (Kraus & Turner, 1967; Wüest & Lorke, 2003). Higher wind energy and convective cooling is associated with weaker stratification and more mixing, while heating from solar radiation results in stronger stratification and the suppression of mixing (Imboden & Wüest, 1995). Over the summer period, weather patterns can influence the relative importance of these

processes, where the passage of cold fronts has been associated with increased mixing (MacIntyre *et al*.2009) and the transition between warm and cold air masses linked to mixing and nutrient upwelling (MacIntyre *et al*. 2006). Over longer timescales, predicted increases in stratification strength, duration and shallower epilimnion depths due to climate change (Hondzo & Stefan, 1991; Persson *et al.*, 2005; Jankowski *et al.*, 2006) are also likely to impact on cross thermocline mixing, resulting in more sustained hypolimnetic oxygen depletion (Jankowski *et al.*, 2006; Foley *et al.*, 2012) and a consequent lengthening of time for the accumulation of the hypolimnetic SRP pool.

This study examines differences in physical forcing and the temporal variability in SRP internal loading from the hypolimnion to the epilimnetic, pelagic phytoplankton over the summer stratified period (June to October) for two consecutive years. We chose to study these dynamics in a typical, stratifying, temperate zone eutrophic lake. In addition, we compare these hypolimnetic fluxes to estimates of epilimnetic sediment and external catchment sources, and consider the wider implications for hypolimnetic loading from potential future changes to physical forcing. We test the following hypotheses:

- (i) Variability in the lake thermal structure over time plays a significant role in the transfer of SRP to the epilimnion from the hypolimnion;
- (ii) Internal hypolimnetic SRP loading mechanisms vary in importance over sub-seasonal timescales; and
- (iii) The total SRP load received by epilimnetic pelagic phytoplankton in a given summer is significantly influenced by the interannual variation in the hypolimnetic SRP load.

Methods

Study site

Esthwaite Water (54°21'N, 3°0'W) is a small, glacially-scoured lake, in the English Lake District, with a surface area of 0.96 km², a total volume of 6.7×10^6 m³, and an average depth of 6.9 m (Mackay *et al.*, 2012). The average residence time for the lake is 100 days (Maberly *et al.*, 2006). Its catchment area of 17 km² has a sedimentary geology of Silurian shales, mudstones and sandstones. Land use in the catchment is predominantly pastoral agriculture surrounding small settlements, with some forest on steeper slopes (Reynolds & Irish, 2000). The relatively low resident population is substantially enlarged by seasonal tourism. Previous work has found that external sources alone cannot account for the phosphorus concentration in the lake water (Hall *et al.*, 2000), implying that internal loading forms an important component of the phosphorus budget of the lake. The lake was also the site where some of the first studies into sediment phosphorus release were conducted by Mortimer (1941; 1942). Recent analysis has classified the lake as eutrophic based on the OECD (1982) classification (Maberly *et al.*, 2006).

Meteorological and Hydrographic Data

High resolution meteorological and hydrographic data were provided by the UK Centre for Ecology and Hydrology (CEH) Automatic Water Quality Monitoring Station (AWQMS) in the north basin of the lake and a meteorological station on the shore (see Rouen, George & Hewitt, 2001; Madgwick *et al.*, 2006 for more details) (Fig. 1). Wind speed was measured at 2.9 m above the lake with a Vector A100L2-WR cup anemometer with optical rotation sensing (Vector Instruments, Rhyl, Wales) and solar radiation was measured using a Kipp & Zonen CNR1 Net Radiometer (Kipp & Zonen B.V, Delft, Holland), both obtained as hourly averages from the AWQMS in the north basin of the lake. Additional data

on the thermal structure of the lake were obtained as two minute averages from a thermistor chain attached to the buoy, consisting of 12 Platinum resistance thermometers (PRTs) (Labfacility Ltd, Bognor Regis, UK) spaced at one metre intervals to a depth of 11.5 metres. Bathymetric data were taken from Mackay et al. (2012).

Daily discharge data were provided from the gauging station at Eel House Bridge located approximately 1 kilometre downstream from the lake on Cunsey Beck (Fig.1 inset), its primary outflow, by the Environment Agency for England and Wales. To adjust the discharge at Eel House Bridge to that of the outflow from the lake, a correction factor of 0.92 was used, based on the difference between the catchment areas of the outflow point and that of the gauging station, weighted by rainfall. At the seasonal and interannual timescales of interest to us in the present study, it was assumed that the total inflow to the lake was equal to the outflow.

Meteorological forcing

To examine the strength of physical forcing, measures of wind stress and changes to the weekly average heat content of the lake were calculated for both years. The vertical turbulent wind energy flux, P_{10} (W m⁻²), a measure of the physical wind forcing over the lake, was calculated from Wüest *et al.* (2000):

$$P_{10} = \rho_{air} C_{10} W_{10}^3 \,, \tag{1}$$

where ρ_{air} is the density of air (1.2 kg m⁻³), C_{10} is the drag coefficient $\approx 1.4 \times 10^{-3}$ (Hicks, 1972) and W_{10}^{-3} is the cube of wind speed at 10 m, rescaled from 2.9 m, following Amorocho and DeVries (1980).

The rate of change in lake heat content from week *j*-1 to week *j*, L_{heat} (J s⁻¹ m⁻²), was calculated from the thermistors as:

$$L_{heat} = \frac{C_p \rho_w \left[\left(\sum_{i=1}^{12} T_i V_i \right)_j - \left(\sum_{i=1}^{12} T_i V_i \right)_{j-1} \right]}{A_0 t_{week}},$$
(2)

where c_p and ρ_w are the specific heat capacity at constant pressure (4200 J kg⁻¹ K⁻¹) and density of water (1000 kg m⁻³) respectively, t_{week} is the number of seconds in a week, T_i is the temperature (K) of each of the 12 thermistors, V_i is the surrounding volume of water (m³), 1 m thick for each of the top 11 thermistors and 5 m thick for the bottom layer and A_0 is the lake surface area (m²).

Water column stability

To investigate the effect of water column stability on the variability of SRP supply to the epilimnion, we calculated the Schmidt stability, S (J m⁻²), a measure of the strength of stratification in the lake (Hutchinson, 1957) as:

$$S = -\frac{g}{A_0} \int_0^{z_{max}} (z - z_v) A_z (\rho_{max} - \rho_z) dz , \qquad (3)$$

where g is the acceleration due to gravity (9.8 m s⁻²), z and z_{max} are the water depth and maximum water depth (m) respectively, A_z is the cross-sectional area at depth z (m²), ρ_{max} and ρ_z (kg m⁻³) are the maximum density of freshwater and density of water at depth z, respectively and z_v is the centre of volume of the lake:

$$z_{\nu} = \frac{1}{V} \int_0^{z_{max}} z A_z dz, \qquad (4)$$

where $V(m^3)$ is the lake volume.

Daily values of the depth of the bottom of the epilimnion, top of the hypolimnion and the centre of the epilimnion, hypolimnion and metalimnion were calculated for the study period in both years. The daily-average epilimnion depth was calculated using the AWQMS PRT chain, as the minimum depth where water temperature had >1 °C difference from the top thermistor (0.5 m) (following Mackay *et al.*, 2011), while the top of the hypolimnion was calculated as the maximum depth at which there was a >1 °C temperature difference from the bottom thermistor (11.5 m). The centres of the epi- and hypolimnion were calculated as the difference between these values and the surface or bottom of the lake respectively, and the centre of the metalimnion was calculated as the mid-point between the epilimnion and hypolimnion centre depths.

Chemical measurements

Calculations of the hypolimnetic load were made using SRP measurements taken from three depths (0.5 m, 11 m, 14 m) at the pelagic sampling site (Fig. 1), located at the deepest point in the lake, where vertical oxygen profiles were also carried out at 1 m intervals using a Hydrolab Quanta® Water Quality Measurement System (Loveland, Colorado, USA). Samples were taken weekly during June to October 2008 and September to October 2009, and fortnightly, from June to August 2009. 1L water samples were filtered in the field using a sealed filtration unit and Whatman GF/C filters to minimise contact with the air, transferred into pre-acid washed bottles, and then analysed on the same day to give SRP concentrations using the molybdenum blue method of Murphy and Riley (1962) following Stephens (1963). Oxygen profiles were interpolated to daily values following Jones *et al.* (2008), then weekly averaged and combined with lake bathymetric data to calculate the volume of the lake that was anoxic and the area of sediment overlain by anoxic water, taken to be that with oxygen concentration < 1 mg m⁻³ (Nürnberg, 1988).

Measurement of the external SRP load was carried out on the main lake inflow, Black Beck, which constitutes ~50% of the total water discharge into the lake (Davison *et al.*, 1980) and drains ~80% of the catchment area. A distinction was made within this inflow between SRP from diffuse sources (the concentration of which we assumed was representative of all diffuse inflows to the lake) and the main point source, Hawkshead Sewage Treatment Works (STW) – which discharges into Black Beck just upstream of the lake. We differentiated these by sampling approximately 300 m up- and 200 m down-stream of the STW (Fig. 1). Water samples were taken approximately fortnightly at each site from June to October 2008 and 2009.

SRP loading calculations

The focus of this study was the calculation of the hypolimnetic SRP supply, which includes both the episodic entrainment and detrainment of the hypolimnion and the more incremental vertical diffusion over the thermocline. In addition, the internal loads from the sediment-epilimnion interface and the external point and diffuse loads were also calculated (Fig. 2). All SRP calculations were carried out in milligrams and then converted to kilograms.

Daily Hypolimnetic Entrainment

The epilimnion entrains water and SRP from below when deepening, and detrains water and SRP when shoaling. As SRP is readily consumed in the epilimnion, entrained water has typically a higher concentration of SRP than the detrained water leaving the epilimnion. Following Soranno *et al.* (1997), we define entraining and detraining events as deepening and shoaling of the epilimnion by at least 1 m. To calculate the SRP fluxes due to these events, the concentration profile was calculated in two steps. Firstly, a linear interpolation of SRP concentration was carried out between the bottom of the mixed layer

and 11 m and between the measured concentrations at 11 m and 14 m. It was assumed that the SRP concentration throughout the mixed layer was the same as that measured at 0.5 m depth. Miller (2008) undertook an earlier summer long study on Esthwaite Water, regularly measuring SRP at each metre depth. Comparing the fully resolved profles in that study with the sub-sampled linearised approximation showed that the linearised method overestimates the SRP between the mixed layer and 11 m by 27% and underestimates the SRP between 11 m and 14 m by 10%. We therefore applied this correction to our linearly interpolated data. The daily flux caused by epilimnion deepening or shoaling, H_{ent} (mg d⁻¹), was then calculated as:

$$H_{ent} = \frac{\sum C_i' V_i}{\Delta t},\tag{5}$$

where Δt is the change in time, equal to one day, V_i (m³) is the volume of each metre-depth layer *i* that is entrained or detrained each day, calculated from the daily change in epilimnion depth and the lake bathymetry and C'_i is the previous day's SRP concentration (mg m⁻³) in that layer, the summation being carried out over the full depth range that is entrained or detrained. The daily values of H_{ent} were averaged to weekly values and converted to kilogrammes for the load calculations. We estimated the error associated with the linearization approximation of SRP concentration using a standard error of the difference (Fowler, Cohen & Jarvis, 1998), comparing the overall load estimate using the metre interval profiles and the sub-sampled linearised approximation. This was converted to a percentage of the fully resolved profile and used to calculate an error estimate of the overall load from vertical entrainment in this study.

Daily Hypolimnetic Vertical Diffusion

The vertical diffusive flux rate of SRP, H_{vd} , (mg d⁻¹) was calculated as:

$$H_{vd} = K_z^m \frac{\Delta C}{\Delta z} A_m, \tag{6}$$

where the concentration gradient $\Delta C/\Delta z$ was calculated between the centre of the epilimnion and centre of the hypolimnion and A_m is the surface area at the depth of centre of the metalimnion, this depth being calculated as a monthly average. K_z^m is the vertical eddy diffusivity (m² d⁻¹), at the centre of the metalimnion, calculated using the heat flux method of Jassby & Powell (1975). The daily values of H_{vd} were averaged to weekly values and converted to kilogrammes for the load calculations. The error was again estimated using percentage standard error of the difference from the Miller (2008) data based on the method above.

Summertime Epilimnetic Load

The total summertime SRP load from the sediment to the overlying epilimnion, I_{epi} (mg), is the sum of the daily flux over the study period:

$$I_{epi} = \sum_{j=1}^{m} K_{sed} S_j , \qquad (7)$$

where S_j (m²) is the area of sediment directly overlain by epilimnetic water on each day, *j*, and *m* is the number of days in the study period. The sediment release rate, K_{sed} , is taken to be 0.46 mg m⁻²d⁻¹, the average summer release rate from a study by Steinman *et al.* (2009), investigating an oxygenated littoral site in Mona Lake, a moderately eutrophic lake similar to Esthwaite Water. The study of Steinman *et al.* (2009) also quoted a range of values for

release rates at the littoral study site $(0 - 1.1 \text{ mg m}^{-2}\text{d}^{-1})$ and these were used to calculate a percentage standard error, which was then used to provide an error estimate for the load calculation in this study.

Summertime External Load

The external diffuse, E_d (mg), and point, E_p (mg), total SRP load estimates for the study period and their associated errors were calculated based on the method of Walling and Webb (1981) from Cassidy & Jordan (2011):

$$E_d = \sum_{i=1}^n (C_{usi} Q_{pi} D_i), \tag{8}$$

$$E_p = \sum_{i=1}^n ((C_{dsi} - C_{usi}) D_i Q_{pi}/2), \tag{9}$$

where *i* represents each sampling period, there being *n* sampling periods in total. For each period *i*, C_{usi} is the concentration of SRP in Black Beck upstream of the STW (mg m⁻³), C_{dsi} is the SRP concentration in Black Beck downstream of the STW (mg m⁻³), Q_{pi} is the average discharge for all the lake inflows (m³ d⁻¹), and D_i is the number of days in that sampling period (~14). Thus, C_{usi} is taken as the SRP concentration of all inflows to the lake except for the STW discharge. The discharge for E_p is that only from Black Beck, being 50% of Q_{pi} . For comparison with long term average conditions, these external load calculations were also carried out taking Q_{pi} equal to the 30-year average discharge for each sampling period.

Analysis by Cassidy and Jordan (2011) suggested that this method with a sampling interval similar to that in this study underestimates the true phosphorus load, based on high frequency measurements, by around 50%, therefore a correction of 50% was added to the load estimates in the present study. The range of values reported in the Cassidy and Jordon

(2011) study for the external load estimation method were used to calculate a percentage standard error of the method. This percentage error was then applied to the load calculations in this study to provide an error estimate. The error estimates for each SRP source were used to calculate an error range for the total summertime load, presented in Table 2.

Results

Physical conditions

It proved useful to distinguish three separate periods in the summer season: an earlysummer period from day 152 to 203 (1st June to 22nd July), a mid-summer period between days 204 and 245 (23rd July to 2nd September) and a late-summer period from day 246 to 280 (3rd September to 7th October). The start of the mid-summer period was chosen to coincide with a time at which the lake was equally stable in both years (Fig. 3c), whilst the end of the mid-summer period represented the week when hypolimnetic SRP reached its maximum in 2008. In early-summer there was less warming and more wind mixing in 2008 than in 2009 (Fig. 3a - b, Table 1), causing a deeper mixed layer and lower Schmidt stability (Fig. 3c - d). The pattern in physical conditions reversed during the mid-summer when 2008 experienced half of the wind mixing of the same period in 2009 and a slight warming in contrast to the gentle cooling in 2009 (Fig. 3a - b, Table 1). As a result, during the mid-summer period the average mixed depth was about 20% deeper in 2009 than 2008 and the stability about 30% less. In the late-summer period, the wind mixing and net cooling eroded the thermal stability and induced overturn at about day 280 in both years.

Anoxia

The development and size, both in water volume and sediment area covered, of the deep water anoxia largely reflected the trends seen in the physical lake conditions. In particular, in mid-summer 2008, a much larger volume and sediment area were anoxic compared to 2009, representing a 39% difference in anoxic volume and 16% difference in anoxic sediment area during this period between the two years (Table 1).

Hypolimnetic SRP

The SRP mass in the deep waters of the hypolimnion followed a similar pattern of increase during the early-summer in both years (Fig. 4). During the mid-summer, however the pattern of hypolimnetic SRP diverged between years, with a continued increase in SRP in 2008, in contrast to little overall change during the mid-summer in 2009. In both years, most of the SRP was lost by the end of the summer.

Hypolimnetic SRP loading into the epilimnion

Vertical diffusion and vertical entrainment showed distinct sub-seasonal patterns (Fig. 5a, 5b). During the early- and mid- summer, the vertical entrainment of SRP was very low, with only 18% and 27% of the total summer entrained load occurring between the start of the study period and day 245 in 2008 and 2009 respectively (Fig. 6a, 6b). Large fluxes took place throughout the late summer of 2008, but only at the end of the summer in 2009 (Fig. 5a, 5b). The diffusive flux also increased through the season, which resulted in the diffusive load more than doubling between the early- and mid-summer periods, accounting for 54% and 84% of the total summer diffusive load by day 245 in 2008 and 2009 respectively (Fig. 6a, 6b). Though the diffusive flux peaked at the end of mid-summer in 2009, it continued to rise until the end of summer in 2008 (Fig. 5a, 5b).

Interannual variability

The overall summer SRP load to the lake differed by 31% between years (Table 2). Whilst both the external loading and internal epilimnetic loading changed little between years, there was a large interannual difference in hypolimnetic loading (Fig. 7, Table 2). This change in hypolimnetic flux altered the relative contribution of internal sources to the summer SRP budget, being 34% of the total in 2009 and 50% in 2008.

Average stream discharge levels during the study periods in 2008 and 2009 were 0.8 m^3s^{-1} and 0.7 m^3s^{-1} respectively, both of which were considerably higher than the 30-year

average for the stream of 0.5 m³s⁻¹. The corresponding residence times over the study period in 2008 and 2009 were 99 and 111 days, respectively, compared to the 30 year average for that period of 159 days. The discharge pattern in both years resulted in larger diffuse fluxes than point source fluxes in both years (Fig. 7). When loads are recalculated using the 30-year average discharge figures, it is clear that external loads in 2008 and 2009 were about 25% higher than might be typically expected (Table 2). Thus if 2008 had been a typical year for discharge, the internal supply would have been about 56% of the total. Calculations based on the maximum and minimum discharge years for the summer period over the 30-year time series indicated that the internal loads measured in this study might account for anything from 22% to 80% of the total SRP load to the lake. On average during 2008 and 2009 about 40 to 50% of the total external phosphorus load was in the form of SRP.

Discussion Linking the weather to SRP release

Three periods were identified to understand the progression of hypolimnetic SRP loading over the summer. In the early-summer of both years, the hypolimnetic SRP pool was small, as the anoxic, reducing conditions required for phosphorus sediment release or water column transformation had only been present for a short period of time (Mortimer, 1941). SRP fluxes to the epilimnion were therefore also small. The SRP pool was located in the deepest water and so was likely to be little affected by the influence of the weather. The initial accumulation of SRP followed an approximately linear trend, a pattern which has been broadly observed for total phosphorus in other lake hypolimnia, following the onset of stratification (Larsen et al., 1981; Wodka et al., 1983; Soranno et al., 1997). This linear trend was also reproduced by the growing proportion of the lake sediment and water volume that became anoxic, reflecting the relationship between hypolimnetic anoxia and hypolimnetic SRP (Mortimer, 1941; Gachter, Meyer & Mares, 1988). Differences between years in deep water temperature, which can affect the rate of SRP release (Holdren & Armstrong, 1980), were not seen in Esthwaite Water, where the mean temperature from the two deepest thermistors at 10.5 m and 11.5 m, were consistently warmer in all periods of the summer in 2009 than 2008 by an average of 0.58°C, suggesting that the differences seen in SRP accumulation were not due to temperature-mediated changes in the sediment release rate.

By the start of mid-summer in both years, the hypolimnetic SRP pool had expanded sufficiently far up the water column to be noticeably affected by vertical mixing, losing SRP to, and gaining oxygen from, the waters above. Differences in weather conditions occurring during the mid-summer resulted in two very different pathways for hypolimnetic SRP accumulation and late-summer hypolimnetic SRP fluxes between the two years. A decrease of only 0.7 m s⁻¹ in mid-summer average wind speed from 3.0 to 2.3 m s⁻¹ resulted in a

halving of wind energy flux from 2009 to 2008 (Table 1). As the less windy 2008 was also accompanied by a net warming, rather than the net cooling experienced over the same period in 2009, the resulting thermal structure in 2008 was more stable than in 2009. This increase in stability reduced downward oxygen flux and allowed the build-up of higher SRP concentrations. In the late-summer of both years, the lake gradually destratified and overturned, mixing the hypolimnetic SRP pool throughout the water column. Thus, the size of the hypolimnetic flux was determined not by mixing events during the late-summer period, but by the size of the hypolimnetic SRP pool at the start of the period.

Importance of understanding interannual variability

In Esthwaite Water the hypolimnetic SRP loading to the epilimnion was twice as large in 2008 as 2009, resulting in the total summertime loading to be a third higher in 2008 than 2009 (Fig. 7). This change was consistent with the sizeable decrease in deep-water anoxia (Table 2) effected by the differing mid-summer weather conditions between the two years. That differing weather conditions can have such a large impact on anoxia and therefore phosphorus loading for a lake is striking. In fact the two years had untypically high flow rates, which would have resulted in higher than normal external loads. Furthermore, the average meteorological conditions over the summer were not that different, suggesting the ratio of internal to external loading over many years would likely be somewhat greater than that shown for just the two years here. This variation puts into context the estimates made in many previous studies on nutrient budgets using single years or assuming a consistent load from internal sources (Wodka *et al.*, 1983; Marsden, 1989; Heinz, Ilmberger & Schimmele, 1990). The fact that both the hypolimnetic and external loads can show large interannual variability needs to be considered when lakes are assessed for water quality targets and

progress towards recovery following catchment and lake interventions (e.g. Hering *et al.*, 2010).

Previous studies have not specifically examined sub-seasonal changes in hypolimnetic SRP loading, although Soranno et al. (1997) did investigate the hypolimnetic entrainment of total phosphorus (TP) in the large and deep Lake Mendota. They too suggested that differences in meteorological conditions altered entrainment, but argued that it would be an increase in storms that would cause greater mixing and higher entrainment of TP. In fact, in their study the most significant entrainment also took place in the late summer after the deepwater TP pool had been built up, with the stormier conditions in late summer one year drawing up a greater proportion of this TP than the calmer conditions experienced in the comparison year. It was not, though, reported what proportion of the TP in Lake Mendota was SRP and therefore likely to be affected by the extent of anoxia, so a direct comparison between the two lakes is not possible. Nevertheless, it poses the question as to whether lake morphology may influence whether an increase in wind mixing would ultimately increase, by promoting upward entrainment, or decrease, by inhibiting deoxygenation, summertime internal loading of nutrients. Over longer timescales than those studied here, other issues such as permanent burial of phosphorus in the sediments or loss through the outflow are important determinants of internal loading and lake recovery times (Katsev et al., 2006; Lewis et al., 2007).

Broader climate influences

Understanding the drivers of the physical forcing processes is important for elucidating how year-to-year variations in weather conditions might be anticipated to influence the hypolimnetic flux of SRP, both in terms of its timing and overall size. Synoptic weather patterns such as the El Nino Southern Oscillation and the North Atlantic Oscillation

and their influence on the passage of cold fronts and the transition between warm and cold air masses has been found to impact on stratification, mixing and the flux of nutrients in lakes, both in terms of external and internal loading (Gerten & Adrian, 2001; Winder & Schindler, 2004; MacIntyre *et al.*, 2006; MacIntyre *et al.*, 2009).

Secular climate change effects on thermal structure, hypolimnetic anoxia and phosphorus concentrations (North *et al.*, 2014) are also likely to influence the hypolimnetic SRP flux. Changes already experienced in lakes include higher thermal stabilities (Persson *et al.*, 2005; Jankowski *et al.*, 2006), longer periods of stratification resulting in increased deep water anoxia (Foley *et al.*, 2012), as well as shallower mixed layers (DeStasio *et al.*, 1996). The implication from our study in this context is that stronger stratification will impact more on hypolimnetic SRP loading through increasing the extent and duration of hypolimnetic anoxia and the concomitant increased size of the hypolimnetic SRP pool, than through the release of phosphorus via cross-thermocline mixing events during the early- and midsummer.

Changes to river flow may also affect the influence of internal loading on epilimnetic nutrient supply. Future changes to discharge regimes are expected to be highly variable (Milly, Dunne & Vecchia, 2005), but in many areas, including the north-west of England where Esthwaite Water is situated, large decreases in summer discharge are predicted (Fowler & Kilsby, 2007). In these areas, internal loading would become an even greater proportion of the phosphorus budget than is currently the case. Jones *et al.* (2011) showed that when summer discharge rates decrease, lakes with a high proportion of internal load are more susceptible to increases in phytoplankton biomass than lakes dominated by diffuse loading.

This study has examined temporal variability in hypolimnetic loading of SRP and physical forcing conditions to explore their influence on the overall summertime SRP load to

a small, eutrophic lake. We have shown that the lake thermal structure had a significant role in determining the hypolimnetic SRP supply, the hypolimnetic sources of SRP varied over sub-seasonal timescales and interannual variability in hypolimnetic SRP loading was significant relative to the total load reaching the epilimnion. Conceptually, the sub-seasonal variability in summertime weather conditions impacts on stratification strength and crossthermocline mixing, which in turn influences oxygenation of the hypolimnetic waters and the development of anoxia up through the water column as the summer progresses. These processes have an important influence on phosphorus release from the sediments, its accumulation in the hypolimnion and the fluxes to the epilimnion. Detailed, continuous data, such as that supplied from the network of automatic monitoring buoys in GLEON (http://www.gleon.org) is required for understanding these processes on the relevant timescales.

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Tables

Table 1 Average meteorological and lake hydrographical data over the different summer periods for Esthwaite Water in 2008 and 2009. Figures in parentheses are absolute differences from 2009 values for Air temperature, Solar radiation and Wind speed and 2008 values expressed as a percentage of 2009 values for all other data.

	2008				2009			
Variable	Whole period	Day 152 to 203	Day 204 to 245	Day 246 to 280	Whole period	Day 152 to 203	Day 204 to 245	Day 246 to 280
Air								
temperature	13.9	13.7	14.4	11.9	14.4	15.1	15.0	12.6
(°C)	(0.5)	(1.4)	(0.6)	(0.7)				
Solar								
radiation	131	171.7	125	77.7	142.1	197.5	117.3	89.3
$(W m^{-2})$	(11.1)	(25.8)	(-7.7)	(11.6)				
Wind speed								
at 10m	2.4	2.6	2.3	2.4	2.6	2.4	3.0	2.5
$(m s^{-1})$	(0.2)	(-0.15)	(0.7)	(0.04)				
Vertical								
wind energy								
flux	72.5	71.2	49.9	101.4	80.5	65.0	99.8	80.4
$(mW m^{-2})$	(90%)	(109%)	(50%)	(126%)				
Change in								
heat content	-2.5	12.5	2.6	-32.5	-0.9	14.9	-9.4	-16.1
$(J s^{-1} m^{-2})$	(261%)	(84%)	(-28%)	(202%)				
Schmidt								
stability	79.9	94	102.4	32.2	81.1	121.0	78.0	25.7
$(J m^{-2})$	(99%)	(78%)	(131%)	(125%)				
Epilimnion								
depth	-5.5	-4.7	-4.4	-8.1	-5.5	-3.7	-5.5	-8.2
(m)	(100%)	(126%)	(79%)	(99%)				
Anoxic lake								
volume	866,067	564,820	1,466,273	627,815	937,566	1,176,265	1,052,541	417,676
(m ³)	(92%)	(48%)	(139%)	(150%)				
Anoxic								
sediment	212 102	247.062	120 (0)	276 522	222 764	250 400	271.052	210.261
area	313,183	247,963	430,686	2/6,533	322,764	350,499	371,952	219,361
(m ⁻)	(9/%)	(/1%)	(116%)	(126%)				

Table 2 Summary of total summertime SRP loading (kg) to Esthwaite Water from different sources in 2008 and 2009. Figures in parentheses are calculated using the 30-year average discharge and \pm values are the product of the load estimate and percentage standard error or standard error of differences specified in the methods.

Source	Туре	2008	2009	2008 - 09 Average
External	Point	98 ±18(99)	62 ±11 (55)	80 ±14 (77)
	Diffuse	137 ±25 (85)	167 ±30 (110)	$152 \pm 27(98)$
Total External		235 (184)	229 (165)	232 (175)
Internal	Entrainment	151 ±60	51 ±20	101 ±40
	Diffusion	62 ± 16	41 ±11	52 ±13
Total .	Hypolimnetic	213	92	153
	Epilimnetic	23 ± 12	24 ± 12	24 ±12
Т	otal Internal	236	116	176
	Total	471	345	408

Figure Legends

Figure 1 Esthwaite Water showing sampling sites and the location of the shore weather station and AWQMS buoy. Location of Eel House Bridge gauging station relative to the lake inset A.

Figure 2 The different external and internal SRP fluxes considered in Esthwaite Water.

Figure 3 a) Weekly averages of vertical wind energy flux (mW m⁻²), (b) weekly change in lake heat content (J s⁻¹ m⁻²), (c) daily values of Schmidt stability (J m⁻²), and (d) daily values of epilimnion depth (m). Dotted lines show division of summer time periods: early-summer, days 152 to 203; mid-summer, days 204 to 245; and late-summer, days 246 to 280.

Figure 4 Deep water (>10m) SRP pool (kg) in 2008 and 2009. Dotted lines show division of summer time periods: early-summer, days 152 to 203; mid-summer, days 204 to 245; and late-summer, days 246 to 280.

Figure 5 Weekly average SRP fluxes (kg d^{-1}) for Esthwaite Water over the study period from the hypolimnetic sources of vertical entrainment and vertical diffusive loading for a) 2008 and b) 2009. Dotted lines show division of summer time periods: early-summer, days 152 to 203; mid-summer, days 204 to 245; and late-summer, days 246 to 280.

Figure 6 Cumulative SRP load (kg) from vertical diffusion and entrainment in a) 2008, b) 2009.

Figure 7 Average daily SRP flux (kg d^{-1}) from the different sources for the study period during 2008 and 2009.



Fig. 2















