

THE LONG-TERM RESPONSE OF LAKE NUTRIENT AND CHLOROPHYLL CONCENTRATIONS TO CHANGES IN NUTRIENT LOADING IN IRELAND'S LARGEST LAKE, LOUGH NEAGH

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ABSTRACT

The long-term response of chlorophyll-*a* (chl-*a*) to changing lake water nutrient concentrations and increasing water temperature was investigated in Lough Neagh, a large, hypereutrophic lake in Northern Ireland. Trends in external and internal nutrient loading and their relation to lake nutrient concentrations were also established. Lake water concentrations of total P (TP) have increased since the 1990s but were not correlated with catchment inputs, which showed no trend. The characteristics of internal loading of P have changed since the mid-1990s, with an earlier and larger mass of P released from the sediments each summer. Catchment inputs of total oxidised N (NO_x) decreased from the peak value of 10,186T/yr in 1995 to 5,396T/yr in 2011, coinciding with a reduction in lake water concentrations. External inputs and lake concentrations of NO_x were highly correlated ($R=0.88$). Water temperature increased approximately 1C and was a predictor of variation in chl-*a* from 1974 to 2012. After the peak chl-*a* concentration in 1993, dissolved inorganic N (DIN) also became an important predictor, accounting for almost half of the 44% variance explained by a hierarchical partition model. Decreasing log (DIN:TP) ratios suggest that N limitation of chl-*a* has become more important in the lake recently.

INTRODUCTION

Cultural eutrophication remains a major threat to freshwater systems globally (Wurtsbaugh *et al.* 2019) and over-enrichment of lakes can lead to undesirable effects on water quality such as elevated concentrations of chlorophyll and anoxic conditions. Climate-induced water temperature increases have also had considerable impacts on the functioning of shallow lakes (Carvalho and Kirika 2003) impacting chemical, physical and biological processes (Pettersson *et al.* 2003; Köhler *et al.* 2005). Water quality across Europe continues to decline (European Environment Agency 2018) despite management measures aimed to improve ecological status implemented under the European Water Framework Directive (WFD) (European Commission 2000). Many of the management measures focus on nutrient control, however, after any reduction of nutrient inputs from the catchment, water quality improvements can be impeded due to the release of P from the lake sediment (Phillips *et al.* 1994; Søndergaard *et al.* 2013). While lakes can respond well to reductions in N loading (e.g. Shatwell and

Köhler 2019) internal P regeneration may act as a considerable source of P (Nürnberg 1987), especially in eutrophic lakes (Søndergaard *et al.* 1999) such as Lough Neagh in Northern Ireland (Gibson *et al.* 2001). Internal release of P is enhanced by factors such as increasing temperature, decreasing nitrate concentrations and increasing pH (Jensen and Andersen 1992) and it can impact the stoichiometric composition of lake water chemistry, influencing primary production limitation (Ding *et al.* 2018). Though it is widely acknowledged that P frequently limits primary production, N can be also limiting in eutrophic lakes, especially where N fixing phytoplankton do not compensate for low N availability (Shatwell and Köhler 2019). Lough Neagh is well studied and has had numerous catchment measures implemented since the 1980s, including the upgrade of sewage treatment works and catchment-wide controls on diffuse pollution from agricultural sources. Despite these measures, the 2020 WFD TP status was Bad (139µg/L) and well exceeded the upper threshold that is compatible with Good Ecological Potential (24µg/L). Current targets aim to lower the TP concentration

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to between 49 $\mu\text{g/L}$ and 97 $\mu\text{g/L}$, which is the range for the Poor status category; these targets take no account of internally released P. In order to set realistic water quality objectives, it is important to understand the characteristics of both internal and external nutrient loading as well as trends in nutrient concentrations and primary production.

We used long-term monitoring results for Lough Neagh to describe how water concentrations of nutrients have changed in response to both external and internal nutrient inputs. The main dataset was from 1974–2012 but some variables had values to 2016. We described long-term trends in lake water P, N and temperature and their influence on chlorophyll-*a* (chl-*a*) over the period (1974–2012) and before and after peak chl-*a* concentrations in 1993. We explored N and P loading trends from the catchment (1984–2011) and P internal load (mass balance trends: annual 1984–2013 and summer 1984–2014). Trends in the volume of river water inflow were investigated and the correlation of lake water nutrient concentrations with the mass of external loading was calculated. We investigated the timing of lake water nitrate depletion and the magnitude of subsequent P remobilisation from lake sediment. We also investigated changes in chl-*a*:TP ratios, lake water chemistry stoichiometry and potential N limitation of primary production.

MATERIALS AND METHODS

STUDY SITE

Lough Neagh has an area of 383 km^2 and volume of 3.45 $\times 10^9\text{m}^3$. It is shallow, hypereutrophic and polymictic with a mean and maximum depth of 8.9m and 34m, respectively. A full description of the lake is given in Wood and Smith (1993).

WATER SAMPLING AND ANALYSES

Integrated water samples were collected at a mid-lake station in 10m water depth weekly (1974–92) or fortnightly (1993 to present). The sampling location was representative of overall lake water chemistry conditions (Gibson *et al.* 2000). Chl-*a* was determined according to Talling and Driver (1963). Total P (TP) and soluble reactive P (SRP) were measured according to Eisenreich *et al.* (1975) and Murphy and Riley (1962), respectively. Filtered samples (0.45 μm) were used to determine total oxidised nitrogen (NO_x, the sum of nitrate and nitrite) and ammonium based on Chapman *et al.* (1967). Dissolved inorganic nitrogen (DIN) was the sum of NO_x and ammonium. Total Kjeldahl N (TKN) was determined on unfiltered samples (Stevens 1976). Total N (TN) was the sum of NO_x and TKN. Water temperature was recorded at 10m, which was taken

as representative of the water column temperature given that the mean depth is 8.9m.

LAKE NUTRIENT LOADING AND SEDIMENT RELEASE

The loadings of TN, NO_x and TP to Lough Neagh were estimated using results from the eight major inflowing rivers, (daily river flow data, available from 1984–2011) and nutrient concentrations in the rivers from water samples collected weekly. The river nutrient concentration and flow results were used to calculate the loadings for each year using flow weighted means and interpolation (Johnes 2007).

As the monitored catchments represented 86% of the Lough Neagh catchment, the nutrient load to the lake (1984–2011) was estimated using a conversion factor (Smith 1993) and by dividing the sum of the loads from the monitored catchments by 0.86. If >4% of flow data for a year was missing, then nutrient load for that year was not derived. The nutrient and flow data for the outflow were used to calculate the lake nutrient output. The mass of P released from the sediment was estimated using: (whole lake P mass at end of time period - whole lake P mass at beginning of time period) - (P mass input - P mass output).

The trends of water column N depletion and release of sediment P were determined. The month within which the NO_x concentration fell below 0.06mg/L was identified; Gibson *et al.* (1992) found that the summer (July–September) average nitrate concentration fell from 0.20 to <0.05mg/L over the 1971 to 1980 period, so 0.06mg/L was chosen as a threshold for the depletion of NO_x through assimilation by phytoplankton. We also identified the month that the SRP concentration began to increase above 0.010mg/L (where the previous month was below this value) and this was the threshold used to indicate the start of sediment P release as described by Gibson and Stewart (1993). Lake water concentration results were available weekly up to 1992, but fortnightly thereafter. We could not identify these times more precisely than monthly for the whole 1974–2012 period.

STATISTICAL ANALYSES

The measurements for water temperature and the concentrations of chl-*a*, SRP, TP and NO_x in Lough Neagh water, at weekly intervals from 1974 to 1992—and fortnightly up to 2012—were used to calculate monthly mean values. The long-term trends and seasonality were then investigated using generalised additive models (GAMs).

The additive model for each variable fitted a smooth function to describe the long-term trend and a smooth function to describe the average seasonal pattern (Equation 1).

$$y = \beta_0 + f_1(\text{year}) + f_2(\text{doy}) + \varepsilon, \varepsilon \sim N(0, V\sigma^2), \quad (1)$$

$$V \sim \text{AR}(1)$$

Where β_0 is the overall mean and $f()$ is a smooth function; cubic regression splines were used for the long-term trend (year) with cyclic cubic regression splines for the seasonal pattern (doy, day of year). The monthly mean concentrations were transformed using natural logs. As some of the SRP and NO_x values were below the limits of detection (LODs), they were treated as censored observations. The ROS method (Helsel 2005) was applied using the NADA package in R (Lee 2013; R Development Core Team 2014) to impute such values to take account of these LODs. The *mgcv* library in R (R Development Core Team 2014; Wood 2017) was used to fit the GAMs (Hastie and Tibshirani 1990). The function *gamm* in *mgcv* was used to incorporate an autocorrelated error structure (order 1) into the model fitting. Figures generated from the additive models displayed the estimated smoothed nonparametric regression line for each covariate effect for the long-term trend and seasonal pattern (i.e., year and day of year, respectively) with shaded 'variability' bands to illustrate ± 2 standard errors (SEs). Covariates were expressed as deviation from their mean of the time series.

The trends in N:P ratios and catchment nutrient loading were described using nonparametric regression models. The *sm* regression function in the *sm* library in R (Bowman and Azzalini 2014) was applied to the log of mean annual nutrient ratios and annual catchment nutrient loading in order to fit smooth nonparametric long-term trends (e.g. Ferguson *et al.* 2008).

The functions for the GAMs and the non-parametric regressions provide inferences on the significance of the nonparametric effects through approximate tests, such as approximate *F*-tests (Hastie and Tibshirani 1990). Mann-Kendall (MK) tests were used to describe the direction of any changes in the variables. Hierarchical partitioning (HP) (Chevan and Sutherland 1991) investigates all multiple regression models jointly in order to find the most likely causal factors (MacNally 2002) and was used here to uncover the relationship between chl-*a*, DIN, TP and water temperature. This technique uncovers the tested predictor variables with the most explanatory power in relation to chl-*a*. Hierarchical partitioning calculates the independent effects (distinct from partial correlation) of each explanatory variable and is an effective method for variables that may be collinear as it dampens the effects of multicollinearity (MacNally 1996). For a set of predictor variables, HP averages the effect of each parameter on goodness of fit measures, in our case R^2 , across all possible 2^K models, for *K* predictor variables (MacNally 2002). This allows the explanatory effect of each parameter to be separated into

an independent effect and a joint effect in common with the other variables. The method can provide insight into potential explanatory relationships. For each of our tested variables, the independent and joint effects are presented as a percent of the total variance explained (MacNally 2000). Hierarchical partitioning (HP) and associated randomisation tests analyses were completed using the *hier.part* package (Walsh and MacNally 2013) in R. Preliminary pairwise plots (Appendix I) showed linearity between chl-*a*, the nutrients and water temperature demonstrating suitability for the HP method.

RESULTS

CATCHMENT LOADING AND LAKE WATER CONCENTRATION OF N AND P

Total N from the catchment was strongly correlated with catchment NO_x load; $R^2=0.85$, $P<0.001$, $n=16$, and so NO_x was used as an indicator of TN as TKN data were unavailable since 2002. For the data available for TN river loading (1984–2002, three missing years), NO_x made up a mean of 66% (SD=6%) of the TN; similar to the value of 64% found by Gibson *et al.* (1992). Total oxidised N loading to Lough Neagh from the catchment (1984–2011) demonstrated a significant trend (nonparametric regression $P<0.05$; Fig. 1a; Table 1); the load generally increased from 1984 until a peak value of 10,186T/yr was reached in 1995, then decreased to 5,396T/yr at the end of the time series. Mean TP loading from the catchment was 606T/yr from 1984 to 2011; catchment inputs were variable from year to year and no significant trend was evident (Fig. 1b; Table 1). Trends in the volume of river inflow were not apparent.

The long-term GAM of the log of lake NO_x (Fig. 2a; $P<0.001$; Table 1) revealed decreasing concentrations after the mid-1990s peak (0.83mg/L in 1996) until the end of the data sequence (0.33mg/L in 2012). A significant decrease in concentration was evident after the mid-1990s (MK $P<0.01$) but no significant trend before this. The annual seasonal cycle of lake water NO_x (Fig. 2b) was identical to that found by Gibson *et al.* (1992) using results for the 1975 to 1987 period, showing assimilation by phytoplankton, which reduced the concentration (lowest by June) followed by mineralisation, which increased it.

The log of lake water TP concentration (GAM $P<0.001$; Fig. 3a; Table 1), showed a generally increasing trend from 1974 to 2012 (MK $P<0.001$). Peak mean annual TP concentration, 164µg/L, was reached in 1997 and concentrations remained high thereafter. A spring lake water TP minimum similar to that described by Gibson and Stewart (1993) was evident (Fig. 3b). The log of lake water SRP concentration (GAM $P<0.001$; Fig. 3c; Table 1), also

showed a general increasing trend over the 1974 to 2012 period (MK $P < 0.001$). Soluble reactive P has gradually increased since the early 1990s. Peak lake water SRP concentration occurred in 2005

(92 $\mu\text{g/L}$) and remained relatively high until the end of the data series; 2012 mean concentration was 72 $\mu\text{g/L}$. A spring lake water SRP minimum was also evident (Fig. 3d).

The catchment loading of NO_x and the lake concentrations of NO_x (1984–2011) were positively correlated ($R=0.88$; $P < 0.001$; Fig. 4a). Lake water concentrations of the nutrient decreased in line with falling inputs over the time series. In contrast, TP input from the catchment and lake concentration of TP (1984–2011) were not correlated ($R=0.25$; $P > 0.05$; Fig. 4b) and showed no trend. The increasing lake TP concentration was not reflected by the catchment input of TP, which showed no significant trend in direction.

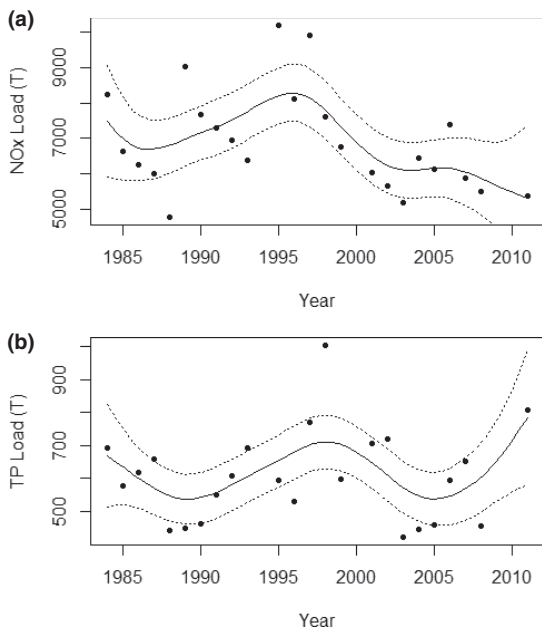


Fig. 1—Nonparametric regression of total oxidised nitrogen (NO_x) (a) and total P (TP) (b) loading from the Lough Neagh catchment in tonnes (T), 1984–2011.

INTERNAL LOADING OF P

The annual (1984–2013) and summer (1984–2014) lake water nutrient mass balances were estimated for TP. Significant changes were not evident at the annual scale, however, increases in the summer mass of sediment TP release have occurred (MK $P < 0.05$). A change in the magnitude of release has occurred, commencing in the 1990s. From 1984 to 1994 the mean summer release of TP was 107T, and from 1996 to 2014 the mean TP release increased to 249T (Fig. 5). The detailed monthly analysis of NO_x and SRP (Fig. 6) showed that lake water NO_x was depleted earlier on in the year and, subsequently, SRP was released from the sediment, indicated by a sudden rise in the lake water SRP concentration.

Table 1—Smoothed regression models (Sm Reg) for the catchment input of total oxidised N (C_NO_x, T/yr), catchment input of total P (C_TP, T/yr) and the log ratio of dissolved inorganic N and total P (DIN:TP). Generalised additive models (GAM) for log total oxidised N (NO_x, mg/L), log TP (TP, $\mu\text{g/L}$), log soluble reactive P (SRP, $\mu\text{g/L}$), water temperature at 10m depth (Temp 10m, C) and log chlorophyll-*a*, (Chl-*a*, $\mu\text{g/L}$). Direction of trends over tested time periods provided by Mann Kendall tests (MK). $P < 0.05$ *, $P < 0.01$ **, $P < 0.001$ *, NS is not significant.**

Model and time period	Variable	Significance	Trend (MK) and time period
Sm Reg 1984–2011	C_NO _x	*	Decreasing* 1984 – 2011
	C_TP	NS	NS 1984 – 2011
Sm Reg 1974 –2016	DIN:TP	**	Decreasing*** 1974 – 2016
GAM 1974– 2012	NO _x	***	NS 1974 – 2012
			NS 1974 – 1996
			Decreasing** 1997 – 2012
	TP	***	Increasing*** 1974 – 2012
	SRP	***	Increasing*** 1974 – 2012
	Temp 10m	***	Increasing*** 1974 – 2012
			NS 1974 – 1995
			Increasing* 1996 – 2012
Chl- <i>a</i>	***	NS 1974 – 2012	
		Increasing*** 1974 – 1993	
		Decreasing*** 1994 – 2012	

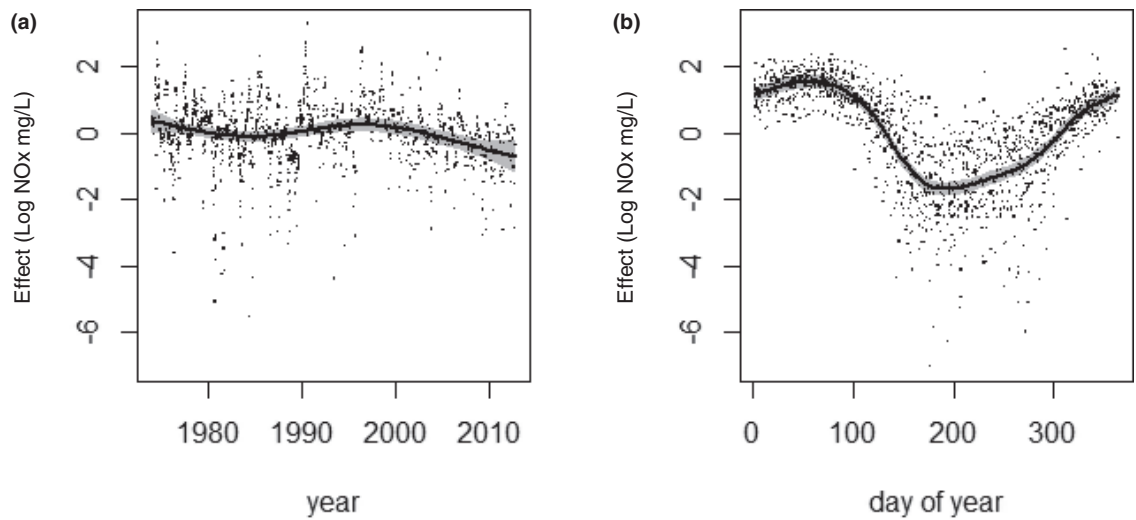


Fig. 2—Long-term trend (a) and average seasonal pattern (b) for log total oxidised nitrogen (Log NO_x, mg/L) concentration from Jan 1974 to Dec 2012 as responses in additive nonparametric models. The shaded region identifies ± 2 SE from the estimate and points are the partial residuals for each covariate respectively (indicating e.g., the remaining long-term trend and variation after fitting the smooth seasonal pattern and vice versa).

This commenced earlier as the time series progressed (1984–2012), from about June rather than July (Fig. 6).

LAKE WATER STOICHIOMETRY, WATER COLUMN TEMPERATURE AND CHL-*A*,

The log of the annual average mass ratio of DIN:TP has decreased significantly over the time series (1974–2016), nonparametric reg. $P < 0.01$; MK $P < 0.001$ (Table 1), especially since the mid-1990s (Fig. 7). The mean log (DIN:TP) ratio was 1.43 before chl-*a* peak concentration in 1993 and was 1.08 afterwards; ratio values were lower and less variable after the mid-1990s (Fig. 7).

Water temperature at 10m (1974–2012) showed a significant increasing trend (GAM and MK $P < 0.001$; Table 1). The increase was more rapid and significant after the mid-1990s (MK $P < 0.05$ after 1995 and > 0.05 before; Table 1); the increasing pattern of water temperature over the time series was driven by the increasing values after the mid-1990s (Fig. 8). Mean annual water temperature (10m) for 1974–95 was 9.88°C, increasing to 10.61°C afterwards (1996–2012).

Nonparametric trends were evident in the log of chl-*a* concentrations (GAM $P < 0.001$; Fig. 9a; Table 1); values increased from 1974 until the peak of 75 µg/L (1993), then decreased to 44 µg/L in 2012. Monotonic trends in chl-*a* concentrations were not apparent over the entire time but a significant increase was evident up to the peak in 1993 (MK $P < 0.001$) and a decrease was evident after 1993 (MK $P < 0.001$; Table 1). Seasonal variation

in chl-*a* was also present (Fig. 9b); the modeled concentration was high for much of the year, from March to October, with a peak in April–May and a small increase in August–September. By testing all possible multiple regression models for the log of annual mean chl-*a* concentration through HP we found that for the three predictor variables tested: mean annual water temperature at 10m, log of mean annual DIN and TP, 13% of variation was explained (1974–2012). Water temperature was identified as the most important variable and had the strongest effect on chl-*a* (HP randomisation test $P < 0.05$; 1974–2012) out of the three predictor variables, accounting for 77% of the explained variation (Table 2). We also investigated the influence of the three variables before and after the chl-*a* peak in 1993. During the period of increasing chl-*a* concentrations the model for log chl-*a* was very weak (HP $R^2 < 0.01$, 1974–93). A large change, however, was apparent after 1993 when concentrations of chl-*a* decreased, HP showed that the three predictor variables accounted for 44% of variation in log chl-*a* concentration (1994–2012). Log DIN concentration and water temperature independent effects accounted for 46% and 47% of variation explained, respectively, (Table 2); both were significant (randomisation test $P < 0.05$). Dissolved inorganic N was positively associated with chl-*a* and temperature was negatively associated (Appendix I, b and c, respectively). The log ($x+1$) of the annual average ratio of chl-*a*:TP generally decreased after the peak chl-*a* concentration 1993, and remained relatively low until the end of the data series (Appendix II).

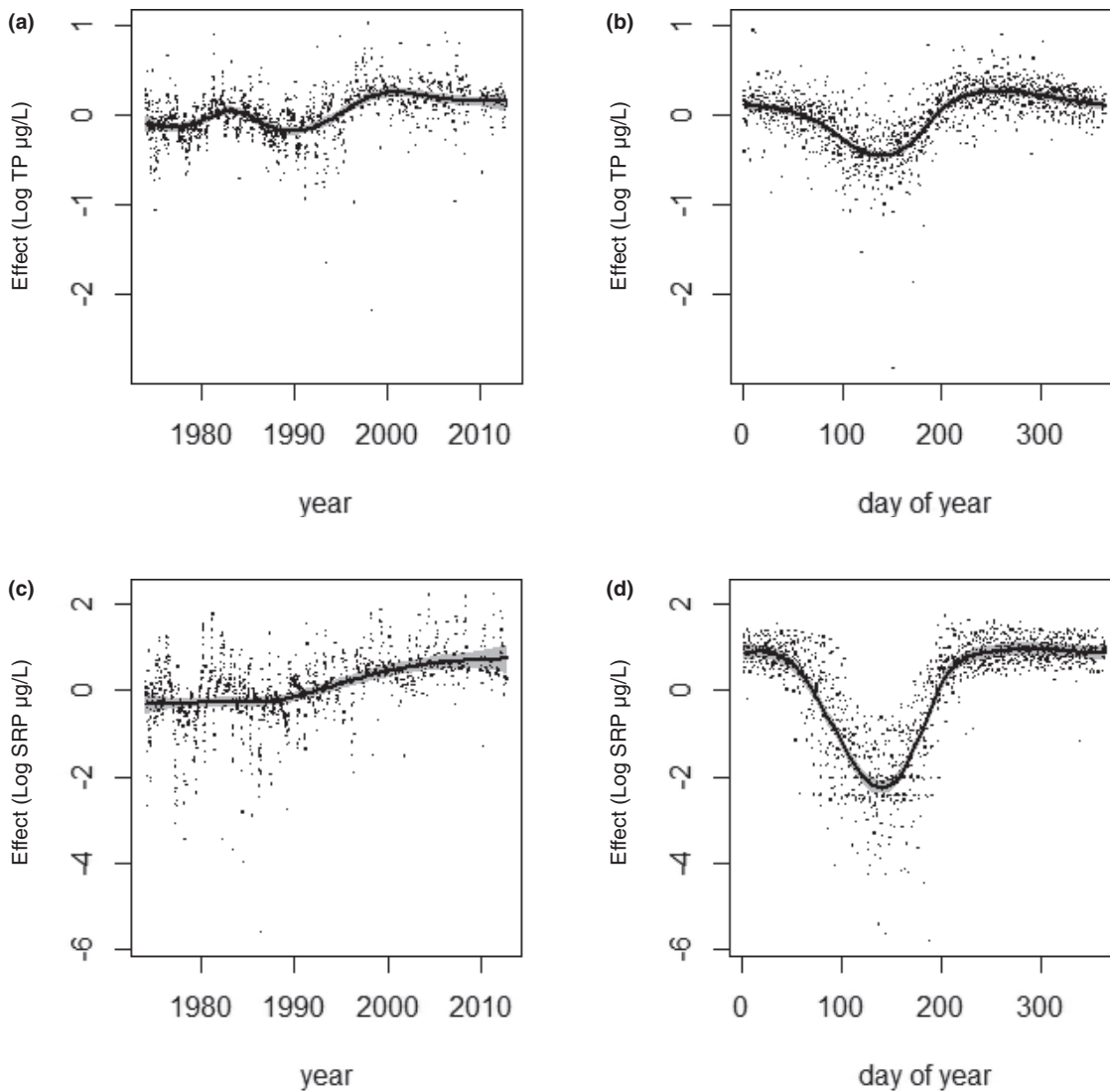


Fig. 3—Long-term trend and average seasonal pattern for log total phosphorus (Log TP, $\mu\text{g/L}$; a and b respectively), and log soluble reactive phosphorus (Log SRP, $\mu\text{g/L}$; c and d) Jan 1974 to Dec 2012 as responses in additive nonparametric models. The shaded region identifies ± 2 SE from the estimate and points are the partial residuals for each covariate respectively (indicating e.g., the remaining long-term trend and variation after fitting the smooth seasonal pattern and vice versa).

DISCUSSION

THE INPUT OF NUTRIENTS AND THE LAKE WATER CONCENTRATION OF NUTRIENTS

The considerable length of the dataset allowed us to reveal trends in water chemistry and show that lake water quality variables underwent significant change after the mid-1990s. We showed that water concentration of NO_x was closely correlated with catchment loading (Fig. 4a) indicating that the lake was responding to decreased N loading from the catchment, which was apparent after the mid-1990s. The poor correlation between catchment inputs of

P and lake water concentrations (Fig. 4b) and results of the lake P mass balance (Fig. 5) indicate that lake water P dynamics are dominated by in-lake processes instead of catchment inputs. The increasing values of lake TP (Fig. 3a) are likely to be driven by the SRP concentration increase in the Lough (Fig. 3c). A very similar lake water nutrient response to reduced N and P loads in a eutrophic lake is described by Köhler *et al.* (2005). Internal loading from P has been identified as one of the reasons why many eutrophic lakes do not respond well to lake water quality restoration efforts (Søndergaard *et al.* 2007) and Lough Neagh with its increasing

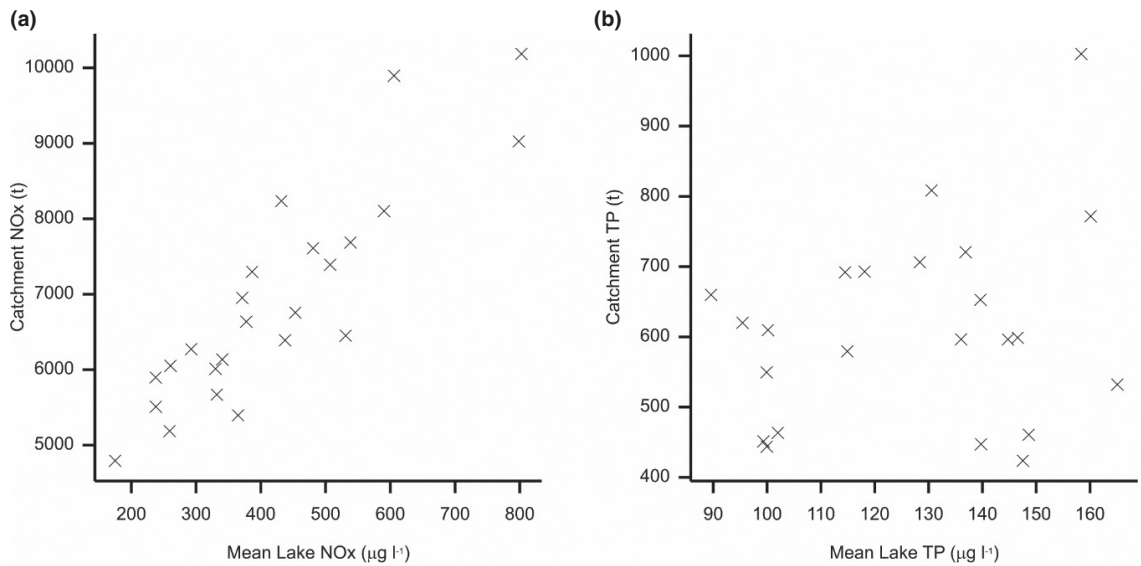


Fig. 4—Annual mean lake water concentration for total oxidised nitrogen (NO_x; µg/L) and catchment loading of NO_x tonnes (T) per year (a) and annual mean lake water concentration for total P (TP; µg/L) and catchment loading of TP (T) per year (b).

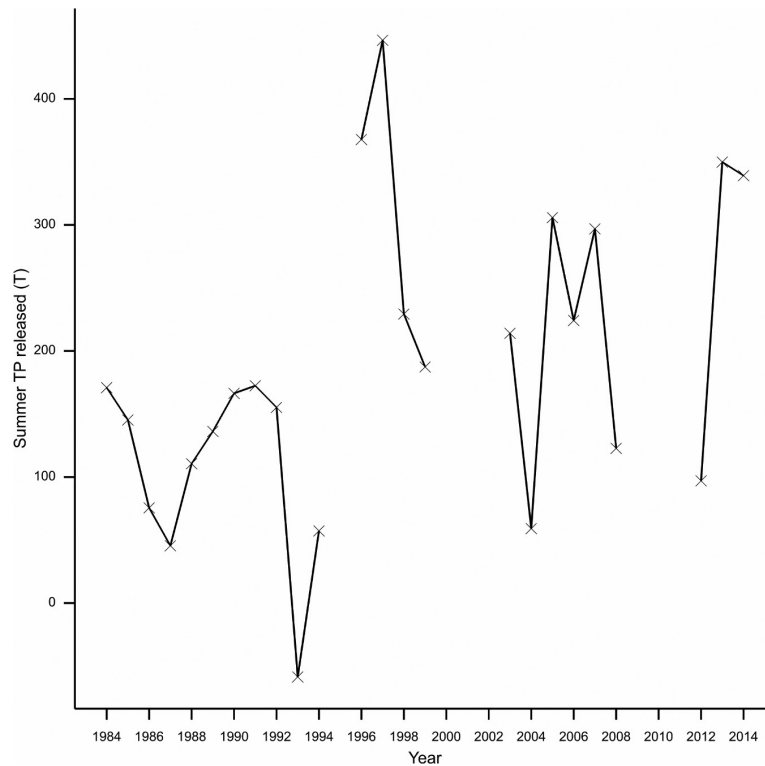


Fig. 5—Net release of total P (T) for summer (June, July, August) 1984–2014.

mass of summer P release is experiencing the negative impacts of internal loading. The greatest mass of internal P in Lough Neagh is released in the summer when higher temperatures and low oxygen conditions accelerate P release (Gibson *et al.* 2001);

coinciding with the most biologically active time in northern temperate lakes. Our observed earlier start to P release in the summer is likely contributing to this greater mass of P released. The average annual cycles of NO_x (Fig. 2b), P (Fig. 3b and 3d) and chl-*a*

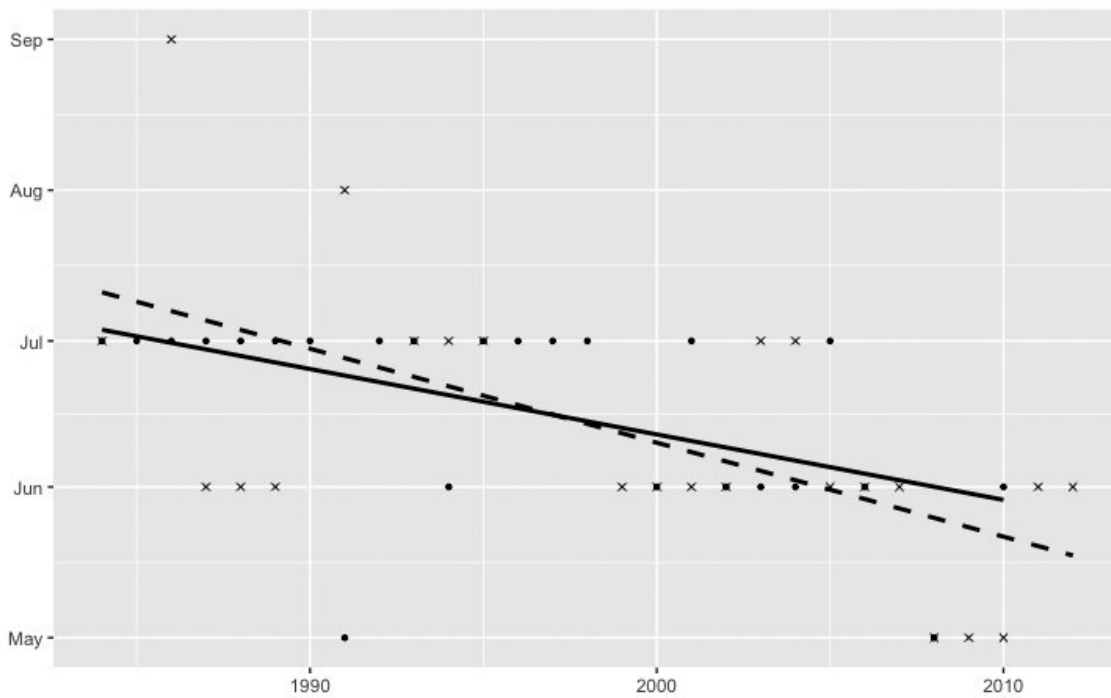


Fig 6—Temporal trends in commencement of total oxidised N (NO_x) depletion (concentration of $\text{NO}_x < 0.06\text{mg/L}$) and soluble reactive P (SRP) sediment release (concentration of SRP was $>10\mu\text{g/L}$), 1984–2012. The temporal trend of NO_x is represented by dots and the solid line, while that of SRP is represented by crosses and the dashed line.

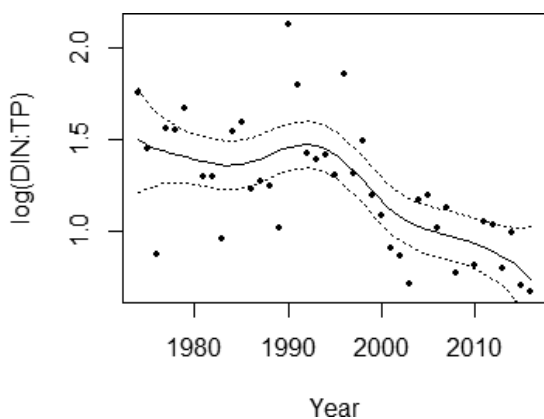


Fig. 7—Log of mean annual mass ratio of dissolved inorganic N (DIN) and total P (TP) in Lough Neagh 1974–2016, $n=41$.

(Fig. 9b), were similar to well-established patterns (Gibson 1993; Gibson and Stewart 1993). However, our more detailed analysis of the N and P seasonal cycles in Lough Neagh (Fig. 6) showed that there have been changes in the time of year that NO_x was depleted through assimilation by phytoplankton and in the start and mass of P released from the sediment. Iron compounds have an important role in binding P in the sediments of Lough Neagh as there is very

little calcium carbonate in the sediment (Rippey 1980; Fletcher 1980). This means that iron mediated release of P (Davison 1993) is the major release mechanism, and this can occur in sediments that are not completely anoxic (McKean 1986; Moore and Reddy 1994; Smith *et al.* 2011). Elevated lake water nitrate concentrations help maintain a high redox potential at the sediment interface, keeping the iron bound P fixed (Jensen and Andersen 1992). Release of P from the lake sediment after the depletion of nitrate in the summer has been previously described in Lough Neagh (Gibson *et al.* 2001), however key changes have been observed since then in this study, specifically earlier annual depletion of NO_x from the water column and subsequent release of P from the sediment (Fig. 6). We also noted an increase in the average mass of P released (1984–2014) (Fig. 5). Our results show that these changes were established by 2000. Factors such as the observed decreasing nitrate and increasing water temperature have been shown to enhance SRP release from eutrophic lake sediment (Jensen and Andersen 1992). The observed increase in water column temperature in Lough Neagh will likely further impact release. This means that the effectiveness of P control measures in the catchment, with the aim of reducing lake P will be limited. Internal loading inputs are considerable in large lakes such as Lough Neagh where intensive use of catchment land have resulted in a large mass

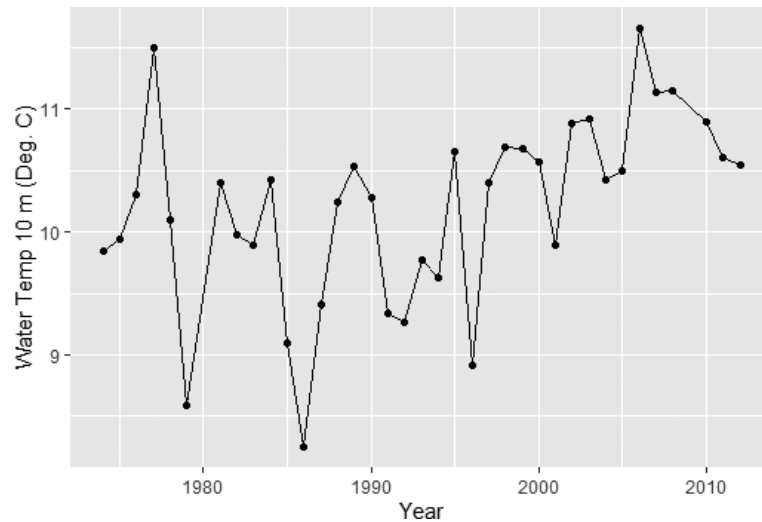


Fig. 8—Mean annual water temperature at 10m (C), 1974–2012.

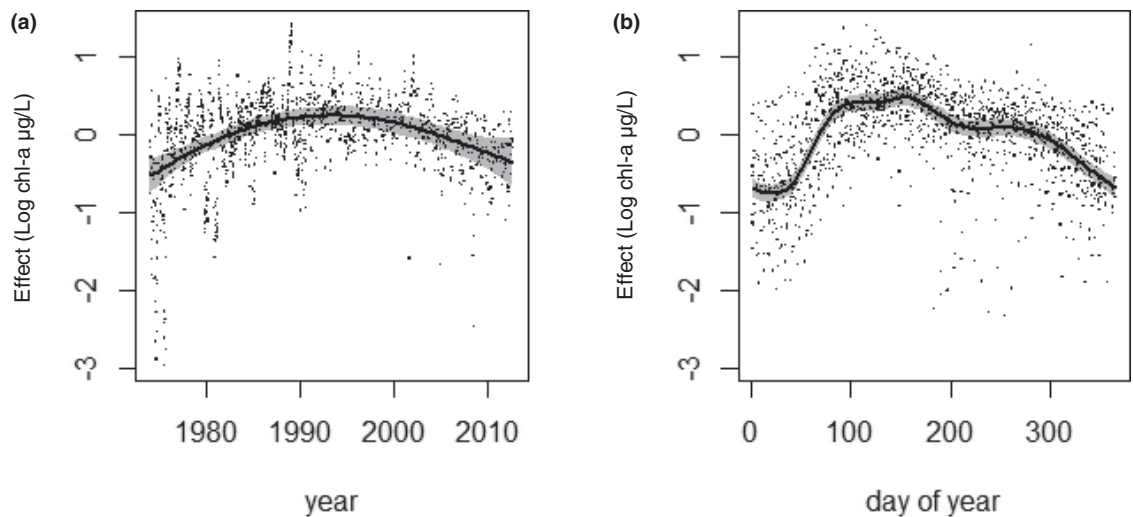


Fig. 9—Long-term trend (a) and average seasonal pattern (b) for log chlorophyll-*a* concentration (Log chl-*a*, µg/L) from Jan 1974 to Dec 2012 as responses in additive nonparametric models. The shaded region identifies ± 2 SE from the estimate and points are the partial residuals for each covariate respectively (indicating e.g., the remaining long-term trend and variation after fitting the smooth seasonal pattern and vice versa).

of P, deposited over many years, in the lake sediment (Søndergaard *et al.* 1999).

WATER CHEMISTRY STOICHIOMETRY, WATER COLUMN TEMPERATURE AND CHL-A

Nitrogen and P are two of the most important nutrients in primary production and lake water stoichiometry determines nutrient limitation (Redfield 1958). Knowing the ratios of the most available form of these nutrients in hypereutrophic lakes can help with predicting biological quality.

Dissolved inorganic N: total P (DIN:TP) ratios are commonly used as indicators of N and P limitation in phytoplankton (Bergström 2010; Ptacnik *et al.* 2010). Log transformed ratios are more appropriate to use in ecological stoichiometry as transformation helps to avoid errors such as bias towards P limitation (Isles 2020). Mass DIN:TP ratios less than 2.6 can indicate N limitation (Kolzau *et al.* 2014); the natural log of 2.6 is 0.96. In Lough Neagh log mean annual ratios have been below 0.96 more frequently since 2001, than any time period previously recorded (Fig. 7) indicating

Table 2.—Hierarchical partitioning of the variables in chlorophyll-*a* (chl-*a*) regression models, showing the independent and joint contributions of each variable to the explained variance in the log of annual mean chl-*a*. DIN – log of annual mean dissolved inorganic N, TP – log of annual mean total P, Water temp – annual mean water temperature at 10m. Randomisation test $P < 0.05$ *.

Time period	Parameter	Independent contribution to r^2	Joint contribution to r^2	Independent / r^2 (%)
1974 – 2012	DIN (log)	0.012	0.010	9.064
	Water temp*	0.102	-0.010	77.100
	TP (log)	0.018	-0.017	13.836
	Total	0.133	-0.017	100.000
1994 – 2012	DIN (log)*	0.204	0.147	46.322
	Water temp*	0.205	0.102	46.678
	TP (log)	0.031	0.001	7.000
	Total	0.440	0.249	100.000

increased N limitation in recent years. The observed decrease in log (DIN:TP) was influenced by the decrease in lake water N and increase in lake P brought about by P remobilisation from the sediments. Low concentrations of bioavailable N can limit phytoplankton over the long term, even with high concentrations of available P (Shatwell and Köhler 2019). The role of N can become more important in controlling primary production after nutrient reduction in some shallow lakes (Moss *et al.* 2005). Ratios of chl-*a*:TP have been used to provide information on potential P limitation (Spears *et al.* 2013) and in Lough Neagh the generally declining values of log ((chl-*a*:TP) + 1) since 1993 to the end of the data series indicate that factors other than P are limiting primary production by phytoplankton.

Of the variables tested in HP, temperature was identified as the only significant predictor of chl-*a* over the entire time series (Table 2). This negative association may be linked to zooplankton predation of phytoplankton over the entire time series. Fitzsimons and Andrews (1993) showed that zooplankton grazing was an important factor in regulating phytoplankton abundance and that temperature likely played an important role in zooplankton population density in the late 1970s. However after 1993 a large change occurred in the relationship between chl-*a*, nutrients and water temperature; DIN became a significant predictor of chl-*a*, further supporting the case of increased N limitation after the mid-1990s. Hierarchical partitioning also identified water temperature as having a large independent effect on chl-*a*, after the peak value in 1993, similar in magnitude to the effect of DIN, this relatively large influence of temperature may be linked to temperature driven phenological changes in zooplankton, which have been shown to directly impact phytoplankton biomass through increased predation (Gerten and Adrian 2000). Air temperature was found to be the most important variable explaining zooplankton

biomass and abundance by (Cremona *et al.* 2020) with increasing temperatures increasing metazooplankton abundance and biomass. Our results show that primary production was not limited by SRP, TP was not identified as a major predictor in the HP analyses and the GAMS show that chl-*a* decreased since the mid-1990s when we observed increasing SRP concentrations (Fig. 3c, Fig. 9a).

Zebra mussels do not appear to have had a large impact on the lake since they appeared in 2005. They are established in the Lough in low numbers and did not appear until 2005, well after the observed downward trend in phytoplankton biomass. They have not expanded well in the Lough due to lack of suitable habitat, poor water exchange between the originally infested bay and the rest of the lough, suboptimal water quality in the infested bay and the Allee effect (McLean 2012).

Our work demonstrates that a broader view would be helpful for river basin management plans, taking into account both external and internal sources and their characteristics in order to set achievable P targets. Lake water N concentrations were well correlated with N catchment inputs, however, despite no significant increase in catchment inputs of P we observed increasing P concentrations in the lake. The lack of correlation between inputs of P and lake water P means that measures in the catchment may have less impact than expected at lowering lake P. The increase in lake water concentrations of P was likely brought about by the more prolonged and larger release of sediment P in the latter years of the data series. Subsequent changes in lake water stoichiometric composition influenced primary production. Our analyses of chl-*a* show that although temperature has always been an important influence, changes have occurred and DIN has become an important predictor of chl-*a* concentrations after the mid-1990s, this, together with the log (DIN:TP) and log (chl-*a*:TP) ratios support the case of increased N limitation of phytoplankton production in the lake.

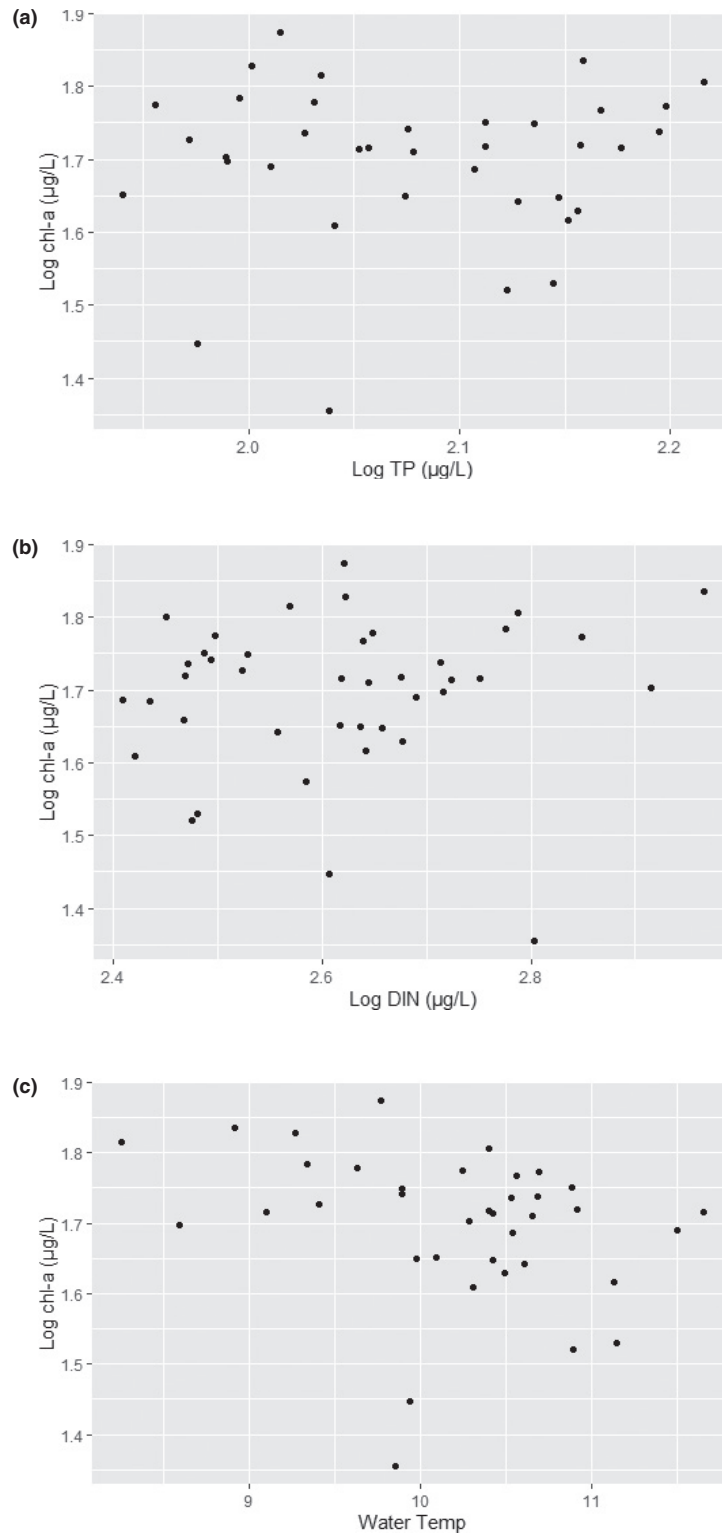
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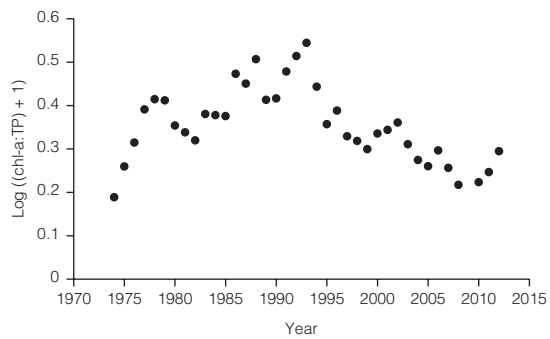
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Appendix I—Log of annual mean chlorophyll-*a* (Log chl-*a*, $\mu\text{g/L}$), 1974 to 2012, plotted against: log of annual mean total P (Log TP, $\mu\text{g/L}$), (a), log of annual mean dissolved inorganic N (Log DIN, $\mu\text{g/L}$), n=(b) and water temperature (C) at 10m depth (Water Temp) (c), n=37.



Appendix II—Log of annual mean ((chl- a :TP)+1), 1974 to 2012, n = 38.