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Water quality effects following establishment of the invasive *Dreissena polymorpha* (Pallas) in a shallow eutrophic lake: implications for pollution mitigation measures

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Abstract

This study investigates whether ecosystem alteration occurred in a shallow, lowland lake following establishment of the alien zebra mussel, *Dreissena polymorpha* (Pallas). Measurements of total phosphorus (TP) loads, lake TP concentrations, phytoplankton (chlorophyll *a*) and transparency levels for the period 1990-2008 were examined to determine the water quality effects of *D. polymorpha*. The period of time also included the implementation of catchment measures aimed at reducing phosphorus (P) loading to the lake. A range of loading-response models was also tested to explore changes in the net sedimentation rate for P. Results show that while high TP loads from the catchment were reduced, TP concentrations in the lake remained high after *D. polymorpha* invasion. Decoupling of the previous chlorophyll *a* –TP relationship also occurred. Results from a TP loading-response model that closely simulated observed concentrations in the lake prior to establishment of *D. polymorpha* indicated that measured TP post establishment was statistically higher than predicted for the same conditions but without the presence of *D. polymorpha*. Data presented in the paper highlight the need to consider the potential impacts of invasive species in evaluations of the effectiveness of measures aimed at mitigating aquatic pollution.

Key words: biotic invasion, mass-balance, nutrient, ecosystem alteration, budget, Water Framework Directive

Introduction

Understanding the influence that individual and interacting multiple stressors have on ecosystem functioning is fundamental in managing the impacts of humans on the environment (Liu et al., 2013). Cultural eutrophication, caused by over enrichment of water bodies by nutrients, notably phosphorus (P) but also nitrogen (N), linked to anthropogenic activity, is a major cause of poor water quality worldwide (Schindler et al., 2008; Johnson et al., 2010; Liu et al., 2012; Carey et al., 2013; Carvalho et al., 2013). Lakes, and to a lesser extent rivers, are especially sensitive to nutrient enrichment. The number of lakes exhibiting eutrophication effects has risen substantially over the last decade (Smith & Schindler, 2009; Seitzinger et al., 2010), and is likely to increase further in coming years owing to climate change and an extensification and intensification of human activity (Moss, 2011; Crossman et al., 2013). More severe and extensive eutrophication problems in the future are particularly likely without the effective implementation of measures aimed at reducing inputs of P and N to water bodies and a reversal of their aquatic impacts (Liu et al., 2012; McGonigle et al., 2012).

The risks of nutrient enrichment and other forms of degradation of water bodies have provoked a response by policy-makers and legislators at national and international levels (Maguire et al., 2009). For example, national water pollution legislation of member states of the European Union (EU) has been subsumed within the Water Framework Directive (WFD). The WFD seeks to achieve good chemical and ecological status in water bodies, defined as close to predisturbance (or reference) conditions (European Commission, 2000), by the end of the current implementation period (end of 2015). One way of achieving this objective is through P remediation measures aimed at reducing the availability of nutrients to aquatic organisms (European Commission, 2000; Allan, 2012). However, eutrophication remains a major problem in Europe (Schulte et al., 2010; Jordan et al., 2012), even where measures have been implemented (Doody et al., 2012). Consequently, the water quality objectives of the WFD are only likely to be achieved in about 50% of waterbodies to which they apply by the end of 2015 (European Environment Agency, 2010).

Effective mitigation schemes for P require a sound scientific basis to their design (Doody et al., 2012; Kroger et al., 2013), and the active engagement of all interested parties in implementation (Wright & Fritsch, 2011). Part of the scientific basis is a clear understanding of the reasons why particular water bodies do not meet or are at risk of failing to meet good status (Barnes et al., 2009). In some cases, the reasons will be obvious, such as failure to decrease external P loads from the catchment. In others, the confounding factors may be less evident and, for example, reflect non-linearity in cause-effect relationships (Rockström, 2009), such as those caused by hysteresis (Spears et al., 2012; Jarvie et al., 2013a,b), or the activities of invasive species (Strayer, 2010; Davis, 2013).

The remobilisation of P in sediments can potentially confound recovery (Søndergaard et al., 2003; Withers & Jarvie, 2008). Retention processes in lakes temporarily remove and/or transform P from the water column for storage in the surface sediment. Phosphorus, bound in sediment to redox-sensitive iron compounds or fixed in labile forms (Selig et al., 2002), may be remobilised at a later stage allowing the opportunity for biotic assimilation, with net sedimentation rate indicating whether sediment acts as an overall source or sink for P in a lake. Sediment-bound P is released under low redox conditions in a form (PO_4) that is readily available for biological uptake (Moore et al., 1998), and can occur while other parts of a lakebed are experiencing net sedimentation. The release of P from sediments may continue for decades (May et al., 2011) and can continue to support primary productivity after external loadings of P have been reduced (Welch & Jacoby, 2001).

The invasive zebra mussel (*Dreissena polymorpha,* Pallas) has become established in many lakes across western Europe and North America, profoundly impacting both the ecological (Ozersky et al., 2012) and economic (Connelly et al., 2007) status of invaded water bodies by affecting the cycling of P. Whether *D. polymorpha* accentuates or attenuates P concentrations in the water column appears to depend, primarily, on initial conditions in the water body (Fahnenstiel et al., 1995; Maguire et al., 2003; Qualls et al., 2007; Higgins et al., 2008; Cha et al., 2013). Where P is readily available, P is filtered from the water column by *D. polymorpha* and subsequently amalgamated in biodeposits rejected or excreted in pseudofeces or faeces, respectively. The organically and nutrient enriched biodeposits settle on the sediment, stimulating microbial activity at the sediment-water interface, reducing dissolved oxygen levels and effectively fuelling the release of PO_4 from the sediment (Newell, 2004; Bykova et al., 2006). However, increased releases of dissolved P into the water column may not necessarily be marked by greater phytoplankton abundance because *D. polymorpha* may also exact strong grazing pressure resulting in reduced phytoplankton biomass and increased transparency of the water column (MacIsaac, 1996; Brines Miller & Watzin, 2007; Higgins & Zanden, 2010). These activities may ultimately result in increased transfer of energy and biomass from the pelagic to the benthos in well mixed or shallow systems (Ward & Ricciardi, 2007; Gergs et al., 2009; Higgins & Zanden, 2010). The establishment of *D. polymorpha* in eutrophic lakes can, therefore, lead to apparent improvements in lake water quality (Zhu et al., 2006; Fishman et al., 2009; Higgins & Zanden, 2010). Where measures aimed at mitigating eutrophication have been introduced, the establishment of *D. polymorpha* could conceivably have a positive influence on their apparent effectiveness, although few studies have demonstrated this in practice (Nicholls & Hopkins, 1993; Dzialowski & Jessie, 2009; Chapra & Dolan, 2012). Several studies have reviewed the cultivation of *D. polymorpha* to improve the quality of water in impaired systems (Elliott et al., 2008; McLaughlan & Aldridge, 2013).

D. polymorpha populations have become established in many lakes in Ireland since the 1990s (Minchin & Moriarty, 1998), including Lough Sheelin (Fig. 1), a shallow, alkaline (>100mgl^{-1} $CaCO_3$) lowland lake and the focus of the current study. Falling lake water quality, largely as a result of the intensification of agriculture in the catchment, has been a problem since at least the 1970s (Champ, 1993; EPA, 1994; Keys & Gibbons, 2006). More recently, multiple point sources such as wastewater treatment plants (WWTPs), industry and septic tanks have significantly contributed to the large exports of P entering the lake (Kerins et al., 2007; Greene et al., 2011). Attempts to improve water quality have largely targeted P. A brief period of recovery in water quality was documented during an early attempt to reduce external loadings of P (1990-1992) that restricted the spreading of livestock manure during winter months (Champ, 1993). From 1998 - 2008, however, several phases of catchment-scale P mitigation were implemented (Greene et al., 2011). Completion of an upgrade to and expansion of treatment facilities at a WWTP and the issue of an integrated pollution prevention control license to a meat processing plant, both located in the catchment, occurred in 1999 (Kerins et al., 2007). An interim P removal regime was introduced at a second WWTP in the catchment in 2003. Catchment-wide, septic tank bye-laws were officially introduced in 2004, following minor improvements initiated in 2000. Agricultural bye-laws to regulate the storage and management of livestock wastes were in place by 2003 (Keys & Gibbons, 2006), and have since been superseded by national regulations under the Nitrates Directive. Licensing of trade discharges to water, septic tank compliance, pollutant investigations and farm surveys were also introduced in 2003. Past declines in water quality, together with the continued presence of diffuse and point sources of P in the catchment, have resulted in Lough Sheelin being identified as a lake at high risk of not meeting the water quality objectives of the WFD (Anon, 2005). The lake is particularly suitable for *D. polymorpha* (Maguire & Sykes, 2004). Establishment of a community of *D. polymorpha* occurred in 2003, by 2006 the population had the ability to filter the total volume of the lake within 13 days (Kerins et al., 2007; Millane et al., 2008) and were incorporated into the diet of high level consumers (Millane et al., 2012).

In the current study available observation data from the long-term monitoring of Lough Sheelin, together with TP loading data from the catchment, were used to examine components of the lake ecosystem prior to and following the introduction of *D. polymorpha*. A series of analyses were aimed at determining whether any discernible shifts occurred in external TP loads, TP concentrations, phytoplankton (Chl a) and transparency levels in the lake and whether these alterations were accompanied by a modified chlorophyll *a* - TP relationship. Given that *D. polymorpha* has potential to alter P sedimentation rates in lakes, a variety of loading-response models that estimate in-lake P concentrations using a range of approximations for the retention of P in sediment were tested for suitability in order to explore timeseries changes in the net sedimentation rate for P.

Materials and Methods

Study site description

Lough Sheelin (53°08' N, 7°33' W, 65.4 m above mean sea level) (Fig. 1) has a mean depth of 4.5 m, a surface area of 18.1 km^2 and a volume of 81.5 x 10^6 m^3. The lake receives water from 10 rivers draining a catchment of 256 km^2 and has a hydrological residence time of six months. Located in the drumlin region of the central-northern part of Ireland, agriculture, and in particular grassland supporting c.150 cattle km^{-2}, is the main land use in the catchment. The northern, upland part of the catchment is predominately underlain by impermeable strata, while the southern extent, where the lake is situated, is characterised by more permeable carboniferous limestone. Glacial drift deposits blanket the bedrock, providing the catchment with its distinctive drumlin landscape and, because of their low permeability, protecting aquifers from surface contamination.

Assembly of research database and exploratory analysis

Data for Lough Sheelin referred to in the current study were extracted from a database developed by Inland Fisheries Ireland and comprise monthly measurements of concentrations of TP (μg l^{-1}), chlorophyll *a* (μg l^{-1}) and water transparency (secchi depth, m) for the period 1990 to 2008. The database also included measurements of TP concentrations collected three times per week at monitoring stations located on seven of the ten rivers draining into the lake (draining the subcatchments of Bellsgrove, Carrick, Crover, Halfcarton, Mountnugent, Ross and Schoolhouse). Water flow rates (m^3 sec^{-1}) for the seven rivers were collected as daily mean flows. The concentration of TP (μg l^{-1}) in unfiltered water samples was determined using methods based on Murphy & Riley (1962); digestion followed Eisenreich et al. (1975). The concentration of chlorophyll *a* (μg l^{-1}) was determined by hot methanol extraction and measured spectrophotometrically (Talling, 1974). Concentrations of

TP from the three unmonitored rivers draining into Lough Sheelin were estimated based on levels in rivers draining neighbouring subcatchments with similar soil and landuse (Greene et al., 2011). Information regarding the invasion and establishment of *D. polymorpha* in the lake was obtained from Kerins et al. (2007) and Millane et al. (2008, 2012).

Total phosphorus, chlorophyll *a*, flow and secchi depth data were divided according to hydrological year (1st October in year n to 30th September in year n+1) in preparation for analysis. Exploratory analysis revealed that several data points for 2000 and 2001 were missing. As a consequence, the years 2000 and 2001 were excluded from the study. Linear regression analysis and ANOVA (analysis of variance) were used in determining the degree of significance ($p < 0.05$) of changes in average annual flow-weighted load of TP entering the lake from external sources (i.e. external loadings of TP, or TP_{in}) and average annual concentration of TP in the lake (TP_{lake}) from 1990-1997 and 1998-2008. These two periods bracket the commencement of sustained efforts to mitigate transfers of P to water bodies in the catchment. In addition a grouping of monitoring data from before the onset of *D. polymorpha* invasion (1990-1999) was used as a control reference against which to compare P and chlorophyll *a* dynamics post *D. polymorpha* establishment (2004-2008). Both earlier year groupings included attempts of P remediation in the catchment (1990-1992) that involved limiting the spreading of livestock manure over the winter.

Reconstruction of the TP budget of Lough Sheelin

A TP budget for Lough Sheelin was reconstructed using TP data for the hydrological years 1990-2008 (excluding 2000 and 2001). The annual net retention of TP ($t\ yr^{-1}$) in the lake (TP_{net}) for each year of data was calculated according to the mass-balance eqn 1 (Jorgensen & Vollenweider, 1989) in which all TP inputs are balanced by equal outputs and biotic assimilation, unless storage in the lake sediments takes place.:

$$TP_{net} = (TP_{load} - TP_{out}) - (TP_{end} - TP_{start}) \qquad (1)$$

where:

TP_{net} is the net TP uptake (+) or release (-) ($t\ yr^{-1}$)

TP_{load} is the external TP load ($t\ yr^{-1}$)

TP_{out} is the TP load at lake outflow ($t\ yr^{-1}$)

TP_{end} is the lake water TP mass at end of year ($t\ yr^{-1}$)

TP_{start} is the lake water TP mass at beginning of year (t yr^{-1})

The total annual TP load (t yr^{-1}) entering the lake from the entire catchment was calculated as the cumulative total TP_{load} (t yr^{-1}), comprising loads from: (i) measurements at monitoring stations on seven tributaries; (ii) estimates for the remaining three unmonitored tributaries; and (iii) estimates of direct runoff. Annual TP_{load} (t yr^{-1}) entering the lake from each of the seven monitored tributaries was calculated using the load estimation method in eqn 2:

$$TP_{load}\,(t\ yr^{-1}) = \left[\sum_{1}^{n}(\mathrm{TP}) * (\mathrm{dmf}) / \sum_{1}^{\mathrm{n}}(\mathrm{dmf})\right] * \left(\sum_{1}^{365.25}\mathrm{dmf}\right) \qquad (2)$$

where:

TP is the measured TP concentration ($\mu g\ l^{-1}$) from each monitored river

dmf is the measured daily mean flow ($m^3\ sec^{-1}$) from each monitored river

n is the number of days in the hydrological year that TP samples were taken

Annual TP_{load} (t yr^{-1}) entering the lake from the stretch of river downstream from a nutrient monitoring point was determined using a conversion factor for TP load per unit area derived from the corresponding monitored data. For the three unmonitored tributaries, annual TP_{load} (t yr^{-1}) was extrapolated from estimates of TP load derived from neighbouring, monitored rivers with similar soil types and land uses. Annual TP_{load} (t yr^{-1}) from direct runoff was also estimated using a conversion factor derived from a combination of measurements relating to the seven monitored subcatchments. The TP load leaving the lake at the Inny outlet (TP_{out}) was calculated using the TP flow-weighted method described in eqn 2. The change in storage of TP_{lake} (t yr^{-1}), was calculated from the difference between the TP concentrations measured in the lake at the beginning and end of each hydrological year.

Calibration of TP loading - response models

The monitoring of variations in lake water quality is frequently constrained by the availability of resources (Haith et al., 2012). A mass balance modelling approach that estimates in-lake P concentrations as a function of P loading from the catchment and other lake parameters provides a viable, cost-effective alternative to in-situ measurements (Johnes et al., 2007; Özkundakci et al., 2010; Chapra & Dolan, 2012). Vollenweider first presented a mass balance model for P in lakes, based on the assumption that lake TP concentration can be estimated if the rates of TP inputs and the TP sedimentation rate are known (Vollenweider, 1975). According to Brett & Benjamin (2008), the most commonly used TP loading-response models today can be broadly categorised into three groups, based on whether TP concentrations are estimated using: (i) a TP sedimentation coefficient, σ, (e.g. OECD (1982) general and shallow model); (ii) a TP retention coefficient, R (Dillon & Rigler, 1974); or (iii) a combination of both (Prairie, 1989) (Table 1).

The annual flow-weighted TP load, TP_{in} ($\mu g\ l^{-1}$), exported to the lake from the catchment was calculated as the cumulative total TP_{load} ($t\ yr^{-1}$) (calculated from eqn 2 divided by the cumulative annual hydrological flow, Q ($m^3\ yr^{-1}$)). Values for R, the TP retention coefficient in the Dillon & Rigler (1974) model, were calculated using a series of eight R estimation models (Table 2). Annual lake flushing rates ($\rho\ yr^{-1}$), a metric of the frequency of lake water renewal, were determined by dividing the cumulative hydrological load (Q $m^3\ yr^{-1}$) by the estimate of lake volume (81.5 x $10^6\ m^3$). Lake water residence time (τ_w) was calculated as the inverse of the flushing rate, ρ (Brett & Benjamin, 2008). Lake areal hydraulic loading rate (q_s $m\ yr^{-1}$), the inflow water volume applied over the surface area of Lough Sheelin, was determined from cumulative hydrological load (Q) divided by lake surface area (A_L). Lake TP concentration, TP_{lake}, was calculated from an annual average of measured TP concentrations in the lake. The final TP parameter, L (areal TP loading rate $g\ m^2\ yr^{-1}$), was calculated using the formula:

$$L = (Q * TP_{in})/A_L \qquad (3)$$

where

L is the areal TP loading rate ($g\ m^2\ yr^{-1}$)

Q is the cumulative annual hydrological flow ($m^3\ yr^{-1}$)

TP_{in} is the annual flow-weighted TP load ($\mu g\ l^{-1}$)

A_L is the lake surface area (km^2)

The accuracy of predictions from the loading-response models was evaluated by root mean square error (RMSE) analysis, comparing predicted values with measured values, described in eqn 4.

$$RMSE = \sqrt{\sum_{i=1}^{n} (TP_{\text{lake}} - TP_{\text{pred}})^2 / n} \quad (4)$$

where:

TP_{lake} is the measured TP concentration in lake averaged over a year (µg l^{-1})

TP_{pred} is the predicted lake TP concentration for the same year (µg l^{-1})

n is the number of years of data in the study

The TP loading-response model that showed the highest prediction accuracy in the grouped years prior to *D. polymorpha* invasion (1990-1999) was used to represent the long-term TP loading-response relationship in the lake system before establishment of *D. polymorpha*, and for predicting expected TP_{lake} concentrations for the period post-establishment of the invasive in 2004. Using ANOVA, if the measured TP_{lake} was significantly ($p < 0.05$) greater than predicted concentrations then increased internal loading of TP was assumed to have occurred. Conversely, if the opposite occurred and there was a decline in estimated TP concentrations, then the difference was attributed to the additional amount of TP retained in the sediments (Qualls et al., 2007).

Evaluation of chlorophyll *a* - TP relationships

The strength of the logarithmic linear relationship between chlorophyll *a* and TP concentrations (Dillon & Rigler, 1974) in Lough Sheelin, based on averaged annual data, was determined for the periods both pre and post establishment of *D. polymorpha*.

The general regression equation used was:

$$\log \text{Chl a} = \text{a} + \text{b} * \log \text{TP} \quad (5)$$

where:

log Chl a is the log of chlorophyll *a* (µg l^{-1})

log TP is the log of TP (µg l^{-1})

a and b are estimated model coefficients for the regression intercept and slope, respectively.

A test of parallelism was applied to the regression models to assess the significance ($p < 0.05$) of differences in slope and intercept for the periods pre and post establishment of *D. polymorpha* (Kleinbaum et al., 1998). The statistical analysis was implemented in PRISM 5 Graphpad software (Motulsky, 2007).

Results

Temporal trends in lake parameters

According to linear regression and ANOVA results, external loadings of TP to the lake were significantly lower ($p < 0.05$) in the period following implementation of P mitigation measures (1998-2008 mean = TP 66 μg l^{-1}) when compared with the period 1990-1997 (mean = TP 95 μg l^{-1}). However, despite this difference in external loadings pre- and post-implementation of measures aimed at reducing P loading from the catchment, an increase (ca. 20%) in mean, in-lake TP concentrations occurred between the periods 1990-1997 (overall mean = 25 μg l^{-1}) and 1998-2008 (overall mean = 31 μg l^{-1}) (Fig 2a). According to the Carlson (1977) trophic status index (TSI) for TP, the lake was classed eutrophic in 1993, and was still in the same status by 2008. The TSI for chlorophyll *a* showed a similar eutrophic trajectory until 2005, when movement to a meso-eutrophic status occurred. Concentrations of TP_{lake} and chlorophyll *a* were generally related during the period 1990 to 1997 and up to 2003 (Fig 2b), with rises and falls in both parameters accompanied by concurrent changes in transparency. However, the chlorophyll *a* - TP relationship appears to change abruptly from 2004, with variations in one variable no longer matched by similar sign changes in the other.

TP budget

Estimated annual net loads of TP peaked in 1994 (26 t yr^{-1}) and were positive in all years except 2004, when negative TP_{net} indicates release of TP to the water column (1.76 t yr^{-1}).

TP loading-response models

Fig. 3 shows regression lines for the relationship between measured TP_{lake} concentrations for 1990-2008 and the TP_{lake} values predicted from the three TP loading-response models that use τ_w (lake water residence time) as a scaling factor for the TP sedimentation rate, σ: Foy (1992)(Foy, 1992), OCED 1982 - general and shallow lakes models, and the Prairie (1989) model that uses a combination of estimations of σ and R. The RMSE values of predictions for the periods 1990-2008, 1990-1999 (pre establishment of *D. polymorpha*) and 2004-2008 (post establishment of *D. polymorpha*) are shown in Table 3. Output from the OECD (1982) shallow model had the lowest overall RMSE (24.5 μg l^{-1}) of the models using σ, i.e. the smallest deviation from observed concentrations of TP in the lake, and was therefore the most efficient model to use σ of those tested in this study. The model proposed by Foy (1992) produced similar predicted values to the OCED (1982) shallow model. Notably, predictions from the OCED (1982) general and Prairie (1989) models deviated most from measured values, these two models over-predicted TP. Regression lines between measured and predicted TP_{lake} concentrations ,based on models that use the retention coefficient (R) to describe the sedimentation of TP, for the period 1990-2008 are shown in Fig. 4. Eight different estimations of R were used: the Ostrofsky (1978b) model showed the lowest overall RMSE (11.9 $\mu g\ l^{-1}$), whereas predictions by the Larsen & Mercier (1976) model had the highest overall RMSE (25.2 $\mu g\ l^{-1}$). Based on the RMSE values generated, the model that best described the lake system in 1990 – 1999 was Ostrofsky (1978b). Consequently this model was used to predict baseline data against which changes in TP_{lake} following establishment of *D. polymorpha* could be compared (where the baseline data represent estimated in-lake concentrations of TP in the absence of *D. polymorpha* for the period 2004). The results of ANOVA showed that measured TP_{lake} values following establishment of *D. polymorpha* were significantly ($p < 0 .05$) higher than those predicted using the Ostrofsky (1978b) model.

Chlorophyll *a* and TP relationships

Linear regression relationships for log chlorophyll *a*-log TP for the time prior to and post establishment of *D. polymorpha* are shown in Fig. 5. The relationship was highly significant ($p < 0.05$) before invasion, but not significant for the period 2004-2008. The changes in slopes and intercepts between the two periods were statistically significant ($p < 0.05$).

Discussion

Data for 1990 to 2008 demonstrate that, overall, external loadings of TP to Lough Sheelin significantly declined ($p < 0.05$) following a peak in the early 1990s and remained relatively low until 2008 (Fig 2a). However, some inter-annual variability was apparent, presumably because of differences over time in rainfall, the number and state of point and diffuse sources and the occasional occurrences of pollutant spills (Greene et al., 2011). Despite this significant, overall fall in TP loads from the catchment, TP concentrations in the lake did not show a similar decrease, remaining at early 1990s and higher levels though to 2008. Some variability is evident, however. For example, from 1990 to 1998, a decrease in TP concentrations in the lake associated with decreased external loadings from the catchment is similar to the loading-response relationship reported elsewhere (Jeppesen et al., 2005; Köhler et al., 2005; Søndergaard et al., 2005). The relationship changed markedly in the early 2000s, however. Despite an overall significant reduction of TP loading in the period during which measures aimed at reducing P loads from the catchment had been implemented, TP concentrations in the lake did not decrease in a similar manner observed previously in 1990 to 1992. This suggests that the change in the TP loading-response relationship after 2004 could have been a result of some other factor, and one that was not influential in the early 1990s.

The lake TP budget results indicate that overall the lake sediment functioned as a net sink for TP, with an estimated 73% of TP retained in sediments since 1990. The amount of TP incorporated into sediment also appeared to be greater than TP lost to the outflow, despite the estimated hydrological residence time being just six months. Compared with deep lakes, where a redox dependent accumulation of P occurs in the anoxic hypolimion during stratification, shallow lakes are usually well mixed and oxidised throughout the water column, encouraging sediment retention (Padisák & Reynolds, 2003; Søndergaard et al., 2003). Lough Sheelin is a polymictic lake; the lake is too shallow for thermal stratification to develop (O'Sullivan & Reynolds, 2005). Brett & Benjamin (2008) suggest that lakes with short hydraulic retention times may receive relatively greater contributions of allochthonous, mineral-bound particulate phosphorus (PP) than lakes with longer hydraulic retention times. Lakes with shorter hydraulic retention times may then display greater sedimentation of TP.

Loading-response models for TP in lakes have been used in many studies to predict the value of one model parameter as a function of another, or to examine the aquatic impacts of proposed TP loading reductions (Søndergaard et al., 1999; Coveney et al., 2005; Girvan & Foy, 2006). The OECD (1982) shallow and Ostrofsky (1978b) models were both associated with relatively low RMSE values in the current research. The Ostrofsky (1978b) model gave a better fit than other models using TP retention coefficients fitted to the loading-response model of Dillon & Rigler (1974) because it predicted the highest rate of TP retention for a given hydraulic load (average R = 0.67). Statistically lower predicted TP compared with measured concentrations after 2004 provide further evidence for increased release of TP from sediments to the water column, thereby leading to elevated TP concentrations in the lake that could not have been accounted for by the model parameters. This explains the tendency of the Kirchner & Dillon (1975) and Nürnberg (1984) models to most accuracy predict TP_{lake} concentrations in the years following establishment of *D. polymorpha*; both of these models describe lower coefficients for R compared with the Ostrofsky (1978b) model. By comparison, the OECD (1982) and Foy (1992) models consistently overestimated TP_{lake}, possibly owing to the bias in the model structure on the loss of TP mass in the lake through the outflow rather than sedimentation.

Evidence from loading-response models suggest that the net P sedimentation rate was reduced following the establishment of *D. polymorpha*, increasing the rate of internal loading. Internal loading of P from the sediment is frequently reported as a main cause hindering the recovery of shallow lakes following reductions in the external load of P entering the lake (Jeppesen et al., 2005; Phillips et al., 2005; Søndergaard et al., 2007), with estimations of TP released from sediments shown to correlate positively with annual average concentrations of TP (May et al., 2011; Spears et al., 2012). Similarly, *D. polymorpha* can alter P sedimentation rates (Bykova et al., 2006; Turner, 2010). Greater deposition of organic matter enhances microbial activity at the sediment-water interface, intensifies nutrient remineralisation, decreases oxygen penetration into the sediments, thus creating conditions to support denitrification and release iron bound P in dissolved form (Jensen & Andersen, 1992; Turner, 2010).

Understanding the extent to which biotic invasion and native species loss alter whole-ecosystem properties remains a fundamental ecological challenge (Sutherland et al., 2013). In the context of *D. polymorpha*, large populations are known to modify food web structure and alter ecosystem function (Miehls et al., 2009; Ozersky et al., 2012; Wikstrom & Hillebrand, 2012) by selective consumption of phytoplankton through filtration (Bastviken et al., 1998; Hwang et al., 2011). This filtration behaviour results in large reductions in the biomass of edible phytoplankton (MacIsaac, 1996), increases in water clarity (Zhu et al., 2006), and alterations in the habitat complexity of benthic communities (Burlakova et al., 2012), providing additional habitat for zebra mussels to colonise (Higgins & Zanden, 2010). Accordingly, the observations made in this study show that not only did P dynamics alter after the invasion of *D. polymorpha* but the ratio of chlorophyll *a* to TP concentrations changed, marked by a substantial decline in chlorophyll *a* concentrations with no commensurate fall in TP level evident. Transparency also increased in the lake from 2004. *D. polymorpha* biomass in Lough Sheelin is recorded as almost doubling (3.73×10^6 to 6.36×10^6) from 2005 to 2006 (Millane et al., 2008). Zebra mussel population levels usually reach a stable state 7 to 12 years after initial colonisation (Burlakova et al., 2006), i.e. roughly between 2011 and 2014 in the case of Lough Sheelin. The observational and modelled data reported here suggest that *D. polymorpha* may have had a tangible effect on water quality several years before population size was expected to have reached carrying capacity. Furthermore, although initial trophic status determines *D. polymorpha* behaviour on invasion, post-establishment the magnitude and extent of influences of resident *D. polymorpha* on water quality are primarily related to the abundance and biomass of the population (Vanderploeg et al., 2002; Burlakova et al., 2006), as these parameters correspond directly to filter-feeding. While the available data do not provide unequivocal evidence of the processes that caused the observed changes, these observed effects would appear to be deserving of consideration in any assessment of the effectiveness of measures aimed at improving water quality in Lough Sheelin, and in other lakes that have been invaded by zebra mussels.

Phytoplankton biomass, one of the four biological quality elements for lake ecological classification cited in the WFD, is typically quantified according to levels of chlorophyll *a* concentration (Kasprzak et al., 2008; Carvalho et al., 2013). Phytoplankton can be sensitive to additions of P in conditions where growth rate is P limited (Vollenweider, 1976). The most commonly adopted response to eutrophication is the implementation of measures aimed at reducing P loads from external and internal sources in order to reduce phytoplankton biomass (Phillips et al., 2008; Søndergaard et al., 2011; Lyche-Solheim et al., 2013; Spears et al., 2013). Reduced concentrations of P are generally assumed to lead, directly, to improved ecological status of water bodies. The use of chlorophyll *a* – TP models as a basis for managing lake water quality is therefore not straightforward; the results from this study suggest that revised assessment methods are required for lakes that have undergone ecosystem changes as a result of invasive species. Considering the expense involved in implementing P regulation, an unequivocal demonstration of the continued effectiveness of P reductions at controlling and reducing eutrophication is necessary, including in lakes invaded by *D. polymorpha*. As *D. polymorpha* has been reported to alter P dynamics substantially in invaded lakes, usually masking a nutrient problem, a sudden decline in *D. polymorpha* biomass could result in the recurrence of substantial eutrophication in the absence of P management. An incomplete understanding of the range and magnitude of aquatic effects of an alien species, therefore, may mean that even well-conceived and expensive measures to mitigate P and other stresses are put at risk or even reversed (Strayer, 2010). These other stresses may in some cases include climate change, as the close connections between climate change and invasive species are increasingly acknowledged (Pyke et al., 2008)

Conclusions

Lowland shallow lakes are highly susceptible to the adverse effects of nutrient enrichment because they accumulate a variety of loads transferred from anthropogenic activities in the catchment, but may also be subjected to internal loading. All sources of nutrients, especially P, require attention under the WFD. Limited resources often mean that in reality evaluations of the effectiveness of measures aimed at reducing catchment losses of P to water bodies are not detailed enough. Identifying and targeting the critical sources of P that are impairing lake ecosystems assume great importance. Comprehensive estimates of the P balance of a lake facilitate understanding of trajectories of P in lakes, providing an insight into potential responses to P remediation and offering evidence of discernible shifts in the system. Although an observational, rather than experimental, study, data provided here showed that conditions in Lough Sheelin changed significantly following *D. polymorpha* establishment. Any effects of invasive species were outside the control of management measures aimed at relaxing eutrophication pressures. The impacts of invasive species on ecological functioning, especially in the context of other changing pressures such as climate change, thus needs to be considered in any evaluation of the effectiveness of measures aimed at mitigating aquatic pollution.

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Tables

Table 1. Formulae and references for the five total phosphorus (TP) loading-response models used in the study

Model type[a]	Reference	Model formula[a]
σ	Foy (1992)	$TP_{lake} = \frac{1.234(TP_{in})^{0.991}}{(1+\sqrt{\tau_w})^{1.130}}$
σ	OECD (1982) general	$TP_{lake} = 1.55\left(\frac{TP_{in}}{1+\sqrt{\tau_w}}\right)^{0.82}$
σ	OECD (1982) shallow	$TP_{lake} = 1.02\left(\frac{TP_{in}}{1+\sqrt{\tau_w}}\right)^{0.88}$
σ plus R	Prairie (1989)	$TP_{lake} = \frac{L(1-0.30\tau_w{}^{40}L^{1.1}z^{0.25})}{q_s}$
R	Dillon & Rigler (1974)	$TP_{lake} = \frac{L(1-R)}{q_s}$

[a]σ = TP sedimentation rate (the fraction of TP in the lake water column that enters the sediment)

R = TP retention coefficient (the fraction of TP loading to the lake that gets retained in the sediment)

TP_{lake} = Annual TP concentration in lake (μg l^{-1})

TP_{in} = Annual flow-weighted load of TP entering the lake from external sources (μg l^{-1})

τ_w = Water residence time of lake (yr^{-1})

L = Areal TP loading rate (g m^2 yr^{-1})

z = Mean lake depth (m)

q_s = Areal hydraulic loading rate (m yr^{-1})

Table 2. Models used to generate the retention (R) formula for the Dillon and Rigler (1974) TP loading-response model in Table 1

Reference	**Model formula**[a]
Vollenweider (1975)	$R = \frac{10}{10+q_s}$
Dillon & Kirchner (1975)	$R = \frac{13.2}{13.2+q_s}$
Chapra (1975)	$R = \frac{16}{16+q_s}$
Ostrofsky (1978a)	$R = \frac{24}{30+q_s}$
Nürnberg (1984)	$R = \frac{15}{18+q_s}$
Larsen & Mercier (1976)	$R = \frac{1}{1+\rho^{0.5}}$
Kirchner & Dillon (1975)	$R = 0.43\ \exp(-0.27\ q_S) + 0.57\ \exp(-0.0095\ q_S)$
Ostrofsky (1978b)	$R = 0.2\exp(-0.043 q_S) + 0.57\exp(-0.0095 q_S)$

[a]R = TP retention coefficient (the fraction of TP loading to the lake that gets retained in the sediment)

qs = Areal hydraulic loading rate (m yr^{-1})

ρ = Lake flushing rate (yr^{-1})

Table 3. Root mean square error **(**RMSE) values for TP_{lake} from TP loading-response models for the hydrological years 1990-2008

Model	**RMSE (TP µg l^{-1})**		
	Full time period (1990-2008)	**Pre *D. polymorpha* (1990-1999)**	**Post *D. polymorpha* (2004-2008)**
σ			
OECD (1982) shallow	24.5	26.6	13.8
Foy (1992)	25.1	27	14.6
OECD (1982) general	49.1	52.4	33.4
R			
Ostrofsky (1978b)	11.9	10.7	12.8
Chapra (1975)	13.2	12.8	13.8
Ostrofsky (1978a)	11.9	10.7	12.8
Dillon & Kirchner (1975)	14.6	16.1	12.7
Kirchner & Dillon (1975)	15.5	18.4	10.7
Nürnberg (1984)	16.1	19.1	11.1
Vollenweider (1975)	18	21.7	11.9
Larsen & Mercier (1976)	25.2	31.6	11.9
σ plus R			
Prairie (1989)	49.1	52.8	31.7

Figure captions

Fig. 1 Location of Lough Sheelin and its catchment in the upper reaches of the Shannon International River Basin District, Ireland. The boundaries of the seven monitored tributaries are delineated and named

Fig. 2 Time series plot showing **(a)** annual flow-weighted TP loading to Lough Sheelin (TP_{in}) and average annual TP concentration in the lake (TP_{lake}) for the hydrological years 1990 -2008; **(b)** Time series plot of annual average TP concentration (TP_{lake}), chlorophyll *a* concentration and secchi depth in Lough Sheelin for the hydrological years 1990-2008. NB data for the years 2000 and 2001 were incomplete and therefore not included in the analysis

Fig. 3 Plots showing the regression relationships between measured $\log_{10}TP_{lake}$ and predicted $\log_{10}TP_{lake}$ concentrations ($\mu g\ l^{-1}$) in Lough Sheelin for the time before (1990-1999) and following (2004-2008) *Dreissena polymorpha* invasion. Predicted TP_{lake} concentrations were obtained from the three TP loading models that use τ_w as a scaling factor for σ (OECD 1982 general, OECD 1982 shallow and Foy 1992) and from the Prairie 1989 model, which uses a combination of estimates of σ and R

Fig. 4 Plots showing the regression relationships between measured $\log_{10}TP_{lake}$ and predicted $\log_{10}TP_{lake}$ concentrations ($\mu g\ l^{-1}$) in Lough Sheelin for the time before (1990-1999) and following (2004-2008) *Dreissena polymorpha* invasion. Predictions were calculated using the Dillon and Rigler (1974) TP loading-response model. The model used eight different estimations of R (Table 2)

Fig. 5 Relationship between $\log_{10}$ chlorophyll *a* and $\log_{10}$ TP concentrations in Lough Sheelin for the hydrological years 1999 to 2008, separated into the periods prior to (1990-1999) and following (2004-2008) the establishment in the lake of zebra mussels (*Dreissena polymorpha* (Pallas, 1771))

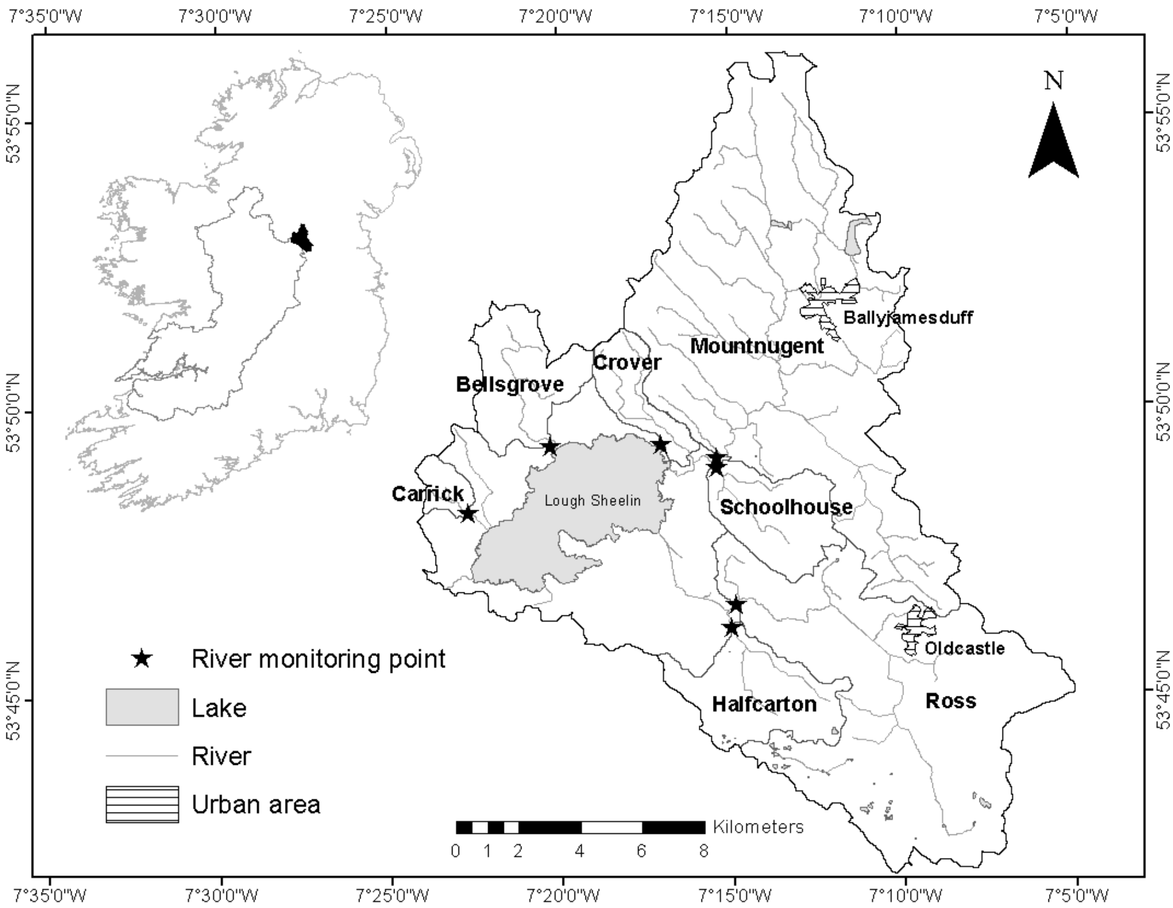
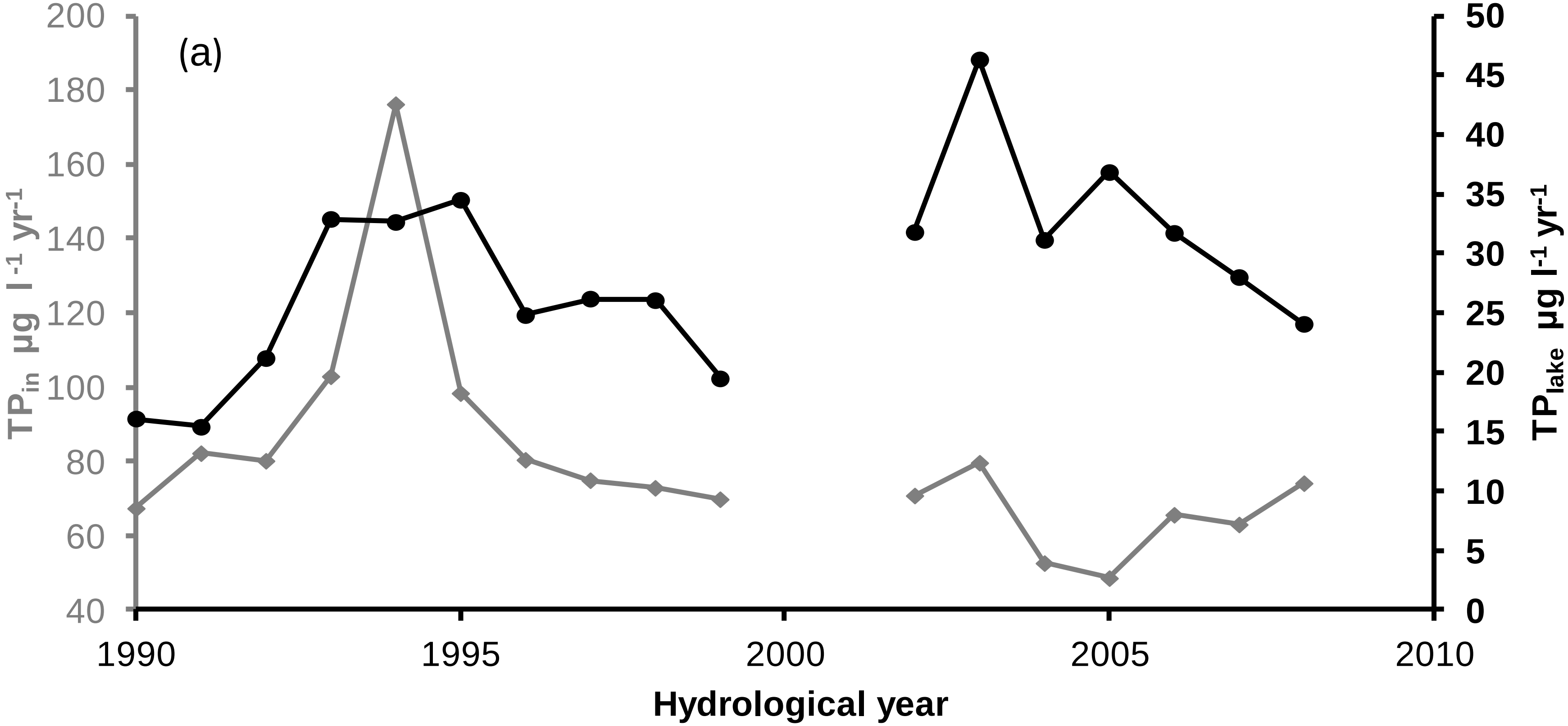
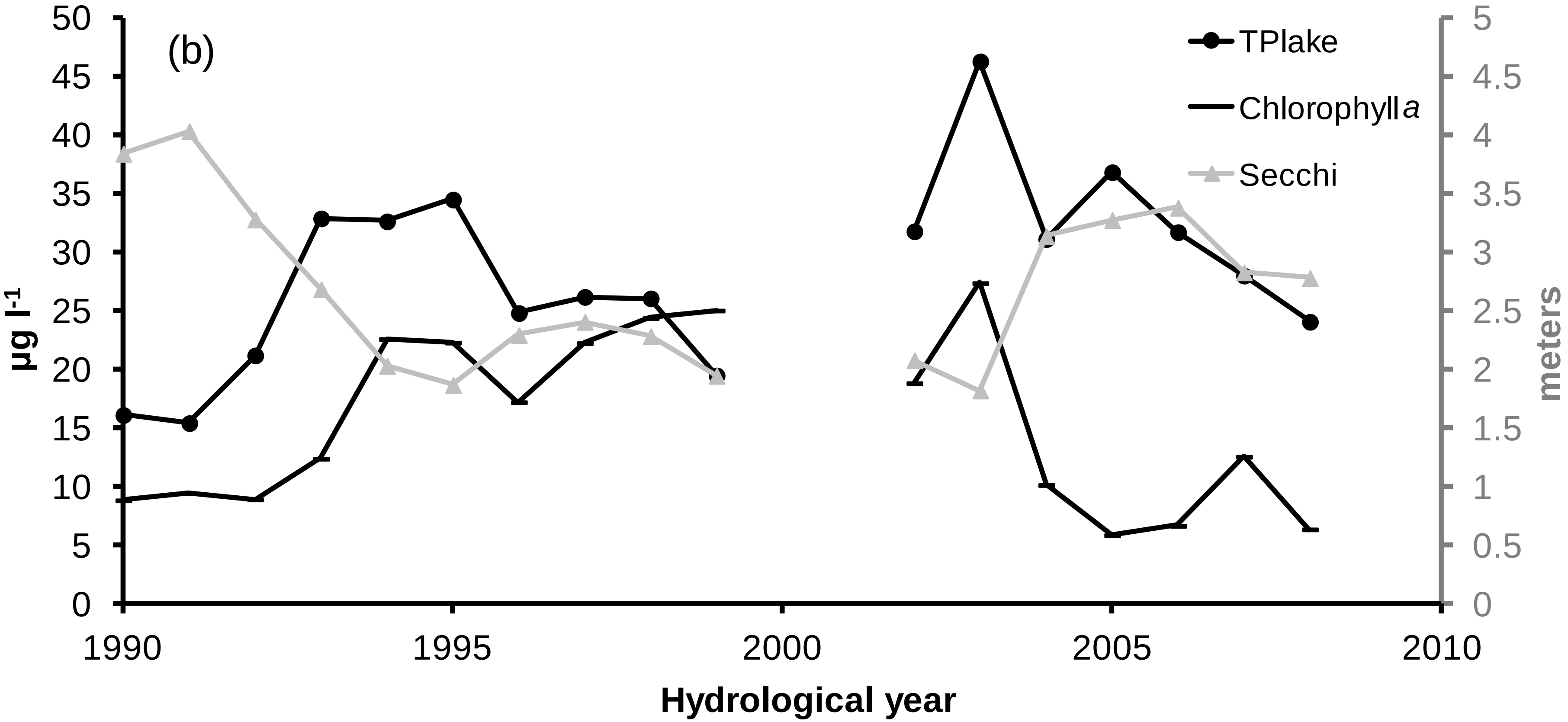

7°35'0"W
7°30'0"W
7°25'0"W
7°20'0"W
7°15'0"W
7°10'0"W
7°5'0"W
53°55'0"N
53°50'0"N
53°45'0"N
N
Ballyjamesduff
Mountnugent
Crover
Bellsgrove
Carrick
Lough Sheelin
Schoolhouse
Oldcastle
Halfcarton
Ross
River monitoring point
Lake
River
Urban area
Kilometers
0 1 2 4 6 8

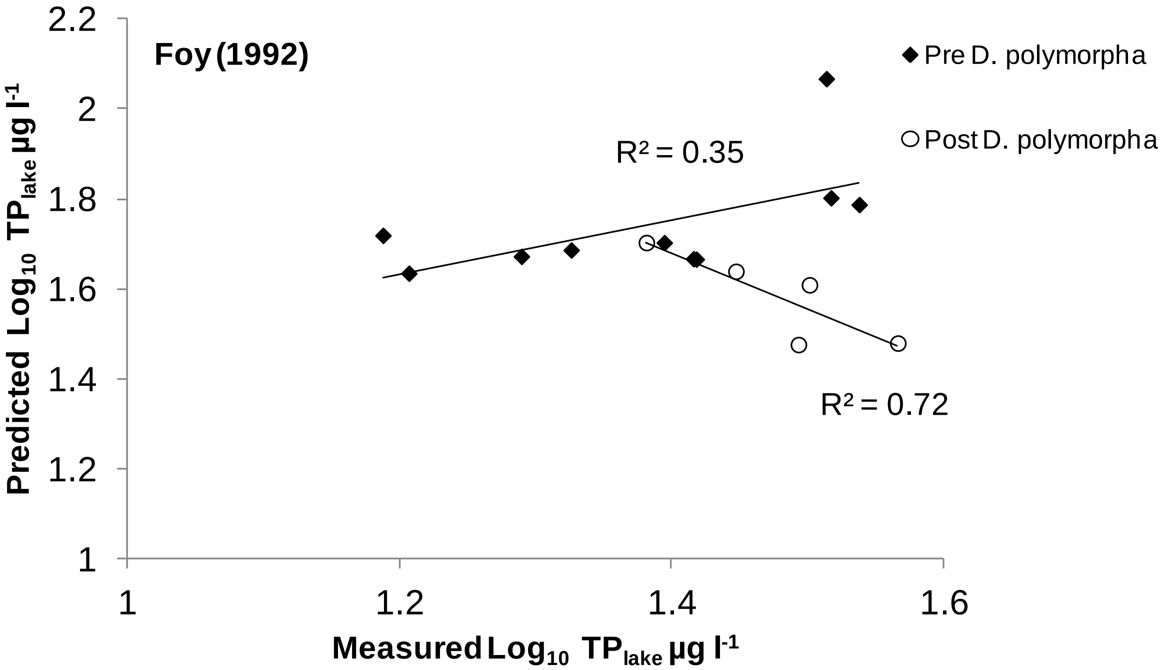
Fig. 1


(a)
200
180
160
140
120
100
80
60
40
TP_{in} µg l^{-1} yr^{-1}
50
45
40
35
30
25
20
15
10
5
0
TP_{lake} µg l^{-1} yr^{-1}
1990
1995
2000
2005
2010
Hydrological year

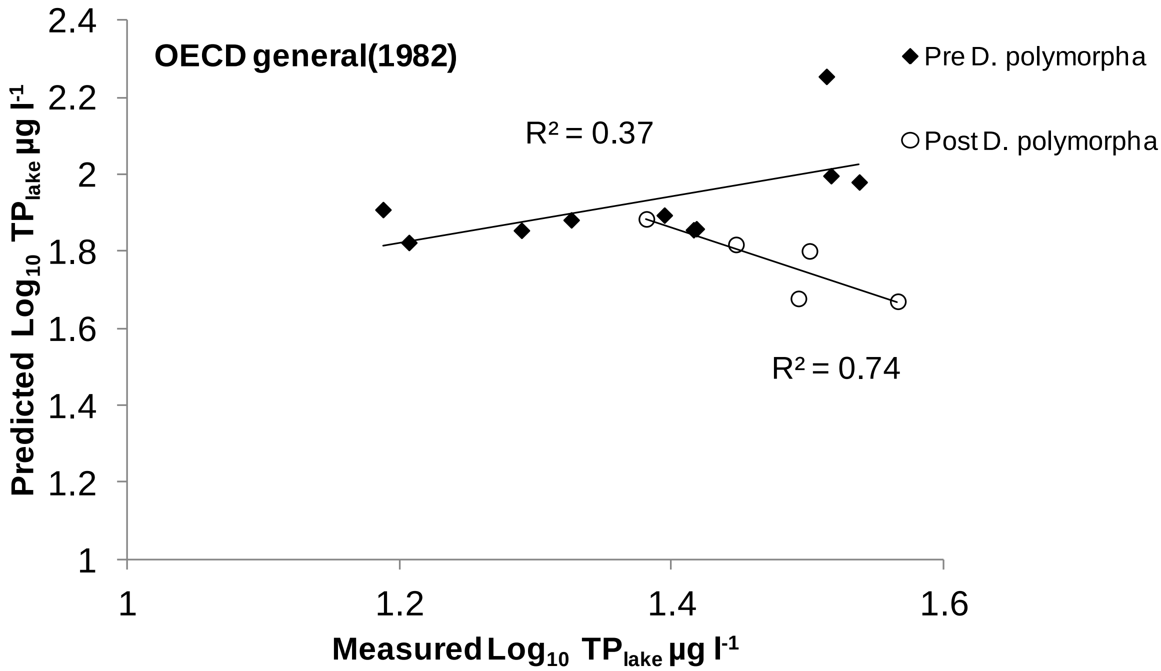


(b)
TPlake
Chlorophyll a
Secchi
µg l-1
meters
Hydrological year
50
45
40
35
30
25
20
15
10
5
0
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
1990
1995
2000
2005
2010

Fig. 2



Foy (1992)
Pre D. polymorpha
Post D. polymorpha
R² = 0.35
R² = 0.72
Predicted Log10 TPlake µg l-1
Measured Log10 TPlake µg l-1
2.2
2
1.8
1.6
1.4
1.2
1
1.2
1.4
1.6



OECD general(1982)
Pre D. polymorpha
Post D. polymorpha
R² = 0.37
R² = 0.74
Predicted Log10 TPlake µg l-1
Measured Log10 TPlake µg l-1
2.4
2.2
2
1.8
1.6
1.4
1.2
1
1.2
1.4
1.6

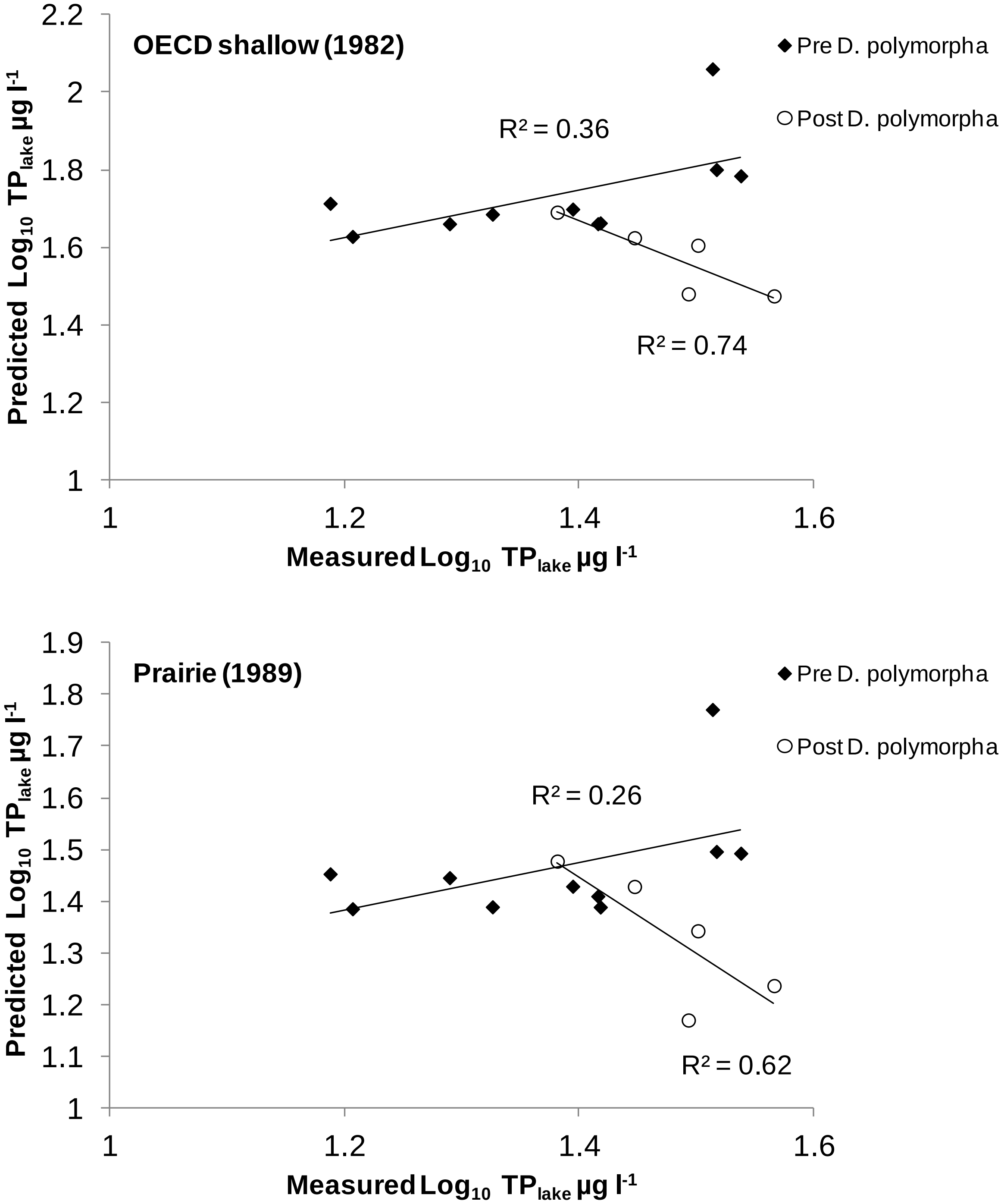
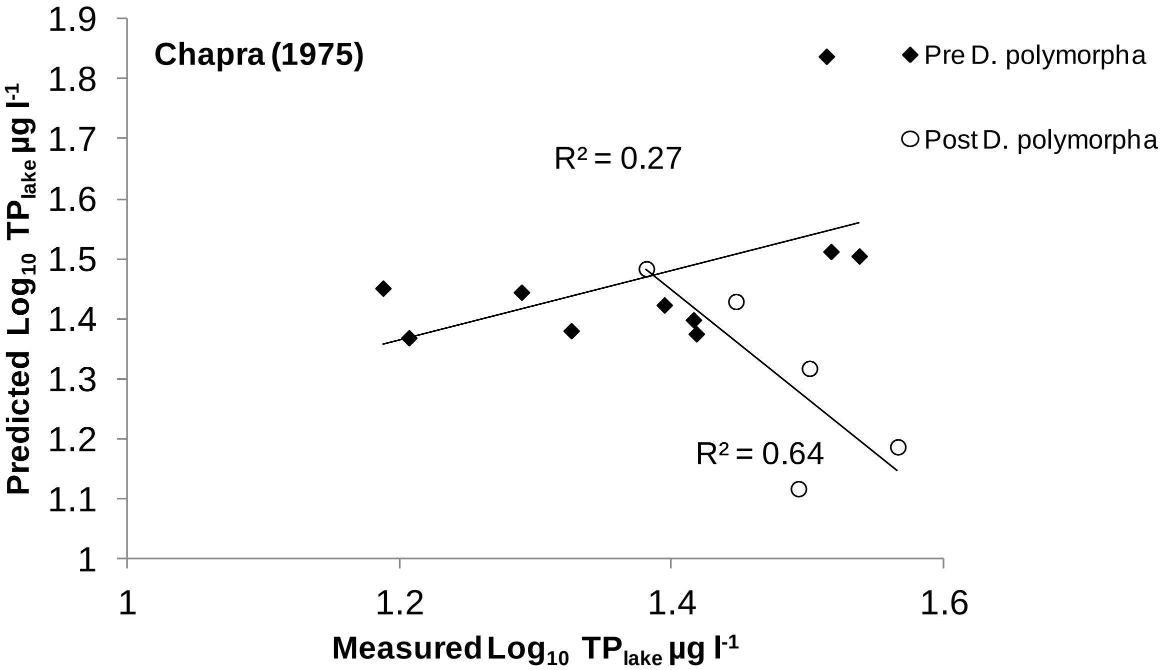
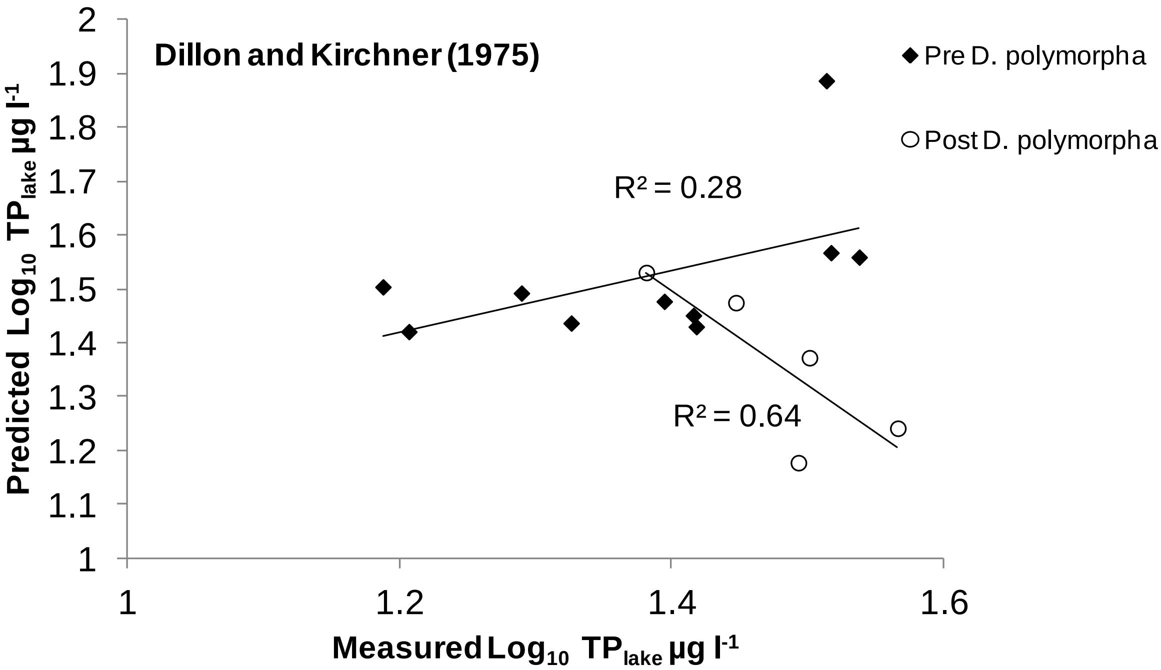

OECD shallow (1982)
Pre D. polymorpha
Post D. polymorpha
R² = 0.36
R² = 0.74
Predicted Log10 TPlake µg l-1
Measured Log10 TPlake µg l-1
Prairie (1989)
Pre D. polymorpha
Post D. polymorpha
R² = 0.26
R² = 0.62
Predicted Log10 TPlake µg l-1
Measured Log10 TPlake µg l-1

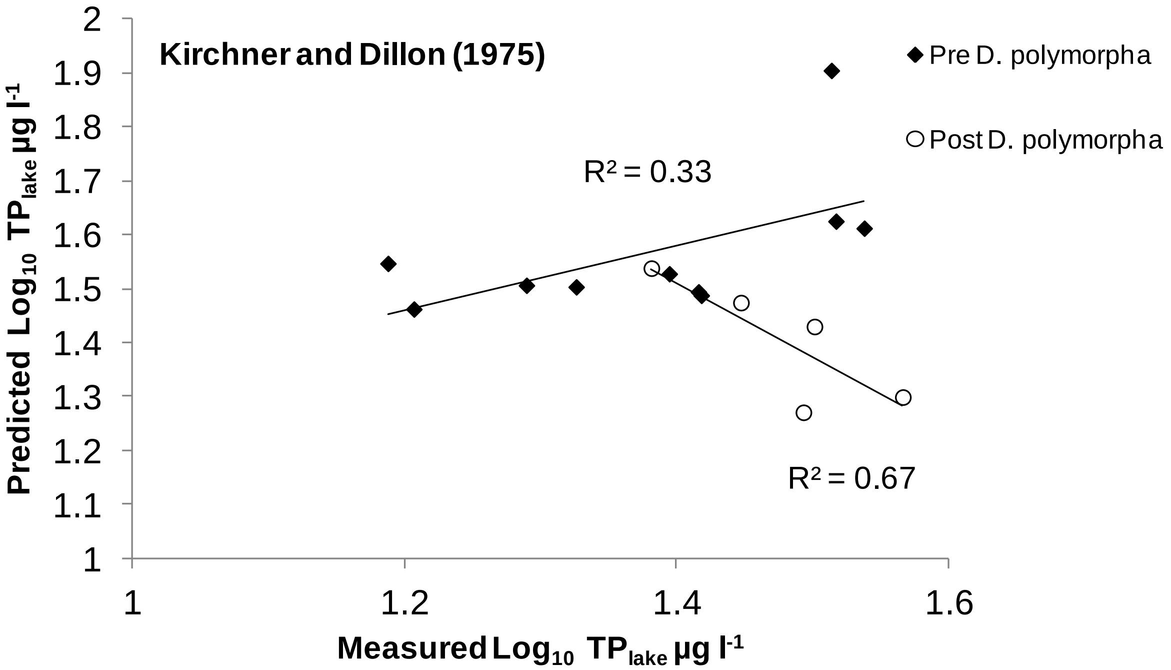
Fig. 3

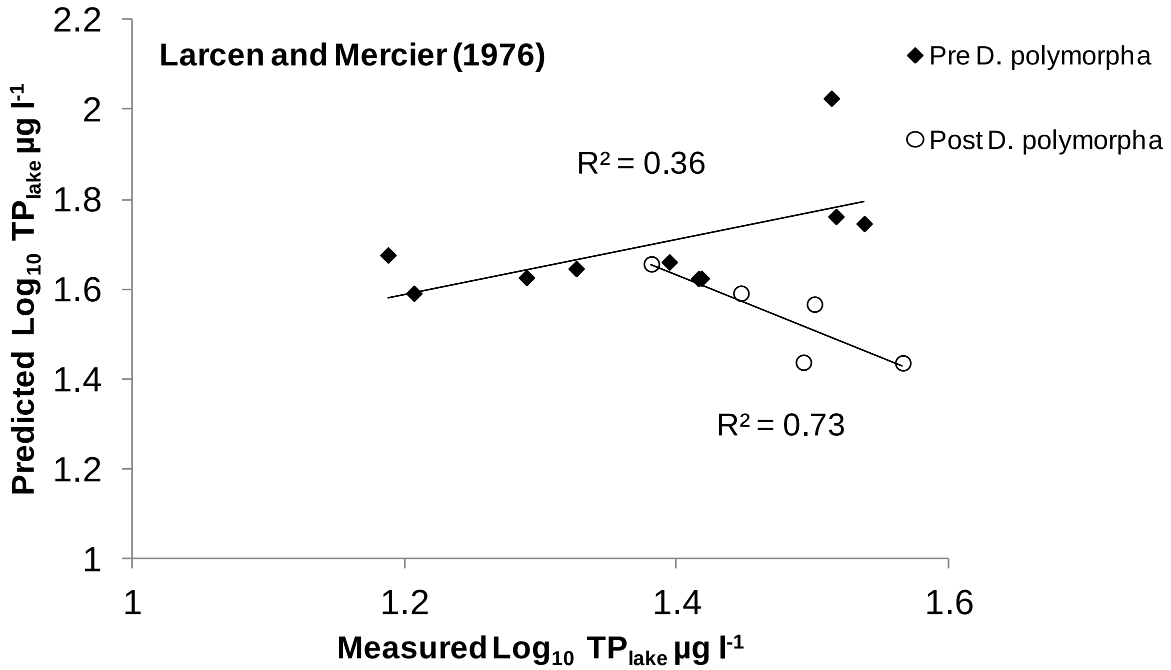


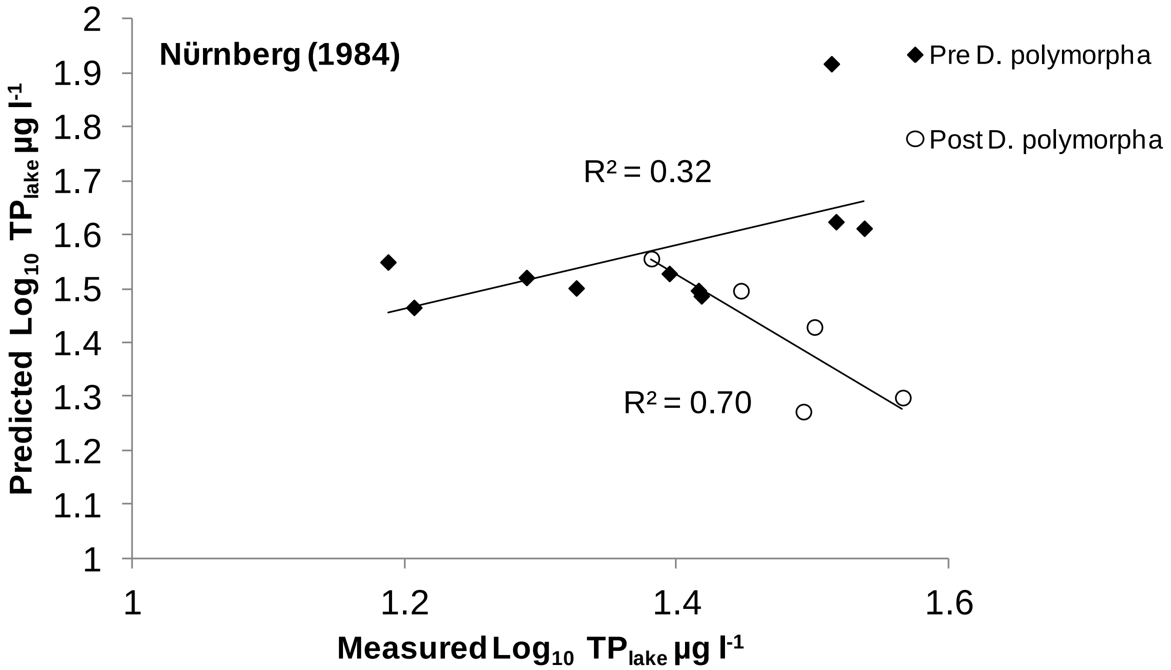
Chapra (1975)
Pre D. polymorpha
Post D. polymorpha
R² = 0.27
R² = 0.64
Predicted Log10 TPlake µg l-1
Measured Log10 TPlake µg l-1
1
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
1
1.2
1.4
1.6



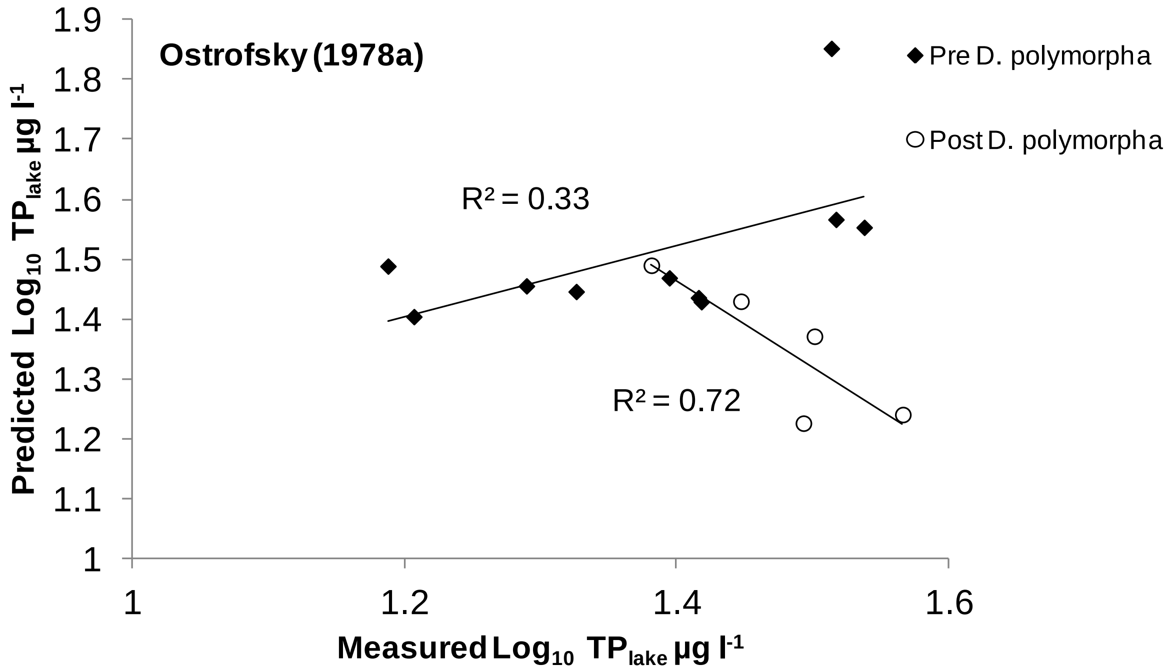
Dillon and Kirchner (1975)
Pre D. polymorpha
Post D. polymorpha
R² = 0.28
R² = 0.64
Predicted Log10 TPlake µg l-1
Measured Log10 TPlake µg l-1
1
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2
1
1.2
1.4
1.6


Kirchner and Dillon (1975)
Pre D. polymorpha
Post D. polymorpha
$R^2 = 0.33$
$R^2 = 0.67$
Predicted Log_{10} TP_{lake} µg l^{-1}
Measured Log_{10} TP_{lake} µg l^{-1}
2
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
1.2
1.4
1.6

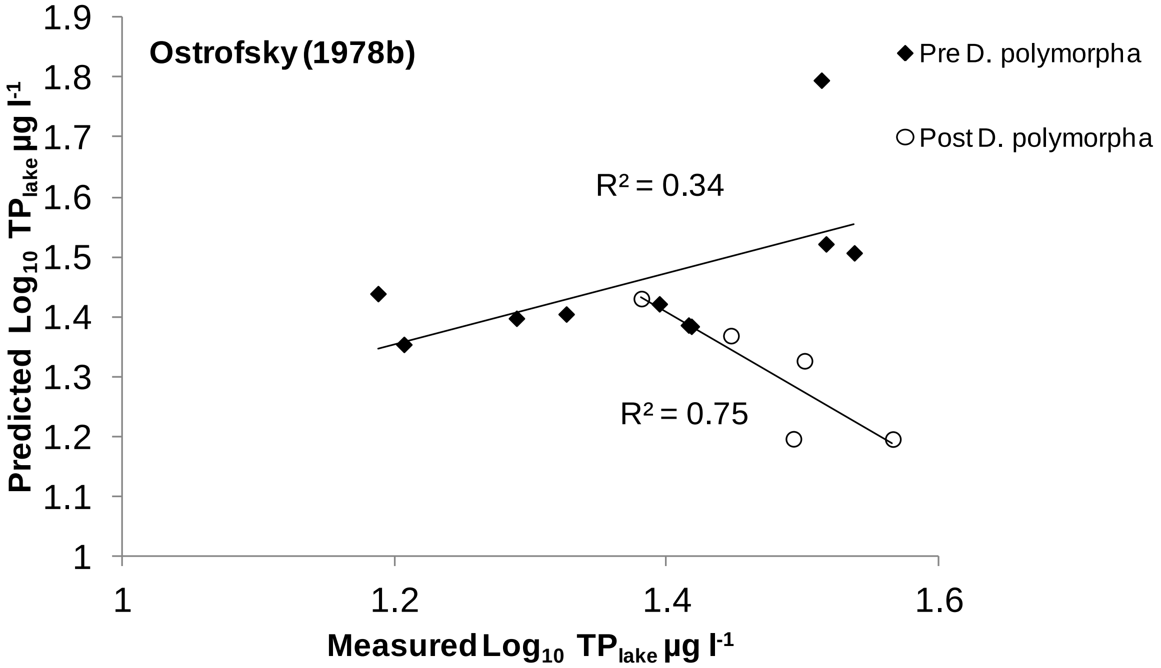

Larcen and Mercier (1976)
Pre D. polymorpha
Post D. polymorpha
$R^2 = 0.36$
$R^2 = 0.73$
Predicted Log_{10} TP_{lake} µg l^{-1}
Measured Log_{10} TP_{lake} µg l^{-1}
2.2
2
1.8
1.6
1.4
1.2
1
1.2
1.4
1.6



Nürnberg (1984)
Pre D. polymorpha
Post D. polymorpha
R² = 0.32
R² = 0.70
Predicted Log10 TPlake µg l-1
Measured Log10 TPlake µg l-1
2
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
1
1.2
1.4
1.6



Ostrofsky (1978a)
Pre D. polymorpha
Post D. polymorpha
R² = 0.33
R² = 0.72
Predicted Log10 TPlake µg l-1
Measured Log10 TPlake µg l-1
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
1
1.2
1.4
1.6


Ostrofsky (1978b)
Pre D. polymorpha
Post D. polymorpha
R² = 0.34
R² = 0.75
Predicted Log10 TPlake µg l-1
Measured Log10 TPlake µg l-1
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
1
1.2
1.4
1.6

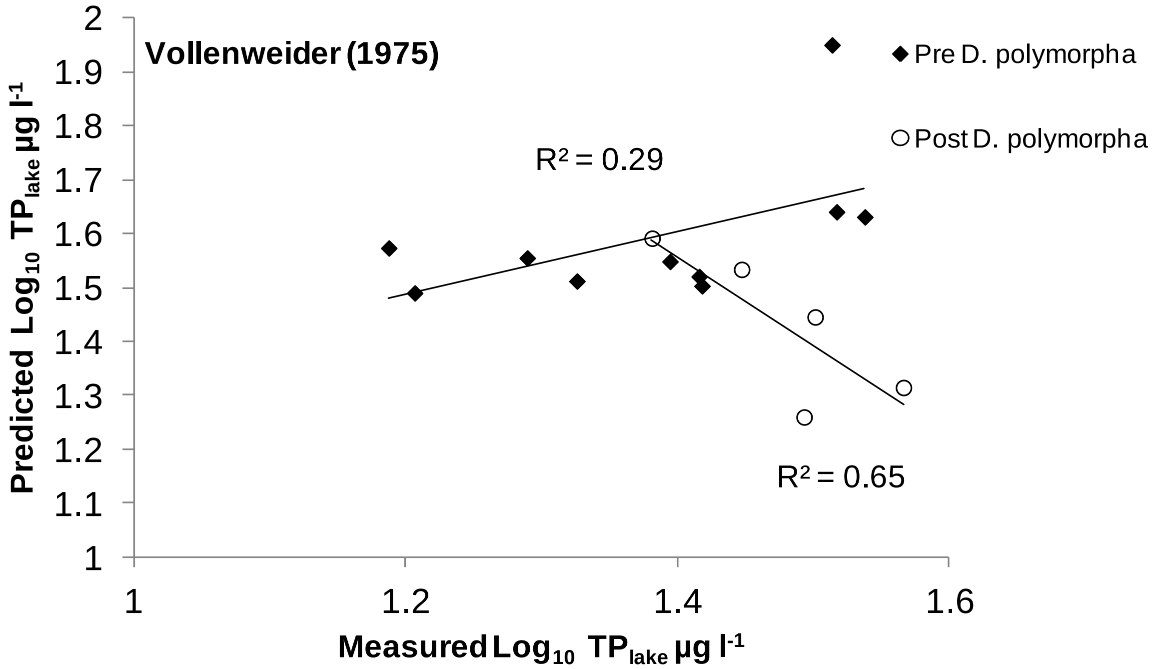

Vollenweider (1975)
Pre D. polymorpha
Post D. polymorpha
R² = 0.29
R² = 0.65
Predicted Log10 TPlake µg l-1
Measured Log10 TPlake µg l-1
2
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
1
1.2
1.4
1.6

Fig. 4

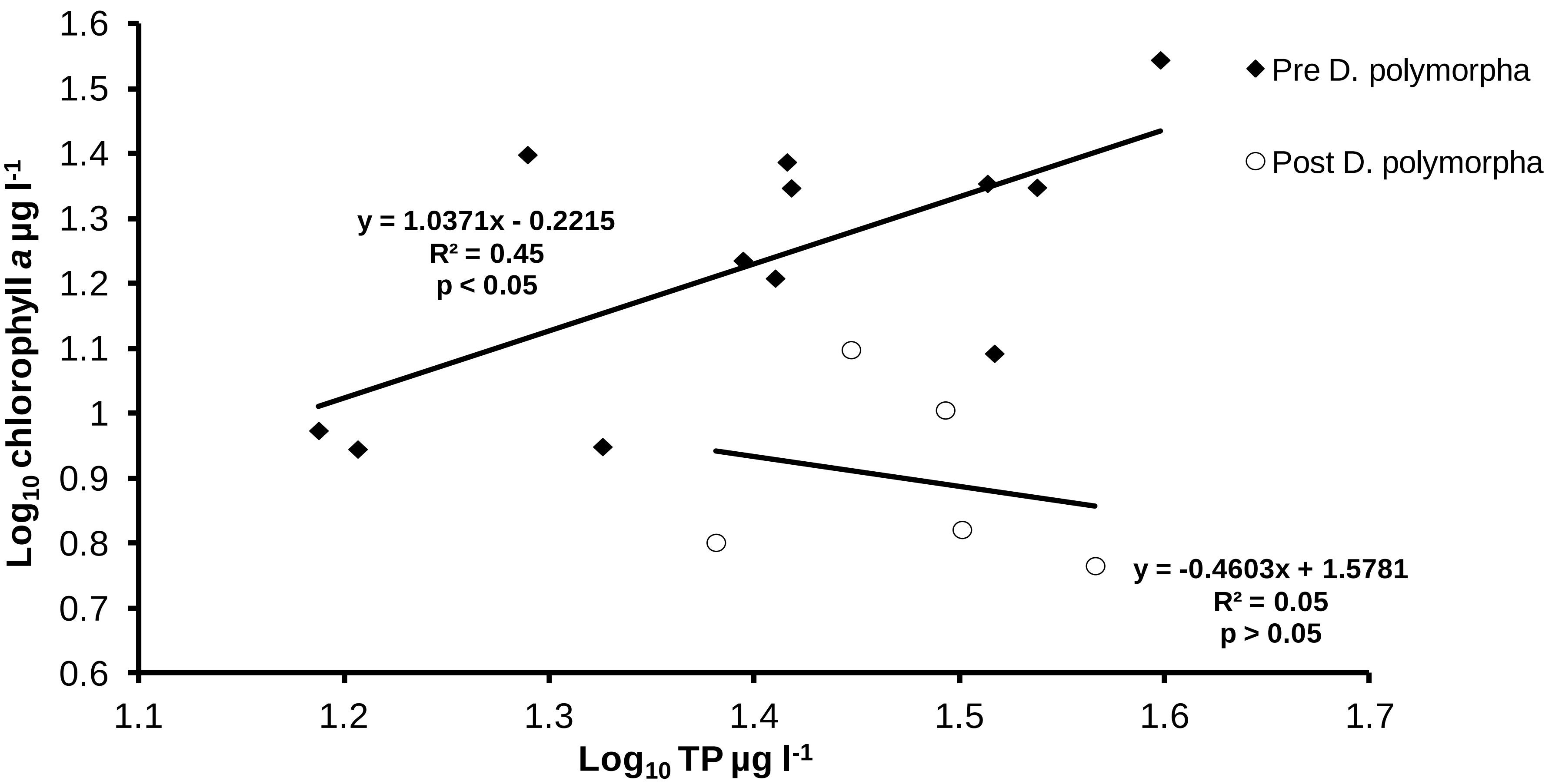

1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
1.1
1.2
1.3
1.4
1.5
1.6
1.7
Log10 chlorophyll a µg l-1
Log10 TP µg l-1
Pre D. polymorpha
Post D. polymorpha
y = 1.0371x - 0.2215
R² = 0.45
p < 0.05
y = -0.4603x + 1.5781
R² = 0.05
p > 0.05

Fig. 5