

## Article (refereed) - postprint

---

Carvalho, L.; Miller, C.; Spears, B.M.; Gunn, I.D.M.; Bennion, H.; Kirika, A.; May, L.. 2012 Water quality of Loch Leven: responses to enrichment, restoration and climate change. *Hydrobiologia*, 681 (1). 35-47.

[10.1007/s10750-011-0923-x](https://doi.org/10.1007/s10750-011-0923-x)

© Springer Science+Business Media B.V. 2011

This version available <http://nora.nerc.ac.uk/15914/>

NERC has developed NORA to enable users to access research outputs wholly or partially funded by NERC. Copyright and other rights for material on this site are retained by the rights owners. Users should read the terms and conditions of use of this material at <http://nora.nerc.ac.uk/policies.html#access>

**This document is the author's final manuscript version of the journal article, incorporating any revisions agreed during the peer review process. Some differences between this and the publisher's version remain. You are advised to consult the publisher's version if you wish to cite from this article.**

The final publication is available at [link.springer.com](http://link.springer.com)

Contact CEH NORA team at  
[noraceh@ceh.ac.uk](mailto:noraceh@ceh.ac.uk)

**Title**

Water quality of Loch Leven: responses to enrichment, restoration and climate change.

**Authors**

L. Carvalho<sup>1</sup>, C. Ferguson<sup>2</sup>, B. M. Spears<sup>1</sup>, I. D. M. Gunn<sup>1</sup>, H. Bennion<sup>3</sup>, A. Kirika<sup>1</sup> and L. May<sup>1</sup>

<sup>1</sup>Centre for Ecology & Hydrology, Bush Estate, Penicuik, Midlothian EH26 0QB, UK.

<sup>2</sup>Department of Statistics, University of Glasgow, University Gardens, Glasgow G12 8QW, UK.

<sup>3</sup>Environmental Change Research Centre, Department of Geography, University College London, Gower Street, London, WC1E 6BT, UK.

Corresponding author: Laurence Carvalho Email [laca@ceh.ac.uk](mailto:laca@ceh.ac.uk); telephone +44 (0)131 445 8540; fax +44 (0)131 445 3943

**Keywords:**

Lake, recovery, chlorophyll *a*, phosphorus, nitrogen, temperature, rainfall, *Daphnia*

This paper has not been submitted elsewhere in identical or similar form, nor will it be during the first three months after its submission to *Hydrobiologia*

## **Abstract**

It is usually assumed that climate change will have negative impacts on water quality and hinder restoration efforts. The long term monitoring at Loch Leven shows, however, that seasonal changes in temperature and rainfall may have positive and negative impacts on water quality. In response to reductions in external nutrient loading, there have been significant reductions in in-lake phosphorus concentrations. Annual measures of chlorophyll *a* have, however, shown little response to these reductions. Warmer spring temperatures appear to be having a positive effect on *Daphnia* densities and this may be the cause of reduced chlorophyll *a* concentrations in spring and an associated improvement in water clarity in May and June. The clearest climate impact was the negative relationship between summer rainfall and chlorophyll *a* concentrations. This is highlighted in extreme weather years, with the 3 wettest summers having very low chlorophyll *a* concentrations and the driest summers having high concentrations. To predict water quality impacts of future climate change, there is a need for more seasonal predictions from climate models and a greater recognition that water quality is the outcome of seasonal responses in different functional groups of phytoplankton and zooplankton to a range of environmental drivers.

## Introduction

Monitoring at Loch Leven has spanned periods of increasing and decreasing nutrient loads (Bennion et al., 2001; [May et al., this volume](#)) and of changing climate (Ferguson et al., 2008). This paper examines how the loch has responded to changes in these pressures, and to restoration activities, providing a valuable case-study of how a shallow lake ecosystem reacts to change.

Nutrient enrichment is recognised as one of the most widespread pressures threatening the quality of freshwaters (Carvalho & Moss, 1995; Smith et al., 2006). Over recent decades, great efforts have been made to restore enriched systems, largely through reductions in point-sources of nutrients entering lakes. The recovery of lake ecosystems is not, however, as immediate or as effective as often hoped (Jeppesen et al., 2005; Moss et al., 2005; Carvalho et al., 1995). Attempts to restore lakes are often hindered by internal loading from nutrients that have stockpiled in the lake's sediments (Sas, 1989; Søndergaard et al., 2007; Spears et al., 2007a). More recently, a possible influence of climate change on lake recovery has also been highlighted (Battarbee et al., 2005; Whitehead et al., 2009). The effects of this on lake ecosystems are poorly understood, but it is often assumed that rising temperatures will lead to a deterioration in water quality as this will stimulate phytoplankton growth, particularly that of bloom-forming cyanobacteria (Paerl & Huisman, 2008). However, changes in temperature also affect the growth and reproduction of zooplankton grazers (Elmore, 1983; Hanazato & Yasuno, 1985) and changes in other climate parameters, such as rainfall, may have confounding influences. Long term monitoring records, such as those from Loch Leven, are invaluable in providing observational evidence of how lake ecosystems respond to multiple pressures. They can also help us understand the relative strengths of the key drivers of water quality.

This paper examines annual and seasonal trends in the main water quality variables at Loch Leven (phosphorus, nitrogen and chlorophyll *a* concentrations and Secchi depth transparency) in relation to changes in potential key drivers, specifically the zooplankton grazer community, the timing of reductions in external nutrient load and the weather. It examines these changes in relation to water quality targets set by the Loch Leven Area Management Advisory Group (LLAMAG, 1993) and in relation to more recent targets set under the Water Framework Directive (WFD) (European Parliament, 2000).

## Methods

### *Site details*

Loch Leven is the largest shallow lake in Great Britain (lake area 13.3 km<sup>2</sup>, mean depth 3.9 m, maximum depth 25.5 m), and is situated in lowland Scotland, UK (56° 12' N, 3° 22' W; altitude 107 m). Historically, the loch received phosphorus (P)-rich effluent from a woollen mill (Holden & Caines, 1974). Inputs were progressively reduced from a peak in the 1960s and early 1970s and the mill ceased using P-based materials in 1989 (LLCMP, 1999; [May et al., this volume](#)). Sewage treatment works within the catchment were also a major source of P to the loch (Bailey-Watts & Kirika, 1987) and, in response to severe eutrophication problems, tertiary treatment and effluent diversion measures were introduced at these works in the 1990s to reduce the nutrient load from this source ([May et al., this volume](#)).

As a result of these changes, the total phosphorus (TP) loading, which had risen to 20 t P y<sup>-1</sup> by 1985, was reduced to 8 t P y<sup>-1</sup> by 1995 (Bailey-Watts & Kirika 1999; [May et al., this volume](#)) and remained at this level in 2005 ([May et al., this volume](#)). Since 1995, diffuse nutrient loads from agriculture have also been targeted through the introduction of buffer strips along the Pow Burn although the impact of this is currently unclear ([May et al., this volume](#)).

Water quality targets for restoring the ecological health of Loch Leven were originally set by the Loch Leven Area Management Advisory Group (LLAMAG, 1993). The targets were based on the water quality required to support aquatic plants growing to 4.5 m depth, based on historical plant survey records (West, 1910) and using the method outlined by D'Arcy et al. (2006). Those targets are 40 µg l<sup>-1</sup> annual mean TP, 15 µg l<sup>-1</sup> annual mean chlorophyll *a* and 2.5 m annual mean Secchi disc depth. The target for TP is consistent with that inferred from a diatom-phosphorus transfer function for the pre-enrichment period of the loch (Bennion et al., 2004).

More recent water quality targets for Loch Leven are being set under the EU Water Framework Directive (European Parliament, 2000), and new UK Environmental Standards for TP for supporting good ecological status under the WFD are also being implemented (UK TAG, 2008). The new TP standards for the loch are more stringent than those set by LLAMAG (1993). The good/moderate (G/M) boundary TP target for a shallow, high alkalinity loch in Scotland, such as Loch Leven, is 32 µg l<sup>-1</sup> (annual geometric mean) and the moderate/poor (M/P) boundary is 46 µg l<sup>-1</sup>. New European standards for chlorophyll *a* concentrations in lakes have also been developed (Carvalho et al., 2008) and are formally being agreed by the European Commission as part of the Intercalibration process for the WFD. The G/M class boundary for chlorophyll *a* for a shallow, high alkalinity lake, such as Loch Leven, is 7.5 µg l<sup>-1</sup> (annual arithmetic mean; Carvalho et al., 2006). Loch Leven is, however, near the 3 m mean depth boundary between shallow and very shallow lake types; a site-specific target based on a lake's specific mean depth and alkalinity is, therefore, considered more appropriate. Site-specific chlorophyll *a* targets for Loch Leven would be 11 µg l<sup>-1</sup> for the G/M boundary and 22 µg l<sup>-1</sup> for the M/P boundary (Carvalho et al., 2009).

#### *Water sampling, storage and analysis*

Loch Leven has been monitored on a weekly to fortnightly basis since 1968. Sampling for water chemistry and plankton was carried out by boat from a mid-basin station, just off Reed Bower. Integrated water samples (between the water surface and about 0.25 m above the lake bed) were collected in duplicate at the site using a weighted polythene tube. As a result of fluctuations in water level, sample depths varied from 3.0 to 3.5 metres. Water clarity was measured using a Secchi disk at the Reed Bower station and at the South Deeps when Secchi depth was observed to exceed water depth at Reed Bower. When access to the Reed Bower station was restricted, surface water samples were collected from the sluices at the outflow using a bucket.

Open water crustacean zooplankton samples were collected at the Reed Bower and centre loch sites. Samples were preserved in 4% formaldehyde solution. Sampling and counting methods for estimating *Daphnia* densities are detailed in [Gunn et al. \(this volume\)](#).

On return to the laboratory, sub-samples of filtered (Whatman® GF/C) water were taken from each of the duplicate samples for analysis of SRP, nitrate-nitrogen (NO<sub>3</sub>-N) and soluble reactive silicate (SRSi), and similarly from unfiltered water for analysis of TP. Samples for chlorophyll *a* analysis were prepared by filtering 400 ml of lake water through a GF/C filter. The filter was stored frozen until analysis.

Filtered water was analysed for SRP following the method of Murphy & Riley (1962). TP was determined using a sulphuric acid-potassium persulphate digestion on unfiltered samples to convert all forms of P to SRP. This was then measured using a modified version of Murphy & Riley (1962) as described by Wetzel and Likens (2000). Nitrate was determined using a SEAL AQ2 analyser (SEAL Analytical Limited) by the sulphanilamide/NEDD reaction which produces a reddish-purple dye (HMSO, 1981). SRSi was analysed according to Golterman et al. (1978) using a spectrophotometer fitted with a 10mm flow-cell.

Chlorophyll *a* was analysed following a methanol extraction method (frozen filters submersed in 90% methanol overnight in a dark fridge) modified from Holm-Hansen & Riemann (1978). The following day, the tubes were centrifuged for 10 minutes at 2500 r.p.m. Chlorophyll *a* was measured spectrophotometrically at 665 nm with a turbidity correction conducted at 750 nm. The concentration of chlorophyll *a* was determined using a standard calibration equation (APHA, 1992).

Monthly mean air temperature and cumulative rainfall totals were calculated from daily measurements recorded at a meteorological station on the shore. For daily air temperature, an average daily temperature was calculated as [(maximum + minimum)/2]. Data gaps were filled using regression equations relating monthly weather data at Loch Leven with monthly records from the Royal Air Force base at Leuchars, 44 km north-east of Loch Leven (<http://www.metoffice.gov.uk/climate/uk/stationdata/>).

### *Statistical methods*

Seasonal means were calculated for winter (D, J, F), spring (M, A, M), summer (J, J, A) and autumn (S, O, N) by averaging monthly means for all variables, except rainfall, for which cumulative seasonal rainfall was computed. Annual means were then estimated from seasonal means. This nested approach for estimating monthly, then seasonal, and finally annual means was necessary due to variation in the sampling frequency over the 40 year period, with weekly summer sampling, a common feature in the early monitoring years, biasing averages based on raw sampling data.

For each variable for the trend analysis, two time periods were considered. These were 1968 to 2007 (full 40 years of monitoring) and 1988 to 2007 (last 20 years after major external nutrient load reductions); annual means were also considered for some variables in 2008. In some cases comparisons were also made between the first (1968-1977) and last (1998-2007) decade on record. As a result of the absence of *Daphnia* from the lake between 1968 and June 1970, and different zooplankton sampling sites and methods being used in the early 1970s, trends in *Daphnia* density were investigated from 1975 onwards, only. A natural log transformation was applied to all of the data, except air temperature and cumulative rainfall, to help to stabilize the variance. For *Daphnia*, the constant 0.01 was added before logarithmic transformations were applied, to remove zeros.

Additive and non-parametric regression models (Hastie & Tibshirani; 1990, Bowman & Azzalini; 1997) were developed to model trends and seasonality in the main water quality parameters and potential key drivers of water quality (grazers, air temperature, rainfall). Statistical analyses were carried out to investigate, trends over the 40 year period, seasonal patterns throughout the year and trends over 40 years for each season individually, for each variable of interest. In each model, smooth functions are fitted for each explanatory variable to enable flexibility in the nature of trends detected (i.e. linear, non-linear, non-parametric). For all models, approximate F-tests (Hastie & Tibshirani, 1990) were used to test hypotheses concerning the significance of non-parametric trends and to assess whether linear (instead of nonparametric) relationships are appropriate. Analyses were carried out using R software (<http://www.r-project.org>). Figures and tests for seasonal trends were produced in R using the *sm* library (Bowman & Azzalini, 1997), in particular, the *sm.regression* function. Further details of the R code are described in Ferguson et al. (2008). Figures are provided for each season, which display the fitted nonparametric regression line for trend over the 40 year period along with shaded bands to display a reference band that represents ‘no effect’, i.e. where the curve is expected to lie if there is no evidence of change over time (see Bowman & Azzalini, 1997, for details). For other basic statistics (linear regression, correlation and t-tests) analyses were carried out using Minitab version 14.

## Results

### *Annual trends in target water quality indicators*

Highly significant trends ( $p < 0.001$ ) were observed for all three water quality indicators (TP, chlorophyll *a*, Secchi depth). TP concentrations declined from an annual mean of over  $100 \mu\text{g l}^{-1}$  in the early 1970s to concentrations below the LLAMAG target of  $40 \mu\text{g l}^{-1}$  in recent years (Figure 1a). The declining trend was non-linear, with a rapid decline in concentrations in the early 1970s, a slight increase in the early 1990s and another rapid decline in 2007 and 2008 (to  $32 \mu\text{g l}^{-1}$  and  $33 \mu\text{g l}^{-1}$ , respectively), the latter being at or near the WFD good status target of  $32 \mu\text{g l}^{-1}$ .

Chlorophyll *a* concentrations had a similar rapid decline in concentrations in the early 1970s, from annual means of over  $90 \mu\text{g l}^{-1}$  to values around  $40 \mu\text{g l}^{-1}$  by the mid-1970s. Since then, annual mean concentrations have fluctuated, mainly between  $30 \mu\text{g l}^{-1}$  and  $50 \mu\text{g l}^{-1}$  (Figure 1b). No significant trend was observed when only the last 20 years (1988-2007) were considered ( $p=0.814$ ). Chlorophyll *a* levels were relatively low in 2007 ( $26 \mu\text{g l}^{-1}$ ) and 2008 ( $25 \mu\text{g l}^{-1}$ ), but were still well above both LLAMAG and WFD good status targets of  $15 \mu\text{g l}^{-1}$  and  $11 \mu\text{g l}^{-1}$ , respectively. As such, the loch would be classified as having poor ecological status under the WFD. Comparing variability in chlorophyll *a* and TP concentrations (Figure 2), there is a highly significant positive relationship ( $p < 0.001$ ), indicating that the two are highly inter-dependent. There is, however, some evidence for a levelling off of the relationship at TP concentrations below about  $70 \mu\text{g l}^{-1}$ , particularly for the low TP years of 2007 and 2008. The first two years of the monitoring 1968 and 1969 are also large outliers in the regression with more chlorophyll than would be predicted from TP concentrations (Figure 2).

Secchi disc depths also showed a rapid improvement in the early 1970s, increasing from annual means of around 1.0 m to about 1.5 m by the mid-1970s. Since then, water clarity has been relatively stable with values generally ranging from 1.2 to 1.7 m, although in terms of

visibility there have been some particularly poor years (1998, 1999) and particularly good years with annual means of 2.0 m or above (1980, 2000) (Figure 1c). Secchi depth transparencies in 2007 and 2008 were slightly above average (1.63 m and 1.61 m), but were well below the LLAMAG target of 2.5 m.

#### *Seasonality and seasonal trends in bio-available nutrients*

Concentrations of SRP showed significant trends for the spring and winter seasons (Table 1). Trends in spring concentrations have been non-linear, with concentrations declining slightly in the 1980s and increasing slightly from the 1990s, onwards. Winter SRP concentrations show a more consistent linear declining trend. Comparing the seasonality in SRP concentrations for the first (1968-1977) and last (1998-2007) decade of the monitoring period (Figure 3a), it can be seen that SRP concentrations have declined for most months of the year, with only the spring months showing little change.

Non-parametric regression indicated no significant trends in nitrate-N (N) concentrations for any of the four seasons (Table 1). Winter N concentrations in 1992 (December 1991 to February 1992) were, however, extremely low. Removing this outlier, winter N concentrations showed a highly significant increasing linear trend ( $p = 0.003$ ). Comparing the seasonality in N concentrations for the first (1968-1977) and last (1998-2007) decade of the monitoring (Figure 3b), concentrations were much higher for the first six months of the year in the last decade than in the earlier decade. In contrast, there has been little change in N concentrations in the second half of the year, although concentrations in August, September and October were lower in the most recent decade than the first, with levels below analytical detection limits ( $0.01 \text{ mg l}^{-1}$ ) being recorded more frequently in August.

SRSi concentrations showed highly significant, decreasing trends for spring, summer and winter periods (Table 1). Comparing the seasonality in SRSi concentrations for the first (1968-1977) and last (1998-2007) decade of monitoring (Figure 3c), it can be seen that concentrations have declined for all months of the year. Since 2000, concentrations in March and April frequently remained below  $0.5 \text{ mg l}^{-1}$ .

#### *Trends in weather and Daphnia grazers*

Air temperature showed a highly significant, increasing linear trend in spring and significant, increasing trends in autumn and winter (Table 1, Figure 4). Summer was the only season not to have a significant warming trend, although the summers from 2003-2006 were all warmer than average, with 2003 being the warmest summer of the 40 year monitoring period (i.e. 1.6 degrees warmer than the 30 year average of  $13.3 \text{ }^\circ\text{C}$  calculated from the 1971-2000 summer means). The most anomalous air temperature was recorded in the winter of 1989, when the mean winter temperature was  $5.8 \text{ }^\circ\text{C}$ , almost  $3^\circ$  above the 30 year average of  $2.9 \text{ }^\circ\text{C}$  (based on 1971-2000 winter means).

Winter rainfall showed a significant increasing trend over the monitoring period (Table 1, Figure 5) and an approximate F-test highlighted that a nonparametric trend was not required here and that a linear trend was more appropriate. All seasons, however, showed large variability in rainfall. The years 1990, 1995, 2000 and 2007 had particularly wet winters with over 150 mm more cumulative rainfall than the 30 year average of 293 mm (1971-2000 winter mean). The years 1976, 1996 and 2006 had particularly dry winters with at least 120 mm less cumulative rainfall than the 30 year average. The wettest summers over the 40



year monitoring period were 1985, 1988, 2007 and 2008 with more than 300 mm cumulative rainfall (compared with the 1971-2000 30 year average of 196 mm). The driest summer, by far, was 1995 with only 64 mm of rain.

Since 1975, *Daphnia* densities have shown no significant trends for the four seasonal means (Table 1). However, when densities over the last two decades are compared, it is clear that densities have increased markedly in May, although the difference between the two decades is not quite statistically significant ( $p=0.079$ ). A general decline in densities is also apparent between July and October when these two decades are compared (Figure 6).

#### *Seasonal trends in chlorophyll a and secchi depth*

Analysis of seasonal trends reveals significant non-linear declining trends for spring, summer and winter chlorophyll *a* concentrations (Table 1), although reductions in the latter two seasons were largely confined to the first decade of monitoring (Figure 7). If trends are only considered for the last 20 years (1988-2007), only the spring season shows evidence of decreasing concentrations, although this trend is not quite significant ( $p=0.085$ ). What is even more evident from the raw data are the particularly low chlorophyll *a* concentrations that have been recorded in May since 2000, with concentrations frequently below  $10 \mu\text{g l}^{-1}$ . These were significantly different to concentrations of more than  $100 \mu\text{g l}^{-1}$  that were often recorded in this month during the first six years (1968-1973) ( $p<0.001$ ). Low summer chlorophyll *a* concentrations in recent years (1985, 2004, 2007 & 2008) were associated with very wet summers. Similarly some of the driest summers had the highest chlorophyll concentrations (1994, 1995 and 2006). Correlations between log summer rainfall and summer chlorophyll *a* concentrations reveal a changing relationship over the 40 years, with a very weak relationship observed for the first two decades, 1968-1987 ( $r = 0.021$ ,  $p = 0.938$ ) and a significant negative relationship for the last two decades, 1989-2008 ( $r = -0.495$ ,  $p = 0.026$ ). Regression analysis was carried out to consider other potential drivers of summer chlorophyll (nutrients, air temperature and *Daphnia* abundance), but only rainfall showed a significant response.

Analysis of trends in Secchi disc depth by season reveals a highly significant increasing trend in spring, largely driven by increases in the early 1970s (Table 1, Figure 8). Similar to chlorophyll *a*, the months of May and June have become particularly clear in recent years, with Secchi depths of 3 m or more often being recorded from 2000 onwards, compared with values of less than 1 m for the first three years of the monitoring record.

## **Discussion**

Annual and seasonal trends in water quality parameters at Loch Leven for the periods 1968-2002 and 1988-2002 were reported by Ferguson et al. (2008). This paper brings this analysis up-to-date by considering a full 40 years of monitoring data (1968-2007) and focusing more on changes since 2000. These trends are also discussed in relation to new targets set in response to the WFD.

#### *Annual trends in target water quality parameters*

The very abrupt decline in TP and chlorophyll *a* concentrations and the increase in Secchi depth in the early 1970s occurred prior to any reductions in external nutrient loads and

coincided with the return of *Daphnia* populations to the lake in 1970 after an absence of 15-20 years (Gunn et al., this volume; May & Spears, this volume). This highlights how significant *Daphnia* grazing is to the water quality of Loch Leven. The impact on TP concentrations, as well as chlorophyll *a* concentrations, indicates an important contribution of phytoplankton cells to the overall TP budget in the water column and hence the potential importance of zooplankton grazing pressure in the maintenance of water quality. Since the mid-1970s, the continuing decline in TP concentrations is most likely a response to the reductions in external loadings of P from the catchment (Bailey-Watts & Kirika, 1999; May et al., this volume). The fact that the annual mean TP concentrations in 2007 and 2008 were below LLAMAG target concentrations of 40  $\mu\text{g l}^{-1}$ , and at or near the UK TAG (2008) good/moderate status class boundary, is some evidence that the restoration measures put in place at this site have been a success. However, it is possible that the extremely wet summers of 2007 and 2008 may have contributed to this achievement. Climatic factors regulating the magnitude of internal loading may have also contributed to the declining trend in annual average TP concentrations (Spears et al., this volume).

In contrast, annual mean chlorophyll *a* concentrations and Secchi depths appear to show a levelling off of a response to the reductions in external P loads that took place since the late 1980s. One possible explanation is that, for most of the monitoring period, P has been in excess for much of the year and has not, therefore, generally limited annual phytoplankton standing crops. A similar lack of response has been observed in other lakes recovering from eutrophication (Jeppesen et al., 2005; Moss et al., 2005) and are commonly due to P release from the sediments sustaining phytoplankton populations. A second possible explanation could be that other factors, such as climate change or grazer densities, may affect the strength of the relationship between annual mean chlorophyll *a* and TP concentrations. This is supported by the TP-chlorophyll regression, which indicates the two biggest outliers in the relationship are associated with 1968 and 1969 when *Daphnia* grazers were absent. In addition to this, it may be that annual measures of chlorophyll *a* mask improvements and/or deteriorations in particular seasons; seasonal trends may be more enlightening, as seasonal processes and consequent relationships between variables (e.g. chlorophyll and P, chlorophyll and grazers) change throughout the year (Ferguson et al., 2009).

#### *Potential for nutrient limitation of phytoplankton*

The changing seasonality in SRP concentrations over the 40 year monitoring period highlights a general reduction in concentrations for much of the year, although significant declining trends were only shown for winter. The seasonality of SRP suggests that concentrations are now getting low enough to potentially limit phytoplankton population growth from February through to June. The late summer and autumn peaks in SRP are almost certainly due to internal loading from the P-rich loch sediments (Spears et al., 2007a). The declines observed in the August SRP maximum since the mid-1990s are most likely due to enhanced regulation of P fluxes from the sediments, as analyses of the P content of the sediments suggest that the reservoir of sediment-P remains plentiful (Spears et al., 2007a). It is also interesting to note that the late summer/autumn peak has been almost restricted to August over the last decade (1998-2007) compared with June to September in the first decade (1968-1977) of monitoring. This is very comparable to the pattern of recovery observed in another shallow lake, Barton Broad, 10-15 years after sewage diversion (Phillips et al., 2005).

As there is no evidence of increased nitrate-N concentrations in the main inflows (Defew, unpublished data), it is not clear what is driving the increasing winter nitrate-N concentrations

in the loch. However, the summer minimum of nitrate-N can probably be explained by two major processes: direct uptake by phytoplankton and denitrification. The latter process, through microbial oxidation of organic carbon, is greatly increased during warmer temperatures (Johnston et al., 1974) and may be one reason why nitrate-N concentrations now reach potentially limiting concentrations for phytoplankton population growth ( $<0.1 \text{ mg l}^{-1}$ ) during late summer. Although this could give nitrogen-fixing cyanobacteria a competitive advantage over other algae (Schindler, 1977), there is no strong evidence of this occurring in Loch Leven. In general, N-fixing cyanobacteria, such as *Anabaena*, tend to peak earlier in the summer in Loch Leven, before N-limitation is most likely to occur.

As we have no SRSi loading data, it is not clear what is causing the significant declines in SRSi concentrations in the loch in spring, summer and winter. SRSi loading would be expected to increase with the increasing winter rainfall, although in-lake concentrations would not be expected to be greatly affected. This suggests that the reductions in lake concentrations may be due more to greater uptake by diatoms. Diatoms do appear to have become the dominant algal group in the loch for much of the year (Carvalho, unpublished data). Only in spring are SRSi concentrations reduced to potentially limiting concentrations for diatom growth (Reynolds, 2006). This may be an important factor in the reduction in spring chlorophyll *a* concentrations, as there has been little change in the other potentially limiting nutrients during this season and diatoms consistently dominate the spring flora.

#### *Seasonal trends in climate, grazers, chlorophyll a and Secchi depth*

The seasonal climate trends are similar to those described by Ferguson et al. (2008), i.e. warmer springs and wetter winters. The additional 5 years of monitoring data also reveal that autumn and winter periods are becoming significantly warmer. The results of trend analysis of *Daphnia* densities contrast with the earlier study, with no significant trends apparent since 1975, compared with the highly significant increasing trends recorded from 1968-2002 (Ferguson et al., 2008). This highlights the fact that the latter was driven largely by the absence of *Daphnia* in the first few years of the monitoring period. The only evidence of increasing *Daphnia* densities is for spring, particularly the month of May, with lower densities more common now over much of the summer and autumn (Figure 6). Gunn et al. (this volume) have shown a significant declining trend in mean summer *Daphnia* monthly maxima over the study period. There is, therefore, no evidence that summer *Daphnia* densities have responded positively to the observed increased coverage by macrophytes (Dudley et al., this volume). The lower mean and maxima densities in summer cannot be explained by lower food quantity, as summer chlorophyll trends show no significant decline since 1988. The decline over the last decade may, therefore, be due to either poorer quality food for *Daphnia* (e.g. inedible or toxic algae) or to increased predation by zooplanktivorous fish.

The enhanced *Daphnia* populations in May are certainly one of the most plausible reasons for the reductions in May chlorophyll *a* concentrations and improvements in May/June water clarity, although declining SRSi concentrations limiting diatom growth are likely to be a major contributory factor too.

Variability in summer chlorophyll *a* concentrations over the last two decades does appear to be increasingly in response to variability in climate, specifically summer rainfall. The best summers, in terms of reduced chlorophyll *a* concentrations, are associated with particularly

wet summers (1985, 2007 and 2008) and the worst summers with particularly dry conditions (1994, 1995 and 2006).

### *Climate change and lake recovery*

Detailed analyses of the seasonal trends indicate responses to changes in both nutrients and climate. There appear to have been significant responses in in-lake P concentrations to the reductions in point-source nutrient loading. In terms of chlorophyll *a* concentrations, warmer temperatures potentially have direct physiological effects (e.g. enhanced growth rates) on plankton communities (Elmore, 1983; Hanazato & Yasuno, 1985; Reynolds, 2006) and it is generally assumed that this will result in an increase in phytoplankton or zooplankton abundance. The negative relationship observed at Loch Leven, with reduced spring chlorophyll *a* and warmer spring water temperatures, suggests an indirect response, probably due to a strong positive effect of water temperature on grazer densities (Ferguson et al., 2007). The consequent increases in May/June water clarity may be a key factor driving the recolonisation of deeper water by submerged aquatic plants (Dudley et al., [this volume](#); May & Carvalho, 2010) and consequent benefits to associated biodiversity (Carss et al., [this volume](#); Gunn et al., [this volume](#); Winfield et al., [this volume](#)), although other factors, such as changes in wind disturbance of sediments, may also be important (Spears & Jones, 2010). The most obvious climate impact on water quality was the beneficial effect of very wet summers, which in recent decades has been significantly associated with low summer chlorophyll *a* concentrations. The most direct cause of this is probably increased phytoplankton loss processes through enhanced flushing from the loch (Bailey-Watts et al, 1990). This is likely to particularly affect slow-growing phytoplankton, such as bloom-forming cyanobacteria (Reynolds & Lund, 1988). Increased flushing will also help the long-term success of restoration, by exporting P released from internal sediment sources during the summer *via* the outflow (Spears et al., 2007b). As the outflow of Loch Leven is controlled, increased summer rainfall may also be partly retained in the loch, which may simply dilute loch phytoplankton populations.

The long term research at Loch Leven is helping us understand how shallow lakes respond to both lake restoration and climate change. It is usually assumed that climate change will have negative impacts on water quality, but this research suggests that some seasonal changes in air temperature and rainfall patterns may actually have positive effects. To predict water quality responses to future climate change, there is a clear need for better seasonal predictions from climate models and a greater understanding of how different functional groups of phytoplankton and zooplankton respond to these seasonal changes.

### **Acknowledgments**

Most of the sample collection and analysis for this research was funded by the Natural Environment Research Council with additional support from the European Union (FP6 Integrated Project 'Euro-limpacs: European project to evaluate impacts of global change on freshwater ecosystems' GOCE-CT-2003-505540). The authors also gratefully acknowledge Kinross Estates for providing access to the loch and for assistance with fieldwork. Loch Leven is part of the UK Environmental Change Network (<http://www.ecn.ac.uk/>).

## References

- APHA, 1992. Standard Methods for the Examination of Water and Wastewater, 18th edition, American Public Health Association, Washington.
- Bailey-Watts, A. E. & A. Kirika, 1987. A re-assessment of the phosphorus inputs to Loch Leven (Kinross, Scotland): rationale and an overview of results on instantaneous loadings with special reference to runoff. *Earth Sciences* 78: 351-367.
- Bailey-Watts, A. E. & A. Kirika, 1999. Poor water quality in Loch Leven (Scotland) in 1995, in spite of reduced phosphorus loadings since 1985: the influences of catchment management and inter-annual weather variation. *Hydrobiologia* 403: 135-151.
- Bailey-Watts, A. E., A. Kirika, L. May & D. H. Jones, 1990. Changes in phytoplankton over various time scales in a shallow, eutrophic: the Loch Leven experience with special reference to the influence of flushing rate. *Freshwater Biology* 23: 85-111.
- Battarbee, R. W., N. J. Anderson, E. Jeppesen & P. R. Leavitt, 2005. Combining palaeolimnological and limnological approaches in assessing lake ecosystem response to nutrient reduction. *Freshwater Biology* 50: 1772-1780.
- Bennion, H., J. Fluin, P. Appleby & B. Ferrier, 2001. Palaeolimnological investigation of Scottish freshwater lochs. Final report to SNIFFER No. SR(00)02. ENSIS Ltd, University College London.
- Bennion, H., J. Fluin & G.L. Simpson, 2004 Assessing eutrophication and reference conditions for Scottish freshwater lochs using subfossil diatoms. *Journal of Applied Ecology* 41:124-138.
- Bowman, A. & A. Azzalini, 1997. Applied Smoothing Techniques for Data Analysis, Clarendon Press, Oxford, UK.
- Carss, D., B. M. Spears, L. Quinn & R. Cooper, this volume. Long-term variations in waterfowl populations in Loch Leven: identifying discontinuities between local and national trends. *Hydrobiologia* 00: 000-000.
- Carvalho, L., M. Beklioglu & B. Moss, 1995. Changes in a deep lake following sewage diversion - a challenge to the orthodoxy of external phosphorus control as a restoration strategy? *Freshwater Biology* 34: 399-410.
- Carvalho, L. & B. Moss, 1995. The current status of a sample of English Sites of Special Scientific Interest subject to eutrophication. *Aquatic Conservation* 5:191-204.
- Carvalho, L., G. Phillips, S. Maberly & R. Clarke, 2006. Chlorophyll and Phosphorus Classifications for UK Lakes. Final Report to SNIFFER (Project WFD38), Edinburgh, October 2006, 81 pp.
- Carvalho, L., A. Solimini, G. Phillips, M. van den Berg, O-P. Pietiläinen, A. Lyche, S. Poikane & U. Mischke, 2008. Chlorophyll reference conditions for European Intercalibration lake types. *Aquatic Ecology* 42: 203-211.

Carvalho, L., A. G. Solimini, G. Phillips, O.-P. Pietiläinen, J. Moe, A. C. Cardoso, A. Lyche Solheim, I. Ott, M. Søndergaard, G. Tartari & S. Rekolainen. 2009. Site-specific chlorophyll reference conditions for lakes in Northern and Western Europe. *Hydrobiologia* 633: 59-66.

D’Arcy, B. J., May, L., Long, J., Fozzard, I. R., Greig, S. & Brachet, A., 2006. The restoration of Loch Leven, Scotland, UK. *Water Science Technology* 53: 183-91.

Dudley, B., I. D. M. Gunn, L. Carvalho, I. Proctor, M. T. O’Hare, K. J. Murphy, A. Milligan, this volume. Changes in aquatic macrophyte communities in Loch Leven – evidence of recovery from eutrophication? *Hydrobiologia* 00: 000-000.

Elmore, J. L., 1983. The influence of temperature on egg development times of three species of *Diatomus* from subtropical Florida. *American Midland Naturalist* 109: 300-308.

European Parliament, 2000. Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000, establishing a framework for community action in the field of water policy. Official Journal of the European Communities, L327/1: 1-72.

Ferguson C. A., A. W. Bowman, E. M. Scott & L. Carvalho, 2009. Multivariate varying-coefficient models for an ecological system. *Environmetrics* 20: 460-476.

Ferguson, C. A., L. Carvalho, E. M. Scott, A. W. Bowman & A. Kirika, 2008. Assessing ecological responses to environmental change using statistical models. *Journal of Applied Ecology* 45: 193-203.

Ferguson C. A., E. M. Scott, A. W. Bowman & L. Carvalho, 2007. Model comparison for a complex ecological system. *Journal of the Royal Statistical Society Series A* 170: 691-711.

Golterman, H. L., R. S. Clymo & M. A. M. Ohnstad, 1978. Methods for physical and chemical analysis of freshwaters, 2<sup>nd</sup> Edition. Blackwell Scientific, Oxford.

Gunn, I. D. M., M. T. O’Hare, P. S. Maitland & L. May, this volume. Long-term trends in Loch Leven invertebrate communities. *Hydrobiologia* 00: 000-000.

Hanazato, T. & M. Yasuno, 1985. Effect of temperature in the laboratory studies on growth, egg development and first parturition of five species of Cladocera. *Japanese Journal of Limnology* 46: 185-191.

Hastie, T. & R. Tibshirani, 1990. *Generalized Additive Models*, Chapman and Hall, London.

HMSO, 1981. *Methods for the Examination of Waters & Associated Materials: Book Number 40, Oxidised Nitrogen in Waters*. HMSO, London.

Holden, A. V. & L. A. Caines, 1974. Nutrient chemistry of Loch Leven, Kinross. *Proceedings of the Royal Society of Edinburgh, B*, 74: 101-121.

Holm-Hansen, O. & B. Riemann, 1978. Chlorophyll *a* determination: improvements in methodology. *Oikos* 30: 438-447.



Jeppesen, E., M. Søndergaard, J. P. Jensen, K. Havens, O. Anneville, L. Carvalho, M. F. Coveney, R. Deneke, M. T. Dokulil, B. Foy, D. Gerdeaux, S. E. Hampton, S. Hilt, K. Kangur, J. Kohler, E. H. H. R. Lammens, T. L. Lauridsen, M. Manca, M. R. Miracle, B. Moss, P. Noges, G. Persson, G. Phillips, R. Portielje, S. Romo, C. L. Schelske, D. Straile, I. Tatrai, E. Willen & M. Winder, 2005. Lake responses to reduced nutrient loading – an analysis of contemporary long-term data from 35 case studies. *Freshwater Biology* 50: 1747-1771.

Johnston, D. W., A. J. Holding & J. E. McCluskie, 1974. Preliminary comparative studies of Denitrification and Methane Production in Loch Leven, Kinross, and other Freshwater Lakes *Proceedings of the Royal Society of Edinburgh, B*, 74: 123-134.

LLAMAG, 1993. Loch Leven Area Management Advisory Group Report, Scottish Natural Heritage, Battleby, Perth, UK.

LLCMP, 1999. Loch Leven Catchment Management Plan: The Report of the Loch Leven Area Management Advisory Group.

May, L. & Carvalho, L. (2010) Maximum growing depth of macrophytes in Loch Leven, Scotland, United Kingdom, in relation to historical changes in estimated phosphorus loading. *Hydrobiologia* 646: 123 – 131.

May, L. L. H. Defew, H. Bennion & A. Kirika, this volume. Historical changes (1905-2005) in external phosphorus loads to Loch Leven, Scotland, UK. *Hydrobiologia* 00: 000-000.

May, L. & B. M. Spears, this volume. A history of scientific research at Loch Leven, Kinross, Scotland. *Hydrobiologia* 00: 000-000.

Moss, B., T. Barker, D. Stephen, A. Williams, D. Balayla, M. Beklioglu & L. Carvalho, 2005. Consequences of reduced nutrient loading on a lake system in a lowland catchment: deviations from the norm? *Freshwater Biology* 50: 1687-1705.

Murphy, J. & J.P. Riley, 1962. A modified single solution method for the determination of phosphate in natural waters. *Analytica Chimica Acta* 27: 31-36.

Paerl, H. W. & J. Huisman, 2008. Blooms like it hot. *Science* 320: 57-58.

Phillips, G., A. Kelly, J. Pitt, R. Sanderson & E. Taylor, 2005. The recovery of a very shallow eutrophic lake, 20 years after the control of effluent derived phosphorus. *Freshwater Biology* 50: 1628–1638.

Reynolds, C. S., 2006. *The Ecology of Phytoplankton*. Cambridge University Press, Cambridge.

Reynolds, C. S. & J. W. G. Lund, 1988. The phytoplankton of an enriched, soft-water lake subject to intermittent hydraulic flushing (Grasmere, English Lake District). *Freshwater Biology* 19: 379-404.

Sas, H., 1989. *Lake restoration by reduction of nutrient loading*. Academia Verlag Richartz GmbH. St. Augustin.

Schindler, D. W., 1977. The evolution of phosphorus limitation in lakes. *Science* 195: 260-262.

Smith, V. H., S. B. Joye & R. W. Howarth, 2006. Eutrophication of freshwater and marine ecosystems. *Limnology and Oceanography* 51: 351-355.

Søndergaard, M., E. Jeppesen, T. Lauridsen, S. C. H. van Nes, R. Roijackers, E. Lammens & R. Portielje, 2007. Lake restoration: successes, failures and long-term effects. *Journal of Applied Ecology* 44: 1095–1105.

Spears, B. M., L. Carvalho, R. Perkins, A. Kirika & D. M. Paterson, 2007a. Sediment P cycling in a large shallow lake: spatio-temporal variation in phosphorus pools and release. *Hydrobiologia* 584: 37-48.

Spears, B. M., L. Carvalho & D. M. Paterson, 2007b. Phosphorus partitioning in a shallow lake: implications for water quality management. *Water and Environment Journal* 21: 47-53.

Spears B. M., L. Carvalho, R. Perkins, A. Kirika & D. M. Paterson, this volume. Long-term variation and regulation of internal phosphorus loading in Loch Leven *Hydrobiologia* 00: 000-000

Spears, B. M. & I. D. Jones, 2010. The long-term (1979-2005) effects of the North Atlantic Oscillation Index on wind-induced wave mixing in Loch Leven (Scotland). *Hydrobiologia* 646: 49-59.

UK TAG, 2008. UK Environmental Standards and Conditions (Phase 2). Final Report (SR1-2007), March 2008, SNIFFER, Edinburgh.

West, G., 1910. A further contribution to a comparative study of the dominant phanerogamic and higher cryptogamic flora of aquatic habitat in Scottish lakes. *Proceedings of the Royal Society of Edinburgh* 30: 65-181.

Wetzel, R. G. & G. E. Likens, 2000. *Limnological Analyses*, Third Edition. Springer, New York.

Whitehead, P. G., R. L. Wilby, R. W. Battarbee, M. Kernan & A. J. Wade, 2009. A review of the potential impacts of climate change on surface water quality. *Hydrological Sciences* 54: 101-123

Winfield, I. J., C. E. Adams, J. D. Armstrong, R. Gardiner, A. Kirika, J. Montgomery, B. M. Spears, D. C. Stewart, J. E. Thorpe & W. Wilson, this volume. Changes in the fish community of Loch Leven: untangling anthropogenic pressures. *Hydrobiologia* 00: 000-000.



## Table

**Table 1** Nonparametric regression test results for seasonal trends in concentrations of Ln soluble reactive phosphorus (SRP), Ln nitrate-N, Ln soluble reactive silicon (SRSi), air temperature, cumulative rainfall, Ln *Daphnia* densities, Ln total phosphorus (TP), Ln chlorophylla and Ln Secchi depth (p-value for Approximate F-test). Values in bold type indicate a significant non-parametric trend from 1968-2007, except Ln *Daphnia* densities (1975-2007)

| Variable | Ln SRP       | Ln Nitrate-N | Ln SRSi      | Air Temp.    | Rainfall     | Ln <i>Daphnia</i> | Ln TP        | Ln chlorophyll | Ln Secchi    |
|----------|--------------|--------------|--------------|--------------|--------------|-------------------|--------------|----------------|--------------|
| Spring   | <b>0.005</b> | 0.139        | <b>0.004</b> | <b>0.004</b> | 0.307        | 0.394             | <b>0.003</b> | <b>0.001</b>   | <b>0.007</b> |
| Summer   | 0.196        | 0.078        | <b>0.004</b> | 0.452        | 0.482        | 0.166             | 0.052        | <b>0.004</b>   | 0.119        |
| Autumn   | 0.127        | 0.577        | 0.701        | <b>0.005</b> | 0.248        | 0.671             | 0.472        | 0.217          | 0.067        |
| Winter   | <b>0.029</b> | 0.359        | <b>0.042</b> | <b>0.029</b> | <b>0.040</b> | 0.253             | 0.306        | <b>0.023</b>   | 0.195        |

## Figure captions

**Fig. 1** Annual mean concentrations of (a) total phosphorus and (b) chlorophyll *a*, and (c) Secchi depth in Loch Leven, 1968-2008, in relation to LLAMAG water quality targets

**Fig. 2** Relationship between annual mean chlorophyll*a* and TP concentrations with quadratic regression fit

**Fig. 3** Seasonality in monthly mean concentrations of (a) soluble reactive phosphorus (SRP), (b) nitrate-nitrogen and (c) soluble reactive silicon (SRSi) in Loch Leven for two decades: 1968-1977 and 1998-2007

**Fig. 4** Trends in seasonal mean air temperature at Loch Leven, 1968-2007; shaded reference band for 'no effect' shows where the curve is expected to lie if there is no evidence of change over time; note that each plot has a different scale on the y-axis

**Fig. 5** Trends in seasonal cumulative rainfall at Loch Leven, 1968-2007; shaded reference band for 'no effect' shows where the curve is expected to lie if there is no evidence of change over time

**Fig. 6** Seasonality in *Daphnia* densities in Loch Leven for two decades: 1988-1997 and 1998-2007

**Fig. 7** Trends in seasonal mean Ln chlorophyll *a* concentrations in Loch Leven, 1968-2007; a shaded reference band for 'no effect' shows where the curve is expected to lie if there is no evidence of change over time

**Fig. 8** Trends in seasonal mean Ln Secchi depth in Loch Leven, 1968-2007; a shaded reference band for 'no effect' shows where the curve is expected to lie if there is no evidence of change over time

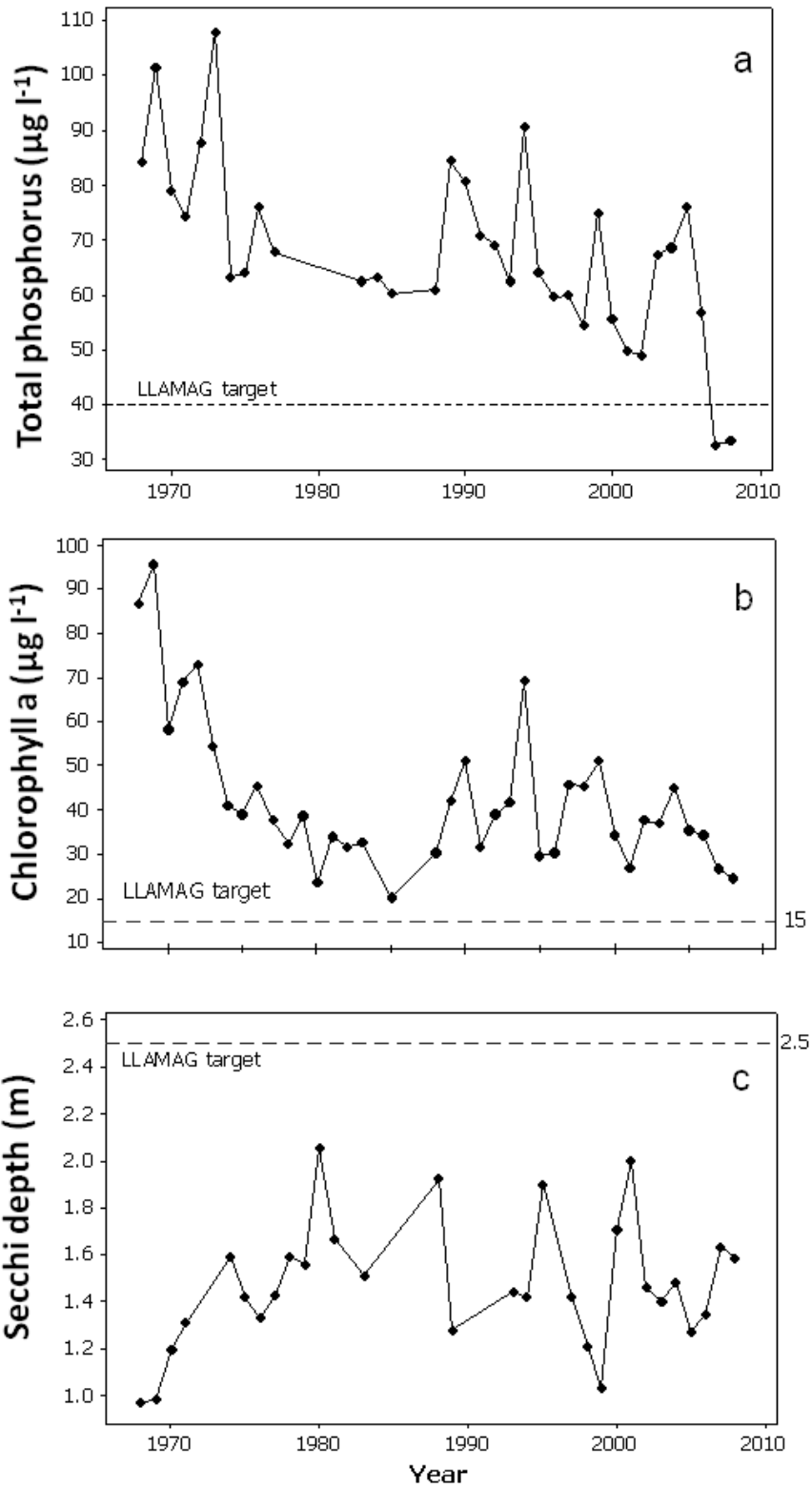


Figure 1

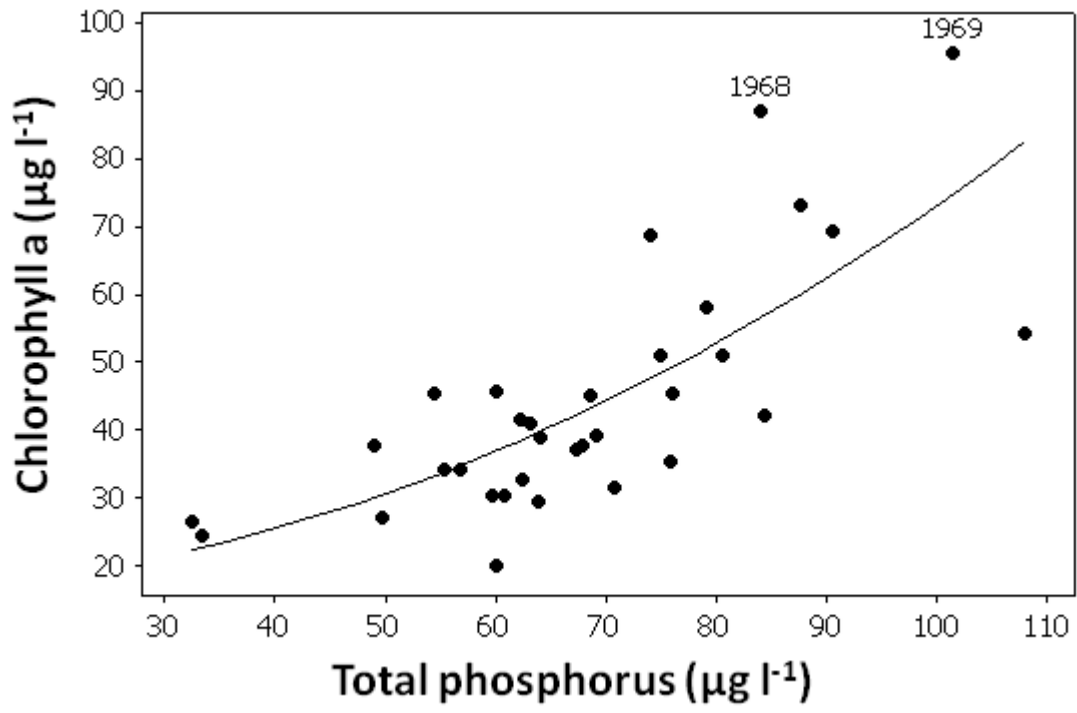


Figure 2.

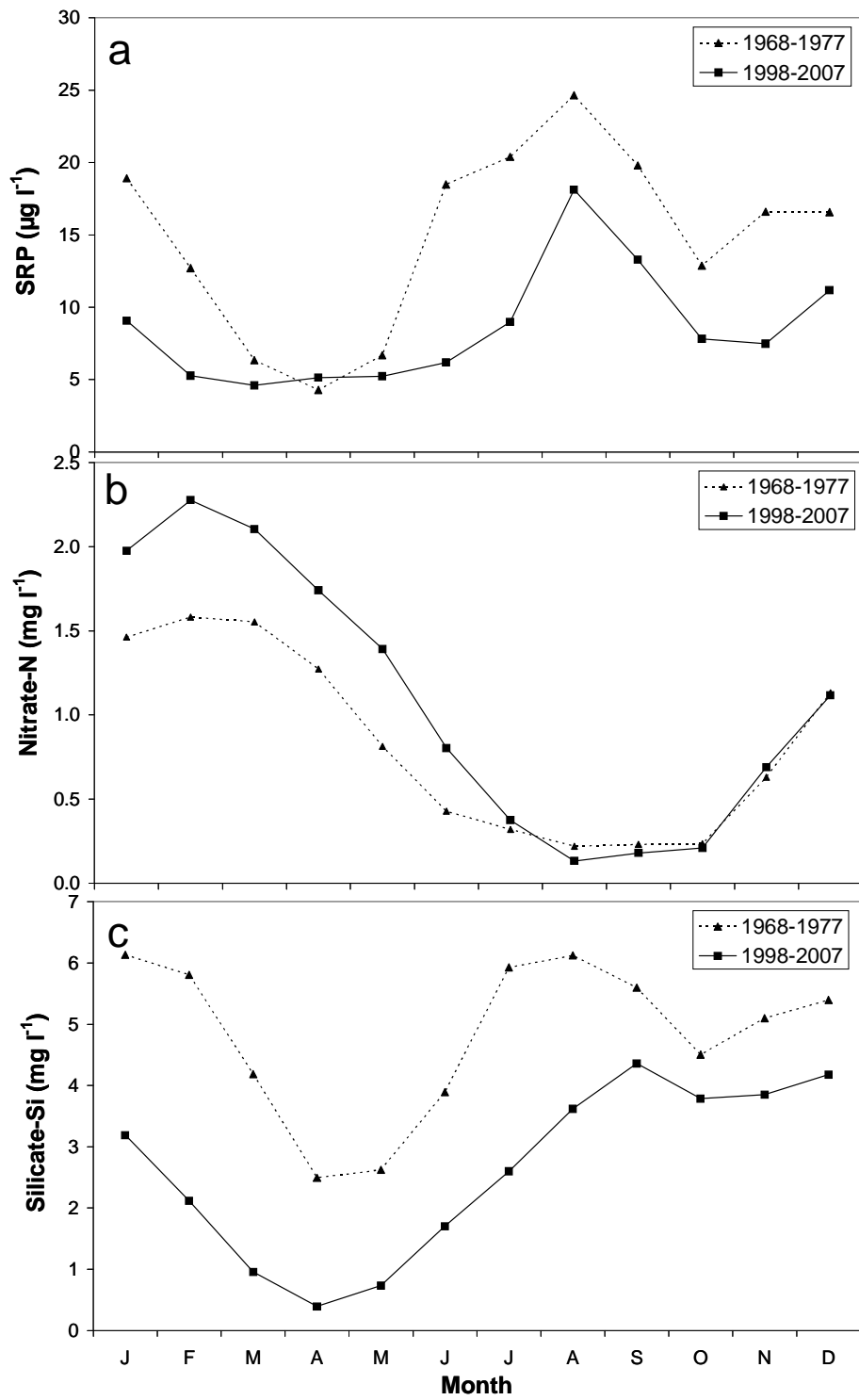


Figure 3.

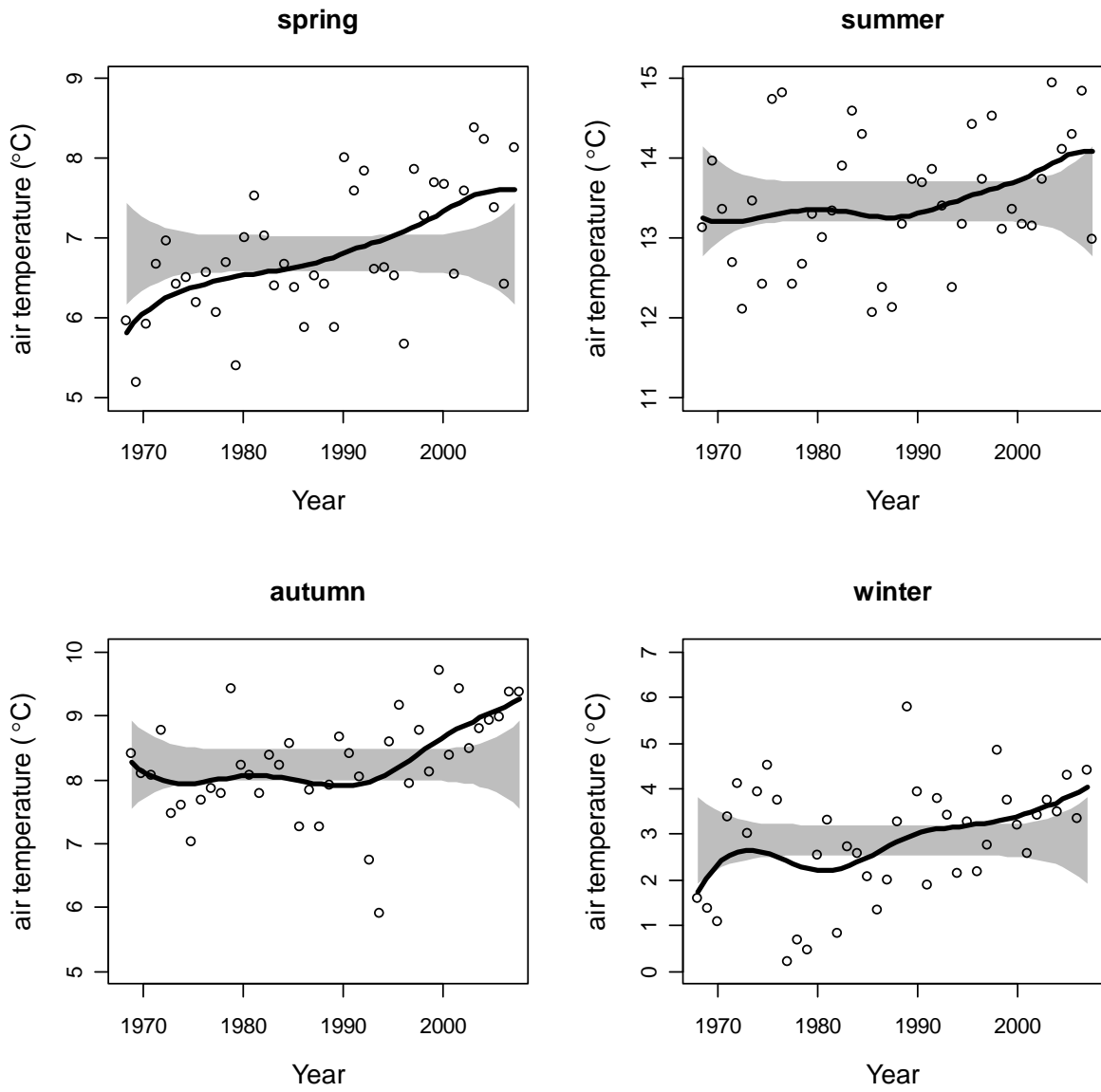


Figure 4.

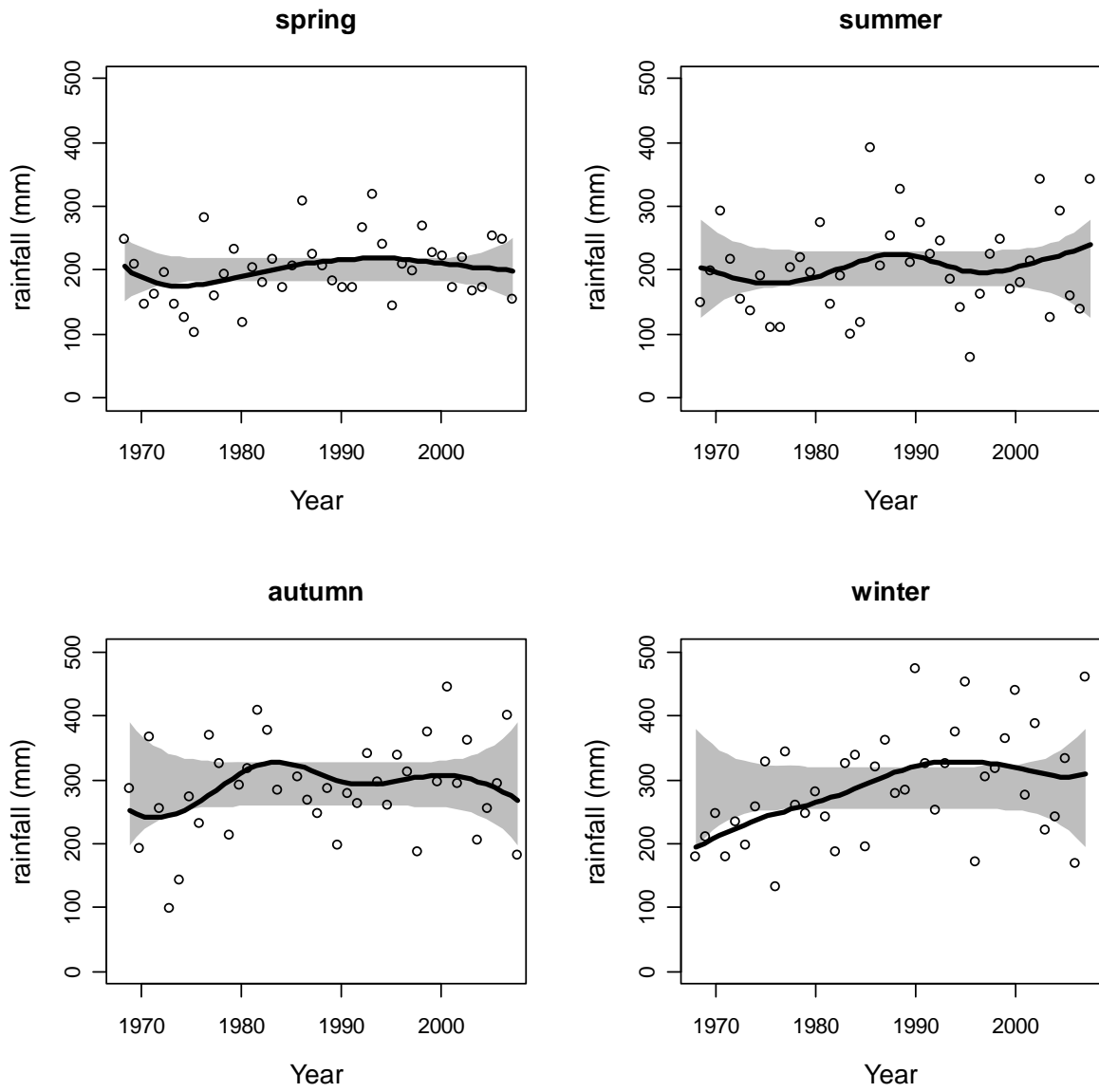


Figure 5.

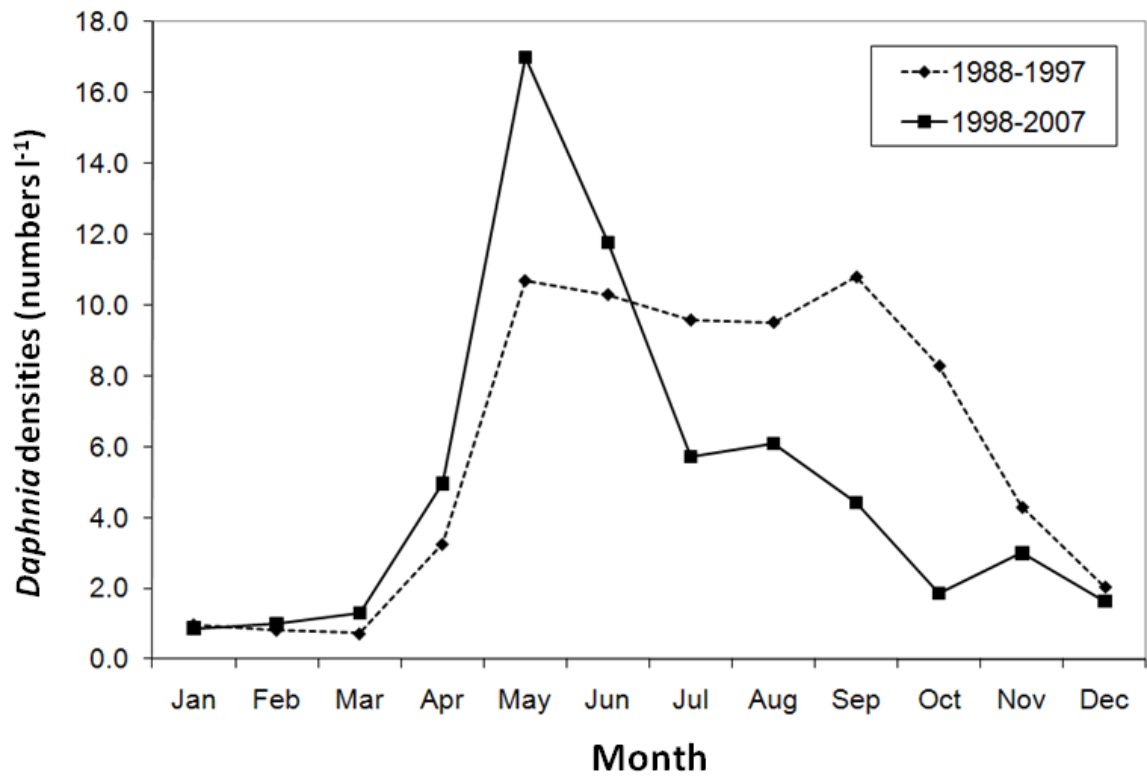


Figure 6.



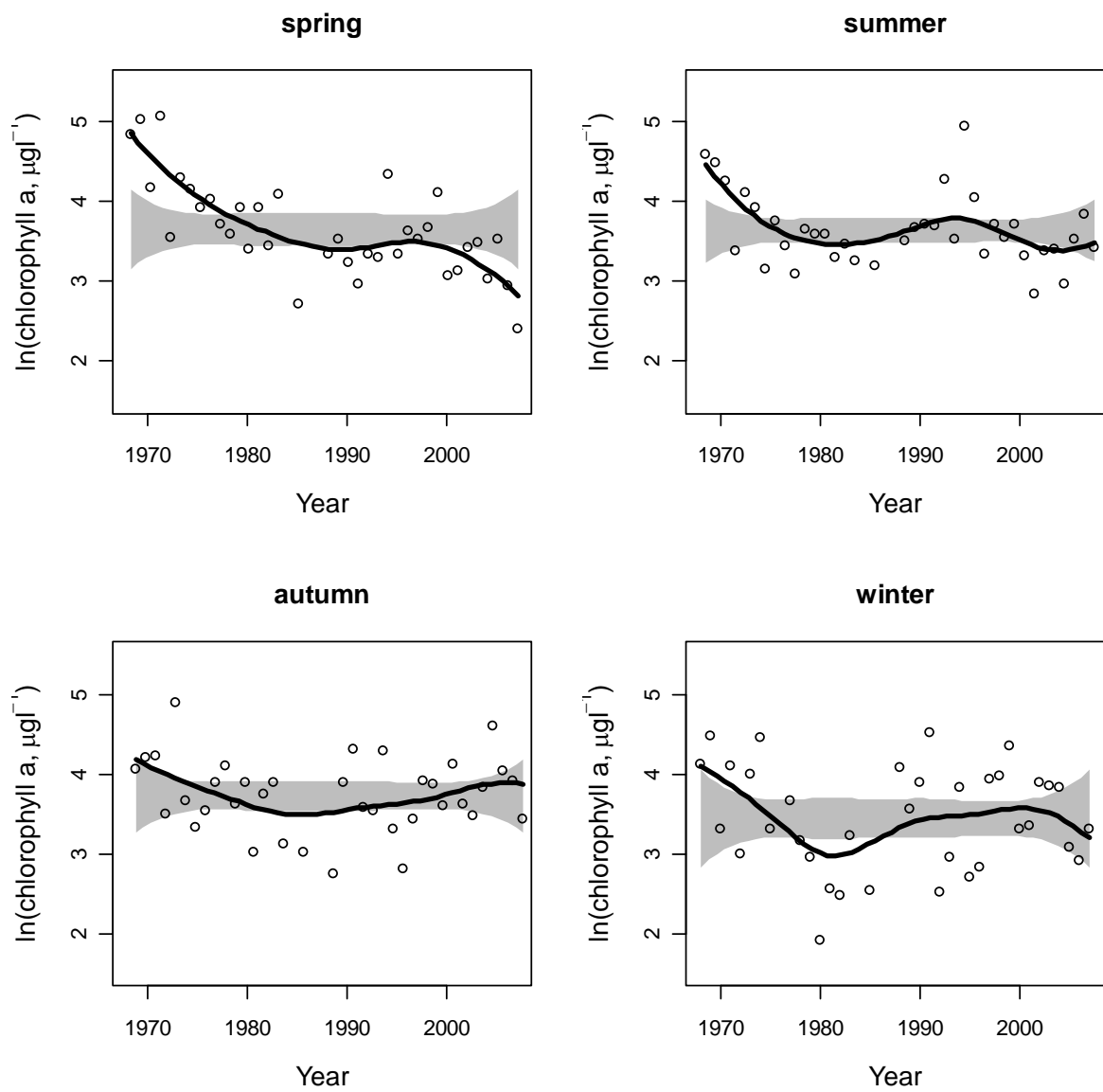


Figure 7

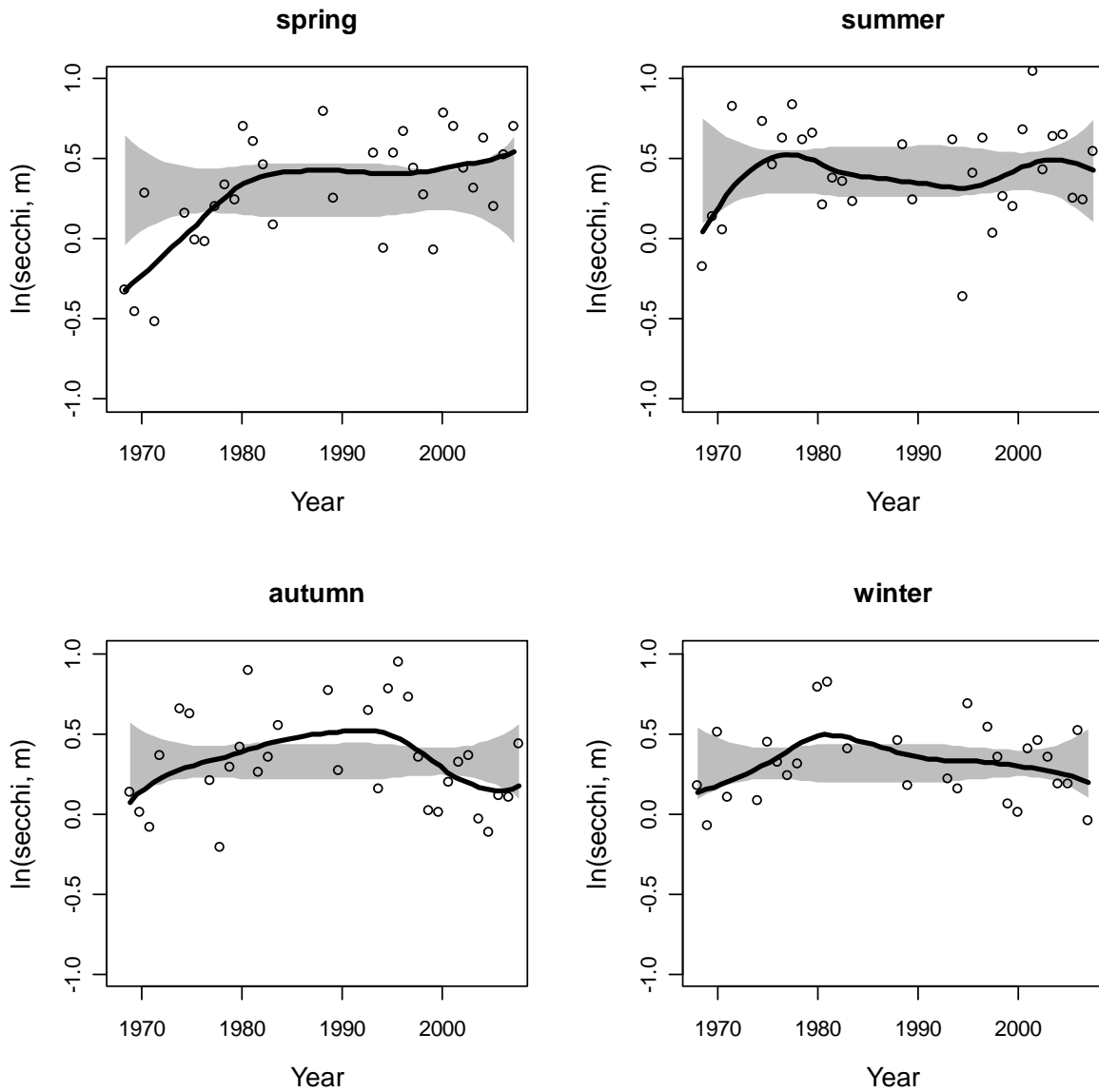


Figure 8.