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Carbon gains, losses, and feedbacks in shallow, eutrophic lakes of phytoplankton and macrophyte dominance

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Soren M. Brothers

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Preface

All parts of this work were conducted at the Leibniz-Institute of Freshwater Ecology and Inland Fisheries, Department of Ecosystem Research, Müggelseedamm 301, 12587, Berlin, Germany. This work was carried out from 15.03.2010 until 26.06.2013 within the framework of the TERRALAC-Project (http://terralac.igb-berlin.de) under the supervision of Dr. Jan Köhler and Dr. Sabine Hilt.

List of Manuscripts

This thesis monograph presents data which are included in the following manuscripts, all of which are either submitted or in press. For all manuscripts my contribution included the experimental design, data collection, data analysis, conception, and writing of the manuscript.

Brothers S.M., Hilt S., Meyer S. and Köhler J. 2013. Plant community structure determines primary productivity in shallow, eutrophic lakes. *Freshwater Biology* doi:10.1111/fwb.12207.

Brothers S.M., Hilt S., Attermeyer K., Grossart H.-P., Kosten S., Lischke B., Mehner T., Meyer N., Scharnweber K. and Köhler J. In press. A regime shift from macrophyte to phytoplankton dominance enhances carbon burial in a shallow, eutrophic lake. *Ecosphere*.

Brothers S.M., Köhler J., Attermeyer K., Grossart H.-P., Meyer N. and Hilt S. A feedback loop links brownification and anoxia in a temperate, shallow lake. Submitted to Limnology and Oceanography.

The following manuscript also includes data from this research.

Scharnweber K., Syväranta J., Hilt S., Brauns M., Vanni M.J., **Brothers S.M.**, Köhler J., Knežević-Jarić J. and Mehner T. Whole-lake experiments demonstrate subsidy of benthic food webs in shallow lakes by terrestrial particulate organic carbon. Under review, Ecology.

Contents

Zusammenfassung

Seen werden zunehmend als wichtige Komponente im globalen Kohlenstoffkreislauf anerkannt. Natürliche Veränderungen und anthropogene Aktivitäten beeinflussen die Struktur der Artengemeinschaft von Seen, was Auswirkungen auf den Transport und Umsatz von Kohlenstoff hat. Diese Arbeit konzentriert sich auf die Beziehung zwischen Kohlenstoffkreislauf und der Gemeinschaftsstruktur der Primärproduzenten in kleinen Flachseen. Diese sind der weltweit häufigste Seentyp und weisen durch ihren im Vergleich zur Fläche großen Umfang eine intensive aquatisch-terrestrische Kopplung auf. In Flachseen treten oft Regimewechsel zwischen Makrophyten- und Phytoplankton-Dominanz auf. Diese können potenziell große Konsequenzen für den regionalen Kohlenstoffkreislauf haben. In dieser Dissertation vergleiche ich einen Klarwassersee mit submersen Makrophyten und einen trüben, Phytoplankton-dominierten See hinsichtlich Verfügbarkeit, Umsatz und Export von organischem und anorganischem Kohlenstoff. Des Weiteren habe ich den Effekt der erhöhten Zufuhr von terrestrischem Kohlenstoff auf den internen Kohlenstoffumsatz untersucht.

Sowohl die Tagesgänge der pelagischen Sauerstoff-Konzentrationen als auch Fluoreszenz-basierte Messungen der Primärproduktion bewiesen, dass die Präsenz von submersen Makrophyten eine höhere jährliche Brutto-Primärproduktion im Vergleich zu einem Phytoplankton-dominierten See mit ähnlichen Nährstoffkonzentrationen ermöglicht. Ein einfaches, auf den empirischen Daten basierendes Model zeigt, dass diese Unterschiede in der Brutto-Primärproduktion typisch sind für moderat eutrophe Seen mit einer mittleren Tiefe von unter 3 bis vier Metern. In diesen Seen leistet die benthische Primärproduktion den Hauptbeitrag zur Primärproduktion des ganzen Sees. Daraus wird ersichtlich, dass Regimewechsel von Makrophyten- zur Phytoplankton-Dominanz in Flachseen die Verfügbarkeit von autochthonem organischem Kohlenstoff für das Nahrungsnetz reduzieren.

Paläolimnologische Analysen in Sedimentkernen beider Seen wiesen darauf hin, dass der Verlust der Makrophyten mit einer vierfachen Zunahme der Kohlenstoff-Speicherraten einhergeht, und somit zu einer großen Veränderung der Dynamik des Kohlenstoffkreislaufs im See führt. Unsere Kohlenstoff-Massenbilanzen zeigen, dass die Erhöhung der Kohlenstoff-Speicherung im Sediment nicht durch die Erhöhung der Primärproduktion oder durch externe Quellen, sondern durch erhöhte der Effizienz der Speicherung begründet war. Dies geht mit einer reduzierten benthischen Mineralisierungsrate und einer erhöhten Calcitfällung einher und führt zu reduzierten Kohlendioxid-Emissionen.

Eine Periode ungewöhnlich hoher Niederschläge mit erhöhten Wasserständen führte im Phytoplankton-dominierten See zu zu einem starken Anstieg der Konzentrationen an

gelöstem organischem Kohlenstoff (DOC) und zu anoxischen Bedingungen. Es wurde postuliert, dass zwischen diesen Prozessen eine positive Rückkopplung besteht. Die hohen Wasserstände und DOC-Konzentrationen reduzierten die Lichtversorgung und damit die Primärproduktion im Benthal und erhöhten die pelagischen Respirationsraten. Dadurch verringerte sich die Sauerstoffverfügbarkeit im Hypolimnion. Die dadurch erzeugten Redox-Verhältnisse führten zu einer Freisetzung großer Mengen an Nährstoffen, DOC und Eisen aus dem Sediment. Die während des gesamten Sommers andauernden anoxischen Verhältnisse in Wassertiefen unter 1 m führten zu einem fast vollständigen Verlust von Fischen und Makroinvertebraten. Zusätzlich wurde der pH-Wert im Pelagial signifikant erniedrigt und die Kohlenstoffdioxid-Emissionen im Vergleich zu früheren Jahren verzehnfacht.

Insgesamt trägt diese Dissertation wesentliche Aspekte zum besseren Verständnis der Bedeutung des Benthals für den Kohlenstoffkreislauf in Flachseen bei. Der Anteil der benthischen Zone an der Primärproduktion in kleinen Flachseen wurde in Relation zur Gesamtproduktion des Systems quantifiziert. Letztlich zeigt diese Arbeit, dass die Gemeinschaftsstruktur der Primärproduzenten eines eutrophen Flachsees die Verfügbarkeit und den Umsatz von Kohlenstoff signifikant beeinflusst. Regimewechsel in Flachseen können durch Änderungen im internen Kohlenstoffkreislauf deren Rolle im globalen Kohlenstoffkreislauf verändern.

Summary

Lakes are increasingly being recognized as an important component of the global carbon cycle, yet anthropogenic activities that alter their community structure may change the way they transport and process carbon. This research focuses on the relationship between carbon cycling and community structure of primary producers in small, shallow lakes, which are the most abundant lake type in the world, and furthermore subject to intense terrestrial-aquatic coupling due to their high perimeter:area ratio. Shifts between macrophyte and phytoplankton dominance are widespread and common in shallow lakes, with potentially large consequences to regional carbon cycling. I thus compared a lake with clear-water conditions and a submerged macrophyte community to a turbid, phytoplankton-dominated lake, describing differences in the availability, processing, and export of organic and inorganic carbon. I furthermore examined the effects of increasing terrestrial carbon inputs on internal carbon cycling processes.

Pelagic diel (24-hour) oxygen curves and independent fluorometric approaches of individual primary producers together indicated that the presence of a submerged macrophyte community facilitated higher annual rates of gross primary production than could be supported in a phytoplankton-dominated lake at similar nutrient concentrations. A simple model constructed from the empirical data suggested that this difference between regime types could be common in moderately eutrophic lakes with mean depths under three to four meters, where benthic primary production is a potentially major contributor to the whole-lake primary production. It thus appears likely that a regime shift from macrophyte to phytoplankton dominance in shallow lakes would typically decrease the quantity of autochthonous organic carbon available to lake food webs.

Sediment core analyses indicated that a regime shift from macrophyte to phytoplankton dominance was associated with a four-fold increase in carbon burial rates, signalling a major change in lake carbon cycling dynamics. Carbon mass balances suggested that increasing carbon burial rates were not due to an increase in primary production or allochthonous loading, but instead were due to a higher carbon burial efficiency (carbon burial / carbon deposition). This, in turn, was associated with diminished benthic mineralization rates and an increase in calcite precipitation, together resulting in lower surface carbon dioxide emissions.

Finally, a period of unusually high precipitation led to rising water levels, resulting in a feedback loop linking increasing concentrations of dissolved organic carbon (DOC) to severely anoxic conditions in the phytoplankton-dominated system. High water levels and

DOC concentrations diminished benthic primary production (via shading) and boosted pelagic respiration rates, diminishing the hypolimnetic oxygen supply. The resulting anoxia created redox conditions which led to a major release of nutrients, DOC, and iron from the sediments. This further transformed the lake metabolism, providing a prolonged summertime anoxia below a water depth of 1 m, and leading to the near-complete loss of fish and macroinvertebrates. Pelagic pH levels also decreased significantly, increasing surface carbon dioxide emissions by an order of magnitude compared to previous years.

Altogether, this thesis adds an important body of knowledge to our understanding of the significance of the benthic zone to carbon cycling in shallow lakes. The contribution of the benthic zone towards whole-lake primary production was quantified, and was identified as an important but vulnerable site for primary production. Benthic mineralization rates were furthermore found to influence carbon burial and surface emission rates, and benthic primary productivity played an important role in determining hypolimnetic oxygen availability, thus controlling the internal sediment loading of nutrients and carbon. This thesis also uniquely demonstrates that the ecological community structure (i.e. stable regime) of a eutrophic, shallow lake can significantly influence carbon availability and processing. By changing carbon cycling pathways, regime shifts in shallow lakes may significantly alter the role of these ecosystems with respect to the global carbon cycle.

1 Introduction

1.1 Relevance of Lakes to the Global Carbon Cycle

The global carbon cycle plays a fundamental role in controlling our planet's climate and productivity, and only recently have we begun to understand that inland waters are a highly important component of this cycle (Cole *et al.*, 2007; Tranvik *et al.*, 2009). It is now believed that less than a third of the carbon transported from terrestrial environments to lakes and streams is exported to the oceans, with the rest being either buried in sediments or mineralized and emitted to the atmosphere as carbon dioxide (CO_2) or methane (CH_4) (Tranvik *et al.*, 2009). Inland waters represent a relatively unstable biome, however, as climate change scenarios predict a significant global redistribution in the regional abundances of lakes (Tranvik *et al.*, 2009). Furthermore, shifts between alternative ecological regimes (for instance, from clear-water macrophyte dominance to turbid phytoplankton dominance) are widespread (Folke *et al.*, 2004, Vermaire *et al.*, 2012), with potential implication for lake carbon cycling. To understand the current and future roles of lakes within the global carbon cycle, an improved understanding of the factors influencing lake carbon cycling is needed. Downing *et al.* (2006) suggest that 99% of the world's lakes are small (under 2.5 km^2), and such lakes are also predicted to be those most severely affected by climate change (Tranvik *et al.*, 2009) while also being highly susceptible to ecological regime shifts (Scheffer *et al.*, 1993a). This thesis therefore explores the carbon cycling characteristics, and their underlying mechanisms, of two shallow lakes in northeastern Germany; one turbid lake dominated by phytoplankton (Kleiner Gollinsee, here referred to as phytoplankton dominated), and another lake which features a substantial submerged macrophyte community and a higher water clarity (Schulzensee, here referred to as macrophyte dominated).

Many basic aspects of carbon cycling in lakes remain poorly understood. For instance, terrestrial-derived (allochthonous) organic carbon is a fundamental component of most lake food webs (e.g., del Giorgio *et al.*, 1999; Cole *et al.*, 2006), whose relative importance generally declines as primary production within a lake increases (e.g., Carpenter *et al.*, 2005). However, the loading of allochthonous organic carbon into many lakes has been increasing in recent decades, as signaled by rising concentrations of dissolved organic carbon (e.g., Clark *et al.*, 2010). The precise mechanisms behind this trend (referred to as "brownification") are poorly understood (Roulet and Moore, 2006), and its effects on lake primary productivity and food webs remain unclear (Klug, 2002). High rates of primary production, in turn, have been associated with lower CO_2 emissions to the atmosphere (Balmer and Downing, 2011) and

elevated carbon burial rates (Heathcote and Downing, 2012), and thus large-scale changes in lake productivity can influence the role of lakes in the global carbon cycle. Blindow *et al.* (2006) found, however, that a eutrophication-linked regime shift from macrophyte to phytoplankton dominance negatively influenced net primary production, indicating a potentially complex link between alternative ecological regimes and lake carbon cycles. Understanding how carbon cycling is related to ecological characteristics is important both on a local scale (for instance, risk assessments for hazardous waste disposal in lakes; Andersson and Sobek, 2006) and a global scale (considering the sensitivity of climate to atmospheric CO_2 and CH_4 concentrations; Tranvik *et al.*, 2009).

The research presented within this thesis adopts a variety of tools and approaches, including fluorometric measurements, paleolimnological analyses, diel (24-hour) oxygen curves, and carbon mass balances to quantify the whole lake carbon cycles of the two study lakes. I especially focused on the metabolic and ecological characteristics which determined the fate of carbon in each system, since little is yet known about the relationship between ecological regime shifts and lake carbon cycling (Tranvik *et al.*, 2009). My primary goals were thus to identify how alternative regimes influenced the annual primary productivity of shallow lakes, and to understand the effects of alternative regimes on the fate of carbon in these lakes, whether as permanent burial in the sediments or as surface carbon emissions. I Furthermore aimed to identify the main processes responsible for an unexpected five-fold increase in dissolved organic carbon (DOC) observed over two years in one of the study lakes, and which led to severely anoxic conditions which prompted the collapse of the higher trophic levels of the food web.

1.2 Controls of Carbon Gains and Losses in Lakes

Organic carbon, a core component of all biological systems and food webs, may be created either by aquatic plants (converted from dissolved CO_2), or from plants which derive their CO_2 from the atmosphere. Organic carbon may thus be autochthonous (produced within a given lake), or allochthonous (fixed from atmospheric CO_2, and subsequently imported to a lake). Whether organic carbon is autochthonous or allochthonous can make a large difference to lake food webs and carbon cycling. Different consumer groups have been widely linked to alternative carbon sources (Cole *et al.*, 2006); for instance, zooplankton communities often favour autochthonous carbon, and benthic macroinvertebrates often favour allochthonous carbon (e.g., Marcarelli *et al.*, 2011). Most lakes in the world are supersaturated with CO_2 relative to the atmosphere (Cole *et al.*, 1994). Although CO_2 emissions are also influenced by

catchment processes (Maberly *et al.*, 2012), high CO_2 concentrations in many lakes are typically associated with allochthonous subsidies to lake food webs (e.g., Pace *et al.*, 2007; Cole and Prairie, 2009). This may be somewhat surprising, however, as allochthonous organic carbon is often more recalcitrant than autochthonous carbon, and also cannot be mineralized as readily as autochthonous carbon under anoxic conditions (Bastviken *et al.*, 2004a). An overabundance of either type of organic carbon can lead to spatial or temporal metabolic imbalances which may result in anoxia, with deleterious effects to species richness (Townsend *et al.*, 1992; Nürnberg, 1996). The structure and functioning of lake wood webs are thus integrally linked to the availability and processing of organic carbon.

As each type of organic carbon is produced separately, each has its own mechanisms influencing its supply to lake food webs. Regarding autochthonous carbon, a generally positive relationship exists between nutrient concentrations and phytoplankton primary production in lakes (Smith, 1979). Increasingly, however, studies have reassessed whether this generalization applies to whole-lake primary productivity, as it may ignore the effect of decreasing benthic production due to light limitation by elevated phytoplankton concentrations (Vadeboncoeur *et al.*, 2001; Vadeboncoeur, *et al.*, 2002; Blindow *et al.*, 2006). This shading effect is especially important in small, shallow lakes, or lakes with low depth ratios, whose benthic zones may be shallow enough to support a major share of a lake's total primary productivity (Vadeboncoeur *et al.*, 2002, 2008).

Allochthonous carbon is typically transported into lakes from the watershed, either through the surface and groundwater flows as DOC and particulate organic carbon (POC), or directly from the vegetation surrounding a lake (for instance, emergent macrophytes and litterfall from overhanging trees). Concerning DOC and POC imports, physical processes such as watershed discharge (Dillon and Molot, 2005; Sadro and Melack, 2012; Heathcote *et al.*, 2013) as well as chemical processes such as iron reduction/oxidation (redox) cycles in the watershed (Knorr, 2013) can both influence a lake's annual allochthonous carbon load. The watershed is also influenced by changes in atmospheric deposition chemistry, with potential implications for lake DOC concentrations even when removed from local anthropogenic influences (e.g., Monteith *et al.*, 2007). Furthermore, large quantities of organic carbon are typically stored in lake sediments, and changes in lake chemistry may prompt an increase in internal carbon loading into lakes as well (Skoog and Arias-Esquivel, 2009). Increases in the internal loading of DOC and nutrients can in turn have positive or negative effects on autochthonous primary production, depending on the quantity of DOC and nutrients loaded, as well as the physiological status of a given phytoplankton community (Klug, 2002). In order

to predict the supply and quality of organic carbon available to a lake food web, a comprehensive understanding of the lake and watershed physical and chemical parameters is thus necessary.

Although the carbon availability to lake consumers is important to questions of food web dynamics, the fate of this carbon, whether exported, buried, or emitted to the atmosphere as CO_2 or CH_4, is more frequently the focus of studies concerned with the role of lakes within the global carbon cycle. As mentioned previously, the majority of carbon which enters most lakes is either buried in a lake's sediments or emitted directly to the atmosphere (Cole *et al.*, 2007). These processes are highly significant to the global transfer and cycling of carbon; lakes and reservoirs are expected to annually bury more than three times more organic carbon than oceans, and emissions to the atmosphere from inland waters are expected to be on the same order of magnitude as emissions from fossil fuel combustion, deforestation, and atmospheric uptake by oceans (Tranvik *et al.*, 2009 and references therein). Although carbon gains and losses are occasionally directly linked (for instance, watershed erosion leading to high carbon burial rates, as described by Heathcote *et al.*, 2013), lake metabolism (the balance between gross primary production and gross respiration rates) often mediates a lake's carbon cycle. Specifically, the balance between gross primary production and gross respiration determines, to a large extent, whether a lake will be a net sink or source of CO_2 with respect to the atmosphere. Furthermore, this metabolic balance of a lake can affect chemical parameters such as pH, which can further influence carbon emission rates by changing the fraction of dissolved inorganic carbon (DIC) that exists as CO_2 (Bade and Cole, 2006; Finlay *et al.*, 2009).

1.3 Influence of Regime Shifts on Shallow Lakes

Scheffer *et al.* (1993a) described a situation whereby the structure of a lake ecosystem could switch rapidly between alternative stable regimes. Specifically, they suggested that submerged macrophytes establish clear-water conditions in shallow lakes by a variety of ecological mechanisms, but that eutrophication could increase turbidity to a point where submerged macrophyte growth is prevented and a new turbid equilibrium is established (Scheffer *et al.*, 1993a). Since each stable regime is self-reinforced, either regime could potentially dominate at intermediate nutrient concentrations. The fundamental concept behind regime shift theory has since expanded considerably to include a broader range of ecosystem types (Folke *et al.*, 2004; Barnosky *et al.*, 2012) and time scales (Hughes *et al.*, 2013) to which it may apply. Even though regime shifts in shallow lakes have been subject to the

longest and most intensive research, their relationship with lake carbon cycling remains poorly defined (Tranvik *et al.*, 2009).

There are several reasons to believe that regime shifts between macrophyte and phytoplankton dominance could strongly influence organic carbon availability. Submerged macrophyte communities can play an important ecosystem function by increasing the available surface area to epiphyton production, while positively influencing the light climate by reducing phytoplankton abundance through a variety of mechanisms (Scheffer *et al.*, 1993a; Hilt and Gross, 2008). It is thus feasible that a regime shift resulting in the loss of submerged macrophytes may lead to major changes in a lake's food web structure and metabolic processes independently of ambient nutrient concentrations. As discussed earlier, the metabolism of a lake is a fundamental factor determining lake carbon cycling, but few studies have linked regime shifts to changes in primary production (e.g., Blindow *et al.*, 2006) and food web structure (e.g., Sand-Jensen *et al.*, 2000). Concerning the relationship between primary production and regime shifts, previous studies have focused on lakes featuring broad differences in nutrient availability (which are frequently, though not necessarily, linked with alternative regimes), thus obscuring the singular importance of differences in community structure. Furthermore, previous studies have adopted a variety of approaches, either excluding certain primary producer groups such as periphyton (Mitchell, 1989) or focusing separately on net (Blindow *et al.*, 2006) or gross (Liboriussen and Jeppesen, 2003) primary production. The conclusions drawn from these studies have thus been inconsistent, and are difficult to harmonize.

Although little is known about the relationship between alternative regimes and primary production in shallow lakes, even less is known about the effect that alternative regimes may have on the fate of carbon in shallow lakes. As with primary production, studies examining lakes across a broad gradient of nutrients have linked high levels of enrichment with increased carbon burial rates (Heathcote and Downing, 2012) and lowered surface CO_2 emissions (e.g., Kosten *et al.*, 2010; Balmer and Downing, 2011). Although the specific importance of regime shifts may partially be captured by such broad-scale studies, it is impossible to exclude the effects of differences in nutrient availability. Given the common occurrence of regime shifts, and the fact that they are predicted to become increasingly widespread (Barnosky *et al.*, 2012), understanding their effects on carbon availability and processing in lakes is essential for predicting the future role of lakes in the global carbon cycle.

1.4 Formulation and Structure of Thesis

An improved understanding of carbon cycling in shallow lakes is necessary to understand regional and global carbon cycles. However, given the ongoing and predicted widespread changes to shallow lake ecosystem structures (via regime shifts) and even global lake distributions from changing precipitation patterns (e.g., Tranvik *et al.*, 2009), it is particularly important that the underlying mechanisms governing lake carbon cycling be defined so that more realistic predictions may be made in future carbon cycling models. This thesis thus investigates whether a regime shift from macrophyte to phytoplankton dominance can alter the availability and processing of carbon in shallow lakes. Rather than a cursory examination of a large number of systems, I chose to approach this topic by thoroughly comparing two similar lakes, so that the mechanisms behind differences in their carbon cycles could be better defined and potentially linked to their ecosystem structure. During the course of this study, a natural, sudden increase in DOC concentrations was observed in one of our study lakes. I chose to include an analysis of this event within the thesis, as it directly represents a potentially widespread phenomenon which has serious implications to lake food webs, and is furthermore intricately linked to the carbon cycling processes already described elsewhere within the thesis.

The primary hypotheses of this thesis are:

(i) The annual whole-lake gross primary production (GPP) of a shallow lake featuring a submerged macrophyte-epiphyton community is greater than in a phytoplankton-dominated system with similar nutrient concentrations.

(ii) A shallow, eutrophic, macrophyte-dominated lake features lower rates of carbon burial than a phytoplankton-dominated lake with similar nutrient concentrations and annual carbon loading rates.

(iii) An observed increase in DOC concentrations and water levels would negatively affect benthic primary production, with consequences to hypolimnetic oxygen availability.

I have addressed each of these hypotheses in three separate manuscripts which are currently either submitted or in press. The methods and results of these manuscripts are here reorganized into a single cohesive document. I furthermore present an overall analysis of the cumulative significance of this research, especially regarding how these findings are relevant to our improved understanding of the role of lakes within the global carbon cycle.

2 Materials and Methods

2.1 Study Sites

Kleiner Gollinsee (53°01'N, 13°35'E, hereafter referred to as Gollinsee) and Schulzensee (53°14'N, 13°16'E) are small, shallow, eutrophic lakes (Table 1) located in a moderately low-lying rural area of northeastern Germany. Schulzensee contains non-rooted submerged macrophytes (primarily *Ceratophyllum submersum* L.) and colony-forming cyanobacteria (*Aphanothece stagnina* (Sprengel) A. Braun), and features a slightly greater water clarity than Gollinsee at similar nutrient concentrations (Table 1). The only aquatic primary producers in Gollinsee are phytoplankton and periphyton (attached algae which grow as epiphyton on macrophyte surfaces or as epipelon on muddy sediments). Neither lake features surface in- or outflows, and both lakes are naturally sheltered, and are thus expected to experience only minor wind-driven resuspension. Both lakes are located in forested watersheds, and are completely encircled by alder trees (*Alnus glutinosa* (L.) Gaertn), a reed belt (*Phragmites australis* (Cav.) Trin. ex Steud.), and stands of floating-leaved water lilies (*Nymphaea alba* L. and *Nuphar lutea* L.). Although the lake surface area occupied by submerged macrophytes is relatively small (20 to 25%), I here refer to Schulzensee as macrophyte dominated following Hilt and Gross (2008), who suggest that this coverage is high enough to influence phytoplankton production, and thus water clarity. A comparison of Secchi disk readings, DOC concentrations, and chlorophyll *a* (chl *a*) concentrations indicated that transparency in our study lakes was much more strongly predicted by phytoplankton chl *a* concentrations (t-test; $r^2 = 0.37$, $P < 0.001$) than DOC ($r^2 = 0.005$, $P = 0.79$). This suggests that these lakes are appropriate for a study of biological controls which influence the dominance of different plant groups and whole-lake GPP. As phytoplankton was the primary biotic factor determining water clarity and thus the GPP of other primary producers in Gollinsee, this lake is here referred to as phytoplankton dominated.

In November 2010, approximately two weeks prior to ice cover, plastic curtains were installed into both lakes, roughly dividing each into equal north and south halves. Maize (*Zea mays (L)*) leaves and stems were added into the southern half of each lake side, as part of a separate study on lake food web processes. The plastic curtains, which sealed the two lake halves from the water surface to the sediments, remained undisturbed for the following years of analysis. For the first year of primary production and carbon cycling analyses (early April 2010 to early April 2011), data from December 2010 to April 2011 are presented for the north (control) side of each lake. As the ice cover period during this winter extended from

December 2010 to mid-March 2011, the impact of the lake division on primary production and carbon cycling during these months was considered to be minimal. During a period of rising water levels from mid 2011 to mid 2012, flooding along the lake shores in Gollinsee influenced both lake halves in a similar fashion, and were considered to be a stronger driving force than the relatively small one-time addition of maize leaves in 2010. Therefore, data presented during this 2011 and 2012 study period in Gollinsee is presented as the mean of both lake halves.

Table 1. General lake characteristics during initial study year (early April 2010 to early April 2011) with standard error of the mean.

	Gollinsee (phytoplankton-dominated)	Schulzensee (macrophyte-dominated)	*P*
Surface area (m^2)	33,000	39,000	-----
Z_{mean} (m)	1.7	2.2	-----
Z_{max} (m)	2.9	4.2	-----
% Littoral area	18	32	-----
Chlorophyll *a* ($\mu g\ L^{-1}$)	23 ± 3 (*n* = 21)	13 ± 3 (*n* = 19)	0.02
$Z_{secchi\ mean}$ (m)	1.4 ± 0.1 (*n* = 17)	1.9 ± 0.1 (*n* = 16)	< 0.001
Light attenuation (m^{-1})	1.2 ± 0.1 (*n* = 17)	0.7 ± 0.1 (*n* = 16)	< 0.001
pH	7.9 ± 0.1 (*n* = 20)	7.6 ± 0.1 (*n* = 20)	0.003
Summer benthic O_2 (%)†	9 ± 8 (*n* = 7)	37 ± 10 (*n* = 5)	0.049
Total phosphorus ($\mu g\ L^{-1}$) *	42 ± 3 (*n* = 20)	34 ± 3 (*n* = 20)	0.07
Soluble reactive phosphorus ($\mu g\ L^{-1}$) *	4.7 ± 0.6 (*n* = 13)	4.4 ± 0.6 (*n* = 13)	0.70
Total nitrogen ($mg\ L^{-1}$) *	1.2 ± 0.14 (*n* = 3)	0.9 ± 0.06 (*n* = 17)	0.07
Dissolved nitrogen ($mg\ L^{-1}$) *	1.0 ± 0.1 (*n* = 15)	0.9 ± 0.1 (*n* = 17)	0.49
Dissolved organic carbon ($mg\ L^{-1}$) *	12.3 ± 0.3 (*n* = 16)	11.3 ± 0.3 (*n* = 18)	0.02
Dissolved inorganic carbon ($mg\ L^{-1}$) *	32.2 ± 0.4 (*n* = 20)	33.6 ± 0.4 (*n* = 20)	0.01

† From June, July, and August vertical profiles.

* Epilimnetic, pelagic means.

2.2 General Sampling and Analysis

Pelagic water samples contained equal parts water from 0.5 m, 1 m, and 2 m at the lake centre. Littoral samples mixed sub-surface water equally from three random locations within the reed belt. Both were taken every two to four weeks throughout the first year of the study period (early April 2010 to early April 2011), with monthly sampling continuing in turbid Gollinsee until July 2012. While littoral samples were always taken from within the reed belt, I here refer to the littoral zone as any lake area with macrophytes (submerged, floating-leaved, or emergent). As the lake area coverage of *C. submersum* overlapped with, and was larger than that of floating-leaved macrophytes, only emergent (reeds) and submerged macrophyte surface areas were used to calculate the total littoral area in Schulzensee (Table 1). Measurements of the concentrations of TP, soluble reactive phosphorus (SRP), total nitrogen (TN), dissolved nitrogen (DN), DIC, and DOC were made separately for the littoral and pelagic zones. Chemical analyses were carried out for all water samples following standard laboratory procedures (DEV, 2009). All statistical tests were made using the computer program JMP (Version 7, SAS Institute), and errors are presented as the standard error of the mean.

Monthly vertical profiles were measured for pelagic oxygen (O_2), temperature, and pH from the water surface to the sediments at 50 cm intervals using a Yellow Springs Instruments (YSI, Xylem Inc., Yellow Springs, OH, USA) monitoring probe. YSI probes were also installed at lake-centre monitoring stations from early May 2010 onwards, at a depth of 1.2 m. These probes recorded temperature, O_2, and pH every 10 minutes during the full study period. Light attenuation was measured across the water column from simultaneous light intensity values recorded by two Underwater Spherical Quantum Sensors (LI-193, LI-COR) fixed vertically, 50 cm apart. Secchi disk readings were used to estimate light attenuation on dates that direct measurements were unavailable. Lake-centre monitoring stations measured global radiation every 10 minutes. Global radiation data from Lake Müggelsee (approximately 100 km to the south) were substituted when data were missing from both study lakes. The availability of photosynthetically active radiation (PAR) at depth z (I_z) was calculated from light attenuation and hourly global radiation data (1 W m^{-2} of global radiation being equivalent to a PAR of 2.12 µmol m^{-2} s^{-1}) using the equation:

$$I_z = I_0 \bullet e^{-\varepsilon \cdot z} \quad (1)$$

where I_0 represents the mean surface irradiance and ε represents light attenuation.

2.3 Gross Primary Production

Gross primary production (GPP), or the amount of carbon fixed by all photoautotrophs within a lake, can be highly heterogeneous (e.g., Van de Bogert *et al.*, 2012), and is often therefore difficult to accurately measure. GPP was thus quantified in both study lakes by two independent and parallel approaches during the first study year (early April 2010 to early April 2011). Diel (24-hour) O_2 curves were analyzed from lake-centre monitoring stations, and compared to the summed individual assessments of GPP for each producer group within each lake. Daily GPP rates were calculated by both approaches, and the measured lake productivity parameters were furthermore used to derive a simple productivity model relating GPP to TP concentrations for lakes featuring alternative stable regimes. Diel O_2 curves were analyzed in phytoplankton-dominated Gollinsee until July 2012 to trace metabolic changes in the water column through the observed period of rising DOC concentrations and water levels.

2.3.1 Macrophytes

The direct exchange of carbon dioxide (CO_2) and O_2 between the aquatic environment and the submerged segments of floating-leaved water lilies or emergent reeds was expected to be minimal (Brix and Schierup, 1990; Smits *et al.*, 1990). For these groups, I therefore calculated only the total carbon content (for later estimates of allochthonous carbon loading), and the underwater surface area (for epiphyton and biofilm bacteria calculations), as described further below. For whole-lake GPP calculations, I included only the submerged macrophyte *C. submersum*. The total surface area occupied by *C. submersum* in Schulzensee was calculated by Geographic Information System (GIS) mapping, using Global Positioning System (GPS) data delineating the habitat boundary. Fixed-volume maximum biomass samples were harvested from four locations and dried at 80°C to a constant dry weight (dw). The plant volume inhabited (PVI) by *C. submersum* was determined by measuring the water depth limits of occurrence at 24 points along the lake periphery during the period of maximum biomass (July 2010). The maximum *C. submersum* biomass was calculated by multiplying PVI by dw m^{-3} and was converted to carbon using total carbon values measured with a vario EL CHNOS Element Analyzer (Elementar Analysensysteme, Hanau, Germany). GPP was calculated by multiplying the summer biomass by a gross production rate-to-harvest ratio of 1.5, determined by Best (1982) for *C. demersum* in a shallow lake in the Netherlands, and was estimated to last for an active growing period of six months of the year (following observations).

2.3.2 Periphyton

The biomass and GPP of periphyton on submerged plastic strips (transparent polypropylene sheets with a slightly textured surface; IBICO, Germany) was considered to be similar to that growing directly on the submerged surfaces of macrophytes (epiphyton) and the benthic surface (epipelon), corrected for a gradient in light availability. This approach has been used previously and is considered valid for eutrophic systems (e.g., Eminson and Moss, 1980; Köhler *et al.*, 2010). Plastic strips were installed in early April 2010 in the open-water and littoral zone of each lake at a depth of 1.2 m, with one end in contact with the sediments to allow access to grazers. Subsamples were harvested monthly during the ice-free period. During the 2011 and 2012 period of rising water levels, plastic strip exposures were only carried out in the pelagic (open water) zone of Gollinsee. In order to provide relatively comparable data to 2010 values, plastic strips were again exposed at a depth of 1.2 m, but were suspended from an anchored buoy (as rising water levels no longer allowed for direct contact with the sediments at this depth in the open water zone).

Large plastic strips (2 cm x 22 cm) were transported in open plastic cylinders in a humid insulated box to a laboratory, where they were brushed and washed with filtered lake water to remove periphyton. The resulting solution was filtered to provide chl *a* concentrations using high-performance liquid chromatography (HPLC, Waters, Millford, MA, USA), following methods in Shatwell *et al.* (2012). Small plastic strips (1 cm x 5 cm) were transported in sealed tubes filled with filtered lake water, and were used for *in vivo* absorption and fluorometric laboratory measurements. Periphyton GPP on the plastic strips was measured using a pulse amplitude modulated fluorometer (Phyto-PAM EDF, Walz, Effeltrich, Germany).

For optimum calculations of periphyton GPP at all times of day and at multiple water depths, light-saturated photosynthesis (P_{max}) and photosynthetic efficiency at low light (α) were adopted, using data from rapid light curves measured by the Phyto-PAM fluorometer which provided values fitted to a model of Eilers and Peeters (1988). Periphyton GPP at varying depths (P_z, µg C L^{-1} h^{-1}) was calculated using the equation of Webb *et al.* (1974):

$$P_z = P_{max} \bullet \text{chl } a \bullet (1 - e^{\wedge}(-\alpha \bullet I_z \bullet P_{max}^{-1})) \quad (2)$$

where epiphyton GPP was calculated at 50% of the mean macrophyte depth, and epipelon GPP was calculated at the mean habitat depth of the littoral and open-water zones. The carbon

assimilation rates for P_{max} and α (C_{assim}, g C g chl *a*$^{-1}$ h^{-1}) were calculated from the formula (adapted from Kromkamp and Forster, 2003):

$$C_{assim} = Y \bullet PAR \bullet 0.0036 \bullet a^* \bullet E \quad (3)$$

where Y is the quantum yield of photosystem II, PAR is the intensity of photosynthetically active radiation (µmol m^{-2} s^{-1}), 0.0036 converts µmol s^{-1} into mol h^{-1}, and a* is the specific absorption of periphyton (m^2 g chl *a*$^{-1}$), calculated as the absorption of photosynthetic pigments (m^{-1}, measured by a Varian spectrophotometer) divided by the HPLC-derived chl *a* concentration (g chl *a* m^{-3}). E is the efficiency of carbon assimilation (0.766 g C mol^{-1}), calculated as the slope between the electron transport rates and carbon assimilation rates from ^{14}C measurements in Lake Müggelsee (J. Köhler, unpublished data). Kromkamp and Forster (2003) explicitly include the ratio between Photosystems I and II in their productivity calculations, yet here this ratio is contained in E. Y was calculated using the formula (from Genty *et al.*, 1989):

$$Y = (F_m - F_I) \bullet F_m^{-1} \quad (4)$$

where F_m is the fluorescence induced by saturating light flashes, and F_I is the fluorescence induced by incrementally lower light intensities. As detritus was expected to influence our measurements of the absorption of photosynthetic pigments (a_p), these were corrected using a previously established relationship from Lake Müggelsee (r^2 = 0.95, *n* = 174; J. Köhler, unpublished data):

$$a_p = 0.647 \bullet a_{t,676} + 0.527 \bullet a_{t,626} - 0.215 \bullet a_{t,438} + 0.096 \quad (5)$$

where $a_{t,\lambda}$ is the measured absorption (m^{-1}) at wavelength λ.

Measurements were made at room temperature (24°C), and P_{max} rates were thus corrected to lake temperatures using a previously established relationship from Lake Müggelsee (r^2 = 0.73, *n* = 148; J. Köhler, unpublished data):

$$P_{max\,T} = P_{max} \bullet (0.409 + 0.1487 \bullet T) \bullet (0.409 + 0.1487 \bullet 24)^{-1} \quad (6)$$

where T is water temperature (°C). An exponential regression of this dataset provides a Q_{10} value of 1.88, which is comparable to the commonly adopted Q_{10} of 2 for phytoplankton production (e.g., Gilbert *et al.*, 2000).

Epiphyton GPP was calculated from the periphyton production in the littoral zone of each lake, and production rates were applied to the underwater surface area of macrophytes. To calculate the available surface area for epiphyton GPP, direct measurements of stem diameter, mean depth of occurrence, and plant density (per m^2) were made for *P. australis* and *N. alba*. Total lake coverage estimates were available from direct measurements taken in 2007 (A. Becker, unpublished data), and GPS measurements in 2010, and the mean value of both estimates was applied. A mean available surface area of 427 cm^2 g dw^{-1} was considered for *C. submersum* (Armstrong *et al.*, 2003). For daily available surface area estimates throughout the year, a quadratic growth curve was applied, using the total measured surface area as a mid-summer maximum, and measured dead or dormant fractions of *P. australis* (75% in Gollinsee; 48% in Schulzensee) and *C. submersum* (10%) as a winter minimum (considered December 1st 2010 to March 31st 2011). Linear relationships were applied between direct measurements.

Epipelon (benthic periphyton) GPP was calculated from the periphyton production in the littoral and open-water zones of each lake. As well-established natural benthic periphyton communities were observed in both lakes throughout the year, monthly production measurements were applied to the periphyton biomass of long-exposure plastic strips for calculating annual production curves. Over-wintering strips under ice could only be retrieved from Schulzensee, but minor differences before and after ice cover suggested that long-exposure strips had likely reached maximum biomasses in both lakes.

2.3.3 Phytoplankton

Phytoplankton GPP was calculated from monthly measurements of chl *a*, fluorescence, and light attenuation using a parallel approach to that described for periphyton. Mean whole-lake chl *a* concentrations were applied, calculated as the weighted mean of measured pelagic and littoral chl *a* concentrations according to the percentage each habitat occupied in each lake. Direct spectrophotometer measurements were made, but bleaching to correct for detritus occasionally produced unreliable absorption (a_p) values. The minimum normalized fluorescence of dark-adapted phytoplankton at red excitation ($F_{0,\ 658}$) had previously been found to provide good estimates of a_p for phytoplankton in Lake Müggelsee ($r^2 = 0.90$, $n = 176$; J. Köhler, unpublished data), and phytoplankton a_p was thus calculated as:

$$a_p = (0.00150 \bullet F_{0,658} + 0.082) \bullet \text{chl } a^{-1} \qquad (7)$$

where $F_{0,658}$ was measured by a Phyto-PAM fluorometer, and chl *a* was measured by HPLC (mg m^{-3}).

The fluorescence of water samples was measured within three hours of sampling using the modular version of a Phyto-PAM fluorometer equipped with a 10 mm cuvette, and water was filtered for HPLC analyses. Production calculations from fluorometric measurements followed the same methods described for periphyton. Phytoplankton GPP was calculated for each 10 cm layer of the water column, applying Equation 2. Each measurement was multiplied by the estimated water volume at a specific depth, and the sum of these measurements was used to calculate daily whole-lake phytoplankton production.

2.3.4 Cyanobacteria

The primary production of the colony-forming cyanobacteria (*A. stagnina*) was determined by another researcher within the same project (S. Meyer, unpublished data), and is here applied to the whole-lake calculated GPP rates. *A. stagnina* were observed at the littoral sediments and water surface, and only in macrophyte-dominated Schulzensee. The GPP of individual colonies was measured using O_2 production data from *in situ* glass bottle incubations and core exposure experiments on five dates (spring to summer 2011). For core exposures, opaque (n = 11) and clear (n = 13) replicates of sediment cores were installed at the lake's mean depth for four hour periods. For glass bottle exposures, single colonies were inserted into 50 mL transparent and opaque glass flasks filled with filtered lake water (0.7 µm), and were incubated for four hours at depths of 0 m, 1 m, 2 m, and 3 m. The gross respiration rates of *A. stagnina* were calculated using the O_2 curves from opaque cores and bottles, and were subtracted from net production rates in transparent cores and bottles to calculate GPP. Daily GPP rates were calculated following Equation 2, as per periphyton production. P_{max} and α values were obtained from the measured relationship between O_2 production and light intensity, and light availability was considered for sediment depths between 1.5 and 3 m, assuming a 20% coverage within that zone (following observations). As colonies were observed at both the benthic environment and occasionally the surface waters, the mean of core and glass bottle GPP values was adopted. Daily rates of *A. stagnina* GPP were calculated for the 80 day period within which experiments were carried out, and mean

rates were extended over the entire nine month ice-free period of the year for whole-lake annual GPP calculations.

2.3.5 Diel Oxygen Curve

Daily GPP rates were calculated using diel O_2 curves provided by YSI probes. Gross nighttime respiration rates were calculated as the mean change in O_2 (per 10 minutes) from dusk until dawn, and were subtracted from net production rates calculated by the same methods for the following day to provide GPP. Although lake-centre diel O_2 curves were expected to capture some metabolic activity from the benthic and littoral zones, it has been established that this approach is highly spatially sensitive (Van de Bogert *et al.*, 2012), and we thus here considered that these data may contain a strong pelagic bias. As with other studies, variations in dissolved O_2 due to physical factors (e.g., water mixing) and a heterogeneous distribution of primary production in the lakes provided occasionally unreliable diel curves (Coloso *et al.*, 2008). These were excluded from our analyses, as the distribution of false negative values was unevenly distributed, and thus did not appear to reflect random patterns in water mixing (Staehr *et al.*, 2010, and further discussed in section 4.1).

Diel O_2 curves were corrected for atmospheric O_2 fluxes following Gelda and Effler (2002), using lake-centre wind speed data recorded every 10 minutes by a meteo multiprobe (ecoTech, Bonn, Germany). Fluxes were further adjusted for periods of stratification, when surface O_2 concentrations from profiles differed from values provided by installed probes. As compartmental fluorescence-based calculations of GPP could not be made during the winter ice-cover period from December 1st 2010 to March 15th 2011 due to the highly variable light climate related to changes in snow and ice thickness, winter O_2 curves were adopted for the full-year GPP estimates of each lake. Production values are expressed in carbon units using a respiratory quotient of one. Statistical tests were made using JMP (Version 7, SAS Institute).

2.4 Gross Respiration

Whole-lake gross respiration rates were estimated for individual groups in both lakes during the initial study year. This was done to provide some information concerning the annual net primary production of each lake (defined as gross primary production minus plant respiration), and was also necessary for the ecosystem carbon budget constructed for each lake (described in section 2.5). Daily gross respiration rates were furthermore calculated from diel O_2 curves in Gollinsee until July 2013 (following methods described above for GPP),

though as these were suspected of providing a spatial pelagic bias (Van de Bogert *et al.*, 2012), they were thus not adopted for whole-lake respiration estimates.

2.4.1 Plants

As plant respiration rates were not directly measured in this study (except in the case of *A. stagnina*), I derived first-order estimates of plant community respiration rates by joining biomass and production data with observed literature relationships for separate plant groups. When available, maximum literature estimates were applied so as to standardize any error between plant group respiration rates, and also to define the maximum significance that plant respiration may have played with respect to other (secondary) respiration groups.

For phytoplankton, I considered that a maximum of 40% of phytoplankton GPP may have been lost to respiration, based on the results of Platt *et al.* (1991). Similarly, a maximum respiration estimate of 60% GPP was adopted for *C. submersum* (Best, 1982 and references therein). Liboriussen and Jeppesen (2006) present the relationship between periphyton biomass and respiration rates at two different times of the year from plastic strip exposures which were similar to our own methodological approach. Slightly more accurate estimates of periphyton respiration rates were thus derived by applying the relationship observed by Liboriussen and Jeppesen (2006) in July to the measured periphyton biomass values from March to August in our study lakes, and their September values to my measured biomasses from September to February. As with GPP, respiration rates for *A. stagnina* colonies were measured directly by O_2 curves using *in situ* core exposures and glass bottle experiments (described above), adjusting daily respiration values to daily water temperature fluctuations based on the measured relationship between water temperature and O_2 consumption rates.

2.4.2 Bacteria

Bacterial respiration rates were estimated from bacterial production values which were measured by another subproject within the same research group (K. Attermeyer, unpublished data). A common bacterial growth efficiency of 30% was considered for bacteria in both lakes, which is typical for eutrophic lakes (e.g., Biddanda *et al.*, 2001). Bacterial production (BP) was measured separately for different groups, following procedures detailed in Attermeyer *et al.* (in press). Briefly, L-^{14}C-leucine was incorporated into the protein fraction following the protocols of Simon and Azam (1989; water) and Buesing and Gessner (2003; sediments and biofilm). Water samples (5 mL) were incubated with L-^{14}C-leucine (Hartmann Analytic, Braunschweig, Germany; specific activity 306 mCi mmol^{-1}) to a final concentration

of 80 nmol L^{-1}. Formaldehyde (4% final concentration) was added to the controls before the incubation, and after one hour to all samples. Samples were filtered onto a 0.2 µm cellulose nitrate filter (Whatman, Dassel, Germany) and incubated in 5% trichloroacetic acid (TCA) for five minutes. Next, filters were washed twice with sterile filtered lake water and once with 50% ethanol. Each filter was transferred into 20 mL scintillation vials with 500 µL ethyl acetate to dissolve the filter for 15 minutes, after which 10 mL of scintillation cocktail (Ultima GoldTM, PerkinElmer Inc.) were added. The next day, disintegrations per minute (dpm) were counted on a liquid scintillation analyzer (TriCarb 2810 TR, PerkinElmer Inc., Illinois, USA).

Sediment and biofilm BP were measured from surface (1 cm) sediment samples and plastic strip exposures used for measuring periphyton production, respectively. BP was determined at *in situ* temperatures (± 2°C). L-^{14}C-leucine was diluted with unlabelled L-leucine (Merck, Darmstadt, Germany) to achieve higher tracer concentrations. 30 µmol L^{-1} (final concentration) was determined to be the saturating concentration for the sediments of these lakes. TCA was used to stop the blanks before leucine addition, and after one hour to stop the incubation of the samples (5% final concentration). Samples were then sonicated for one minute at five to six Watts (Branson Sonifier 150, Connecticut, USA) and subsequently processed with multiple washing steps following Buesing and Gessner (2003). 250 µL of the alkaline extract were placed into a 20 mL scintillation vial and 5 mL of a scintillation cocktail (Ultima Gold XR, PerkinElmer Inc.) were added. The next day, disintegrations per minute (dpm) were counted on a liquid scintillation analyzer (TriCarb 2810 TR, PerkinElmer Inc., Illinois, USA). Net disintegrations per minute were converted to pmol L^{-1} d^{-1} according to Simon and Azam (1989), applying an isotope dilution factor of two (Kirchman, 1993). The conversion from volume (L) to gram dry weight (g dw) for bacterial production was carried out following standard dry weight (dw) determination at 105°C. Areal production rates for biofilm bacteria were applied to the submerged surface area of macrophytes (as described previously for epiphyton GPP calculations) for whole-lake estimates.

2.4.3 Zooplankton

Zooplankton respiration rates were estimated from zooplankton biomass measurements (B. Lischke, S. Schmidt-Halewicz, unpublished data) using a biomass-to-respiration conversion factor of 0.115 g C g C^{-1} d^{-1} (Andersson and Kumblad, 2006 and references therein). Zooplankton samples were taken monthly during ice-free periods from April 2010 to April 2011, from the littoral and pelagic zones of each lake. A 40 L mixed

epilimnetic water sample was used to provide a 50 mL sub-sample which was immediately fixed with acidified Lugol's solution (Hoehn *et al.*, 1998) to stain the ciliates. The remaining water was filtered through a 55 µm mesh, and these crustacean samples were fixed with 4% sugar formalin (Haney and Hall, 1973). Samples were counted at the genus or species level, and volume (ciliates and rotifers) or size (crustaceans) was measured at the LimSa Gewässerbüro (Konstanz, Germany). Regressions were used to calculate the individual carbon content based on volume or size. Specifically, Telesh *et al.* (1998) was used for rotifers, Müller and Geller (1993) for ciliates, and Dumont *et al.* (1975) for crustaceans. A carbon content of 50% dry weight (dw) was assumed (Gaedke, 1992 and references therein).

2.4.4 Macroinvertebrates

Macroinvertebrate respiration was estimated from macroinvertebrate biomass measurements (J. Diekmann, submitted), using biomass-to-respiration conversion factors for different macroinvertebrate groups (classified by feeding type; Andersson and Kumblad, 2006 and references therein). Sampling was carried out on eight occasions from April to November 2011. As detailed estimates were unavailable for 2010, respiration rates were estimated from 2011 biomass measurements. Samples were collected from different habitat zones (eulittoral zone: 0 to 1 m depth, sublittoral zone: 1 to 2 m depth, and profundal zone: greater than 2 m depth) following a transect from the lakeshore. As no macroinvertebrates could be found in the profundal zones, further analyses were restricted to the littoral zones. A 0.6 m^2 area was sampled using a kick net (250 µm mesh size) and the substrate was fixed in ethanol. Samples were transferred to the laboratory where individuals could be picked from the samples. Species were determined to the lowest possible taxonomic division and wet weight (ww) was obtained for each sampling occasion. Analyses focused on the most abundant taxonomic groups. Literature values were used to correct for the effects of weight loss due to preservation in ethanol (Leuven *et al.*, 1985; González *et al.*, 2002; von Schiller and Solimini, 2005; Wetzel *et al.*, 2005). To convert to dw, measured ww:dw ratios were applied, and a carbon content of 45% dw was adopted (Peters, 1983; Wetzel, 2001). The ash-free dry weight of gastropods was calculated from species-specific traits (body length, shell width or shell height) measured for individuals from three sampling occasions (April, June, and November 2011), and applying independent regressions (M. Mährlein, unpublished data).

2.4.5 Fish

Fish respiration was estimated from fish biomass using a biomass-to-respiration conversion factor of 0.033 g C g C^{-1} d^{-1} (Andersson and Kumblad, 2006 and references therein). Fish biomass was quantified by Wanke (2011), as part of another subproject within the same research group. In October 2010 and 2011, standardized fishing campaigns were conducted using Nordic multi-mesh gillnets and electrofishing techniques. Eight gillnets were set perpendicular to the shore line from dusk until dawn. Sampling by electrofishing was conducted by applying 15 dips for 15 seconds at each of six randomly chosen locations. Biomass caught per unit effort (BPUE, g ww net $^{-1}$ h^{-1}) was calculated for each campaign. BPUE between the years differed significantly (Mann Whitney *U*, Gollinsee: $U_{16} = 64.00$, $P = 0.015$; Schulzensee: $U_{16} = 48.00$, $P = 0.002$), likely due to a severe fish kill that occurred in both lakes as a consequence of a long and cold winter from 2009 to 2010. High abundances of young-of-the-year planktivorous fish occurred in both lakes during 2010, but decreased in 2011. Biomasses were converted to carbon units assuming that ww was 25% dw (Brey *et al.*, 2010), and that dw was 45% carbon (Peters, 1983; Wetzel, 2001).

To estimate the total fish biomass of each lake in 2010, more detailed biomass estimates from 2011 were applied, adjusting for the proportional differences observed in standardized sampling campaigns between years. Fish abundance was estimated in October 2011 using a mark-recapture approach. During five consecutive days, fish were caught using an electrofishing device, anesthetized with clove oil, and measured. Fish weight was estimated using our own length-mass regression. Coded wire tags (Northwest Marine Technology, Inc., USA) were inserted into the snout region to tag the fish. After the first day of tagging, all caught fish were visually inspected for tags and further checked using magnetic detectors. The number of recaptured fish was recorded. To estimate population abundances, a Schnabel multiple-census approach was adopted, adjusted by Chapman (Ricker, 1975):

$$N = [\sum(Ct \bullet Mt)] \bullet (R + 1)^{-1} \quad (8)$$

where N is the estimate of the total population abundance, Ct is the number of fish captured during time (t), Mt is the number of marked fish captured during time (t) and R is the total number of fish recaptured during the same period. A Poisson variable was used for 95% confidence limits of abundance estimates, as listed in Ricker (1975).

To obtain fish biomass (g ww per lake), fish abundances were multiplied by the geometric mean of the wet weight of all tagged fish. Rough estimates were applied for the

biomass of scarce hybrid species, whose low numbers did not allow for an abundance estimate from mark-recapture techniques. Similarly, it was not possible to obtain mark-recapture abundance estimates for sunbleak (*Leucaspius delineatus*, Heckel), as the small body size of this fish species made tagging impossible. Therefore, the proportion of biomass associated with sunbleak was applied from the total biomass measured from prior samplings.

2.5 Carbon Balances

The carbon mass balance here adopted considers that the quantity of carbon entering each lake in one year (C_{in_M}) equals the quantity of carbon loss in the same year (C_{out_M}). Carbon burial in lake sediments (measured by dated sediment cores) is thus considered a carbon loss. I adapted the methods of Andersson and Sobek (2006) for carbon mass balances and ecosystem budgets to our smaller lakes. I thus defined a carbon mass balance as:

$$DOC_{in} + DIC_{in} + OC_{litter} + DOC_{wet} + OC_{mac} = DOC_{out} + DIC_{out} + C_{emission} + C_{sed} \quad (9)$$

with DOC_{in} and DIC_{in} representing the groundwater input of DOC and DIC. OC_{litter} is the carbon input from tree litterfall, DOC_{wet} (estimated as 1 g C m^{-2} yr^{-1} from Andersson and Sobek, 2006) is the DOC input from precipitation, and OC_{mac} is the carbon input by floating-leaved and emergent macrophytes. DOC_{out} and DIC_{out} represent the losses of DOC and DIC by groundwater, $C_{emission}$ represents the net carbon losses to the atmosphere (as CO_2), and C_{sed} represents carbon burial in lake sediments. All values are presented in g C m^{-2} yr^{-1}.

The carbon ecosystem budget, also adapted from Andersson and Sobek (2006), assumes that the total quantity of organic carbon gained within a lake over the course of a year (OC_{in_E}) is equivalent to the total quantity of organic carbon processed or lost over the same time period (OC_{out_E}). I thus define the ecosystem carbon budget as:

$$DOC_{in} + OC_{litter} + DOC_{wet} + GPP = DOC_{out} + C_{photo} + C_{sed} + R \quad (10)$$

with GPP representing annual gross primary production. C_{photo} represents the organic carbon loss by photo-oxidation and R represents ecosystem respiration. Values are presented in g C m^{-2} yr^{-1}. Photo-oxidation was estimated to be 13.1 g C m^{-2} yr^{-1}, from a lake with a comparable Secchi depth to these study lakes (Granéli *et al.*, 1996).

2.5.1 Groundwater

Groundwater carbon import and export rates were measured by N. Meyer as part of another subproject within the same research group. Data from sixteen piezometer wells in the vicinity of each lake were used to determine groundwater flow directions (S. Rudnick, unpublished data). Groundwater tables were compared to changes in lake water levels, precipitation (recorded continuously at each lake), and estimates of evapotranspiration, providing monthly estimates of the quantitative gain and loss of groundwater at each lake. Two separate wells (up to five meters deep) were installed in the groundwater flow path entering each lake, four to six meters from the lake shores. Groundwater samples in these wells were extracted from two to three meters below the soil surface for carbon (DOC and DIC) analyses. These data were joined to total groundwater import and export flow rates to calculate the total carbon gains and losses by groundwater.

2.5.2 Litter Loading

Any loaded organic carbon produced using CO_2 from outside the aquatic environment is here considered allochthonous. This included leaves from trees (OC_{litter}) as well as floating-leaved (*N. lutea* and *N. alba*) and emergent (*P. australis*) macrophytes. OC_{litter} was calculated from four floating leaf traps (5 m x 1 m) installed along the shore of each lake for a full year beginning July 2011. For floating-leaved macrophytes, plant density was recorded per square meter, and the total lake coverage area was provided by calculations for epiphyton GPP (as described previously). To calculate the carbon contribution of *P. australis*, reeds growing within and directly beyond the lake shore were included to account for loading during periods of high water levels or by leaching into the shoreline sediments and groundwater. Detailed measurements of reed area and density per m^2 were made along the periphery of each lake. Maximum (mid-July) biomass estimates involved twenty random samples of floating-leaved and emergent macrophytes. Macrophytes were cut at the sediment surface, dried at 60°C for two days, and weighed. The mean carbon content of water lilies (38.3 ± 0.6%, both lakes combined) was measured by a vario EL CHNOS Element Analyzer, and mean values for reeds (45.6 ± 1%) were applied from Mille-Lindblom *et al.* (2006). It was assumed that the maximum quantity of living organic carbon in emergent and floating-leaved macrophytes was equivalent to the annual quantity of carbon loaded into the aquatic environment by these groups.

2.5.3 Carbon Burial

Sediment cores (65 and 95 cm in length in Gollinsee and Schulzensee, respectively) were retrieved with Uwitec corers (9 cm diameter, Mondsee, Austria) from the open-water zone of each lake, at a location roughly halfway between each lake's centre and shoreline. As sedimentation rates are often greatest at the deepest point of a lake (e.g., Petterson *et al.*, 1993), these coring locations were chosen to reduce any systematic spatial bias in sedimentation rates. However, due to the similarity between maximum and mean depths (Table 1), the lack of surface in- or outflows, and the small size of both lakes, significant or systematic variations in sediment burial rates between lake sites were considered unlikely.

Sediment cores were sliced at each 1 cm depth, and sediment materials were stored in plastic cups sealed with Parafilm (M) to avoid moisture loss. Samples remained in a cool (~ 10°C), dark location until processing. Sediments were analyzed by Flett Research laboratories (Winnipeg, Canada) for ^{210}Pb, ^{137}Cs, and ^{226}Ra isotope signals to determine sedimentation rates within the past 150 years. Separate cores were taken from proximate locations within each lake for determining loss-on-ignition (LOI) at 450ºC for two hours (for organic carbon) and 900ºC (for $CaCO_3$, or calcite), as well as direct organic and total carbon measurements by a vario EL CHNOS Element Analyzer. Organic carbon was calculated as 50% LOI at 450ºC (Håkanson and Jansson, 1983). The burial rates of organic carbon, total carbon, and calcite were calculated as the product of the total sedimentation rate at a given depth (from dating) and the fraction which each element or compound constituted at the equivalent depth.

Two transparent sediment traps were installed at the center of each lake to measure sediment deposition rates. Traps were stationed at the deepest point of each lake to minimize errors from resuspension (Bloesch and Uehlinger, 1986). Each trap was carefully installed at a depth at which the bottom of the trap was within approximately 30 cm of Z_{max} in order to reduce any direct disturbance of the sediment surface during installation. Wind-driven resuspension was expected to be generally low, however, as both lakes were located in landscape depressions and surrounded by trees. Deposited material was collected biweekly throughout the ice-free period, and was immediately transported to the laboratory for filtration. The total carbon content of filters was measured by a CHNOS Element Analyzer. Following Sobek *et al.* (2009), the carbon burial efficiency of each lake was calculated as the carbon burial rate (from sediment core dating) divided by the carbon deposition rate (from sediment traps).

2.5.4 Carbon Emissions

Surface-to-air CO_2 fluxes were calculated throughout the study year by joining surface pCO_2 concentrations to pH and temperature profiles, using lake-centre wind speed data recorded by ultrasound every 10 minutes by a meteo multiprobe (ecoTech, Bonn, Germany). CO_2 emission rates were calculated following Cole and Caraco (1998), adjusting for chemical enhancement following Bade and Cole (2006), and references therein. The concentration of pCO_2 in surface waters was calculated from DIC concentrations, pH, and temperature, adjusting for the concentration of calcium ions ($CaCO_3^0$, $CaHCO_3^+$, and $CaOH^+$) following Gelbrecht *et al.* (1998), and references therein. Conservative pCO_2 concentrations were calculated for each lake by accounting for a possible measured pH bias of 0.2 from DOC effects (Herczeg *et al.*, 1985; Cole *et al.*, 1994). Although methane (CH_4) emissions can be an important source of greenhouse gases released by lakes to the atmosphere, their contribution to the mass transfer of carbon is generally considered to be minor (e.g., Tranvik *et al.*, 2009). As an initial investigation of sediment core exposures in these lakes further confirmed that the benthic CH_4 losses were significantly lower than CO_2 losses (D. Zak, unpublished data), CH_4 emissions were not included in this analysis. Reeds may also channel CO_2 directly between the sediments and the atmosphere (Brix *et al.*, 1996), yet I here considered this process to be external to the aquatic lake environment, and thus excluded it from carbon emission estimates.

2.6 Primary Productivity Model

To expand the applicability of these results across a wider range of nutrient availability, productivity measurements from these study lakes were used to produce a conceptual model describing GPP as a function of total TP availability in the water column at alternative plant community structures. For practical purposes, the TP gradient presented may be considered the springtime ambient TP concentration in a lake prior to partitioning by separate primary producer groups. Model parameter values are provided in Table 2.

A trade-off was considered to occur between TP assimilation by planktonic (TP_p) and benthic ($TP_b = 1 - TP_p$) primary producers. This approach simplified the complex interactions between primary producer groups, presenting only the outcome of competitive interactions. It does not, for instance, consider more specific parameters such as light fluctuation variables (e.g., spectral composition), although important in eutrophic systems (Schubert and Forster, 1997). As Hill functions have previously been found to provide suitable descriptions of the feedbacks between phytoplankton and macrophytes (Scheffer, 1990; Scheffer *et al.*, 1993b),

such an approach was adopted. The partitioning of TP_p between phytoplankton and macrophytes was thus calculated as:

$$TP_p = (TP_m - TP_0) \bullet TP^n \bullet (TP^n + k_p^n)^{-1} + TP_0 \qquad (11)$$

where TP_0 and TP_m represent the initial and maximum phytoplankton shares of the phosphorus pool, respectively. For lakes without submerged macrophytes, these were set to 0.5 and 1, respectively. For lakes with submerged macrophytes, a smaller share of TP was considered to be sequestered by phytoplankton, and these values were thus set to 0.2 and 0.9. A common power coefficient of 3 was applied (e.g., Scheffer *et al.*, 1993b; van Nes *et al.*, 2003), and the half-saturation concentration of TP (k_p) was set to 14 mg m^{-3} following Behrendt and Opitz (1996).

Phytoplankton biomass (as chl *a*) was described as a function of TP_p by a Droop-type model, following Köhler *et al.* (2000):

$$\text{chl } a = TP_p \bullet (TP_p \bullet (q_0 \bullet q_{max}^{-1}) + k_P) \bullet (q_0 \bullet (k_p + TP_p))^{-1} \qquad (12)$$

and periphyton biomass (chl *a*) was calculated according to TP_b and light intensity:

$$\text{chl } a = TP_b \bullet (TP_b \bullet (q_0 \bullet q_{max}^{-1}) + k_P) \bullet (q_0 \bullet (k_p + TP_b))^{-1} \bullet I_z \bullet (I_z + k_I)^{-1} \qquad (13)$$

where q_0 and q_{max} are the minimum and maximum cell quota (from Behrendt and Opitz, 1996), k_I is the half-saturating light intensity (from Köhler *et al.*, 2010), and I_z is the light intensity at depth z (applying lake mean depth for epipelon and 50% mean depth for epiphyton and submerged macrophytes). Algal primary production was estimated from these modeled biomasses along with mean photosynthesis parameters from measured values and light availability. I_z was adopted for periphyton production (Eq. 1), while the mean PAR intensity at a mixed-water depth (I_{mz}) was applied for phytoplankton, calculated from mean surface irradiance (I_0), light attenuation (ε) and depth (z), following the equation:

$$I_{mz} = I_0 \bullet e\text{^}(-\varepsilon \bullet z) \bullet (\varepsilon \bullet z)^{-1} \qquad (14)$$

with light attenuation (ε) being dependent upon phytoplankton biomass, the specific absorption of phytoplankton (a^*), and non-algal light attenuation (ε_0):

$\varepsilon = a^* \bullet \text{chl } a_p + \varepsilon_0$ (15)

Table 2. Productivity model parameters.

	Definition	Phytoplankton	Periphyton	Submerged Macrophytes
P_{max} (g C g chl a^{-1} d^{-1})	Maximum production	25 [1]	35 [1]	-----
α (g C g chl a mol^{-1} m^{-2})	Specific efficiency of production	3 [1]	5 [1]	-----
a* (m^2 g chl a^{-1})	Specific absorption of chl a	18.3 [1]	-----	-----
ε_0 (m^{-1})	Background attenuation	0.61 [1]	-----	-----
I_0 (mol m^{-2} d^{-1})	Mean PAR at water surface	19 [1]	-----	-----
Chl a_{max} (g chl a m^{-2})	Maximum biomass	-----	-----	2.1 [2]
n	Power coefficient	-----	-----	3 [3]
k_p (mg P m^{-3})	Half-saturation TP for chl a	14 [4]	14 [4]	50 [5]
k_I (mol m^{-2} d^{-1})	Half-saturation I for chl a	-----	2 [2]	4.7 [2]
q_0 (g P g chl a^{-1})	Minimum cell quota	0.28 [4]	0.28 [4]	-----
q_{max} (g P g chl a^{-1})	Maximum cell quota	1.4 [4]	1.4 [4]	-----

Data from [1] present study, [2] Köhler *et al.* (2010), [3] van Nes *et al.* (2003), [4] Behrendt and Opitz (1996), [5] Jeppesen *et al.* (1990)

For submerged macrophytes, biomass (chl *a*) was calculated as:

$\text{chl } a = \text{chla}_{max} \bullet TP_b \bullet (TP_b + k_p)^{-1} \bullet (1 - e^{\wedge}(-\alpha \bullet I_{sm} \bullet \text{chla}_{max}^{-1}))$ (16)

where chla_{max} is the maximum biomass of submerged macrophytes (g chl a m^{-3}) at light and nutrient saturation and α is the initial slope of the biomass-light model (from Köhler *et al.*,

2010). The surface area available to epiphyton communities was considered to be 427 cm^2 g dw^{-1} (mean for *C. demersum* from Armstrong *et al.*, 2003) and 166 g dw g chl a^{-1} was applied, adapted from Pokorný and Rejmánková (1983) and Osmond *et al.* (1981). Self-shading by submerged macrophytes (I_{sm}) was calculated following Equation 6 in van Nes *et al.* (2003). Submerged macrophyte GPP was calculated from the modeled biomass of *C. submersum* following Best (1982).

2.7 Brownification Analysis

During the period of rising water levels and DOC concentrations in Gollinsee (2011 to 2012), multiple abiotic and biotic parameters in this lake were examined in order to identify the mechanisms responsible for increasing DOC concentrations, as well as their relationship to metabolic responses within the lake. Following procedures outlined for the initial study year, pelagic chl *a*, DOC, DIC, iron (Fe), and nutrient (TP, SRP, dissolved inorganic and organic nitrogen) concentrations were measured upon each sampling campaign. Sampling campaigns were carried out every four weeks from April 2011 to March 2012, and then again in June and July 2012. Dissolved organic nitrogen (DON) was calculated as the difference between total nitrogen (TN) and dissolved inorganic nitrogen (DIN). Fe concentrations were measured using an ICP-OES analyzer with an iCAP 6000-Duo (Thermo Fisher Scientific, Waltham, MA, USA). Furthermore, as high DOC concentrations have been known to increase thermal stratification in shallow lakes (Fee *et al.*, 1996; Houser, 2006), temperature loggers (Thermistor, USA) were suspended from buoys along depth intervals of 0.5 m from the surface to the sediments to track changes in water temperature. Each logger took continuous (every 30 s) measurements of water temperature. Temperature loggers were installed in 2011 from May to November, and in 2012 from June to November. To track metabolic changes, diel O_2 curves, periphyton growth, bacterial production, and surface CO_2 emissions were also examined during this period, following methods described for the initial study year.

To identify the compartmental origin of DOC in Gollinsee lake water, three-dimensional fluorescence excitation-emission matrices were produced. Independent fluorophores were identified by N. Meyer (unpublished data) using a parallel factor analysis (PARAFAC) following Stedmon *et al.* (2003), with a thirteen-component model according to Cory and McKnight (2005). For comparison with surface water samples from the lake centre, the fluorescence of DOC was also measured within the flooded reed and alder belt (sampled in November and December 2011 and January, July, September, October, and December 2012) and in the groundwater near the lake (in August and September 2012, taken from two

wells located four to six meters from the lake shore, with groundwater located two to three meters below ground level). Pore water samples from the adjacent degraded peatlands were measured in September and December 2012. Pore water from one meter deep in the peatlands was collected by suction cups (n = 2) and dialysis "peeper" pore water samplers (n = 9). Peatland pore water samples were taken from locations near the limit of the lake-flooded area, 4 to 10 cm below the water surface. Following the nomenclature of Cory and McKnight (2005), Strohmeier *et al.* (2013) classified component 1 (C1) as typical of wetland soils, and component 12 (an oxidized quinone, Q3) as typical of groundwater samples, and PARAFAC analyses for Gollinsee thus focused on these factors.

3 Results

3.1 Lake Conditions

Over the course of the initial study year, there were no statistically significant differences between study lakes with regards to nutrient (TP, SRP, TN, DN) concentrations (Table 1). One high SRP outlier in Gollinsee was removed from analyses as it could not be explained by natural conditions or methodological error, although this did not alter the statistical significance of SRP differences between study lakes. Mean chl *a* concentrations were highest in phytoplankton-dominated Gollinsee, and light transmission was lower (Table 1), suggesting that the desired conditions for our study (comparing two lakes with alternative stable regimes at similar nutrient concentrations) were reasonably well met. Although pH values were generally within the same range in both lakes (7.6 to 7.9), mean values were higher in Gollinsee than Schulzensee (Table 1).

In Gollinsee, the littoral zone consisted of *P. australis* (15% of the total lake area) and *N. alba* (3% of the lake area, Table 1). These corresponded to maximum epiphyton-available surface areas of 1400 m^2 on *P. australis* and 1500 m^2 on *N. alba*. In Schulzensee, the littoral zone consisted of *P. australis* (10% of the lake area), *N. alba* (12% of the lake area), and *C. submersum* (22% of the lake area, or 8% of the lake volume, Table 1). These corresponded to maximum epiphyton-available surface areas of 1500 m^2 on *P. australis*, 7700 m^2 on *N. alba*, and 5600 m^2 on *C. submersum*.

3.2 Gross Primary Production

Measured periphyton biomasses on long-exposure littoral plastic strips were only slightly higher in macrophyte-dominated Schulzensee (7.6 ± 1.3 µg chl *a* cm^{-2}) than in phytoplankton-dominated Gollinsee (5.0 ± 1.3 µg chl *a* cm^{-2}; t-test, $n = 3$, $P = 0.23$). Alternatively, long-exposure biomasses on open-water strips were slightly lower in macrophyte-dominated Schulzensee (5.6 ± 2.6 µg chl *a* cm^{-2}) than in Gollinsee (7.9 ± 2.6 µg chl *a* cm^{-2}; $n = 3$, $P = 0.56$). A significantly higher full-year epiphyton GPP was thus calculated for macrophyte-dominated Schulzensee (Table 3; t-test, $n = 365$, $P < 0.0001$), but no significant difference in epipelon GPP was identified between the lakes (Table 3; $P = 0.50$). Differences in total periphyton GPP between lakes were found to be most pronounced during summer months (June to August), when a higher light attenuation in Gollinsee diminished benthic epipelon GPP, and a greater littoral surface area in Schulzensee boosted epiphyton production (Fig. 1A). Detritus correction factors provided mean specific absorption

values of 19 ± 3 m^2 g chl a^{-1} in Gollinsee and 10 ± 3 m^2 g chl a^{-1} in Schulzensee, within the range to be expected for algae from the literature (Tilzer, 1983 and references therein).

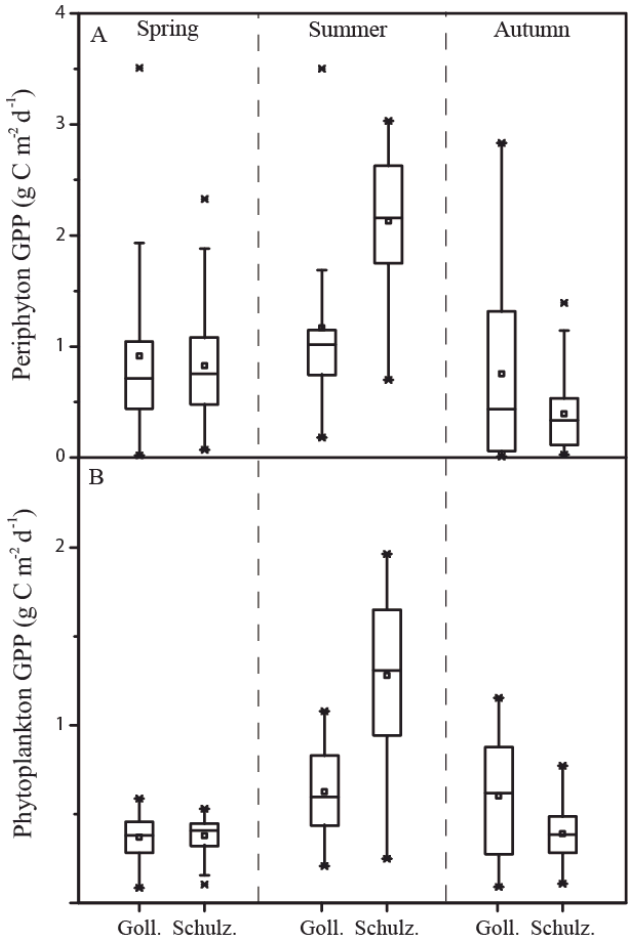

Figure 1**.** Seasonal comparison of A) periphyton and B) phytoplankton GPP between lakes (g C m^{-2} d^{-1}). Boxes represent the upper quartile, median, and lower quartile, and whiskers represent the 5th and 95th percentiles. Central squares represent the mean, and crosses designate minimum and maximum values. Goll. represents Gollinsee, and Schulz. represents Schulzensee.

Pelagic chl *a* concentrations in phytoplankton-dominated Gollinsee were significantly higher than those in macrophyte-dominated Schulzensee (Table 1). Despite this, a higher mean depth in Schulzensee provided roughly 20% higher depth-integrated annual phytoplankton GPP rates in the macrophyte-dominated lake (Table 3; P = 0.0006), with the difference between systems being greatest during summer months (Fig. 1B). Detritus correction factors for phytoplankton absorption provided mean specific absorption values of 12 ± 1 m^2 g chl a^{-1} in Gollinsee and 17 ± 1 m^2 g chl a^{-1} in Schulzensee, which were 20 to 30% lower than direct measurements without detritus corrections, and similar to literature values

(Tilzer, 1983 and references therein). *C. submersum* and *A. stagnina*, the two primary producers which occurred only in Schulzensee, accounted for 8% of the total estimated GPP in this lake (approximately 4% each; Table 3). The mean maximum biomass measured for *C. submersum* was 316 ± 97 g dw m^{-3} (n = 4). The mean GPP of *A. stagnina* from core exposures (11 ± 0.3 g C m^{-2} yr^{-1}) was lower than that from glass bottle experiments (34 ± 1 g C m^{-2} yr^{-1}), which was attributed to the greater amount of light-exposed surface area for floating *A. stagnina* colonies.

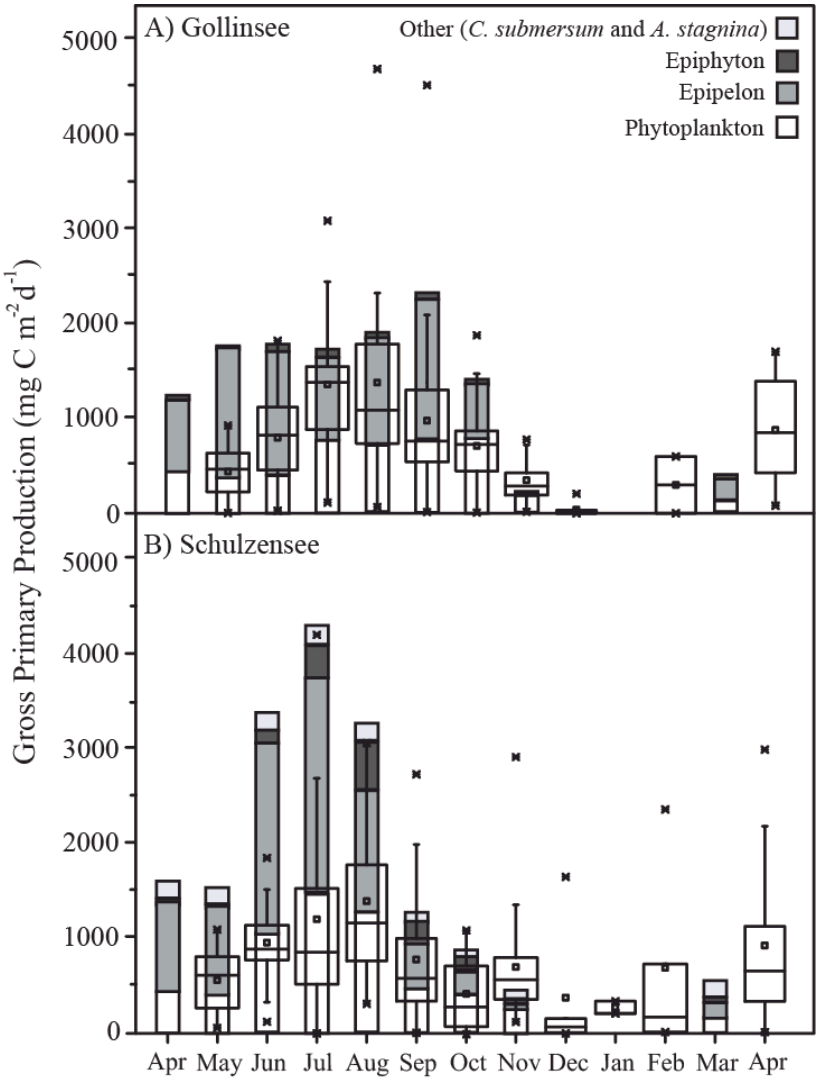

Figure 2. Monthly GPP (mg C m^{-2} d^{-1}) in A) Gollinsee and B) Schulzensee. Boxplots present O_2 curve-derived GPP, with boxes representing the upper quartile, median, and lower quartile, and whiskers representing the 5th and 95th percentiles. Central squares represent the mean, and crosses designate minimum and maximum values. Columns present compartmental GPP calculations. One high outlier (7160 mg C m^{-2} d^{-1}) is excluded from Schulzensee in February as it occurred during ice break, when fluxes may have been poorly quantified.

Whole-lake annual GPP rates were 40% higher in macrophyte-dominated Schulzensee (586 ± 23 g C m^{-2} yr^{-1}) than in phytoplankton-dominated Gollinsee (408 ± 23 g C m^{-2} yr^{-1}; t-test, $n = 365$, $P < 0.0001$). Most of this observed difference was due to the contribution of the submerged macrophyte-epiphyton complex and *A. stagnina* in Schulzensee. Summer GPP measurements from diel O_2 curves (approximately 1400 mg C m^{-2} d^{-1} in both lakes) were comparable to the whole-lake summertime GPP rates independently calculated in phytoplankton-dominated Gollinsee (1600 to 1900 mg C m^{-2} d^{-1}, Fig. 2A), but significantly lower than the summertime GPP rates calculated for macrophyte-dominated Schulzensee (3600 to 4400 mg C m^{-2} d^{-1}, Fig. 2B). Instead, diel O_2 curves in Schulzensee appeared to better represent calculated phytoplankton GPP (Fig. 2B). Winter GPP measured by O_2 curves was significantly higher in Schulzensee (900 ± 200 mg C m^{-2} d^{-1}) than in Gollinsee (100 ± 200 g C m^{-2} d^{-1}; t-test, $P = 0.004$).

To better compare approaches, a more detailed analysis of diel O_2 curves and compartmental GPP was carried out for both lakes for the first five days of July (Fig. 3) and September (Fig. 4). For these dates, positive GPP rates from diel O_2 curves appeared to provide an accurate representation of whole-lake and phytoplankton GPP in Gollinsee and Schulzensee, respectively. Although compartmental GPP calculations showed relatively steady daily GPP rates during this period, a noisy O_2 signal resulted in only three of the five dates from diel O_2 curves reflecting this. Summertime O_2 curves in Schulzensee, however, displayed a steady rhythm which closely matched daytime length (Fig. 3B). Diel O_2 curves in Schulzensee thus provided no negative GPP values during this period, and the mean GPP of phytoplankton calculated by the fluorometric approach (2.0 ± 0.2 g O_2 m^{-3} d^{-1}) did not differ significantly from O_2 curve-derived GPP rates (1.8 ± 0.2 g O_2 m^{-3} d^{-1}; $P = 0.48$). In September, relatively irregular O_2 curves were observed in both lakes (Fig. 4). This is especially evident in Gollinsee's September diel O_2 curves (Fig. 4A), when maximum O_2 concentrations regularly occurred overnight, providing frequent negative GPP rates despite an apparent net ecosystem autotrophy. The mean of GPP rates derived from positive curves in Schulzensee (0.7 ± 0.1 g O_2 m^{-3} d^{-1}), however, again closely matched phytoplankton GPP (0.8 ± 0.1 g O_2 m^{-3} d^{-1}) (Fig. 4B). The GPP rate predicted by Schulzensee's diel O_2 curves if negative values were included would be much lower (0.2 ± 0.2 g O_2 m^{-3} d^{-1}).

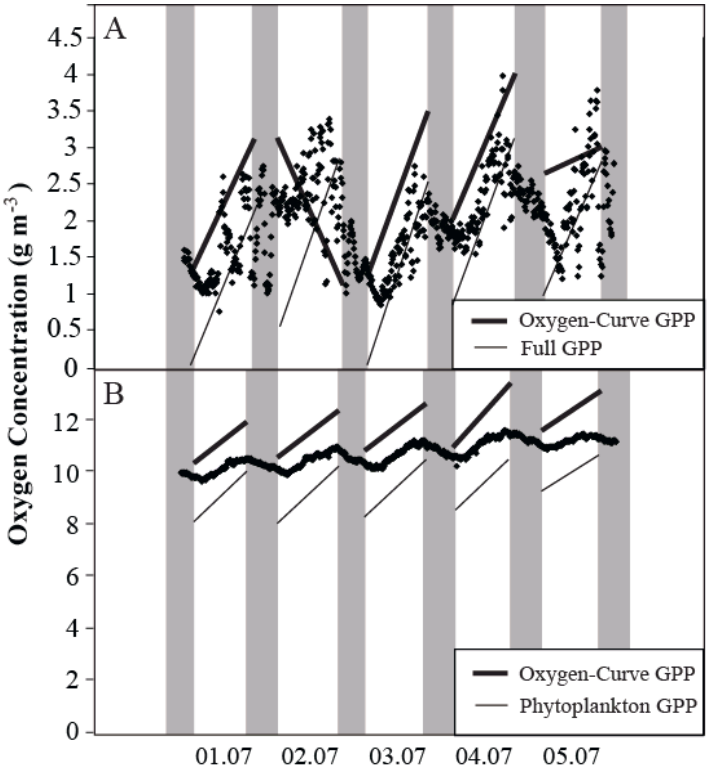

Figure 3. Oxygen curves from 1 July to 5 July, 2010, showing day (clear) and night (shaded) periods for A) Gollinsee and B) Schulzensee.

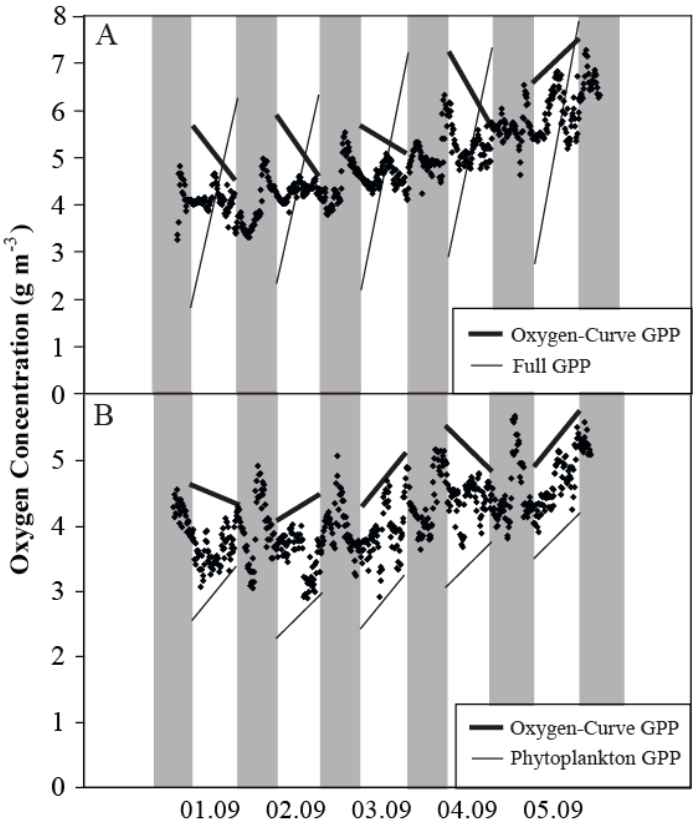

Figure 4. Oxygen curves from 1 September to 5 September, 2010, showing day (clear) and night (shaded) periods for A) Gollinsee and B) Schulzensee.

3.3 Gross Respiration

Compartmental estimates of gross respiration rates for the initial study year indicated similar whole-lake values between systems (Table 3, Table 4). Due to the reliance upon literature relationships for these values, the range of error could not be presented, and thus these may only be considered first-order estimates. The majority of respiration in both lakes was associated with sediment bacteria (50 to 60%) and plants (20 to 30%; Table 3).

Table 3. Mean production and respiration estimates for the initial study year (2010 to 2011).

Producer group	Gollinsee (phytoplankton-dominated)			Schulzensee (macrophyte-dominated)		
	B (mg C m^{-2})	Gross production (g C m^{-2} yr^{-1})	Respiration (g C m^{-2} yr^{-1})	B (mg C m^{-2})	Gross production (g C m^{-2} yr^{-1})	Respiration (g C m^{-2} yr^{-1})
Phytoplankton	-----	141	51	-----	182	57
Epipelon	-----	243	90	-----	258	85
Epiphyton	-----	10	3	-----	33	20
C. submersum	-----	-----	-----	-----	27	16
A. stagnina	-----	-----	-----	-----	22	13
Sediment bacteria	-----	440	308	-----	352	246
Biofilm bacteria	-----	2	2	-----	17	12
Pelagic bacteria	-----	34	24	-----	29	20
Zooplankton	582	-----	22	635	-----	24
Macroinv.	704	-----	8	2464	-----	27
Fish	1339	-----	16	1336	----	16

Note: “B” refers to biomass, and “macroinv.” refers to macroinvertebrates.

3.4 Carbon Cycling

Regarding carbon inputs, allochthonous carbon loading into both lakes was dominated by emergent macrophytes (Fig. 5), though their input was calculated to be nearly three times greater in phytoplankton-dominated Gollinsee than in macrophyte-dominated Schulzensee (Table 4) due to higher measured reed densities (184 culms m^{-2} in Gollinsee, 45 culms m^{-2} in Schulzensee). Mean groundwater DOC concentrations were 7.4 ± 1.6 mg L^{-1} in Gollinsee and 7.3 ± 1.9 mg L^{-1} in Schulzensee, and mean groundwater DIC concentrations of 41.4 ± 2.3 mg L^{-1} in Gollinsee and 40.4 ± 2.6 mg L^{-1} in Schulzensee. Although total resulting groundwater gains and losses of DOC and DIC were minor relative to other inputs (Fig. 5), our data indicated that both lakes received a net gain of groundwater carbon (Table 4).

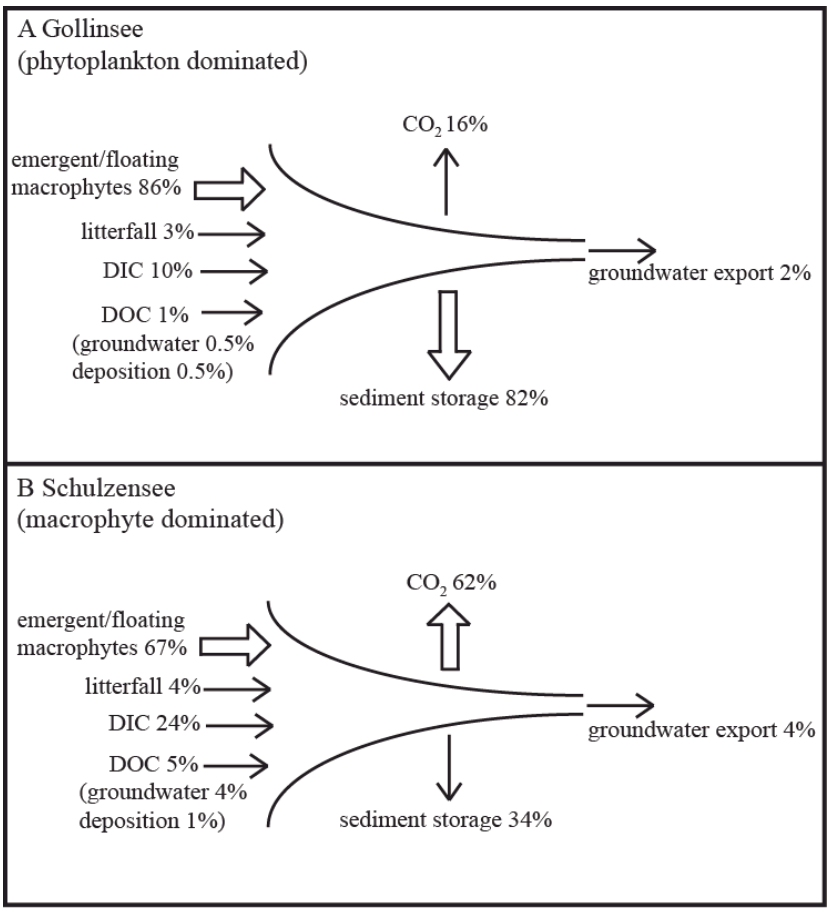

Figure 5. Synthesis of carbon flux estimates in A) Gollinsee and B) Schulzensee, from mass balances (figure style adapted from Tranvik *et al.*, 2009).

Regarding carbon losses for each lake, mean areal sediment deposition rates (from sediment traps) did not differ significantly between lakes (Gollinsee = 681 ± 130 g m^{-2} yr^{-1}, Schulzensee = 708 ± 140 g m^{-2} yr^{-1}; t-test, $P = 0.89$). The carbon fraction of freshly deposited sediments, however, was significantly higher in macrophyte-dominated Schulzensee (mean =

37 ± 1%) than in phytoplankton-dominated Gollinsee (28 ± 1%) (t-test, $P < 0.0001$). Mean calculated carbon deposition rates were therefore somewhat higher in Schulzensee (285 ± 65 g C m^{-2} yr^{-1}) than Gollinsee (191 ± 63 g C m^{-2} yr^{-1}), although the difference between lakes was not statistically significant ($P = 0.30$). Regarding dated sediment cores, dating errors are difficult to quantify due to possible fluctuations in ^{210}Pb inputs, historic sediment mixing, and ^{210}Pb diffusion in the upper sediments. I therefore do not present specific errors for sediment core chronologies, but instead note that the degree of uncertainty in dating increases exponentially in deeper sediment layers, and suggest error ranges (with a 95% confidence interval) of 10 to 20 years within the past dated 100 years (following Binford, 1990). The accuracy of sediment core dating was, however, validated by measuring ^{137}Cs (which typically peaks at 1963, the year of the nuclear Test Ban Treaty signing) as an independent tracer (e.g., Appleby, 2001). In Gollinsee, the peak ^{137}Cs input was identified at 30 to 31 cm deep, which corresponded to a constant rate of supply (CRS) model extrapolated depth of 30.5 cm for 1963. In Schulzensee, the peak ^{137}Cs input was identified at 28 to 29 cm deep, which correctly fell between CRS modeled depths for 1956 (31 to 32 cm deep) and 1974 (24 to 25 cm deep). Due to the close correspondence between ^{210}Pb and ^{137}Cs approaches in both lakes, these sediment chronologies may reasonably be considered reliable.

In phytoplankton-dominated Gollinsee, a CRS model from ^{210}Pb dating provided total carbon burial rates at the earliest dated segments (roughly 1860 to 1960) which were relatively stable (~ 50 g C m^{-2} yr^{-1}). Carbon burial rates gradually increased over a period dated from roughly 1960 to 2000, after which they appeared to become again relatively stable (mean = 196 g C m^{-2} yr^{-1}). During this period, Gollinsee experienced a four-fold increase in organic carbon burial (Fig. 6), and a seven- to eight-fold increase in inorganic carbon burial. The increase in inorganic carbon burial appears to be associated almost entirely with a seven-fold increase in calcite ($CaCO_3$) burial over the same period. Macrofossil analyses identified high concentrations of the oospores of *Characeae sp.* (submerged macrophytes typically associated with clear-water conditions) in sediments dated as recently as 1977, followed by lower concentrations in more recent sediments (data not shown). Leaf fossils from *Potamogeton sp.* (another submerged macrophyte species) were also found in deeper layers (most recently ~ 1900), indicating a possible earlier diversity of submerged macrophytes in this lake. Submerged macrophytes are no longer found in this lake. The dated period when sedimentation rates began to rise (~ 1960) coincided with a single layer of high sediment loading, and the construction period of a nearby military airport (out of operation since 1990). Together, these factors strongly suggest that the period of increasing sedimentation rates from

1960 to 2000 corresponds to a shift from a macrophyte-dominated to a phytoplankton-dominated regime, resulting from a disturbance associated with nearby anthropogenic activities.

In macrophyte-dominated Schulzensee, a CRS model from ^{210}Pb dating provided carbon burial rates that did not follow any particular or sustained pattern across the dated segment of the sediment core, and sediments in the top 10 cm were poorly consolidated. Organic carbon (Fig. 6) and $CaCO_3$ burial rates are roughly equivalent between early (pre-1930) and more recent (~ 2000) dated periods. Current carbon burial rates in Schulzensee were therefore considered to be the total mean carbon burial rate across the full core, excluding a temporary peak dating to the 1950's as well as the recent (post-2000) poorly consolidated sediments. This provided a mean carbon burial rate of 53 g C m^{-2} yr^{-1}, which was roughly equivalent to the pre-shift carbon burial rates calculated for Gollinsee (~ 50 g C m^{-2} yr^{-1}).

Comparing sediment burial rates between lakes for the layer dated nearest 2000 indicated recent total sediment burial rates of approximately 673 g m^{-2} yr^{-1} in Gollinsee and approximately 220 g m^{-2} yr^{-1} in Schulzensee. Dividing these sediment burial values by our measured sediment deposition rates (from sediment traps) suggested that the sediment burial efficiency in Gollinsee was nearly 100%, but only approximately 30% in Schulzensee. Comparing carbon deposition data (from sediment traps) to carbon burial data (from dated sediment cores), and estimating a range of error from the mean fraction of the standard deviation to the mean of replicate sediment traps provided carbon burial efficiency estimates of 102 ± 14% in Gollinsee compared to 19 ± 30% in Schulzensee.

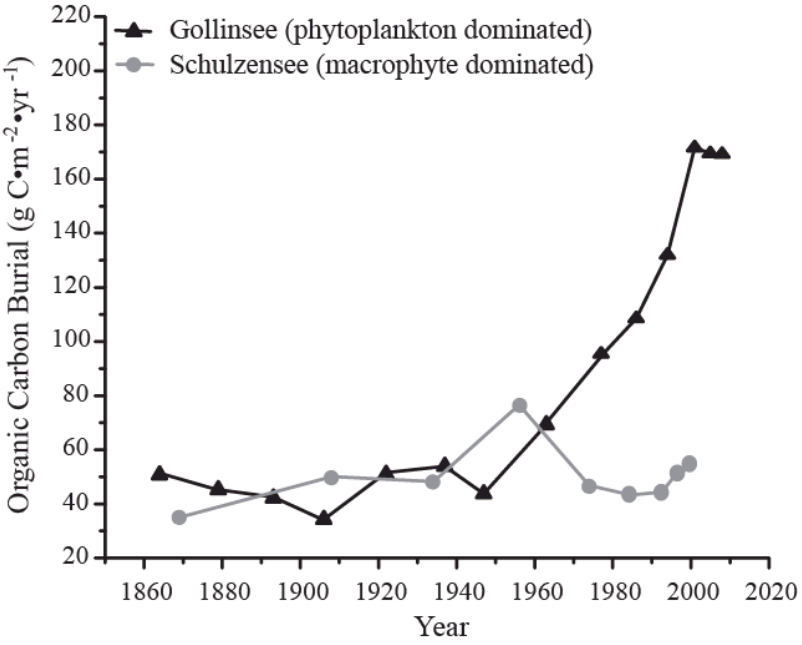

Figure 6. Historic changes in organic carbon burial rates in Gollinsee and Schulzensee, determined from CRS models from dated sediment cores.

Concerning carbon losses to the atmosphere, both lakes were generally supersaturated with pCO_2, yet full-year CO_2 emissions were highest in macrophyte-dominated Schulzensee (Table 4). Pelagic pCO_2 concentrations (derived from DIC concentrations) were also significantly higher in Schulzensee (5.5 ± 0.6 g CO_2 m^{-3}) than in phytoplankton-dominated Gollinsee (2.8 ± 0.6 g CO_2 m^{-3}; t-test, n = 20, P = 0.002), with chemical enhancement increasing estimated annual fluxes by approximately 30% in both systems. Although groundwater DIC represented a larger proportion of the loaded carbon in Schulzensee (Fig. 6), similar groundwater DIC concentrations and net loading rates (Table 4) in both lakes suggest that the significant difference observed in pelagic DIC concentrations (and surface emissions) is most likely due to differences in within-lake heterotrophy (respiration - GPP), rather than differences in hydrology (Stets *et al.*, 2009) or catchment productivity (Maberly *et al.*, 2012).

Carbon mass balances approached equilibrium for both lakes, indicating that the major processes described may be considered reasonably well defined (Table 4). These carbon balances show that, of the annual carbon losses in phytoplankton-dominated Gollinsee, approximately 82% was permanently buried and 16% was emitted to the atmosphere (the remainder being lost via groundwater). Of the annual carbon losses in macrophyte-dominated Schulzensee, 34% was permanently buried in the sediments, and 62% was emitted to the atmosphere (Fig. 5). Ecosystem budgets of both lakes were imbalanced by approximately 15%. This imbalance suggests that the net heterotrophic balance of each lake calculated as the

difference between total respiration and GPP rates (Table 4) may not be accurate, as is evident from the generally more heterotrophic lake conditions observed in Schulzensee (Table 1). These differences are likely due the imprecision of estimated plant and bacterial respiration rates, as discussed in more detail in section 4.2.

Table 4. Full-year carbon gains and losses in study lakes (g C m^{-2} yr^{-1}).

	Carbon budget applied (ecosystem budget = E, mass balance = M)	Gollinsee		Schulzensee	
		In	Out	In	Out
$DOC_{groundwater}$	E, M	1	1	6	1
$DIC_{groundwater}$	M	25	3	33	6
DOC_{wet}‡	E, M	1	-----	1	-----
OC_{litter}	E, M	7	-----	6	-----
OC_{mac}	E, M	214	-----	92	-----
C_{photo}§	E	-----	13	-----	13
$C_{emission}$	M	-----	39	-----	96
C_{sed}	E, M	-----	196	-----	53
Gross primary production	E	408†	-----	586†	-----
Gross respiration	E	-----	524	-----	535
Mass balance		248	239	138	156
Ecosystem budget		631	734	691	602

† Adjusted for winter GPP with under-ice diel O_2 curves.

‡ from Andersson and Sobek (2006).

§ from Granéli *et al.* (1996).

3.5 Primary Productivity Model

The empirical data collected during the first study year were applied to previously established conceptual relationships between TP availability and GPP, illustrating that at moderate TP concentrations and low mean lake depths most GPP can be supplied by either phytoplankton (in lakes without submerged macrophytes) or benthic algae (in lakes with submerged macrophytes) (Fig. 7A). This model suggests that with increasing TP, macrophyte–dominated lakes would first exhibit reductions in epipelon GPP, followed by

losses in submerged macrophyte and epiphyton GPP, leading eventually to a full phytoplankton dominance of lake GPP (Fig. 7A). A hump-shaped relationship is thus suggested to exist between total GPP and TP in macrophyte-dominated, clear-water lakes (Fig. 7B). At intermediate TP concentrations, the GPP of a clear-water regime is therefore higher than that of a turbid regime (Fig. 7B), reflecting the empirical results. Due to the important role of benthic GPP, the difference between regimes diminishes sharply as the mean lake depth increases, and disappears completely beyond mean depths of 3 to 4 m (Fig. 7D, 7F). At higher TP concentrations, phytoplankton and periphyton communities dominate, and the model suggests that the response of GPP to further increases in TP concentrations is relatively weak, since periphyton GPP becomes increasingly light limited, and self-shading by phytoplankton restricts increases in areal pelagic GPP.

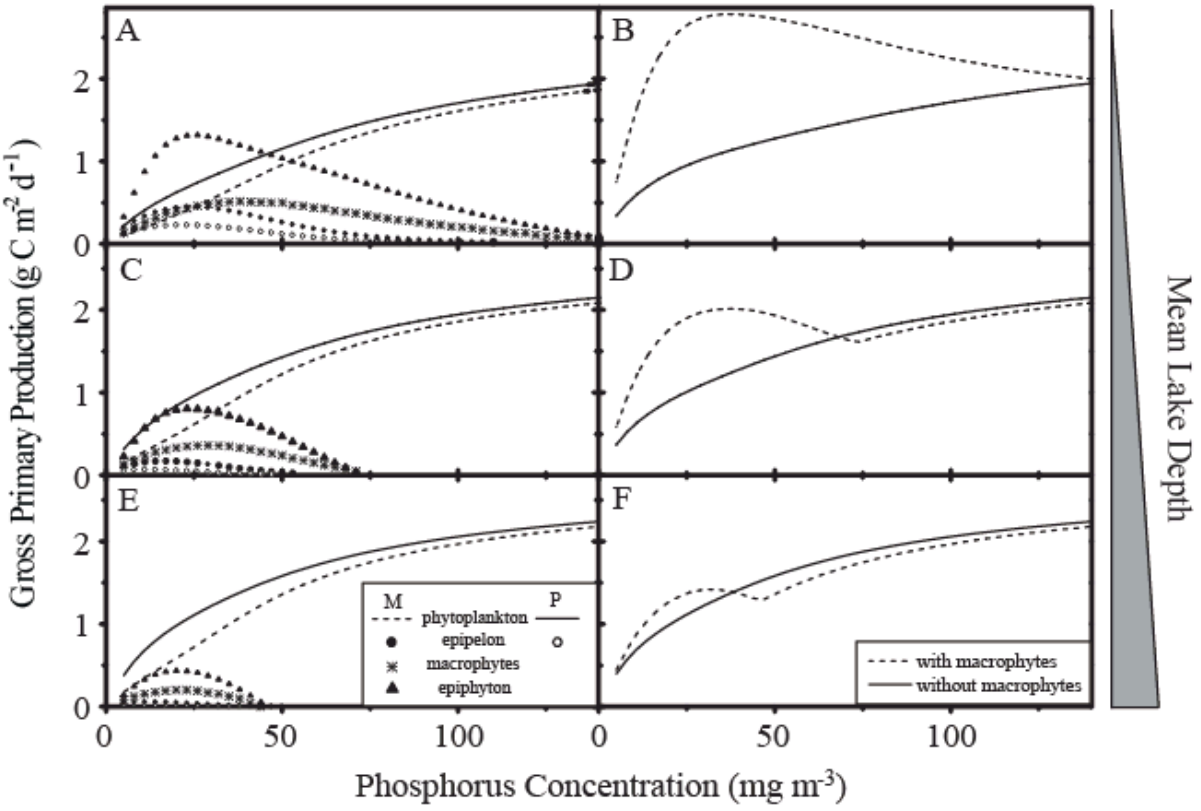

Figure 7. Conceptual model displaying the theoretical response of individual primary producer group (left boxes) and whole-lake (right boxes) GPP (g C m^{-2} d^{-1}) to TP availability with ("M") and without ("P") submerged macrophytes. Model outputs are provided for lakes of mean depth 1.5 m (top), 2.5 m (middle), and 3.5 m (bottom).

3.6 Brownification

Initial (2010) DOC concentrations were approximately 10 mg L^{-1}, began to rise in May 2011, and rose to approximately 55 mg L^{-1} by June 2012, when maximum water levels (Fig. 8) and DOC concentrations (Fig. 9A) were recorded. Concentrations of Fe, TP, SRP, DIN, and DON had also increased dramatically by 2012 (Fig. 9B-F), with most parameters beginning to increase most strongly during January and February 2012. Temperature loggers and profiles revealed a strengthening in summertime thermal stratification, and thus a diminishing mixing depth between each consecutive study year. Specifically, 2010 water temperatures had remained relatively consistent throughout the water column, but by 2012 temperatures dropped sharply below a depth of 1 m, providing an 11ºC thermal gradient across the 3 m water column. Comparing these data to vertical YSI profiles from 2010, surface summertime (June to August) water temperatures remained relatively consistent between years (Fig 9G; t-test, $P = 0.44$), while a significant decrease in the mean benthic temperatures over the same periods is recorded (Fig 9H; t-test, $P < 0.001$).

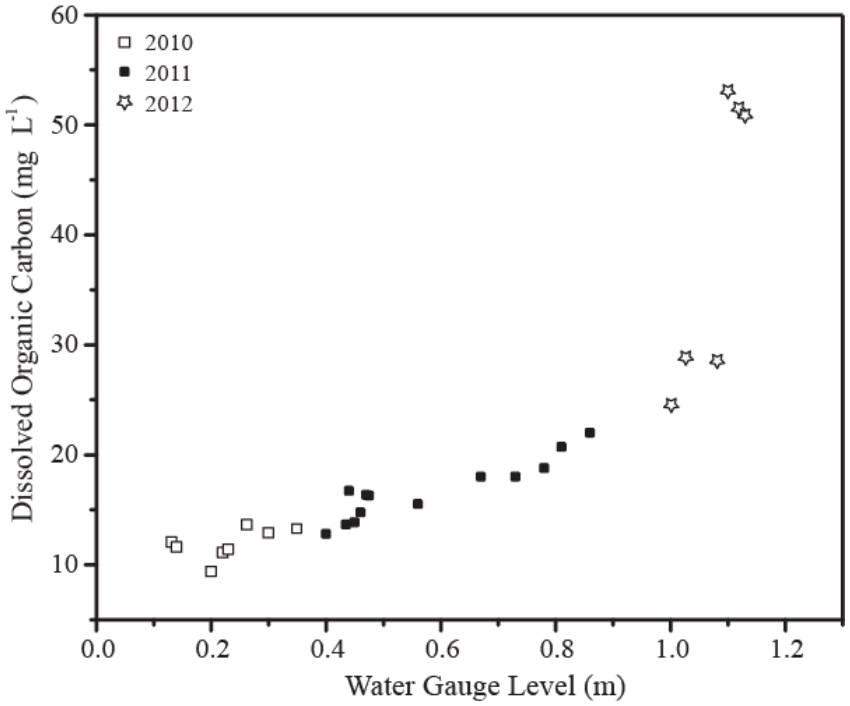

Figure 8. Relationship between rising water levels and dissolved organic carbon concentrations in Gollinsee.

In 2010, anoxic conditions were measured during brief summer periods, and only near the sediment surface of the deepest parts of the lake. In 2011, these anoxic conditions were occasionally observed in the water column below 2.5 m, and more frequently than in 2010 (observed in late June and late August, with oxygenated waters reaching the sediments in July). In 2012, anoxia became a defining characteristic of Gollinsee, lasting from April to November and occasionally extending to the water surface (Fig. 10). This was associated with a three-year decline in the euphotic zone depth (calculated as 1% PAR from light attenuation measurements), with 2012 furthermore representing the first year at which the mean lake basin depth was below the euphotic zone (Fig. 11).

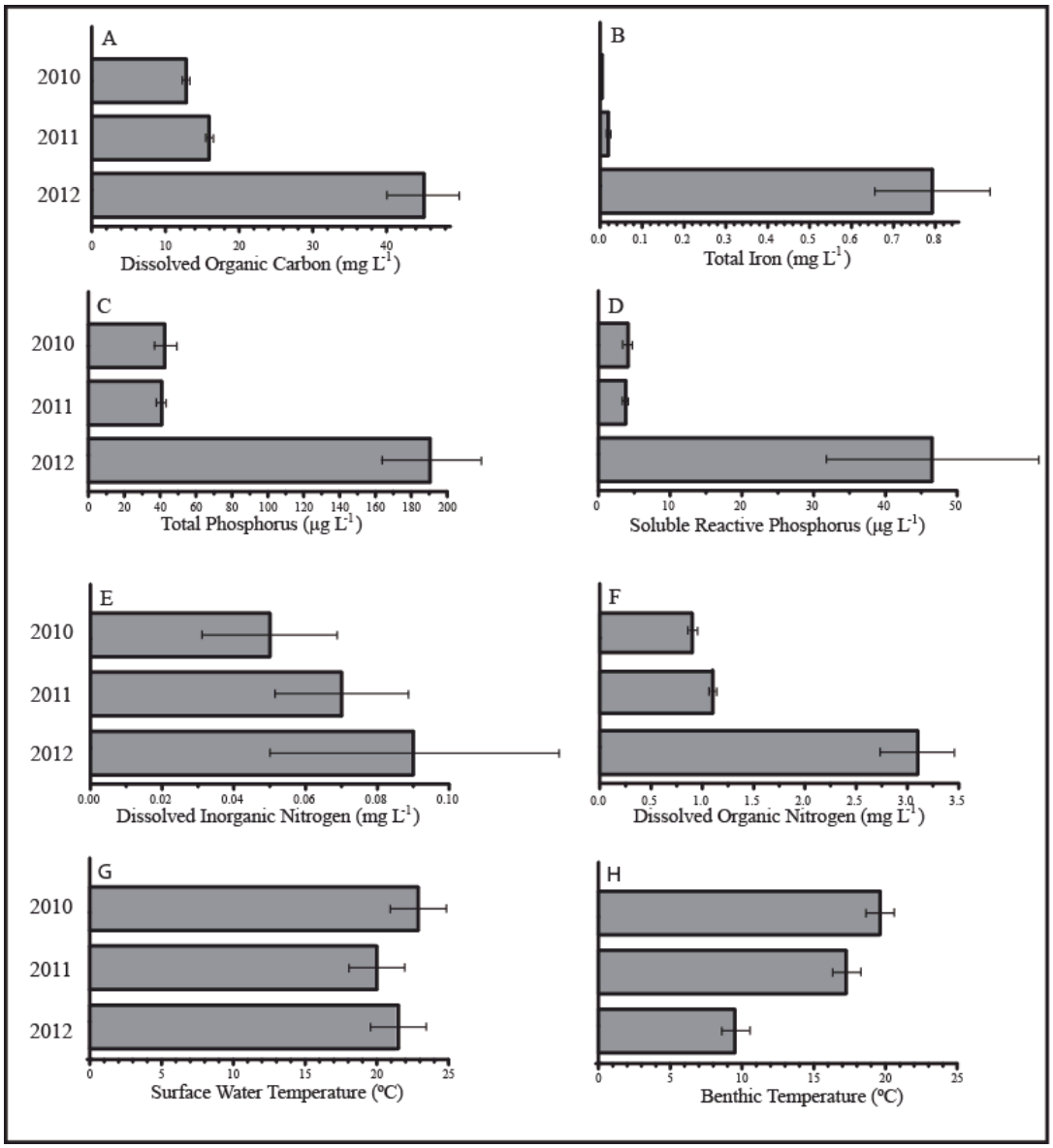

Figure 9. Abiotic lake characteristics for 2010 to 2012, with standard error of the mean. All values are spring/summer means, except G and H, representing summer values.

Regarding parallel factor (PARAFAC) analyses of DOC, component names C1 and Q3 (Cory and McKnight, 2005) were used to separate DOC of groundwater and terrigenous peatland origin. Component C1 is more likely to be found in peatland samples, whereas Q3 is more prominent in shallow groundwater (Strohmeier *et al.*, 2013). A low percentage of the Q3 component in Gollinsee's lake water relative to the groundwater (Fig. 12) suggested that the groundwater did not play a major role as a DOC source in Gollinsee, and was thus not responsible for the observed increase in lake water DOC concentrations in 2011. Instead, lake water and water in the alder and reed belts appeared to be dominated by water originating from the surrounding flooded peatlands (Fig. 12). In 2012, however, PARAFAC analyses identified a significant increase in the fluorescence component Q3 in lake waters (t-test, $P < 0.001$), but without any significant change in the C1 component.

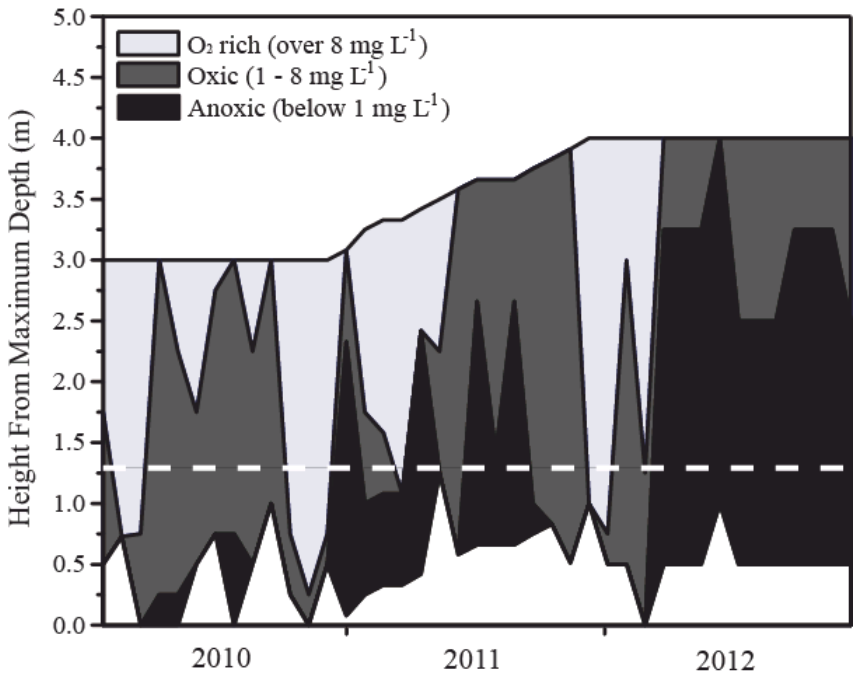

Figure 10. Lake oxic status from 2010 to 2012, compiled from vertical oxygen concentration profiles and daily monitoring station measurements. The top represents the maximum lake surface level, and the bottom white areas reflect sediment depths at different profiling locations and dates within the lake. A dotted line represents the mean basin depth.

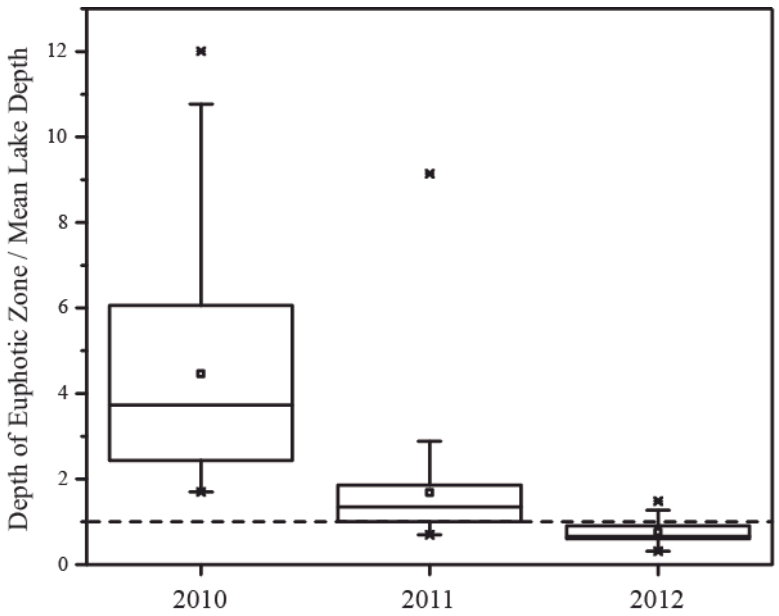

Figure 11. Change in euphotic zone depth (as 1% PAR limit) divided by the estimated mean basin depth. Boxes represent the upper quartile, median, and lower quartile, and whiskers represent the 5th and 95th percentiles. Centered squares represent the mean value, and crosses designate minimum and maximum values in the dataset. A dotted line represents a ratio of one, below which the mean basin depth is beyond the euphotic zone.

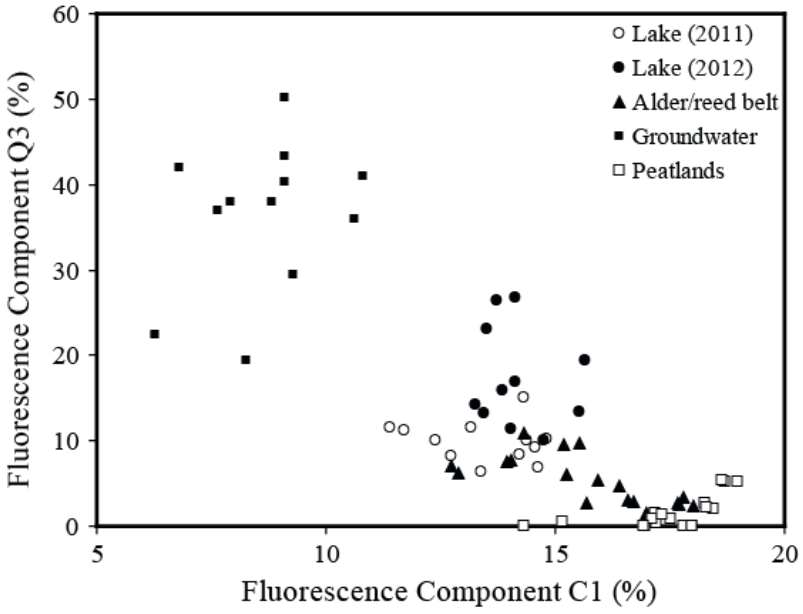

Figure 12. Parallel factor (PARAFAC) analysis of dissolved organic carbon origins in Lake Gollinsee.

Comparing the metabolic lake characteristics between 2010, 2011, and 2012 suggested equally profound changes to the lake ecosystem. Decreasing Secchi depths (Fig. 13A) were accompanied by an increase in pelagic chl *a* concentrations (Fig. 13B), coupled to a decrease

in mean summer periphyton growth (Fig. 13C). A total decline in pH levels (Fig. 13D) accompanied increasing pelagic GPP (Fig. 13E) and respiration (Fig. 13F) rates. Furthermore, a significant increase in surface CO_2 emissions (Fig. 13G) was coupled to a decline in DIC concentrations (Fig. 13H), suggesting perhaps that a decline in pH, rather than an increase in ecosystem heterotrophy (and thus net DIC production), was responsible for the increase in CO_2 emissions.

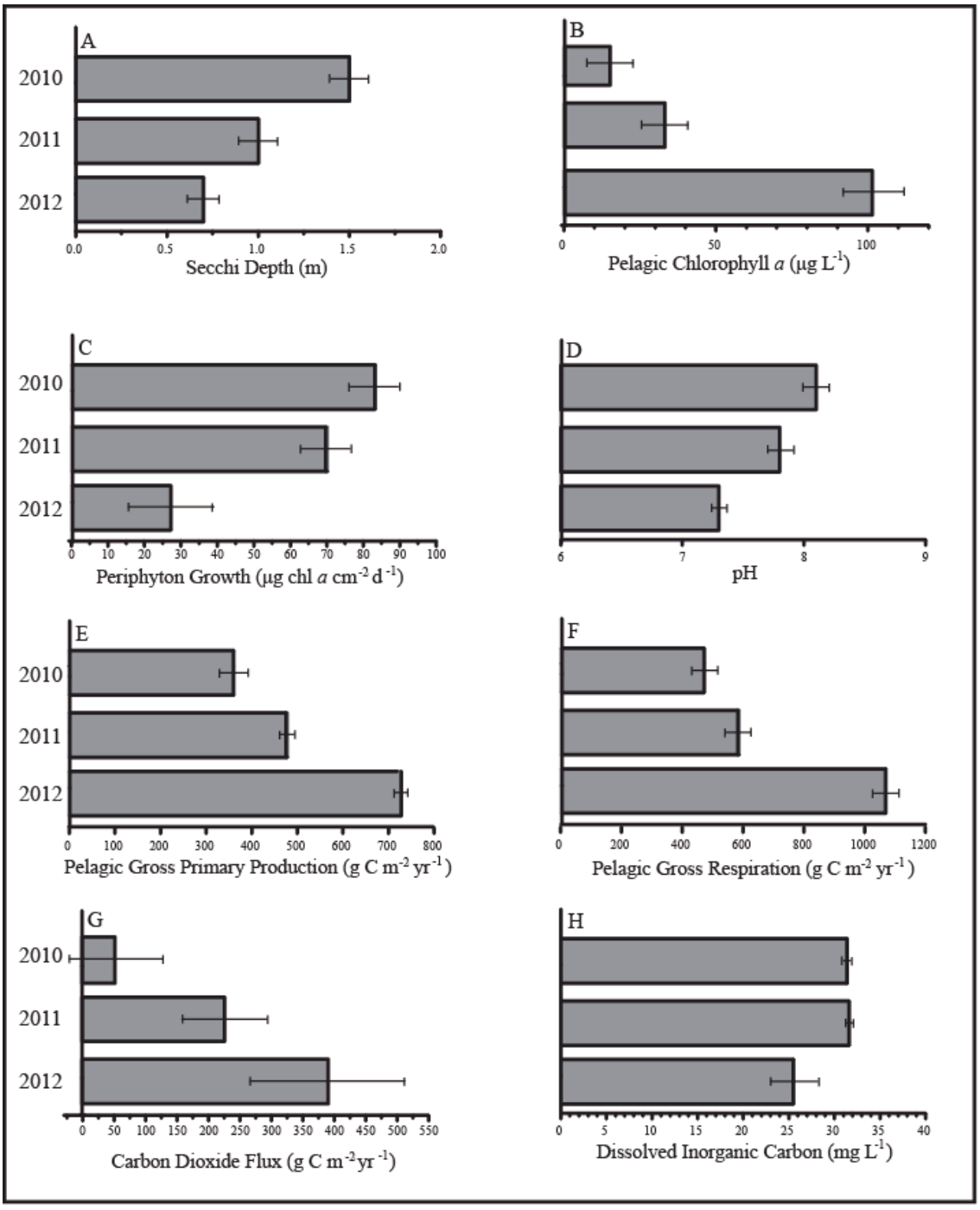

Figure 13. Metabolic and biological lake characteristics for 2010 to 2012, with standard error of the mean. All values are spring/summer means, except C, representing summer values.

4 Discussions

4.1 Gross Primary Production

My results demonstrate that a shallow eutrophic lake featuring a submerged macrophyte community can support a higher full-lake annual GPP than a phytoplankton-dominated lake of comparable morphometry and nutrient concentrations, thus supporting my initial hypothesis. Although nutrients play an important role in broadly limiting or propelling ecosystem productivity, these data suggest that the relationship between GPP and nutrient status may be discontinuous in bistable systems. Lower whole-lake GPP rates in the phytoplankton-dominated lake were attributed to the lowered water clarity and presence of fewer primary producer groups. These conclusions were illustrated by a simple primary productivity model which suggested that the presence of a submerged macrophyte-epiphyton complex in a shallow lake improves benthic light availability, and consequently allows for a greater whole-lake GPP than would be expected for a phytoplankton-dominated lake at similar pelagic TP concentrations. It is furthermore likely that the difference in GPP between these two lakes was higher than these data suggest, due to the possible underestimation of epipelon GPP in the open-water areas of Schulzensee. Periphyton biomass on plastic strips did not differ significantly between study lakes, but this was suspected to be an error due to the localized effect of floating-leaved water lilies in Schulzensee, which shaded the strips intended as open-water exposures. This was supported by data from the following year, when the monthly periphyton biomass accumulation on open-water strip exposures was higher in macrophyte-dominated Schulzensee (1.77 ± 0.2 µg chl *a* cm^{-2}) than in phytoplankton-dominated Gollinsee (1.08 ± 0.2 µg chl *a* cm^{-2}; t-test, $P = 0.05$).

The GPP rates in these lakes during the first study year were comparable to those in other studies of similar systems. Areal phytoplankton GPP rates (ranging from 140 to 180 g C m^{-2} yr^{-1}) were similar to literature values for other lakes with comparable nutrient concentrations (e.g., 200 to 300 g C m^{-2} yr^{-1} from del Giorgio and Peters, 1993; 100 to 400 g C m^{-2} yr^{-1} from Liboriussen and Jeppesen, 2003). Epipelon GPP rates (~ 250 g C m^{-2} yr^{-1}) were also in the same range as values published for other shallow lakes (500 g C m^{-2} yr^{-1} from Vadeboncoeur and Lodge, 1998; 100 to 1700 g C m^{-2} yr^{-1} from Üveges *et al.*, 2011). Whole-lake GPP values in the literature are typically expressed as daily summertime rates, and were found to range from 1 to 7 g C m^{-2} d^{-1}. Summertime (June to August) GPP in Gollinsee (1.8 ± 0.2 g C m^{-2} d^{-1}) and Schulzensee (3.7 ± 0.2 g C m^{-2} d^{-1}) both fell within this range, with rates being significantly higher in macrophyte-dominated Schulzensee (t-test, $P = 0.005$).

A comparison of daily estimates (Fig. 3, Fig. 4) verified our fluorometric approach to calculating daily GPP rates, and indicated that errors in GPP calculated from diel O_2 curves may arise from seasonal shifts in the distribution of primary production, and possibly changes in lake mixing patterns. This confirmed the results of Van de Bogert *et al.* (2012), who found a high degree of spatial sensitivity to diel O_2 curves. Concerning whole-lake GPP calculations, the discrepancy between approaches in this study was greatest in the macrophyte-dominated lake, where the littoral and benthic zones were expected to play a larger role in whole-lake GPP. This difference was also largest during the summer, when the submerged macrophyte-epiphyton complex GPP was highest (Fig. 2B). Diel O_2 curves in macrophyte-dominated Schulzensee aligned well with calculated phytoplankton GPP, suggesting that these O_2 curves essentially measured pelagic processes. In phytoplankton-dominated Gollinsee, O_2 curves more closely resembled whole-lake GPP. This may have been due to the slightly shallower mean depth of Gollinsee (with the benthic zone positioned nearer to the installed YSI probes), as well as the smaller contribution of the littoral zone to whole-lake GPP in this lake. The detailed comparisons of approaches further showed that diel O_2 curves in Gollinsee provided regularly negative GPP values in September (despite an overall apparent ecosystem autotrophy, Fig. 4B), while our compartmental approach indicated that whole-lake GPP during this period was dominated by epipelon. This spatial distance between monitoring probes and primary producers thus appeared to make diel O_2 curve analyses unsuitable for estimating whole-lake (or even phytoplankton) GPP during this period. Staehr *et al.* (2010) suggest that positive and negative data be both included in diel O_2 curve analyses on the assumption that sudden or unexpected changes in O_2 concentrations are the result of random water mixing events (providing an equal number of false positive and false negative values). These results suggest that the adoption of such an approach may be inappropriate for small lakes with a highly heterogeneous distribution of primary producers, and may significantly ultimately underestimate whole-lake ecosystem GPP.

This study focused on gross primary production, yet it is important to note that others such as Blindow *et al.* (2006) and Mitchell (1989) instead measured net primary production (NPP, the difference between GPP and plant respiration). While I focused on GPP so as to define the full role of plants with the lake carbon cycle, NPP is important to consider for food web dynamics as it represents the supply of autochthonous organic carbon available to consumers. Furthermore, differences in GPP do not always translate directly to NPP, as plant respiration rates are not constant (e.g., Blindow *et al.*, 2006). Neither approach adopted in this study provided estimates of algal respiration, yet plant respiration rates calculated for the

ecosystem carbon budget provided mean NPP estimates of 372 g C m^{-2} yr^{-1} in macrophyte-dominated Schulzensee and 264 g C m^{-2} yr^{-1} in phytoplankton-dominated Gollinsee. My conclusions regarding the relationship between GPP and plant community structure thus appear to hold true when considering NPP as well. Therefore, not only did aquatic plants fix more CO_2 in macrophyte-dominated Schulzensee, but more of this organic carbon remained annually available to consumers at higher levels of the food web.

The primary productivity model bridges new empirical data to previously established relationships, thus expanding the results from these lakes into a broader theoretical framework of the relationship between shallow lakes, primary production, and regime shifts. Specifically, the primary productivity model predicts that a macrophyte-dominated, shallow lake would generally support higher rates of GPP than a more turbid, phytoplankton-dominated lake across an intermediate range of TP availability. A perturbation (anthropogenic or natural) which leads to the loss of submerged macrophytes and epiphyton at moderate nutrient concentrations may thus result in an immediate decrease in whole-lake GPP, provided that the disturbance does not significantly change the nutrient supply of the system. Within the parameters described for these study lakes, the predicted difference between total GPP for alternative regimes disappears at mean lake depths greater than 4 m, or TP concentrations higher than 150 μg L^{-1}. While this TP range may be applicable to other lakes with similar DOC concentrations to our study systems, much lower DOC concentrations would result in a larger modeled depth range across which macrophyte-dominated lakes would exhibit a higher GPP than phytoplankton-dominated lakes. Similarly, the TP threshold at which differences in GPP exist between regimes varies with mean depth, with shallower mean depths providing higher TP thresholds. As discussed above, differences in GPP between systems do not always match differences in NPP (e.g., Blindow *et al.*, 2006), and thus the specific model output may differ slightly when NPP is considered.

The primary productivity model here presented is among the first to describe the relationship between GPP and nutrients for lakes subjected to regime shifts. A similar model by Genkai-Kato *et al.* (2012) described a sudden increase in whole-lake GPP following a regime shift from periphyton to phytoplankton dominance, yet the lake type and mechanisms involved in their study and this research are not analogous. Genkai-Kato *et al.* (2012) focused exclusively on lakes which were already lacking submerged macrophytes, and the regulation of internal TP release by periphyton loss was a key mechanism by which their model predicted the relationship between regime shifts and whole-lake GPP. The primary productivity model presented in this thesis did not account for an additional TP release from

the sediments in a turbid regime, which is fitting as it describes lakes at a TP range below which periphyton production is expected to disappear completely from phytoplankton shading (Liboriussen and Jeppesen, 2006). It is also worth noting that the submerged macrophyte species (*C. submersum*) included in this model is rootless, and rooted species may influence ambient nutrient conditions differently by using nutrients mainly from the sediments. However, all submerged macrophytes would theoretically influence phytoplankton nutrient availability by boosting epiphyton GPP, and may additionally suppress phytoplankton GPP by other mechanisms such as allelopathy (Hilt and Gross, 2008) and by providing refuge to phytoplankton-grazing zooplankton (Timms and Moss, 1984). Overall, the primary productivity model introduced in this thesis reflects conditions that are common in many small, shallow lakes capable of undergoing regime shifts (Scheffer *et al.*, 1993a), and the general relationship here illustrated may thus be considered widely relevant.

4.2 Carbon Cycling

Carbon burial and surface emission rates differed greatly between systems, providing strong evidence that their carbon cycling and processing also differed greatly. Specifically, phytoplankton-dominated Gollinsee buried a much larger fraction of the loaded carbon than macrophyte-dominated Schulzensee, supporting my second hypothesis. Microfossil analyses of the sediment core in Gollinsee furthermore showed that this lake previously contained a submerged macrophyte community, and that carbon burial rates during this early period were comparable to carbon burial rates in macrophyte-dominated Schulzensee. These results suggest that a regime shift from macrophyte to phytoplankton dominance is linked to a major increase in carbon burial efficiency, resulting in higher carbon burial rates. During our initial study year, nearly all of the deposited carbon in phytoplankton-dominated Gollinsee would have been buried in the sediments, compared to only 20% in the macrophyte-dominated Schulzensee. This difference in carbon burial efficiency indicated that carbon which reached the sediments in Gollinsee was less likely to return to the aquatic environment, a conclusion which was supported by the lower pelagic DIC concentrations and surface CO_2 emission rates in Gollinsee.

Of the carbon inputs to both lakes, most (70 to 90%) of the allochthonous carbon load in the initial study year came from the surrounding vegetation. For autochthonous carbon inputs, the annual whole-lake GPP was lower in Gollinsee than Schulzensee, and the primary productivity model would suggest that the recent loss of a submerged macrophyte community in Gollinsee likely resulted in a net decline in the availability of autochthonous organic

carbon. The largest calculated source of allochthonous carbon to Gollinsee was the shoreline reed community, which was not expected to have increased significantly over the observed period of rising carbon burial rates since eutrophic conditions tend to have a negative impact on reed communities (van der Putten, 1997). Comparing these study lakes, a regime shift-mediated increase in carbon burial efficiency thus appears to provide a more likely explanation for the historic increase in carbon burial rates in Gollinsee than an increase in watershed carbon loading (which was quantified, and small due to the lack of surface in- and outflows), nutrients (which did not differ significantly between systems), or autochthonous GPP (which was lower in Gollinsee, and expected to decline with the loss of submerged macrophytes).

A high carbon burial efficiency in Gollinsee may most likely be a symptom of low benthic mineralization rates. Although only few data were available for benthic respiration rates, the available data on summertime sediment O_2 demand (here converted to carbon units assuming a respiratory quotient of one) indicated that benthic carbon mineralization rates were higher in Schulzensee (mean = 168 ± 33 g C m^{-2} yr^{-1}, n = 14) than in Gollinsee (mean = 73 ± 23 g C m^{-2} yr^{-1}, n = 30; t-test, P = 0.02; K. Attermeyer, S. Meyer, unpublished data). Changes in hypolimnetic O_2 concentrations were another independent measure of sediment respiration which indicated lower sediment mineralization rates in Gollinsee than Schulzensee. Although both lakes were shallow, their sheltered position decreased wind exposure enough to regularly allow for a vertical O_2 concentration gradient. During a relatively strong and stable period of stratification in July 2010, hypolimnetic O_2 concentrations in phytoplankton-dominated Gollinsee decreased at a rate of 2.6 mg O_2 m^{-2} d^{-1} (corresponding to a net respiration rate of 0.4 g C m^{-2} yr^{-1}). During the same month, hypolimnetic O_2 concentrations in macrophyte-dominated Schulzensee decreased at a rate of 123 mg O_2 m^{-2} d^{-1} (corresponding to a net respiration rate of 17 g C m^{-2} yr^{-1}). These rates represent the difference between gross (24 hour) respiration and daytime primary production rates. Therefore, the difference in gross benthic respiration rates between the lakes may be higher than these data suggest, as benthic primary production was calculated to be higher in Schulzensee than in Gollinsee during this period.

While benthic mineralization rates appear to be generally greater in macrophyte-dominated Schulzensee, these data also show that some deposited carbon in Gollinsee was mineralized at the sediment surface and not immediately buried. This suggests that an annual carbon burial efficiency approaching 100% in Gollinsee may be the result of a more complex process whereby DIC released from the sediments has a greater chance of being

reincorporated into phytoplankton or calcite and returned to the sediments, rather than being emitted to the atmosphere. Calcite precipitation is frequently associated with high pH values and a low ecosystem heterotrophy (Kalff, 2002), and a seven-fold increase in calcite burial in Gollinsee from 1960 to 2000 indicates that it may have played such a role in this lake. In the most recent (top) sediment layers, inorganic carbon associated with calcite only represents a small proportion (under 5%) of the total carbon mass buried, yet $CaCO_3$ altogether represents roughly 30% of the total sediment burial. The influence of calcite on deposition (and thus total sedimentation) rates may in fact be higher than this, as calcite crystals frequently produce detritus aggregates which also increase the sedimentation of other nutrients and organic matter (Kalff, 2002).

Although the estimated whole-lake gross respiration rates used for carbon balances were similar between lakes, a comparison of direct measurements of benthic metabolism to the relative imbalance of our ecosystem budgets suggests that true carbon mineralization rates are likely higher than calculated for Schulzensee and lower in Gollinsee. Our ecosystem budgets furthermore indicate that sediment bacteria were likely the dominant source of respiration in both lakes (Table 3). As a higher benthic O_2 demand and generally more heterotrophic conditions (lower pH and higher DIC concentrations) were observed in macrophyte-dominated Schulzensee (at similar groundwater carbon loading rates), it may appear somewhat counter-intuitive that sediment bacterial production (and thus calculated respiration) rates were highest in phytoplankton-dominated Gollinsee. It is important to consider, however, that the application of a common bacterial growth efficiency (BGE) value of 30% provided only a rough, first-order estimate of the bacterial contribution to whole-lake respiration rates. In fact, BGE values from below 5% to 60% may be anticipated (del Giorgio and Cole, 1998). A positive relationship between bacterial production and BGE (del Giorgio and Cole, 1998) may have provided Schulzensee with a lower BGE, resulting in a proportionally higher release of DIC to the aquatic environment. There is also evidence to suggest that a diminished exposure to light may increase the BGE of bacterial communities (e.g., Pullin *et al.*, 2004) providing another mechanism whereby a phytoplankton-dominated regime may be associated with a higher BGE (and thus carbon burial efficiency). Other factors identified by del Giorgio and Cole (1998) as influencing BGE (such as nutrient concentrations) did not differ significantly between these systems. Even if the BGE was similar between lakes, bacterial production was only measured in the top 1 cm sediment layer, and bacterial metabolism may have also be substantial at deeper layers (Graf, 1987; Rothfuss *et al.*, 1997). As bacterial production was not measured below the surface sediments, I cannot

rule out that bacterial production or growth efficiency in deeper layers differed between these study lakes.

Although precise, year-round estimates of benthic mineralization rates were unavailable, Sobek *et al.* (2009) established a strong negative relationship between benthic O_2 exposure time and organic carbon burial efficiency across 27 study lakes. Mixing events and seasonal benthic primary productivity in both of our study systems resulted in full-year benthic O_2 concentrations which did not differ significantly between lakes during the initial study year (Gollinsee mean = 33 ± 8%, Schulzensee mean = 27 ± 8%, n = 16; t-test, P = 0.6). Profiles taken during the (2010) summer months alone, however, measured significantly higher benthic O_2 concentrations in Schulzensee (37 ± 10%) than in Gollinsee (9 ± 8%; Table 1) despite the higher sediment O_2 demand described above. With seasonally lower hypolimnetic O_2 concentrations, the frequency of hypoxia or anoxia at the sediment level would increase, with potentially negative consequences to secondary benthic communities. Cole and Pace (1995) found that anoxic conditions led to higher abundances of sediment bacteria, but a slower doubling time. They further suggest that this could lead to higher rates of organic matter preservation, which would be consistent with our own findings. A greater summertime O_2 supply rate to the sediments in Schulzensee due to higher epipelon production rates could have therefore contributed to the lower carbon burial efficiency in this macrophyte-dominated lake. The lower light availability and higher benthic instability in phytoplankton-dominated lakes such as Gollinsee would both likely decrease the epipelon productivity (and thus benthic O_2 availability) in such systems (Kufel and Ozimek, 1994; Vermaat *et al.*, 2000; Genkai-Kato *et al.*, 2012).

My data suggest that benthic primary and secondary production influence carbon burial efficiency, and thus carbon burial rates. They also suggest that benthic GPP in shallow macrophyte-dominated lakes benefit from the higher degree of water clarity associated with this regime type. However, as benthic productivity is generally most important to shallow lakes (e.g., Vadeboncoeur *et al.*, 2008), it is possible that these conclusions apply mostly to eutrophic lakes that are shallow enough to permit benthic primary production. Lake morphology has indeed been found to play an important role in explaining large-scale patterns in sediment respiration (den Heyer and Kalff, 1998) and carbon burial (Ferland *et al.*, 2012) rates, and previous studies of large-scale patterns in carbon burial have tended to focus on lakes which are one or more orders of magnitude larger than those included in this study (e.g., Heathcote and Downing, 2012). Therefore, while other anthropogenically-linked processes such as watershed erosion (Theissen *et al.*, 2012; Heathcote *et al.*, 2013) and nutrient loading

(Heathcote and Downing, 2012) have been shown to increasing carbon burial rates, the research in this thesis suggests that the loss of a submerged macrophyte community may be an equally important yet previously overlooked process.

4.3 Brownification-Anoxia Feedback Loop

My initial hypothesis regarding the observed brownification in Gollinsee in 2011 and 2012 was that rising DOC concentrations would result in a significant loss of benthic primary production. As the results of the initial year of this study found benthic primary production to be a major component of the whole lake GPP, and the hypolimnion was already O_2-poor relative to Schulzensee, this was expected to have major implications to the whole-lake metabolism. An analysis of the available data from 2010 to 2012 supported this hypothesis, with a large decrease in epipelon production occurring at the same time as an onset in severely anoxic conditions. However, these data furthermore imply a more complicated process, whereby the loss of benthic primary production may have played a key role in establishing a feedback loop between loaded DOC from the flooded peatlands, anoxic conditions, and the internal loading of DOC from within the lake basin.

The full observed process may be described as occurring in two stages. Comparing 2010 and 2011, an increase in water levels, DOC, and nitrogen concentrations was observed. There was no apparent increase in TP concentrations, yet mean pelagic chl *a* concentrations doubled, and diel O_2 curves indicated a minor increase in GPP. Pelagic bacterial production also increased, which could be due to either (or both) high DOC or phytoplankton concentrations. However, diel O_2 curves measured a comparable increase in respiration and GPP rates over this period (Fig. 13E, F), hinting perhaps that the high respiration rates in 2011 were predominantly fueled by the increased phytoplankton production. Elevated DOC and phytoplankton concentrations furthermore both contributed to the diminished Secchi depths, and thus an overall decrease in the size of the euphotic zone. This reduced transparency negatively impacted primary production in the hypolimnion. Together with a DOC-driven strengthening of summer stratification, this resulted in a more severe anoxia than observed previously. Anoxic conditions in lakes are frequently attributed to boosted respiration rates in the hypolimnion due to high epilimnetic phytoplankton productivity (e.g., Nürnberg, 1995). Although bacterial growth efficiencies may shift rapidly, providing constant sediment respiration rates (Schwaerter *et al.*, 1988), Ask *et al.* (2012) observed a negative relationship between benthic respiration and DOC concentrations in boreal Swedish lakes. We also observed a net decline in sediment bacterial production and benthic temperatures, indicating

that sediment respiration rates did not likely increase in Gollinsee. The hypolimnetic anoxia observed in Gollinsee therefore appeared instead to reflect a strong decline in hypolimnetic GPP relative to gross respiration, rather than boosted sediment respiration rates due to the increased sedimentation of phytoplankton biomass.

A qualitative comparison of the DOC pool and rising water levels in 2010 and 2011 yielded a steady positive relationship (Fig. 8). In 2012, this relationship was decoupled, with DOC concentrations rising dramatically without an associated increase in water levels. Anoxic conditions in 2011 thus appeared to be driven by a decline in water mixing and benthic primary production due to rising water levels in parallel to the increased input of DOC leached from the flooded degraded peatlands. Low hypolimnetic O_2 concentrations have long been associated with internal nutrient loading (e.g., Behrendt *et al.*, 1993; Hamilton *et al.*, 1997), and Zhang *et al.* (2013) have shown that this process can result directly from the loss of benthic algae. In 2012, the prevailing lack of oxygen, loss of benthic periphyton, and altered redox conditions thus increased the internal loading of DOC and nutrients. The full process described is graphically represented in Figure 14. The high internal DOC and nutrient loading associated with sediment-level anoxia can result from the reductive dissolution of FeOOH, releasing associated organic carbon into the water column (e.g., Skoog and Arias-Esquivel, 2009). A large increase in Fe concentrations observed in 2012 confirms this process involving sediment redox conditions (Knorr, 2013; Riedel *et al.*, in press) which has also been linked to brownification in lakes (Kritzberg and Ekström, 2012). Dillon and Molot (2005) found that DOC, nutrient, and Fe increases can be linked to runoff conditions which could also produce similar redox conditions, but the lack of surface inflows to Gollinsee suggest that this was not likely an important factor in this lake. Since changes in these redox-dependent processes are related to certain thresholds in redox potential, they provide a suitable explanation for the sudden increase in DOC and nutrient concentrations during January and February 2012, more than six months after the initial increase in water levels and leached DOC concentrations.

As Gollinsee has no surface in- or outflows, the flooding of adjacent degraded peatlands was originally considered to be the most likely source of increasing DOC concentrations. This was confirmed by PARAFAC analyses, which showed that in 2011 the DOC in the alder and reed belts had similar optical properties to the DOC within the adjacent degraded peatlands which had been flooded by the lake. In 2012, however, PARAFAC analyses identified an increase in the DOC fluorescence component Q3. Although this component is typically associated with groundwater (Strohmeier *et al.*, 2013), the observed

increase in Q3 was not associated with a decrease in the C1 component, as apparent in groundwater samples (Fig. 12). Cory and McKnight (2005) described a significant positive relationship between component Q3 and aliphatic carbon content, which has further been linked to algal carbohydrates (McKnight *et al.*, 1994). As the significant increase in component Q3 occurs at the same time as the observed loss of benthic periphyton and increase in epilimnetic phytoplankton production, it appears possible that benthic algal breakdown and/or phytoplankton-exudated DOC contributed to the changed character of the DOC pool in 2012. To test whether the breakdown of benthic periphyton could have explained the increase in DOC concentrations in 2012, I compiled rough estimates of the maximum possible carbon contribution of epipelon. These estimates were derived from the carbon content of full-year periphyton exposures on plastic strips in 2010 (data not shown) coupled with the benthic surface area lying below the mean euphotic zone in 2012 (1.7 m). This analysis indicated that even a full dissociation of epipelon below this depth could only likely account for 5% or less of the observed increase in DOC concentrations from 2011 to 2012, suggesting that most of this increase in DOC concentrations was more likely released from the sediments by redox-driven processes. Furthermore, McKnight *et al.* (1992) found that aromatic carbon may be sorbed to hydrous iron oxides, which could also result in a measured higher proportion of the component Q3 in the DOC. This is a possibility in our study lake, as our observed proportional increase in Q3 coincided with the onset of anoxic conditions in the lake, and major increases in Fe and nutrient concentrations in the water column (Fig. 9).

Internal nutrient loading in 2012 boosted chl *a* concentrations and epilimnetic GPP rates. Dramatic increases in pelagic DOC and chl *a* concentrations together resulted in a strongly reduced euphotic zone, restricting ecosystem GPP solely to the epilimnion. Furthermore, high DOC concentrations strongly increased thermal stratification in the system, providing benthic temperatures approximately 10ºC cooler than in 2010 and thus negatively affecting sediment respiration rates and hypolimnetic O_2 availability. While diel O_2 curves yielded an increase in both GPP and respiration rates from 2011 to 2012, the calculated increase in respiration rates was greater than the increase in GPP, suggesting that elevated DOC concentrations likely subsidized the high pelagic respiration rates. Additionally, since these respiration rates were derived from nighttime O_2 consumption rates, they did not include other factors such as the photo-oxidation of DOC to CO_2 by solar ultraviolet radiation, which has been known to increase eight-fold upon the doubling of humic DOC concentrations (Lindell *et al.*, 2000), and which is also boosted by low pH conditions (Gennings *et al.*, 2001).

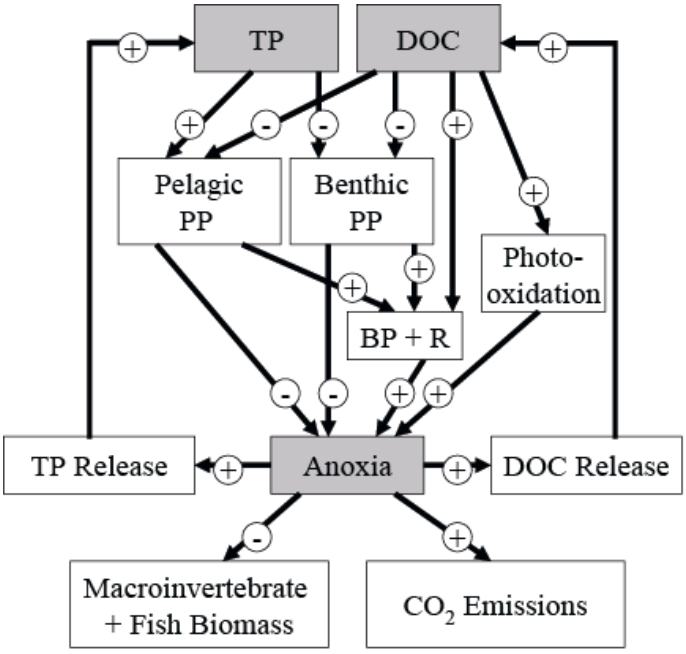

Figure 14. Processes leading to anoxia in a shallow lake dominated by benthic primary production (PP), showing a brownification-anoxia feedback loop. "BP + R" represents bacterial production and respiration.

The ecological consequences of the brownification-anoxia feedback loop in Gollinsee were severe. This feedback loop facilitated a persistent state of anoxia which occasionally extended to the water surface, resulting in the near-complete loss of macroinvertebrate and fish populations. In 2011, Gollinsee was estimated to contain approximately 2.5 g dry weight m^{-2} of fish (across five species), and 1.6 g dry weight m^{-2} of macroinvertebrates (across six classes) (K. Scharnweber, unpublished data). Attempts were made in September 2012 to quantify the fish and macrozoobenthos productivity. For fish, too few individuals could be found in 2012 to produce reliable estimates of whole-lake populations, and these only consisted of one fish species (sunbleak). Macroinvertebrate numbers were also severely reduced to a point below which the full populations could be reliably quantified, and became dominated by Diptera (mostly chironomids, which can adapt to anoxic conditions). These reductions in population size and species richness were directly attributed to the severe anoxia during that summer period, as observed by other studies (e.g., Townsend *et al.*, 1992). These results are in line with recent model simulations by Jones *et al.* (2012), which suggest that the negative effects of DOC shading of hypolimnetic primary production (here linked to a brownification-anoxia feedback loop) may outweigh the positive effects of DOC on resource availability and the fertilization of autochthonous production by TP.

Concerning overall changes to lake carbon cycling, the relatively high pH in 2010 (mean = 8.1 ± 0.1) declined in the following years with values dropping as low as 7.0 at the surface and 6.6 in the hypolimnion. Although a decline in pH may have been related to humic substances leached from the surrounding flooded peatlands or to a decline in groundwater pH from 2010 to 2011 (data not shown), a high degree of variability between measurements in 2011 and 2012 indicated a strong effect of within-lake metabolism (i.e. respired CO_2) on pH. The loss of benthic primary production and increase in epilimnetic net respiration rates would both reduce pH levels. The lowered pH resulted in a roughly 20% larger fraction of the DIC pool as pCO_2, increasing surface emissions. Diminishing pelagic DIC concentrations in 2012 furthermore indicated that CO_2 losses to the atmosphere during this period were greater than could be supported by the net heterotrophy within the lake. Previous studies have linked increasing CO_2 emissions from lakes to high precipitation, and attributed this increase to the mineralization of loaded DOC (Rantakari and Kortelainen, 2005). The data from Gollinsee suggest that internal DOC and nutrient loading may follow externally-driven brownification events, facilitating higher CO_2 emissions to the atmosphere via a decreased pH (likely resulting in part from a decline in benthic primary production). Furthermore, methane emissions are frequently exacerbated by anoxic conditions (Bastviken *et al.*, 2004b), and although they could not be quantified in this study, they likely increased as well. The widespread occurrence of such redox-dependent feedback loops with brownification in shallow lakes could have significant long-term implications to the global carbon cycle and food web of shallow lake ecosystems. As climate change is expected to increase precipitation events and watershed DOC loading (Clair *et al.*, 1999), it is possible that the process here described could occur even in lakes that are far from any direct anthropogenic impacts. In light of recent initiatives to decrease nutrient loading in many regions, the current widespread brownification phenomenon may thus increase the significance of DOC as a driver of O_2 depletion and anoxia in aquatic systems.

4.4 Synthesis

By focusing on multiple aspects of carbon cycling over a period of several years, this research provides a rare insight into the complex and variable nature of carbon cycling in shallow lakes, with potential implications to our understanding of the general role of lakes within the global carbon cycle. Tranvik *et al.* (2009) stated that inland waters bury or emit to the atmosphere roughly two thirds of the carbon they receive from the terrestrial environment. As the flux of carbon to the atmosphere generally seems to be greater than carbon burial rates,

lakes have thus been increasingly characterized as natural transport channels for terrestrial carbon to the atmosphere (Cole *et al.*, 2007). However, it is important to note that, partly due to the fact that both study lakes were relatively closed systems, 70 to 90% of the allochthonous carbon imported to these lakes during our initial study year was derived from the surrounding vegetation (especially the reed and tree belt surrounding the lake). This is relatively young terrestrial carbon (being fixed only recently from atmospheric CO_2), suggesting that most of the carbon emitted from these lakes during this year was likely derived (directly or indirectly) from plants which had only recently removed this carbon from the atmosphere. With respect to atmospheric CO_2 concentrations, this means that the net annual contribution from such lakes may be at equilibrium (if most of the loaded carbon is annually returned to the atmosphere through emissions) or subtractive. Many small, closed-system lakes, even when exhibiting high surface emissions, may thus be net carbon sinks with respect to the atmosphere on an annual or decadal time horizon. However, it is important to note that this condition was reversed in Gollinsee, when flooding and redox reactions led to a strong increase in surface CO_2 emissions, and that carbon mass balances in other biological regions such as the boreal zone, have found peatlands (and thus presumably older carbon) to be a dominant source of allochthonous carbon into lakes (Molot and Dillon, 1996). Unlike previous years, the change in Gollinsee represented a release of older carbon sources which had previously been buried in the lake sediments or surrounding degraded peatlands. The release of this carbon into the atmosphere would thus be additive with respect to atmospheric CO_2 concentrations.

Altogether, these studies stress the importance of benthic metabolism to carbon cycling and ecosystem productivity in shallow lakes. Benthic primary production was found to be an important source of autochthonous organic carbon in both study lakes, and the susceptibility of this production to shading by phytoplankton, DOC, and water column height appeared to play a key initial role in setting off the observed brownification-anoxia feedback loop. Furthermore, benthic mineralization rates appeared to play a pivotal role in decreasing carbon burial efficiency in phytoplankton-dominated Gollinsee, changing it into a strong sink of terrestrial carbon upon the loss of its submerged macrophyte community. Although carbon burial rates in Gollinsee could not be quantified for 2012, a large increase in surface carbon emissions in this year may have signaled a proportional shift whereby the lake became a larger net source of carbon with respect to the atmosphere. These changing conditions further appeared to indicate a sensitivity of lake carbon cycling to a threshold of hypolimnetic O_2

availability, whereby high carbon burial rates produced by hypoxic conditions may have been reversed by the establishment of anoxic conditions and associated redox reactions.

Due to the importance of the benthic zone, many of the mechanisms described in this thesis, however, may only apply to shallow eutrophic lake ecosystems where nutrients are not limiting and where changes in light and O_2 availability may severely impact benthic metabolic processes. Small lakes (under 2.5 km^2) are expected to comprise the majority (99%) of lake systems, and lakes of the size here studied represent roughly a third of the global lake surface area (Downing *et al.*, 2006). However, as described with the primary productivity model, the patterns observed in these study lakes may differ for other systems, such as highly humic lakes in the boreal zone. On the other hand, large eutrophic lakes which are shallow enough to experience high levels of benthic primary production over large areas (for instance, Lake Erie in North America) may feature some parallel mechanisms to those observed in these study lakes. This study thus represents an important step towards an improved understanding of the mechanistic relationships between carbon cycling, ecological community structures, and food webs in shallow, eutrophic lakes.

4.5 Final Outlook: Scaling Up

In an attempt to quantify the role of inland waters with respect to the global carbon cycle, Tranvik *et al.* (2009) mention that little is yet known about how the widespread occurrence of regime shifts will change their predictions. This is an important question, as studies such as that by Sand-Jensen *et al.* (2000) and Vermaire *et al.* (2012) have already identified major losses of submerged macrophyte communities in lakes, with regime shifts being often linked to anthropogenic activities. Furthermore, Barnosky *et al.* (2012) suggest that the occurrence of potentially deleterious regime shifts may be on the rise. The results of this thesis suggest that the loss of submerged macrophyte communities in shallow lakes would likely result in lakes becoming a greater carbon sink with respect to the global carbon cycle. In these study lakes, however, this outcome appeared to be the result of a decline in primary production and benthic mineralization rates, and thus such regime shifts may have a net negative impact on lake productivity and food webs. Furthermore, current climate change predictions suggest that many regions around the world will experience higher precipitation rates (Tranvik *et al.*, 2009), and thus the observed brownification-anoxia feedback loop may potentially become an increasingly widespread phenomenon, resulting in the release of high quantities of previously buried carbon to the atmosphere.

As atmospheric CO_2 concentrations continue to rise, many further changes to the global carbon cycle, and the role of lakes within it, are bound to change. The terrestrial productivity in arid zones was found by Donohue *et al.* (2013) to have already increased by roughly 12% from CO_2 fertilization in recent decades, while Schippers *et al.* (2004) suggested that a similar process may occur for aquatic plants in lakes as well. Changes in atmospheric deposition chemistry have also already increased the transport of DOC from catchments into lakes (Monteith *et al.*, 2007). As the quantity of allochthonous carbon loaded annually into lakes increases, so will the annual quantity of carbon either emitted to the atmosphere or buried in sediments. As discussed earlier, the net balance of these carbon fates depends on the metabolic conditions with the lake, and the immediate net effect of each process with regards to atmospheric CO_2 concentrations depends largely on the source of carbon (whether from fresh vegetation or previously buried carbon). An improved understanding of the mechanisms underlying lake carbon processing, as provided by this research, is thus necessary to make sense of broad patterns in carbon cycling with potentially overlapping processes, for instance linking carbon burial rates to latitude (Brothers *et al.*, 2008) lake morphometry (Ferland *et al.*, 2013), erosion (Heathcote *et al.*, 2013), and nutrient loading (Heathcote and Downing, 2012).

With climate change scenarios predicting a large-scale redistribution of precipitation patterns, changes in lake sizes and distribution may influence the global carbon cycle. Large-scale changes in precipitation patterns such as those predicted by Tranvik *et al.* (2009) could thus feasibly be joined to large-scale regional biome carbon stock data (e.g., Malhi *et al.*, 1999; Buffam *et al.*, 2011) for more meaningful predictions of changes in carbon cycling. The boreal zone is perhaps the most significant region for the future changing role of lakes within the global carbon cycle as it contains the Earth's largest soil carbon reserves (Malhi *et al.*, 1999) along with a high occurrence of lakes (Downing *et al.*, 2006), and is predicted to be among the regions most severely affected by upcoming changing precipitation patterns (Tranvik *et al.*, 2009). However, the temperate zone, whose processes may be better represented by the lakes described in this thesis, is also expected to experience major changes in precipitation patterns (Tranvik *et al.*, 2009) while being subject to more frequent and direct anthropogenic disturbances. Globally, Tranvik *et al.* (2009) suggest that inland waters currently emit up to 1.4 Pg C yr^{-1} to the atmosphere, which is similar to the amount estimated by Burgermeister (2007) to be emitted to the atmosphere by deforestation (1.6 Pg C yr^{-1}). Tranvik *et al.* (2009) further suggest that lakes globally bury 0.6 Pg C yr^{-1} in their sediments. If a large proportion of global lakes were to experience regime shifts similar to those examined in this thesis, and with the same results to carbon cycling characteristics, the global

annual sequestration of carbon by lakes could be significantly increased, to the point that lakes could feasibly sequester more carbon annually than forests (1.4 Pg C yr^{-1}; Malhi *et al.*, 1999). Brothers *et al.* (2012) found that the carbon stock of flooded soils was directly related to their DOC release into the water and the subsequent pelagic CO_2 production. The final outcome of natural flooding events such as that observed at Gollinsee is therefore likely to depend upon the soil carbon characteristics of the terrestrial environment surrounding a lake. However, a comparable rise in DOC concentrations and water levels in both Gollinsee and Schulzensee from 2010 to 2011 (data not shown) suggests that lake metabolism and perhaps stable regime also play an important role in this regard, since no subsequent brownification-anoxia feedback loop occurred in macrophyte-dominated Schulzensee. Although the net impact of rising water levels and CO_2 emissions on carbon burial is not yet clear, it is important that future global carbon cycling models take these processes into account. By describing the underlying mechanisms behind several aspects of carbon cycling in shallow lakes, this research provides an important step towards a fuller understanding of the global carbon cycle and the processes affecting it.

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Statement of Academic Integrity

I hereby declare, that the dissertation entitled “Carbon gains, losses, and feedbacks in shallow, eutrophic lakes of phytoplankton and macrophyte dominance” is my own work. No sources other than those indicated have been used. All collaboration that has taken place with other researchers is indicated. This thesis has not been submitted for a doctoral degree at any other institution.

Hiermit erkläre ich, dass die Dissertation mit dem Titel “Carbon gains, losses, and feedbacks in shallow, eutrophic lakes of phytoplankton and macrophyte dominance” meine eigene Arbeit ist. Sie wurde nur unter der Verwendung der angegebenen Hilfen und Hilfsmittel angefertigt. Kooperationen mit anderen Wissenschaftlern wurden angegeben. Diese Dissertation wurde an keiner anderen Universität eingereicht.

Berlin, 25.06.2013

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Soren Brothers

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Curriculum Vitae

Personal

Name	Soren Michael Brothers
Birth	19. December 1982 in Mississauga, Canada
Citizenship	United Kingdom

Education

present	**Universität Potsdam (Potsdam, Germany), Leibniz-Institute for Freshwater Ecology and Inland Fisheries** Doctoral student, Biology.
2008 - 2010	**Université du Québec à Montréal (Montreal, Canada)** M.Sc., Biology.
2006 - 2007	**McGill University (Montreal, Canada)** Independent researcher, non-degree student.
2001 – 2005	**University of British Columbia (Vancouver, Canada)** B.Sc., major in biology (conservation biology), minor in political science.

Work/Volunteer

2012	**Field course teaching assistant, Potsdam University**
2010 - 2013	**Researcher, Leibniz-Institute of Freshwater Ecology and Inland Fisheries**
2009	**Field research and laboratory assistant, Université du Québec à Montréal**
2008	**Teaching assistant, Université du Québec à Montréal**
2007	**"Green Team" volunteer for the International Society of Limnology (SIL) conference in Montreal, Canada**
2006 – 2008	**Paleolimnology independent researcher, McGill University**
2005 – 2006	**General assistant, English-language editor at the Citizen's Alliance for Saving the Atmosphere and earth (CASA), Osaka, Japan**
2004 – 2005	**Plant Biology Research Assistant, University of British Columbia**
2005	**Conservation biology field work assistant, University of British Columbia**

Presentations

2013 **American Society of Oceanography and Limnology (ASLO) (New Orleans, USA)**

Köhler J., **Brothers S.M.** and Hilt S. "Shifts from turbid to clear-water state increase primary productivity but decline C burial in shallow lakes and lowland rivers" (oral presentation)

2012 **American Society of Oceanography and Limnology (ASLO) (Otsu, Japan)**

Brothers S., Hilt S., Kosten S., Mehner T., Meyer N. and Köhler J. "Regime shifts influence carbon fate in small, shallow lakes." (oral presentation)

2011 **The 7th international shallow lakes conference** (Wuxi, China)

Köhler J., **Brothers S.** and Hilt S. "Macrophyte versus phytoplankton dominance of shallow lakes: effects on productivity and carbon budget." (oral presentation)

2011 **Deutsche Gesellschaft fur Limnologie (DGL) (Freising, Germany)**

Brothers S., Köhler J., Hilt S., Attermeyer K., Meyer N., Scharnweber K., Mehner T., Nützmann G. and Caspar P. "The effects of plant community structure on primary production and carbon fate in shallow lakes." (oral presentation)

2009 **Hydro-Québec Eastmain-1 Workgroup meeting (Montreal, Canada)**

Brothers S. "Metabolic Differences between Boreal Lakes and a Young Boreal Reservoir in Quebec." (oral presentation)

2009 **Groupe de recherche interuniversitaire en limnologie et en environnement aquatique (GRIL) (Quebec, Canada)**

Brothers S. "La respiration pélagique et benthique d'un réservoir boréal et des lacs avoisinantes." (oral presentation)

2007 **Groupe de recherche interuniversitaire en limnologie et en environnement aquatique (GRIL) (Quebec, Canada)**

Brothers S. "A Multi-Scale Analysis of Factors Affecting Changes in Lacustrine Sedimentation Rates." (poster presentation)

Publications

Brothers S.M., Hilt S., Meyer S. and Köhler J. 2013. Plant community structure determines primary productivity in shallow, eutrophic lakes. *Freshwater Biology* doi:10.1111/fwb.12207.

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Jan Köhler (PhD supervisor)
Leibniz-Institut für Gewässerökologie und Binnenfischerei
Tel: +49(0)3064181687
Email: koehler@igb-berlin.de

Sabine Hilt (PhD supervisor)
Leibniz-Institut für Gewässerökologie und Binnenfischerei
Tel: +49(0)3064181677
Email: hilt@igb-berlin.de

Paul del Giorgio (M.Sc. supervisor)
Université du Québec à Montréal
Tel: 514-987-3000, ext. 2072
Email: del_giorgio.paul@uqam.ca

Yves Prairie (M.Sc. supervisor)
Université du Québec à Montréal
Tel : 514-987-3000, ext. 4870
Email: prairie.yves@uqam.ca