Effects of warming and nitrogen enrichment on carbon turnover in a littoral wetland

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Effects of Warming and Nitrogen Enrichment on Carbon Turnover in a Littoral Wetland

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"Grau, teurer Freund, ist alle Theorie

Und grün des Lebens goldner Baum."

Mephistopheles, Faust I

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Summary

Since the beginning of the Industrial Revolution in the 18th century, global mean surface temperature has risen by 0.74°C ± 0.18°C. This increase is largely attributed to the anthropogenic emission of greenhouse gases such as carbon dioxide (CO_2). A further temperature increase of 1.4 to 6.4 °C has been predicted by the Intergovernmental Panel on Climate Change (IPCC) to occur by the end of this century. Additionally, extensive uses of fertilizers, land-use changes and emission of nitrous oxide (N_2O) have seriously altered the global nitrogen cycle. These global environmental changes may have serious impacts on ecosystems, but the nature and magnitude of these impacts are not well understood at present.

Aim of this dissertation was to assess effects of elevated temperature and nitrogen enrichment on important components of the carbon cycle in ecosystems, specifically on the decomposition of plant litter and whole-ecosystem metabolism in a freshwater wetland. To this end, a set of heatable enclosures was set up in a littoral marsh of a lake. Half of the enclosures were heated to a target temperature of 4°C above ambient water temperature, whereas the other half served as unheated controls. Furthermore, half of the heated and half of the unheated enclosures where monthly fertilized with nitrate to an initial concentration five times higher than in the marsh. Enclosures were made of a double-layer of uncoloured polypropylene cylinders 120 cm high and with an inner diameter of 142 cm. The cylinders were pushed into the sediment to about 20 cm depth and fixed with three rebars (300 cm x 2 cm). Rates of plant litter decomposition and ecosystem metabolism were determined in these enclosures in three different experiments.

In a first experiment we tested for possible combined effects global warming and nitrogen supply on decomposition on leaf-litter. Experimentally elevated temperature had a pronounced effect on the decomposition, causing significantly faster decomposition of *Phragmites australis* leaves. This stimulation was counteracted, however, by an inhibition of decomposition in response to elevated nitrogen supply. As a result, decomposition in enclosures that were both heated and enriched with nitrogen proceeded at almost the same rate as in control enclosures. These results imply that increases in temperature predicted by global-change scenarios may lead to accelerated litter decomposition and shift wetlands from net carbon sinks to sources of CO_2 This would have profound implications for the global carbon cycle. However, sustained nitrogen supply, which is

likely to occur in concert with warming, may limit and even reverse the stimulation of decomposition by elevated temperature.

In a second experiment, the possible impact on litter decomposition of elevated atmospheric CO_2 concentrations during growth of deciduous trees was tested. It was hypothesized that elevated CO_2 concentrations would lower litter quality by increasing the lignin concentration, C:N ratio and/or C:P of leaf litter. As a result, it was expected that litter grown under elevated CO_2 would decompose more slowly than litter from control trees, but that elevated temperature during decomposition would offset the negative effect of reduced litter quality. Leaves for this experiment were collected from a free-air CO_2 enrichment experiment (FACE) located in a mixed, fully-grown forest stand dominated by *Prunus avium, Tilia platyphyllos, Carpinus betulus, Acer campestre, Quercus petraea and Fagus sylvatica.* All six species were used, resulting in 12 different litter types. Contrary to expectations, litter chemistry remained largely unaffected by elevated CO_2 concentrations during the growing season. Lignin concentrations were unaffected in litter from four of the six species and *Acer* and *Quercus* leaves contained significant less, rather than more lignin when grown under conditions of elevated CO_2 levels. Similarly, the C:N and C:P ratios of litter showed no consistent response across all species and were decreased, rather than increased in three or four, respectively, of the six species. Decomposition rates tended to be higher when leaves were grown at elevated CO_2 levels but this effect could not be clearly related to changes in litter quality except for *Acer* and especially *Quercus* where faster decomposition correlated with lower litter lignin concentrations. Higher amounts of nonstructural carbohydrates may account for the observed effect in the other species where leaves grown at elevated CO_2 concentrations decomposed faster. Overall, elevated temperature had surprisingly little effect on decomposition rates, especially of recalcitrant leaves that remained longer in the field than the more rapidly decomposing species. This lack of a clear positive temperature effect may have been due to declines of dissolved oxygen concentrations in the enclosures.

In a third experiment, the influence of elevated temperature and nitrogen deposition on ecosystem metabolism was tested. This experiment revealed an inhibition of both gross primary production (GPP) and ecosystem respiration (ER) by nitrogen enrichment, whereas experimental warming had no effect. Patterns across treatments of GPP and ER were strikingly similar, suggesting that GPP might have been limited by rates of nutrient recycling in benthic organic matter, which was likely to dominate ER. There was no clear indication that the nitrogen-

induced inhibition of GPP and ER was due to exacerbated phosphorus limitation, the element that appeared to be in shortest supply. Instead, it may have been caused by a cascading effect triggered by an inhibition of organic matter decomposition by elevated nitrate concentrations, particularly of recalcitrant organic carbon compounds such as lignin.

In summary, results of the present dissertation revealed a stimulating effect of elevated temperature on the decomposition of *Phragmites* leaves, but a similar effect on leaf litter from a range of deciduous tree species was not observed, possibly due to the negative consequences of declines in dissolved oxygen concentrations in enclosures. Exposure of leaves to elevated CO_2 concentrations only produced a strong effect in two of six leaf species, although a similar tendency was also apparent in most other cases. Elevated nitrogen supply counteracted the acceleration of *Phragmites* decomposition and also impacted ecosystem metabolism in that both gross primary production of algae and whole-ecosystem respiration were reduced except in winter. Nitrogen enrichment thus appears to buffer warming effects on ecosystem processes and could potentially prevent wetlands from shifting from a CO_2 sink to a CO_2 sources when global temperature increases further in the future.

Zusammenfassung

Seit Beginn der Industriellen Revolution im 18. Jahrhundert hat sich die globale mittlere Jahrestemperatur um 0.74°C ± 0.18°C erhöht. Dieser Anstieg ist hauptsächlich auf den anthropogenen Ausstoss von Kohlenstoffdioxid (CO_2) zurückzuführen. Ein weiterer Anstieg um etwa 1.4 – 6.4 °C wird vom Intergovernmental Panel on Climate Change (IPCC) bis zum Ende des Jahrhunderts prognostiziert. Darüber hinaus hat der intensive Einsatz von Stickstoffdünger in der Landwirtschaft und die Emission von Stickoxiden den globalen Stickstoff-Kreislauf stark verändert. Diese globalen Umweltveränderungen haben mit hoher Wahrscheinlichkeit starke Einflüsse auf Ökosysteme. Die Art und das Ausmass der zu erwartenden Veränderungen sind nach dem derzeitigen Stand der Wissenschaft jedoch kaum abzuschätzen.

Ziel dieser Doktorarbeit war die Untersuchung der Einflüsse erhöhter Temperaturen und Stickstoffdeposition auf wichtige Teile des Kohlenstoffkreislaufs, speziell auf den Abbau von Blattmaterial und den Gesamtkohlkenstoffumsatz in Schilfröhrichten. Für diese Untersuchungen wurden im Schilfgürtel eines Sees experimentell beheizbare Mesokosmen installiert. Die Hälfte der Mesokosmen wurde so beheizt, dass die Wassertemperatur in ihnen jeweils 4°C höher als die umgebende Seetemperatur war, die übrigen Mesokosmen dienten als ungeheizte Kontrollen. Zusätzlich wurde jeweils die Hälfte der geheizten und ungeheizten Mesokosmen monatlich mit Nitrat gedüngt, wobei die Zielkonzentration in den gedüngten Mesokosmen fünfmal höher war als die Nitratkonzentration im See. Drei verschiedene Experimente zum Abbau von Blattmaterial und Metabolismus wurden in diesen Mesokosmen durchgeführt.

Im ersten Experiment wurde der gemeinsame Einfluss von erhöhter Temperatur und Stickstoffdeposition auf den Abbau von Blattmaterial untersucht. Die experimentelle Erhöhung der Temperatur hatte einen starken Einfluss auf den Abbau und verursachte einen signifikant schnelleren Abbau der Blätter von *Phragmites australis*. Stickstoff wirkte tendenziell inhibierend auf den Abbau und wirkte dadurch der Erhöhung der Abbaurate durch Erwärmung entgegen. Dies führte dazu, dass die Blattabbaugeschwindigkeit in geheizten und gedüngten Mesokosmen ungefähr gleich hoch war wie in den (ungeheizten und ungedüngten) Kontrollmesokosmen. Diese Ergebnisse lassen darauf schließen, dass die globale Erwärmung zu einem schnelleren Abbau von organischem Material führen könnte und Feuchtgebiete von Kohlenstoffsenken zu Kohlenstoffquellen werden könnten. Gravierende Auswirkungen auf den globalen

Kohlenstoffkreislauf könnten die Folge sein. Eine in Zukunft sehr wahrscheinlich erhöhte Stickstoffdeposition könnte jedoch die Erhöhung der Abbauraten limitieren oder sogar umkehren.

In einem zweiten Experiment wurde untersucht, wie sich erhöhte CO_2-Konzentrationen während des Wachstums von Laubblättern auf den Streuabbau auswirken. Es wurde angenommen, dass erhöhte CO_2-Konzentrationen die Blattqualität aufgrund einer höheren Ligninkonzentration und veränderter C:N- und/oder C:P-Verhältnisse vermindern. Aufgrund ihrer geringeren Qualität könnten Blätter, die bei höheren CO_2 Konzentrationen gewachsen sind, langsamer abgebaut werden. Dieser Effekt könnte jedoch durch höhere Temperaturen wieder aufgehoben werden. Die Blätter für dieses Experiment wurden von einem CO_2-Begasungs-Experiment in einem Mischwald mit *Prunus avium, Tilia platyphyllos, Carpinus betulus, Acer campestre, Quercus petraea and Fagus sylvatica* gesammelt. Von allen sechs Arten wurden jeweils Blätter gesammelt die unter erhöhten CO_2-Konzentrationen gewachsen waren und Kontrollblätter, die unter normalen Konzentrationen gewachsen waren. In vier der sechs untersuchten Arten hatte CO_2 keinen Einfluss auf die Ligninkonzentration. *Acer* und *Quercus* enthielten sogar weniger Lignin. Die Verhältnisse von C:N und C:P zeigten ebenfalls kein klares Bild. Drei der sechs Arten hatten sogar niedrigere anstatt höhere Kohlenstoff-Nährstoff-Verhältnisse. Der Abbau war tendenziell schneller bei Blättern, die unter höheren CO_2-Konzentrationen gewachsen waren, die Abbaugeschwindigkeit liess sich jedoch nicht eindeutig mit einer veränderten Blattchemie korrelieren. Ausgenommen davon waren *Acer* und *Quercus*, bei denen ein schnellerer Abbau mit niedrigeren Ligninkonzentrationen korrelierte. Der schnellere Abbau von Blättern, die unter höheren CO_2-Konzentrationen gewachsen waren, könnte durch einen höheren Anteil von gut abbaubaren Kohlenhydraten verursacht worden sein, die nicht strukturgebundenen sind. Insgesamt war der Einfluss der erhöhten Temperatur gering, speziell bei schwer abbaubaren Blättern, die sehr lang im Röhricht exponiert waren. Dies wurde wahrscheinlich durch geringe Sauerstoffkonzentrationen in den Mesokosmen während der Sommermonate verursacht.

Im dritten Experiment wurde der Einfluss von erhöhter Temperatur und Stickstoffdüngung auf den Gesamtkohlenstoffhaushalt im Röhricht untersucht. Dieses Experiment zeigte eine Inhibierung der Bruttoprimärproduktion und der Ökosystem-Respiration durch Stickstoff, jedoch keinen Temperatureffekt. Diese Ergebnisse deuten darauf hin, dass die Bruttoprimärproduktion möglicherweise indirekt durch eine Inhibierung der Ökosystem-Respiration und der damit verbundenen verminderten Nährstoffrezyklierung limitiert wurde. Der Mechanismus dieser

Limitierung ist jedoch nicht geklärt. Es ist denkbar, dass durch die experimentelle Stickstoffzugabe eine bestehende Phosphorlimitierung verschärft wurde. Ein anderer möglicher Effekt ist eine Inhibierung des Abbaus von ohnehin schwer abbaubaren Verbindungen. Dies könnte zu der erwähnten verminderten Nährstoffrezyklierung geführt haben und dadurch wiederum die Bruttoprimärproduktion limitiert haben.

Zusammenfassend zeigen die Ergebnisse der vorliegenden Arbeit einen schnelleren Abbau von *Phragmites*-Blättern. Ein entsprechender Effekt bei verschiedenen anderen Laubarten konnte jedoch nicht eindeutig nachgewiesen werden, was möglicherweise durch niedrige Sauerstoffkonzentrationen in den Mesokosmen verursacht wurde. Erhöhte CO_2-Konzentrationen während des Blattwachstums veränderten nur in zwei von sechs Fällen den Abbau deutlich, wobei bei den anderen vier Arten jedoch Tendenzen festgestellt wurden. Erhöhte Stickstoffdeposition führte bei *Phragmites* zu einem verminderten Abbau und verminderte geringfügig, aber systematisch die Bruttoprimärproduktion und Ökosystem-Respiration - ausser im Winter, w die Umsatzraten sehr niedrig waren. Es scheint deshlab möglich dass erhöhte Stickstoffdeposition die stimulierenden Effekte erhöhter Temperatur auf den Streuabbau abpuffern könnte und dadurch verhindern, dass Feuchtgebiete von Kohlenstoffsenken zu Kohlenstoffquellen für die Atmosphäre werden, wenn die Klimaerwärmung weiter voranschreitet.

Introduction

Since the beginning of the Industrial Revolution in the 18th century, the emission of greenhouse gases such as carbon dioxide (CO_2) and nitrous oxide (N_2O) has dramatically increased due to burning of fossil fuels and intensive land use (Forster et al., 2007). Over the last 250 years the concentration of CO_2 has increased globally by about 100 ppm (36%), from 275-285 ppm in the pre-industrial era to 379 ppm in 2005; N_2O concentrations have increased simultaneously from 270 ppb to 319 ppb (Forster et al., 2007). Greenhouse gases reduce the Earth's loss of heat into space and thereby contribute to global atmospheric warming through the greenhouse effect. Greenhouse gases are essential to maintain the Earth's surface temperature; without them Earth would be too cold to sustain life (Karl & Trenberth, 2003). However the massive combustion of fossil fuels led to an increase of greenhouse gases which in turn raised global mean surface temperature by 0.74°C ± 0.18°C since the beginning of last century, with the highest rates of increase in the last two decades (Trenberth et al., 2007). With massive anthropogenic emissions of greenhouse gases continuing, further warming of the atmosphere and Earth's surface currently seems inevitable. Accordingly, the Intergovernmental Panel of Climate Change (IPCC) predicts a further rise between 1.4 and 3.8°C (scenario B2, local environmental sustainability) to between 1.4 and 6.4°C (scenario A1, rapid economic growth; Meehl et al., 2007) by the year 2100. With human demography and demands for agricultural commodities increasing, the transformation in the Haber-Bosch process of inert dinitrogen gas (N_2) to reactive nitrogen species has also greatly increased during the last 100 years from ~15 Tg N in 1860 to 187 Tg N in 2005 (Galloway et al., 2008).

The consequences for the biosphere of these profound changes in global carbon and nitrogen cycles and their complex interactions are only beginning to be understood. Nitrogen enrichment causes, for example, changes in rates of primary production, plant tissue chemistry and decomposition of organic matter (Aerts, 1997; Aerts, van Logtestijn, & Karlsson, 2006; DeForest, Zak, Pregitzer, & Burton, 2005; Finlay, Khandwala, & Power, 2002; Galloway et al., 2003; Holland, Braswell, Sulzman, & Lamarque, 2005; Norby, Cotrufo, Ineson, O'Neill, & Canadell, 2001). Elevated carbon dioxide concentrations in the atmosphere have often been found to increase lignin concentrations and to change the C:N ratio of deciduous leaves (Hättenschwiler, Bühler, & Körner, 1999; Hirschel, Körner, & Arnone, 1997). Because of the

tight connection of the N- and C-cycle a change in N-input triggers also changes in the C-cycle (Vitousek et al., 1997).

Wetlands play an important role in the global carbon cycle. Although, they only cover about 6% the Earth's land surface (Mack, Schuur, Bret-Harte, Shaver, & Chapin, 2004; Mitsch & Gosselink, 2000), they store considerable amounts of carbon because primary production often exceeds decomposition (Mitsch et al., 2000). For example, in wetlands composed of *Phragmites australis* (Cav.) Trin. ex Steud., the net annual aboveground production may be up to 10 kg dry matter per m^2 for the most productive sites, although 1-2 kg m^2 are more typical values (Brix, Sorrell, & Lorenzen, 2001). Climatic changes may affect the C-cycle in wetlands in complex ways. Increased temperatures may lead to later freezing and earlier ice-breakup in the northern hemisphere (Magnuson et al., 2000), resulting in an extended growing season and increased annual primary production (Jonasson, Michelsen, Schmidt, & Nielsen, 1999; McKee et al., 2002). As a consequence of increased productivity in wetlands, litter production will be increased as well, which in turn may lead to augmented litter decomposition. Another scenario is that warming leads to faster litter decomposition than litter accumulation and therefore to a depletion of the long-term C-stores. This shift of wetlands from a carbon sink to a carbon source would than feed back on atmospheric CO_2 concentrations and hence on climate.

The aim of this dissertation was to test in a series of controlled experiments for the combined effects of global warming and nitrogen supply on important processes of the carbon cycle. Special emphasis was placed on litter decomposition (Chapters 1 and 2) but whole-ecosystem metabolism was also considered in one study (Chapter 3). In addition, one study assessed the interplay between elevated CO_2 concentrations in the atmosphere during plant growth and elevated temperature during decomposition of plant litter (Chapter 2). All experiments were conducted in a set of enclosures that were installed in a littoral freshwater marsh composed of an important wetland plant (the cosmopolitan common reed, *Phragmites australis*) and that could be experimentally heated and fertilized.

In the first experiment the combined influence of sustained nitrogen loading and elevated temperature on litter decomposition was tested. Decomposition was expected to increase with increasing temperature, as has been found in comparisons across climatic zones in terrestrial ecosystems (Liski, Nissinen, Erhard, & Taskinen, 2003; Moore et al., 1999) and in a range of also terrestrial studies in which experimental heating mimicked elevated temperatures caused by climate change (Bryant, Holland, Seastedt, & Walker, 1998; McHale, Mitchell, Bowles, &

Bowles, 1998; Shaw & Harte, 2001; Sjögersten & Wookey, 2004). Results from the heating experiments in terrestrial environments have to be interpreted with caution, however, as the experimental manipulation may confound effects of elevated temperature with side effects caused by decreasing water availability, which seriously affects microbial decomposers. To circumvent this problem, the present study was carried out in a permanently inundated marsh. Prediction of nitrogen enrichment effects on decomposition is less straightforward than prediction of temperature effects. Although nitrogen is in short supply relative to the C:N demand ratios of decomposers, N enrichment is unlikely to increase decomposition rates of leaf material because phosphorus is generally in shortest supply in fresh waters and thus the limiting factor of ecosystem processes in the freshwater systems. This should result in a neutral effect of N addition on decomposition. However, N enrichment has also been observed in some studies to inhibit decomposition. Carreiro et al. (2000) presented evidence that such adverse effects of N enrichment are due to the suppression of ligninolytic fungal enzyme activity. Other studies, however, found no (e.g. Carreiro et al., 2000; Hobbie & Vitousek, 2000) or stimulating effects (e.g. Carreiro et al., 2000; Hobbie, 2000; Hobbie et al., 2000). The main goal of the experiment reported in Chapter 1 was to ascertain how N enrichment resulting from sustained N deposition affects decomposition and to test for possible combined effects of elevated temperature and nitrogen. The study involved a standard litter-bag experiment with leaves of *Phragmites australis* exposed in heated, fertilized and control enclosures as well as in unfenced control plots in the marsh. The litter was later retrieved to determine leaf mass remaining. Use of two mesh sizes (0.5 and 10 mm) was intended to distinguish effects mediated by detritivorous macroinvertebrates by and microbial decomposers.

In the second experiment the response of leaf litter decomposition to leaves grown under conditions of elevated carbon dioxide was tested. Assessing effect of elevated carbon dioxide concentrations is important because these conditions have potential to increase lignin concentrations of deciduous leaves (Coley, Massa, Lovelock, & Winter, 2002; Cotrufo, Briones, & Ineson, 1998; Poorter et al., 1997) and lignin is a key factor controlling rates of leaf decomposition in freshwater ecosystems (Gessner & Chauvet, 1994). This suggests that decomposition rates of litter from trees grown under elevated carbon dioxide levels are reduced. In addition, nitrogen concentrations in leaf tissue might become reduced in plants expose to elevated CO_2 concentrations, because enhanced carbon supply for photosynthesis may result in a dilution of nitrogen-containing leaf constituents. This effect has been observed in various studies (e.g. Cotrufo et al., 1998; Norby, Long, Hartz-Rubin, & O'Neill, 2000). Lowered N

concentrations in plant litter excaerbates stoichiometric constraints on microbial decomposers and detritivores, which in turn may lead to reduced decomposition rates. Thus, we hypothesized that exposure of leaves to elevated CO_2 levels during the growing season lowers decomposition rates as a result of higher lignin and/or lower N concentrations. We also hypothesized that reduced decomposition rates could be counteracted, however, by elevated temperatures. To test these predictions, a litter-bag experiment was conducted similar to the one described above. Leaf litter was collected from deciduous trees exposed to elevated carbon dioxide concentrations in a free-air carbon dioxide enrichment (FACE) experiment (Pepin & Körner, 2002). Leaves from a total of six species (*Fagus sylvatica* L., *Quercus petraea* Liebl., *Carpinus betulus* L., *Acer campestre* L., *Tilia platyphyllos* Scop. and *Prunus avium* L.) and their corresponding control leaves exposed to ambient carbon dioxide concentrations were collected in tree canopies just before leaf fall. Each of the twelve different leaf types was enclosed in separate leaf bags and exposed in enclosures and later retrieved to determine litter mass remaining.

In the last experiment we tested for the influence of warming and nitrogen enrichment on whole-ecosystem metabolism (sensu Odum, 1956), which combines primary production and respiration by all organisms in a given ecosystems. Gross primary production (GPP) is the process that fixes CO_2 and transforms it to organic carbon in the form of biomass, whereas ecosystem respiration (ER) is the complementary process that leads to the mineralization of organic carbon to CO_2. The ratio of both processes (GPP/ER) describes whether a system is net heterotrophic or autotrophic. In net autotrophic systems, GPP exceeds ER and the system can store or export organic carbon. In net heterotrophic systems, ER exceeds GPP and the system mineralizes more organic C than was produced by primary production within the system's boundaries (Staehr & Sand-Jensen, 2006). Effects of elevated temperature and nitrogen on ecosystem metabolism have not been previously tested. They are also difficult to predict since different processes contributing to overall metabolism may respond differently to temperature and/or nitrogen supply. Higher temperature is expected to increase rates of ecosystem processes (Davidson & Janssens, 2006; Staehr et al., 2006), leading to enhanced ecosystem metabolism. Excessive nitrogen supply, in contrast, may inhibit some heterotrophic processes, such as ligninolysis (Carreiro et al., 2000), and may thus reduce ecosystem respiration. The net effect on whole-ecosystem metabolism has not been assessed yet. Therefore, the aim of the experiment reported in Chapter 3 was to test for the effects of elevated temperature and nitrogen supply on whole-ecosystem metabolism. This was achieved by measuring diel changes in dissolved oxygen

concentrations (Odum, 1956) in the enclosures described above that were subject to experimental warming and nitrogen enrichment.

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Combined effects of nutrient addition and elevated temperature on leaf litter decomposition

Arne Hammrich, Sabine Flury and Mark O. Gessner

Introduction

Global mean surface temperature has risen by 0.74°C ± 0.18°C since the beginning of last century (Trenberth et al., 2007). Further warming has been predicted by the Intergovernmental Panel on Climate Change (IPCC), depending on the scenario, to range from 1.4 - 3.8°C (scenario B2, local environmental sustainability) to 1.4 - 6.4°C (scenario A1, rapid economic growth) for the year 2100 (Meehl et al., 2007). It is broadly accepted that the massive anthropogenic emission of greenhouse gases such as CO_2 is a main reason for this rise in temperature. However, since the Industrial Revolution in the mid 19th century not only the concentration of CO_2 has risen, but also the bioavailability of nitrogen, due to combustion of fossil fuels, intensive land use and the Haber-Bosch process, which converts nonreactive N_2 to reactive NH_3 mainly for fertilizer production (Galloway et al., 2008; Gruber & Galloway, 2008).

Nitrogen and carbon cycling in ecosystems are tightly linked (Vitousek et al., 1997). Nitrogen enrichment causes, for example, changes in primary production, litter chemistry and decomposition of organic carbon (Aerts, 1997; Aerts, van Logtestijn, & Karlsson, 2006; DeForest, Zak, Pregitzer, & Burton, 2005; Finlay, Khandwala, & Power, 2002; Galloway et al., 2003; Holland, Braswell, Sulzman, & Lamarque, 2005; Norby, Cotrufo, Ineson, O'Neill, & Canadell, 2001). The complex interactions of nitrogen and carbon cycles are only beginning to be understood. About 1500 Pg carbon, twice as much as contained in the atmosphere, is globally bound in soils and litter (Houghton, 2007). Decomposition, the counteracting process of primary production, of these vast carbon pools is therefore a potential source of greenhouse gases and further global temperature increases. It is currently unclear whether these carbon stores will remain carbon sinks or shift to become carbon sources when atmospheric CO_2 concentrations and N availability continues to rise.

A number of studies have been conducted to investigate effects of nitrogen supply on litter decomposition. Results have varied. Several authors have reported no effect of nitrogen on decomposition (e.g. Carreiro, Sinsabaugh, Repert, & Parkhurst, 2000; Hobbie & Vitousek, 2000), others found inhibitory effects (e.g. Carreiro et al., 2000; Magill & Aber, 1998), and still others have observed stimulating effects (Carreiro et al., 2000; Hobbie, 2000; Hobbie et al., 2000). Knorr et al. (2005) relate these seemingly contradictory results to differences in litter chemistry. Accordingly, decomposition of high-quality litter is stimulated by high loads of external nitrogen, whereas decomposition rates of low-quality litter are reduced. The underlying reason may be suppression of phenol oxidase by high nitrogen loads (Knorr et al., 2005; Osono, 2007; Sinsabaugh, Carreiro, & Repert, 2002).

Assessing the influence of elevated temperature on litter decomposition appears to be straightforward and has been the subject of numerous studies. Several of them have increased temperature experimentally to test for effects of warming on decomposition (Bryant, Holland, Seastedt, & Walker, 1998; McHale, Mitchell, Bowles, & Bowles, 1998; Shaw & Harte, 2001; Sjögersten & Wookey, 2004), and others have compared decomposition rates across different climatic zones (Liski, Nissinen, Erhard, & Taskinen, 2003; Moore et al., 1999). Decomposition rates determined in these studies increased with increasing temperature, although temperature effects may have been confounded with decreasing water availability when temperatures increased (Zelles et al., 1991).Decreasing humidity resulting from higher temperatures seriously affects bacterial and fungal decomposers, so that results of those studies must be interpreted with caution.

Global warming experiments in permanently flooded wetlands do not suffer from the problem of coupled changes in temperature and moisture, as water never becomes limiting for the decomposer community. Furthermore, although they only cover a relatively small part (6%) of the earth's land surface, wetlands play an important role in the global cycles of carbon, nitrogen and other elements (Mack, Schuur, Bret-Harte, Shaver, & Chapin, 2004; Mitsch & Gosselink, 2000) and tend to sequester carbon because decomposition often cannot keep pace with primary production (Mitsch et al., 2000). For example, in wetlands composed of *Phragmites australis* (Cav.) Trin. ex Steud, the net annual aboveground production may be up to 10 kg dry matter per m^2 for the most productive sites (Brix, Sorrell, & Lorenzen, 2001), although 1-2 kg per m^2 are more typical values (Brix et al., 2001), and a large fraction of the refractory stem material may not be turned over in one year (Gessner, 2000; Hietz, 1992). Increases in temperature such as

those predicted by the IPCC (2007) may lead to enhanced litter decomposition, and shift wetlands from net carbon sinks to sources of atmospheric CO_2. Such temperature effects have not been experimentally investigated in aquatic environments under field conditions.

Studies addressing possible interactive effects of elevated temperature and nitrogen supply are rare. Bryant et al. (1998) placed litter bags in three different vegetation types along a natural temperature gradient and fertilized part of the experimental plots with ammonium nitrate. They found no effect of nitrogen enrichment on decomposition and suggested that moisture availability was the overriding factor controlling decomposition rate.

The aim of this study was to assess effects of elevated temperature, nitrogen enrichment, and the interaction of these two factors of global environmental change on litter decomposition. By simulating global warming in mesocosms positioned in a permanently aquatic marsh, we avoided the confounding effect of experimentally increased temperature on water availability. Mesocosms were also enriched with nitrate to assess whether warming and increased nitrogen availability may have synergistic effects on decomposition rates.

Material & Methods

The experimental site was located in a littoral marsh dominated by common reed, *Phragmites australis* (Cav.) Trin. ex Steud., on the eastern shore of Lake Hallwil near Meisterschwanden in Central Switzerland. Lake Hallwil is a eutrophic meromictic moraine lake at 449 m above sea level. It has a surface area of 10.2 km^2, a volume of 0.292 km^3 and a maximum depth of 48 m. The theoretical water residence time is 3.8 a (Märki & Schmid, 1983; Scheidegger, Stöckli, & Wüest, 1994). The stand is permanently flooded, extends about 850m along the shore line and is up to 20m wide. The maximum water depth within the marsh is about 1m; the average depth is about 0.5m.

To test for combined effects of elevated temperature and nitrogen amendment, we used a randomized block design with four blocks. Each block consisted of two heated and two unheated enclosures and an additional unfenced control plot to test for possible artifacts caused by the enclosures. Treatments were randomly assigned within blocks. Water temperature in the heated

enclosures was increased to a target temperature of 4 °C above the ambient water temperature to simulate IPCC Scenario A2 (Meehl et al., 2007). One heated and one unheated enclosure per block were each fertilized by monthly addition of $Ca(NO_3)_2$ solution to a target concentration five times above the ambient lake concentration.

Enclosures were made of a double-layer of uncolored polypropylene cylinders 120 cm in height and with an inner diameter of 142 cm. The cylinders were pushed into the sediment to about 20 cm depth and fixed with three large rebars (300 cm x 2 cm) and braces. Temperature in the enclosures was controlled by two-point regulators (FCR 13A, Shinko Technos Company Ltd.; Osaka, Japan). Two control units were used per block, each regulating one pair of one heated and one unheated enclosure. The control units were connected to three platinum thermocouples (Pt 100), one each for the two enclosures and the surrounding lake. Heating was achieved by four electrical heating elements (300 W, jbl; Neuhofen, Germany) per enclosure. A submersible, permanently running pump (model 1046, Eheim; Deizisau, Germany) minimized formation of temperature and chemical gradients in the enclosures. Temperature in all enclosures and the lake was recorded at 30-minute intervals (Minilog, 8 bit temperature loggers, Vemco; Halifax, Canada).

We used standard litter-bags with two mesh sizes to determine decomposition rates of *Phragmites australis* leaf litter (Boulton & Boon, 1991). Coarse-mesh bags (10-mm mesh size) allowed macroinvertebrates to access the leaves, whereas fine-mesh bags (0.5 mm) were intended to measure microbial decomposition only. Fully brown leaf blades were collected in early November from standing dead *Phragmites* shoots in Lake Hallwil and air-dried at room temperature. The dried leaves were weighed in batches of 5.00±0.05 g and placed in the litter bags. Six randomly selected batches were immediately freeze-dried to determine moisture content. Before enclosing the remaining leaf batches in the litter bags, they were sprayed with lake water to make them pliant and thus prevent breakage. The bags were then closed, stored overnight at 4°C, and deployed in the field the next day. Pairs of fine-mesh and coarse-mesh bags were tied to a bamboo stick and then submerged in each enclosure or unfenced control plot.

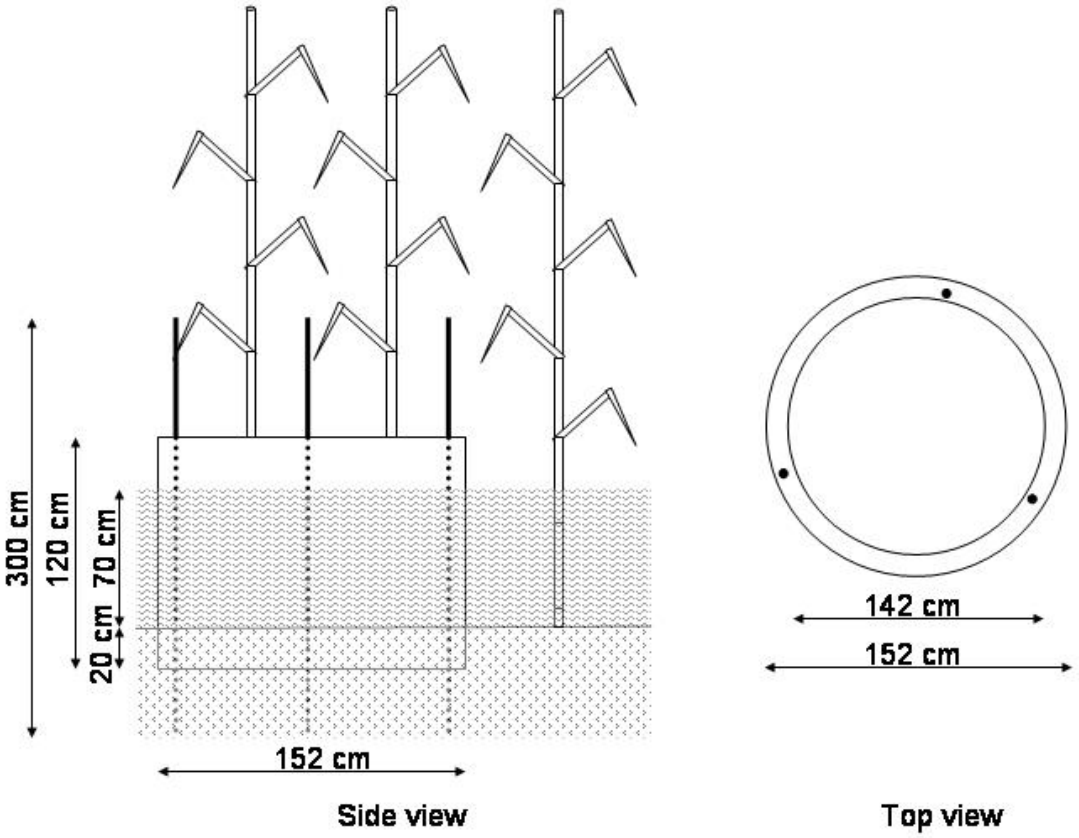

Figure 1. Lateral (left) and top view (right) of an enclosure in the littoral reed stand of Lake Hallwil.

Bags were retrieved from the field after 33, 70, 104, 132, 159, 188 and 222 days and returned to the laboratory in a cooling box. The leaf material remaining in the bags was cleaned with filtered lake water from macroinvertebrates and adhering debris, freeze-dried, and weighed to the nearest 0.01 g to determine litter mass loss.

Decomposition of *Phragmites australis* was described as dry mass remaining over time. The decay rate coefficient, *k*, was normalized for temperature using the following equation:

$$m(t) = m_o \cdot e^{-k \cdot \int_{to}^{t} e^{\frac{\ln Q_{10}}{10} \cdot T(t')} dt'}$$

where *m(t)* is the litter mass remaining at time *t*, m_0 is the initial litter mass and *T* is the daily mean temperature. Q_{10} denotes a factor, first introduced by van t'Hoff, by which a chemical reaction rate is accelerated when temperature increases by 10 °C. It typically ranges between 2 and 3. The integral in the exponent is a proxy of heat energy experienced by the litter during decomposition in the field. This approach is analogous to fitting a degree-day model, but assumes an exponential rather than linear dependence of litter mass loss on temperature. Decay

rate coefficients, k, were calculated for each enclosure and mesh size by fitting least-squares in iterative cycles in which Q_{10} values were varied from 0.5 to 10.0 in 0.1 steps. Q_{10} values corresponding to the best-fitting regressions differed slightly among enclosures, as judged from the calculated coefficients of determination (r^2). Since we were primarily interested in comparing decay coefficients, we subsequently used a constant Q_{10} obtained by averaging across all treatments and enclosures. The k values for all treatments were then recalculated based on this average Q_{10}. Regression analyses were performed with MATLAB (R2007b, The MathWorks, Inc.; Natick, MA, USA).

Model performance was assessed by fitting linear regressions between the measured data and the data predicted by the model. The predicted values were used as the independent variable, the measured values as dependent variable. A perfect model would provide a line passing through the origin with a slope of unity. This null-hypothesis that the intercept = 0 and slope = 1 was tested with a simultaneous F-test (Dent & Blackie, 1979).

Coefficients of determination (r^2) are insufficient to judge if a model is accurate. Suppose, for example, a very precise model that leads to a regression line with a slope of 1 but an intercept very different from 0. This case cannot be properly assessed based on r^2, because r^2 would be close to one even though the model is inaccurate. Consequently, we used the so-called modeling efficiency (MEF) instead of r^2 to evaluate model accuracy and precision (Tedeschi, 2006). MEF is the proportion of variation explained by the line $Y_{measured} = X_{predicted}$:

$$\mathrm{MEF} = 1 - \frac{\sum_{i=1}^{n}(Y_i - X_i)^2}{\sum_{i=1}^{n}(Y_i - \overline{Y})^2},$$

where Y_i are measured values and X_i are values predicted by the model. Similar to r^2, MEF can assume values between 0 (no relation between modeled and measured data) and 1 (perfect fit).

Sensitivity of estimated decay coefficients to variation in Q_{10} was assessed by varying Q_{10} in a stepwise fashion to ±60% and evaluating the resulting percent change of k as percent deviation from the k-values calculated based on the initial Q_{10}.

Repeated-measures ANOVA was used to test for effects of elevated temperature and nitrogen enrichment on litter mass loss. ANOVAs were carried out with the five warming and nitrogen

treatments (unheated, unfertilized = Δ0°; unheated, fertilized = Δ0°N; heated, unfertilized = Δ4°; heated, fertilized = Δ4°N; L = unfenced control plot) and mesh size as categorical variables, sampling date as repeated-measures variable, position in the reed stand as blocking factor, and percent litter mass remaining as response variable. Planned linear contrasts were subsequently used to test for mesocosm effects (control mesocosms vs. unfenced control plots), for effects of experimental warming (heated vs. unheated enclosures), nitrogen enrichment (fertilized vs. unfertilized enclosures both within one temperature regime and between temperature regimes). Differences among *k*-values were tested by ANOVA and planned contrasts in the same manner, except that sampling date was not included as a repeated measure. Finally, we tested in a third ANOVA for differences in the time needed until 60% of the initial leaf mass had been lost (T_{60}).

Results

Experimental warming was successful, although the intended 4°C above ambient lake temperature was not always reached (Figure 2). Nevertheless, on average, the temperature in the heated enclosures was 3.9°C higher than the lake temperature. In the heated and fertilized enclosures the temperature was 3.3°C higher than in the surrounding lake.

Litter decomposition in all enclosures followed a sigmoid mass loss pattern (Figure 3). After an initially rapid mass loss, decomposition slowed between day 105 and 159 but later accelerated again. Although mass loss was similar in all treatments during the first 104 days, differences began to emerge among treatments during the following months. Leaves in coarse-mesh bags decomposed faster than leaves in fine-mesh bags ($P < 0.001$). Leaves deployed in the unfenced control plots decomposed the fastest and leaves submerged in the fertilized but unheated enclosures (Δ0°N) were the slowest to decompose. Litter mass remaining in fine-mesh bags after 222 days ranged from 44.7 ± 4.0% in the unfenced control plots to 57.8 ± 3.8% in Δ0°N enclosures. Corresponding values in coarse-mesh bags were 15.0 ± 4.2% in the unfenced control plot to 35.8 ± 13.9% in Δ0°N enclosures. Heating generally accelerated decomposition ($P = 0.001$).

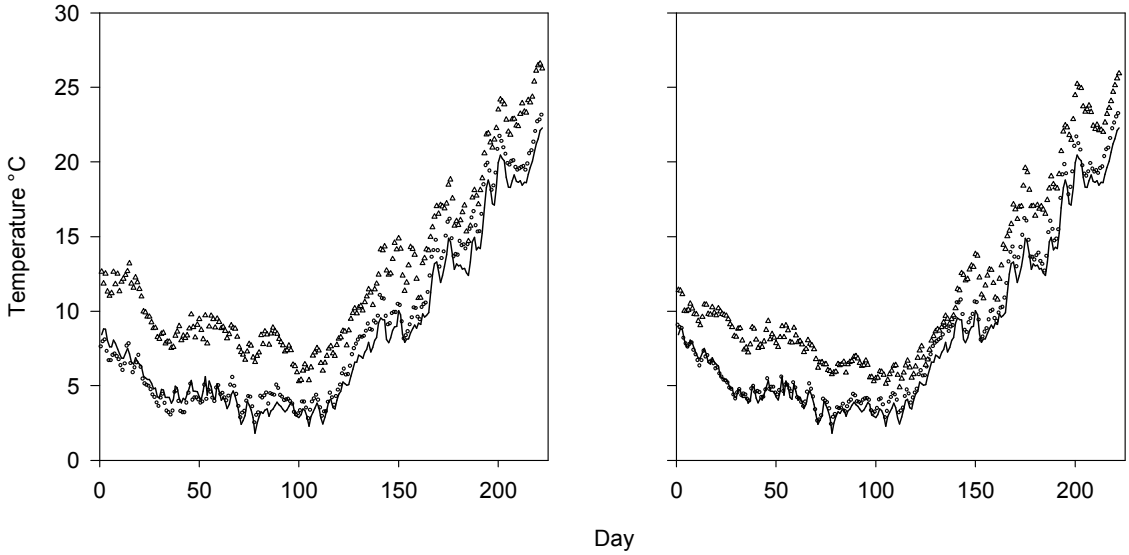

Figure 2. Daily mean temperatures during the decomposition experiment in the reed stand of Lake Hallwil. The left panel shows temperatures in unfertilized enclosures (symbols) and the unfenced control plots (solid line), the right panel shows temperature in fertilized enclosures (symbols) and the unfenced control plots (solid line). Circles denote unheated enclosures, triangles denote heated enclosures.

The only exceptions were leaves from coarse-mesh bags in Δ0°N enclosures, where leaf mass loss was exceptionally fast after day 188. Nitrate addition tended to slow decomposition. This effects was particularly prominent when the fertilized enclosures were heated (P = 0.005), whereas in unheated enclosures the effect of nitrogen addition was not statistically significant (P = 0.08).

Table 1. Parameters of linear regressions of measured over modeled data from all four types of enclosures (unheated, unfertilized = Δ0°; unheated, fertilized = Δ0°N; heated, unfertilized = Δ4°; heated, fertilized = Δ4°N) and the unfenced control plots. Errors are SEM (N = 4). MEF = Modeling Efficiency according to Tedeschi (2006).

Mesh-size	Treatment	Slope	Intercept	r^2	MEF	*F*	*P*
Coarse	Lake	0.96±0.05	0.47±3.74	0.99	0.94	4.48	0.06
	Δ0°	0.95±0.06	3.79±4.83	0.99	0.97	0.50	0.62
	Δ0°N	0.88±0.05	8.66±4.06	0.99	0.95	3.29	0.10
	Δ4°	0.92±0.06	5.35±4.24	0.99	0.96	1.18	0.36
	Δ4°N	0.94±0.06	2.97±5.07	0.98	0.95	2.04	0.20
Fine	Lake	1.06±0.09	-0.49±5.57	0.98	0.94	1.12	0.38
	Δ0°	1.12±0.09	-6.84±6.04	0.98	0.95	0.80	0.49
	Δ0°N	1.08±0.04	-6.49±2.89	1.00	0.98	1.96	0.21
	Δ4°	0.97±0.05	1.46±3.46	0.99	0.98	0.17	0.84
	Δ4°N	1.04±0.07	-3.29±5.15	0.98	0.97	0.24	0.79

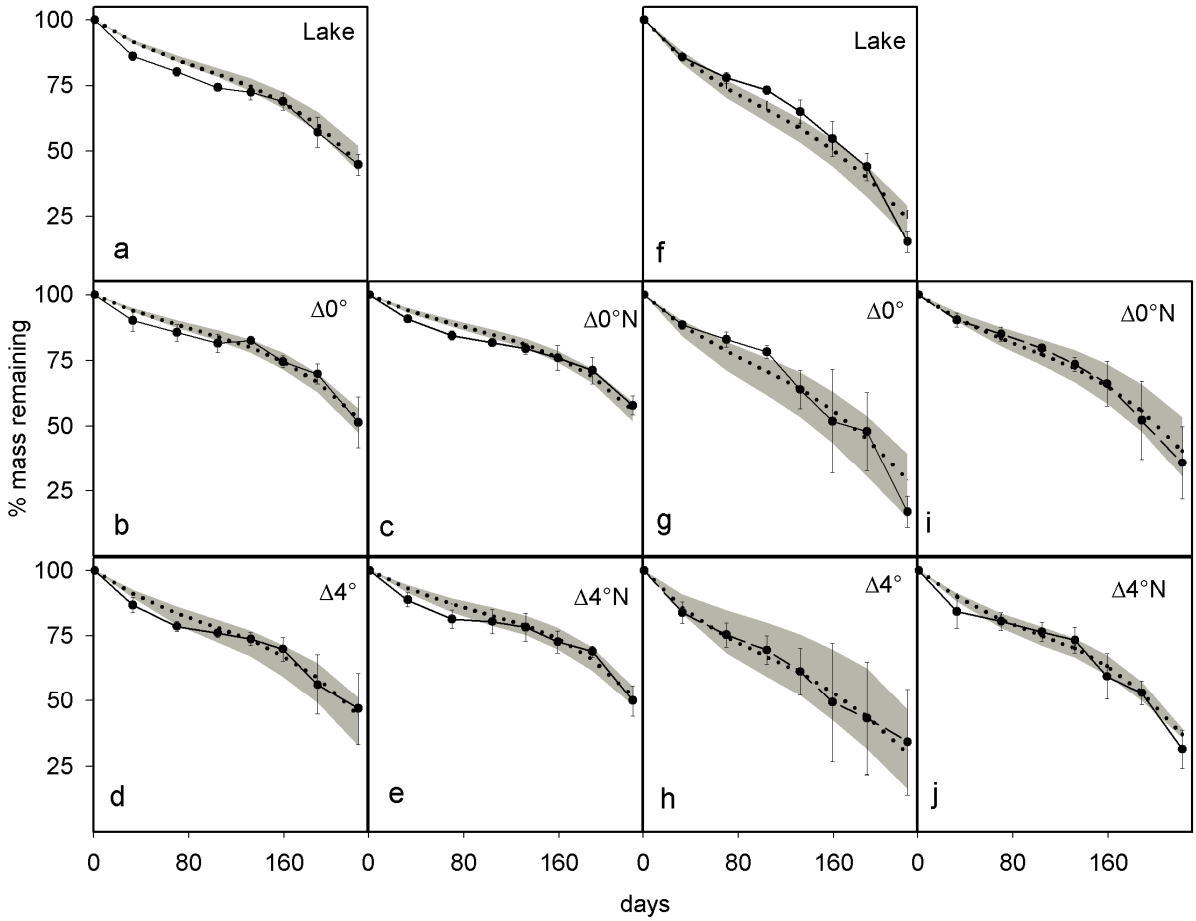

Figure 3 **Litter mass remaining over time in four types of enclosures (unheated, unfertilized = Δ0°; unheated, fertilized = Δ0°N; heated, unfertilized = Δ4°; heated, fertilized = Δ4°N) and unfenced control plots (Lake) in a freshwater marsh. Fine-mesh bags are shown on the left (a-e), coarse-mesh bags on the right (f-j). Error bars depict standard deviations. Grey areas show the range of predicted values (minimum to maximum) by an exponential temperature model around the predicted mean (dotted line).**

Comparisons of temperature-normalized decay rate coefficients, *k*, also indicated faster decomposition in unfenced control plots than in the enclosures ($P < 0.001$) and nitrogen addition resulted in reduced *k*-values ($P = 0.03$; Figure 4). However, the observed temperature effect was no longer significant ($P = 0.13$) after temperature correction of the litter mass loss data.

Fitted Q_{10} values from the first model run ranged from 1.0 to 6.0 and the average Q_{10} was 2.5 (SD = 0.6, N = 40). This average was used for all subsequent model runs aimed at comparing temperature-normalized decay rate coefficients among treatments. The litter mass remaining predicted by the exponential temperature model was very similar to the values actually measured in all cases (Figure 3). The average mismatch between predicted and measured values was 2.2% for fine-mesh bags and 3.3% for coarse-mesh bags.

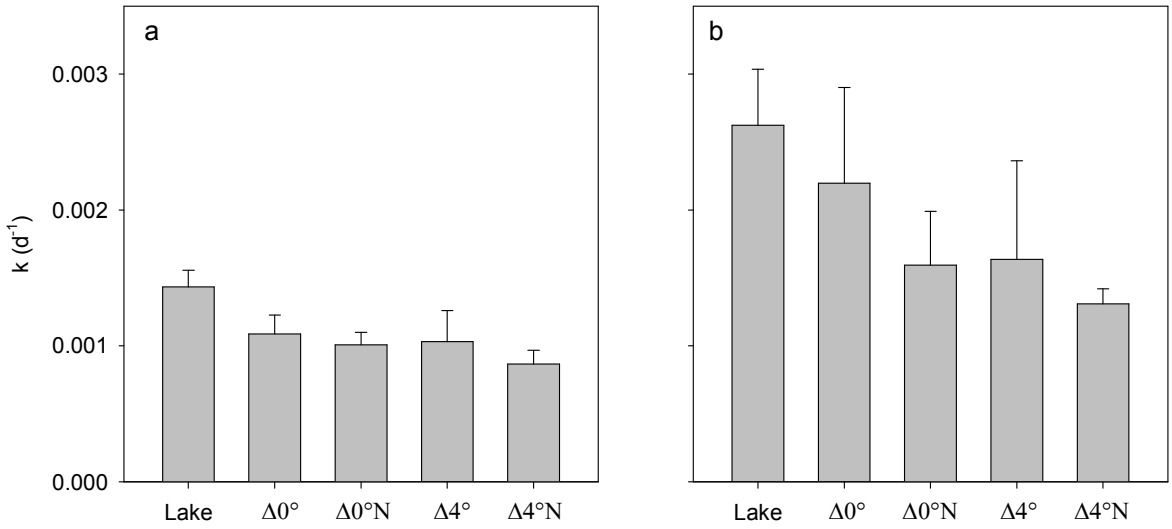

Figure 4. Decay rate coefficients, *k*, of decomposing *Phragmites australis* leaves in fine (a) and coarse (b) mesh bags in four types of enclosures (unheated, unfertilized = Δ0°; unheated, fertilized = Δ0°N; heated, unfertilized = Δ4°; heated, fertilized = Δ4°N) and unfenced control plots (Lake) in a freshwater marsh. Error bars show standard deviations.

However, during the first phase of decomposition (up to day 104) the litter mass remaining in fine-mesh bags was systematically overestimated (by about 5%), whereas after day 104 the measured values were always within the range of the predicted litter mass remaining. The model also tended to underestimate the mass remaining in coarse-mesh bags exposed in unfenced control plots and in control enclosures (Δ0°) during the initial stages of decomposition. The mismatch in these two cases was about 5%, whereas the average mismatch between predicted and measured values during subsequent decomposition stages was generally much smaller.

The model's tendency to overestimate the litter mass remaining in fine-mesh bags during the initial decomposition stages resulted in slopes slightly smaller than unity for the relation between measured and predicted litter mass remaining (Figure 4). In contrast, these slopes tended to be slightly greater than one for litter from coarse-mesh bags, although the regression slope neither deviated statistically from unity nor did the intercept deviate from zero (Figure 5). The modeling efficiency (MEF) ranged from 0.94 to 0.98, indicating an excellent match between the model predictions and measured values. Results of the sensitivity analysis are shown in Figure 6. For clarity, values for all unheated treatments (unfenced control plots, Δ0° and Δ0°N) were grouped.

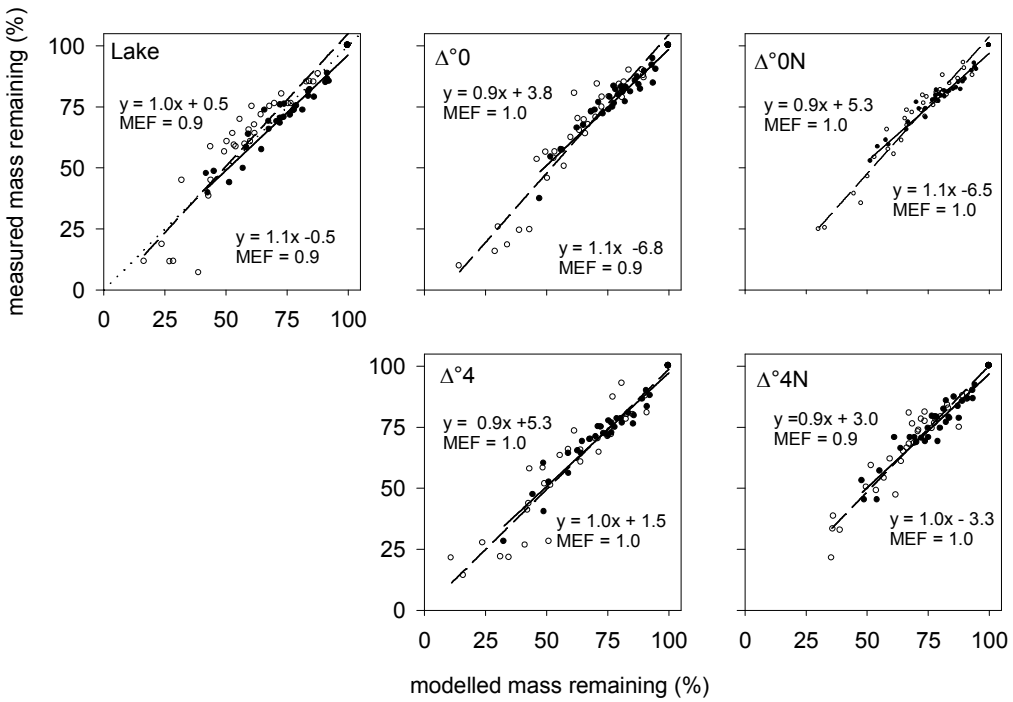

Figure 5 **Measured versus predicted litter mass remaining in four types of enclosures (unheated, unfertilized = Δ0°; unheated, fertilized = Δ0°N; heated, unfertilized = Δ4°; heated, fertilized = Δ4°N) and unfenced control plots (Lake) in a freshwater marsh. Closed symbols and solid lines depict fine-mesh bags, open symbols and dashed lines depict coarse-mesh bags. MEF = Modeling Efficiency according to Tedeschi (2006).**

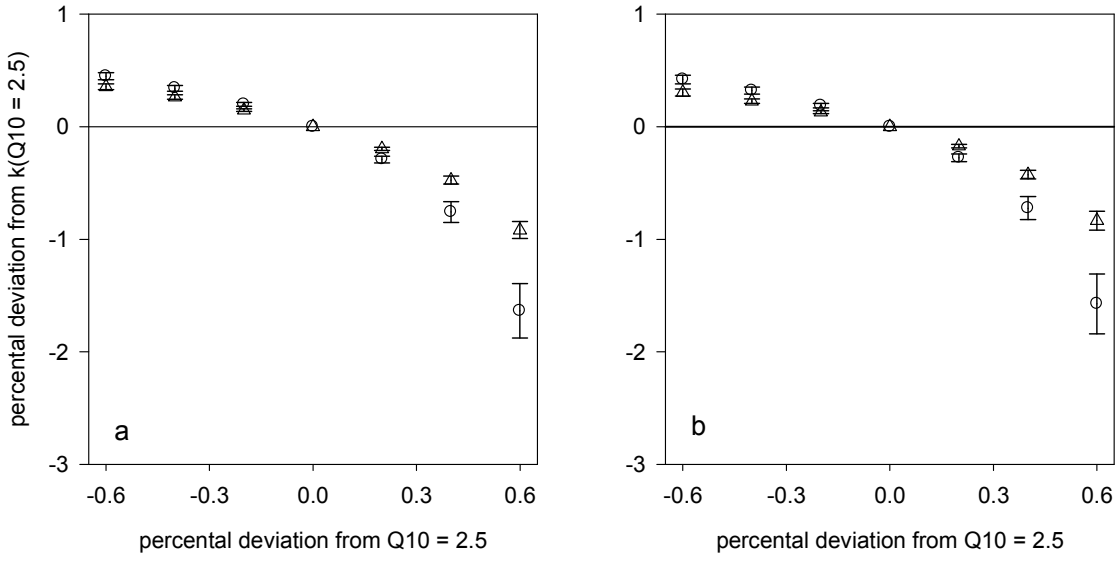

Figure 6**. Sensitivity of the decomposition rate *k* to variations of the Q_{10}-value. X-axes show the percent deviation from a Q_{10} of 2.5. Y-axes show the resulting decay coefficients (k) as percent deviation from the coefficients obtained at Q_{10} = 2.5. Panel a shows results from of fine-mesh bags, panel b of coarse-mesh bags. Circles refer to means in unheated enclosures and unfenced control plots and triangles to means in heated enclosures. Error bars denote standard deviations.**

Response of this group to varying Q_{10} was notably different from the response of samples from heated enclosures (Δ4°and Δ4°N), when the Q_{10} was changed by more than +30%. In this situation, the *k*–values for samples from heated enclosures were much more sensitive than the unheated samples, changing by more than 100% when Q_{10} was changed by 60%. The response of *k* observed for unheated enclosures was well below 100% in the tested range of Q_{10} values. Mesh size had no effect on the sensitivity of *k* to changes in Q_{10}.

Discussion

Results from the present field mesocosms experiment in which we tested for effects of simulated global warming and nitrogen enrichment on litter decomposition suggest an interaction between warming and nitrogen supply. Specifically, we found evidence that nitrogen enrichment decreases decomposition rates of *Phragmites* leaf litter, thus potentially counteracting the acceleration of decomposition caused by temperature rises in the range predicted by global-change scenarios for the next few decades.

Experimental warming had a pronounced effect on decomposition, causing significant differences in decomposition dynamics of *Phragmites australis*. Leaves decomposed significantly faster in heated enclosures than in enclosures maintained at ambient temperature. Although the model we used to describe decomposition as a function of time and temperature tended to overestimate litter mass remaining in fine mesh bags during the initial decomposition stages, the overall prediction of mass loss was excellent for both temperature regimes and nitrogen treatments. The average Q_{10} of 2.5 that we obtained is well supported by literature data (Davidson, Janssens, & Lou, 2006; Zhou, Sherry, An, Wallace, & Luo, 2006) and thus lends additional confidence that our model predictions are accurate.

The initially rapid mass loss that we observed may have been caused by leaching of soluble litter constituents and decomposition of highly labile compounds such as simple sugars and other nonstructural carbohydrates. However, attempts to improve predictions for this initial phase by introducing in the model separate terms for different litter constituents (Carpenter, 1981; Moorhead & Sinsabaugh, 2006) were not successful in that suitable parameter values for all tested conditions were not found. Differences in decay rate coefficients, *k*, of litter from different

enclosures were no longer significant after temperature correction, indicating that faster litter mass loss in heated enclosures was entirely due to the experimental temperature rise. As our *k*-values were corrected for temperature, we could not directly compare decomposition rates of the present study with literature data. However, half-lives of submerged *Phragmites* leaves in a similar reed stand as in Lake Hallwil were about six months (Gessner, 2000), which agrees with the present findings. Hietz (1992) reported much slower decomposition rates at several sites in Lake Neusiedl, Austria. However, Lake Neusiedl differs in many respects from Lake Hallwil (e.g. salinity) and its *Phragmites* marsh is up to 6 km wide. This greatly limits hydrological exchange and has consequences for oxygen regimes and other environmental and biotic factors that can affect decomposition.

Nitrogen had an inhibitory effect on decomposition in our study. Leaves from fertilized enclosures decomposed at significantly lower rates than the leaves placed in enclosures without added nitrogen. The circumstances under which, and the mechanisms by which increased nitrogen supply affects rates of litter decomposition are not well understood. Magill & Aber (1998), for example, found an inhibitory effect of nitrogen on the decomposition of pine, maple and birch leaves, and Carreiro et al. (2000) also observed that decomposition of oak was inhibited by nitrogen addition, whereas the decomposition of rapidly decomposing dogwood leaves was stimulated. Based on a meta-analysis of nutrient-enrichment experiments, Knorr et al. (2005) concluded that nitrogen inhibits decomposition when (i) litter quality is low (e.g. high lignin content) and (ii) fertilization rates exceed 2-20 times the anthropogenic deposition level. The nitrate concentration chosen in our experiments was five-fold above ambient, which is within this critical range identified by Knorr (2005). Sinsabaugh et al. (2002) provide evidence that high nitrogen supply inhibits especially lignin degradation but stimulates the degradation of cellulose. Fast decomposition of high-quality litter under high nitrogen supply thus could be due to stimulation of cellulolysis (Osono, 2007). Dinka et al. (2004) found the lignin concentration of *Phragmites* leaves from Lake Neusiedl to be less than 10%, whereas Flury (2008) found about 17% lignin in leaf litter from Lake Hallwil collected in a different year. Based on the present data it is not clear whether this latter concentration is sufficiently high to attribute the observed negative influence of nitrate on decomposition to an inhibition of ligninolysis.

An alternative explanation might be that nitrate fertilization exacerbated phosphorus limitation of microbial litter decomposers by facilitating primary producers and other competitors for phosphorus. This effect has been reported in other studies (Debusk & Reddy, 2005; Stallcup,

Ardón, & Pringle, 2006; Stelzer, Heffernan, & Likens, 2003). However, nutrient analyses of monthly water samples taken during the experiment do not support this idea. Phosphorus concentrations were usually higher in enclosures than in the unfenced control plots and they also failed to show clear pattern among the different nitrogen and temperature treatments. Over the whole sampling period phosphorus rather tended to increase in nitrogen-enriched and/or heated enclosures compared to unheated and unenriched enclosures

Another factor potentially controlling litter decomposition is oxygen availability. Water exchange in our enclosures was greatly restricted and could therefore have caused oxygen depletion if heterotrophic activity was sufficiently high. Both heating and/or fertilization of the enclosures fostered algal production and even resulted in algal blooms and subsequent decomposition of this labile organic matter could have contributed to oxygen declines, especially in summer at high temperatures. Phenoloxidase is a critical enzyme of lignin degradation that requires molecular oxygen (Freeman, Kim, Lee, & Kang, 2004), suggesting that decomposition may have been curbed by an inhibitory effect on lignin degradation. However, activities of microbial decomposers and detritivores, and hence the utilization and degradation also of other litter constituents, may have been reduced at low oxygen concentrations as well. An indication that oxygen declines in enclosures may indeed have been important in slowing decomposition in enclosures is the fact that decomposition was consistently faster in the unfenced control plots. This observation points to an artifact caused by the enclosures. However, although the oxygen conditions thus created in our enclosures were artificial in our experiment, they may well reflect real impacts that may be expected in more extensive marshes under warmer and nutrient-richer conditions in the future. Large areas in such marshes often have reduced horizontal water exchange, similar to the conditions in our enclosures. A corollary is that an important effect of global warming and nitrogen enrichment on litter decomposition in these marshes might be mediated indirectly by oxygen regimes rather than by temperature regimes or direct nitrogen effects.

Faster decomposition in coarse-mesh litter bags suggests that detritivores promoted decomposition. However, detritivore feeding (or any mechanical losses that might have occurred) did not alter the pattern of decomposition among treatments, which was similar for litter from fine-mesh and coarse-mesh bags. This indicates that warming and nitrogen enrichment influenced either microbial decomposers only or microbial decomposers and detritivores were affected in the same way.

A remarkable result of the present study is the almost perfect elimination of the temperature stimulation of decomposition by nitrogen enrichment. Decomposition in enclosures that were both heated and enriched with nitrogen proceeded at almost the same rate as in control enclosures (Δ0°). This indicates that nitrogen enrichment balanced the observed acceleration of decomposition in response to elevated temperature. This would slow the mineralization of organic matter and consequent release of CO_2 to the atmosphere. The implication is that freshwater marshes would not become important sources of additional CO_2 in the future. Rather their carbon balance would remain unchanged in spite of elevated temperature, provided that nitrogen supply continues to be high.

Increases in temperature predicted by global-change scenarios may lead to enhanced litter decomposition, and shift wetlands from net carbon sinks to sources of greenhouse gases. This would have profound implications on the global carbon cycle. However, warming and elevated nitrogen deposition are also likely to increase primary production and may alter litter chemistry (Norby et al., 2001). This in turn may lead to faster litter decomposition, possibly also of anaerobic decomposition processes such as methanogenesis (Boon & Mitchell, 1995). Brix et al. (2001) pointed out the delicate balance between wetlands acting as a source or sink for greenhouse gases. Even when wetlands sequester carbon, they emit considerable amounts of methane, which has an approximately 20 times greater global warming potential than CO_2 (Forster et al., 2007). As a consequence, wetlands may act as net contributors to global climate change even when their carbon balance suggests a role as a carbon sink.

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Response of leaf litter decomposition to atmospheric carbon dioxide, enrichment, elevated temperature, and sustained nitrogen deposition

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Introduction

Anthropogenic emissions of carbon dioxide (CO_2) resulting from the burning of fossil fuels and intensive land use have dramatically increased atmospheric CO_2 levels since the Industrial Revolution (Forster et al., 2007). Within the last two centuries, the average global concentration of CO_2, the most important greenhouse gas, has risen from about 280-300 ppm to currently about 380 ppm (Forster et al., 2007). Projections by the Intergovernmental Panel on Climate Change (IPCC) suggest that a further rise is very likely, with concentrations between 730 and 1020 ppm expected by 2100 (Meehl et al., 2007). The impacts of such high CO_2 levels on the Earth's ecosystems, while potentially profound, are only beginning to be understood.

In addition to direct effects on plants, elevated concentrations of atmospheric CO_2 and other greenhouse gases have been identified as the main reason for a rise in global mean surface temperature, which has increased by 0.74°C ± 0.18°C since the beginning of the last century (Trenberth et al., 2007). With elevated emissions of CO_2 continuing, further warming appears to be inevitable, although the extent is difficult to predict in view of the inherent complexities and the uncertainties surrounding human responses to the anticipated change. Accordingly, the IPPC predicts an additional temperature increase by 2100 of 1.4 - 3.8°C in their scenario B2, which assumes local environmental sustainability, and of 1.4 - 6.4°C in their scenario A1, which is based on the assumption of rapid economic growth (Meehl et al., 2007).

A critical process in many ecosystems that is likely to be affected by both elevated temperature and CO_2 levels in the atmosphere is the decomposition of plant litter. Altered rates of decomposition in turn may have profound consequences for the global carbon cycle, by affecting

the balance between carbon fixation through primary production and carbon mineralization, and thus exert an important feedback on the climate system. Wetlands are an important component in the global carbon budget. As rates of primary production often exceed rates of decomposition, i.e. decomposition does not keep pace with primary production, many wetlands tend to sequester carbon (Mitsch & Gosselink, 2000). If elevated temperature, as predicted in global-change scenarios, accelerates decomposition in these systems, important carbon stores may be lost. However, whether global carbon stocks in wetlands will indeed be released in response to global warming is currently unclear (Davidson & Janssens, 2006).

One mechanism by which decomposition rates may be reduced are changes in leaf chemistry induced by elevated CO_2 concentrations in the atmosphere. (e.g. Coley, Massa, Lovelock, & Winter, 2002; Cotrufo, Briones, & Ineson, 1998; Cotrufo, Ineson, & Rowland, 1994; Onoda, Hirose, & Hikosaka, 2007; Poorter et al., 1997). Such chemical changes can persist after leaf senescence and thus alter also the chemical composition of litter with consequent effects on decomposition (Rier, Tuchman, & Wetzel, 2005). Changes in litter lignin concentrations may be particularly important in this respect, because lignin is a highly recalcitrant leaf constituent that is often a key determinant of decomposition rate, either alone or in conjunction with litter nutrient concentrations (e.g. Gallardo & Merino, 1993; Gessner & Chauvet, 1994; Melillo, Aber, & Muratore, 1982). If nutrient concentrations are important, then elevated CO_2 levels may also influence litter chemistry and decomposition by diluting the N and/or P pools in leaves as a result of increased carbon availability but unchanged nutrient supply (Cotrufo et al., 1998; Norby, Long, Hartz-Rubin, & O'Neill, 2000). Both effects have been repeatedly observed (Booker, 2000; Booker et al., 2005; Cotrufo et al., 1998; Hall, Stiling, Moon, Drake, & Hunter, 2006; Norby, Cotrufo, Ineson, O'Neill, & Canadell, 2001), although no effects were found in several other studies (Blaschke et al., 2001; Hoorens, Aerts, & Stroetenga, 2002; Luo, Calfapietra, Liberloo, Scarascia-Mugnozza, & Polle, 2006). In a review on CO_2-enrichment effects on litter decomposition, Norby et al. (2001) concluded, therefore, that CO_2-enrichment effects on litter decomposition strongly depend on the experimental methods used and the specific plant types examined, and Booker et al. (2000) suggested that the magnitude of litter-quality changes induced by elevated CO_2 concentrations is unlikely to alter decomposition substantially.

The aim of the experiment presented here was to assess effects of elevated CO_2 concentrations on the decomposition of various deciduous leaf types, and how decomposition of these leaves is

influenced under climate change scenarios predicted for the year 2100. Specifically, we hypothesized that exposure of leaves to elevated CO_2 levels during the growing season lowers decomposition rates by increasing lignin concentrations and/or C:N or C:P ratios of the leaf litter. Furthermore, we expected that CO_2-induced reductions in decomposition rates would be counteracted by elevated temperature. To test these hypotheses, we collected senescent leaves from a Free-Air CO_2 Enrichment (FACE) site in a mature forest and used them in a decomposition experiment conducted in a series of enclosures set up in a freshwater marsh. The experimental facility in the marsh allowed us to increase the ambient water temperature in a subset of enclosures and thus to assess the interplay of effects caused by warming during decomposition and by elevated CO_2 levels during plant growth.

Material & Methods

The experimental site was located in a permanently flooded reed stand on the eastern shore of Lake Hallwil near Meisterschwanden, Switzerland (47°17' N, 8°14' E). Lake Hallwil is a eutrophic meromictic moraine lake at 449 m above sea level. The reed stand is composed of common reed, *Phragmites australis* (Cav.) Trin. ex Steud, with occasional small patches of lakeshore bulrush, *Schoenoplectus lacustris* (L.) Palla, at the lakeward margin. The reed stand extends about 850m along the shore line and is between 6 and 20m wide.

The effect of elevated temperature on rates of litter decomposition was tested with an experimental setup that allowed us to heat enclosures in the reed stand to a target temperature of 4 °C above ambient water temperature. The cylindrical enclosures were 120 cm in height and 142 cm in diameter and were made of a double layer of uncolored polypropylene. They were pushed about 20 cm into the sediment. Temperature was controlled by two-point regulators (FCR 13A, Shinko Technos Co., Ltd.; Osaka, Japan). A total of 16 enclosures were arranged in four blocks perpendicular to the shore line. Each block comprised one heated and one unheated enclosures plus an additional unfenced control plot. Two temperature control units were used per block, each regulating a pair of one heated and one unheated enclosure. Heating was achieved by four electrical heating elements (300 W, jbl; Neuhofen, Germany) per enclosure. A submersible pump (model 1046, Eheim; Deizisau, Germany) in each enclosure ensured gentle stirring of the water to minimize the build-up of temperature and chemical gradients.

Leaves for this experiment were collected in autumn 2005 from a free-air CO_2 enrichment (FACE) experiment near Basel, Switzerland (47°28′ N, 7°30′ E; Pepin & Körner, 2002). The FACE facility was located in a mixed, fully-grown forest stand dominated by *Fagus sylvatica* (L.) and *Quercus petraea* (Matt.) Liebl., with *Carpinus betulus* (L.), *Acer campestre* (L.), *Tilia platyphyllos* (Scop.) and *Prunus avium* (L.) as additional broad-leaved species. CO_2 was released through laser-punched tubes which were fixed in the branches of the trees exposed to elevated CO_2 levels. CO_2 concentration in the canopies of these trees was elevated to 520 ppm during daylight hours in the growing season. The CO_2 enrichment started in May 2001. Therefore trees had been exposed to elevated CO_2 concentrations for five growing seasons at the time when the leaves were collected. At least one tree per species was subject to elevated CO_2 levels and at least one tree to ambient CO_2 levels. A tower crane equipped with a gondola was positioned in the center of the stand and provided access to virtually every spot within the forest canopy. This allowed us to collect leaves from defined areas within the canopies of CO_2-enriched and control trees from each of the six broad-leaved species. Leaves were individually picked in the canopies at a late state of senescence, air-dried and stored until used in the experiment. We collected leaves from all six broad-leaved tree species exposed to both ambient and elevated CO_2 concentrations. This resulted in a total of 12 litter types.

In mid-November, litter of these 12 types was weighed in batches of 1.20±0.05 g, sprayed with lake water to make them pliant and prevent breakage, and placed in litter bags. Coarse-mesh bags (10-mm mesh size) were used to allow detritivores to feed on litter, whereas fine-mesh bags (0.5 mm) were intended to determine microbial decomposition only. Four randomly selected samples per tree species and CO_2 treatment were immediately freeze-dried to determine moisture content and then ground to pass a 0.5-mm screen for chemical analyses. These four samples per species were used to determine the initial cellulose, lignin, nitrogen and phosphorus concentrations in the litter. Cellulose and lignin contents were estimated with the acid-detergent fiber method (Gessner, 2005). Nitrogen and phosphorus were simultaneously determined after peroxodisulfate oxidation following Ebina et al. (1983).

All other bags were sealed and stored overnight at 4 °C until deployment the next day in the field. Pairs of one fine and one coarse-mesh bag per tree species and CO_2 treatment were tied to a bamboo-stick and submerged in the enclosures and unfenced control plots. The litter bags were removed after 79 (*Prunus*), 93 (*Tilia*), 126 (*Acer*), 141 (*Carpinus*), 233 (*Quercus*) and 237 (*Fagus*) days. These periods were chosen according to the expected decomposition rates of the

different species such that all species were at a similar decomposition stage at the time of removal. Litter from trees of a given species subjected to elevated and ambient CO_2 conditions, respectively, were always retrieved together. Samples were transported to the laboratory in a cooling box and the leaves individually cleaned with lake water from adhering macroinvertebrates, debris and sediment. The cleaned leaves were freeze-dried and weighed to the nearest 0.01 g to determine litter dry mass remaining.

Decomposition rate coefficients (k) were calculated by assuming an exponential decay model:

$$k = \frac{-1}{t} \ln\left(\frac{m_t}{m_i}\right),$$

where t is the exposure time in the field in days, m_t the litter dry mass remaining after retrieval of the leaves from the field, and m_i is the initial dry mass.

Differences in decomposition rate coefficients (k-values) were tested by ANOVA performed with leaf species, CO_2 treatment, temperature treatment, and mesh type as predictive variables. As some of the predictive variables showed different results for coarse-mesh and fine-mesh bags, we subsequently tested effects for both mesh sizes separately. In these ANOVAs we tested for differences in k-values with leaf species, CO_2 treatment and temperature treatment as predictive variables. Tukey's test was used following the ANOVAs to test for differences among leaf species and temperature treatments. Differences in litter chemistry (cellulose, lignin, N and P) among leaf species and CO_2 treatment were also tested by ANOVA with leaf species and CO_2 treatment as predictive variables, and Tukey's test was again used to test for differences among leaf species and CO_2 treatment.

Results

On average the temperature in the heated enclosures was 2.4°C higher than in the lake. In the heated and fertilized enclosures an increase of 2.8°C was achieved (Figure 1). Especially when lake temperature rose very fast, experimental heating could not keep pace. Nevertheless, the

temperature in heated enclosures was always higher than in the control enclosures and unfenced control plots.

Nitrogen concentrations in leaves grown under ambient CO_2 conditions ranged from 0.6% in *Fagus* to 1.3% in *Tilia* (Figure 2a). CO_2 enrichment resulted in higher N concentrations in *Prunus*, *Tilia* and *Carpinus* ($P < 0.05$) and in a lower concentration in *Acer* ($P < 0.05$), whereas no influence on *Quercus* and *Fagus* was observed. Phosphorus concentrations varied by a similar magnitude, from 0.025-0.06%, in leaves grown under ambient CO_2 conditions (Figure 2b). As for N, P concentrations of leaves exposed to elevated CO_2 levels were higher in *Prunus*, *Tilia* and *Carpinus*, lower in *Acer*, and showed little response in *Fagus*. However, in *Quercus* leaves, P concentrations of leaves exposed to elevated CO_2 levels were about 70% higher than in leaves grown at ambient CO_2 levels (Figure 2b).

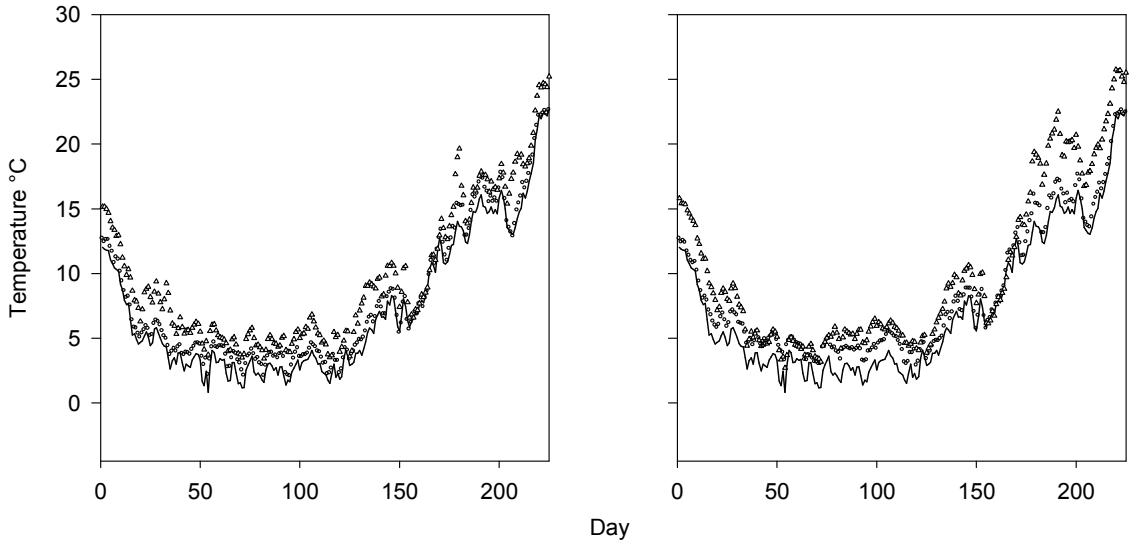

Figure 1. Daily mean temperatures during the decomposition experiment in the reed stand of Lake Hallwil. The left panel shows temperatures in unfertilized enclosures (symbols) and the unfenced control plots (solid line), the right panel shows temperature in fertilized enclosures (symbols) and the unfenced control plots (solid line). Circles denote unheated enclosures, triangles denote heated enclosures.

Table 1. Precental mass remaining of initial dry mass of all six different deciduous leaf species grown under ambient and elevated atmospheric CO_2 levels. Errors denote standard deviations.

Mesh-size	Temperature treatment	CO_2 level	*Tilia*	*Prunus*	*Carpinus*	*Acer*	*Quercus*	*Fagus*
Fine	Lake	Ambient	81.0±2.1	53.2±7.4	63.8±3.2	49.7±5.0	63.7±6.7	60.8±0.9
	Lake	Elevated	70.1±1.3	46.8±3.22	59.4±1.7	41.7±28.0	42.0±5.4	67.2±11.9
	Ambient	Ambient	83.3±1.4	62.5±5.6	79.3±6.6	61.9±3.7	69.9±2.1	68.7±3.8
	Ambient	Elevated	69.4±3.1	57.5±4.1	69.8±9.6	61.0±3.5	51.0±7.0	69.4±3.5
	Elevated	Ambient	81.6±4.9	52.3±6.1	70.3±13.9	58.5±4.3	71.0±4.3	65.8±4.7
	Elevated	Elevated	66.3±1.4	52.9±1.9	67.5±4.8	59.8±3.7	52.7±4.6	65.0±5.1
Coarse	Lake	Ambient	76.9±3.4	36.6±2.4	75.2±6.2	29.3±19.9	56.0±5.6	46.9±3.5
	Lake	Elevated	63.9±5.0	34.1±7.2	70.1±13.7	27.8±18.9	22.1±6.0	41.3±14.9
	Ambient	Ambient	77.0±8.2	37.9±26.8	45.6±39.6	37.1±26.7	56.4±8.2	58.5±22.4
	Ambient	Elevated	59.8±12.9	25.6±27.5	48.0±34.1	53.9±10.5	26.1±7.5	61.4±15.6
	Elevated	Ambient	77.4±4.5	39.2±8.6	71.0±3.8	48.7±3.9	63.8±5.3	52.9±5.2
	Elevated	Elevated	65.3±2.3	33.8±8.8	69.1±2.6	49.8±5.2	44.1±6.2	60.5±2.1

Differences in structural carbon constituents among leaves exposed to ambient and elevated CO_2 levels were generally less pronounced than differences in nutrients. Cellulose concentrations of leaves not subject to CO_2 enrichment ranged from 18% in *Prunus* to 38% in *Fagus* (Figure 3a) CO_2 enrichment during the growing season had no consistent effect on the cellulose concentration of the six leaf species. Concentrations were lower in *Carpinus* and *Acer* when leaves were grown under elevated CO_2 conditions, but were unaffected in *Prunus*, *Tilia* and *Fagus*. As for P, the strongest effect was observed in *Quercus* leaves, where concentrations in leaves grown under CO_2-enriched conditions increased by 35%. *Prunus*, *Tilia* and *Carpinus* contained about 10% lignin irrespective of the CO_2 conditions under which the leaves were grown (Figure 3b), and *Acer* (12%) and *Fagus* leaves (26%) were also unaffected by CO_2 enrichment. In *Quercus*, however, the lignin concentration decreased strongly from 23% (ambient CO_2) to 14% (elevated CO_2; $P < 0.05$).

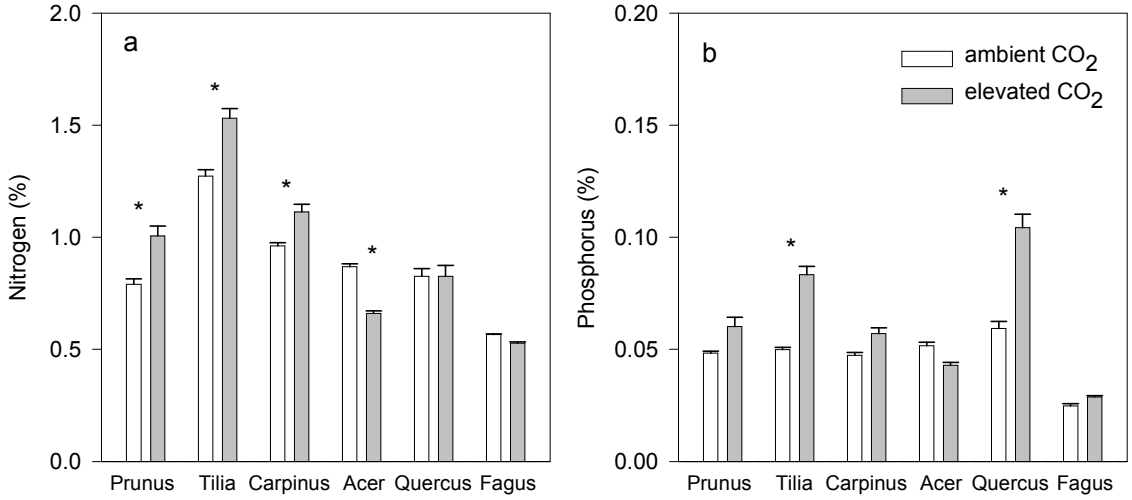

Figure 2. Concentrations of N (a) and P (b) in six different deciduous leaf species grown under ambient (white bars) and elevated (grey bars) atmospheric CO_2 levels. Error bars denote SEM (N = 4). Asterisks denote significantly (P < 0.05) different concentrations between leaves of a given species exposed to ambient and elevated CO_2 levels.

Decomposition rate coefficients, *k*, of litter in fine-mesh bags ranged from 0.0019d^{-1} (*Fagus*) to 0.0089 d^{-1} (*Prunus*; Figure 4a-l). Leaves grown under elevated CO_2 conditions often decomposed faster than leaves from ambient CO_2 conditions ($P < 0.05$). *Acer* and *Quercus* leaves showed especially large differences. This CO_2 effect was more apparent in the unfenced control plots, where it occurred in 10 of 12 cases, but was less prominent in enclosures. Leaves in the unfenced control plots decomposed almost always faster than leaves in the control enclosures and even in the heated enclosures. *Prunus*, *Tilia*, *Carpinus* and *Acer* leaves decomposed faster in heated than in unheated enclosures, although the acceleration at elevated temperature was not pronounced. For *Fagus* leaves, this effect was only observed with leaves grown under ambient CO_2 conditions, and decomposition of *Quercus* leaves did not show any response to elevated temperature.

Decomposition rate coefficients of litter in coarse-mesh bags varied more than tenfold, from 0.0012d^{-1} (*Fagus*) to 0.0126 d^{-1} (*Prunus*; Figure 4m-x). *Acer* and *Quercus* leaves grown under elevated CO_2 conditions decomposed faster than leaves of these species exposed to ambient CO_2 levels during the growing season ($P = 0.001$), whereas the other four species did not show the same response to CO_2 enrichment. This is the same pattern across species that was observed for leaves in fine-mesh litter bags. The response patterns to the temperature treatments, in contrast, partially differed from those observed for litter decomposing in fine-mesh bags. Although similar to the general pattern in fine-mesh bags, *Prunus* and *Carpinus* decomposed fastest in the

unfenced control plots, at intermediate rates in the heated enclosures, and slowest in the unheated enclosures. The four other species showed either no temperature response (*Tilia*) or slower decomposition in heated than in unheated enclosures (*Acer*, *Quercus*, *Fagus*). As a result, separate ANOVAs for the two mesh sizes resulted in a significant temperature effect between heated and unheated enclosures for fine-mesh bags ($P = 0.032$) but not for coarse-mesh bags ($P = 0.38$).

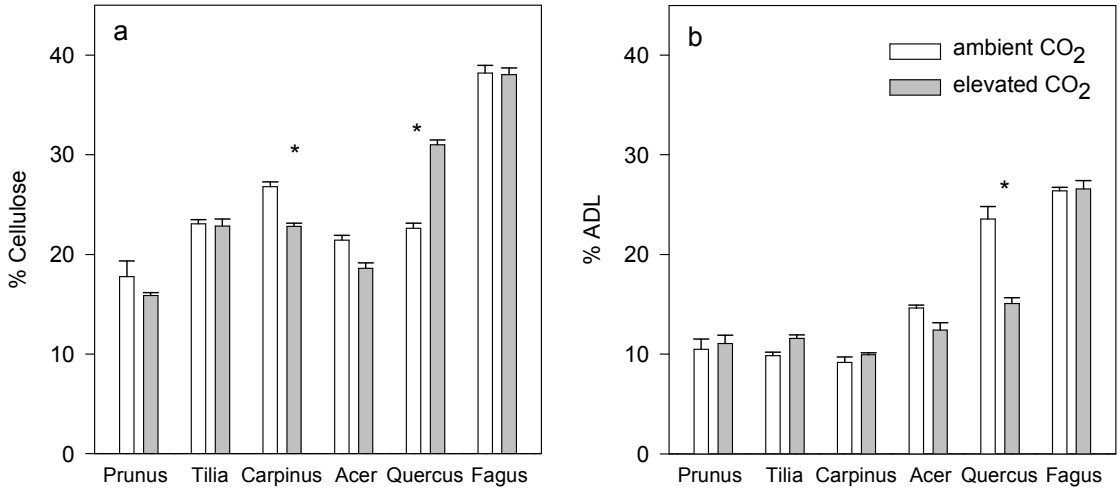

Figure 3. Concentrations of cellulose (a) and acid-detergent lignin (b) in six different deciduous leaf species grown under ambient (white bars) and elevated (grey bars) CO_2 levels. Error bars denote SEM (N = 4). Asterisks denote significant ($P < 0.05$) different contents within one species between the two CO_2 levels.

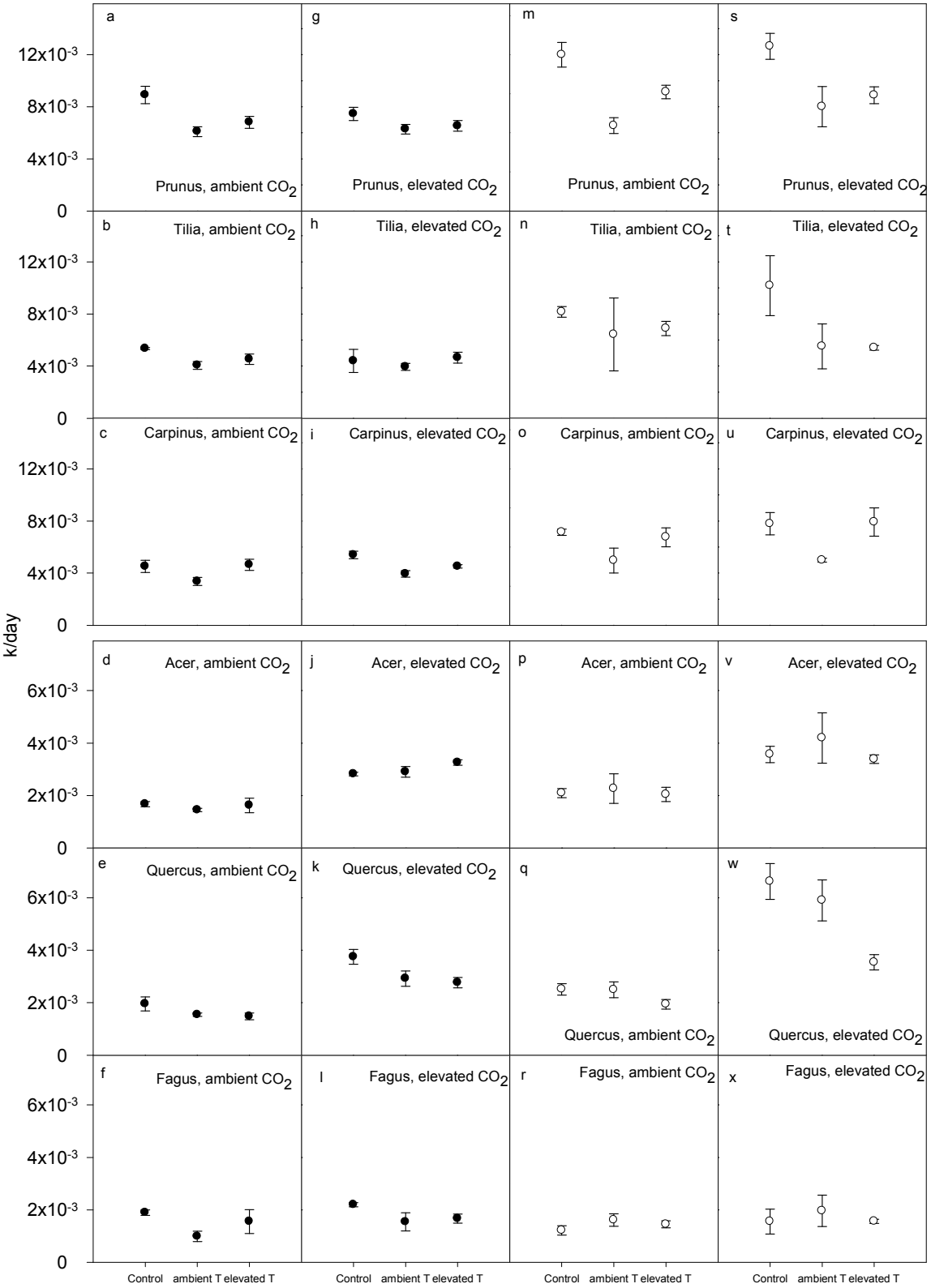

Figure 4. Decomposition rate coefficients (*k*) of leaves from six different deciduous tree species exposed during the growing season to ambient and elevated CO_2 levels, respectively. Filled symbols refer to data from fine-mesh bags, open symbols to coarse-mesh bags. Error bars denote SEM (N = 4). Note different scaling on y-axis in top 3 rows and bottom 3 rows.

Much of the overall variation in decomposition rates among the 12 litter types was statistically explained by the initial lignin concentration of the litter as a measure of leaf recalcitrance (Figure 5). In contrast, the initial concentrations of N or P were not related to decomposition rate (Figure 5) and consideration of N or P as predictive variables in addition to lignin concentration did not or only marginally increase the strength of the relationships with lignin alone (data not shown).

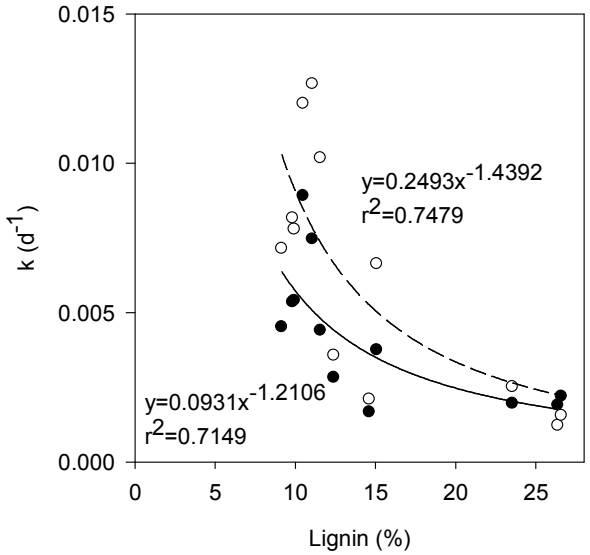

Figure 5. Relationships between lignin and decomposition rate (*k*) of leaf litter collected from six deciduous tree species subject to ambient and elevated CO_2 levels during the growing season. Open circles and broken lines depict coarse-mesh bags, filled circles and solid lines depict fine-mesh bags.

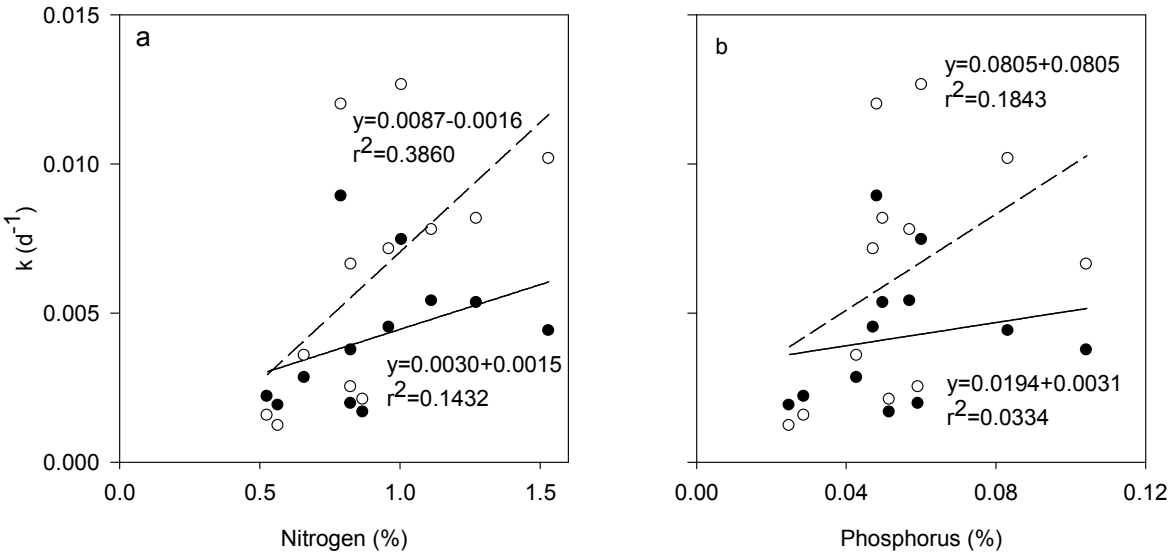

Figure 6. Relationships between N (a) and P (b), respectively, and decomposition rate (k) of leaf litter collected from six deciduous tree species subject to ambient and elevated CO_2 levels during the growing season. Open circles and broken lines depict coarse-mesh bags, filled circles and solid lines depict fine-mesh bags.

Discussion

Contrary to our expectations, CO_2 enrichment influenced the litter chemistry of the faster-decomposing species (*Prunus*, *Tilia* and *Carpinus*) in that the concentrations of N and P were higher in leaves exposed to elevated CO_2 concentrations than in the corresponding leaves exposed to ambient CO_2 concentrations. These results are at variance with a range of other studies that found lower N concentrations in leaves exposed to elevated CO_2 concentrations (e.g. Kasurinen, Riikonen, Oksanen, Vapaavuori, & Holopainen, 2006; Knops, Naeem, & Reich, 2007; Lindroth, Kinney, & Platz, 1993; Norby & Iversen, 2006). In a comprehensive meta-analysis, Norby et al. (2001) noted on average a 7.1% decrease of N in leaves grown under elevated CO_2 conditions. However, they also point out that in more natural experimental conditions (e.g. in FACE-experiments) the CO_2 effect becomes weaker. Moreover, a weaker CO_2 effect was evident in leaves that contained less than 10 mg N mg g^{-1} leaf dry mass (Norby et al., 2001). As leaves in the present study were collected at a FACE site in a mature forest and only *Tilia* had more than 10 mg g^{-1} leaf dry mass under ambient CO_2 conditions, our results are less at odds with published data than they may first appear to be.

The increase in litter N concentrations in *Prunus*, *Tilia*, and *Carpinus* in response to CO_2 enrichment raises the question of how the extra N is acquired. A possible explanation may be increased root growth when extra carbon is fixed under elevated CO_2 conditions (O'Neill, Luxmoore, & Norby, 1987; Pritchard et al., 2008), which increases the likelihood of encountering and mining nitrogen-rich spots in the soil. Rastetter et al. (1997) simulated root growth and found different reactions concerning the N uptake at different time scales: In the short term (less than 1 year), C:N ratio increases, whereas at the decadal time scale N uptake increases as a result of a net N flux from the soil to the tree, which could account for lower C:N ratios in leaves.

Among the numerous studies that have assessed effects of elevated CO_2 levels on leaf lignin concentrations, most found an increase in plants grown at elevated CO_2 (e.g.Hanson, Carpenter, Armstrong, Stanley, & Kratz, 2006; Kasurinen et al., 2006; Lindroth et al., 1993). Other studies, however, observed a decrease (Knops et al., 2007; Sanità Di Toppi et al., 2003) or found no effect (Blaschke et al., 2001; Luo et al., 2006). These variable outcomes are also reflected in the non-consistent response across leaf types in the present study. The three faster-decomposing

species (*Prunus*, *Tilia* and *Carpinus*) tended to have higher lignin concentrations when grown at elevated CO_2 concentrations, but the differences were small and *Fagus*, the most recalcitrant species, showed no response. *Acer* and especially *Quercus* leaves had even significantly lower lignin concentrations when they were grown under elevated CO_2 concentrations, in stark contrast to our expectations. One important limitation of the present study is, however, that for most leaf types it was not possible to collect leaves from more than a single tree. Although differences in litter chemistry within the canopy of individual trees have been found to be as large as among trees (S. Hättenschwiler, pers. comm.), this limitation in the experimental design could have biased our results on CO_2 effects.

Litter lignin concentration was a good predictor of decomposition rate across the 12 leaf types examined in the present study. The two variables showed a hyperbolic relationship, as has previously been observed in other types of ecosystems such as forests and streams (e.g. Gallardo et al., 1993; Gessner et al., 1994) which accounted for over 70% of the variation in decomposition rates in both fine-mesh and coarse-mesh litter bags. This result together with a body of literature data underpins the eminent role of lignin as a factor controlling rates of litter decomposition in a variety of ecosystems. This conclusion is further supported by the response of *Quercus* and *Acer* leaves to CO_2 enrichment. The lower lignin concentrations in these species when leaves were exposed to elevated CO_2 concentrations were clearly reflected in faster decomposition rates.

In addition to lignin, N and/or P concentrations in litter have been found to be related to decomposition rates over a wide range of litter types (e.g. Enríquez, Duarte, & Sand-Jensen, 1993). In the present study with a much narrower range of litter qualities, similarly strong relationships were not found, although litter N concentration explained almost 40% of the variation in decomposition rates in coarse-mesh bags. However, this latter relationship could have been confounded by lignin concentration, which was correlated with N concentration (r^2 = 0.65), and it did not emerge for fine-mesh bags (r^2 = 0.14). Likewise, there was no indication that the P concentration of litter had an influence on decomposition rate in either fine-mesh or coarse-mesh bags, and neither P nor N concentration could explain the CO_2-induced differences in decomposition rates that were found in the present study.

Ten out of 12 samples placed in the unfenced control plots decomposed at least slightly faster when grown under conditions of elevated CO_2, but variation in none of the tested litter

constituents (N, P, cellulose and lignin) could explain the CO_2-induced differences in litter decomposition across this broad range of leaf types. A possible explanation for this mismatch might be that the main effect of CO_2-enrichment on litter chemistry in the four species other than *Acer* and *Quercus* was an increase in concentrations of non-structural carbon compounds. Such an increase has indeed been observed both at the FACE site where the leaves for the present experiment were collected (Hoch, Richter, & Körner, 2003) and in other CO_2 enrichment experiments (Körner, 2003; Onoda et al., 2007). Non-structural carbon compounds include compounds such as carbohydrates (mainly starch, sucrose, glucose and fructose), lipids and sugar alcohols (cyclithols and sorbitol). These labile compounds are likely to determine decay rates during the initial stages of litter decomposition and may have been instrumental in causing the faster decomposition of leaves grown at elevated CO_2 in the present study.

In contrast to CO_2, elevated temperature consistently increased decomposition rates of litter in fine-mesh bags, although even this temperature effect was relatively weak or absent, especially for *Quercus* and *Fagus* leaves. That warming did not result in faster decomposition, unlike our previous observations for reed leaves (Chapter 1), may be due to oxygen depletion in the enclosures. The water volume of our enclosures (~800 l) was relatively small and water exchange restricted. This could have led to oxygen depletion, with negative effects on decomposition, particularly in summer and in heated enclosures. Algal growth on fine-mesh bags (pers. obs.) could have further limited water exchange inside the fine-mesh bags. This explanation is in line with our observation that the warming effect was weakest for *Quercus* and *Fagus* leaves, which were retrieved only at the end of June and in early July, respectively, when water temperature was about 23°C. Furthermore, decomposition of all litter types was generally faster in the unfenced control plots where water exchange was unrestricted than in the enclosures.

In coarse-mesh bags, stimulation of decomposition by warming was strongest for two of the faster-decomposing species, *Prunus* and *Carpinus*, whereas no temperature effect was found for *Acer* and *Fagus* leaves or decomposition of *Quercus* leaves was even slower. Furthermore, no differences were found in these three leaf species between litter from fine-mesh and coarse-mesh bags decomposing in heated enclosures. A possible explanation for this observation is that detritivores were more strongly affected by oxygen depletion than microbial decomposers. Although leaf shredding caddis-flies were present at our study site (pers. obs.), the main

detritivore in our samples was an isopod, *Asellus aquaticus*, indicating that oxygen conditions were insufficient especially for insect detritivores.

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Influence of warming and nitrogen enrichment on whole-ecosystem metabolism

Arne Hammrich and Mark O. Gessner

Introduction

Since the Industrial Revolution in the 18th century the impact of humans on earth and its climate has been profound and complex. Combustion of fossil fuels has dramatically increased the emission of greenhouse gases, particularly of carbon dioxide, in the last two centuries (Forster et al., 2007). As a result, earth's global mean surface temperature has risen by 0.74°C ± 0.18°C over the last 100 years 1906–2005; (Trenberth et al., 2007) and climate-change models predict further warming of 1.8-6.4 °C to occur by 2100 (Meehl et al., 2007). Similarly, the annual production of reactive nitrogen species has increased more than tenfold from ~15 Tg N in 1860 to 187 Tg N in 2005 (Galloway et al., 2008), accompanied by atmospheric concentrations of nitrous oxide (N_2O), another potent greenhouse gas, that have increased from 270 to 319 ppb (Forster et al., 2007). These dramatic changes can have important consequences on ecosystems, including on key biogeochemical processes.

Primary production and respiration are arguably the two most important processes in ecosystems. Primary production binds CO_2 in plant biomass, which is subsequently released again through respiration by the plants themselves and a wide range of consumers and microbial decomposers. Gross primary production (GPP) is defined as the photosynthetic fixation of carbon. The complementary process is referred to as ecosystem respiration (ER); it is the sum of the respiratory activities of all organisms in an ecosystem and results in the mineralization of organic carbon to CO_2. Primary production and respiration combined are referred to as ecosystem metabolism (sensu Odum, 1956), the difference as net ecosystem productivity (NEP), and the ratio of both processes (GPP/ER) describes whether a system is net heterotrophic or autotrophic. In net heterotrophic systems, ER exceeds GPP and more organic C is respired than is produced by primary production within the system's boundaries (Staehr & Sand-Jensen, 2006). In net autotrophic systems, GPP exceeds ER and the system can export or store organic carbon. The

balance between CO_2-fixing processes (GPP) and CO_2-releasing processes (ER) thus determines the capacity of ecosystems to sequester carbon.

The effects of elevated temperature and nitrogen supply on ecosystem metabolism are largely unknown. Primary production in aquatic ecosystems is frequently limited by nutrient supply. Phosphorus is often the limiting factor in fresh waters, but there is evidence that nitrogen may be equally important (Elser et al., 2007), suggesting that primary production might be enhanced by nitrogen enrichment. Conversely, rates of some heterotrophic processes such as plant litter decomposition may be reduced when nitrogen supply is high (Carreiro, Sinsabaugh, Repert, & Parkhurst, 2000; Knops, Bradley, & Wedin, 2002). Therefore, the net effect of N enrichment on ecosystem metabolism and net ecosystem productivity (NEP) is not easy to predict as it may depend on the relative strength of positive and negative N effects on GPP and ER. For example, in a comprehensive study on four lakes in Wisconsin, USA, Cole et al. (2000) enriched three lakes with ammonium nitrate. This fertilization enhanced primary production but also stimulated ecosystem respiration to a similar extent and thus led to only small changes in net ecosystem productivity.

Temperature in the physiological range of organisms influences all biological processes (Davidson & Janssens, 2006). Ecosystem respiration is therefore expected to increase in response to warming. Although primary production may also respond to warming, photosynthesis tends to be less sensitive to temperature than respiration (Allen, Gillooly, & Brown, 2005). This suggests that the balance of GPP and ER is shifted towards ER when temperature is elevated. However, experimental tests of the role of temperature on ecosystem metabolism in lakes have not been conducted and other field studies on the combined effect of elevated temperature and nitrogen supply on ecosystem metabolism are also lacking.

The present study set out to test for the combined effects of elevated temperature and nitrogen supply on ecosystem metabolism in a freshwater marsh. To this end, we measured diel changes in dissolved oxygen concentrations in a series of experimental enclosures set up in a littoral marsh and then used these data to derive various parameters describing ecosystem metabolism. Experimental heating and/or nitrate enrichment of subsets of the enclosures allowed us to assess ecosystem effects of both warming and increased nitrogen supply as important components of global environmental change.

Material & Methods

The study site was located in a littoral reed stand on the eastern shore of Lake Hallwil near Meisterschwanden, Switzerland (47°17'N, 8°14'E). Lake Hallwil is a eutrophic meromictic lake in Central Switzerland, located in a morainal landscape at 449 m above sea level. The lake has a surface area of 10.2 km^2, a volume of 0.292 km^3 and a maximum depth of 48 m. The theoretical water residence time is 3.8 a (Märki & Schmid, 1983; Scheidegger, Stöckli, & Wüest, 1994). The reed stand was permanently aquatic and composed of common reed *Phragmites australis* (Cav.) Trin. ex Steud with small patches of lakeshore bulrush *Schoenoplectus lacustris* (L.) Palla occurring at the lakeward margin.

A randomized block design with four blocks was used to test for the combined effects of elevated temperature and sustained nitrogen deposition on ecosystem metabolism. Each block consisted of two heated and two unheated enclosures. The targeted water temperature in the heated enclosures was 4°C above the ambient lake water temperature to mimic the IPCC A2 scenario (Meehl et al., 2007). One heated and one unheated enclosure per block were fertilized monthly by adding a concentrated $Ca(NO_3)_2$ solution to a final target concentration five times above ambient. An additional unfenced control plot was delineated in each block to assess the occurrence of any enclosure artifacts.

An inner cylinder (142 cm in diameter) was nested in a larger outer one (152 cm in diameter) to minimize lateral heat loss. The cylinders were 120 cm in height and pushed about 20 cm into the sediment. They were fixed with three iron bars (300 cm length, 2 cm diameter). Temperature in the enclosures was controlled by two-point regulators (FCR 13A, Shinko Technos Company Ltd., Osaka, Japan). Two control units were used per block, each regulating a pair of one heated and one unheated enclosure. The control units were connected to three platinum thermocouples (Pt 100), one each for the two enclosures and the surrounding lake. Heating was achieved by four electrical heating elements (300 W, jbl; Neuhofen, Germany) per enclosure. A submersible pump (model 1046, Eheim; Deizisau, Germany) was running permanently to minimize the build-up of temperature and chemical gradients in the enclosures.

Metabolism in enclosures was calculated based on diel changes in oxygen concentrations in the enclosures (Odum, 1956). Oxygen concentrations were monitored at four occasions in 2007, one

in each season. Measurements were made for three days in all enclosures of one block simultaneously before the oxygen probes were moved to the next block. After two weeks, when oxygen had been monitored once for three days in all blocks, the complete cycle was repeated for another two weeks. The optical oxygen probes (model ldo 101) and loggers (model hq40d) used were purchased from Hach-Lange, Düsseldorf, Germany. They recorded oxygen concentration, temperature and barometric pressure at 15-minute intervals. All probes were carefully cleaned and calibrated in water-saturated air before each three-day deployment. Drift of the oxygen probes was determined by Winkler titration both before and after each measurement period.

Following Chapin III et al. (2006) we define gross primary production (GPP) as the sum of C-fixation, and ecosystem respiration (ER) as the respiratory sum of all organisms. The difference of GPP and ER is defined as net ecosystem productivity (NEP). It is positive in autotrophic ecosystems and negative in heterotrophic ecosystems. Another common measure to evaluate whether an ecosystem is auto- or heterotrophic is the ratio of GPP and ER, with ratios <1 denoting heterotrophic and ratios >1 autotrophic ecosystems.

Any change in oxygen concentration at a given time is due to NEP and the diffusive gas exchange (D) with the atmosphere (Cole et al., 2000). Thus:

$$NEP = \Delta[O_2] - D$$

where positive values denote an addition of oxygen to the system (GPP) and negative values denote a loss of oxygen (ER). The diffusive flux is a function of the piston velocity, *k*, the oxygen concentration in water and the saturation concentration of oxygen in water at a given temperature:

$$D = k ([O_2] - [O_2]_{sat})$$

The saturation concentration of oxygen was calculated according to Wüest et al. (1992). Estimates of *k* were based on gas exchange measurements of an inert tracer gas, sulfur hexafluoride (SF_6). During the spring, each of the 16 enclosures was spiked with SF_6-saturated water and the decrease in concentration measured over four days. The saturated water was prepared by sparging Nanopure water in stoppered bottles with a mixture of SF_6 and N_2 (10%

SF_6, 90% N_2). Two syringe needles were inserted in the rubber stoppers, one reaching below the water level to inject the tracer gas, the other remaining above the water level to release excess gas. After 4 hours of bubbling, the needles were removed and the bottles stored overnight in a refrigerator (4 °C). This ensured losses of SF_6 during storage to be small. The next day the total water volume of each individual enclosure was estimated by measuring depth at ten spots and the enclosures then spiked with 6.5 to 8 ml of SF_6 saturated water to reach a target concentration of 60 pg l^{-1}. The submersible pumps in the enclosures ensured complete mixing.

Duplicate water samples were taken with 50-ml gas-tight glass syringes 1, 18, 42, 67 and 91 hours after addition of the SF_6. Syringes were filled with 25 ml of water, leaving no headspace, and sealed with a three-way valve. In the laboratory, the syringes were topped with 25 ml of N_2 and vigorously shaken for 30 s to let most of the SF_6 escape into the gaseous phase. SF_6 in the headspace was measured with a gas chromatograph (Fisions GC 8000, Milan, Italy) equipped with a molecular sieve 5Å column (6 feet x 1/8 inches, 80/100 mesh, Alltech; Deerfield, IL, USA) operated at room temperature. SF_6 was detected and quantified with an electron-capture detector (ECD Fisions 800, Milan, Italy) kept at 350 °C. For details see Cirpka et al. (1993) and Schlatter et al. (Schlatter, Wuest, & Imboden, 1997).

Piston velocity was calculated for each time interval between two consecutive water samplings and averaged over time following the method of Ledwell (1982) as described in Crusius (2003):

$$k = \frac{SF_{6,i} - SF_{6,f}}{(t_i - t_f) \cdot A \cdot C_{surf}}$$

where SF_6 is the total number of moles of SF_6 in the enclosure, A is the water surface area of the enclosures (1.58 m^2), t stands for time in hours and C_{surf} is the difference between the measured SF_6 concentration in water and the equilibrium concentration of SF_6 with air (mol m^{-3}). Indices *i* and *f* denote the beginning and end of the considered time interval. Piston velocity *k* for oxygen was calculated from *k* for SF_6 using the ratio of Schmidt numbers (Sc); this ratio allows calculating *k* for any gas if *k* for another gas at a given temperature is known (Cole & Caraco, 1998):

$$\frac{k_{O_2}}{k_{SF_6}} = \left(\frac{Sc_{O_2}}{Sc_{SF_6}} \right)^n$$

The exponent *n* is dependent on wind speed and was assumed to be -2/3, corresponding to wind speeds within the reed stand below 3 m s^{-1} (Crusius et al., 2003). Schmidt numbers for a given gas and temperatures were calculated from a third-order polynomial Wanninkhof (1992):

$$Sc = a - bT + cT^2 - dT^3$$

where *a*, *b*, *c* and *d* are regression coefficients and *T* is temperature in °C. Coefficients for both O_2 and SF_6 were taken from Wanninkhof (1992).

Ecosystem respiration (ER) was assumed to equal NEP during the night, in the absence of photosynthesis. Nighttime ER was assumed to equal daytime ER (e.g. Carignan, Blais, & Vis, 1998). GPP was calculated as the sum of NEP and ER.

Three ANOVAs were carried out to test for effects of elevated temperature, nitrogen enrichment and season on GPP, ER and GPP/ER. The five warming and nitrogen treatments (unheated, unfertilized = Δ0°; unheated, fertilized = Δ0°N; heated, unfertilized = Δ4°; heated, fertilized = Δ4°N; L = unfenced control plot) and season were used as categorical variables, and GPP, ER and GPP/ER, respectively, as response variable. Planned linear contrasts were subsequently used to test for effects of experimental warming (heated vs. unheated enclosures), nitrogen enrichment (fertilized vs. unfertilized enclosures), and enclosure effects (unheated and unfertilized control enclosures vs. unfenced control plots) and differences between seasons.

Results

Experimental warming was less effective than intended (Figure 1), especially during periods when water temperature in the reed stand rose very fast, such as in April, when the experimental heating could not keep pace with the natural warming. Nevertheless, the temperature in heated enclosures was always higher than in the control enclosures and unfenced control plots, resulting

in a mean annual temperature in the heated enclosures that was 3.1 °C higher than in the unfenced control plots.

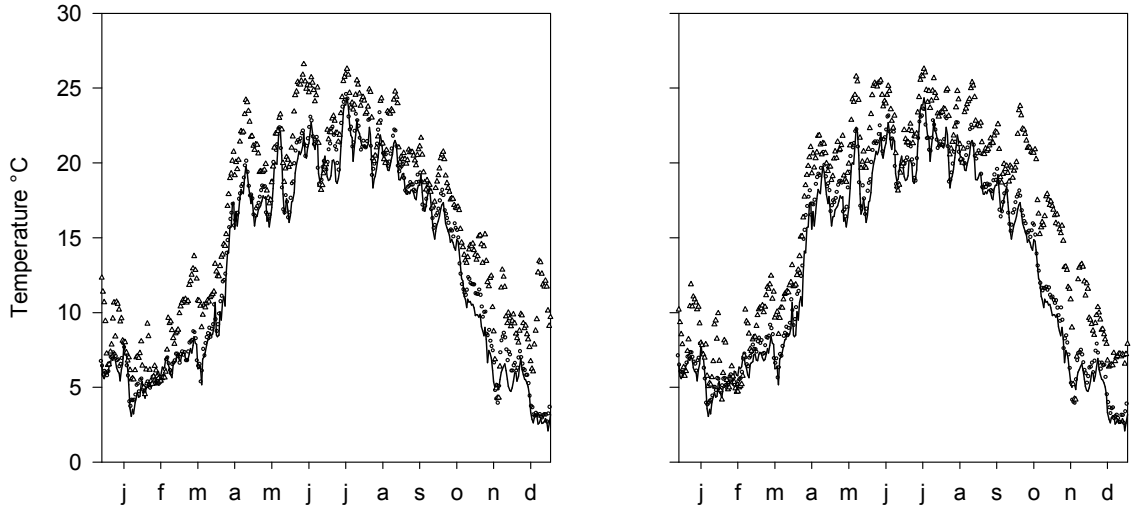

Figure 1. Daily mean temperatures in 2007 in the reed stand of Lake Hallwil. The left panel shows temperatures in unfertilized enclosures (symbols) and the unfenced control plots (solid line), the right panel shows temperature in fertilized enclosures (symbols) and the unfenced control plots (solid line). Circles denote unheated enclosures, triangles denote heated enclosures.

Nitrogen enrichment was more effective during the first half of the year when nitrogen concentrations in the fertilized enclosures were on average 2.5 times higher than in the unfenced control plots (Figure 2). During the second half of the year concentrations were about 1.9 times higher. The large error bars for the fertilized enclosures result from the sampling scheme. Samples were taken before and after nitrate addition to the enclosures. Over the 4 weeks between two subsequent nitrogen additions, concentrations in the enclosures declined to the base level measured in the unfertilized enclosures and unfenced control plots. Phosphorus concentrations decreased much more strongly during spring than nitrogen concentrations (Figure 3). Between February and April phosphorus decreased from 12 $\mu g\ l^{-1}$ to about 3 $\mu g\ l^{-1}$ in the unfenced control plots and remained low until December when concentrations started to increase again. Phosphorus concentrations in all enclosures were generally slightly higher than in the control plots throughout the year. The resulting molar N:P ratios ranged from 47 to 642. The lowest ratios were observed in unfertilized enclosures during spring highest in fertilized enclosures during summer and fall. On annual average the N:P ratio in fertilized enclosures was 166 (Δ0°) and 210 (Δ4°), in heated enclosures the ratio was 459 (Δ0°N) and 491 (Δ4°N). In the unfenced Lake control the N:P ratio averaged annually at 359.

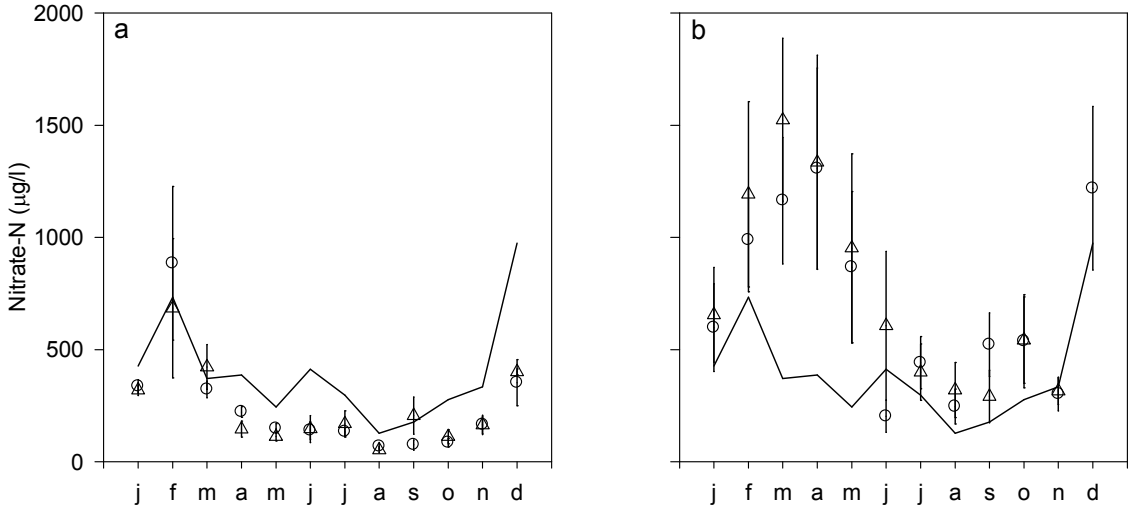

Figure 2. Dynamics of nitrate concentrations in the reed stand of Lake Hallwil during 2007. The left panel shows unfertilized enclosures (symbols) and the control plots (solid line), the right panel shows fertilized enclosures (symbols) and the control plots (solid line). Circles denote unheated enclosures, triangles denote heated enclosures. Error bars denote SEM, N = 4.

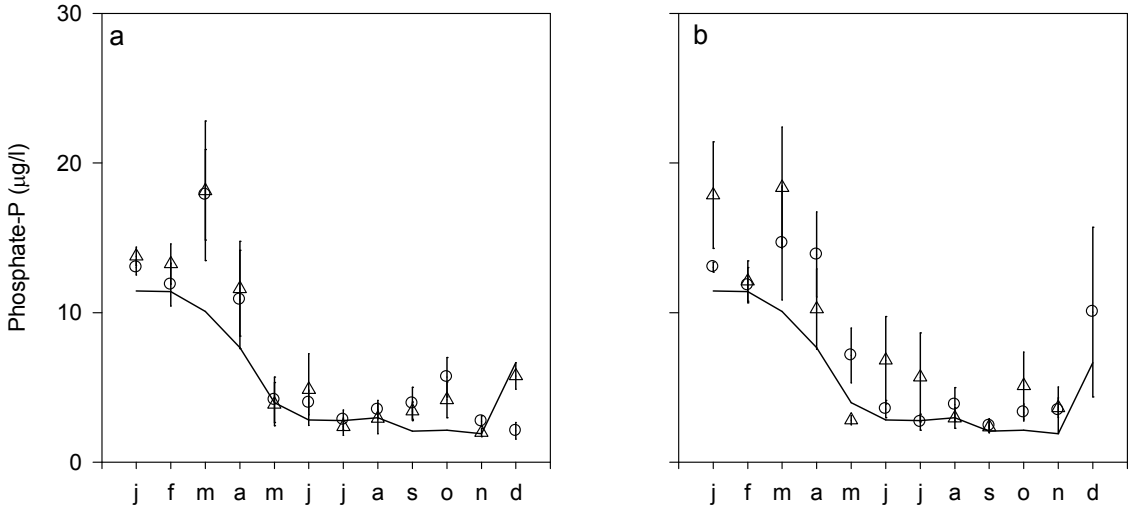

Figure 3. Concentrations of phosphorus in 2007 in Lake Hallwil. The left panel shows unfertilized enclosures and the control plots (solid line), the right panel shows fertilized enclosures and the control plots (solid line). Circles denote unheated enclosures, triangles denote heated enclosures. Error bars denote SEM, N = 4.

SF_6 tracer concentrations declined at similar rates in all enclosures (Figure 4). Only during the first measurement (T0) a larger variance of SF_6 concentrations between different enclosures was found, which was probably caused by the fact that the SF_6 was not yet evenly mixed within the water in the enclosure. In later measurements this discrepancy diminished. As the decrease in SF_6 concentrations was very similar in all enclosures, we averaged all measured piston velocities (k) and used this average of 0.010 ± 0.001 (SD) m h^{-1} for all enclosure types and the unfenced control plots.

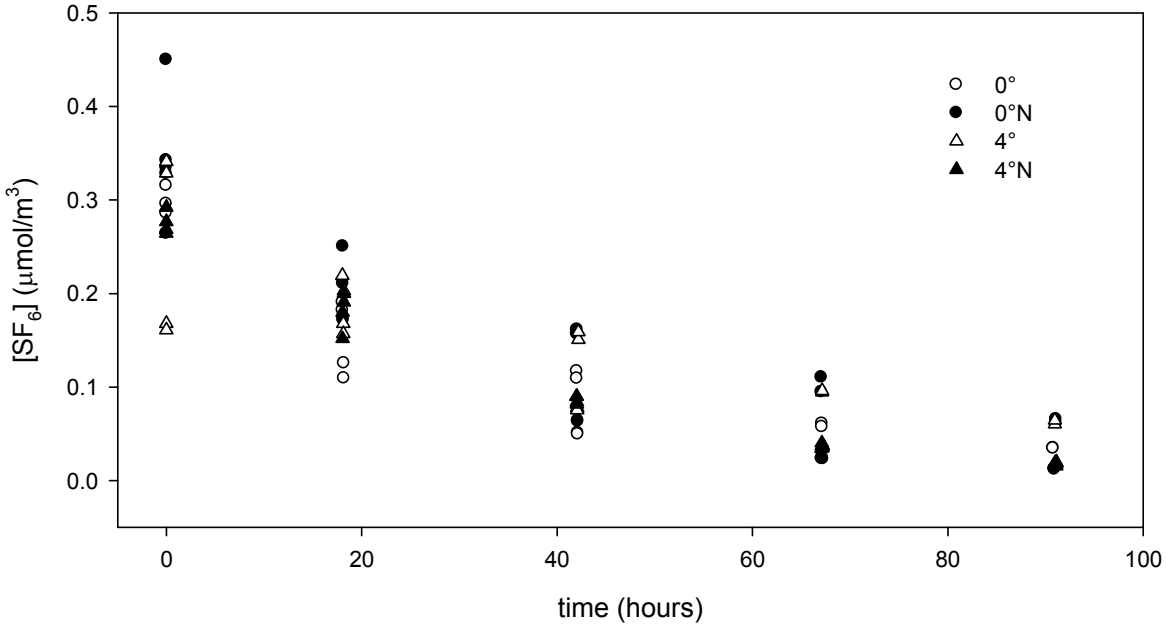

Figure 4. Changes over time in the concentration of an inert tracer gas, SF_6, in four different enclosure types: ambient temperature, unfertilized = 0°; ambient temperature, fertilized = 0°N; heated, unfertilized = 4° and heated, fertilized = 4°N. N = 4 for each enclosure type.

Oxygen concentrations were generally low (saturation < 50%) in the enclosures regardless of the treatment (Figure 5). There was tendency that heated enclosures showed higher oscillations than unheated ones, whereas fertilized enclosures tended to have higher concentrations than unheated enclosures.

Ecosystem Respiration (ER) was lowest in winter (Figure 6) increased several fold in spring ($P < 0.001$) to decline again in summer and fall. Fertilized enclosures showed lower respiration rates than unfertilized enclosures ($P = 0.008$), a tendency that was apparent in all seasons but winter, irrespective of experimental warming. A temperature effect on ER was not apparent ($P = 0.64$). Gross Primary Production (GPP) showed the almost exact same pattern as ER, with highest rates in spring and lowest rates in winter. There was again a significant difference between spring and all other seasons ($P < 0.001$) but not between summer, fall and winter ($P = 0.12$ to 0.38). Furthermore, nitrogen addition inhibited ER ($P < 0.001$), whereas experimental warming had no significant effect on GPP ($P = 0.60$).

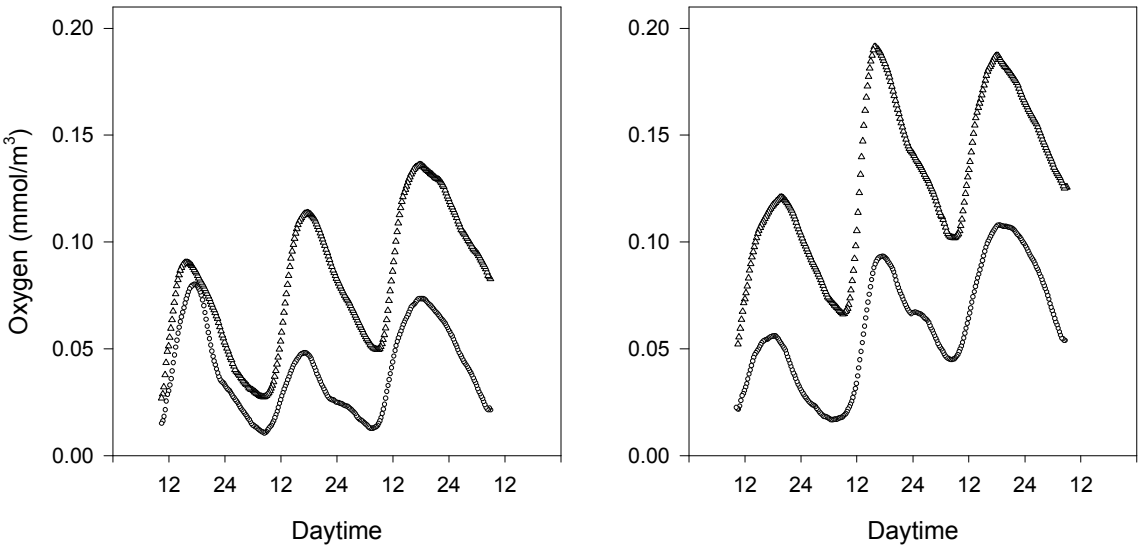

Figure 5. Diel oxygen osciallations during three days in July. The left panel shows oxygen concnetrations in unfertilized enclosures, the right panel shows temperature in fertilized enclosures. Circles denote unheated enclosures, triangles denote heated enclosures.

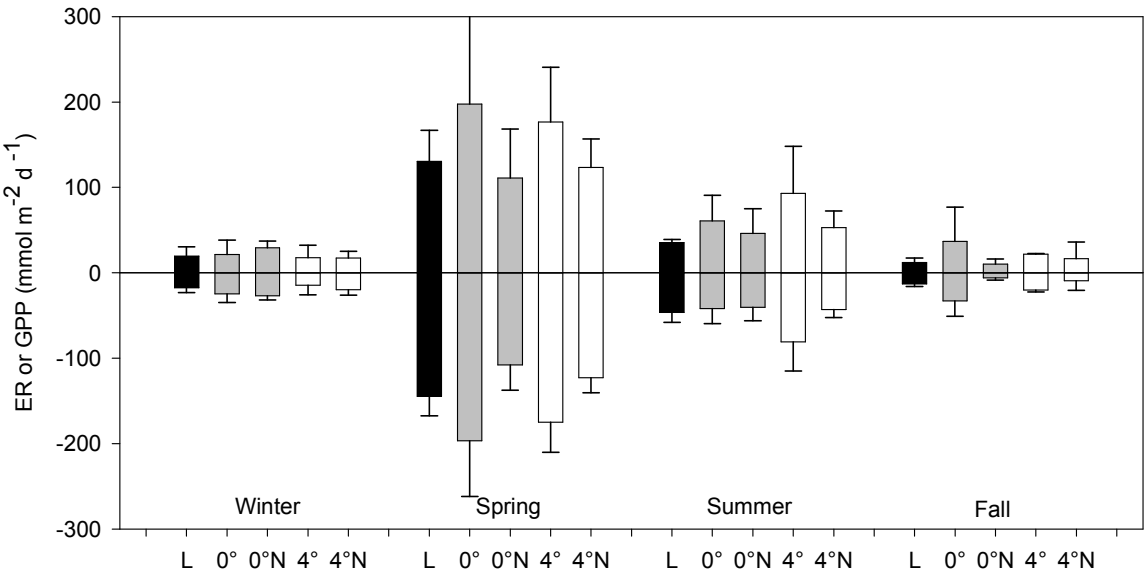

Figure 6. Gross Primary Production (GPP; positive values) and Ecosystem Respiration (ER; negative values) in four seasons and different enclosure types (ambient temperature, unfertilized = 0°; ambient temperature, fertilized = 0°N; heated, unfertilized = 4°; and heated, fertilized = 4°N) and unfenced control plots (L). Error bars denote SEM (N=4).

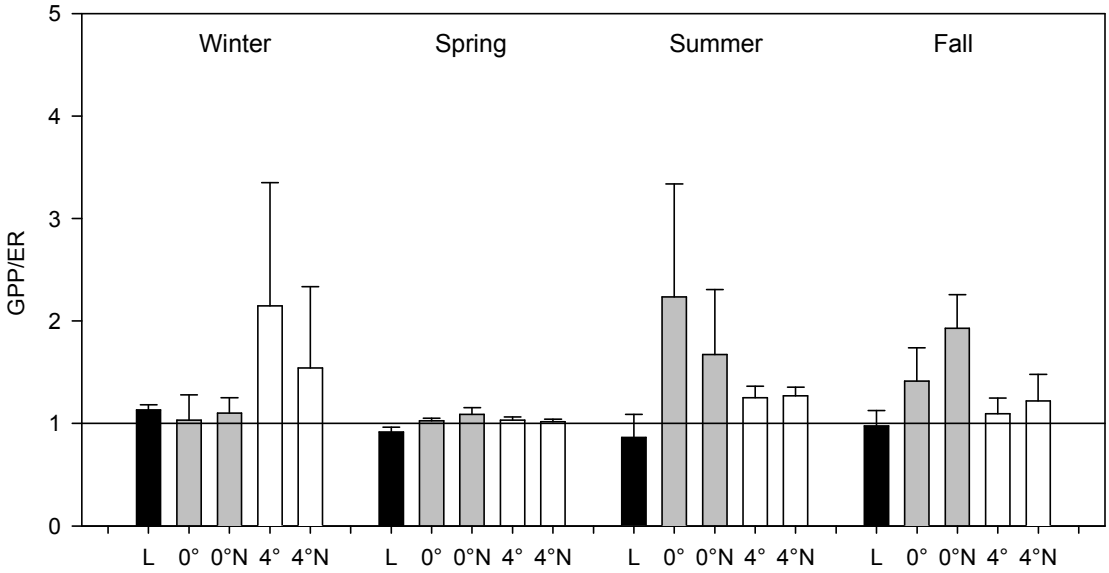

Figure 7. GPP/ER ratios in all four seasons in all four enclosure-types (ambient temperature, unfertilized = 0°; ambient temperature, fertilized = 0°N; heated, unfertilized = 4° and heated, fertilized = 4°N) and the unfenced control plots (L). Error bars denote SEM (N=4). Values <1 denote net heterotrophic, values >1 net autotrophic conditions.

GPP/ER ratios in spring were very close to unity regardless of the treatment (Figure 7). In all other seasons GPP/ER ratios in the enclosures tended to be greater than one. Highest ratios for unheated enclosures were found in summer and fall. In heated enclosures the highest ratios occurred in winter. Neither nitrogen enrichment nor experimental warming had a significant effect on the GPP/ER ratio ($P = 0.93$ for nitrogen, and $P = 0.85$ for temperature). In the unfenced control plots the ratio remained close to one throughout the year. Frequency distributions of GPP/ER ratios indicate a shift towards autotrophic conditions in the enclosures compared to the unfenced control plots (Figure 8). Experimental warming increased the incidence of GPP/ER >1 from 53.8% in unheated enclosures to 66.7% in heated enclosures. In unheated and fertilized enclosures, GPP/ER ratios >1 occurred almost 20% more often than in unheated and unfertilized enclosures, and enclosures subject to both heating and fertilization had GPP/ER ratios >1 less often than enclosures that were either heated or fertilized.

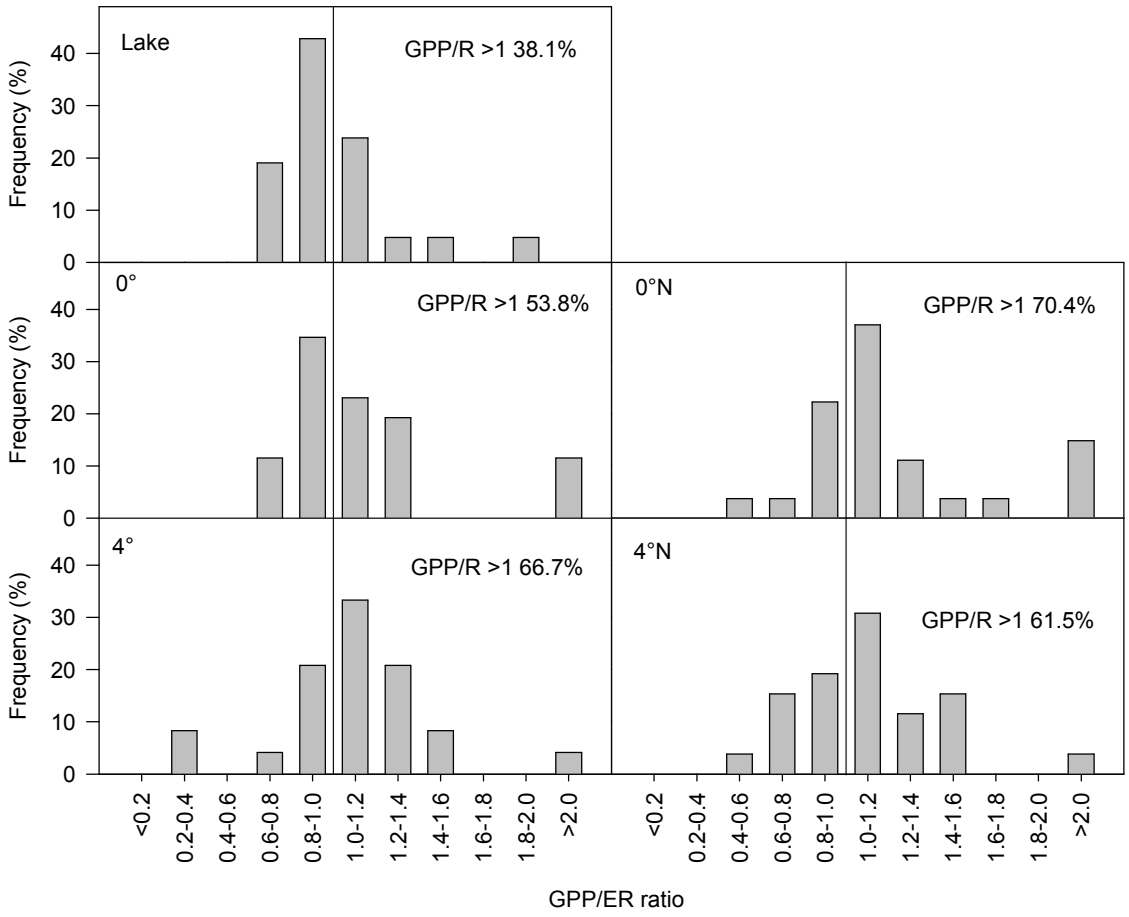

Figure 8. Frequency distribution of GPP/ER ratios for all five treatments (ambient temperature, unfertilized = 0°; ambient temperature, fertilized = 0°N; heated, unfertilized = 4° and heated, fertilized = 4°N and the lake controls). Values <1 denote net heterotrophic, values >1 net autotrophic conditions.

Discussion

An intriguing result of the present study was the almost perfect balance between gross primary production (GPP) and ecosystem respiration (ER), which suggests that the two processes are tightly linked. This raises the question of which of the two processes may control the other. Either GPP controls ER in the sense that low GPP restricts supply of organic carbon for ER, or ER controls GPP by limiting the supply of recycled nutrients such as phosphorus and nitrogen required by primary producers. Measurements of microbial production rates (Buesing and Gessner (2006) indicate that most of the heterotrophic metabolic activity in the reed stand derives from the litter layer and sediment, whereas processes in the water column and on submerged biofilms are negligible. The reed stand is indeed characterized by a thick litter layer all year round, corresponding to an annual average carbon stock of about 370 g m^{-2} (Buesing,

2002). This large reservoir of organic carbon, even though much of it is relatively recalcitrant, makes it highly unlikely that carbon fixation by GPP in the water column and submerged biofilms was critical in fuelling total-system respiration. However, given that the water and nutrient exchange in enclosures was greatly restricted, it seems plausible that mineralization of organic matter in the enclosures was an important source of nutrients for primary producers. This would imply that nutrient recycling was the rate-limiting step of GPP and that nutrients released as a result of organic matter mineralization were rapidly channeled into GPP to build new biomass. Such coupling could explain the almost perfect balance between GPP and ER and is also in line with the very small net ecosystem productivity that we observed in the enclosures.

Which nutrient was limiting in the present study? N:P ratios of 47 to 642 indicate that phosphorus was the critical element. Phosphorus concentrations were also low overall and decreased during the spring to remain low for most of the remaining year. Moreover, immediately after addition of nitrate to enclosures, N:P ratios in enclosures receiving extra nitrogen were several fold higher than in control enclosures, suggesting that phosphorus limitation could have been exacerbated by nitrogen enrichment. It is unlikely, however, that ER and GPP were affected by this shift in N:P ratios because the total amount of available phosphorus was not reduced by nitrogen enrichment. Further, the concentrations of phosphorus in enclosures, although low in general, even tended to be higher, rather than lower, in nitrogen-enriched enclosures. Thus, phosphorus limitation may account for an overall low activity of ER and GPP but it cannot explain the observed differences between control and nitrogen-enriched enclosures.

As heterotrophic metabolic activity in the reed stand mainly occurs in the litter layer and sediment (Buesing et al., 2006), reduced decomposition of organic matter could account for lower ER and GPP in fertilized enclosures. Other studies (Chapter 1; Carreiro et al., 2000; Magill & Aber, 1998) indicate that elevated nitrogen concentrations can be inhibitory to plant litter decomposition. Decomposition of highly recalcitrant organic matter is particularly affected, possibly because phenol oxidase is suppressed by high nitrogen loads (Knorr, Prentice, House, & Holland, 2005; Osono, 2007; Sinsabaugh, Carreiro, & Repert, 2002). If most of the plant litter and other organic matter accumulating on the sediment are recalcitrant, then the metabolism in enclosures would mainly derive from low-quality carbon. This would mean that ER (and nutrient recycling) is controlled by the decomposition of low-quality carbon. Consequently, when decomposition of this material is inhibited, for example in response to high nitrogen loads, a

cascade of processes ranging from plant litter mineralization and nutrient recycling to algal GPP may be affected.

The GPP/ER ratios in the unfenced control plots suggest that the reed stand is a heterotrophic system. This contrasts the general tendency of wetlands to sequester carbon (Bridgham, Megonigal, Keller, Bliss, & Trettin, 2006) and also appears to be at variance with earlier estimates of microbial productivity which suggested the reed stand to be a hot spot of heterotrophic metabolic activity (Buesing et al., 2006). The argument by Buesing & Gessner (2006) was based on their estimate that carbon demand by microbes exceeds the carbon supply by above-ground plant production. Although for methodological reasons the estimate of bacterial productivity by Buesing & Gessner (2006) may be an overestimate (Gillies, Kuehn, Francoeur, & Neely, 2006), the microbial carbon demand is clearly high. However, horizontal water movement driven by the prevailing westerly winds can transport large amounts of planktonic carbon and dissolved oxygen into the reed stand and thus boost heterotrophic microbial activity. This labile carbon and oxygen would not be available in the enclosures, thus curbing overall heterotrophic activity, including ER, and leading to a greater tendency of net autotrophy

Calculation of ER and GPP from diel changes in oxygen concentration is based on the premise that respiration at night equals respiration during the day. However, as shown by Bender et al. (1987), daytime respiration can be higher than nighttime respiration, due to several biochemical pathways. The error introduced by this imprecision is small, because GPP and ER would increase in equal proportions. Therefore, the ratio of GPP and ER would be little affected.

In summary, our results suggest that GPP and ER were closely coupled and that GPP may rely on the delivery of nutrients recycled in the course of benthic organic matter decomposition. In contrast, reliance on recycled nutrients cannot explain the observed reduction in ecosystem metabolism caused by the enrichment of enclosures with nitrate, because there was no clear indications that the inhibition was caused by exacerbated phosphorus limitation, the element that appeared to be in shortest supply. Instead, the inhibition may have been due to a cascading effect triggered by inhibition of organic matter decomposition by elevated nitrate concentrations, particularly of recalcitrant organic carbon compounds such as lignin. Further studies could provide a better understanding of the complex controls and mutual dependencies of ER and GPP.

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Outlook

The work presented in this dissertation is the first attempt to investigate effects of climate warming and nitrogen enrichment on litter decomposition in an aquatic ecosystem under field conditions. The results of these experiments are promising but often not clearcut. One possible reason for this is, in part, that for technical reasons the experimental warming was nearly always below the intended 4°C above ambient lake temperature. For future experiments a different technique for temperature regulation should be considered. A second, perhaps more important point is that that oxygen concentrations in the enclosures were below levels in the lake, due to restricted water exchange. Decomposition rates in the enclosures were generally lower in the enclosures than in the unfenced lake controls, regardless of the treatment. It is likely that these differences in decomposition rates were caused by low oxygen concentrations. However, as this artifact was the same among all treatments, they are unlikely to change the general outcome of the presented experiments, in spite of its marked influence.

The present study suggests that nitrogen had an inhibitory effect on decomposition processes. Other studies in terrestrial ecosystems have shown inhibitory effects of nitrogen on litter decomposition as well (e. g. Magill & Aber (1998), but the mechanisms by which increased nitrogen supply affects decomposition rates are not well understood. Knorr et al. (2005) concluded that nitrogen inhibits decomposition when (i) litter quality is low (e.g. as a result of high lignin content) and (ii) fertilization rates exceed 2-20 times the anthropogenic deposition level of nirogen. The nitrate concentration chosen in our experiments was five-fold above ambient, which is within this critical range identified by Knorr (2005). Sinsabaugh et al. (2002) provide evidence that high nitrogen supply inhibits lignin degradation although it the cellulose degradation was stimulates. Better understanding of these mechanisms is essential for better predictions of effects of future global environmental change on carbon flows in aquatic ecosystems that are dominated by vascular plants.

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