A feedback loop links brownification and anoxia in a temperate, shallow lake

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Abstract

This study examines a natural, rapid five-fold increase in dissolved organic carbon (DOC) concentrations in a temperate shallow lake, describing the processes by which increased DOC resulted in anoxic conditions and altered existing carbon cycling pathways. High precipitation for two consecutive years led to rising water levels and the flooding of adjacent degraded peatlands. Leaching from the flooded soils provided an initial increase in DOC concentrations (from a 2010 mean of 12 ± 1 mg L^{-1} to a maximum concentration of 55 mg L^{-1} by June 2012). Increasing water levels, DOC, and phytoplankton concentrations reduced light reaching the sediment surface, eliminating most benthic primary production and promoting anoxia in the hypolimnion. From January to June 2012 there was a sudden increase in total phosphorus (from 57 μg L^{-1} to 216 μg L^{-1}), DOC (from 24.6 mg L^{-1} to 51.5 mg L^{-1}), and iron (from 0.12 mg L^{-1} to 1.07 mg L^{-1}) concentrations, without any further large fluxes in water levels. We suggest that anoxic conditions at the sediment surface and flooded soils produced a dramatic release of these chemicals that exacerbated brownification and eutrophication, creating anoxic conditions which persisted roughly six months below a water depth of 1 m, and extended periodically to the water surface. This anoxia resulted in a near-complete loss of macroinvertebrate and fish populations, and surface carbon dioxide (CO_2) emissions increased by an order of magnitude relative to previous years. A brownification-anoxia feedback loop reduced benthic primary and secondary production and increased CO_2 emissions in a shallow lake.

Introduction

Many freshwater systems in mid- to high-latitudes of the northern hemisphere have experienced a gradual, long-term increase in dissolved organic carbon (DOC) concentrations in recent decades (Roulet and Moore 2006; Clark et al. 2010). This trend has been dubbed ‘brownification’ (Kritzberg and Ekström 2012). Despite a large number of recent studies, the ultimate causes and consequences of this phenomenon remain poorly understood, and strongly debated (Clark et al. 2010). In general, DOC strongly influences the light attenuation, nutrient supply, and metal toxicity of lakes, and can thus significantly alter the metabolic balance of an ecosystem (Williamson et al. 1999). For instance, it has long been recognized that DOC can boost ecosystem respiration rates (Williamson et al. 1999), while diminishing primary production by shading (Jones 1992; Carpenter et al. 1998). Furthermore, high concentrations of DOC can abiotically deplete oxygen (O_2) by promoting photo-oxidation (Lindell et al. 2000), and can decrease the water mixing depth in shallow lakes (Fee et al. 1996), diminishing the supply of O_2-rich waters to deeper layers during stratified periods. In terms of biodiversity, anoxia typically results in significant declines in the biological richness and diversity of a given ecosystem (Townsend et al. 1992). The full effects of DOC on aquatic ecosystems may be complex, and thus whole-lake studies of rising DOC concentrations (Sadro and Melack 2012) are important yet rare sources of information regarding the net metabolic responses of lakes to high DOC concentrations, and are necessary for the meaningful prediction of trends at broader temporal and spatial scales.

The frequently observed metabolic responses to increasing DOC concentrations (such as boosted microbial respiration and photo-oxidation rates, and suppressed primary production) all potentially lead to the rapid depletion of dissolved O_2 in aquatic systems, and may thus promote anoxia. Anoxic conditions at the sediment surface are potentially exacerbated by intensified thermal stratification due to brownification. They have also been found to strongly influence geochemical fluxes, boosting the internal benthic release of DOC, phosphate, iron, and manganese (Skoog and Arias-Esquivel 2009). There thus exists a linkage between ecosystem metabolism (creating anoxic conditions) and geochemical responses, producing the potential for positive or negative feedback mechanisms. From a carbon cycling perspective, a sustained shift towards a greater heterotrophy (defined as respiration minus primary production) could theoretically turn a lake into a greater net carbon source to the atmosphere, with broad implications for regional carbon balances.

In this study, we analyzed changes in the abiotic and metabolic parameters of a shallow lake in northeast Germany over three consecutive years. During this time, our study lake experienced a pronounced natural brownification during two years, associated with a major increase in water levels during a period of high precipitation. We hypothesized that increasing DOC concentrations were due to leaching from the flooding of adjacent degraded peatlands, and that the severe anoxia eventually observed in this system was the result of a loss of benthic primary production by DOC shading as well as boosted ecosystem respiration rates. We furthermore hypothesize that the metabolic-geochemical linkage constitutes a feedback loop which will augment anoxic conditions.

Methods

Study site

Kleiner Gollinsee (53°01’N, 13°35’E, hereafter referred to as Gollinsee) is a small (surface area = 0.03 km^2), shallow (Z_{mean} = 1.7 m, Z_{max} = 2.9 m; 2010 values), and eutrophic lake located in a low-lying rural region of northeastern Germany. It features no sizeable surface in- or outflows. The lake is completely encircled by alder trees (*Alnus glutinosa* L.). Primary production within the lake consists of phytoplankton (36%), epiphyton (2%), and epipelon (62%; 2010 values, Brothers et al. 2013*a*). Gollinsee features no submerged macrophytes, and the littoral zone is dominated by water lilies (primarily *Nymphaea alba* L.) and a shoreline reed belt (*Phragmites australis* Trin. ex Steud.).

Unusually high precipitation caused the water levels of Gollinsee to rise gradually, beginning in the summer of 2011. By the following summer (2012), lake water levels were approximately 1 m higher than in previous years, and the lake surface area had expanded to a point where it flooded an adjacent area of degraded peatlands. These peatlands are located directly beyond the alder belt, and extend to the north and south of the lake beyond the limits of the flooded lake area in 2012. They are fully degraded (decomposed) peatlands (H10 on the von Post scale, Puustjärvi 1970), featuring amorphous, unrecognizable plant structures, and lacking free water. The catchment area beyond the peatlands is dominated by rusty brown soils (dystric cambisols) with pine forests (*Pinus sylvestris*).

In November 2010, prior to the increase in water levels, a plastic curtain had been installed and 2000 kg of maize leaves had been added to one side of the divided lake as a tracer for terrestrial particulate organic carbon with a distinct δ^{13}C signature in an unrelated experiment (Attermeyer et al. 2013). This curtain remained undisturbed throughout the 2011 to 2012 period of increasing water levels. Except when explicitly stated, we here present mean data for both lake halves.

Water sampling and analysis

Pelagic water samples were taken every four weeks from April 2010 to March 2012, and then again in June and July 2012. Samples included equal portions of water generally from 0.5 m, 1 m, and 2 m water depths (always above the thermocline, with precise sampling depths varying with mixing depths). Samples were transported to the laboratory in a dark cooler, and were analyzed within 12 to 24 hours of sampling. Light attenuation was measured along the entire water column from simultaneous light intensity values recorded by two Underwater Spherical Quantum Sensors (LI-193, LI-COR) fixed vertically at 50 cm apart. Secchi disk readings were also recorded for each sampling date, and were used to estimate light attenuation on dates when direct measurements were unavailable or unreliable. Vertical profiles of O_2 concentrations, pH, and temperature were made during each sampling visit using a Yellow Springs Instruments (YSI, Xylem) monitoring probe.

Water samples were analyzed for concentrations of total phosphorus (TP), soluble reactive phosphorus (SRP), dissolved nitrogen (DN), and dissolved inorganic carbon (DIC) following standard procedures. DOC concentrations in water samples were analyzed with a total organic carbon (TOC) Carbon-Analyser (TOC 5000, Shimadzu). Iron (Fe) concentrations were measured using an inductively coupled plasma optical emission spectrometer (ICP-OES) with an inductively coupled argon plasma (iCAP) 6000-Duo (Thermo Fisher Scientific). Pelagic chlorophyll *a* (Chl *a*) concentrations were estimated by filtering lake water for pigment concentration analysis by high-performance liquid chromatography (HPLC, Waters) following methods outlined by Shatwell et al. (2012). Temperature loggers (Thermistor) were suspended from buoys along depth intervals of 0.5 m from the water surface to the sediments. Each logger took continuous (every 30 s) measurements of water temperature. Temperature loggers were installed into the lake in 2011 from May to November, and in 2012 from June to November.

In order to assess the possible sources of DOC within the lake, its composition was compared between water samples from the lake center, flooded reed and alder belt (sampled separately in November and December 2011 and January, July, September, October, and December 2012), the groundwater near the lake (in August and September 2012, taken from two wells located 4 to 6 m of the lake shore, with groundwater located 2 to 3 m below ground level), and in the pore water from the adjacent degraded peatlands (taken in September and December 2012). Pore water from 1 m deep in the peatlands was collected by suction cups ($n = 2$) and dialysis ‘peeper’ pore water samplers ($n = 9$). Peatland pore water samples were taken from locations near the limit of the lake-flooded area, 4 to 10 cm below the water surface. Independent fluorophores were identified by a parallel factor analysis (PARAFAC) of three-dimensional fluorescence excitation-emission matrices following Stedmon et al. (2003), using a thirteen-component model according to Cory and McKnight (2005). Following the nomenclature of Cory and McKnight (2005), Strohmeier et al. (2013) identify component 1 (C1) as typical of peatland soils, and component 12 (an oxidized quinone, Q3) as typical of groundwater samples, and we thus focus specifically on these factors in our analyses.

Lake metabolism

Carbon dioxide (CO_2) surface fluxes were calculated following methods outlined by Cole and Caraco (1998), and adjusted for chemical enhancement following Bade and Cole (2006). Wind speed data were recorded by ultrasound at lake-center monitoring stations every 10 minutes by a meteo multiprobe (ecoTech, Bonn, Germany). The concentration of P_{CO_2} in surface waters was calculated from DIC concentrations, pH, and temperature, adjusting for the concentration of calcium ions ($CaCO_3^0$, $CaHCO_3^+$, and $CaOH^+$) following Gelbrecht et al. (1998). Conservative P_{CO_2} concentrations are calculated for each lake accounting for a possible measured pH bias of 0.2 from DOC effects (Herczeg et al. 1985).

Pelagic gross primary production (GPP) was estimated using diel (24 hour) O_2 curves calculated from O_2 concentrations measured at the lake-center monitoring station YSI probes (Z = ~ 1.2 m). Nighttime ecosystem respiration rates (R) were calculated as the mean decline in O_2 (per 10 minute period) from dusk until dawn, and were subtracted from daytime net production rates calculated by the same method for the following day. As diel O_2 curves from the lake center may be poor at representing full-lake GPP (Brothers et al. 2013*a*), we here consider these data to primarily reflect pelagic metabolism (and during periods of stable stratification, epilimnetic metabolism). GPP and R were corrected for surface O_2 fluxes following methods outlined in Gelda and Effler (2002). O_2 curve-derived metabolic rates are expressed as CO_2, assuming a respiratory quotient of one. All statistical tests were made using the computer program JMP (version 7, Statistical Analysis System Institute), and errors are presented as the standard error of the mean.

In order to examine changes in epipelon (benthic algae) production following an increase in mean water depth and decline in transparency, periphyton (attached algae) growth rates on plastic strips were compared between July 2010 (pre-brownification), July 2011, and July 2012. Plastic strips (2 cm x 22 cm) were installed at a depth of 1.2 m in the open-water zone for four week periods. Upon removal, care was taken to minimize any disturbance to the algae during transport. Strips were transported in open plastic cylinders in a humid insulated box to a laboratory, where they were washed and brushed with filtered lake water to remove periphyton. The remaining solution was filtered for HPLC pigment concentration analysis, following Shatwell et al. (2012).

A previous study (Brothers et al. 2013*b*) found bacterial respiration to constitute the largest heterotrophic fraction of respiration rates in this lake. Consequently, we focus on bacteria as a primary potential candidate for increasing ecosystem heterotrophy (R – GPP). Monthly bacterial production data were available from April 2010 until December 2011 (excluding a period of ice cover from December 2010 to March 2011). Bacterial production (BP) was measured separately in the water and in the sediment (upper first centimeter) by incorporating L-^{14}C-leucine into the protein fraction using the protocols of Simon and Azam (1989) for water, and Buesing and Gessner (2003) for sediments. Mean values were calculated from samples collected in the littoral as well as open zones of the lake, and samples were processed following procedures described in Attermeyer et al. (2013). Net disintegrations per minute (dpm) were converted to pmol L^{-1} d^{-1} following Simon and Azam (1989), applying an isotope dilution factor of two. The conversion from volume (L) to gram dry weight (g dry wt) for bacterial production was carried out following standard dry wt determination at 105°C.

In 2011, the biomass of macroinvertebrates was estimated from eight sampling campaigns from April to November, and fish biomass estimates were obtained in October using a mark-recapture approach (Brothers et al. 2013*b*). As in 2011, kick nets were deployed in September 2012 to estimate the biomass of macroinvertebrates. Fishing campaigns carried out in October 2011 and late September 2012 were standardized, using a combined approach of multi-mesh gillnetting and electrofishing (Brothers et al. 2013*b*).

Results

Abiotic transformations

Initial (2010) DOC concentrations were approximately 12 mg L^{-1}, began to rise steadily in May 2011, and then with the onset of severely anoxic conditions rose rapidly to approximately 55 mg L^{-1} by June 2012 (Figs. 1A, 2A), Concentrations of TP and Fe had also increased dramatically by 2012 (Fig. 1B, C). Furthermore, temperature loggers and profiles revealed a strengthening in summertime thermal stratification (Fig. 1D), and thus a diminished mixing depth between each consecutive study year. Water temperatures in 2010 had remained relatively consistent throughout the water column, but by 2012 temperatures dropped sharply below a depth of 1 m, providing an 11ºC thermal gradient across the 3 m water column. Comparing these data to vertical YSI profiles from 2010, we record a significant decrease in the mean summertime (June to August) benthic temperatures (measured by profiles at the sediment surface; *t*-test, $t = -7.8287$, degrees of freedom (df) = 6, $p < 0.001$), while mean surface temperatures over the same periods were not significantly different between years (Fig. 1D; *t*-test, $t = -0.7188$, df = 5, $p = 0.50$). These changes in lake characteristics coincided with maximum recorded water levels, with DOC, TP, and Fe all increasing most strongly during the winter of 2011 to 2012 (Fig. 2A, B). Dramatic increases in the mean concentrations of dissolved nitrogen (1.3 ± 0.1 mg L^{-1} in 2011 to 2.9 ± 0.1 mg L^{-1} in 2012) and SRP (5.6 ± 4.0 μg L^{-1} in 2011 to 39.0 ± 5.6 μg L^{-1} in 2012) were also observed during this same period.

In 2010, anoxic conditions (considered to be when O_2 concentrations were below 1 mg L^{-1}) were measured during brief summer periods, and only near the sediment surface of the deepest parts of the lake. In 2011, such anoxic conditions were occasionally observed in the water column below approximately 1 to 2 m, and with increasing frequency (observed in late June and late August, with oxygenated waters reaching the sediments in July). In 2012, anoxia became a defining characteristic of Gollinsee, lasting from April to November and occasionally extending to the water surface (Fig. 3).

Regarding PARAFAC analyses of DOC, component names C1 and Q3 (Cory and McKnight 2005) were used to separate DOC of groundwater and terrigenous peatland origin. In 2011, C1 and Q3 values from lake water and water in the alder and reed belts related most closely with those values from water originating from the surrounding flooded peatlands (Fig. 4). By 2012 PARAFAC analyses identified a significant increase in the fluorescence component Q3 in lake waters (*t*-test, $t = 3.9387$, df = 13, $p = 0.002$).

Lake metabolism

The euphotic zone, calculated as the theoretical depth at which 1% of surface light would remain available to primary producers, diminished sharply from 2010 to 2011, and by 2012 was lower than the mean lake depth (Fig. 5). This corresponded to decreasing Secchi depths from 2010 to 2012 (Fig. 6A), as well as increasing DOC (Fig. 1A) and pelagic Chl *a* concentrations (Fig. 6B). These changes were further associated with a decrease in periphyton (attached algae) growth (Fig. 6C) and pH (Fig. 6D). Mean spring and summer (considered 1 March to 31 August, excluding anoxic periods and negative values) pelagic gross primary production (GPP) rates measured from diel O_2 curves increased slightly from 2010 (1.0 ± 0.1 g C m^{-2} d^{-1}) to 2011 (1.3 ± 0.1 g C m^{-2} d^{-1}; *t*-test, $t = 1.6387$, df = 340, $p = 0.10$), but significantly from 2011 to 2012 (2.0 ± 0.1 g C m^{-2} d^{-1}; *t*-test, $t = 4.0510$, df = 340, $p < 0.001$, adjusting areal estimates to a mean measured euphotic zone depth of 1.7 m) (Fig. 6E). Gross respiration rates followed a similar pattern, increasing slightly from 2010 (1.2 ± 0.2 g C m^{-2} d^{-1}) to 2011 (1.6 ± 0.1 g C m^{-2} d^{-1}; *t*-test, $t = 1.1794$, df = 452, $p = 0.24$), and then significantly from 2011 to 2012 (2.9 ± 0.2 g C m^{-2} d^{-1}; *t*-test, $t = 5.6957$, df = 452, $p < 0.0001$) (Fig. 6F). Summertime surface CO_2 emissions also increased significantly from 2011 to 2012 (Fig. 6G; *t*-test, $t = 5.9695$, df = 14, $p < 0.0001$), despite an apparent decline in pelagic DIC concentrations by 2012 (Fig. 6H).

Mirroring the results of our O_2 curves from 2010 and 2011, pelagic bacterial production increased from 36 ± 8 g C m^{-2} yr^{-1} in 2010 (given a mean depth of 1.72 m) to 62 ± 6 g C m^{-2} yr^{-1} in 2011 (given a mean depth of 2 m; $\log_{10}$ transformations, *t*-test, $t = 2.4862$, df = 53, $p = 0.02$). Along with a likely decline in benthic primary production, bacterial production in the surface sediments decreased significantly from 2010 to 2011 (*t*-test, $t = -2.3114$, df = 50, $p = 0.025$).

The biomass of macroinvertebrates in 2011 was estimated to be 1.6 g dry wt m^{-2} across six classes. In 2012, too few individuals were found to reliably estimate the whole-lake population. The macroinvertebrate community became dominated by Diptera, and chironomids in particular. In 2011, Gollinsee contained approximately 2.5 g dry wt m^{-2} of fish (across five species). In 2012, multi-mesh gill nets installed from dusk till dawn remained empty. Following a standardized sampling effort using electrofishing, fish catches remained at zero. A substantial additional effort of electrofishing secured several sunbleak individuals (*Leucaspius delineatus*, Heckel), but no other fish species could be caught. In total, approximately 1 to 5% of the previous year's numbers of sunbleak individuals were captured.

Discussion

Our results support the hypothesis that strong DOC fluxes from terrestrial surroundings could increase lake heterotrophy by fueling pelagic respiration rates while restricting hypolimnetic primary production. As a result, O_2 consumption surpassed O_2 availability, rendering the system anoxic. In our study lake, anoxic conditions appeared to lead to an internal brownification via the reductive dissolution of iron-bound DOC in the sediments (following Skoog and Arias-Esquivel 2009). We suggest that this process resulted in a positive feedback loop which sustained O_2 depletion in the lake (Fig. 7).

Causes of initial DOC increase

The summers of 2011 and 2012 featured unusually high precipitation (201 to 250% above the 1961 to 1990 average for this region), resulting in rising groundwater and lake levels across many of the groundwater-fed lakes in the glacial landscape of northeastern Central Europe (Kaiser et al. 2014). Significant rises in DOC concentrations were subsequently observed in many northeastern German lakes which featured water levels rises between 0.5 and 1 m, and which were surrounded by degraded peatlands (J.

Gelbrecht pers. comm.). High DOC concentrations in pore water samples had also been previously observed during fen rewetting in this area (Zak and Gelbrecht 2007). A large survey of roughly 1,000 lakes in Finland found that the proportion of catchment area occupied by peatlands was the most significant catchment variable in predicting lake TOC concentrations (Kortelainen 1993). Similar trends between long-term precipitation patterns and catchment exports of DOC in North American lakes associated with peatlands (Dillon and Molot 2005) suggest that such processes may be widespread.

As Gollinsee has no surface in- or outflows, we suggest that the flooding of adjacent degraded peatlands was the primary source of the initial (2011) increase in DOC concentrations. This was supported by our PARAFAC analyses, which showed that in 2011 the optical properties of DOC samples taken from the flooded peatlands overlapped with those of DOC taken from the alder and reed belts, which were linked to lake water DOC. A potential limitation of the PARAFAC approach is that while it can provide a valuable insight into the changing characteristics of DOC, it does not measure the concentrations of different DOC components. Instead, PARAFAC analyses represent integral fluorescence signals of DOC samples, which may vary with concentration, molar absorptivity, and quantum efficiency, which are unknown (Stedmon and Bro 2008). Experimental maize additions in late 2010 were not responsible for the observed DOC increase, as the increase occurred in both sides of the divided lake, with no significant differences in 2012 DOC concentrations (*t*-test, $t = 1.3622$, df = 11, $p = 0.20$).

Initial effects of brownification on lake metabolism

Water levels, DOC, and nitrogen concentrations all increased from 2010 to 2011. Although there was no apparent increase in TP concentrations, mean pelagic Chl *a* concentrations doubled, and pelagic diel O_2 curves indicated a slight increase in GPP. Since diel O_2 curves measured a comparable increase in both respiration and GPP rates over the same period, it is likely that the high respiration rates in 2011 were predominantly fueled by the increased phytoplankton production, although the slight increase in pelagic bacterial production could also be driven by high DOC concentrations.

Elevated DOC and phytoplankton concentrations both contributed to diminished Secchi depths and an overall decrease in the size of the euphotic zone. This reduced transparency would have negatively affected primary production in the hypolimnion. A net decline in sediment bacterial production and benthic temperatures suggests that sediment respiration rates did not increase during this period. This notion is supported by Ask et al. (2012), who observed a negative relationship between benthic respiration and DOC concentrations in boreal Swedish lakes. It is, however, possible that changing bacterial growth efficiencies left sediment respiration rates unchanged (Schwaerter et al. 1988). The anoxic conditions observed in the hypolimnion in 2011 therefore appear to reflect a decline in hypolimnetic GPP relative to community respiration, rather than an increase in sediment respiration due to an increased sedimentation of phytoplankton biomass.

Anoxia leads to dystrophication

In 2012, PARAFAC analyses identified an increase in the DOC fluorescence component Q3 in lake water samples corresponding to the apparent loss of benthic primary production and measured increase in epilimnetic phytoplankton production. Cory and McKnight (2005) describe a significant positive relationship between component Q3 and aliphatic carbon content, which has further been linked to algal carbohydrates

(McKnight et al. 1994). It thus appeared possible that benthic algal breakdown and/or phytoplankton-released DOC contributed to the character of the DOC pool in 2012. However, rough estimates derived from full-year periphyton exposures in 2010 (S. Brothers unpubl.) coupled with the benthic surface area below the mean euphotic zone depth in 2012 (1.7 m) indicated that even a full dissociation of periphyton below this depth could only account for ~ 5% or less of the observed increase in DOC concentrations from 2011 to 2012. McKnight et al. (1992) found that aromatic carbon may be adsorbed to hydrous iron oxides, which could also result in a measured higher proportion of Q3 in the DOC. This is a possibility in our study lake, as the proportional increase in Q3 coincided with the onset of anoxic conditions and major increases in Fe and nutrient concentrations in the water column (Fig. 1).

A qualitative comparison of the DOC pool and rising water levels in 2010 and 2011 yielded a steady positive relationship. In 2012, this relationship was decoupled, with DOC concentrations rising dramatically without an associated increase in water levels (Fig. 2A). We thus conclude that anoxic conditions in 2011 were most likely driven by a decline in benthic primary production due to the increased input of DOC leached from the flooded degraded peatlands. Previous studies have established that the loss of benthic algae can boost internal nutrient loading (Zhang et al. 2013). By 2012, the prevailing lack of O_2 would have altered redox conditions at the sediment surface, increasing the internal loading of DOC and nutrients (following Zak and Gelbrecht 2007), and adding substantially to the externally-loaded DOC concentrations from 2011. Such internal DOC and nutrient loading mechanisms have also been previously described by Skoog and Arias-Esquivel (2009). In that study, anoxia at the sediment surface resulted in the reductive dissolution of FeOOH and release of associated organic carbon. Similar processes are assumed to have occurred in our study lake. A large increase in Fe concentrations observed during the winter of 2011 to 2012 indicates a change in sediment redox conditions (Knorr 2013; Riedel et al. 2013), which has been correlated to the flooding of peatlands (Zak and Gelbrecht 2007) and brownification in lakes (Kritzberg and Ekström 2012). Since changes in these redox-dependent processes are related to certain thresholds in redox potential, and since they are a well-established occurrence in this region (Zak and Gelbrecht 2007) they represent the most likely explanation for the sudden increase in DOC and nutrient concentrations during January and February 2012, more than six months after the initial increase in water levels and leached DOC concentrations. Although we do not have direct measurements of benthic primary production, our measured decline in periphyton growth is supported by rough estimates of the percentage of sediment surface area which would receive below 1% of the surface global radiation (thus making benthic primary production impossible). In 2010, our data suggest that 0.1 ± 4% of the sediments would be out of the range of sufficient light for photosynthesis, but by 2012, benthic primary production would have been impossible at 57 ± 5% of the lake's sediment surface area (data not shown).

Phytoplankton production was boosted by the release of nutrients from the sediments and by a compressed mixing depth. The increase in pelagic Chl *a* (~ 80 μg L^{-1}, Fig. 6B) contributed to about 50% of the increase in vertical light attenuation from 2010 to 2012 (assuming a specific absorption of 10 m² (g Chl *a*)$^{-1}$). Regarding the proposed establishment of a brownification-anoxia feedback loop (Fig. 7), the effect of nutrients and DOC thus appeared to be equally important in our study lake. The mean theoretical euphotic zone depth in 2010 (6.8 ± 0.5 m) was deep enough that the water level rise alone was not enough to shade out benthic primary production at the mean lake depth. This suggests that the decrease in light penetration due to DOC and phytoplankton was the primary cause for the loss of benthic GPP. Furthermore, high DOC concentrations increased thermal stratification, providing benthic temperatures approximately 10ºC cooler than in 2010 and thus likely negatively affecting sediment respiration rates. These results support earlier findings on the effects of DOC on thermal stratification in shallow lakes (Fee et al. 1996). To test whether an increased water depth also contributed to a greater stratification, we applied a one-dimensional model (FLake; www.flake.igb-berlin.de). Model runs were based on the mean measured annual courses of meteorological conditions (wind speed, air temperature, global radiation, and humidity, all recorded every 10 minutes at a lake-center monitoring station by a meteo multiprobe), but differed in maximum lake depths (2.9 m in 2010, 3.9 m in 2012) and vertical light attenuation (1.18 m^{-1} in 2010, 2.77 m^{-1} in 2012). This model calculated a temperature difference between near-surface and near-bottom water layers of 0.3°C in 2010 and 14.4°C in 2012 (average from April to September). A loss of transparency alone (with no rise in water levels) would have caused a mean temperature difference of 13.9°C, whereas an exclusive increase in water levels would have resulted in a difference of only 4.3°C. This suggests that the decreasing light penetration due to DOC and phytoplankton played a much larger role than changing water levels in establishing the stronger thermal stratification.

Effects of a brownification-anoxia feedback on metabolism and carbon cycling

By 2012, the increase in ecosystem respiration rates was greater than the increase in GPP, suggesting that both phytoplankton production and elevated DOC concentrations fueled the high pelagic respiration rates. Additionally, since our measurements of respiration rates were derived from nighttime O_2 consumption rates, they do not include other factors such as the photo-oxidation of DOC to CO_2 by solar ultraviolet radiation, which could increase eight-fold upon doubling humic DOC concentrations (Lindell et al. 2000). Nevertheless, the ecological consequences of the changes in Gollinsee by 2012 were severe. The brownification-anoxia feedback loop facilitated a persistent state of anoxia which occasionally extended to the water surface, resulting in the near-complete loss of macroinvertebrate and fish populations. These reductions in population size and species richness could be attributed to the severe summer anoxia, in line with the results of other studies (Townsend et al. 1992). These results suggest that the positive effects of DOC on resource availability and the fertilization of autochthonous production by TP may be outweighed by the negative influence of DOC shading on hypolimnetic primary production and of reduced mixing (as suggested in model simulations by Jones et al. 2012).

The relatively high pH in 2010 (mean = 8.1 ± 0.1) declined in following years with values eventually as low as 7.0 at the surface and 6.6 in the hypolimnion. Although a decline in pH may have been related to humic substances leached from the surrounding flooded peatlands or to a decline in groundwater pH from 2010 to 2011 (data not shown), a high degree of variability between measurements in 2011 and 2012 indicated a strong effect of carbon metabolism (i.e., respired CO_2) on lake pH values. A loss of benthic primary production and net increase in epilimnetic respiration rates would both reduce pH levels. The lowered pH resulted in a roughly 20% larger fraction of the DIC pool as P_{CO_2}, increasing surface emissions. Diminishing pelagic DIC concentrations in 2012 furthermore indicate that CO_2 losses to the atmosphere during this period were greater than could be supported by the net heterotrophy within the lake. By making this lake a greater source of CO_2 to the atmosphere, these changes represent a large shift in the carbon cycling characteristics of this ecosystem.

Previous studies have linked increasing CO_2 emissions from lakes to high precipitation, and associated this increase with the mineralization of loaded DOC (Rantakari and Kortelainen 2005). Our study suggests that internal DOC and nutrient loading may follow brownification events, facilitating higher CO_2 emissions to the atmosphere via a decreased buffer capacity (as the ability of primary producers in the hypolimnion to capture this carbon). Furthermore, methane emissions are frequently exacerbated by anoxic conditions (Bastviken et al. 2004), and although not included in this study, they likely increased as well. We therefore suggest that a widespread occurrence of such feedback loops could have significant implications to the global carbon cycle and food webs of shallow lakes. As climate change is expected to increase precipitation events and watershed DOC loading (Clair et al. 1999), it is possible that the process described in this study could occur even in lakes far from direct anthropogenic effects. This study thus extends our understanding of an important and potentially widespread internal driver in establishing anoxic conditions in lakes. Typically, the onset and duration of summer anoxia is positively linked to phytoplankton production, which in turn is often driven by high total phosphorus (TP) concentrations (Nürnberg 1995). Previous studies of anoxia, however, have focused on a period of significant eutrophication, yet the current brownification phenomenon along with regional decreases in nutrient loading may increase the importance of terrigenous DOC as a driver of anoxia in many lakes. This increasing significance of brownification as a driver of anoxia would be especially true for shallow lakes whose benthic primary production represents a larger fraction of the whole-lake GPP, making these systems more susceptible to heavy losses of primary production by shading. Regional variations in watershed and lake characteristics would thus strongly influence the likelihood and severity of our observed process occurring in another lake. However, the underlying mechanisms linking anoxia to internal brownification via the loss of benthic primary production are biogeochemical processes which may feasibly occur in any shallow lakes where light supply to the benthic zone may be limited by brownification events. We thus suggest that the current global brownification phenomenon should be considered an increasing source of concern as a potential driver of O_2 depletion and anoxia in aquatic systems.

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Table 1. General lake characteristics (May 2010 to April 2011), providing standard error of the mean.

	Gollinsee
Surface area (m^2)	33,000
Z_{mean} (m)	1.7
Z_{max} (m)	2.9
$Z_{secchi\ mean}$ (m)	1.4 ± 0.1 (*n* = 17)
pH	7.9 ± 0.1 (*n* = 20)
Chlorophyll *a* (μg L^{-1})	23 ± 3 (*n* = 21)
Total phosphorus (μg L^{-1})[†]	42 ± 3 (*n* = 20)
Soluble reactive phosphorus (μg L^{-1})[† ‡]	4.7 ± 0.6 (*n* = 13)
Dissolved nitrogen (mg L^{-1})[†]	0.97 ± 0.06 (*n* = 15)
Dissolved organic carbon (mg L^{-1})[†]	12.3 ± 0.3 (*n* = 16)
Dissolved inorganic carbon (mg L^{-1})[†]	32.2 ± 0.4 (*n* = 20)

[†] Epilimnetic, pelagic means.

[‡] One high outlier excluded.

Figure Legends

Figure 1. Abiotic lake characteristics for 2010 to 2012, with standard error of the mean. All values are spring and summer means (March to August), except D, which are summer (June to August) values.

Figure 2. Time course of (A) dissolved organic carbon and changing lake water levels, and (B) total phosphorus and iron in Gollinsee.

Figure 3. Lake oxic status from 2010 to 2012, from vertical oxygen concentration profiles and daily monitoring station measurements. The top represents the maximum lake surface level, and the bottom white area reflects the sediment surface (i.e., the lower limit of oxygen profiles made at different profiling locations and dates within the lake).

Figure 4. Parallel factor (PARAFAC) analysis of dissolved organic carbon origins in Lake Gollinsee.

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

Figure 6. Metabolic and biological lake characteristics for 2010 to 2012, with standard error of the mean. All values are spring and summer means, except C, representing summer values.

Figure 7. Processes leading to anoxia in a shallow lake dominated by benthic primary production (PP), showing a brownification-anoxia feedback loop. ‘BP + R’ represents bacterial production and respiration.

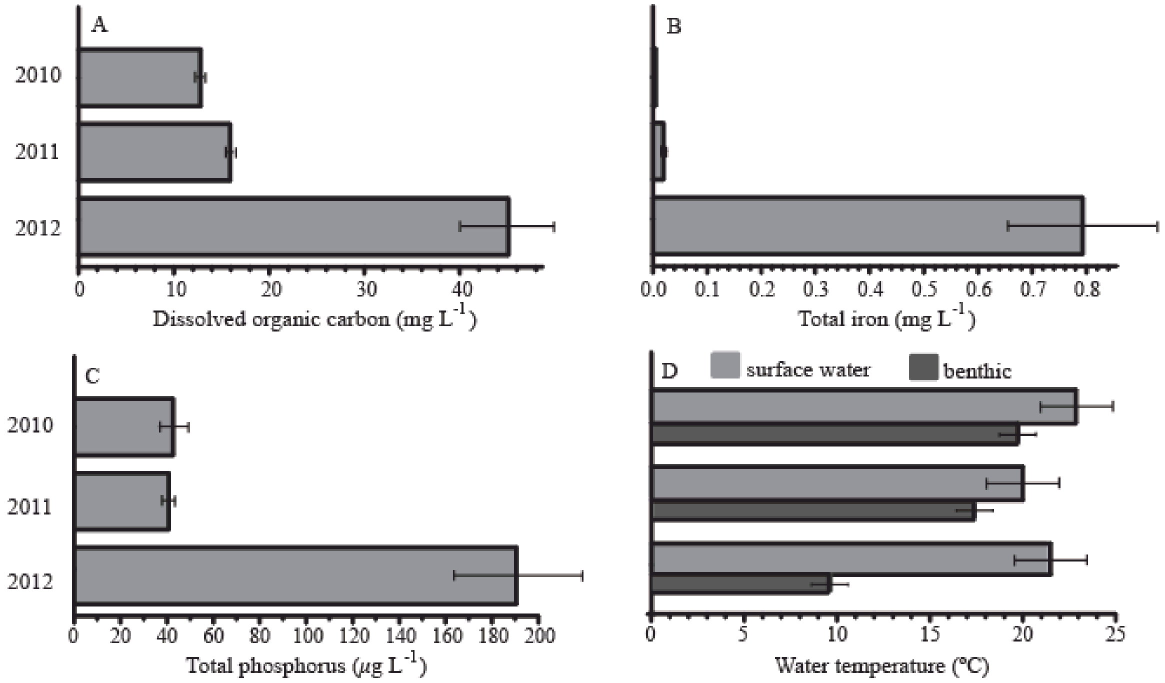

A
2010
2011
2012
0
10
20
30
40
Dissolved organic carbon (mg L-1)
B
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
Total iron (mg L-1)
C
2010
2011
2012
0
20
40
60
80
100
120
140
160
180
200
Total phosphorus (μg L-1)
D
surface water
benthic
0
5
10
15
20
25
Water temperature (°C)

Fig. 1.

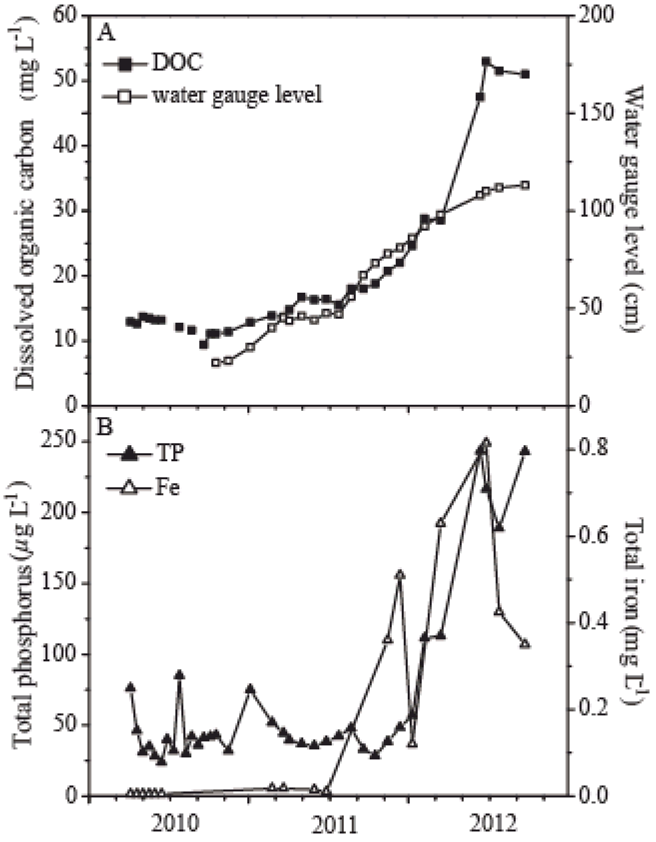

A
DOC
water gauge level
Dissolved organic carbon (mg L^{-1})
Water gauge level (cm)
60
50
40
30
20
10
0
200
150
100
50
0
B
TP
Fe
Total phosphorus (μg L^{-1})
Total iron (mg L^{-1})
250
200
150
100
50
0
0.8
0.6
0.4
0.2
0.0
2010
2011
2012

Fig. 2.

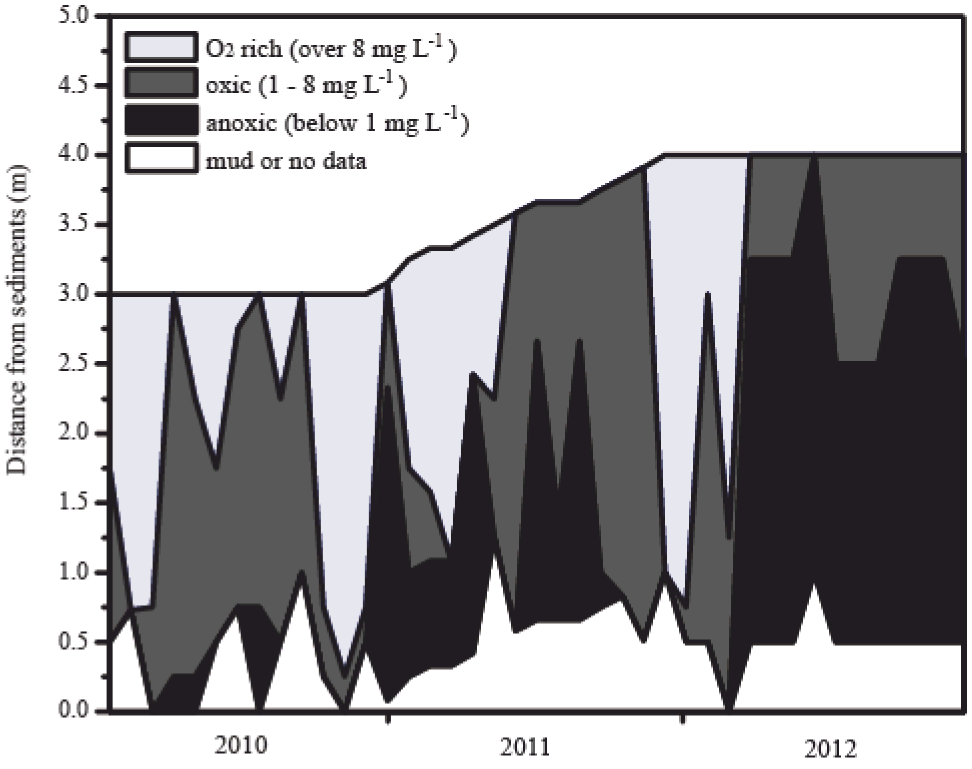
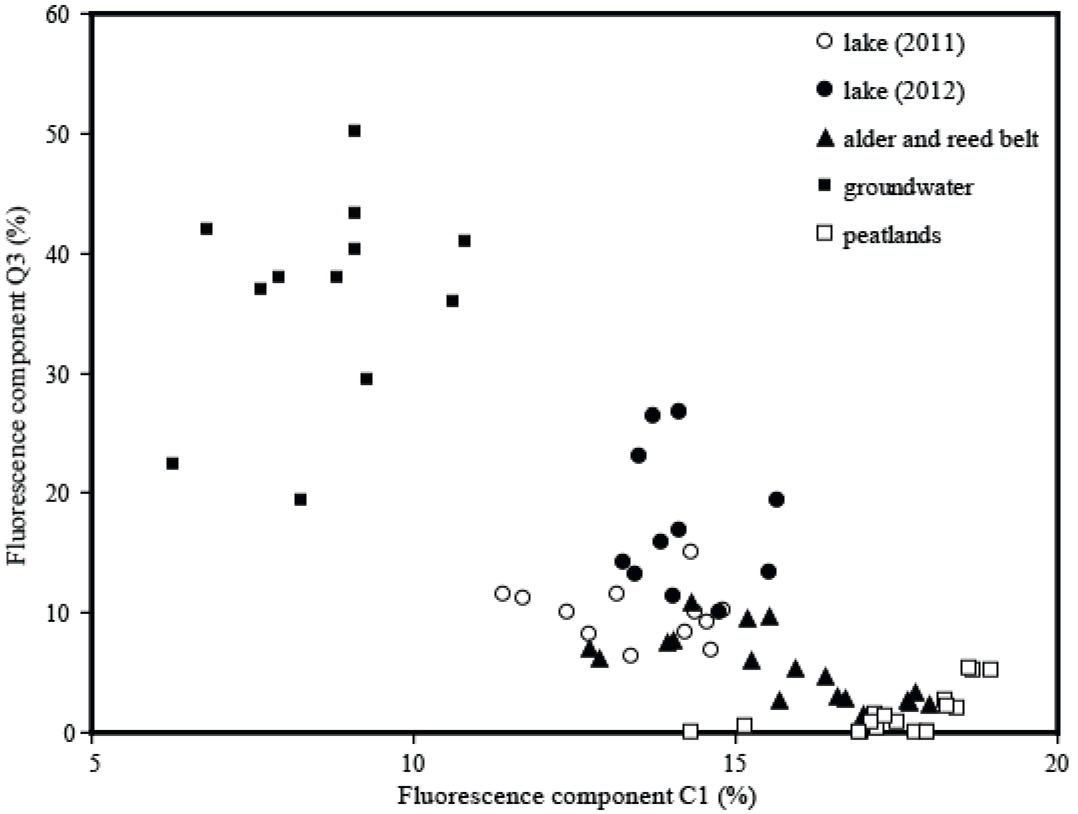

5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Distance from sediments (m)
O₂ rich (over 8 mg L⁻¹)
oxic (1 - 8 mg L⁻¹)
anoxic (below 1 mg L⁻¹)
mud or no data
2010
2011
2012

Fig. 3.



Fluorescence component Q3 (%)
0
10
20
30
40
50
60
Fluorescence component C1 (%)
5
10
15
20
○ lake (2011)
● lake (2012)
▲ alder and reed belt
■ groundwater
□ peatlands

Fig. 4.

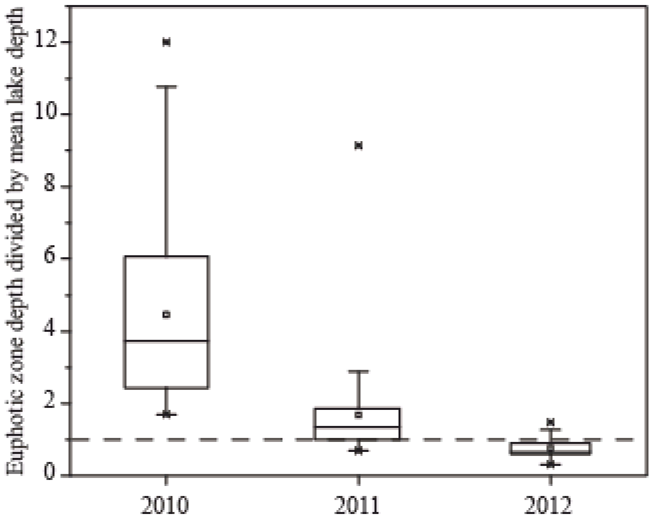

Euphotic zone depth divided by mean lake depth
0
2
4
6
8
10
12
2010
2011
2012

Fig. 5.

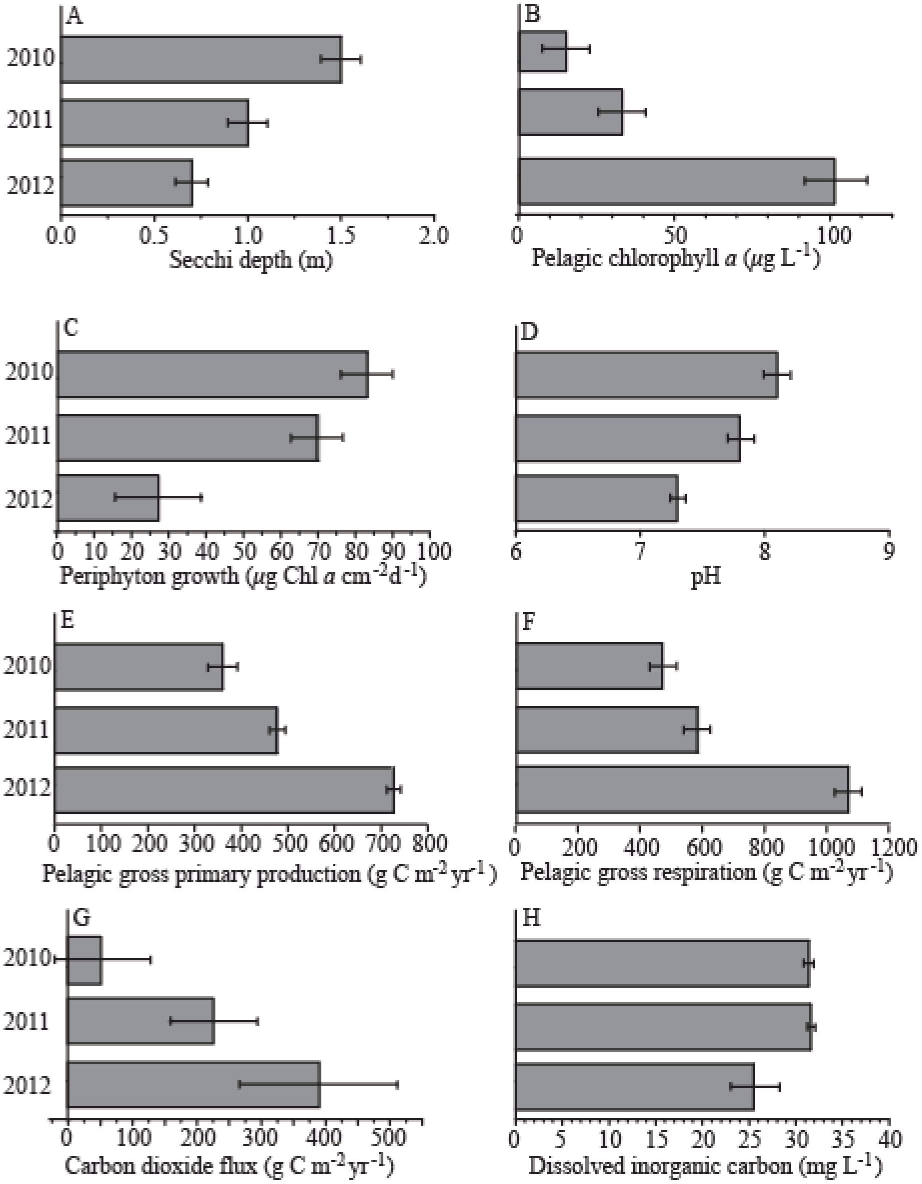

A
2010
2011
2012
0.0 0.5 1.0 1.5 2.0
Secchi depth (m)
B
0 50 100
Pelagic chlorophyll a (μg L-1)
C
2010
2011
2012
0 10 20 30 40 50 60 70 80 90 100
Periphyton growth (μg Chl a cm-2d-1)
D
6 7 8 9
pH
E
2010
2011
2012
0 100 200 300 400 500 600 700 800
Pelagic gross primary production (g C m-2 yr-1)
F
0 200 400 600 800 1000 1200
Pelagic gross respiration (g C m-2 yr-1)
G
2010
2011
2012
0 100 200 300 400 500
Carbon dioxide flux (g C m-2 yr-1)
H
0 5 10 15 20 25 30 35 40
Dissolved inorganic carbon (mg L-1)

Fig. 6.

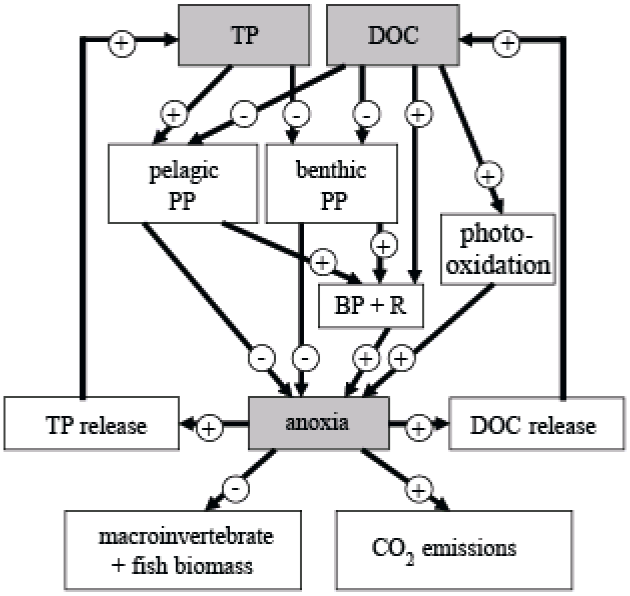

TP
DOC
+
-
-
-
+
+
pelagic PP
benthic PP
photo-oxidation
+
+
BP + R
-
-
+
+
TP release
anoxia
DOC release
+
+
-
+
macroinvertebrate + fish biomass
CO2 emissions
+
+

Fig 7.