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Light may have triggered a period of net heterotrophy in Lake Superior

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Running Head: Light influences heterotrophy in a large lake

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Abstract

Recent studies of Lake Superior, the Earth's largest freshwater lake by surface area, describe it as net heterotrophic (primary production < community respiration), making it a net source of carbon dioxide (CO_2) to the atmosphere. This conclusion is largely based on measurements made between 1998 and 2001. We present a long-term (1968 to 2016) analysis of ice-free (April to November) surface oxygen (O_2) saturation data collected by monitoring agencies. These data indicate that Lake Superior's surface waters are typically supersaturated with dissolved O_2 from May to September (May-September mean is 103.5 ± 0.6%; pooled mean from April, October, and November is 97.6 ± 1.1%, standard error of the mean). However, these data also support prior studies which describe a state of net heterotrophy from 1998 to 2001. We investigated potential triggers for a transient heterotrophic period, and discuss the sources of organic carbon necessary to fuel net heterotrophy in a large oligotrophic lake. We conclude that net heterotrophy likely resulted from an increase in light period and penetration driven by declines in cloud cover, increases in water clarity, and a reduction of winter ice cover following the 1997-98 El Niño. Together, these could have depleted a pre-existing pool of dissolved organic carbon (DOC) via photomineralization and/or photochemical degradation. Our results indicate that Lake Superior is typically net autotrophic (calculated annual CO_2 influx = ~0.4 Tg C). These results highlight how water clarity and aquatic DOC pools may interact to induce net metabolic shifts in large oligotrophic aquatic ecosystems.

Introduction

Given the important role that the Earth's hydrosphere plays in regulating global carbon dioxide (CO_2) concentrations, one of the most important questions facing aquatic scientists today is whether aquatic environments are net CO_2 sources or sinks relative to the atmosphere. Inland waters tend to be net heterotrophic, meaning that they are net sources of CO_2 to the atmosphere (Cole and others 1994; Tranvik and others 2009). However, this condition is generally associated with a steady supply of allochthonous (terrigenous) organic carbon (OC) from their watersheds (Cole and others 2007), and the CO_2 emitted to the atmosphere results from the combined mineralization of autochthonous (in-lake gross primary production, GPP) and allochthonous OC (Cole and others 2002). The degree of heterotrophy in an aquatic ecosystem is thus expected to decrease as the trophic status increases (boosting autochthonous OC production) or as the catchment-to-lake area (CA:LA) ratio decreases, reducing the relative inputs of allochthonous OC (Kelly and others 2001; Balmer and Downing 2011). When both trophic status and allochthonous inputs are extremely low, such as in the oligotrophic subtropical ocean gyres, arguments persist as to the predominant directional flow of CO_2 between the water and atmosphere (del Giorgio and Duarte 2002; Duarte and others 2013; Williams and others 2013).

Lake Superior has a large surface area (82,103 km^2) and a low CA:LA ratio (1.55). Combining this with relatively minor anthropogenic influences, it is a highly oligotrophic system whose biogeochemical processes have been compared to those of oceans (Parkos and others 1969; Johnson and others 1982; Cotner and others 2004). A suite of studies published in the early 2000s found that measured community respiration (CR) rates tended to be higher than GPP rates, indicating a state of net heterotrophy (Cotner and others 2004; Russ and others 2004; Urban and others 2004a). A state of net heterotrophy was further suggested by full-lake carbon budgets (Cotner and others 2004; Urban and others 2005), and studies measuring and/or modelling surface dissolved oxygen (O_2) or CO_2 emissions from the lake to the atmosphere (Atilla and others 2011; Bennington and others 2012; Matsumoto and others 2015). However, prior studies describe Lake Superior as net autotrophic, being typically super-saturated with O_2 and under-saturated with CO_2 relative to the atmosphere (Dobson and others 1974; Weiler 1978; Kelly and others 2001). In Lake Superior, the supply of terrestrial OC from watershed erosion and runoff is minor (~0.4 to 0.9 Tg C y^{-1}; Urban and others 2005 and references therein), and significantly lower than autochthonous phytoplankton production (~10 Tg C y^{-1}; Sterner 2010). Even combined, allochthonous and autochthonous inputs are too low to sustain reported CR rates (13 to 81 Tg C y^{-1}; Urban and others 2005). Such high CR rates could be overestimates due to near-shore biases in measurements (Baehr and McManus 2003; Russ and others 2004; Bennington and others 2012), but updated models of full-lake CO_2 emissions which have attempted to balance the carbon budget still conclude that Lake Superior is net heterotrophic, falling short of explaining why O_2 supersaturation dominated in earlier studies.

Lake Superior is situated in a region of North America which is believed to be strongly affected by teleconnections from the El Niño Southern Oscillation (ENSO) and the Pacific Decadal Oscillation (PDO) (Hoerling and others 1997; Rodionov and Assel 2003). These oscillations work together to influence the climate affecting Lake Superior, shaping trends in precipitation, water circulation, and air temperatures, with the effects of ENSO events being typically greatest during “warm” PDO phases (Rodionov and Assel 2003). The teleconnections, combined with the longer-term effects of climate change on Lake Superior (including gradual but significant reductions of cloud cover and increases in wind speed and solar radiation; Austin and Colman 2007; Desai and others 2009; O’Reilly and others 2015), caused winter lake ice cover to drop dramatically in the winter of 1997-98, and remain low in subsequent years (Assel and others 2003; Wang and others 2012; Van Cleave and others 2014). This has led to the suggestion that Lake Superior underwent a "regime shift" in 1998, precipitated by the El Niño of the previous winter (Van Cleave and others 2014).

The metabolic balance of an aquatic environment, whether net autotrophic or heterotrophic, is often determined by its GPP and CR rates, which can be influenced either directly or indirectly by climate-driven factors such as temperature, light supply, circulation/mixing, and precipitation (Kosten and others 2010; White and others 2012). Given its strong link to cyclical climatic forces, its large size, and low anthropogenic impact, Lake Superior is an ideal ecosystem for studying the effects of climate and water physical characteristics on the metabolic balance of large oligotrophic aquatic environments. While disagreements concerning the net heterotrophy of the oligotrophic subtropical gyres largely revolve around the different methodologies being adopted (Williams 1998; Duarte and others 2013; Williams and others 2013), differing reports of Lake Superior's net heterotrophy appear to follow a timeline where studies using data from the late 1990s onwards tend to report or assume a state of net heterotrophy (e.g., Urban and others 2005; Bennington and others 2012; Matsumoto and others 2015), while earlier reports imply a state of net autotrophy (Weiler 1978; Kelly and others 2001). Such disagreements might result from gradual improvements in our understanding of the biogeochemistry of Lake Superior, though we instead predict that the long-term condition and potential short-term shifts in the lake have likely been overlooked, as they remain unaddressed in the literature. We therefore analyzed all available monitoring datasets for surface dissolved O_2 saturation measurements to test whether Lake Superior tends to be net autotrophic or heterotrophic, and also to determine whether Lake Superior's net metabolic balance has possibly shifted over time. In the event of an identifiable shift, we aimed to determine whether natural variability (teleconnections) and/or anthropogenic climate change might be responsible for inducing such a shift, and identify the most likely mechanism facilitating a supersaturation of CO_2 which annual allochthonous OC inputs could not support.

Methods

Historical climatic, chemical, and physical data for Lake Superior are available from the literature and government monitoring agencies. Regularly sampled and recent surface values are from the U.S. Environmental Protection Agency (EPA) sampling campaigns (1996 to 2016), which were obtained directly from the agency. These provide lake surface water temperatures, dissolved O_2 concentrations, and conductivity (measured by Sea-Bird sensors; Sea-Bird Scientific, USA), as well as water clarity (Secchi depths; Z_{secchi}). EPA sampling campaigns were carried out twice a year (spring, typically April, and summer, typically August), including 19 stations distributed across the entire lake. Springtime oxygen data from 2005 and summertime oxygen data from 2001 were significantly lower than data provided by separate Winkler titrations carried out concurrently at a subset of the same stations. Due to an apparent error in those monitoring data (J. May, EPA, pers. comm.), O_2 saturation values from those periods were removed from analyses.

Long-term surface dissolved O_2 concentrations for Lake Superior were also available from monitoring campaigns made by Environment Canada (EC), from 1971 to 2013 (data available for 19 years across the 42 year period). EC monitoring campaigns typically sampled up to 221 permanent stations established across the entire lake, with surface temperatures measured by an electronic bathythermograph and dissolved O_2 concentrations measured using the modified Winkler iodometric method (Philbert and Traversy, 1973). Sampling campaigns across the lake often lasted from spring (typically May) until fall (typically October). Additional data were retrieved from the National Ocean and Atmospheric Administration's (NOAA) Great Lakes Environmental Research Laboratory dataset (GLERL; Bell 1980a, b). These data were taken from approximately 120 stations across the lake, each station being resampled during the course of six cruises from late May to late November, 1968. Other pre-2000 data for Lake Superior either focused exclusively on CO_2 (Parkos and others 1969; Kelly and others 2001) or only presented data for the hypolimnion (Dobson and others 1974; earlier EPA monitoring data) and could thus not be used in our analysis. Some water clarity data was only available as light attenuation (K_d) values, in which case Secchi depths were calculated using a standard equation $Z_{secchi} = 1.7 / K_d$, which has been validated in both freshwater and marine environments (Poole and Atkins 1929; Idso and Gilbert 1974). The shallowest measurements from each station (typically 0 to 3 m below the surface) are here considered "surface" values. Annual ice extent data were applied from Wang and others (2012), which were calculated from the National Ice Database. As most datasets provided dissolved O_2 concentrations only in mg L^{-1}, O_2 saturation (%) relative to the atmosphere for these data was calculated for the water temperature at those sampling depths and locations.

Comparing the various monitoring datasets, there were only six overlapping months of data from which the agreement between data sources could be examined (May and August 1996, May and August 1997, May 2008, and August 2011). Of these, all mean EPA May values were significantly lower than EC values for the same month, as well as EPA August values in 1997 (there was no significant difference between datasets in August 1996 or August 2011). EPA and

EC May sampling campaigns in these years contained no overlapping dates, with EPA campaigns always occurring earlier in the month than EC campaigns. The significant difference between these datasets thus likely reflects a rapid increase in dissolved O_2 levels across this month. August 1997 EPA and EC sampling campaigns also did not contain overlapping dates, with the EPA campaign occurring later in the month than the EC campaign. Although overall means were significantly different between campaigns for this month (EPA mean = 104.6 ± 1.1%, EC mean = 108.6 ± 0.8%), measured values were (unlike in May campaigns) generally overlapping the same range of values, and thus indicate that the difference between values in this month may be attributed to a more minor within-month variability (data not shown). It is therefore reasonable to conclude that all datasets accurately represent Lake Superior's O_2 saturation at the time of their sampling, and we therefore pooled all available data in our analyses.

We examined relationships between dissolved O_2 data and long-term patterns in potential drivers to determine whether potential shifts in O_2 saturation may be linked to specific drivers. Air and surface water temperatures, precipitation records, watershed runoff, cloud cover, and wind speed for our full study period were drawn from the online U.S. NOAA GLERL database (https://www.glerl.noaa.gov/pubs/tech_reports/glerl-083/UpdatedFiles/). These values represent modeled full-lake characteristics based on measured data, with assumptions and associated data sources provided within individual online files. Studies have shown that phytoplankton production in Lake Superior can be phosphorus limited (Rose and Axler 1998), but is more commonly limited by light availability (Nalewajko and others 1981). The lake has nevertheless experienced a slight long-term decline in total phosphorus (TP) despite no change in soluble reactive phosphorus concentrations (Dove and Chapra 2015), and we thus included TP concentration trends as well in our discussions. Oxygen fluxes between Lake Superior's surface waters and the atmosphere are linked to metabolic processes, with an undersaturation with O_2 typically aligning to a supersaturation of CO_2 (representing a state of net heterotrophy), and vice versa (Russ and others 2004). Data were tested for normality of distribution and equality of variance. When these assumptions were met, or high-*n* non-normal datasets were being compared, Student's *t*-tests or ANOVA tests were adopted. When equality of variance was not met, an unequal variance *t*-test was applied. All statistical tests were carried out using JMP (Version 7; SAS Institute, Cary, N.C., U.S.A.). Standard errors of the mean are provided for data unless otherwise specified.

Results and Discussions

Surface O_2 saturation of Lake Superior varied widely and systematically between months (Fig. 1). A strong seasonality in Lake Superior's dissolved O_2 concentrations has previously been described, with the greatest saturation typically occurring in mid-summer (Weiler 1978; Russ and others 2004). Pooling all available values, April featured the lowest (96.6 ± 0.3%) and July featured the highest mean O_2 saturation (106.7 ± 0.3%). Mean monthly O_2 saturation values were above 100% from May to September (total mean of monthly means is 103.5 ± 0.6%, pooled mean from April, October, and November monthly means is 97.6 ± 1.1%; Fig. 1). The average of all monthly means (April to November, pooling data from 1968 to 2016) is 102.5%, indicating a net supersaturation of surface O_2 in Lake Superior during the ice free months.

Historical variability in oxygen saturation relative to the atmosphere

Prior *in situ* studies have described Lake Superior as net heterotrophic, based on data collected from 1998 to 2001 (Russ and others 2004; Urban and others 2004a). The only months for which there were long-term monitoring data before, during, and after this set of years were May and August. Mean monthly surface O_2 values in May were not significantly different during the 1998-2001 period compared to earlier or later measurements (ANOVA, $p = 0.99$, Fig. 2a), though mean August values were significantly lower and net undersaturated during these years (99.6 ± 2.1%) compared to pre-1998 (106.9 ± 1.8%) and post-2001 values (105.3 ± 1.2%, $p = 0.04$, Fig. 2b). Although earlier (pre-1998) April data were not available, an analysis of all available April O_2 saturation measurements also found O_2 saturation to be significantly lower during the 1998-2001 period (94.9 ± 0.5%) compared to later years (96.9 ± 0.2%, $p = 0.0002$). Long-term monitoring data show that May surface O_2 saturation values can vary widely, occasionally falling below saturation (Fig. 3a). As May is a transitionary month in Lake Superior between April (typically undersaturated in O_2) and June (typically supersaturated; Fig. 1), May saturation values likely depend largely on the sampling time within the month. Long-term monitoring data for the summer months (July and August) are more constrained than those in May, with mean values typically falling between 100 and 110% (Fig. 3b). In showing a general state of O_2 supersaturation in Lake Superior, these data loosely support an *in situ* study which determined Lake Superior to be net autotrophic in 1989 (May to October) and 1990 (August to October), when surface pCO_2 concentrations were undersaturated relative to the atmosphere (Kelly and others 2001). The seasonal resolution provided by the monitoring data in insufficient to alone determine whether Lake Superior was net heterotrophic during any individual year, yet the data show that prior studies supporting net heterotrophy in Lake Superior (Russ and others 2004; Urban and others 2004a) occurred during a period (1998 to 2001) including at least two years (1998 and 2000), and the only known years since 1968, in which the lake was undersaturated in O_2 during the summer months (Fig. 3b).

It has been suggested that the high heterotrophy measured in these studies may be partly due to their proximity to the near-shore environment (as many of the data come from 0 to 21 km of Lake Superior's Keweenaw Peninsula; Bennington and others 2012), yet our analysis of all available measurements found only one month (September) to feature a significant positive relationship (as a linear regression) between the maximum site depth and surface O_2 saturation ($p < 0.0001$), indicating a prevalence of near-shore heterotrophy. For May, June, and July the relationship between O_2 and site depth was always significant and negative, indicating that near-shore zones were likely more autotrophic than off-shore zones during these months. There was no significant relationship for the remaining months for which data was available (data not shown).

It is also worth noting that the monitoring data do not indicate a consistently heterotrophic period 1998 to 2001. Instead, mean August surface O_2 saturation fluctuated widely across these four years, ranging from 92.8 ± 7.1% (1998) to 112.5 ± 7.1% (1999). We were unable to verify whether the especially high O_2 saturation in 1999 was a natural occurrence, or the result of faulty data (neither EC data nor independent Winkler titrations from the EPA were available for that year). However, planktonic CR rates measured in July and August were significantly lower in 1999 than in 1998 ($p = 0.001$; Table 1 in Urban and others 2004a), which could have resulted in higher O_2 saturation in 1999 if there was no similar decline in GPP rates. On the other hand, an analysis of surface CO_2 emissions across this period described peak spring (April) CO_2 emissions in 1999, and potential net heterotrophy in both April and August (as a net CO_2 supersaturation relative to the atmosphere) extending from 2001 to 2003 (Atilla and others

2011). Although the absence of O_2 data from winter months means that an accurate full-year mean O_2 balance with respect to the atmosphere cannot be determined, we conclude that more detailed *in situ* studies may be correct in describing Lake Superior as being net heterotrophic during this period (1998-2001). The long-term monitoring data indicate, however, that this may be the most, and possibly only, net heterotrophic period in Lake Superior's recent history. A further analysis of the potential interannual variability within this period is impossible with the available monitoring data, and is beyond the scope of this study.

Climatic and in-lake factors influencing metabolic balance

The possible existence of a net heterotrophic period in Lake Superior from 1998 to 2001, as indicated by *in situ* studies and long-term monitoring data, aligns temporally with a reported "regime shift" which Lake Superior underwent following the 1997-98 El Niño (Van Cleave and others 2014). We therefore examine a range of climatic and in-lake factors which may have influenced Lake Superior's metabolic balance during this period.

Wind speed (Fig. 4a) and cloud cover (Fig. 4b) did not appear to be strongly linked to the 1997-98 El Niño, pre- and post-El Niño linear slopes being similar to the full-period slopes. Air temperature and ice cover, however, exhibited a large shift in 1998, and were more stable before and after that date (Fig. 5; Van Cleave and others 2014). It is thus possible that these latter factors (air temperature and ice cover) were strongly influenced by the ENSO and PDO, while changes in the former (wind speed and cloud cover) may be more broadly linked to climate change. Lake Superior's mean annual surface water temperatures increased over the full study period (Fig. 6a). Even though surface temperatures have exhibited a downward trend since the 1997-98 El Niño (Fig. 6a), mean values since 1997 (14.85 ± 0.66°C, $n = 19$) remain significantly higher than pre-1997 values (mean = 9.44 ± 0.63°C, $n = 21$; unequal variances t-test, $p < 0.0001$). The apparent slight decline in post-1997 lake surface temperatures agrees with a moderate decline in air temperatures over the lake across this same time period. Secchi depths have also increased significantly since the late 1960s, despite an apparent downward trend since 1998 (Fig. 6b), and spring TP concentrations have declined (data not shown), supporting previous studies which have described increases in Lake Superior's water clarity (Dove and Chapra 2015; Brothers and others 2016).

In considering a possible heterotrophic period from 1998 to 2001, August surface water temperatures associated with the monitoring station data are significantly higher during that period (16.6 ± 0.4°C) than in earlier (13.2 ± 0.2°C) or later years (14.7 ± 0.2°C; $p < 0.0001$). However, no broader significant relationship was apparent between surface O_2 saturation and either the occurrence of El Niño events since 1968, or whether the PDO was in a warm or cold phase. Our analysis of climatic factors thus supports previous research marking the 1997-98 El Niño as an important event for Lake Superior (Van Cleave and others 2014). Since 1997, air temperatures over Lake Superior have remained warmer (Fig. 5), and cloud cover has remained reduced and continues to decline relative to previous recent decades (Fig. 4b). These climatic drivers correspond to an overall increase in water temperatures (Fig. 6a) and a reduced winter ice cover (Fig. 5). As ice cover had previously rebounded after El Niño events (1972-73, 1982-83, 1986-87, 1991-92, Fig. 5), it is possible that the effects of climate change (warmer air temperatures coupled with wind speeds which have continued to rise since 1998, likely due to a reduced air-water temperature gradient; Desai and others 2009) have reduced the resilience of this system (i.e. its ability to return to full-ice winters following El Niño events), prolonging warm, ice-free conditions (Van Cleave and others 2014). As none of the examined climatic drivers differed significantly between the 1998-2001 heterotrophic and 2002-2016 net autotrophic periods, we argue that the generally higher O_2 saturation in the current autotrophic period is not caused by any more recent (2001 to 2003) shift in external drivers. It thus appears likely that the 1997-98 El Niño partially triggered the observed period of relative heterotrophy, while a return to more autotrophic conditions by 2002 does not appear to be linked to further changes in climatic drivers.

In order for a period of net heterotrophy to be established in a large oligotrophic lake such as Lake Superior, a surplus or novel source of OC must be supplied as additional fuel for bacterial respiration, and/or an existing pool of OC must be liberated through changes in environmental conditions, such as water temperature or light availability. Dark-bottle incubations in Lake Superior's western arm identified bacteria as being responsible for ~98% of the planktonic CR (Biddanda and others 2001), and measurements from 2000 and 2001 confirmed that surface gas fluxes were determined by metabolic ratios (GPP:CR; Russ and others 2004). We therefore first consider the possibility of an increase in OC transported into the lake from its watershed. The highest CR rates in the lake are in near-shore zones (< 5 km off-shore), and at shallow depths (Urban and others 2004a; Bennington and others 2012). However, even though watershed runoff is generally an important driver of heterotrophy in aquatic systems and DOC concentrations in Lake Superior tend to be highest near shore (Urban and others 2005), shoreline transects found no relationship between CR rates and proximity to watershed inputs in Lake Superior (Urban and others 2004a). Furthermore, watershed runoff has been significantly lower since 1997 ($n = 17$ years) than in previous years (1973-1996; unequal variance *t*-test, $p = 0.01$, data not shown), and thus changes in terrigenous OC loading cannot explain the lake-wide heterotrophic period. Atmospheric deposition of OC is also unlikely to have increased, as there was no significant difference between pre- and post-1997 precipitation over Lake Superior (Student's *t*-test, $p = 0.87$), and the concentration of OC in precipitation is not known to have changed over this period. Finally, the relationship between maximum site depth and surface O_2 saturation (described above) from this study does not support a general state of near-shore heterotrophy, and instead suggests that near-shore GPP may be equivalent to or greater than near-shore CR throughout most of the ice-free period, perhaps indicative of a high degree of near-shore benthic algal production (Brothers and others 2016).

Planktonic OC mineralization rates can also be boosted by internal resuspension. Resuspension can be an important seasonal source of OC for bacteria in the Great Lakes (Biddanda and Cotner 2002), and Lake Superior's circulation rates and currents increased in strength from 1979 to 2006 (Bennington and others 2010), making the benthic zone susceptible to higher resuspension. Furthermore, 10 to 30% of the materials collected in off-shore sediment traps in the hypolimnion were resuspended, and likely of near-shore origin (Urban and others 2004b). However, increasing resuspension is often associated with reduced water clarity (e.g., Brothers and others 2017), which does not appear to be the case in Lake Superior, whose water clarity has increased in recent decades (Dove and Chapra 2015; Brothers and others 2016; this study). Furthermore, volumetric hypolimnetic CR rates tend to be lower than those closer to the lake surface (Urban and others 2004a), and circulation rates potentially driving resuspension are not known to have declined since 2001. Resuspension is therefore unlikely to explain the observed heterotrophic period of Lake Superior.

As we could not identify any surplus terrigenous or benthic source of OC which might support a heterotrophic period in Lake Superior, it appears likely that a pre-existing pool of OC was liberated through changes in water temperature and/or light availability after the 1997-98 El

Niño. Given that the low August O_2 saturation defining the 1998-2001 heterotrophic period aligns with elevated August surface water temperatures, it is likely that temperature played an important mechanistic role in shifting Lake Superior's metabolic balance. Higher surface water temperatures have been broadly associated with higher degrees of heterotrophy in lakes (Biddanda and Cotner 2002; Kosten and others 2010), and rising temperatures in lakes are expected to shift lakes towards more heterotrophic conditions by promoting an increase in CR rates relative to GPP rates (Yvon-Durocher and others 2010). However, despite higher predicted warming rates, the response of ecosystem metabolism to warming in higher-latitude lakes (such as Lake Superior) may be lower than those in lower latitudes (Kraemer and others 2017). Within the Great Lakes specifically, neither phytoplankton production (measured in Lake Michigan, 1998 to 2000; Lohrenz and others 2004) nor water column CR rates (measured in Lake Superior, 1998 and 1999; Urban and others 2004a) are significantly temperature dependent. A summertime relationship between temperature and R:P ratios was found in the central and western (but not eastern) basins of Lake Superior, but this relationship was negative (Russ and others 2004). It is therefore unlikely that high temperatures alone played a significant direct role in shifting Lake Superior to a period of heterotrophy by selectively increasing CR rates over GPP rates. It remains likely, however, that temperature played an indirect role, via its effects on light availability in the water column.

Effects of light availability on heterotrophy

Cloud cover (Fig. 4b) and light attenuation (Fig. 6b) both declined prior to the 1997-98 El Niño (the latter possibly being linked to reductions in TP concentrations; Dove and Chapra 2015; Brothers and others 2016), yet the sudden and sustained increase in surface water temperatures from 1997 onwards could also interact positively with water column light availability by substantially reducing the ice cover period (Wang and others 2012; Van Cleave and others 2014), thus expanding the annual duration of light exposure in the water column. Mean (spring and summer) Secchi depths of ~13 m since 1997 (compared to 11 m pre-1998) indicate that the lake's photic zone currently extends roughly 27 m below the surface, although photic zone depths of up to 43 m have been recorded (Cotner and others 2004). Light thus penetrates well into the hypolimnion (which in the summer of 1998 typically began ~10 m below the surface), and possibly as far as the subsurface chlorophyll *a* maximum (typically peaking at roughly 25 m below the surface, but ranging from 20 to 40 m; Barbiero and Tuchman 2001). Increased light could influence Lake Superior's metabolic balance either by fueling nearshore benthic GPP (potentially supplying more OC to the pelagic environment), or by promoting direct biotic or abiotic mineralization of the pre-existing pelagic DOC pool.

Benthic GPP can play an important ecological (e.g., fish nutrition) and biogeochemical (e.g., hypoxia formation) role, even in large lakes (Vadeboncoeur and others 2011; Vander Zanden and others 2011; Sierszen and others 2014; Brothers and others 2017), and it has been suggested that littoral benthic production can fuel off-shore water column heterotrophy in oligotrophic lakes (Coveney and Wetzel 1995). Warmer temperatures and reduced ice cover could favor phytoplankton primary production (White and others 2012), yet Lake Superior has likely experienced a minor, long-term (1970s to 2000s) decline in phytoplankton production (Brothers and others 2016), although the interannual algal dynamics since 1997 are unknown. In contrast to declining off-shore phytoplankton GPP, light-saturated periphyton production rates measured in Lake Superior are higher than those typical in smaller lakes (Stokes and others 1970), and benthic GPP may currently represent as much as 36% of the lake's total areal GPP (Brothers and others 2016). Our analysis of the negative relationship between site depth and surface O_2 saturation from May to July (described above) further supports the suggestion that benthic GPP may play an important, driving role in Lake Superior's near-shore metabolism. In shallow lakes, elevated benthic GPP can increase sediment oxygen demand (SOD) and reduce carbon burial efficiency (carbon burial rate / carbon deposition rate; Brothers and others 2013). One potential explanation for such a situation could be a "priming effect", whereby an increase in benthic algal production liberates older, more recalcitrant OC in the surface sediments for bacterial mineralization (Guenet and others 2010). Research on priming effects in freshwater lakes is relatively novel (Guenet and others 2010; Kuehn and others 2014), and its occurrence in these systems remains controversial (Bianchi and others 2015; Catalán and others 2015). However, the presence of a priming effect is well established in terrestrial environments (Guenet and others 2010) as well as in oceans, where the experimental addition of algae to sediments can boost SOD by up to 30% (van Nugteren and others 2009). Although SOD has been considered to be a minor contributor to hypolimnetic O_2 depletion rates in Lake Superior (McManus and others 2003), any potential benefit of benthic GPP to CR rates would be limited to near-shore zones with water column depths less than ~40 m, or off-shore reefs (Edsall and others 1991). To our knowledge, no studies have examined such effects in the shallow zones of Lake Superior, but it seems unlikely that near-shore benthic processes would exert a strong influence on the net heterotrophy of the off-shore sampling sites included in this analysis.

Light can also directly and indirectly influence off-shore pelagic OC mineralization. When exposed to sunlight, Lake Superior's DOC becomes more labile, making it more easily mineralized by bacteria (Biddanda and Cotner 2003). Although exposure to solar UV-B radiation can produce refractory forms of DOC (Benner and Biddanda 1998), this does not seem to be a significant process in Lake Superior (Biddanda and Cotner 2003; Minor and Stephens 2008).

Given a gradually deepening light penetration, and suddenly longer exposure periods to light after 1997 (due to prolonged ice-free seasons), the pool of DOC being exposed to light would increase significantly, potentially boosting bacterial growth in these zones by ~150 to 260% (Biddanda and Cotner 2003). Although UV radiation is attenuated more rapidly than photosynthetically-active radiation, in August 1999 it extended approximately 10 m into Lake Superior's water column (Ma and Green 2004), overlapping much of the water column area likely featuring the highest bacterial abundance and production rates (Biddanda and Cotner 2003). UV radiation can also directly convert DOC to CO_2 via abiotic photomineralization (Granéli and others 1996; Ma and Green 2004). Photomineralization rates in Lake Superior are highly variable, and can produce as much as 1.6 mg DIC L^{-1} in a 10 hour day, though more often fall in the range of 0.03 to 0.06 mg DIC L^{-1} d^{-1}, which is similar to rates measured in oceans (Ma and Green 2004 and references therein). Scaled up to the full lake (assuming a 10 m UV photic zone) and ice-free period (estimated as 250 days), even the low end of these rates would produce ~6 Tg C y^{-1}, which is greater than the CO_2 fluxes to the atmosphere measured during the heterotrophic period (~3 Tg C y^{-1}, Urban and others 2005). UV radiation penetration into the water column can furthermore be negatively related to DOC concentrations (Scully and Lean 1994), with high DOC photodegradation rates due to longer ice-free seasons resulting in deeper UV penetration into the water column. Although likely too deep to experience the direct influence of solar UV radiation, hypolimnetic O_2 consumption rates at sites in Lake Superior's western arm were five to ten times greater than could be explained by local SOD rates and the settling rates of particulate organic carbon, implying a localized drawdown of DOC (McManus and others 2003).

The concept of a long-term (decades to centuries) DOC drawdown linked with elevated temperatures is not new, and has previously been suggested as a potential cause of Lake Superior's carbon budget imbalance (Cotner and others 2004). In addition to facilitating a transient heterotrophic period, a DOC drawdown triggered by the major changes linked to the 1997-98 El Niño could also explain why subsequent El Niño events (2002-03, 2009) did not produce similar heterotrophic conditions, given that the available DOC pool may have been effectively altered or depleted by then. As for earlier El Niño events within the studied timeframe, being of lower intensities than the 1997-98 event, they did not produce the same sustained effect on Lake Superior's water temperature and light climate (Van Cleave and others 2014), and thus may not have been able to liberate the lake's DOC pool. Still, for DOC-light interactions to be responsible for the net heterotrophic period there must be a sufficient pre-existing pool of DOC to draw upon. Lake Superior's DOC concentrations in 1998 averaged ~1.3 mg L^{-1} (Biddanda and others 2001; Biddanda and Cotner 2003; Urban and others 2005), providing a total DOC pool of ~17 Tg C (Urban and others 2005). While DOC drawdown rates in 1998 were sufficient to explain hypolimnetic O_2 depletion rates measured in 2000 and 2001, only 5 to 10% of the DOC pool was being mineralized by bacteria within the average stratified period (Biddanda and others 2001; McManus and others 2003). A rough annual carbon deficit during the heterotrophic period of 0.9 Tg C can be calculated as the difference between total estimated carbon losses (surface CO_2 emissions = 1.3 Tg C y^{-1}; Atilla and others 2011; OC burial = 0.5 Tg C y^{-1}; outflows = 0.1 Tg C y^{-1}; Fig. 7 in Urban and others 2005; total out = 1.9 Tg C y^{-1}) and gains (precipitation = 0.1 Tg C y^{-1}, inflows = 0.9 Tg C y^{-1}; Fig. 7 in Urban and others 2005; total in = 1 Tg C y^{-1}). This annual deficit would amount to a loss of 3.6 Tg C over a period of 4 years (1998 to 2001). For DOC drawdown to support such a deficit would require DOC concentrations to drop by roughly 0.30 mg L^{-1} in the lake. Although we are unaware of any study specifically comparing DOC concentrations across recent decades, reported mean DOC concentrations in 1990 were roughly 1.8 mg L^{-1} (Kelly and others 2001), 0.5 mg L^{-1} higher than the mean value of those measured during the heterotrophic period (1.3 mg L^{-1}, Biddanda and others 2001; Biddanda and Cotner 2003; Urban and others 2005). More recently, offshore mean DOC concentrations measured in spring and summer 2010 were lower still, at ~1.1 mg L^{-1} (Zigah and others 2014). These different concentrations cannot be standardized for full-lake representation, and interannual differences within the heterotrophic period are high, but the overall apparent decline over time is likely greater than would be explained by seasonal drawdown (~ 0.03 – 0.2 mg C L^{-1}, Cotner and others 2004; Urban and others 2005). An apparent increase in DOC concentrations from 1998 (~1.35 mg L^{-1}) to 1999 (~1.45 mg L^{-1}; Fig. 2a, Urban and others 2005) indicates that DOC concentrations in Lake Superior are annually recharged to some extent, and a long-term drawdown of DOC may not be immediately apparent from comparisons between any individual two years. However, these data show that Lake Superior's DOC pool is volatile and may have undergone the drawdown necessary to explain the observed heterotrophic period.

Summary of Natural and Anthropogenic Factors

In the above sections, we have explored the primary natural and anthropogenic drivers which might conceivably be responsible for producing temporary heterotrophic conditions in Lake Superior from 1998 to 2001. These drivers included changes in OC transport to the water column (from watershed loading or internal resuspension), teleconnections (PDO, ENSO), and climatic factors influencing temperature and light availability. Environmental records show that precipitation declined after 1997, making it unlikely that the heterotrophic period was fueled by novel terrigenous OC imports. Historical dissolved O_2 concentrations in Lake Superior do not respond regularly to PDO phases and ENSO events, and so these factors are excluded as dominant or solitary drivers. We argue that potential increases in resuspension and/or increasing benthic metabolism are unlikely to influence distant surface O_2 concentrations measured at monitoring stations, most of which are at sites with maximum depths of over 100 m. Previous studies of plankton communities in the Great Lakes have not been able to establish a significant temperature dependence of the metabolic rates or balance of these communities, and so changes in water temperature alone do not appear to be responsible for this period of net heterotrophy. We therefore argue that a change in light availability is the most likely primary driver of net heterotrophy.

An increase in light supply and availability in Lake Superior occurs at the nexus of many of the above factors. Both increases in light attenuation and warmer waters may have been influenced by the 1997-98 El Niño, given their non-linear trends before and after that event (Fig. 6a, b). Warmer surface waters are further associated with reduced ice cover (Fig. 5) as well as higher wind speeds (Fig. 4b), which may in turn be linked to lower cloud cover (Fig. 4a), although the latter two factors do not appear to have been influenced by the 1997-98 El Niño (given no change in their trends before and after that year), and are thus more likely linked to climate change. A number of biological and abiotic mechanisms by which light could have liberated a pre-existing pool of DOC within the lake are presented. Below, we re-examine the carbon budget of Lake Superior, taking a temporary light-mediated DOC drawdown into consideration.

Carbon budget revisions

Previous attempts at balancing the carbon budget of Lake Superior based on direct measurements have been unsuccessful (Cotner and others 2004; Urban and others 2005). Recent estimates calculated annual OC inputs of 2.4 to 7.7 Tg C, compared to annual outputs of 13 to 81 Tg C (Table 2 in Urban and others 2005). Although this imbalance may be partly explained by the lake's spatial heterogeneity, with carbon budgets being largely derived from near-shore measurements (Bennington and others 2012), it has also been suggested that underestimated phytoplankton GPP or a tightly coupled microbial production loop may be responsible for the imbalance (Cotner and others 2004; Urban and others 2005). Updated phytoplankton GPP measurements are higher than previous estimates (Sterner 2010), and the inclusion of (previously unconsidered) benthic GPP may further boost total GPP estimates (Brothers and others 2016). Still, OC inputs fall short of balancing the carbon budget. We argue that previous carbon budgets were made during a period in which Lake Superior's carbon outputs may have outpaced its inputs, meaning that the basic assumption of the lake being at steady-state equilibrium was not met during the 1998-2001 period. The magnitude of the imbalance may thus be partly linked to the fact that many key measurements were made from relatively few years within the heterotrophic period. For instance, measurements from 1998 to 2000 produced net CO_2 emission estimates of roughly 3 Tg C y^{-1} (Urban and others 2005) while investigations along a longer timespan (1996 to 2006) produced lower CO_2 emission estimates of 1.3 ± 3.2 Tg C y^{-1} (Atilla and others 2011).

Previous ecosystem-level carbon inputs and outputs may be compared to provide a rough estimate of current surface CO_2 fluxes with the atmosphere (Table 1). Estimated carbon mass inputs (precipitation, inflows, and erosion) range from 0.44 to 1.02 Tg C y^{-1} (Table 2 in Urban and others 2005 and references therein). Carbon outflow rates are estimated to be 0.1 Tg C y^{-1}, while measured carbon burial rates range from 0.06 to 2 Tg C y^{-1} (Table 2 in Urban and others 2005 and references therein). The difference between these values indicates that Lake Superior surface emissions may range from a CO_2 efflux of 0.86 Tg C y^{-1} to the atmosphere, to an influx of 1.66 Tg C y^{-1} from the atmosphere to the lake (mean = 0.4 Tg C y^{-1} net CO_2 influx; Table 1). These values fall between previous CO_2 emissions estimates for the heterotrophic period (efflux of 1.3 ± 3.2 Tg C y^{-1}, Atilla and others 2011) and the earlier autotrophic period (influx of 1.9 Tg C y^{-1}, Kelly and others 2001, assuming 250 ice free days in a year). It is furthermore possible to solve for CR, applying phytoplankton GPP estimates of 9.73 Tg C y^{-1} (Sterner 2010) and periphyton GPP estimates of 1.15 Tg C y^{-1} (Brothers and others 2016). Total annual OC inputs to Lake Superior (GPP, precipitation, river inputs, and erosion) are thus roughly 11.62 – 12.20 Tg C, while annual OC outputs (burial and outflow, excluding CR) range from 0.16 to 2.1 Tg C (Urban and others 2005). The difference between these provides CR rates of roughly 9.5 – 12.0 Tg C y^{-1} (mean = 10.78 Tg C y^{-1}), or ~2.4 μg C L^{-1} d^{-1}, which is at the low end of the range of CR rates measured in 1998 and 1999 (Urban and others 2004a). Such CR rates may more reasonably reflect the typical conditions of Lake Superior, and the additional effects of DOC photodegradation on CR, as well as the role of direct DOC photomineralization (which is not included in this budget) may have produced the carbon budget imbalance measured during the heterotrophic period.

Conclusions

In our examination of data from 1968 to 2016, we found that Lake Superior’s surface waters tended to be supersaturated with dissolved O_2 during most of its ice-free period. However, we also identified a possible period of net heterotrophy from 1998 to 2001, in agreement with *in situ* studies made during this period, which appeared to be associated with the El Niño of 1997-

98. A return to previous metabolic conditions by 2002 appeared to occur naturally, without any major corresponding change in climatic conditions. We argue that an increase in water clarity, in association with the climate change and teleconnection effects of higher water temperatures and reduced ice and cloud cover, is likely to be the strongest driver of this heterotrophy, causing the drawdown of the deep-water DOC pool by direct photomineralization and/or photodegradation of recalcitrant DOC. Both *in situ* (Weiler 1978, Russ and others 2004) and modeling studies (Bennington and others 2012; Matsumoto and others 2015), as well as this study (Fig. 1), describe the tendency for Lake Superior to be more autotrophic during the ice-free season and indicate that its most heterotrophic period occurs during the winter months. Although prior studies do not reveal what sources of carbon could potentially drive an annual net heterotrophy in the lake, they do highlight the existence of a bias towards a calculated net autotrophy when considering measurements made only during ice-free months, and further underscore the importance of winter sampling in fully understanding the biogeochemistry of Lake Superior.

The question of heterotrophy vs. autotrophy in the subtropical ocean gyres largely focuses on the accuracy of *in vitro* experiments vs. *in situ* measurements (Williams 1998; Duarte and others 2013; Williams and others 2013). However, there is also a fundamental theoretical component to the debate, being whether terrigenous materials can access these remote environments at a sufficient rate to elevate CO_2 emissions (argued by the heterotrophists), or whether autochthonous phytoplankton GPP is the only possible steady supply of OC in these regions, and must therefore limit bacterial production and respiration rates (argued by the autotrophists). Lake Superior is not the oligotrophic ocean, but many of the characteristics involved in its biogeochemical cycling carry these same fundamental principles of low allochthonous OC inputs and low autochthonous OC production. This overview of the available literature and monitoring data indicates that shifts in light availability may have influenced the biogeochemical cycling of this large aquatic ecosystem, with more light availability (from both longer open-water seasons and deeper-penetrating euphotic zones) leading to a reversal of the lake's fluxes, from being a net sink of atmospheric CO_2 to a temporary net source. The effects of increased light availability on DOC lability, and the overall role DOC photodegradation plays on the oceanic carbon cycle, are well documented in marine environments (Mopper and others 1991; Benner and Biddanda 1998). Water clarity in the oligotrophic ocean can also be variable (Falkowski and Wilson 1992), and given current reductions of the Arctic Ocean ice cover (Walsh and others 2017), similar effects on the net metabolic balance of oceans may be expected. DOC in aquatic ecosystems represents as much as 20% of the planet's OC, and is roughly equivalent to the amount of carbon in the atmosphere (Hedges 1992). These results underline the volatility of such DOC pools, and the role that light can play in transforming large quantities of this pool into atmospheric CO_2 within a relatively short timeframe, with potentially major implications for climate change-induced positive feedback mechanisms between the atmosphere and hydrosphere.

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Figure Legends

Figure 1. Mean monthly surface dissolved O_2 saturation (%) from all available datasets for all years. Boxes represent the upper quartile, median, and lower quartile, with whiskers representing the 5th and 95th percentiles. Centered squares represent the mean value, and crosses designate minimum and maximum values in the dataset (excluding outliers, which are denoted by short horizontal lines). A dotted horizontal line indicates 100% saturation with respect to the atmosphere.

Figure 2. Monthly means of surface dissolved O_2 saturation (%) before, during, and since the identified heterotrophic period. Boxes are calculated by pooling mean annual values for May (a) and August (b) measurements. Early data include 13 years for May, and 5 years for August. Recent data include 7 years for May and 15 years for August. Boxes represent the upper quartile, median, and lower quartile, with whiskers representing the 5th and 95th percentiles. Centered squares represent the mean value, and crosses designate minimum and maximum values in the dataset. A dotted horizontal line indicates 100% saturation with respect to the atmosphere.

Figure 3. Mean May (a) and summertime (b, July and August measurements) surface dissolved O_2 saturation (%) from all available datasets for all available years. Boxes are calculated by pooling data from all stations. Boxes represent the upper quartile, median, and lower quartile, with whiskers representing the 5th and 95th percentiles. Centered squares represent the mean value, and crosses designate minimum and maximum values in the dataset (excluding outliers, which are denoted by short horizontal lines). All data are included, and only years for which both spring and summer data were available are shown. A dotted horizontal line indicates 100%

saturation with respect to the atmosphere, and the apparent transient heterotrophic period is shaded in gray.

Figure 4. Annual means for (a) wind speed and (b) cloud cover over Lake Superior. Dotted lines show linear regressions of data before (1968 to 1997) and after (1998 onwards) the 1997-98 El Niño, and solid lines represent linear regressions for the full period.

Figure 5. Winter ice coverage (columns) and air temperature over Lake Superior (circles). A vertical broad-dashed line marks the 1997-98 El Niño, while two horizontal fine-dashed lines denote the mean air temperatures before and after the El Niño event.

Figure 6. Annual means for (a) water surface temperature and (b) Secchi depth. Dotted lines show linear regressions of data before (1968 to 1997) and after (1998 onwards) the 1997-98 El Niño, and solid lines represent linear regressions for the full period.

Tables

Table 1. Summary of C fluxes in and out of Lake Superior.

Inputs / Outputs	C flux (Tg C y^{-1})	Reference
Shoreline erosion	0.02	Urban and others 2005, and references therein
Rivers	0.4 – 0.9	Urban and others 2005
Precipitation	0.02 – 0.1	Urban and others 2005, and references therein
Total OC loading	0.44 – 1.02	Calculated as sum of above
Lake outflow	0.1	Urban and others 2005
Sediment burial	0.06 – 2.0	Urban and others 2005, and references therein
Total OC export	0.16 – 2.1	Calculated as sum of above
CO_2 exchange with atmosphere (negative values indicate an influx to the lake)	-1.66 – 0.86 (mean = -0.40)	This study, calculated from difference between OC loading and exports
Gross primary production	10.88	Sterner 2010 for phytoplankton, Brothers and others 2016 for periphyton (see text for details)
Community respiration	9.5 – 12.0 (mean = 10.78)	This study, calculated as the difference between OC

		inputs (GPP + total OC loading) and total OC exports

Figures

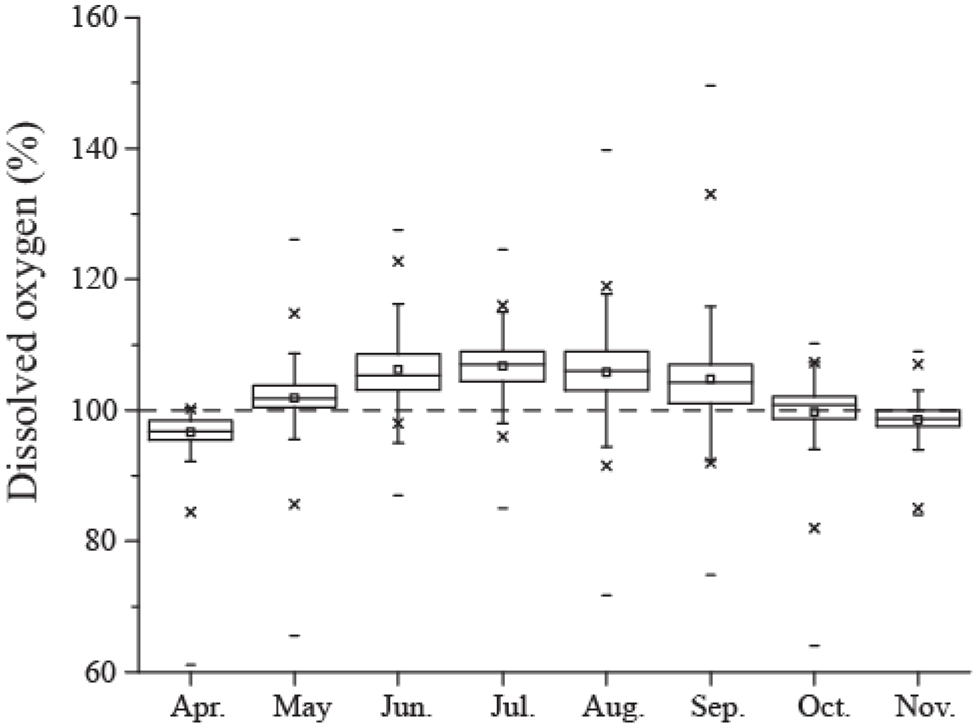
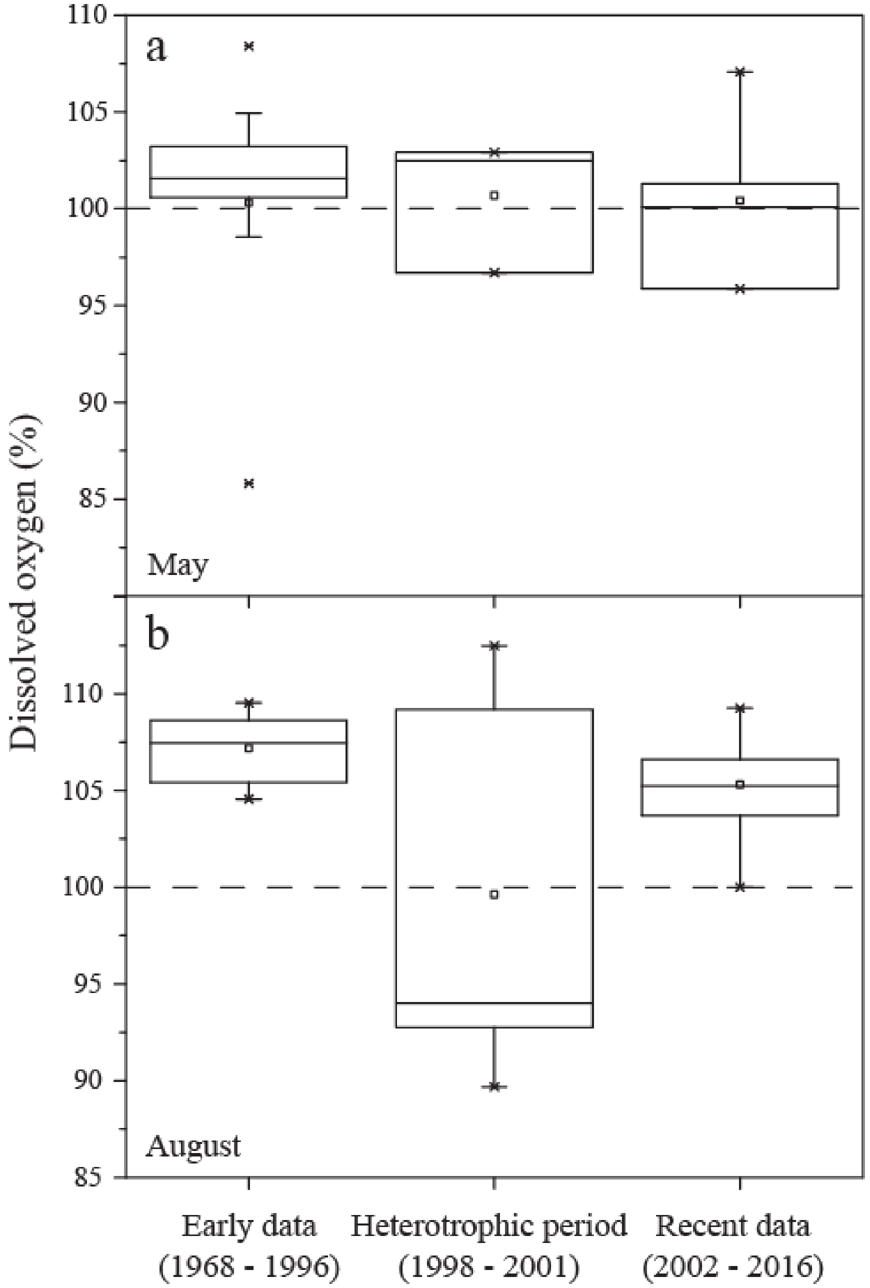


Fig. 1



Dissolved oxygen (%)
a
May
b
August
110
105
100
95
90
85
110
105
100
95
90
85
Early data (1968 - 1996)
Heterotrophic period (1998 - 2001)
Recent data (2002 - 2016)

Fig. 2

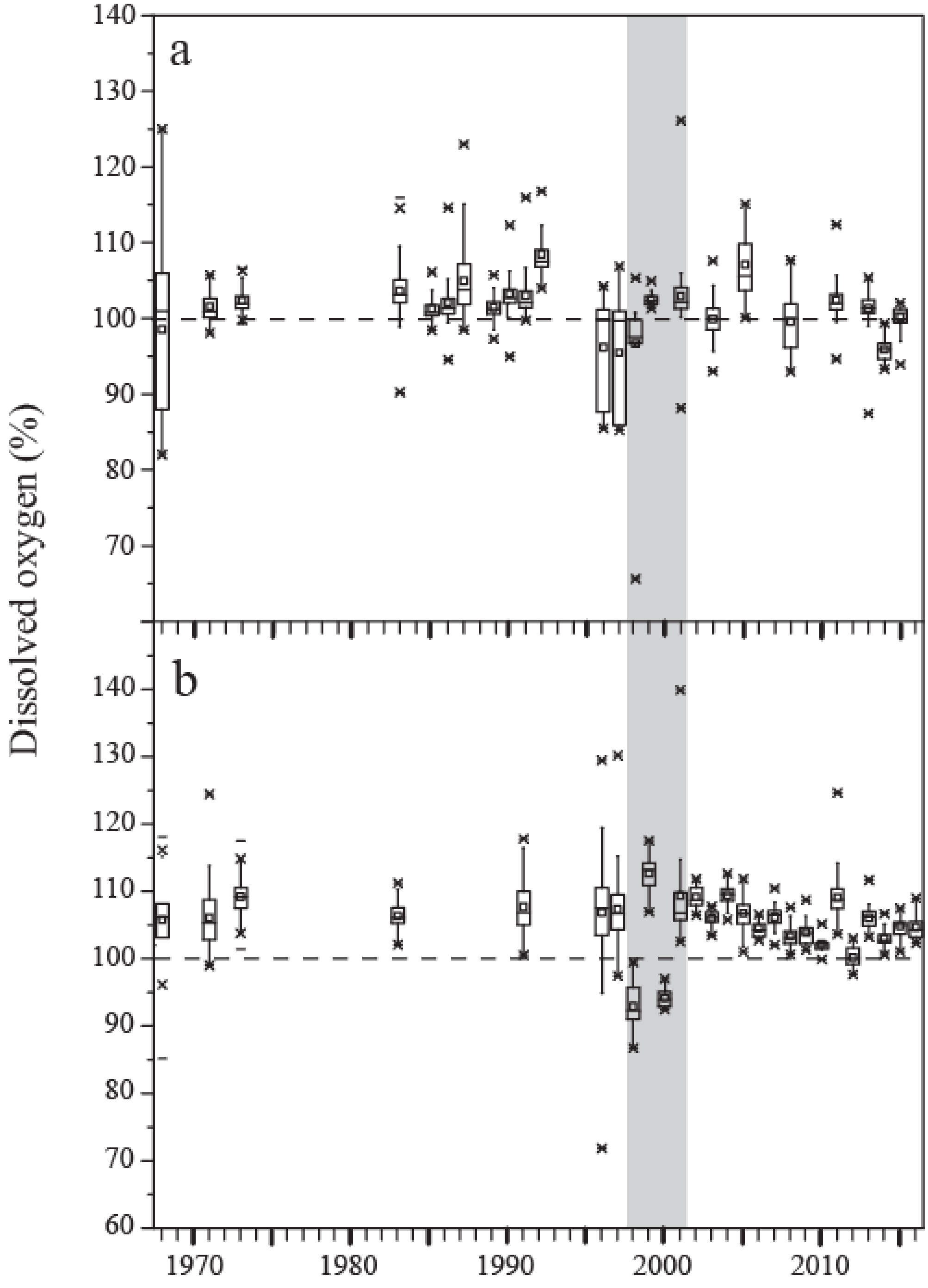
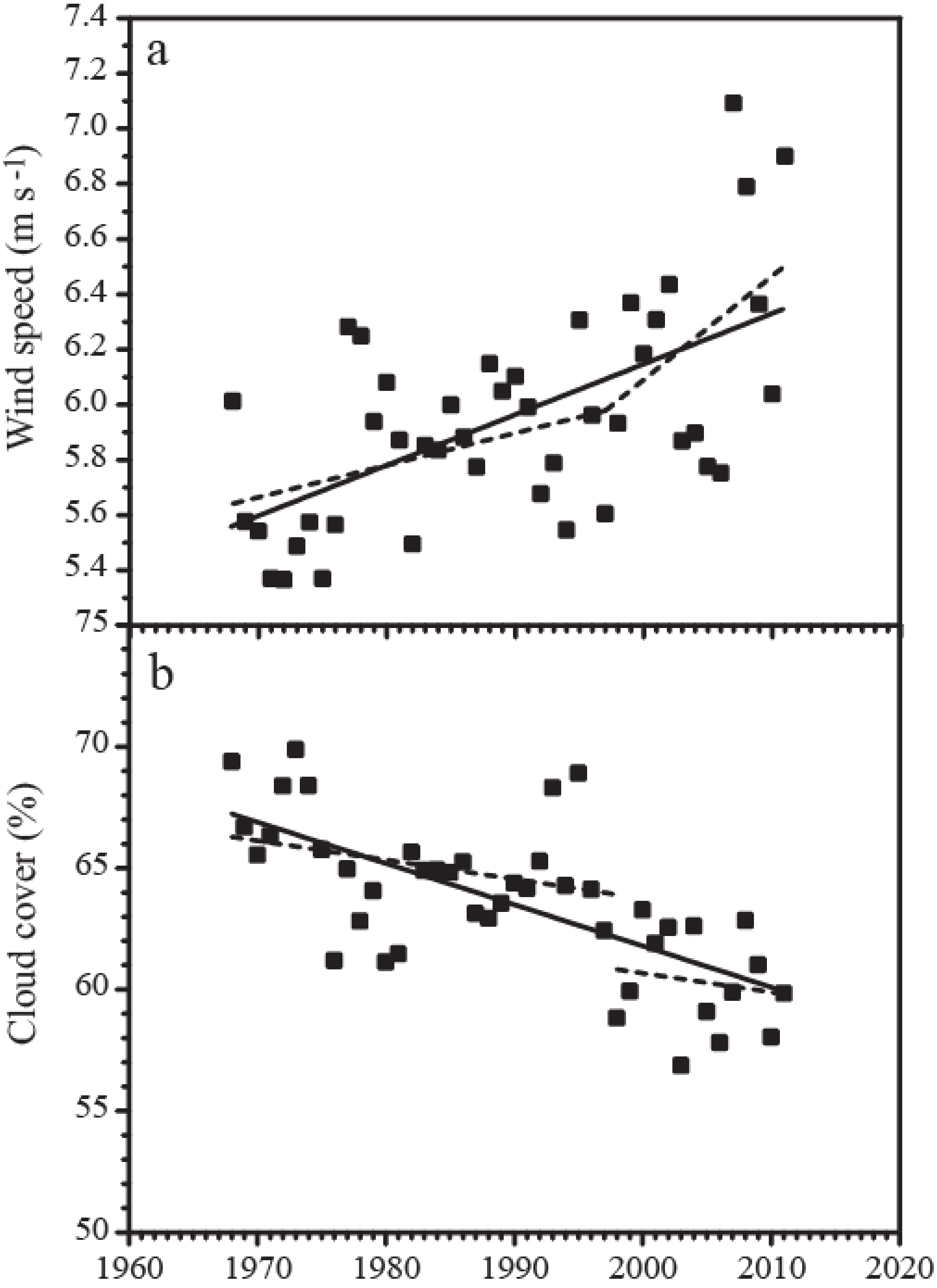

Dissolved oxygen (%)
a
b
140
130
120
110
100
90
80
70
60
1970
1980
1990
2000
2010

Fig. 3



856

857 Fig. 4

858

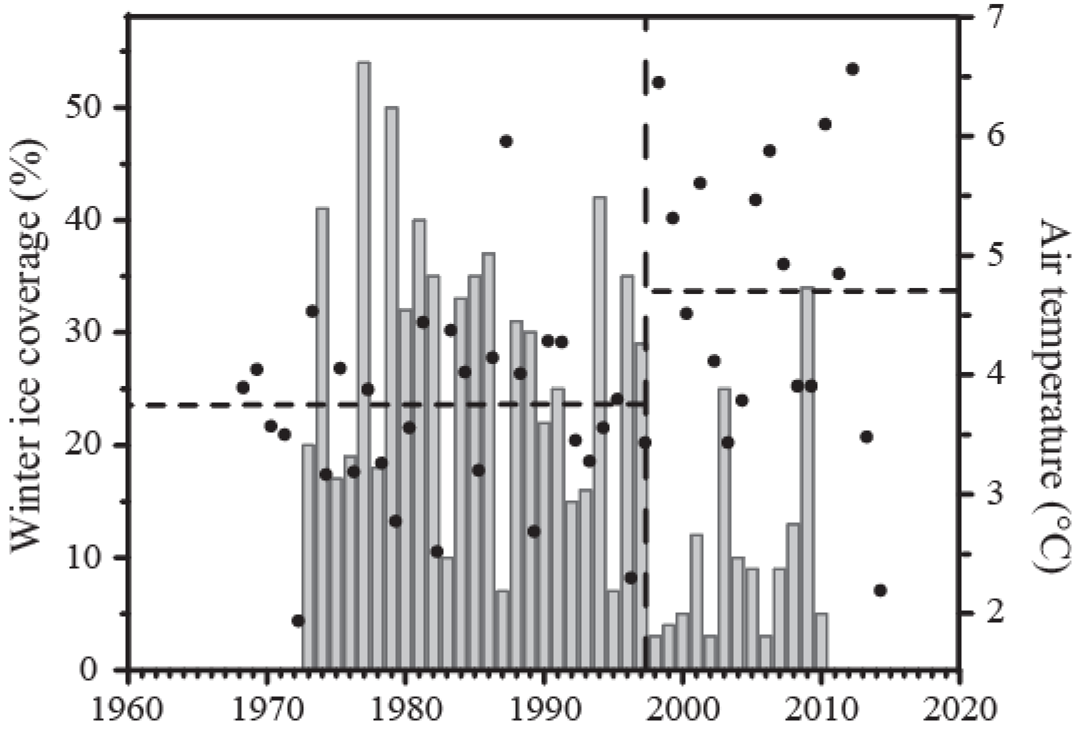

Winter ice coverage (%)
0
10
20
30
40
50
Air temperature (°C)
2
3
4
5
6
7
1960
1970
1980
1990
2000
2010
2020

Fig. 5

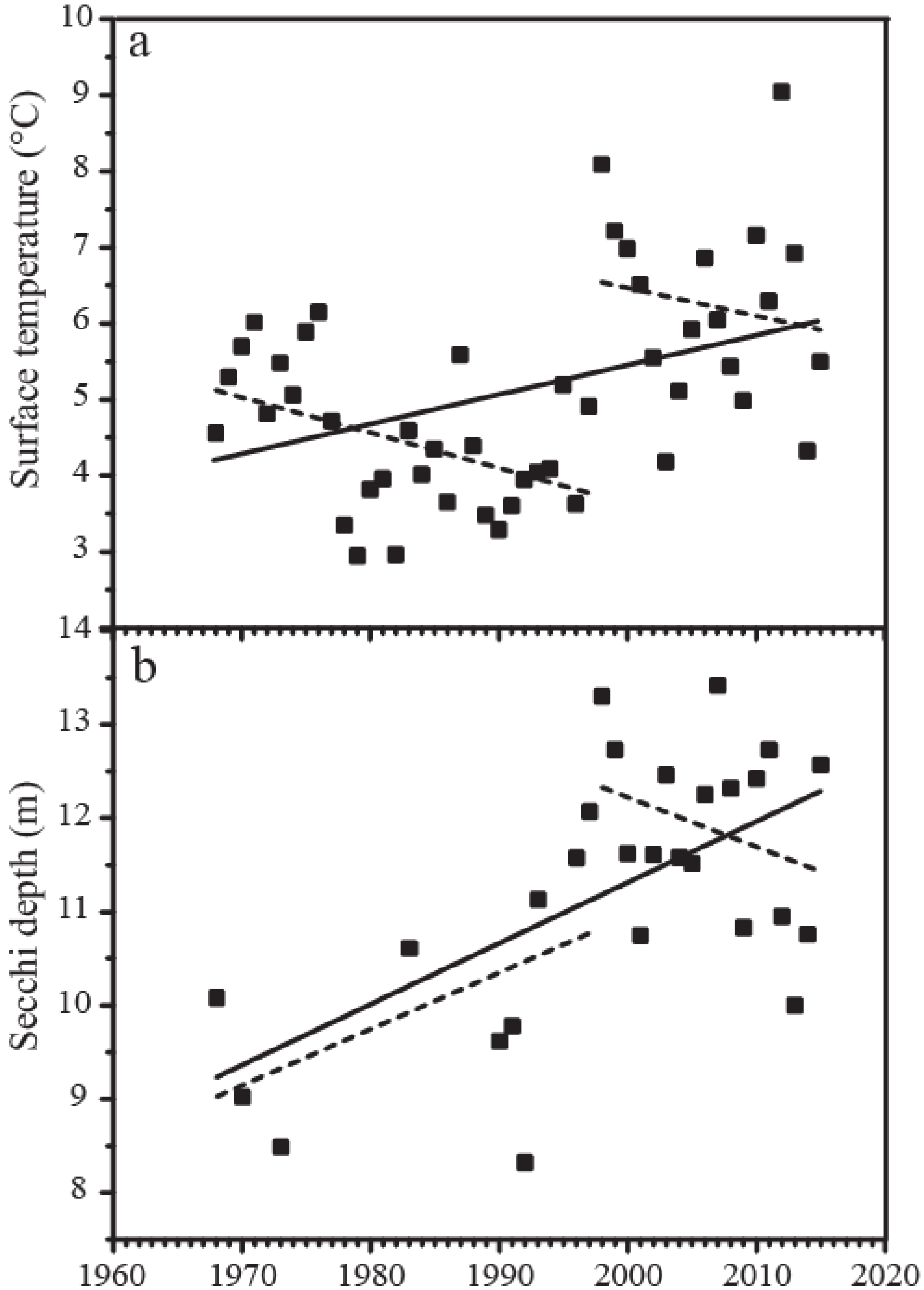

a
b
Surface temperature (°C)
Secchi depth (m)
10
9
8
7
6
5
4
3
14
13
12
11
10
9
8
1960
1970
1980
1990
2000
2010
2020

Fig. 6