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# Carbon Dynamics in Tropical Lake Malawi

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# CARBON DYNAMICS IN TROPICAL LAKE MALAWI

by

Maxon Ngochera

A Dissertation Submitted in
Partial Fulfillment of the
Requirements for the Degree of

Doctor of Philosophy
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at
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# ABSTRACT
# CARBON DYNAMICS IN TROPICAL LAKE MALAWI

by

Maxon Ngochera

The University of Wisconsin – Milwaukee, 2018
Under the Supervision of Dr. Harvey Bootsma

Large lakes of the world play a vital role in the global carbon cycle as they act both as conduits and sinks of terrestrially and atmospherically derived carbon. Lake Malawi, lying at the extreme southernmost end of the East African Rift Valley is one of the largest, deepest and most ancient of the African Great Lakes. In this study, the spatial and seasonal variation of direct measurements of air and water $pCO_2$ were taken for a period of one annual cycle using a vessel of opportunity along the north-south axis of Lake Malawi. These data, together with limnological and meteorological variables, were used to estimate the annual net $CO_2$ flux at the air-water interface.

The data reveal distinct spatial and temporal variation in $pCO_2$ and $CO_2$ flux that is related to hydrodynamic and meteorological conditions that drive nutrient dynamics and phytoplankton productivity. Contemporaneous measurements of lake temperature profiles, nutrients, weather conditions, phytoplankton biomass and seston $\delta^{13}C$ suggest that increased nutrient supply due to vertical mixing and allochthonous inputs promotes high phytoplankton growth rates and $CO_2$ uptake during the cool, mixing season and the hot, rainy season. Spatially, the southernmost region of the lake which is the most nutrient-rich and hence most productive was distinct from the rest of the lake. High $CO_2$ efflux to the atmosphere was observed in this region at the onset of the cool, mixing season probably due to the physical resupply of dissolved inorganic carbon (DIC) from deep waters during upwelling. Seasonally, almost the entire lake was $CO_2$ undersaturated with respect to the atmosphere during the wet, hot season (December to April) and the cool, mixing season (July to September), periods when nutrient supply from river inputs and vertical mixing that promote phytoplankton photosynthesis are high. By contrast, during the hot, stratified season (October and November), $CO_2$ evasion to the atmosphere was observed, possibly driven by high respiration to photosynthesis ratios.

The experiments conducted to determine the influence of river water loading and vertical exchange on the metabolism of Lake Malawi using Linthipe River water and hypolimnetic water from Lake Malawi shows distinct differences. River loading results in $CO_2$ supersaturation implying high respiration rates while hypolimnetic water showed a net consumption of carbon dioxide. Low phytoplankton biomass and particulate organic carbon production were observed in incubation bottles spiked with river water. In contrast, bottles spiked with hypolimnetic water showed high phytoplankton biomass and particulate organic carbon. The high OC: DP ratio compared to lake seston stoichiometry in Linthipe River is responsible for the observed heterotrophy while autotrophy by hypolimnetic water was sustained by the relatively low OC: DP from vertical flux.

Autochthonous primary production constitutes the major source of organic carbon in the lake and although concentrations of DOC and POC are relatively low compared to other lakes, the internal organic carbon inventory is large. The vertical exchange is an important source of DIC to the upper 200 m of the lake and it appears the recycling rate of carbon decreases with depth. A comparison of carbon sedimentation rates and DIC vertical flux rates among different strata in the lake suggests that the carbon recycling efficiency within the epilimnion is 73%, while it is 33% within the anoxic hypolimnion. If carbon is selectively retained while P is efficiently recycled into the epilimnion, $CO_2$ fixation in the epilimnion will be enhanced leading to autotrophy.

Several studies have indicated that the majority of oligotrophic inland waters are net sources of $CO_2$ to the atmosphere. Results from the present study indicate that this paradigm may not apply to large tropical lakes. On an annual basis, Lake Malawi is a net $CO_2$ sink and hence net autotrophic, absorbing 209 to 320 mmol C/m/yr from the atmosphere. Using the Lake Malawi C:P stoichiometry requirements and the carbon mass balance approach, we still determined that the lake is a net $CO_2$ sink. The data further suggest that surface $pCO_2$ variability is driven primarily by biological processes and vertical mixing, with seasonal temperature fluctuations playing a minor role. The variability in $CO_2$ underscores the importance of making measurements with high spatial and temporal resolution to accurately determine air-water gas fluxes in large lakes.

To my Wife, Mercy
my daughters Stella, Tadala, and Takondwa,
my son Stein,

Your love and prayers have seen me through this program.

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I would like to first and foremost thank my wife Mercy. There are no words to express my appreciation for the support, love, prayers, and encouragement she provided to me during the entire process. I will never be able to repay her for the time we were away from each other. She has had to take care of our kids, Stella, Tadala, Takondwa and Stein alone for several months while I was away. To my late dad, Jonasi, mom, Stellia and Sister Annie, education was the best gift you could instill in your son. I will thank you forever for this. Till we reunite again. May Your Souls Rest in Eternal Peace.

I was first introduced to the subject of "Limnology" by Dr. Mangaliso Gondwe who was the lead scientist for the Water Quality Section during the bridging phase of the SADC-GEF Water Quality Project at Senga Bay, Salima. Back then, I would join him for sampling trips at Station 928 and assist with cleaning glassware in the laboratory. But my career would not have developed fully if it was not for the support of Dr. Olaf Weyl, a Research Advisor for the German-funded National Aquatic Resources and Management Project (NARMAP). In addition to initiating water quality monitoring program in Lake Malombe that enhanced my research skills, he also encouraged me to apply for the Fulbright Junior Development Program Scholarship for a Master's Scholarship. Thanks to Dr. Harvey Bootsma who supported me throughout the scholarship application process. Although I had not met Dr. Bootsma in person, he sacrificed his precious time and personal resources to assist me with the application process. I owe my 'Fulbright Scholar' achievement to him. As a supervisor and mentor, I have over the years, learned and acquired a lot of knowledge and skills from him both as a Scientist and a Professional. I will always be grateful to Dr. Bootsma and his family for the unimaginable support.

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A study of this kind, covering the whole stretch of Lake Malawi can be expensive and dangerous. I am very grateful to the management and staff of Malawi Lake Services (MLS) for allowing me to conduct this study using the *MV* Ilala. Funding for this study was partly provided by the International Foundation for Science (IFS) grant, A5105-1 and a University of Wisconsin-Milwaukee Chancellor's Award to me and unspecified support from Dr. Bootsma.

# Chapter 1 - Introduction and Background

## 1.1 Introduction

Since the measurements by C.D. Keeling which showed considerable evidence of rapidly increasing carbon dioxide ($CO_2$) levels in the atmosphere (Keeling 1958), understanding the dynamics of atmospheric $CO_2$ and the influence it has on ecosystem function has been a subject of paramount importance (Farquhar et al. 198). The pre-industrial (circa 1750) atmospheric $CO_2$, estimated at around 280 ± 10 ppm (Etheridge et al. 1996) has continued to rise (Bacastow et al. 1985, IPCC 2000, Keeling and Whorf 2000, Solomon et al. 2007) and based on NOAA, Earth System Research Laboratory measurements, the global average atmospheric $CO_2$ concentration has since then increased by about 40% (https://www.esrl.noaa.gov/gmd/ccgg/trends/global.html) to a level of 406 ppm at the time of this writing. According to Prentice et al. (2001), the increase in atmospheric $CO_2$ is a result of anthropogenic $CO_2$ emissions that are caused by fossil fuel burning, accounting for 75%, land-use change and industries make up the remainder. Carbon dioxide is a greenhouse gas, and its increase in the atmosphere together with methane ($CH_4$) have significant implications for global warming (Lashof and Ahuja 1990, Hofmann et al. 2006). In addition, carbon dioxide is an important part of the carbon cycle, and therefore understanding its major pathways of transport and fate in ecosystems is considered a priority (Halmann and Steinberg 1999).

Photosynthesis and respiration constitute the major processes through which organic carbon in ecosystems is produced and utilized, respectively (Cole et al. 2000). The balance between gross primary production (GPP) and total community respiration (R), the net ecosystem production (NEP), represents the overall metabolic state of an ecosystem (Howarth et al. 1996, Kemp et al. 1997, Staehr et al. 2012), a unique term useful in classifying aquatic ecosystems (Cole et al. 1994). An aquatic ecosystem is said to be net autotrophic when GPP exceeds R (GPP: R > 1) resulting in the export or burial of organic carbon that is produced through the conversion of inorganic nutrients and $CO_2$ (Schindler et al. 1972). On the other hand, net heterotrophy indicates R is greater than GPP (GPP: R < 1) and the system respires more organic carbon than is produced internally. Available evidence suggests that respiration can only exceed GPP if external organic carbon is transported into the system (Cole et al. 2000). Primary production is generally regulated by the supply of plant-limiting nutrients such as phosphorus and nitrogen (Elser et al. 1990) and the quantity of light in the production zone (Fee et al. 1996). Inorganic carbon, especially dissolved carbon dioxide and bicarbonate, is the primary source of carbon for photosynthesis and the production of organic substances (Wetzel 2001). The utilization of inorganic carbon by phytoplankton in aquatic ecosystems is offset by heterotrophic production through the respiration of $CO_2$ by bacteria, algae, large aquatic animals, and by $CO_2$ inputs from the catchment and atmosphere to a lake, or inputs of $CO_2$ – rich waters from the hypolimnion (Seiler and Crutzen 1980, Nojiri et al. 1993, del Giorgio et al. 1999, Cole et al. 2007, Klump et al. 2009, Borges et al. 2014).

There are several methods that are used to determine the metabolic status of aquatic ecosystems (Smith and Hollibaugh 1993). Some studies determine community metabolism by measuring and comparing the various carbon cycle processes, i.e. algal photosynthesis, bacterial and invertebrate respiration (Fee 1973, Schindler 1977, Fee 1990, Schindler et al. 1997). This approach is advantageous in that it provides information about the individual processes that contribute to community metabolism. However, it is very involving and time-intensive as measurements have to be made with the highest spatial and temporal resolution, which in most cases can be challenging especially for very large aquatic ecosystems. It can also lead to inaccurate estimates of community metabolism due to the propagation of errors associated with the measurement of multiple processes. Metabolism has also been measured using radiotracer estimates of bacterial production (del Giorgio et al. 1999, Biddanda and Cotner 2002). Many authors have used the $^{14}C$ tracer technique to quantify primary production, especially in oligotrophic systems (Steemann 1952, Williams and Raine 1979, Bootsma 1993b). However, uncertainties arise with this technique as the approach is not very explicit on whether it approximates gross primary production or net ecosystem production (Karl et al. 1998, Marra 2007). Alternatively, whole-lake ecosystem metabolism can be measured using diel free water measurements of the air-water flux of $CO_2$ and $O_2$ (Lauster et al. 2006, Staehr and Sand-Jensen 2007). This flux represents the net result of all the carbon cycling processes within the lake. If for example, photosynthesis in the aquatic ecosystem is greater than respiration, there will be a negative $CO_2$ flux indicating invasion from the air to the lake. On the other hand, if respiration is higher than photosynthesis, $CO_2$ flux will be positive indicating an evasion from the lake to the air. In this case, respiration is supported by external organic carbon input (Prairie et al. 2002, Hanson et al. 2003, Duarte and Prairie 2005) that exhibits a high C:P loading ratio relative to primary producers in the system (Klump et al. 2009). If there are no external organic carbon inputs into the ecosystem, then respiration should equal or be less than photosynthesis, and the net flux from the lake to the atmosphere will be zero or negative.

Carbon dioxide flux between water and air and the associated gas transfer coefficients have received much attention in the ocean (Wanninkhof et al. 2009) and lakes to determine the biological activity of those ecosystems and infer the interactions with their watersheds (Kling et al. 1991a, Sellers et al. 1995, Dillon and Molot 1997b, Biddanda and Cotner 2002). The current understanding is that the world's oceans represent huge sinks of carbon dioxide due to the "biological pump" – the mechanism by which $CO_2$ is photosynthetically fixed into organic carbon which is then sequestered in the deep sea and in sediments (Takahashi et al. 1999). Measurements made between 1980 and 1989, and 1990 to 1999, reveal that the ocean-atmosphere $CO_2$ flux varies between –1.7 and –1.9 ± 0.6 PgC $yr^{-1}$ (Prentice et al. 2001). These carbon uptake estimates are consistent with global ocean budgets from IPCC Special Reports (IPCC 1996, 2000, 2005). Uptake of $CO_2$ by the oceans is influenced by the carbonate chemistry and it generally increases with an increase in atmospheric $CO_2$ due to the difference of $pCO_2$ at the air-water interface as long as the buffering capacity remains high (Prentice et al. 2001).

Lakes, reservoirs, and peatlands around the world are valuable systems from which essential knowledge of carbon cycling processes can be obtained. While earlier studies focused on the oceans as ultimate sinks for carbon, recent investigations highlight that inland waters also sequester organic carbon. For example, Dean and Gorham (1998) show that, collectively, lakes, reservoirs, and peatlands store approximately 300 Tg C $yr^{-1}$ in their sediments, comparable to burial rates previously reported by Mulholland and Elwood (1982). An assessment of carbon cycling in some large lakes of the world by Alin and Johnson (2007) estimated that a total of 7 Tg of carbon is buried in the sediments annually. More recently, Mendonça et al. (2017) report an estimated organic carbon burial in lakes and reservoirs of approximately 150 TgC $yr^{-1}$. Most of the organic carbon that is buried in lakes is autochthonous produced through primary production within the lakes. Although the oceans cover 71% of the total earth's surface area, the burial efficiency of organic carbon in lakes is more efficient, with a mean of 9% (Alin and

Johnson 2007) compared to less than 0.5% in the oceans (Hedges and Keil 1995) as burial rates from the world's oceans fluctuates between 100 - 200 Tg C $yr^{-1}$ (IPCC 2005, Benson et al. 2012).

There is growing evidence that many inland waters of the world are heterotrophic and hence net sources of $CO_2$ to the atmosphere (Cole et al. 1994, del Giorgio et al. 1997, Dillon and Molot 1997a, Alin and Johnson 2007). It is estimated that inland waters actively process terrestrial carbon and emit up to 1,400 Tg C $yr^{-1}$ (Dean and Gorham 1998, Cole et al. 2007, Tranvik et al. 2009). Recent studies by Raymond et al. (2013) however, report an even higher $CO_2$ evasion rate from inland waters of 2,100 Tg C $yr^{-1}$. The difference in flux rates is due to the accounting for $CO_2$ evasion from streams and rivers (Raymond et al. 2013). An extensive survey of surface $CO_2$ in worldwide distributed lakes showed that over 87% of the lakes studied were supersaturated with $CO_2$ (Duarte and Prairie 2005).

A number of studies indicate a general positive correlation between $pCO_2$ and DOC concentration in aquatic ecosystems (Jonsson et al. 2003, Sobek et al. 2005, Jonsson et al. 2008, Lapierre and del Giorgio 2012). The positive relationship is due to the fact that DOC is a major substrate for heterotrophic bacterial metabolism (Hanson et al. 2003). Similar findings were reported by Hope et al. (1996) for northern Wisconsin lakes, which showed a strong positive correlation of surface $pCO_2$ with DOC. Other studies observe that high $pCO_2$ may also result from the input of highly $CO_2$ supersaturated groundwater (Atilla et al. 2011, McDonald et al. 2013, Borges et al. 2014), and the input of reduced chemical species such as iron or sulfur, the oxidation of which generates acidity and converts bicarbonate to carbon dioxide (Borges et al. 2014). Areal rates of $CO_2$ emission to the atmosphere from individual lakes are inversely proportional to lake surface area (Striegl et al. 2001) because DOC inputs are dependent on the size of the watershed relative to the lake surface area (Urabe et al. 2005). Due to the large watershed to lake surface area ratio, carbon dynamics in small lakes are strongly influenced by external (terrestrial) inputs, resulting in net heterotrophy (Kelly et al. 2001, Alin and Johnson 2007, Roehm et al. 2009, Kortelainen et al. 2013). Indeed, surface $pCO_2$ concentration in small temperate lakes can reach up to 1,000 ppm (Cole et al. 1994, Kelly et al. 2001, Striegl et al. 2001) while even higher concentrations (10,000 ppm) are observed is small bog lakes (Riera et al. 1999). The watershed to lake surface area ratio (WA: LA) for Lake Malawi is small (< 4) compared to the small temperate lakes that can be over 100 (Hope et al. 1996). Climate may also influence DOC loads to lakes. Hecky et al. (2003), reported DOC concentrations for Lake Malawi tributary rivers that are much lower (mean of 233 $\mu$mol $L^{-1}$) than those observed in most temperate rivers (Mulholland and Kuenzler 1979, Meybeck 1981, Schiff et al. 1990, Schiff et al. 1997). Although the Lake Malawi catchment receives rainfall of similar magnitude to that of the Laurentian Great Lakes (800-1200 mm per year), most rivers cease to flow during part of the year due to high evaporation rates. Consequently, DOC loading into Lake Malawi is low because of the low DOC concentrations and limited flows from tributary rivers. In contrast, evaporation rates in temperate regions are small and most rivers continue to flow throughout the year, which facilitates the decomposition of terrestrial material and leaching of DOC (Meybeck 1981, McDowell and Asbury 1994). Measurements of DOC concentrations in Lake Malawi are unusually low which corroborates the observed trends from its watershed (Ramlal et al. 2003). And so it might be expected that $CO_2$ dynamics in Lake Malawi are less influenced by allochthonous DOC than they are in large, temperate lakes.

While there is enough evidence to support heterotrophy in many lakes (Cole et al. 1994, del Giorgio et al. 1997, Prairie et al. 2002), most of these measurements have been conducted in small and medium-sized temperate lakes (Hope et al. 1996) whose response to physical and chemical forcing can be very rapid. The mechanisms that regulate $CO_2$ dynamics in tropical lakes and indeed the African Great Lakes may be different considering their unique features. Lakes Tanganyika and Malawi are extremely oligotrophic, old, deep and complete mixing is restricted because of the permanent thermocline that forms below 200 m (Eccles 1962, Coulter 1968, Eccles 1974). Because of the long hydraulic residence times (114 years for Lake Malawi; 440 years for Lake Tanganyika) and the absence of vertical turnover, significant differences in water chemistry in these large tropical lakes are apparent compared to most large, temperate lakes (Hecky 2000, Katsev et al. 2017). Microbial activity, together with slow mixing in these tropical lakes, favors the accumulation of reduced compounds in their monimolimnion such as $CO_2$, $Mn^{2+}$, $NH_4^+$, $Fe^{2+}$, $H_2S$, and $CH_4$ (Kilham and Kilham 1990, Hecky 2000, Vollmer et al. 2002, Lewis 2010, Katsev et al. 2017). Furthermore, the anoxic conditions persistent in the monimolimnion of these lakes promotes denitrification, and may reduce the release of carbon, while accelerating recycling of dissolved phosphorus (Sobek et al. 2009), which leads to low C:P and N:P supply ratios for the surface mixed layer (Hecky 2000, Katsev et al. 2006). The high vertical flux rates of dissolved phosphorus would promote net $CO_2$ uptake from the atmosphere in these tropical large lakes.

Although Lake Malawi has low chlorophyll *a* concentrations in its open waters, photosynthetic rates are relatively high (Degnbol and Mapila 1982, Bootsma 1993b, Patterson and Kachinjika 1995). The high phytoplankton photosynthetic rates are attributed to the year-round high water temperatures and photosynthetically active radiation (Kilham and Kilham (1990) which results in an efficient breakdown and recycling of nutrients in the epilimnion and relatively high turnover rates of primary productivity (Talling 1965, Bootsma 1993b, Spigel and Coulter 1996, Lewis 2010). Phytoplankton photosynthetic rates measured in Lake Malawi show a distinct seasonal and spatial variation. Seasonally, high rates are observed during the cool, mixing and rainy season while the hot, stratified season displays the lowest rates (Bootsma 1993b, Patterson and Kachinjika 1995). Spatially, the southern part of the lake exhibits the highest photosynthetic rates due to upwelling of nutrient-rich water (Bootsma 1993b, Hamblin et al. 2003a).

## 1.3 Description of Lake Malawi

### *1.3.1 Physical, climatic and hydrological characteristics*

Lake Malawi lies to the southerly most of the East African Great Rift Valley lakes (Fig. 1). These African Great Lakes, Tanganyika, and Malawi are old (Tiercelin and Mondeguer 1991, Cohen et al. 1993) and together with Lake Victoria, occupy a surface area of 130,900 km$^2$, holding approximately 25% of the Earth's available surface freshwater (Bootsma and Hecky 2003). Lake Malawi is the world's fourth largest by volume (7,775 km$^3$), eighth largest by area (29,500 km$^2$), and third deepest (706 m max depth; (Eccles 1974). The lake is oligotrophic, meromictic and anoxic below ~220 m. It is located at an altitude of 500 m and between 9.5$^o$ and 14.3$^o$ south of the equator and is, therefore, able to experience seasonal cycling of wind, temperature, and precipitation. The lake is 560 km long and 75 km wide at its greatest. The climatic conditions of Lake Malawi can be divided into three seasons; the hot, rainy season (December to April), the cool, windy mixing season (May to September) and the hot, stratified season (October to November). Generally, the lake experiences one main rainy season but the northern part of the lake sometimes receives rains twice. The dominant winds in the lake are from the south that blows along the axis of the lake, however, strong southeasterly winds (*mwera* winds) up to 40 km hr$^{-1}$, generating surface waves of 5 m high are more prevalent between May and September (H.A. Bootsma pers. comm.). This period coincides with low air temperatures that result in the overall cooling of the lake. The combination of strong wind speeds and reduced water column temperatures induces vertical mixing and upwelling at the southern end of the lake which brings nutrients to the surface waters. During the rainy season, winds are mostly from the north, (*mpoto* winds) and this period is characterized by high air temperatures which result in warming of the lake surface layer creating a strong thermocline that inhibits vertical mixing transport of nutrients from the deep waters. The highest surface water temperatures in the lake are observed in February and can reach up to 30°C (Patterson and Kachinjika 1995, Wooster et al. 2001). On an annual basis, the surface water temperature variability in Lake Malawi is usually less than 10°C which is negligible compared to temperate lakes. Temperatures below 200 m hardly change and are maintained throughout the year at close to 22°C (Wüest et al. 1996, Vollmer et al. 2002). Water levels in the lake are seasonal and are dictated by river inflow, direct precipitation, and evaporation.

While Lake Malawi has numerous tributary rivers discharging an estimated rate of 29 $km^3$ $yr^{-1}$ of water, the major source of water into the lake is direct precipitation (54 $km^3$ $yr^{-1}$) while evaporation constitutes the highest loss of water from the lake (Owen et al. 1990). The only outlet, Shire River, accounts for less than 20% (12 $km^3$ $yr^{-1}$) of water loss. Because of the relatively small outflow, water balance budget models have considered the lake to be nearly a closed-basin (Spigel and Coulter 1996). This means that most of the nutrients and the organic carbon material are retained and recycled within the lake. While annual rainfall over the lake is comparable to that of the Laurentian Great Lakes, evaporation rates are high due to the year-round high temperatures (Spigel and Coulter 1996). Previous studies have investigated organic carbon and nutrient inputs into Lake Malawi from tributary rivers, the atmosphere, and vertical flux (Bootsma et al. 1999, Hecky et al. 2003). A general observation is that a majority of the nutrients and organic carbon from river inputs is in particulate form, while atmospheric deposition and vertical flux supply primarily dissolved forms of nutrients and organic carbon (Bootsma and Hecky 1999, Kingdon et al. 1999). Deforestation and increasing intensive agriculture, coupled with steep topography, explains the high proportions of particulate material compared to dissolved being transported into the lake from rivers (Hecky et al. 2003).

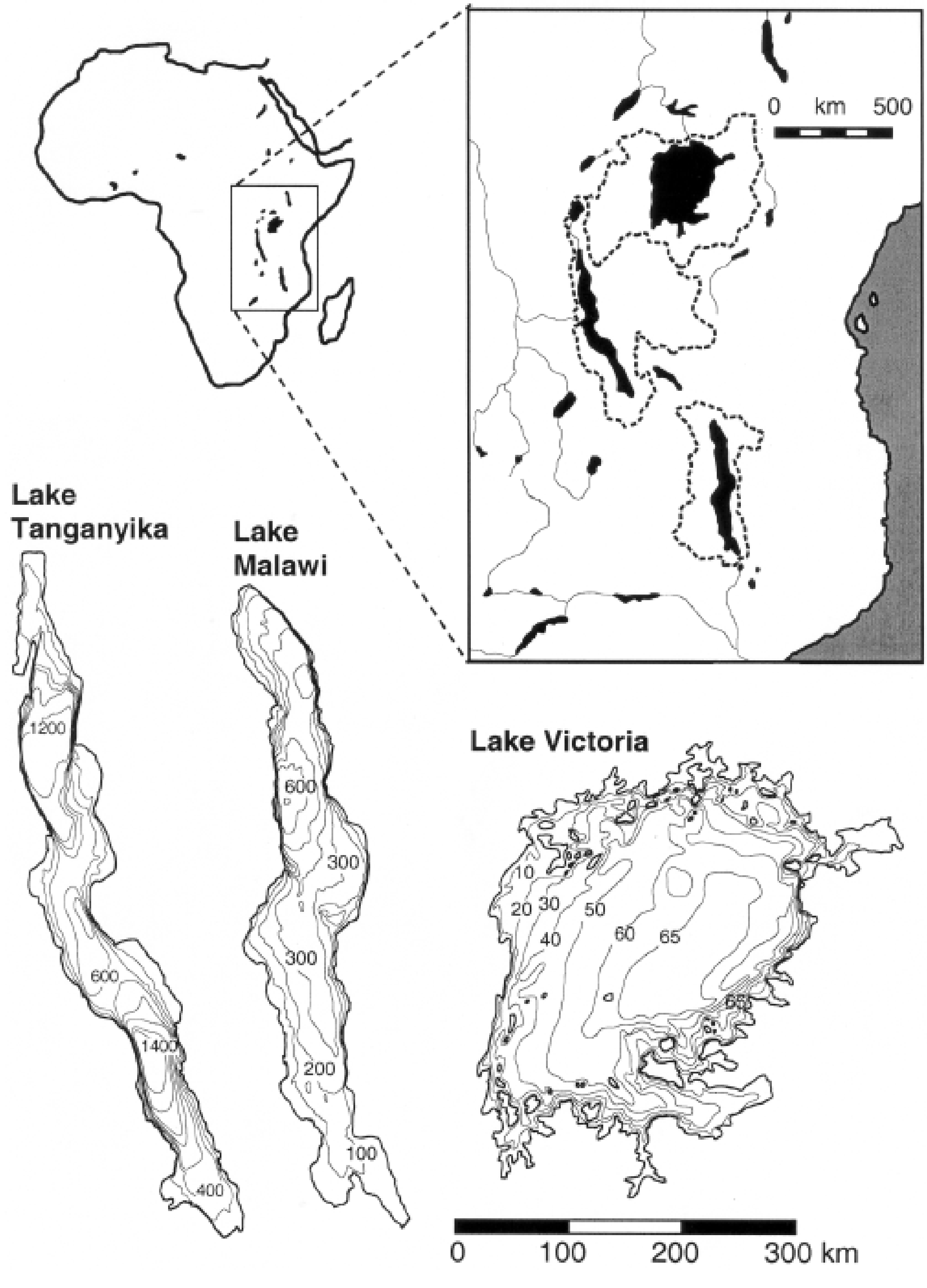


Figure 1: Map of lakes Tanganyika, Malawi, and Victoria, the three East African Great Lakes with associated catchment boundaries (dashed lines). Bathymetric contour depths are provided in meters. Map reproduced from Bootsma and Hecky (2003)

### *1.3.2 Chemistry and Biology*

The open waters of Lake Malawi are nutrient poor but concentrations of dissolved nutrients increase with depth (Bootsma and Hecky 2003). Concentrations of dissolved inorganic nitrogen and soluble reactive phosphorus in the surface waters are less than 0.1 µmol $L^{-1}$ but increase with depth, with ammonia and SRP reaching 25 and 3.2 µmol $L^{-1}$, respectively, in the anoxic monimolimnion below 200 m, (Bootsma and Hecky 1993, Wüest et al. 1996). According to Hecky et al. (1996), the anoxic monimolimnion is the major source of phosphorus and silica to the surface mixed layer, contributing approximately 89% and 88%, respectively while the remainder is supplied by atmospheric deposition and river inputs. The concentration of chlorophyll *a* in the pelagic zone of the lake is also low but phytoplankton photosynthetic rates are high and vary seasonally. Measurements of photosynthetic rates in the lake range between 240 and 520 mg C $m^{-2}yr^{-1}$ (Degnbol and Mapila 1982, Bootsma 1993b). Phytoplankton composition is dominated by Cyanophyta, Chlorophyta, and Bacillariophtya species (Bootsma 1993a, Patterson and Kachinjika 1995, Lehman 1996) but during the hot, stratified season cyanobacteria, dominate the composition because they can fix atmospheric nitrogen as phytoplankton are nutrient limited during this period (Gondwe et al. 2008).

Seston C:P and N:P ratios in Lake Malawi are much higher than the Redfield ratios and are characteristic of moderate P limitation i.e. C:P of 197–257:1 and N:P of 21–40:1 (Hecky and Kilham 1988, Guildford and Hecky 2000, Ngochera and Bootsma 2018). In contrast, the stoichiometry of the nutrients sources to the lake are different and depend on the form of P under consideration i.e. particulate vs. dissolved (Table 2). It is apparent that river loading, atmospheric deposition, and vertical flux have lower TC: TP, DOC: TP and excess DIC: SRP ratios relative to seston, although TC: TDP from river loading is an order of magnitude higher than that of lake seston. Calculation of excess DIC is described in Chapter 2. Since P concentrations dictate photosynthesis while DOC controls respiration, the high P loading into the epilimnion should promote phytoplankton photosynthesis, while organic carbon in the form of either DOC or POC will promote respiration (Hansen et al. 2003, Sobek et al. 2005). However, an important question becomes: what portion of the loaded carbon supports respiration and $CO_2$ production, and what portion of the loaded phosphorus supports phytoplankton photosynthesis? Specifically, what forms of phosphorus are available for phytoplankton primary production, and over what timescales? If all of the carbon and phosphorus from rivers are available, then the C:P load ratio is lower than the seston C:P ratio. This can only occur if phytoplankton fixes extra $CO_2$ from the atmosphere, in which case the lake would be autotrophic. But if all the loaded carbon is available for bacterial utilization, and only the TDP is available to support phytoplankton photosynthesis, then the C:P load ratio is >1500. In this case, even if phytoplankton use all of the loaded P for photosynthesis, they could still not fix as much $CO_2$ as that respired by bacteria, and so the lake would be heterotrophic.

Table 1: Stoichiometric ratios for nutrient loading in Lake Malawi; TOC = total organic carbon, TP = total phosphorus, TDP = total dissolved phosphorus, DOC = dissolved organic carbon, DIC = dissolved inorganic carbon, PC = particulate carbon, PP = particulate phosphorus. Sources: (Hecky and Kilham 1988, Bootsma and Hecky 1999, Guildford and Hecky 2000, Ngochera and Bootsma 2018)

| **Nutient Source** | **TOC:TP** | **TOC:TDP** | **DOC:TP** | **DOC:TDP** | **Seston** |
|---|---|---|---|---|---|
| River Input | 178 | 1562 | 28 | 249 | PC:PP = 197 – 257:1 |
| Atmospheric Deposition | 111 | 207 | 77 | 147 | |
| | | **DIC: TP** | **Excess DIC: SRP*** | | |
| Vertical Mixing<br>Meta - Epilimnion | | 225 | 96 | | |

*estimates from this study

According to Bootsma et al. (1999), Lake Malawi has one of the highest loading rates of P from atmospheric deposition in the world (Fig. 2C). Deforestation, the opening of new agricultural fields and the cultural tradition of burning of grasslands and crop residues are some of the contributing factors to high P loading from atmospheric deposition into the lake. Similar observations have also been reported for the other African Great Lakes i.e Lake Victoria (Tamatamah et al. 2005b), Lake Tanganyika (Langenberg et al. 2003) and Lake Kivu (Bagalwa et al. 2016). The total C:P loading ratio from atmospheric deposition for all C and P species is lower than the seston C:P ratio. If atmospheric loading is a major source of nutrients and carbon to the lake, it will tend to promote autotrophy.

Upwelling/vertical flux is another major source of nutrients to the epilimnion of Lake Malawi. These events are more common at the southernmost end of the lake (Hamblin et al. 2003a) but Eccles (1974) observed weaker events in the northern part of Lake Malawi. The ratio of fluxed DIC: TP from the metalimnion to the epilimnion is similar to the seston stoichiometric ratio. However, the excess DIC: SRP ratio is smaller than that of seston. If internal mixing is the main source of P to the epilimnion and all of the SRP from the vertical exchange is available, then phytoplankton would fix extra $CO_2$ from the atmosphere, in which case the lake would tend to be autotrophic. Vertical mixing in Lake Malawi does not result in a net input of DOC to the epilimnion as previous measurements have indicated that concentrations of DOC are lowest in the hypolimnion and metalimnion compared to the epilimnion (Ramlal et al. 2003). Similar observations were also reported for Lake Superior (Urban et al. 2005).

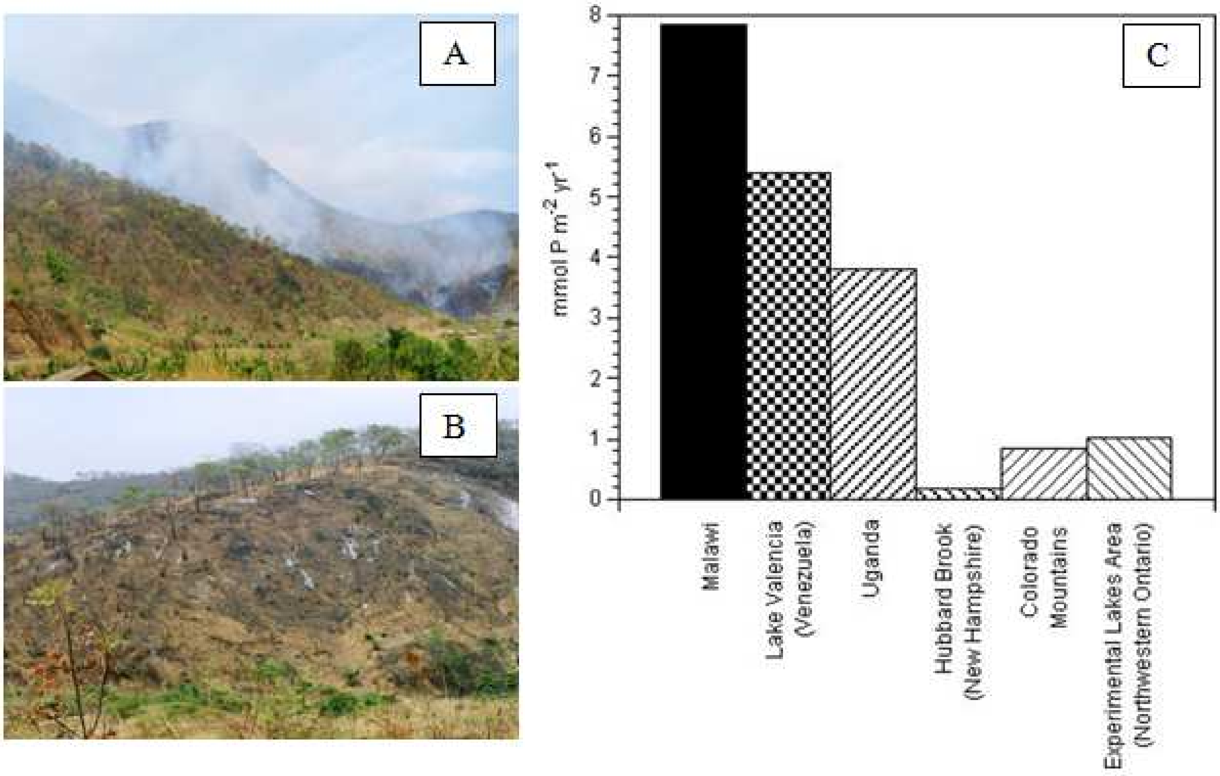


Figure 2: Biomass burning and exposed land (A and B) and a comparison of wet deposition rates for atmospheric phosphorus at various lakes and locations around the world (C). Source: Bootsma et al. (1999).

## 1.4 Research objective, questions, and hypotheses

The focus of this study is on tropical Lake Malawi, a deep and oligotrophic lake at the southernmost of the African Rift Valley. The overall objective of the research is to determine the spatial and temporal variability of surface $pCO_2$ and infer the mechanisms that may be responsible for regulating air-water $CO_2$ exchange in this large lake. To achieve this objective, four main specific questions were addressed. 1) what is the role of this large tropical lake in regional or global carbon budgets? Does the lake act as a net $CO_2$ sink (autotrophic) or a net $CO_2$ source (heterotrophic)? 2) do surface $pCO_2$ and $CO_2$ flux in the lake vary both seasonally and spatially similar to phytoplankton photosynthetic rates? 3) what are the relative roles of river loading and internal cycling in controlling $pCO_2$ flux in the lake? and 4) do the measured rates of lake-atmosphere $CO_2$ exchange reconcile with a carbon mass balance budget for Lake Malawi?

It was hypothesized that surface $CO_2$ concentrations in the lake will vary seasonally according to the previously observed temporal patterns of phytoplankton productivity. Further, it was expected that since the southern part of the lake is the most productive part of the lake, this region will show autotrophy and hence a net sink of atmospheric $CO_2$. To maintain stoichiometric balance in the lake, which has C:P ratios that are high relative to ratios of C:P supply rates from rivers and vertical flux, it was expected that the lake will fix more atmospheric $CO_2$ than it respires, resulting in net autotrophy. This hypothesis is, however, based on the assumption that all the supplied phosphorus will be bioavailable for phytoplankton uptake.

These research objectives were addressed in three different ways. Firstly, whole-lake measurements of air and surface water $pCO_2$ were collected aboard a vessel of opportunity along the north-south axis of Lake Malawi for a period one annual cycle, together with supporting meteorological and limnological parameters. This dataset was used to determine the spatiotemporal $CO_2$ flux in the lake and infer mechanisms regulating it. Secondly, bottle enclosure experiments using Linthipe River and hypolimnetic lake water were conducted to gain insights into the relative importance of each of these sources of C and P in driving photosynthesis and respiration. Lastly, a carbon mass balance was constructed to determine whether the conceptual models of carbon and nutrient dynamics that arise from the data obtained from previous studies, the whole-lake cruises and the river/hypolimnion water experiments are compatible with a carbon mass balance. This mass balance was also used to determine whether the lake is a net $CO_2$ source or sink, and the results compared with the conclusion arrived at by the $CO_2$ flux results.

In addition to this introductory chapter, this dissertation consists of four additional chapters. **Chapter 2** – Spatial and temporal dynamics of $pCO_2$ and $CO_2$ flux in tropical Lake Malawi presents results of the lake-wide cruise measurements of $pCO_2$ and determines the spatial and temporal variability of $CO_2$ flux in the lake. Normalizing the $CO_2$ flux to the entire lake surface area provided vital information on whether the lake is a net $CO_2$ source or sink. **Chapter 3** - The relative role of river loading and internal nutrient cycling in controlling $pCO_2$ flux in tropical Lake Malawi provides results of experiments that were conducted to simulate the potential response of the lake when river and deep lake water is exchanged with epilimnetic waters. **Chapter 4** – A carbon mass balance for Lake Malawi, translates the conceptual model developed for carbon into a numerical representation that summarizes the major sources and sinks of carbon in the lake. This model is a modification of the organic carbon model by Ramlal et al. (2003), with additional inputs of the air-water $CO_2$ exchange and vertical DIC flux to constrain the budget. **Chapter 5 -** Summary and Conclusion, provides a summary and synopsis of the main findings of the study and conclusions of the research study.

# Chapter 2 - Spatial and temporal dynamics of $pCO_2$ and $CO_2$ flux in tropical Lake Malawi

## Abstract

Numerous studies have documented $CO_2$ dynamics in temperate lakes, but only a handful of such studies have been conducted on tropical lakes, and limited direct measurements of the spatiotemporal variability of surface $CO_2$ have been made for the African Great Lakes. Spatial and seasonal variation of direct measurements of air and water $pCO_2$, along with supporting limnological and meteorological variables, were measured using a vessel of opportunity along the north-south axis of Lake Malawi, and these measurements were used to estimate annual net lake-atmosphere $CO_2$ flux and infer mechanisms regulating this flux. Surface $pCO_2$ and $CO_2$ flux varied significantly with season and location. Temporally, the lake was $CO_2$ undersaturated during the hot, wet season (Dec.-Mar.) and the cool, windy mixing season (July-Sept.). In contrast, the lake was $CO_2$ supersaturated at the onset of the mixing season (May) and during the hot, stratified season (October). Concurrent measurements of lake temperature profiles, weather conditions, phytoplankton biomass and seston $\delta^{13}C$ suggest that increased nutrient supply due to vertical mixing and allochthonous nutrient inputs promotes high phytoplankton growth rates and $CO_2$ uptake during the windy mixing season and hot, rainy season. However, unlike the rest of the lake, the southernmost region of the lake was usually $CO_2$ supersaturated, even though phytoplankton productivity is highest in this region. While the upwelling of hypolimnetic water at the southern end of the lake is a major source of nutrients that promote $CO_2$ uptake over large spatial and temporal scales, over shorter time scales (< 1 month) due to phytoplankton

photosynthesis, the $CO_2$ introduced in upwelled water appears to overwhelm the photosynthetic capacity of the lake. Over an annual cycle, the lake appears to be a net $CO_2$ sink with a mean air-lake flux of -264 ± 56 mmol C $m^{-2}$ $yr^{-1}$.

## 2.1 Introduction

Lake ecosystems provide important services to their riparian populations such as provision of food (Molsa et al. 1999, Sarch and Birkett 2000, Weyl et al. 2010), acting as reservoirs of aquatic biodiversity (Ribbink 1988, Martens 1994) and affording numerous economic benefits including hydroelectric power generation, inland water transport, industries, tourism, and wildlife (Bootsma and Hecky 1993, Ogutu-Ohwayo et al. 1997, Cangelosi et al. 2001). In addition, there is a growing appreciation for the role of lakes in the global carbon cycle (Tranvik et al. 2009), serving both as sinks for organic carbon, and as sources/sinks of $CO_2$ (Mulholland and Elwood 1982, Dean and Gorham 1998, Cole et al. 2007, Tranvik et al. 2009). It is estimated that inland waters actively process terrestrial carbon and emit up to 1,400 Tg C $yr^{-1}$ (Dean and Gorham 1998, Cole et al. 2007, Tranvik et al. 2009) while accumulating organic carbon at a rate of 60 Tg C $yr^{-1}$ (Mulholland and Elwood 1982). This is contrary to earlier theories that regarded inland lakes as passive conduits of carbon to the ocean (Schlesinger and Melack 1981, Degens et al. 1991). Net ecosystem production (NEP = GPP - R), the difference between gross primary production (GPP) and community respiration (R), is often used to classify the trophic status of lakes (Hanson et al. 2003). Lakes with positive NEP are classified as autotrophic while those displaying negative NEP are regarded as heterotrophic. While NEP is of ecological significance (Ryther 1956), the methods used to determine GPP and R have often provided differing conclusions and raised a lot of debate (Carignan et al. 2000). Many studies measure changes in dissolved $CO_2$ or $O_2$ to determine photosynthesis or respiration. Historically, bottle incubations have been used, with results interpolated over space and time to derive whole–lake values (Schindler 1977, Fee 1980). In aquatic ecosystems, $pCO_2$ has often been calculated using carbonate equilibria and assuming constant alkalinity due to the scarcity of direct $pCO_2$

measurements (Raymond et al. 2013). However, there may be large uncertainties associated with errors resulting from inaccurate estimation of the components of the carbonate equilibria (Golub et al. 2017). Alternatively, probes have been developed to measure the concentration and dynamics of in situ gases such as $CO_2$ and $O_2$, although their use is somewhat limited owing to their low sensitivity when used in unproductive waters (Carignan 1998). But because $CO_2$ and $O_2$ probes can provide measurements for calculating the net balance between GPP and R (NPP), they provide reliable estimates of net ecosystem metabolism (Sellers et al. 1995, Davies et al. 2003, Hanson et al. 2003).

Numerous studies (Cole et al. 1994, del Giorgio et al. 1997, Cole et al. 2000, Duarte and Prairie 2005, Alin and Johnson 2007) have indicated that most lakes are $CO_2$ supersaturated and are hence net sources of $CO_2$ to the atmosphere. This implies that allochthonous contributions to respiration in these lakes exceed net autochthonous C fixation (Kling et al. 1991b, Cole et al. 1994, Cole et al. 2000, Sobek et al. 2005, Bellido et al. 2009). Temporal fluctuations in lake $CO_2$ concentration can be driven by both biological and physical factors. Biological processes include photosynthesis and respiration. For lakes exhibiting high net phytoplankton photosynthetic rates, utilization of aqueous $CO_2$ is high and results in atmospheric $CO_2$ diffusion into surface waters (Kling et al. 1992, Schindler et al. 1997). Similarly, lakes with high respiration rates have elevated release rates of $CO_2$ to the atmosphere. The available evidence indicates that phosphorus and dissolved organic carbon (DOC) concentrations are the main drivers of metabolism in many lakes (del Giorgio and Peters 1994, Cole et al. 2000, Hanson et al. 2003) where phosphorus promotes $CO_2$ uptake by phytoplankton and DOC promotes microbial respiration. At low DOC concentrations ($< 0.8$ mmol C $L^{-1}$), GPP and R may be at equilibrium and net ecosystem production may be close to zero (Prairie et al. 2002, Hanson et al. 2003).

Physical factors include temperature changes and vertical mixing (upwelling, entrainment due to cooling of surface waters, and eddy diffusion due to wind-induced turbulence). Fluctuations in surface temperature can influence surface $CO_2$ concentration simply due to the influence of temperature on gas solubility (Takahashi et al. 2002, Thomas et al. 2005, Atilla et al. 2011). Vertical mixing can introduce $CO_2$-rich hypolimnetic water to the surface, resulting in $CO_2$-evasion to the atmosphere (Lewis 2010).

Our current understanding of carbon dynamics in lakes may be biased because the majority of observations have been conducted in small to medium size temperate lakes (Hope et al. 1996). It is therefore uncertain whether trends observed in temperate lakes, such as the prevalence of $CO_2$ supersaturation in surface waters (Cole et al. 1994), extend to large, tropical lakes. The mechanisms that regulate $CO_2$ dynamics in large, tropical lakes may be different considering their unique features. For example, the African Great Lakes of Tanganyika and Malawi are old (several million years), deep and meromictic. The long hydraulic residence times and absence of vertical turnover result in significant differences in water chemistry relative to most large, temperate lakes (Hecky 2000, Katsev et al. 2017). The large tropical lakes accumulate high concentrations of dissolved nutrients and $CO_2$ in their hypolimnia. Microbial activity, coupled with the absence of photosynthesis and slow vertical mixing (Vollmer et al. 2002) in the monimolimnion of these tropical lakes favors the accumulation of reduced compounds such as $CO_2$, $Mn^{2+}$, $NH_4^+$, $Fe^{2+}$, $H_2S$, and $CH_4$ (Kilham and Kilham 1990, Hecky 2000, Lewis 2010, Katsev et al. 2017). Additionally, anoxic conditions promote denitrification while accelerating the release of dissolved phosphorus in the deep waters, which may lead to low N:P supply ratios for the surface mixed layer (Hecky 2000, Katsev et al. 2006). Because organic carbon decomposition rates may be reduced under anoxic conditions (Sobek et al. 2009), there may be a selective recycling of P relative to C in the monimolimia of these lakes, which would promote net $CO_2$ uptake from the atmosphere.

A number of studies indicate a general positive correlation between $pCO_2$ and DOC concentration in aquatic ecosystems (Jonsson et al. 2003, Sobek et al. 2005, Jonsson et al. 2008, Lapierre and del Giorgio 2012). But the magnitude of DOC inputs into aquatic systems depends strongly on the watershed to lake surface area ratio (Urabe et al. 2005) with high DOC concentrations observed in aquatic ecosystems with high watershed to lake area ratios (Kelly et al. 2001, Alin and Johnson 2007, Roehm et al. 2009, Kortelainen et al. 2013). The watershed to lake surface area ratio for Lake Malawi is small and in accordance with the expected trends, DOC concentrations in the lake, are low, ranging between 20 and 140 μmol $L^{-1}$ (Ramlal et al. 2003). The DOC concentrations are comparable to those observed in Lake Superior and the open ocean (Druffel et al. 1992, Kelly et al. 2001). In addition, Lake Malawi does not experience large periodic external inputs of dissolved organic carbon from its tributary rivers that would increase DOC concentrations in the lake to promote heterotrophy. Over 80% of the organic carbon transported into the lake from its tributaries is in particulate form (Kingdon et al. 1999). This observation is different from the DOC: POC ratio of >1 reported for most large tropical and temperate rivers (Martins and Probst 1991, Wetzel 2001). Within Lake Malawi, increasing human population is exerting pressure on forests for fuelwood and timber, and land for agricultural purposes, leading to accelerated biomass burning and soil erosion (Bootsma et al. 1996, Cohen et al. 1996, Hecky et al. 2003). The influence of allochthonous DOC on $CO_2$ dynamics in Lake Malawi may, therefore, differ from that in large temperate lakes.

Despite low chlorophyll *a* concentrations in the open waters of Lake Malawi (< 1 μg$L^{-1}$), photosynthetic rates are relatively high, estimated at ~0.7 g C $m^{-2}$ $d^{-1}$ (Degnbol and Mapila 1982, Bootsma 1993b, Patterson and Kachinjika 1995). Phytoplankton abundance is low and comparable to Lake Superior (Guildford et al. 2000), but phytoplankton turnover rates are comparable to those in Lake Erie. This is attributed to the persistent high water temperatures and photosynthetically active radiation (PAR) (Kilham and Kilham (1990) resulting in relatively high rates of primary productivity and an efficient breakdown and recycling of nutrients in the epilimnion of tropical lakes (Talling 1965, Bootsma 1993b, Spigel and Coulter 1996, Lewis 2010). Photosynthetic rates in Lake Malawi vary seasonally with high rates observed during the cool, mixing and rainy season while the hot, stratified season displays the lowest rates (Bootsma 1993b, Patterson and Kachinjika 1995). The lake also displays spatial differences in photosynthetic rates, with the southern part of the lake having the highest rates due to upwelling of nutrient-rich water (Bootsma 1993b, Hamblin et al. 2003a). Hence there is a reason to believe that lake-atmosphere $CO_2$ flux will also vary temporally and spatially.

The current study presents results of monthly in situ surface $pCO_2$ concentrations acquired over one annual cycle along the north-south axis of Lake Malawi. We tested the following hypotheses: (1) Surface $CO_2$ concentrations will vary seasonally according to previously observed seasonality of phytoplankton productivity. (2) Because the southern part of the lake is the most nutrient-rich, with high phytoplankton biomass and photosynthetic rates, that region is a net $CO_2$ sink; (3) While lake surface temperatures are high throughout the year in Lake Malawi, the annual temperature fluctuation is small compared to that in temperate lakes and therefore biological effects will be the main driver of surface $pCO_2$ variability; (4) Selective recycling of dissolved P relative to $CO_2$ into the epilimnion from lower strata will promote net $CO_2$ uptake from the atmosphere.

## 2.2 Materials and Methods

### *2.2.1 Description of Study Site*

Lake Malawi lies between latitudes 9°30’S and 14°30’S and longitudes 033°30’E and 035°30’E at the extreme southern end of the East African Rift valley. The lake is one of the world’s oldest (5 – 10 million years old), largest (29,500 $km^2$) and deepest (max. 700 m) (Bootsma and Hecky 2003). The physical characteristics of Lake Malawi have been described by others (Bootsma and Hecky 1993, Cohen et al. 1993, Vollmer et al. 2002). The open waters of the lake are nutrient poor (concentrations of soluble reactive phosphorus (SRP) and dissolved inorganic nitrogen (DIN) are less than 0.1 $\mu mol\ L^{-1}$), but ammonia and soluble reactive phosphorus increase with depth reaching concentrations of 25 and 3.2 $\mu molL^{-1}$, respectively, in the anoxic monimolimnion below 200 m, (Bootsma and Hecky 1993, Wüest et al. 1996). Phytoplankton biomass in the open lake is low, water clarity is high (PAR extinction coefficient in the open waters range between 0.05 – 0.11 $m^{-1}$; (Bootsma 1993b, Guildford et al. 2000, Ngochera 2006) but phytoplankton photosynthetic rates are high (Degnbol and Mapila 1982, Bootsma 1993b, Patterson and Kachinjika 1995). The climatological conditions over Lake Malawi are divided into three distinct seasons, the hot, wet season (December – April), cool, dry season (May – September) and the hot, stratified season (October – November). The cool, dry season is characterized by relatively low air temperature (20 to 22 °C), accompanied by low surface water temperatures and strong southeast trade winds. During the hot, stratified season, wind speeds decline and air temperatures increase, resulting in lake surface temperatures as high as 29 °C and stronger, shallower stratification. The rainy season is variable but usually extends from December to April.

### *2.2.2. Data Collection*

A lake-wide sampling program on Lake Malawi aboard a passenger ferry, the *MV* Ilala, was conducted for a period of one year in 2013. In the southern region where the *MV* Ilala does not operate, the Fisheries Research Vessel, *RV* Ndunduma and smaller boats were used. While the vessels were underway, an onboard monitoring system was used to make continuous measurements of lake surface $pCO_2$, chlorophyll fluorescence, and temperature. On the *MV* Ilala and *RV* Ndunduma, valves were inserted into the sea-chest plumbing system, allowing lake surface water to be pumped into the onboard monitoring system. On the *MV* Ilala, the hull mounted intake was ~ 2 m below the waterline and the time between intake and measurement was ~ 2 seconds. On the *RV* Ndunduma, the intake depth was ~ 2.4 m and the time from intake to measurements was ~ 3 seconds. On smaller boats, intake tubing was submerged ~0.5 m below the lake surface by attaching to a vertical pole. The south-north cruise on the *MV* Ilala lasted on average about 6 days. For data analysis purposes, the lake was divided into five (5) zones (Fig. 3) based on catchment characteristics (Kidd 1983), previous plankton and water quality observations (Bootsma 1993a, Patterson and Kachinjika 1995), and transect orientation i.e. whether the *MV* Ilala was traveling on a south-north or west-east direction. In each zone, surface water samples (2m) were collected from 2 to 5 stations depending on the size of the zone. Samples were filtered on GF/F filters and analyzed for chlorophyll *a* (Stainton et al. (1977) and stable isotopes of carbon and nitrogen following the methods described in Ngochera and Bootsma (2011).

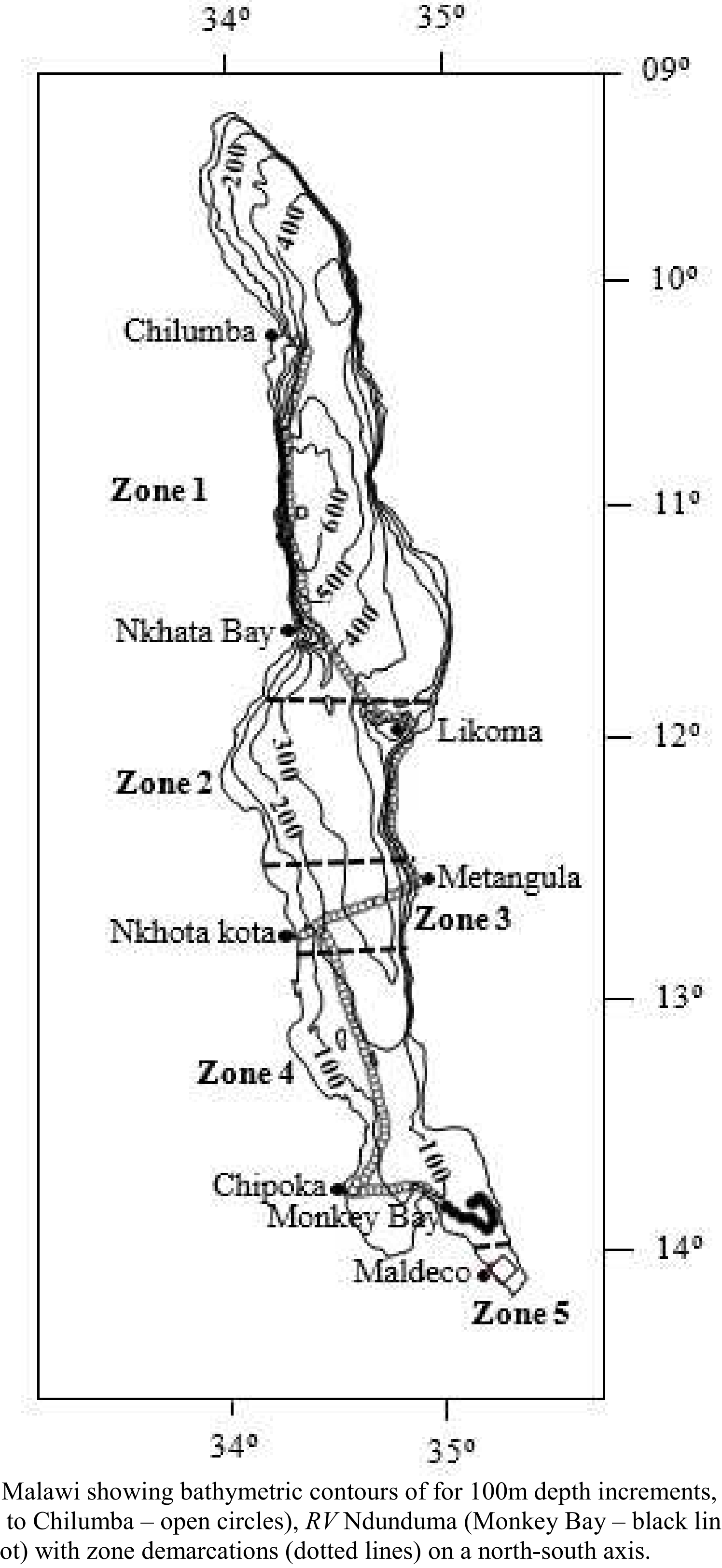


Figure 3: Map of Lake Malawi showing bathymetric contours of for 100m depth increments, sampling route with *MV* Ilala (Monkey Bay to Chilumba – open circles), *RV* Ndunduma (Monkey Bay – black line) and smaller boat (Maldeco – filled red dot) with zone demarcations (dotted lines) on a north-south axis.

### *2.2.3* **$pCO_2$** *measurements*

Surface water $pCO_2$ measurements were made using a real-time, in situ $CO_2$ measuring system. The $CO_2$ system consists of a “wet box” containing a peristatic water pump, an air-water gas equilibrator, a temperature sensor and a chlorophyll fluorometer, and a “dry box” containing a Li-Cor LI-820 infrared gas analyzer (IRGA), an oxygen sensor, a Campbell Scientific CR-1000 controller/logger, and an air pump connected to tubing that circulates air between the equilibrator in the wet box and the gas sensors in the dry box (Fig. 4). Air-water 95% gas equilibration time is < 90 s (Zagorski and Bootsma 2006). Lake water is pumped through the wet box at a rate of 400-500 ml $min^{-1}$ before discharging back to the lake. The dry box has a secondary air intake tube that allowed for measuring ambient air $pCO_2$, approximately 5 m above the lake surface. A solenoid valve was used to switch the air plumbing between the ambient air intake and water-equilibrated air on a 15 min cycle with 12 minutes of water sampling and 3 minutes of air sampling. A Garmin 16-HVS GPS receiver was attached to the logger, allowing all measurements to be georeferenced. Vessel speed reported by the GPS to the controller was used to switch the system on and off so that the system only operated while the vessel was underway. The temperature sensor in the wet box has an accuracy of $\pm 0.1^{o}C$. Several times per day during cruises, a bucket was used to draw water directly from the lake and a hand-held thermometer used to record the lake’s surface temperature. These temperatures were compared with the $pCO_2$ system measurements to determine whether water temperature changed between the point of intake and the point of measurement, as this would affect $pCO_2$ measurements. These measurements indicated that the temperature in the gas equilibrator was slightly warmer than in situ temperature, and so measured temperatures were corrected using the relationship $LST = 0.8289*L_T + 4.34$, ($r^2 = 0.84$, $p < 0.0001$) where LST is the corrected lake surface temperature and $L_T$ is the measured temperature. Measured $pCO_2$ was then corrected for warming to determine in situ surface $pCO_2$. IRGA-reported $pCO_2$ values, which are normalized to a pressure of 1.0 atmospheres, were corrected for local atmospheric pressure (recorded hourly at a lakeshore meteorological station) to determine in situ $pCO_2$. The IRGA was regularly calibrated using $CO_2$-free air (made by circulating atmospheric air through an ascarite column) and a $CO_2$ standard gas (399 ppm ± 2%).

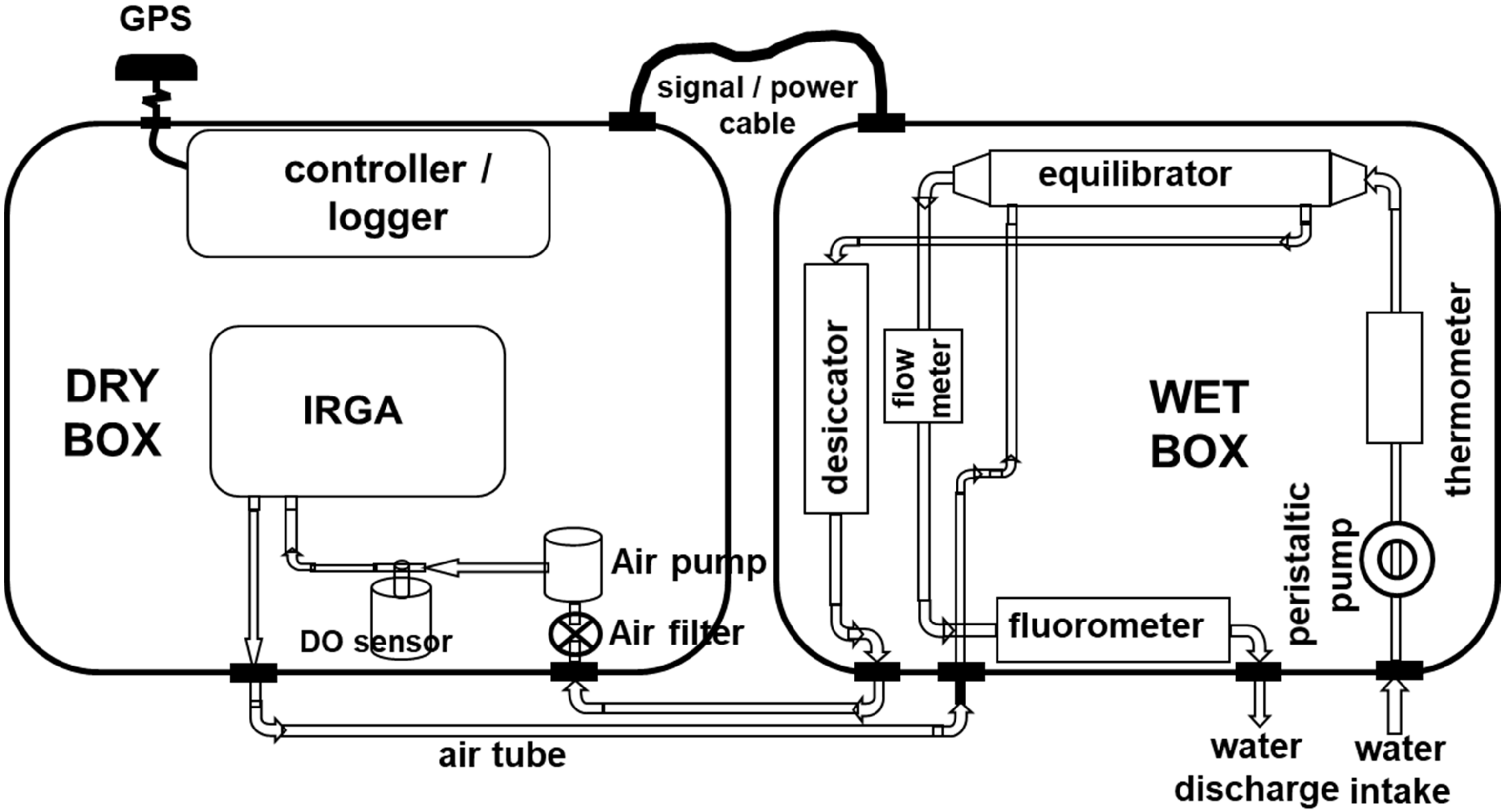


Figure 4: Automated *in situ* monitoring system for surface $pCO_2$, $pO_2$, temperature, and fluorescence. The “wet box” contains a peristatic water pump, an air-water gas equilibrator, a temperature sensor and a chlorophyll fluorometer while the “dry box” houses a Li-Cor LI-820 infrared gas analyzer (IRGA), an oxygen sensor, a Campbell Scientific CR-1000 controller/logger, and an air pump connected to tubing that circulates air between the equilibrator in the wet box and the gas sensors in the dry box. All data are geolocated using coordinates continuously provided by a GPS.

### *2.2.4 Air-water gas flux calculation*

Lake – atmospheric $CO_2$ flux was calculated as

$$\mathbf{F} = \boldsymbol{k}\mathbf{K_o}(\mathbf{pCO_{2w}} - \mathbf{pCO_{2a}}) \tag{1}$$

where $pCO_{2w}$ and $pCO_{2a}$ are the partial pressures of $CO_2$ in surface water and air, respectively (µatm), $K_o$ (mol m$^{-3}$ atm$^{-1}$) is the aqueous phase solubility of $CO_2$ (Weiss 1974) and $k$ is the vertical gas transfer coefficient (cm hr$^{-1}$) which was determined as a function of wind speed, using the model of MacIntyre et al. (2010),

$$\boldsymbol{k_{600}} = \mathbf{2.25}\ \boldsymbol{U_{10}} + \mathbf{0.16} \tag{2}$$

where $k_{600}$ is the transfer velocity (cm hr$^{-1}$) at a temperature of 20$^{o}$C (at which the Schmidt number for $CO_2$ is 600) and $U_{10}$ is the wind speed (m s$^{-1}$) normalized to a height of 10 m above the water surface (Peterson and Hennessey (1978).

We decided to use the MacIntyre et al. (2010) model as opposed to the model of Wanninkhof et al. (2009) because the MacIntyre model is calibrated for wind speeds between 1 and 8 m s$^{-1}$ whereas the Wanninkhof et al. (2009) model is more applicable for wind speeds that are $\geq$ 3 m s$^{-1}$. In addition, the MacIntyre et al. (2010) model does not produce a flux of 0 when wind speed is very low. We frequently observed wind speeds over Lake Malawi that were less than 3 m s$^{-1}$ and so this model is more relevant for those wind categories. Although MacIntyre et al. (2010) provide separate models for daytime and nighttime conditions to account for the effect of nocturnal cooling on near-surface mixing, we used the averaged relationship. According to MacIntyre et al. (2010), the effect of surface cooling is important when wind speeds are very low. Diurnal surface temperature fluctuations in Lake Malawi are highest during the winter period (June-September), but this period is also characterized by consistently higher wind speeds so that the effect of nighttime cooling on near-surface turbulence relative to the effect of wind speed would be very small. *k* values were corrected for temperature following the method described by Jähne et al. (1987),

$$\boldsymbol{k_T = k_{600}\, x\, (600/Sc_T)^n} \tag{3}$$

where $Sc_T$ is the Schmidt number for $CO_2$ at in situ temperature *T* (°C) and *n* depends on water surface conditions and varies from -0.67 to 1 (Cole and Caraco 1998). For purposes of this study, and in agreement with other authors (Alin and Johnson 2007), a value of -0.5 for n was used, which is typical of a wavy water surface free of films (Jähne et al. 1987). The Schmidt number was determined as a function of temperature using the following relationship (Wanninkhof 1992)

$$\boldsymbol{Sc_T = 1911.1 - 118.11T + 3.4527T^2 - 0.04132T^3} \tag{4}$$

where T is the lake surface temperature (LST).

Using the recorded water temperatures, aqueous carbon dioxide concentration $[CO_{2(aq)}]$ was calculated using Henry's solubility constant, $K_h$ (Harned and Davis 1943, Stumm and Morgan 1996) as

$$\mathbf{[CO_{2(aq)}] = pCO_{2(atm)}\ x\ K_h} \tag{5}$$

where $[CO_{2(aq)}]$ is in mol liter$^{-1}$, and $K_h$ in mol liter$^{-1}$ atm$^{-1}$.

Data analyses (descriptive statistics, two-way ANOVA and post hoc tests) were performed using SigmaPlot12.5 and OriginPro8 software to test for significant spatial and temporal variability in the measured parameters. Differences between means were considered significant at $p < 0.05\%$.

### *2.2.5 Interpolation of meteorological data*

Wind speeds over the lake were estimated from a single meteorological weather station in Senga Bay (10 – 20 m from shore depending on the water level) operated by the Senga Bay Fisheries Research Station installed at a height of 3.5m. The Malawi Department of Climate Change and Meteorological Services (DCCMS) has weather stations along Lake Malawi but these are several kilometers from shore and sometimes installed in shielded areas. Initially, estimates of over-lake wind speeds were derived using DCCMS wind data adjusted to over-lake conditions using the relationship of Hsu (1985), but the results compared poorly with previous direct observations of over-lake conditions (Hamblin et al. 2003b). To determine the validity of using Senga Bay wind speeds for the entire lake, data from one northerly station, Likoma Island (Fig. 3) collected between 1997 and 1999 were compared with Senga Bay data over the same period. A one-way ANOVA revealed significant differences in the annual wind speeds between Senga Bay and Likoma (F = 14.08, *F-crit* = 3.85, $p$ =0.00019). Therefore, wind speeds were grouped into four daily periods of 6 hours each and into three seasons: rainy, windy and hot, stratified (Table 2), and correction factors for each season/day period combination were calculated for zones 1 and 2. Data from Senga Bay were used for zones 3 to 5 without corrections as previous direct shipboard measurements (anemometer mounted on *RV* Usipa) revealed no significant difference between wind speeds in those zones and those at Senga Bay (Hamblin et al. 2003b). All wind speeds were adjusted to a common anemometer wind height of 10 m using the power law relationship;

$$\boldsymbol{U_{10} = U_r \, x \, \left(\frac{z}{z_r}\right)^{\alpha}} \tag{6}$$

where $U_r$ is the wind speed at the reference height $z_r$, $U_{10}$ is the wind speed at height $z$, and $\alpha$ is a parameter dependent on surface conditions and atmospheric stability which was set to 0.14 in agreement with the literature (Peterson and Hennessey 1978).

Table 2: Annual mean wind speeds by season and time of the day. The correction factors were used to adjust wind speeds observed at Senga bay for the specific season and time category that the *RV* Ilala was in zones 1 and 2.

| **Season** | **Time of day (hours)** | **Mean Annual Wind Speed (ms$^{-1}$)** | | **Factor** |
|---|---|---|---|---|
| | | **Senga Bay** | **Likoma** | |
| Hot, Stratified | 0 - 6 | 2.82 | 2.89 | 1.02 |
| | 6 - 12 | 3.69 | 3.93 | 1.07 |
| | 12 - 18 | 2.71 | 3.13 | 1.15 |
| | 18 - 24 | 1.50 | 1.87 | 1.25 |
| Hot, Wet | 0 - 6 | 2.92 | 1.71 | 0.59 |
| | 6 - 12 | 2.85 | 2.22 | 0.78 |
| | 12 - 18 | 2.22 | 2.30 | 1.04 |
| | 18 - 24 | 1.93 | 1.28 | 0.66 |
| Cool, Windy | 0 - 6 | 2.93 | 1.73 | 0.59 |
| | 6 - 12 | 3.45 | 2.87 | 0.83 |
| | 12 - 18 | 2.41 | 3.18 | 1.32 |
| | 18 - 24 | 2.04 | 1.39 | 0.68 |

### 2.2.6 Controls of $pCO_2$ in surface waters

In order to understand the main processes controlling the variability of $pCO_2$ in Lake Malawi, we applied the approach of Takahashi et al. (2002) which allows for separation of the surface temperature effect from other effects. The temperature component is what the measured $pCO_2$ temporal variability would be if it was only controlled by temperature, while the non-temperature component is the remaining variability after the temperature influence has been removed. The temperature component ($pCO_{2T}$) and non-temperature component ($pCO_{2B}$) were calculated using the following equations;

$$\boldsymbol{pCO_{2T} = \overline{pCO_2}\ x\ \exp[0.032\ (T - \overline{T}\,)]} \quad (7)$$

$$\boldsymbol{pCO_{2B} = pCO_2\ x\ \exp[0.032\ (\overline{T} -\ T)]} \quad (8)$$

where $\overline{pCO_2}$ and $\overline{T}$ are the annual mean surface $pCO_2$ and temperature, respectively. The value of 0.032°C$^{-1}$ represents the isochemical effect of temperature on $CO_2$ solubility in freshwater and was calculated using the relationship, $\partial \ln pCO_2 / \partial T$ over a range of temperature and corresponding saturation $pCO_2$ values following Atilla et al. (2011). The magnitude of the temperature and non-temperature effects on surface $pCO_2$ are then determined as:

$$\boldsymbol{\Delta pCO_{2T} = (pCO_2\ at\ T_{obs})_{max} - (pCO_2\ at\ T_{obs})_{min}} \quad (9)$$

$$\boldsymbol{\Delta pCO_{2B} = (pCO_2\ at\ T_{mean})_{max} - (pCO_2\ at\ T_{mean})_{min}} \quad (10)$$

with the subscripts "max" and "min" indicating the annual maximum and minimum values. To compare the magnitude of the temperature or non-temperature effects, the ratio and difference of the changes of the temperature and non-temperature effects were calculated:

$$\boldsymbol{(T/B) = \Delta pCO_{2T}/\Delta pCO_{2B}} \quad (11)$$

$$\boldsymbol{(T - B) = \Delta pCO_{2T} - \Delta pCO_{2B}} \quad (12)$$

The temperature effect is important when the ratio (T/B) is greater than 1 or the difference (T–B) is positive while the opposite signifies that non-temperature effects are strong. These effects are similar in magnitude if the ratio is 1 and the difference is 0.

### 2.2.7 Stable isotope analyses

A known volume of water (1000 – 2000ml) was filtered on 24 mm (diameter), 0.7µm pre-combusted GF/F filters. Dried filter samples were packed in tin foil and stored in a desiccator until analysis on a Costech 4010 Elemental Analyzer System coupled by a Thermo Scientific CONFLO IV gas control module to a Thermo Scientific Delta-V Plus Isotope Ratio Mass Spectrometer. Each sample run was preceded by a tin foil blank and standards of acetanilide. During sample runs, an acetanilide control sample was run every twelfth sample. $^{13}C$:$^{12}C$ ratios (expressed as $\delta^{13}C$ values) were determined relative to the PDB carbonate standard and are expressed as $\delta^{13}C$ (‰) values:

$$\boldsymbol{\delta^{13}C = \left[\left(\frac{R_{sample}}{R_{standard}}\right) - 1\right] x\ 1000} \tag{13}$$

where $R = \frac{^{13}\mathrm{C}}{^{12}\mathrm{C}}$

### 2.2.8 Weighted pCO2 and CO2 flux

To calculate seasonal and annual whole-lake $CO_2$ fluxes, zone-specific concentrations of $CO_2$ (µatm) and $CO_2$ fluxes (mmol C $m^{-2}$ $d^{-1}$) were weighted according to the area of each zone. Whole-lake monthly mean and standard deviations of $pCO_2$ and flux (F) were computed as:

$$\textbf{Weighted mean } \mathbf{pCO_2} \textbf{or F} = \frac{\sum(\boldsymbol{A_i}\ \boldsymbol{x}\ \boldsymbol{R_i})}{\boldsymbol{A_t}} \tag{14}$$

$$\textbf{Standard deviation} = \sqrt{\frac{\sum \boldsymbol{A_i}(\boldsymbol{R_i} - \bar{R})^2}{\boldsymbol{A_t}\left(\frac{\boldsymbol{n}-1}{\boldsymbol{n}}\right)}} \tag{15}$$

where $R_i$ is the measured $pCO_2$ or $CO_2$ flux in zone *i* for a specific month, $\bar{R}$ is the weighted mean $pCO_2$ or $CO_2$ flux, $A_i$ is the surface area of zone *i*, and $A_t$ is the total lake surface area.

## 2.3 Results

### *2.3.1 Meteorological conditions*

Weather conditions over the lake display a clear seasonality, with temperatures coolest between June and August (Fig. 5A), coinciding with high wind speeds (Fig. 5B). During this period, persistent southeasterly winds blow across the lake. The wet season (December to April) is characterized by relatively higher air temperatures and low wind speeds. The southern end of the lake cools more than the rest of the lake, with surface temperatures going below 23°C between June and August. Temperature profiles for the three seasons indicate that in the cool, windy period, mean water column temperatures at the southern end of the lake are similar to those recorded in the metalimnion and monimolimnion further to the north (Fig. 6B), reflecting upwelling of deep, cold water to the surface in the southern part of the lake at this time of year (Eccles 1962, Hamblin et al. 2003a).

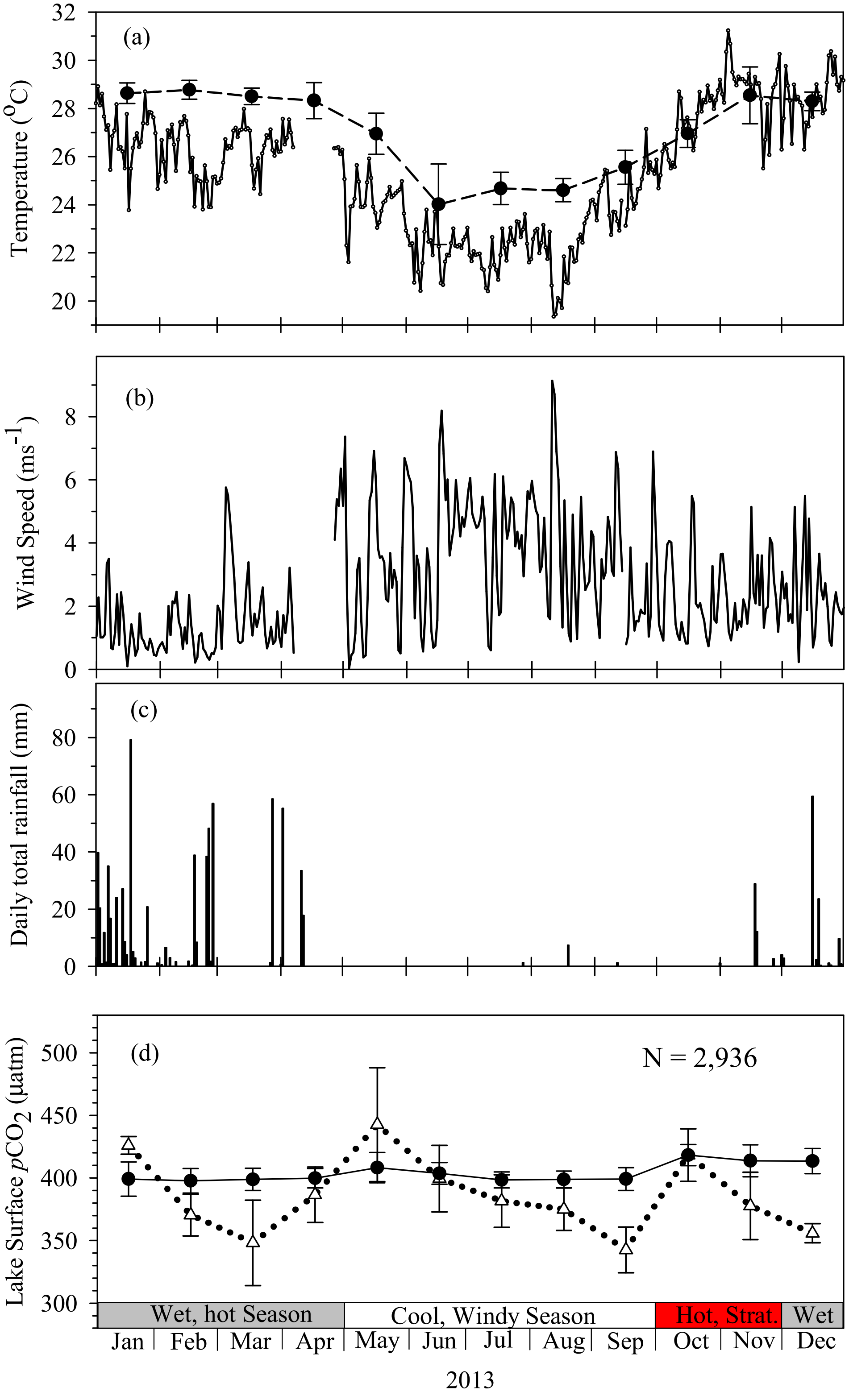


Figure 5: Variation of (A) daily mean air temperature (solid line) recorded at Senga Bay Research Station and whole – lake mean monthly water temperature (symbol and dotted line), (B) daily mean wind speed, (C) daily total rainfall, and (D) monthly mean air (solid line and cycles) and lake surface $pCO_2$ (dotted line and open triangles) with standard deviation.

### *2.3.2 Seasonal and Spatial variations in* **p$CO_2$**

Seasonal and spatial variations of lake surface p$CO_2$ are shown in Figs. 5D, 7 and 8. Surface waters were supersaturated with respect to the atmosphere during the hot, stratified season (October and November), and the early mixing season (May and June). However, during the wet, hot season (February and March) and the cool, mixing season (July to September), almost the entire lake was $CO_2$ undersaturated with respect to the atmosphere. p$CO_2$ measurements were near equilibrium with the atmosphere in April and December. In general, p$CO_2$ values were lowest during the rainy season and highest at the onset of the cool, mixing season (Fig. 5D and 8). Spatially, the southernmost zone (zone 5) displayed higher p$CO_2$ values than the other zones (Fig. 7). The annual mean p$CO_2$ in zone 5 was above saturation while mean p$CO_2$ in zones 1 to 4 was below saturation. To determine if there were significant differences in surface p$CO_2$ over time and among zones, the dataset from each zone was divided into three periods that coincide with the hydrological conditions in the lake i.e. wet season (December – April), windy mixing season (May – September) and hot, stratified season (October – November). The grouped p$CO_2$ data were then subjected to a two-way ANOVA with location and season as the two factors. Significant differences were observed among seasons ($p < 0.001$). A pairwise multiple comparison procedure (Tukey test) showed that differences were only significant between the hot, stratified season and the other two seasons. No significant difference was observed between the rainy and mixing seasons ($p = 0.236$). The analysis also indicates significant differences among zones ($p < 0.001$). However, the difference was only significant between the southernmost zone (zone 5) and the north-central zones (zones 1 to 4). No significant difference was observed among zones 1 to 4 ($p > 0.05$). There was no statistically significant interaction between zone and season ($p = 0.973$).

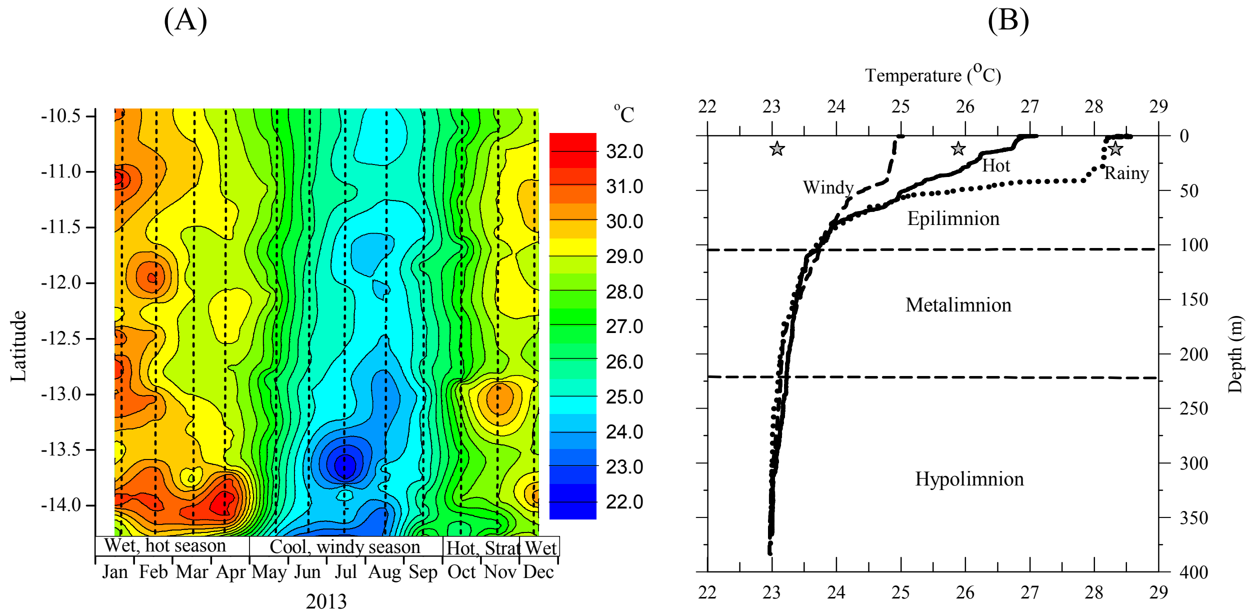


Figure 6: Contour plot of lake surface temperature along the north-south axis of Lake Malawi. Vertical dotted lines indicate cruise dates (A) Temperature-depth profiles measured at the northern station near Nkhata Bay for February, August, and November representing wet and hot, cool and windy and hot stratified seasons (B). Gray stars in (B) indicate depth-averaged temperatures (0 – 20 m) at the southernmost station (Zone 5) for the three climatological seasons and horizontal dotted lines are the water layer boundaries based on Vollmer et al (2002).

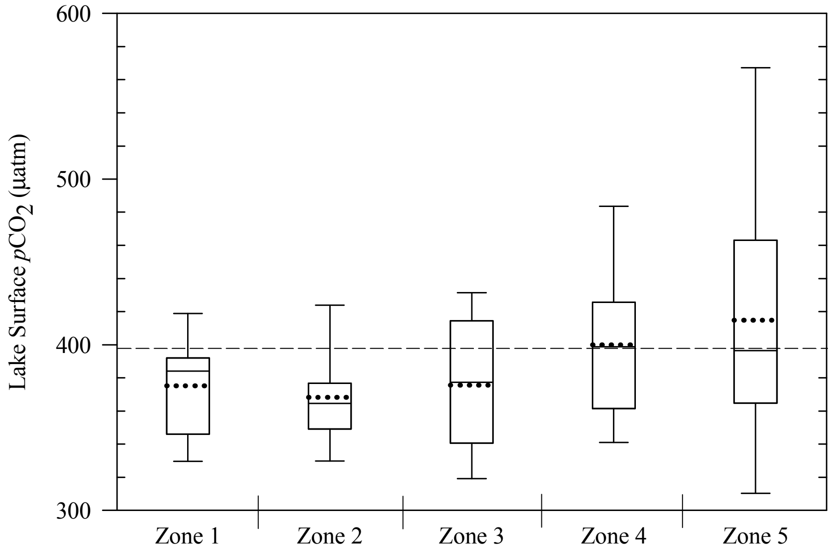


Figure 7: Spatial variation of lake surface $pCO_2$ measured in the five different lake zones. The dotted line of each box plot represents the annual mean, the solid line is the median while the upper and lower lines are the 75th and 25th percentiles, respectively. The upper and lower whiskers are the maximum and minimum $pCO_2$ values. The horizontal dotted line is the annual mean air $pCO_2$.

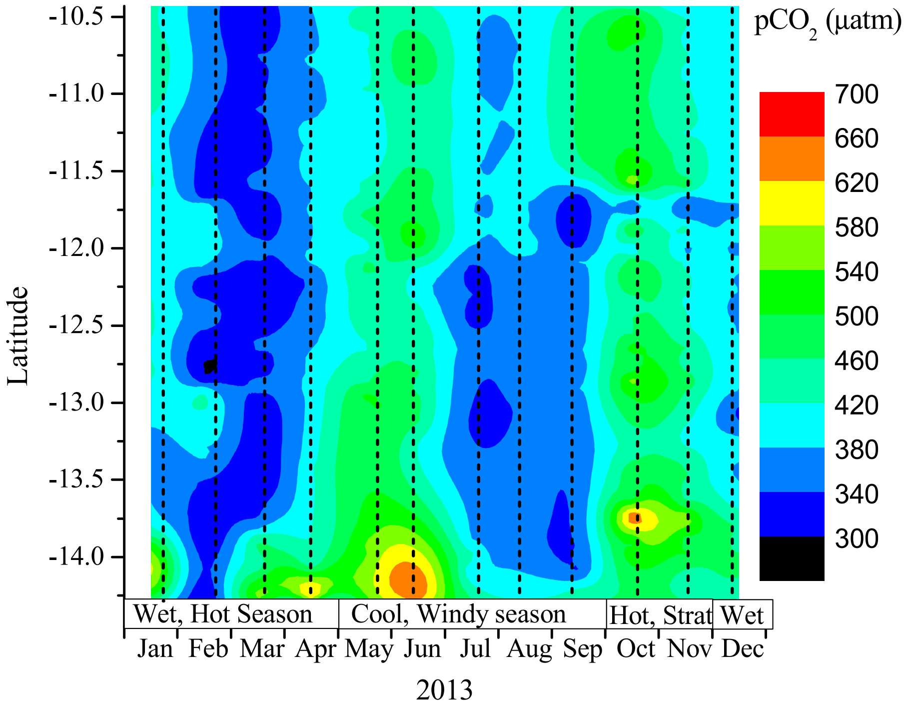


Figure 8: Spatial and temporal variation of surface pCO$_2$ (µatm) in Lake Malawi. Vertical dotted lines represent cruise dates on the south-north axis.

### *2.3.3 Seasonal and spatial variation in $CO_2$ fluxes*

Seasonal and spatial variations in C fluxes are provided in Figs. 9, 10 and Table 3. $CO_2$ fluxes display distinct seasonal patterns that coincide with temporal patterns of phytoplankton abundance and productivity previously observed in the lake (Bootsma 1993a, Patterson and Kachinjika 1995). Net $CO_2$ uptake by the lake is observed during the rainy season and the latter half of the cool, mixing season in all zones while net $CO_2$ efflux was observed at the onset of the cool, mixing season and during the hot, stratified season. The largest $CO_2$ flux into the lake is observed in September while highest evasion to the atmosphere was in May (Fig. 9, Entire lake). The dataset shows the spatial difference between the southernmost area and the rest of the lake. For most of the year, zones 1 to 4 were either net sinks of $CO_2$ or close to equilibrium with the atmosphere (Fig. 9, Table 3). By contrast, there is a net evasion of $CO_2$ from the lake to the atmosphere in zone 5. A two-way ANOVA with location and season as factors shows significant differences among both seasons and locations ($p < 0.001$), with no significant interaction of season and location ($p = 0.816$). Post hoc analysis indicates there was no significant difference between the rainy and mixing season ($p > 0.05$), and no significant difference was observed among zones 1 to 4 ($p > 0.05$). The areal-weighted mean annual $CO_2$ flux for the lake was estimated as –264.44±55.7 (95% CI: – 320.1 to – 208.7) mmol C $m^{-2}$ $yr^{-1}$, indicating that the lake is a net sink of $CO_2$ from the atmosphere (Table 3). Overall, Lake Malawi absorbs a total of 7.7±1.6 (95% CI: 6.1 to 9.3) x $10^{12}$ mmol C $yr^{-1}$ from the atmosphere.

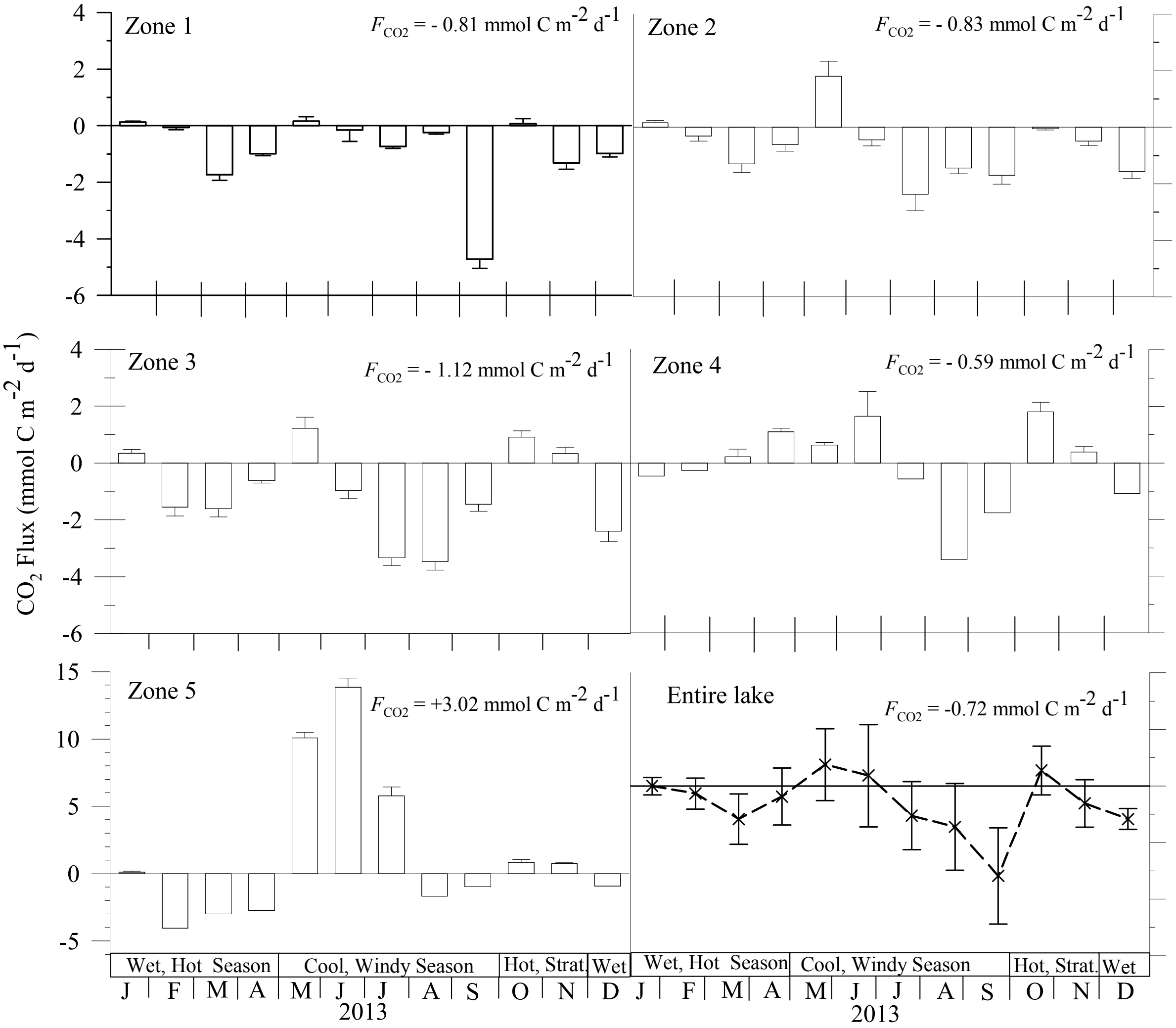


Figure 9: Mean monthly $CO_2$ fluxes and associated standard error bars for the five lake zones. The lower right figure displays monthly mean area-weighted $CO_2$ fluxes for the entire lake. The mean annual C fluxes for each zone and the entire lake are included on the respective plots. Positive fluxes indicate net evasion from the lake to the atmosphere while negative values are an invasion into the lake. Note the different $CO_2$ flux scale for zone 5.

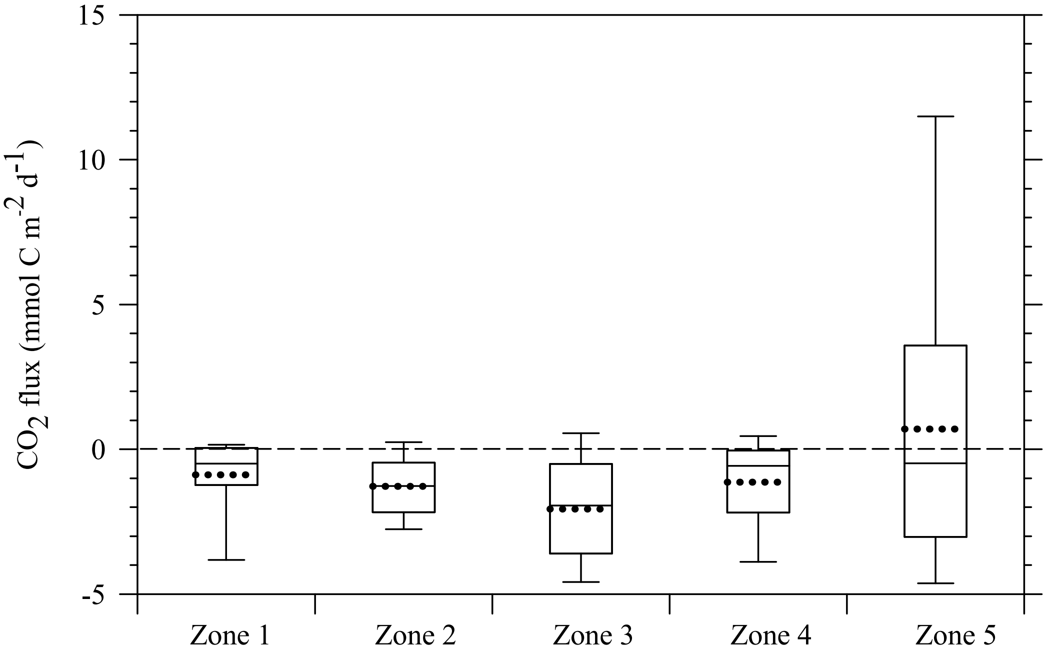


Figure 10: Spatial variation of $CO_2$ flux measured in the five different lake zones. The dotted line of each box plot represents the annual mean, the solid line is the median while the upper and lower lines are the 75th and 25th percentiles, respectively. The upper and lower whiskers are the maximum and minimum $pCO_2$ fluxes. The horizontal dotted line is the equilibrium point where net ecosystem production (NEP) is zero. Positive fluxes indicate net evasion from the lake to the atmosphere while negative values are an invasion into the lake.

Table 3: Zone surface area, annual mean wind speed, mean surface $pCO_2$ and associated $CO_2$ flux calculated using flux equations by MacIntyre et al (2010) and Wanninkhof et al (2009) herein referred to as M2010 and W2009, respectively. $CO_2$ fluxes include 95% confidence interval (C.I) for each zone. Lake-wide $pCO_2$ usable samples were 2,936

| Location | Surface Area ($km^2$) | Mean Wind Speed ($ms^{-1}$) | $\overline{pCO_2}$ (µatm) | M'2010 $\overline{pCO_2}$ flux (mmol C $m^{-2}$ $d^{-1}$) | W'2009 $\overline{pCO_2}$ flux (mmol C $m^{-2}$ $d^{-1}$) | 95% C.I $\overline{pCO_2}$ flux (mmol C $m^{-2}$ $d^{-1}$) |
|---|---|---|---|---|---|---|
| Zone 1 | 14,396 | 2.49 | 380.42 | - 0.80 | - 0.43 | (- 0.90, -0.69) |
| Zone 2 | 5,683 | 1.67 | 369.42 | - 0.83 | - 0.34 | (- 1.04, -0.62) |
| Zone 3 | 1,282 | 2.86 | 376.37 | - 1.12 | - 0.71 | (- 1.31, -0.91) |
| Zone 4 | 7,541 | 2.98 | 392.25 | - 0.59 | - 0.35 | (- 0.75, -0.43) |
| Zone 5 | 303 | 3.45 | 429.79 | +3.02 | +2.06 | (+2.20, +3.84) |
| Daily weighted mean $pCO_2$ flux (mmol C $m^{-2}$ $d^{-1}$) | | | | - 0.72 | - 0.42 | |
| Annual mean $pCO_2$ flux (mmol C $m^{-2}$ $yr^{-1}$) | | | | -264.4±55.7 (95%CI: -320.1 to -208.6) | | |
| Annual basin-wide $pCO_2$ flux (mmol C $yr^{-1}$) | | | | -7.7±1.6 (95%CI: - 9.4 to - 6.1) x $10^{12}$ | | |

### *2.3.4 Seasonal and spatial variation in chlorophyll a and seston $\delta^{13}C$*

A plot of phytoplankton biomass measured as chlorophyll *a* and seston $\delta^{13}$C values shows seasonal (Fig. 11A and C) as well as spatial (Fig. 11B and D) fluctuations in the lake. In general, seston $\delta^{13}$C revealed a seasonal pattern similar to that of chlorophyll *a* concentrations (Fig. 11A and C). Similar results were also observed by Ngochera and Bootsma (2011) who attributed the enriched seston $\delta^{13}$C during the wet and mixing seasons to enhanced phytoplankton growth rates during those periods. Spatially, the southernmost zone 5 which is considered the most productive area in the lake, showed higher chlorophyll *a* concentration and more enriched seston $\delta^{13}$C values than the rest of the lake (Fig. 11B and D). A two-way ANOVA showed significant differences in seston $\delta^{13}$C among both seasons ($p = 0.0105$) and zones ($p =0.0198$). Chlorophyll *a* concentrations were also significantly different among seasons and zones ($p < 0.05$). However, there was no significant interaction of season and zone ($p=0.783$).

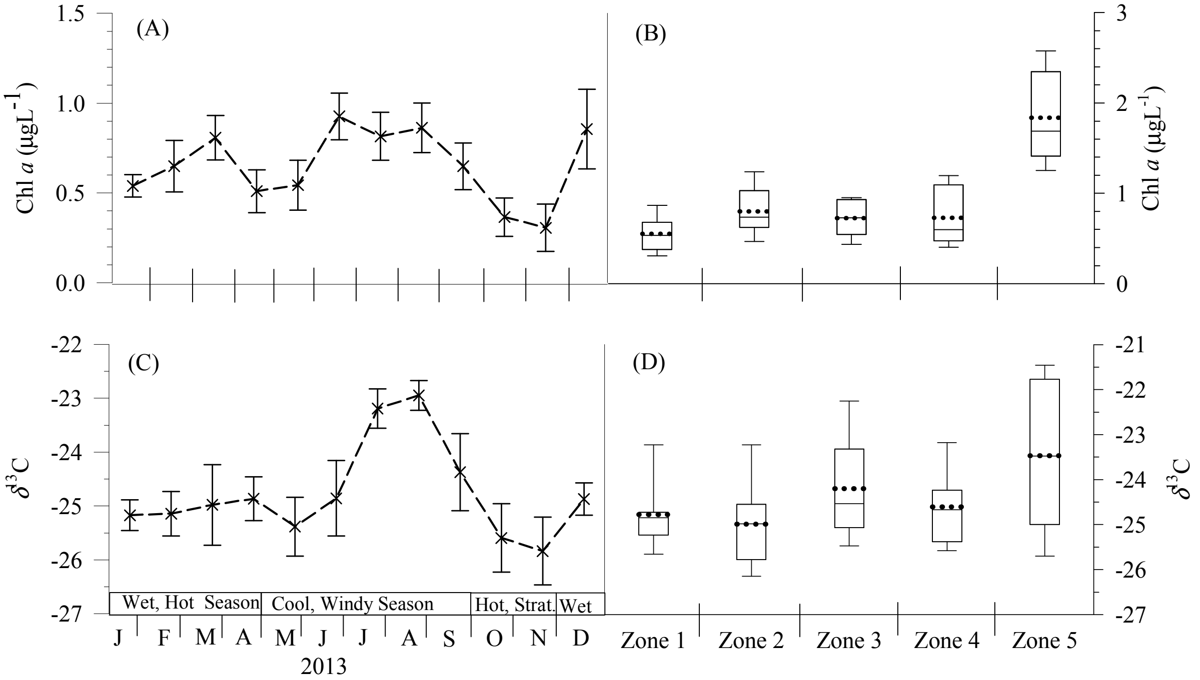


Figure 11: Seasonal and spatial variation of chlorophyll *a* (A and B) and carbon stable isotope (C and D) in surface waters of the lake. Error bars are included in A and C. The dotted line of each box plot represents the annual mean, the solid line is the median while the upper and lower lines are the 75th and 25th percentiles, respectively. The upper and lower whiskers are the maximum and minimum values.

### *2.3.5 Regulation of $CO_2$ and C flux in Lake Malawi*

To determine potential factors regulating surface $CO_2$ concentrations in Lake Malawi, changes in $pCO_2$ over time were decomposed into temperature-driven ($pCO_{2T}$) and non-temperature-driven ($pCO_{2B}$) components (Fig. 12). Because no difference was observed in the seasonal $pCO_2$ variations among zones 1 to 4, the data from these zones were combined and referred to as north-central region and was treated separately from the data for zone 5, referred to as the southernmost region. The dataset shows that seasonal temperature fluctuations have a minimal effect on surface $pCO_2$ because the ratio of T/B is less than 1 and the difference (T – B) is negative (Takahashi et al. 2002, Atilla et al. 2011). The magnitude of non-temperature effects is lowest in the north-central regions, with a T/B ratio of 0.44 and difference (T – B) of –59.55 µatm, while the southernmost region had higher non-temperature effects with T/B ratio of 0.32 and T-B difference of – 252.53 µatm. The significance of non-temperature effects is further underscored by the strong linear relationship between observed $pCO_2$ and $pCO_{2B}$, and the weak relationship between observed $pCO_2$ and $pCO_{2T}$ (Fig. 12C, 12D).

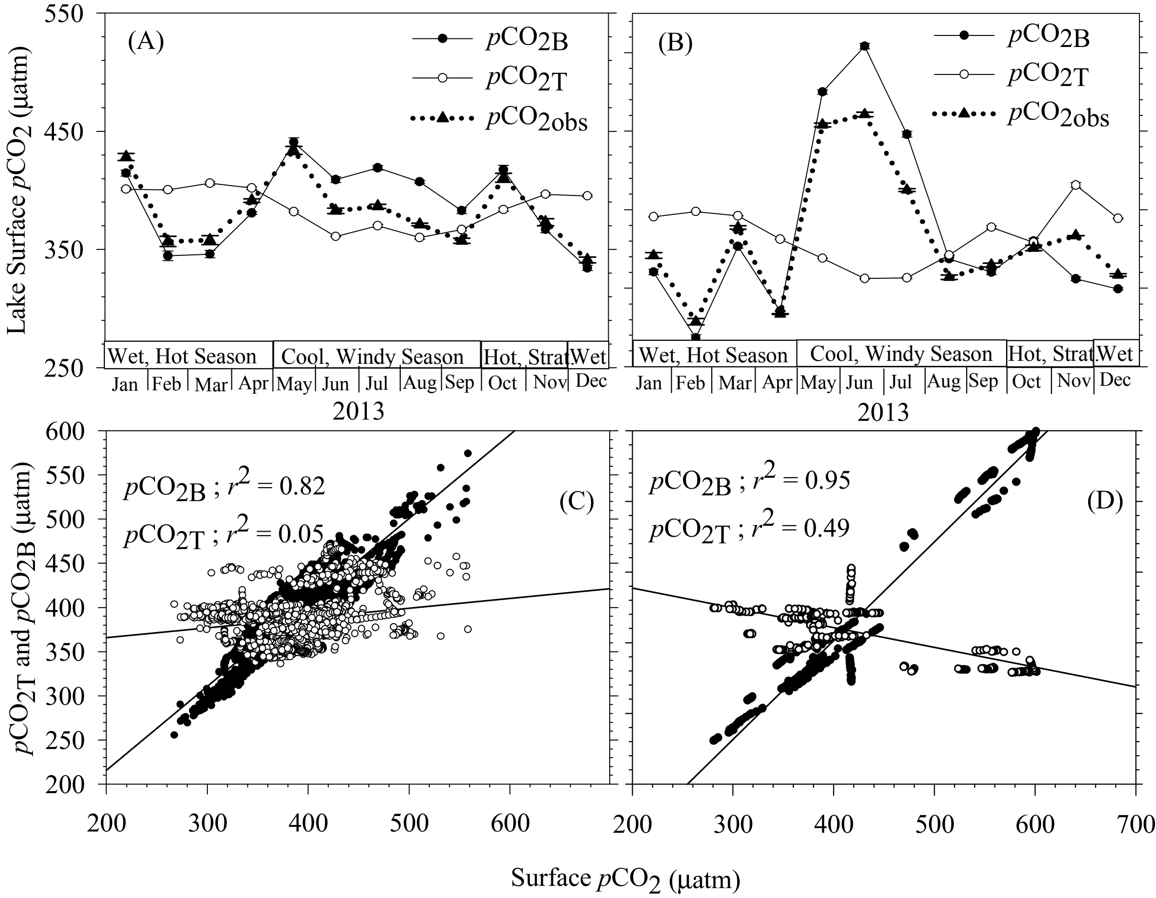


Figure 12: (A) Seasonal variation of observed pCO$_2$ (pCO$_{2obs}$), pCO$_2$ that would result from temperature change alone (pCO$_{2T}$), and pCO$_2$ with temperature effect removed (pCO$_{2B}$) in zones 1 to 4 combined. (B) The same observations for the southernmost zone (zone 5). (C and D) The relationship between measured lake surface pCO$_2$ and the temperature-driven pCO$_2$ (pCO$_{2T}$ - open circles), and the temperature effect removed (pCO$_{2B}$ - filled circles) in zones 1 to 4 (C) and zone 5 (D).

## 2.4 Discussion

The results presented here show distinct differences in $pCO_2$ and $CO_2$ fluxes over time and location that appear to be linked to hydrological and hydrodynamic conditions. With some exceptions, the seasonal pattern of surface $CO_2$ conforms to what might be expected based on previously observed patterns of phytoplankton productivity (Bootsma 1993b, Patterson and Kachinjika 1995, Patterson et al. 2000). Phytoplankton biomass and growth rates in the African Great Lakes vary in space and time (Jackson et al. 1963, Hecky and Fee 1981, Hecky and Kling 1987, Bootsma 1993a, Patterson et al. 2000). In a whole-lake study of phytoplankton photosynthesis, Bootsma (1993b) measured the highest photosynthetic rates during the mixing (June – September) and rainy (December – January) seasons, the same periods when surface $pCO_2$ was below saturation in the present study. Although internal nutrient cycling is important, the $CO_2$ undersaturation observed in the rainy season in Lake Malawi suggests the lake responds rapidly to external nutrient loading. This is perhaps because more than 60% of the river nutrient load is confined to the epilimnion ($P = 4.5 – 7.0$ mmol P $m^{-2}$ $yr^{-1}$), rather than being diluted over the entire water column (Patterson and Kachinjika 1995, Kingdon et al. 1999). Our results show seasonal as well as spatial variability that appears to be related to mixing regimes and the meteorological conditions occurring in the lake. Concurrent measurements of seston C stable isotopes and abundance revealed enriched $\delta^{13}C$ values and high Chl *a* concentrations in the wet (December - March) and mixing periods (May-August) when mixed-layer nutrient concentrations are high. In contrast, depleted $\delta^{13}C$ signals observed during the period of strongest stratification (October and November), coincided with low nutrient and Chl *a* concentrations in the surface mixed layer (Fig. 11A), and hence reduced photosynthetic rates (Bootsma 1993b, Guildford et al. 2007). Similar seasonal patterns in $\delta^{13}C$ were observed in a previous study in the lake (Ngochera and Bootsma 2011). These temporal planktonic $\delta^{13}$C fluctuations reflect seasonal patterns in phytoplankton primary productivity previously measured in the lake (Bootsma 1993b).

Spatially, the southernmost part of the lake (zone 5) was significantly different from the rest of the lake. At the lake's southern end, $pCO_2$ values were high at the same time that phytoplankton biomass and photosynthesis are usually high (Bootsma 1993b). This is the opposite of what we expected. The low surface temperatures during the cool, mixing season in zone 5 (Fig 6A & B) suggest there was upwelling at that time, and the high surface $pCO_2$ values indicate that the excess $CO_2$ supplied with this hypolimnetic water was not completely utilized by phytoplankton (Figs. 7 and 8). While this hypolimnetic water is also nutrient-rich, it appears that there is a lag in community metabolism response to these nutrients. In the initial stage of upwelling, the supply of excess $CO_2$ exceeds the ability of phytoplankton to utilize this $CO_2$. However, in the second half of the mixing season, zone 5 becomes a net sink for $CO_2$. This shift is likely due to loss of $CO_2$ in the initial stages of upwelling (due to evasion to the atmosphere and photosynthetic uptake) combined with recycling and retention of the phosphorus derived from upwelling, so that the ratio of phosphorus to excess $CO_2$ (i.e. the total amount of DIC above that at atmospheric equilibrium) is greater in the second half of the upwelling season. The high seston $\delta^{13}$C values measured in the southernmost zone suggest that phytoplankton growth rates are higher in this area. This region is the most productive part of the lake as it is relatively shallow, weakly stratified, and receives nutrients from the deep nutrient-rich waters during upwelling (Hamblin et al. 2003a). In addition, high chlorophyll *a* concentrations were also measured in this region of the lake (Fig. 11C), as has been observed in previous studies (Bootsma 1993b, Patterson and Kachinjika 1995, Hamblin et al. 2003a).

The lake-atmosphere C fluxes measured for Lake Malawi do not conform to the common tenet that oligotrophic lacustrine and marine systems tend to be net heterotrophic (del Giorgio et al. 1997, Duarte and Agusti 1998, Cole 1999, Duarte and Prairie 2005). The prevalence of net heterotrophic aquatic ecosystems implies that they must receive substantial amounts of allochthonous organic carbon (Prairie et al. 2002, Hanson et al. 2003, Duarte and Prairie 2005) and that organic C:P loading ratios must be high. Once the exported organic carbon enters aquatic ecosystems, it undergoes microbial and photochemical transformations (Cole 1999). However, the generalization of net heterotrophy in oligotrophic aquatic ecosystems has been viewed with some skepticism from both the freshwater (Carignan et al. 2000) and marine perspective (Karl et al. 2003). Prairie et al. (2002) and Hanson et al. (2003) report that there seems to be a tendency for oligotrophic systems to exhibit heterotrophy but ultimately this depends on the concentration of DOC. While Lake Malawi is oligotrophic in nature, $pCO_2$ concentrations and $CO_2$ flux rates measured in the current study suggest that the lake is a net $CO_2$ sink. Several studies have reported a general positive correlation between $pCO_2$ and DOC concentration in aquatic ecosystems (Jonsson et al. 2003, Sobek et al. 2005, Jonsson et al. 2008, Lapierre and del Giorgio 2012). The magnitude of terrestrial dissolved organic carbon inputs into adjacent aquatic systems depends strongly on the watershed to lake surface area ratio (Urabe et al. 2005). Indeed, aquatic ecosystems with a high watershed to lake area ratio display high DOC and $pCO_2$ concentrations, resulting in net heterotrophy (Kelly et al. 2001, Alin and Johnson 2007, Roehm et al. 2009, Kortelainen et al. 2013). For example, $pCO_2$ in small temperate lakes with high watershed to lake surface area ratio can range from 500 and 1,000ppm (Cole et al. 1994, Kelly et al. 2001, Striegl et al. 2001) while $pCO_2$ in small bog lakes can reach 10,000ppm (Riera et al. 1999). The watershed to lake area (WA: LA) ratio for Lake Malawi is small (3.4) compared to the small temperate lakes and bogs that display high DOC and $pCO_2$ concentrations, and is within the range of large African Great lakes (2.8 – 6.7) and the Laurentian Great Lakes (1.6 – 3.7) (Bootsma and Hecky 2003, Morana et al. 2015). In accordance with the general relationship between WA: LA and DOC, concentrations of dissolved organic carbon (DOC) in Lake Malawi are low (Ramlal et al. 2003). While the Lake Malawi watershed receives rainfall similar to that of the Laurentian Great Lakes (800-1200 mm per year), rapid evaporation rates leave many of the tributary rivers dry for much of the year. Hecky et al. (2003) reported DOC concentrations ranging from 125 to 575 $\mu$mol $L^{-1}$ (mean = 233 $\mu$mol $L^{-1}$) for thirteen major Lake Malawi tributaries. These are lower than those reported for most temperate rivers (Mulholland and Kuenzler 1979, Meybeck 1981, Schiff et al. 1990, Schiff et al. 1997). Therefore, the low DOC concentrations from tributary rivers together with limited river flows results in lower DOC loading into Lake Malawi. Unlike in most temperate ecosystems where rivers perennially flow, allowing the terrestrial material to decay and leach DOC (Meybeck 1981, McDowell and Asbury 1994), a higher proportion of terrestrial organic carbon may be retained or remineralized within the Lake Malawi watershed.

Surface $pCO_2$ concentrations observed in Lake Malawi are comparable to those reported for Lake Superior, which also has small catchment to surface area ratio (1.6) and low DOC concentration (Urban et al. 2005, Atilla et al. 2011, Lin and Guo 2016). However, Lake Superior appears to be net heterotrophic even though allochthonous organic matter concentration inputs are low (Urban et al. 2005) but see Atilla et al. (2011). According to Urban et al. (2005) and Cotner et al. (2004), although external organic inputs into Lake Superior are small, heterotrophic production (13 – 81 Tg C $yr^{-1}$) in the lake, exceeds autotrophic production (3 – 8 Tg C $yr^{-1}$) with a GPP: R ratio that ranges between 0.2 and 0.4. Because Lake Superior is holomictic, mixing brings a considerable amount of remineralized DIC from the deep to the surface waters (Cotner et al. 2000, Urban et al. 2005) which results in high $pCO_2$ concentrations in some months (Atilla et al. 2011). By contrast, Lake Malawi is deep and meromictic and has a long hydraulic residence time. The upward mixing of $CO_2$-rich waters in Lake Malawi is only accomplished primarily through localized upwelling events at the southern end of the lake. Another significant difference between these two lakes is hypolimnetic redox conditions. The hypolimnion of Lake Malawi is anoxic and under these conditions organic carbon decomposition rates may be reduced (Sobek et al. 2009), while there may be more efficient recycling of P. As a result, the ratio of excess $CO_2$ to dissolved P provided to the euphotic zone may be lower than the phytoplankton C:P ratio, so that phytoplankton $CO_2$ uptake over the lake as a whole exceeds the flux of $CO_2$ from the hypolimnion to the surface layer, creating a demand for atmospheric $CO_2$.

Global estimates of carbon fluxes often regard tropical lakes as having high surface $pCO_2$ because of persistent high temperatures that should favor high bacterial metabolism (Tranvik et al. 2009, Aufdenkampe et al. 2011, Raymond et al. 2013). But other studies have argued that warm temperatures may also promote biomass production when nutrients are not limiting (Lewis 2010). In fact, the balance between photosynthesis and respiration in temperate and tropical lakes may be comparable, as long as the processes are not substrate-constrained (Lewis 2010). Although Lake Malawi and some other deep tropical lakes are permanently stratified, the vertical temperature gradient is much smaller than in lakes of higher latitude (Lewis 1987). Hence, while complete mixing does not occur, seasonal changes in mixed layer depth and vertical mixing can result in large changes in nutrient supply to the euphotic zone (Hamblin et al. 2003a). Previous phytoplankton dynamics studies provide evidence that the year-round warm temperatures experienced in Lake Malawi result in high phytoplankton metabolic and rapid turnover rates

(Bootsma 1993b, Bootsma and Hecky 2003). Although chlorophyll *a* concentrations are relatively low in Lake Malawi (< 1 µg $L^{-}1$), phytoplankton photosynthetic rates are remarkably high, estimated at 0.7 g C $m^{-2}$ $d^{-1}$ (Degnbol and Mapila 1982, Bootsma 1993b, Patterson and Kachinjika 1995). High photosynthetic rates of up to 1.0 g C $m^{-2}$ $d^{-1}$ are also reported for Lake Tanganyika (Hecky and Fee 1981). So, even though phytoplankton biomass in the African Great Lakes are relatively low and comparable to Lake Superior (Vollenweider 1974, Guildford et al. 2000, Barbiero and Tuchman 2001), photosynthetic rates are high and similar to those observed in Lake Erie (Makarewicz 1993). In fact, if the Laurentian Lake classification standards (Vollenweider 1974) are applied to lakes Tanganyika and Malawi, they would be categorized as eutrophic. Therefore, the observed $pCO_2$ concentrations in Lake Malawi, are in perfect agreement with trends of phytoplankton photosynthetic rates.

The analysis of temperature effect on surface pCO2 indicates that non-temperature processes are the main driver of surface $pCO_2$ variability in the lake. Specifically, it appears that during the rainy season and the latter part of the cool, mixing season phytoplankton photosynthesis drives surface $CO_2$ below saturation while early in the mixing season, vertical mixing provides excess $CO_2$ to the epilimnion. During the hot, stratified season, it seems that decomposition of organic carbon exceeds photosynthesis within the epilimnion, resulting in $CO_2$ supersaturation since surface nutrient concentrations are typically very low during that period. The strong inverse relationship between observed $pCO_2$ and $pCO2_T$ at the southernmost region shows that when zone 5 cools, $pCO_2$ goes up, highlighting the fact that upwelling (which occurs when this zone cools) has a stronger influence on surface $pCO_2$ than temperature.

Our measured mean lake surface $pCO_2$ of 385 µatm and $CO_2$ flux of – 0.3 mol C $m^{-2}$ $yr^{-1}$ are different from earlier estimates ($pCO_2$ = 844 µatm; C flux = +5.3 mol C $m^{-2}$ $yr^{-1}$) in the lake that were calculated by Alin and Johnson (2007) using published pH, alkalinity and dissolved inorganic carbon (DIC) concentrations. Based on these previous estimates, they concluded that Lake Malawi was a net $CO_2$ source to the atmosphere. However, there is likely a large degree of uncertainty in their flux estimates, due to the use of data that was very limited in space and time, and to the errors that can result from calculating $CO_2$ concentration based on other variables within the inorganic carbon system (Raymond et al. 2013). While the current study did not encounter epilimnetic $pCO_2$ values as high as those reported by Alin and Johnson (2007) (the maximum we observed was 758 μatm), it is possible their measurements may have coincided with an episodic mixing event that resulted in high surface $pCO_2$. The data available to Alin and Johnson (2007) could not afford them a temporal analysis like that presented here, limiting their ability to explore mechanisms regulating lake-air $CO_2$ exchange. To further examine whether internal C and P recycling may regulate lake-atmosphere $CO_2$ exchange in Lake Malawi, we compared excess DIC: SRP ratios in the metalimnion and hypolimnion with epilimnetic seston C:P ratios. Excess DIC was calculated as the difference between the volume-weighted mean annual DIC concentration in the metalimnion or hypolimnion and the DIC concentration in the epilimnion. DIC and SRP profile samples were collected on three separate dates in April, August and October 2014 at a station near Nkhata Bay (max. depth 400m), coinciding with the three seasons in the lake. The excess DIC: SRP ratios in the metalimnion and hypolimnion are comparable, 93 and 96, respectively (Table 4) but are much smaller than the mean epilimnetic seston C:P ratio of ~200:1 (Ngochera and Bootsma 2018). The difference between excess DIC:SRP ratios and seston C:P ratios indicates that there is selective retention of carbon and preferential recycling of phosphorus within the hypolimnion (Table 4). If phytoplankton are utilizing all the SRP that is fluxed upwards into the epilimnion from the adjacent water strata, then the upward fluxing $CO_2$ should be augmented with atmospheric $CO_2$.

We compared our measurements of lake-atmosphere $CO_2$ exchange rates with those that would be expected based on the vertical fluxes of excess DIC and SRP and epilimnetic seston stoichiometry. Based on the requirement of a stoichiometric balance in the epilimnion, the net assimilation of $CO_2$ ($CO_{2a}$) can be expressed as a function of the flux of SRP into the epilimnion ($F_{SRP}$) and the C:P ratio of phytoplankton ($C{:}P_{seston}$):

$$\boldsymbol{CO_{2a} = F_{SRP}\ x\ C{:}P_{seston}} \tag{16}$$

If epilimnetic $CO_2$ remains at equilibrium with the atmosphere, then

$$\boldsymbol{CO_{2a} = F_{DIC} + F} \tag{17}$$

where $F_{DIC}$ is the flux of excess DIC from the metalimnion to the epilimnion and F is the lake-atmosphere $CO_2$ flux.

Table 4: Calculated volumes for each depth strata, vertical exchange coefficients (*k*), volume-weighted annual mean DIC and SRP concentrations, excess DIC, annual vertical excess DIC and SRP flux rates and ratios derived from these values. *k* values are from Vollmer et al. (2002) and excess DIC and SRP fluxes values represent annual exchange rate between a stratum and that underlying it.

| Stratum | Volume ($km^3$) | *k* (1/yr) | DIC ($\mu$mol $L^{-1}$) | SRP ($\mu$mol $L^{-1}$) | Excess DIC ($\mu$mol $L^{-1}$) | DIC flux (mmol C $m^2$ $yr^{-1}$) | SRP flux (mmol C $m^2$ $yr^{-1}$) | Excess DIC:SRP |
|---|---|---|---|---|---|---|---|---|
| Epilimnion (0 – 105m) | 2,754 | 0.27 | 2,273±14 | 0.49±0.25 | 0 | 2,320 | 13.4 | 174 |
| Metalimnion (105 – 220m) | 2,310 | 0.056 | 2,371±52 | 1.05±0.63 | 98 | 424 | 4.3 | 100 |
| Hypolimnion (>220m) | 2,711 | | 2,427±46 | 1.61±0.29 | 154 | | | |

The vertical fluxes of excess DIC and SRP are presented in Table 5. Solving for equation (13), $CO_{2a}$ = 2.68 mol C $m^2$ $yr^{-1}$. By comparison, $F_{DIC}$ = 2.32 mol C $m^2$ $yr^{-1}$. The difference between the two, 0.36 mol C $m^2$ $yr^{-1}$, must be made up by the flux of atmospheric $CO_2$ into the lake (F). By comparison, the lake-atmosphere $CO_2$ flux based on lake and atmosphere $pCO_2$ measurements is -0.24 mol C $m^2$ $yr^{-1}$. The difference between the two estimates may be due to 1) underestimation of $CO_2$ fixation from inshore regions as measurements of air-water $pCO_2$ were collected from offshore regions; 2) uncertainty regarding the annual mean SRP and DIC vertical gradients, and 3) error resulting from uncertainty in the estimates of *k* and the wind speeds used to derive *k*. Considering these various sources of uncertainty, the agreement between the two estimates of lake-atmosphere $CO_2$ flux is reasonably good and supports the use of the Macintyre et al. (2010) *k* model. The Wanninkhof et al. (2009) *k* model resulted in an annual flux rate 32% lower than the Macintyre et al. model. The difference is mainly due to the difference between the models at low wind speeds. The MacIntyre model is calibrated for wind speeds between 1 and 8 m $s^{-1}$ whereas the Wanninkhof model is more appropriate for wind speeds that are $\geq$ 3 m $s^{-1}$. Also, the MacIntyre et al. (2010) model does not result in a $CO_2$ flux of 0 even when the lake is calm. We frequently observed wind speeds over the lake that were lower than 3 m $s^{-1}$, underscoring the need for correct model parameterization at low wind speeds

# Chapter 3 - The relative roles of river loading and internal nutrient cycling in controlling $pCO_2$ flux.

## Abstract

Experiments to determine the effects of river nutrient and carbon loading and vertical exchange on the metabolism of Lake Malawi were conducted using hypolimnetic water and water from a major tributary during two seasons; the hot, wet season (January and April) and the cool, mixing season (August). The response to the two organic carbon and nutrient sources was measured through production and consumption of carbon dioxide, the biomass of chlorophyll *a* and particulate stoichiometry. Results show that the addition of river water to lake surface water resulted in $CO_2$ supersatuation, implying high respiration rates. This was corroborated by the low phytoplankton biomass and particulate organic carbon production. In contrast, the addition of hyoplimnetic water to lake surface water showed a net consumption of carbon dioxide indicating high carbon fixation rates resulting in high phytoplankton biomass and particulate organic carbon. Heterotrophy induced by the addition of river water was maintained by the high dissolved organic carbon: dissolved phosphorus (DOC: DP) ratio relative to that of lake seston, while autotrophy was promoted by the relatively low DOC: DP ratio in hypolimnetic water. Since these two mechanisms of organic carbon and nutrient supply to the epilimnion are seasonally distinct, seasonal changes in lake-atmosphere $CO_2$ flux can be expected. Over an annual cycle, vertical mixing is a larger source of nutrients to the epilimnion than river discharge is, which may explain why Lake Malawi appears to be a net $CO_2$ sink.

## 3.1 Introduction

Aquatic ecosystems derive their nutrients from allochthonous inputs and vertical exchange while organic carbon is supplied either by terrestrial loading or from primary production within the ecosystem. However, the relative role that these sources play in shaping ecosystem food webs and biogeochemical processes is a topic that is under debate (Cole et al. 2002). Recently, increasing attention has been given to the role of inland lakes in the global carbon cycle. The available data indicate that most lakes of the world are supersaturated with $pCO_2$ and therefore are net sources of $CO_2$ to the atmosphere (Cole et al. 1994, del Giorgio and Peters 1994, Hansen et al. 2003). One important finding is that the air-water $CO_2$ exchange is dependent on both the external supply of nutrients and carbon from the catchment (France and Peters 1995) and internal cycling of carbon and nutrients (Molot and Dillon 1997, Bachmann et al. 2000, Biddanda and Cotner 2002). According to Smith and Hollibaugh (1997), primary production in freshwater aquatic ecosystems is largely dependent on the availability of nutrients, primarily phosphorus (P), while respiration is dependent on the availability of labile organic material (DOC). Previous studies in Lake Malawi (Eccles 1974, Bootsma and Hecky 1999, Kingdon et al. 1999, Bootsma et al. 2003, Hamblin et al. 2003a), show that river inputs and internal mixing events result in increased phytoplankton production. Specifically increased primary productivity and biomass are observed during the rainy season when river flow is at its highest (Bootsma 1993b) and during the cool, mixing season when vertical mixing prevails (Patterson et al. 2000, Hamblin et al. 2003a). A large survey of Lake Malawi tributaries (Kingdon et al. 1999) revealed a mean ratio of TOC: TDP of about1,500:1. By comparison, in-lake seston C:P ratios range between 197–257:1 (Guildford and Hecky 2000, Ngochera and

Bootsma 2018). In contrast, the vertical exchange ratio of excess dissolved inorganic carbon to dissolved phosphorus (ExcessDIC: DP) reported in Chapter 2 indicates a ratio of 96:1.

Numerous studies have investigated the response of the phytoplankton community to manipulation of nutrient concentrations (Carpenter et al. 2001, Guildford et al. 2003). However, studies that examine the influence of total organic carbon and nutrient inputs from river discharge and internal vertical exchange on $CO_2$ lake-atmospheric exchange are nonexistent for tropical Lake Malawi. Based on the C:P ratios of river loading, internal mixing, and seston in the lake, one might logically expect river loading and internal mixing to have opposite effects on $CO_2$ concentration. However, both sources have several different forms of organic carbon and phosphorus, and the bioavailability of these different forms, as well as their roles in the lake's energy and nutrient cycles, are not known. Several studies indicate that soluble reactive phosphorus (SRP) is the available pool for phytoplankton rather than the particulate phase (Cotner and Wetzel 1992, Auer et al. 1998). Therefore, experiments are needed to determine if the phytoplankton response to C and P inputs from these two sources will be as predicted.

The aim of the current study was to deterime the relative roles of river loading and internal cycling in controlling $pCO_2$ variability in Lake Malawi. We test the hypothesis that since the TOC:TDP ratio of river water is higher than seston C:P, the riverine input will promote net $CO_2$ production while vertical exchange will drive net $CO_2$ uptake because the TOC:DP of hypolimnetic water is lower compared to in-lake seston. To simulate the influence of riverine and vertically fluxed OC and P, we conducted experiments by spiking epilimnetic lake water with river water during the 2014/2015 rainy season and hypolimnetic water in the mixing period when upwelling is strongest.

## 3.2 Methods

### *3.2.1 Sampling and experimental procedure*

The general approach was to incubate epilimnetic water samples that had been spiked with either hypolimnetic water or river water, and monitor changes in aqueous $CO_2$, soluble reactive phosphorus (SRP), DOC, particulate organic C and N, and chlorophyll *a* over time. Water for the hypolimnion spike experiments was collected from a deep location in the northern part of the lake (11.5542°S, 034.3134°E; max. depth 400 m) while water for the river spike experiment was collected from a central station (13.7131°S, 034.6731°E; max. depth 140) and from the Linthipe River, a major Lake Malawi tributary that drains a highly disturbed watershed of approximately 8,560 $km^2$ (Hecky et al. 2003). Epilimnetic samples consisted of water pooled from 15, 20 and 25 m depths, bracketing the depth at which chlorophyll *a* concentration is usually the greatest. This integrated sample was regarded as the control where no river or hypolimnetic water was added. For hypolimnion spike experiments, epilimnetic water was spiked immediately after collection with 5% of hypolimnetic water collected from a depth of 300 m. Likewise, river spike experiments used epilimnetic water mixed with 5% Linthipe River water. The mixture was passed through a 210 µm Nitex nylon mesh to remove zooplankton and any other large particles. A total of 900 ml sample was incubated in 1000 ml clear and dark glass bottles (leaving a headspace of 100 ml) for a period between five and 15 days. Two Teflon tubes (one short, extending down into the headspace, and one long, extending down into the water) were fitted through silicone stoppers into the air-tight bottles. The long tubing was used to draw water from the bottle and circulate it through an air-tight $CO_2$ measurement system that included an in-line gas equilibrator, fluorometer, and micro-thermometer (described in Chapter 2). After flowing through the $CO_2$ system, the water was returned to the incubation bottle through the short tubing. During the day, light bottles were illuminated overhead with an irradiance of approximately 100 µmol photons $m^{-2}$ $s^{-1}$ to simulate the light-dark cycle and light intensity was monitored using a Biospherical quantum sensor (400 – 700nm) as described by Bootsma (1993b). Incubator bottles were placed in a bucket and temperatures were maintained by a continuous slow flow of tap water. Bottles used for dark respiration were covered in black plastic vinyl paper, then wrapped in aluminum foil and kept in a dark place. The temperature in the dark bottles was monitored regularly to make sure it was within the range of light bottles. Samples were run in duplicate. Measurements of $pCO_2$ and temperature were made daily between 4 and 6 am representing dark respiration and 3 to 5 pm for day photosynthesis. In between sample analysis, the system was flushed with distilled water for five minutes. $pCO_2$ measurements were used to calculate aqueous $CO_2$ concentrations by correcting to ambient atmospheric pressure and multiplying by Henry's solubility constant as described in the equation 21. In addition, measurements of pH (using a portable Mettler Toledo SevenGo Duo$^{TM}$), soluble reactive P (SRP), particulate organic C (POC), particulate P (PP), dissolved organic carbon (DOC) and extracted chlorophyll *a* were made at the beginning and end of each experiment. The hypolimnion spike experiments were conducted beginning 30th August 2014 and 29th April of 2015 while the Linthipe River spike experiments were conducted starting from the 19th January 2015. CTD casts (Sea-Bird SBE19 profiler) were made at each of the stations where epilimnetic water was collected to provide initial conditions of temperature, dissolved oxygen, and pH.

## *Chemical analysis*

### *3.2.2 Dissolved organic carbon*

DOC samples were filtered through 0.45µm pore size membrane filters and the filtrate was preserved in phosphoric acid in dark glass, pre-cleaned bottles and kept in a fridge at 4°C until shipped to the University of Wisconsin-Milwaukee School for Freshwater Sciences for analysis. The analysis was done on Shimadzu Total Organic Carbon 5000 analyzer equipped with an ASI-5000 auto sampler using the high temperature combustion catalytic oxidation method. The detection range is 4 µg $L^{-1}$ – 30,000 mg $L^{-1}$. 25 ml DOC samples were acidified with 2-3 drops of 1N HCl to attain a pH of 2 or less, allowing for the purging of all inorganic carbon prior to OC analysis.

### *3.2.3 Particulate organic carbon*

To determine particulate organic carbon, 250 ml of each sample was filtered onto a pre-combusted (500°C for 2 hours) GF/F filter and dried in a desiccator. Samples were shipped to the UWM – School for Freshwater Science and analysis was conducted on a Costech 4010 Elemental Analyzer System coupled by a Thermo Scientific CONFLO IV gas control module to a Thermo Scientific Delta-V Plus Isotope Ratio Mass Spectrometer. Each twelve-sample run was preceded by a blank and an acetanilide control to ensure instrument calibration. Acetanilide standards were run after every twenty-four samples and a standard curve was used to convert the millivolt (mV) spikes in $CO_2$ for each sample to total POC mass. Using the known filtered volumes, POC concentration was determined. To avoid build-up of ash in the combustion column, the column insert containing quartz wool and chromium oxide was replaced after every twenty-four-sample run.

### *3.2.4 $CO_2$ measurements*

$CO_2$ concentration in each of the bottles was determined by measuring the $CO_2$ partial pressure ($pCO_2$) in the bottle, similar to the approach described by Davies et al. (2003). However, instead of using syringes to draw $CO_2$ from the headspace and measuring on a gas chromatograph, $pCO_2$ was measured directly by pumping water from the bottles through an air-water gas equilibrator. The equilibrated air is pumped through Nafion® tubing embedded in silica gel desiccant to remove water vapor, after which the air flow through an infrared gas analyzer (Li-Cor LI-820) which reports $pCO_2$ normalized to 1 atmosphere. $pCO_2$ in the dark and light bottles was measured twice daily, at dawn and dusk to determine dark respiration and net photosynthesis, respectively. Partial pressures of carbon dioxide were converted to aqueous concentrations by correcting to ambient atmospheric pressure (*kPa*) and multiplying by Henry's solubility constant, $K_h$, (Weiss 1974):

$$[CO_2]\ (\mu mol\ L^{-1}) = pCO_2\ (\mu atm)\ x\ \frac{kPa}{101.325}\ x\ K_h \tag{21}$$

### *3.2.5 Soluble reactive (SRP) and particulate phosphorus (PP)*

To determine particulate phosphorus, 250 ml of each sample was filtered onto a pre-combusted GF/F filter and dried in a desiccator. PP samples were analyzed as SRP after persulfate digestion of ashed samples by combustion of filters at 500°C for 2 hours followed by heated digestion using 10 ml of 1M HCL at 105°C for 1 hour. Soluble reactive phosphorus samples were determined spectrophotometrically on the filtrate by the molybdate-ascorbic acid method (Stainton et al. 1977).

### *3.2.6 Chlorophyll a*

To measure chlorophyll a, 250 ml of each sample was filtered onto a GF/F filter under low pressure and low-light conditions wrapped immediately in aluminum foil and kept in a freezer if chlorophyll *a* extraction was not done same day. Chlorophyll *a* on GF/F filters was extracted using a 10 ml mixture of acetone (27%), methanol (68%) and water (5%) and storing in a freezer for 24h. Fluorescence was measured on a Turner Series 10 fluorometer according to Stainton et al. (1977).

# 3.3. Results

## *3.3.1 Physical conditions*

Profiles of water temperature, dissolved oxygen and $CO_2$ at the time of collecting water for the hypolimnetic experiment are provided in Fig. 13. Hypolimnetic experiment 1 (April) was conducted during a strongly stratified period when the epilimnion was relatively shallow, while the second experiment was done during the cool, windy season (August) when mixing depth increased. Mean epilimnetic water temperature was 28.1°C during the hot, wet season (January and April) and 24.9 °C in August. There are no distinct seasonal changes in temperature for waters deeper than 200 m with an estimated mean of 22.98 ± 0.01°C. Measurements of dissolved oxygen show levels that are >50% saturation in the epilimnetic waters (0 – 105 m) but decrease sharply with anoxic conditions prominent between 200 and 210 m (Fig. 13). The concentration of dissolved oxygen was always highest between 20 and 30 m which also approximates the depth of chlorophyll maximum (DCM), (Guildford et al. 2000). The concentration of dissolved $CO_2$ indicates low values in the surface mixed waters with a mean of 12.89 ± 0.11 and 14.17 ± 0.04 $\mu mol\ L^{-1}$ in the hot, wet season and the cool, dry season, respectively. $CO_2$ concentrations increased with depth and a steep gradient is observed at the epilimnion and metalimnion boundary (105 m). Aqueous $CO_2$ for waters deeper than 200 m ranged between 169.22 and 246.40 $\mu mol\ L^{-1}$.

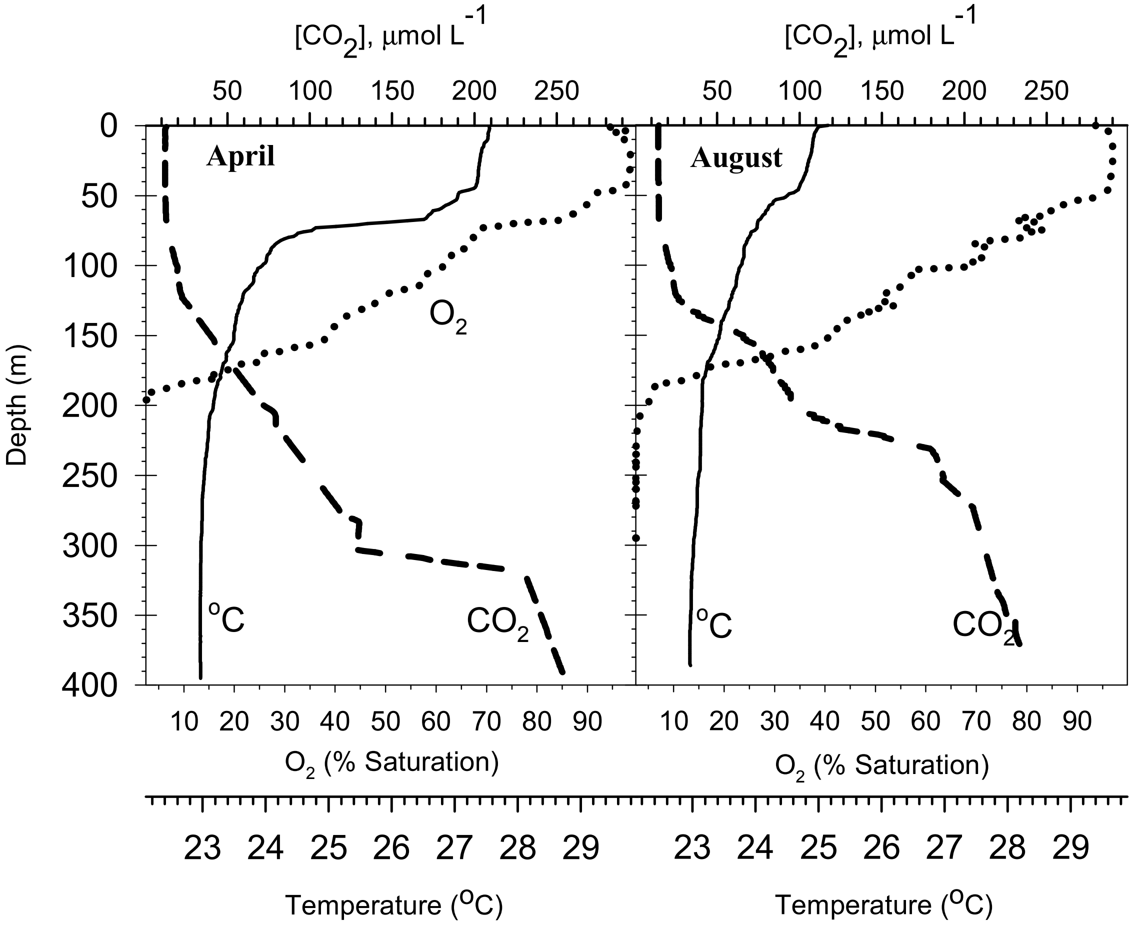
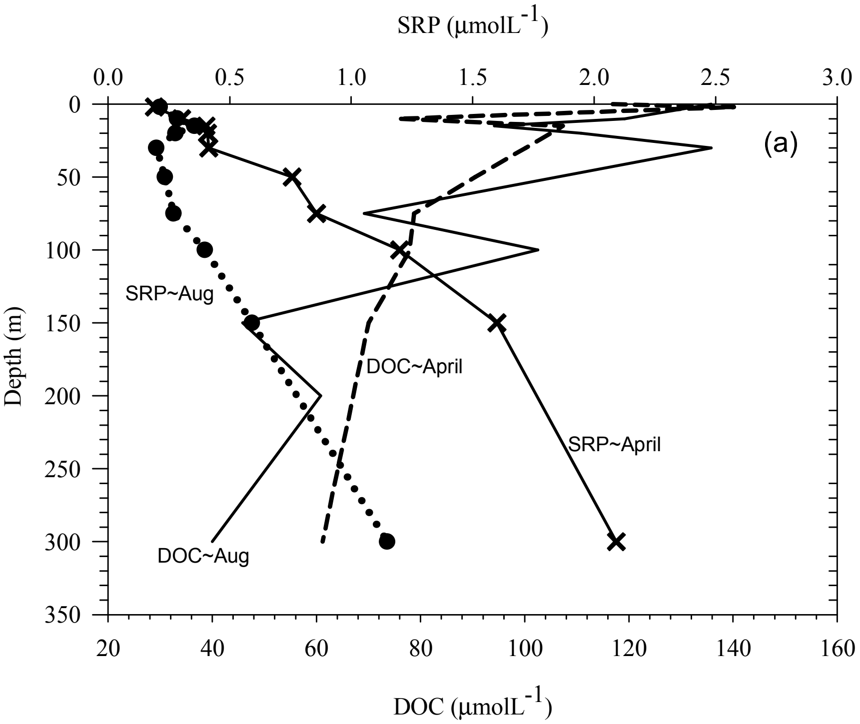


Figure 13: Depth profile of aqueous carbon dioxide, temperature and dissolved oxygen at the northern station of Nkhata Bay, where water for the hypolimnetic experiment was collected from. Profiles were taken on 30th August 2014 and 29th April 2015.

### *3.3.2 Chemical conditions*

#### *3.3.2.1 Lake Malawi*

Profiles of DOC and SRP that were taken at the northern and central locations for the hypolimnetic and river water experiment are provided in Fig. 14. There was no spatial difference in DOC and POC concentration in the epilimnion of the two locations (DOC = 80 to 140 μmol $L^{-1}$ and POC = 10 to 20 μmol $L^{-1}$). At the northern station, DOC declined with depth and ranged between 40 and 60 μmol $L^{-1}$ in the hypolimnion. The POC: DOC ratio in the lake shows that DOC is the dominant pool than POC varying between 0.25 and 0.14 in the epilimnion. As previously observed, soluble reactive phosphorous (SRP) is low in the surface waters but increase with depth (Fig. 14 a & b). SRP concentrations are highest in the hypolimnion. The C:N:P ratio shows distinct differences with strata. For example, in the epilimnion, the observed C:P, N:P, and C:N were 176, 17 and 11, respectively while in the epilimnion ratios of 88, 13 and 7 for C:P, N:P and C:N were recorded, respectively. This signifies an increase in P with depth relative to carbon. The concentration of chlorophyll *a* in the epilimnion of the northern and central station fluctuated between 0.4-0.8 μg $L^{-1}$ and 0.8-1.2 μg $L^{-1}$, respectively.



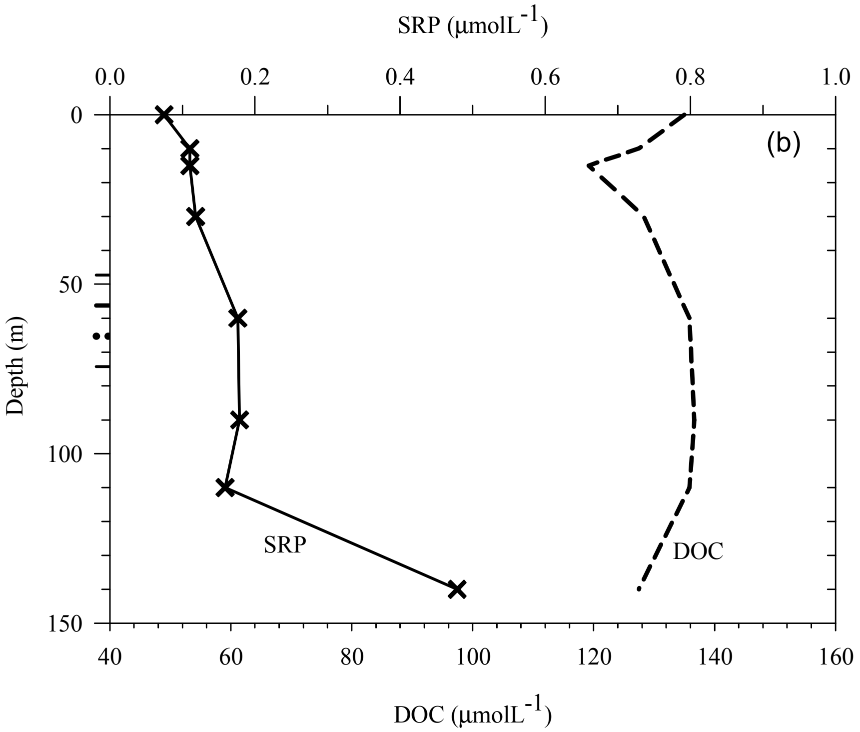


Figure 14: Depth profile of DOC and SRP concentrations at the northern station of Nkhata Bay (a) and central station (b), where water for the hypolimnetic and river experiment was collected from, respectively. Profiles for the northern station were taken on 30th August 2014 and 29th April 2015 while the central station was taken on 19th January 2015.

#### *3.2.1.2 Linthipe River*

The Linthipe River drains one of the most highly disturbed river catchments within Lake Malawi and has unusually high sediment and nutrient loads compared to other tributary rivers (McCullough 1999, Hecky et al. 2003). The estimated total catchment area of Linthipe River is 8,560 $km^2$ consisting primarily of weathered loamy sandy soils. During the 2014/15 rainy season, the river discharged a total of $9.50 \times 10^9$ $m^3$ into the lake (Chapter 4). Estimates of DOC from Linthipe River at the time of conducting the experiment (January 2015), ranged between 280 ± 32 µmol $L^{-1}$. In contrast, POC concentration was estimated at 1500 ± 148 µmol $L^{-1}$ for the same period. This represents a POC: DOC ratio of approximately 5 indicates that most of the organic carbon load from the Linthipe River is in the particulate form. Based on results from Chapter 4, on an annual basis, the volume weighted mean DOC and POC concentrations in Linthipe River were 274 and 989 µmol $L^{-1}$, respectively. By comparison, soluble reactive phosphorus fluctuated between 0.32 and 0.98 µmol $L^{-1}$, representing a POC:DP ratio of 2,187:1 and 1,500:1. The flux of phosphorus (SRP, TDP, and PP) from all rivers into the epilimnion of Lake Malawi fluctuates between 5.4 and 8.4 mmol P $m^{-2}$ $yr^{-1}$ (Bootsma and Hecky 1999). However, a majority of the phosphorus pool is in the particulate form (PP accounts for over 80%). In contrast, most of the phosphorus inputs into the epilimnion from the vertical exchange is in the dissolved form, SRP = 8.1 mmol P $m^{-2}$ $yr^{-1}$ and TDP = 7.7 – 22.4 mmol P $m^{-2}$ $yr^{-1}$ (Bootsma and Hecky 1999).

### *3.3.2 Response to the addition of hypolimnetic water*

The concentration of $pCO_2$ and change in aqueous carbon dioxide [$CO_2$] in the treatment and control bottles are provided in Fig. 15. $pCO_2$ at the start of the experiment was relatively higher in August (Fig. 15a) than those recorded in April (Fig. 15). An increasing trend in $pCO_2$ is observed for all incubation bottles in August. Although all samples increased over time, the light spiked incubation bottle displayed lowest $pCO_2$ throughout the study period. In contrast, the April experiment shows that $pCO_2$ in the dark spiked bottles increased with time while the light spiked bottles declined after day three. For both experiments, $pCO_2$ in the dark spiked bottles were always higher than the controls.

For each experiment, we calculated the difference between the dissolved $CO_2$ in the spiked and control bottles at each time point and plotted these differences against time (Fig. 15c and d). Results show a negative trend for the light bottles for both the August (coefficient of determination $r^2 = 0.33$) and February (coefficient of determination $r^2 = 0.38$) experiments indicating net $CO_2$ consumption and a positive trend in dark bottles signifying $CO_2$ production. Chlorophyll *a* concentration at the start and end of the experiment are provided in Fig. 16 and Table 5. There is a general declining trend in all incubation bottles except for the light spiked bottle. Particulate organic carbon was also highest in the light spiked bottle at the end of the experiment (Fig. 16, Table 5). Unlike chlorophyll *a*, POC was always higher at the end of experiment. The ratio of C:Chl (µmol:µg), a general indicator of nutrient deficiency (either phosphorus or nitrogen) and changes in light conditions (Healey and Hendzel 1979, Healey 1985), varied between 10 and 19 for the initial measurements and 13 to 43 for the final estimates. Chlorophyll *a* and POC concentrations were highest in the spiked light bottles and at the end of the incubation period while in all other bottles chlorophyll *a* and POC were either lower than or comparable to initial conditions (Fig. 17). The DOC: DP ratio shows relatively lower values at the start of the experiment than at the end (Table 5). The POC: PON ratio ranged between 9 and 25 which according to Healey and Hendzel (1979) is within the range of moderate and somewhat extreme nitrogen deficiency.

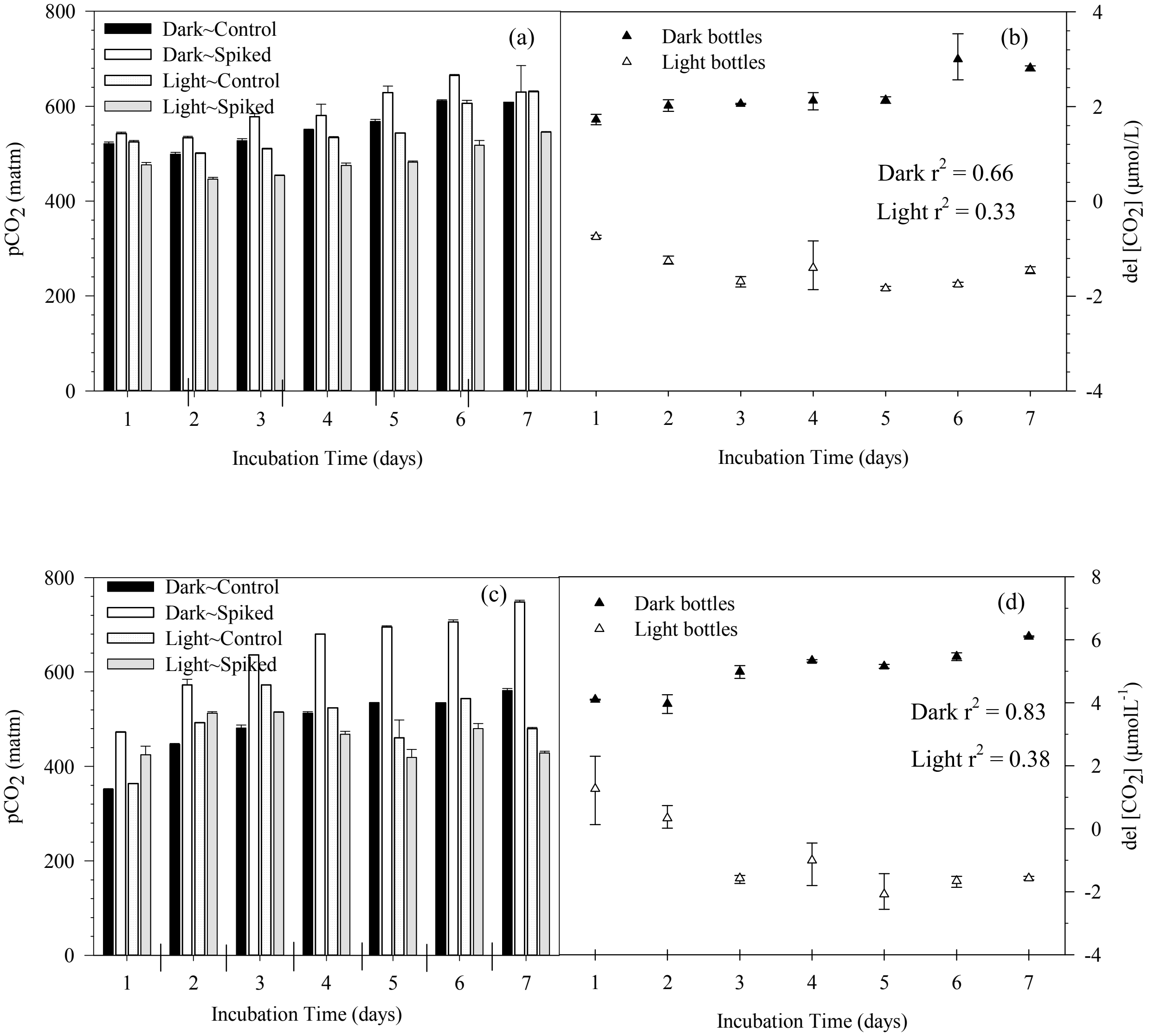


Figure 15. a: Concentration of $pCO_2$ over time in dark and light control (northern station epilimnetic water only) and hypolimnion-spiked bottles (5% of hypolimnetic water). and b: the difference between treatment and control bottle aqueous $CO_2$ concentrations over time for August 2014. Lower panel (c and d), same as above but for April 2015. Ranges (minimum and maximum; vertical lines) and coefficients of determination ($r^2$) are included.

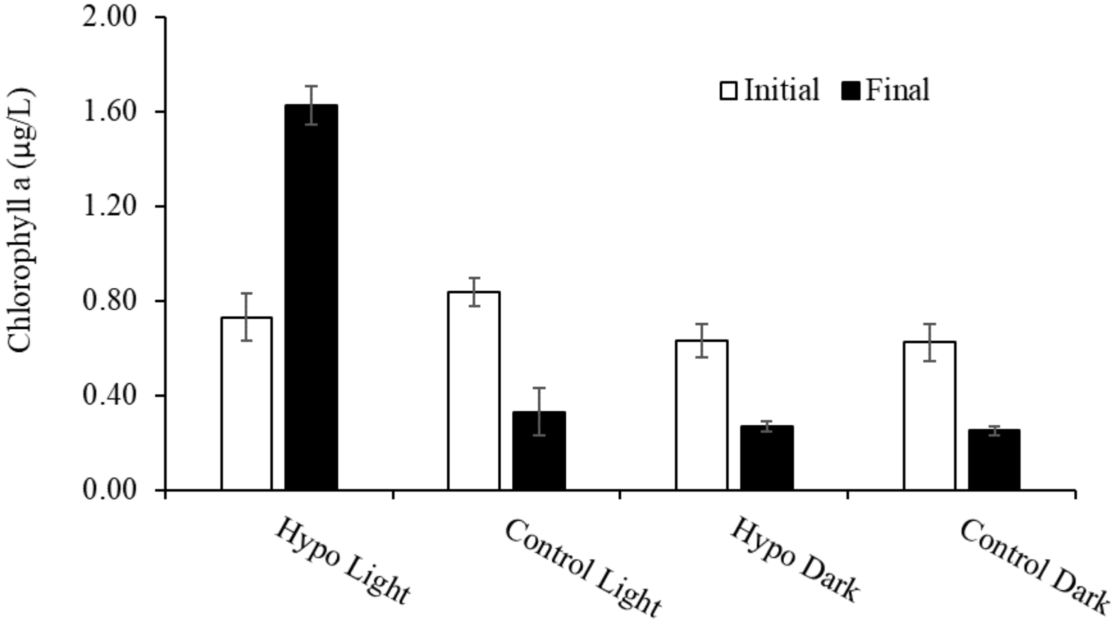


Figure 16: Initial and final concentrations of chlorophyll *a* in the hypolimnetic water experiment. Spiked bottles (5% of hypolimnetic water) and control bottles (northern station epilimnetic water). Vertical lines represent the range between the minimum and maximum of two bottles.

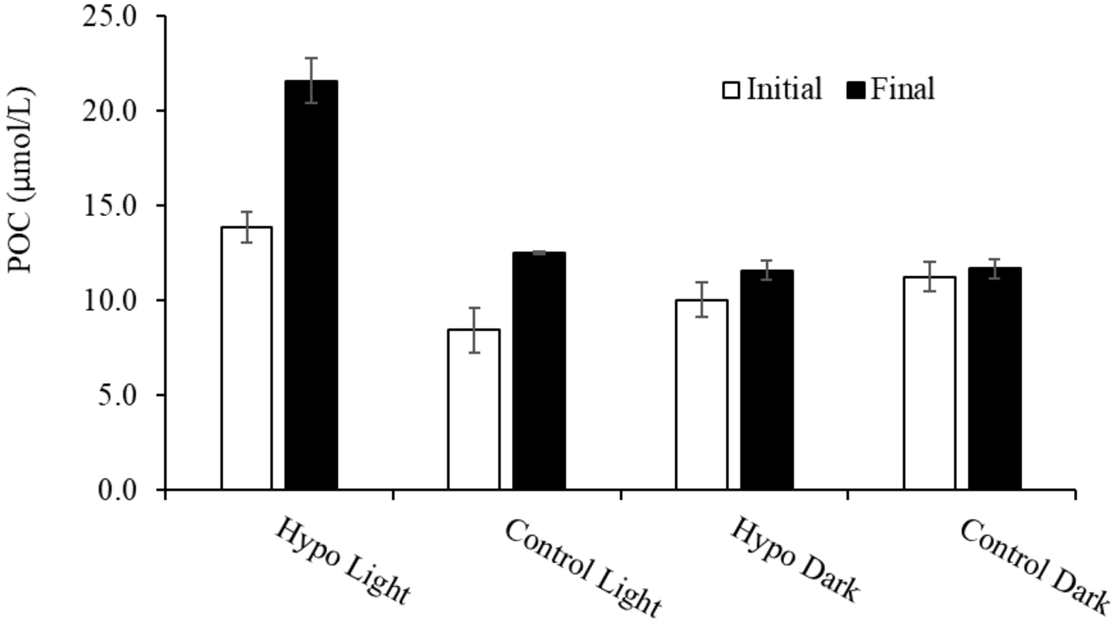


Figure 17: Initial and final concentrations of particulate organic carbon (POC) in the hypolimnetic water experiment. Spiked bottles (5% of hypolimnetic water) and control bottles (northern station epilimnetic water). Vertical lines represent the range between the minimum and maximum of two bottles.

Table 5: Initial and final concentration of various parameters and ratios for the start and end of the experiment in which lake water was spiked with hypolimnetic water.

| Parameter | Initial | | Final | | | |
|---|---|---|---|---|---|---|
| | Light/Dark | | Light Bottles | | Dark Bottles | |
| | Spiked | Control | Spiked | Control | Spiked | Control |
| Chl a (µg/L) | 0.63 - 0.75 | 0.62 - 0.84 | 1.55 - 1.71 | 0.23 - 0.43 | 0.25 - 0.29 | 0.23 - 0.27 |
| DOC (µmol/L) | 109.36 - 122.03 | 92.91 - 107.31 | 141.07 - 149.16 | 109.87 - 110.12 | 140.71- 145.62 | 116.43 - 124.26 |
| SRP (µmol/L) | 1.35 - 1.74 | 0.20 - 0.33 | 0.12 - 0.16 | 0.18 - 0.24 | 0.22 - 0.28 | 0.19 - 0.26 |
| POC (µmol/L) | 10.03 - 13.83 | 8.42 - 11.24 | 20.37 - 22.77 | 12.40 – 12.60 | 11.07 - 12.07 | 11.16 - 12.16 |
| PON (µmol/L) | 0.96 - 1.09 | 0.66 - 0.76 | 2.19 - 2.45 | 0.49 - 0.56 | 1.19 - 1.30 | 0.70 - 0.76 |
| POC:Chl *a* | 16 - 18 | 10 - 18 | 13 | 29 - 54 | 41 - 44 | 45 - 48 |
| DOC:SRP | 63 - 70 | 325 - 465 | 932 - 1,175 | 458 - 610 | 520 - 640 | 477 - 613 |
| POC:PON | 9 - 14 | 11 - 17 | 9 - 10 | 23 - 26 | 10 | 15 |

### *3.3.2 Response to the addition of Linthipe River water*

$pCO_2$ and the concentration of dissolved carbon dioxide [$CO_2$] in the river-spike experiment are provided in Fig. 17. Except for the light control bottles which show relatively stable $pCO_2$ concentration over time, a generally increasing trend in $pCO_2$ is observed for spiked light and dark bottles and the dark control throughout the study period. (Fig. 18a). Both light and dark incubation bottles experienced an increase in $CO_2$ concentration relative to that of controls over time (Fig. 18b).

In all bottles, there is a definite decrease in chlorophyll *a* and POC over the study period, although the change in chlorophyll *a* in the spiked light bottle was small (Fig. 19 and 20). The ratio of POC: Chl (µmol:µg) varied between 42 and 56 for the initial measurements and 10 to 148 for the final estimates. The DOC: DP ratio shows relatively higher values ranging between 614 to 1,609 for the initial measurements and 852 to 1,507 for the final estimates. The POC: PON ratio ranged between 7 and 19 which is within the range of moderate and extreme nitrogen deficiency.

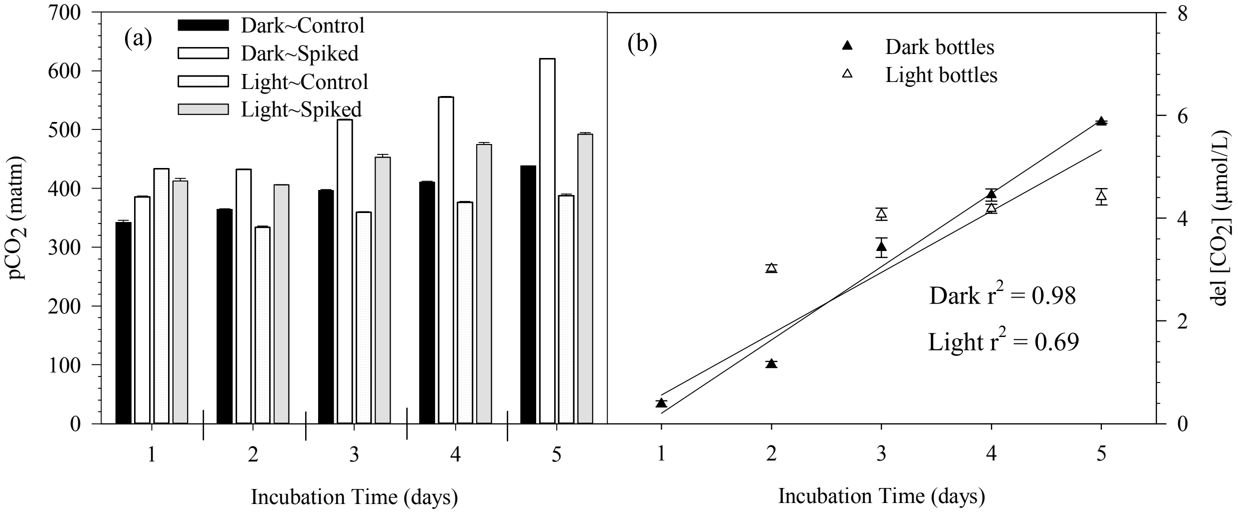


Figure 18: a: Concentration of $pCO_2$ over time in dark and light control and river-spiked bottles (5% of Linthipe River water). b: Difference between spiked and control bottle (epilimnetic water only) aqueous $CO_2$ concentrations over time. Ranges (minimum and maximum; vertical lines) and coefficients of determination ($r^2$) are included.

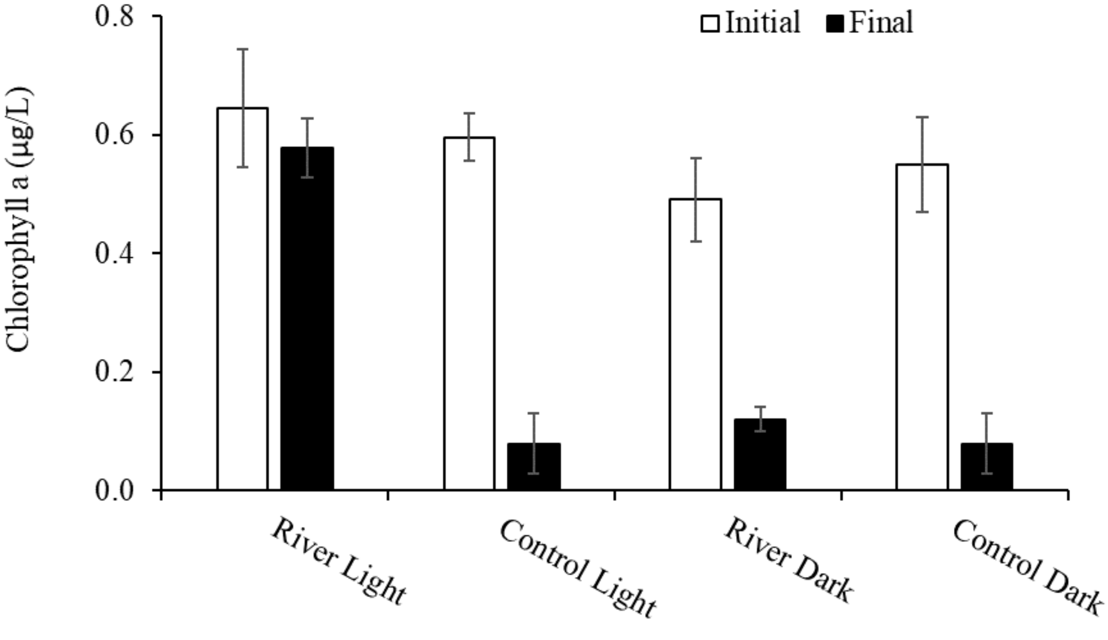


Figure 19: Initial and final concentrations of chlorophyll *a* in the river water experiment. Spiked bottles (5% of Linthipe River water) and control bottles (central station epilimnetic water only).

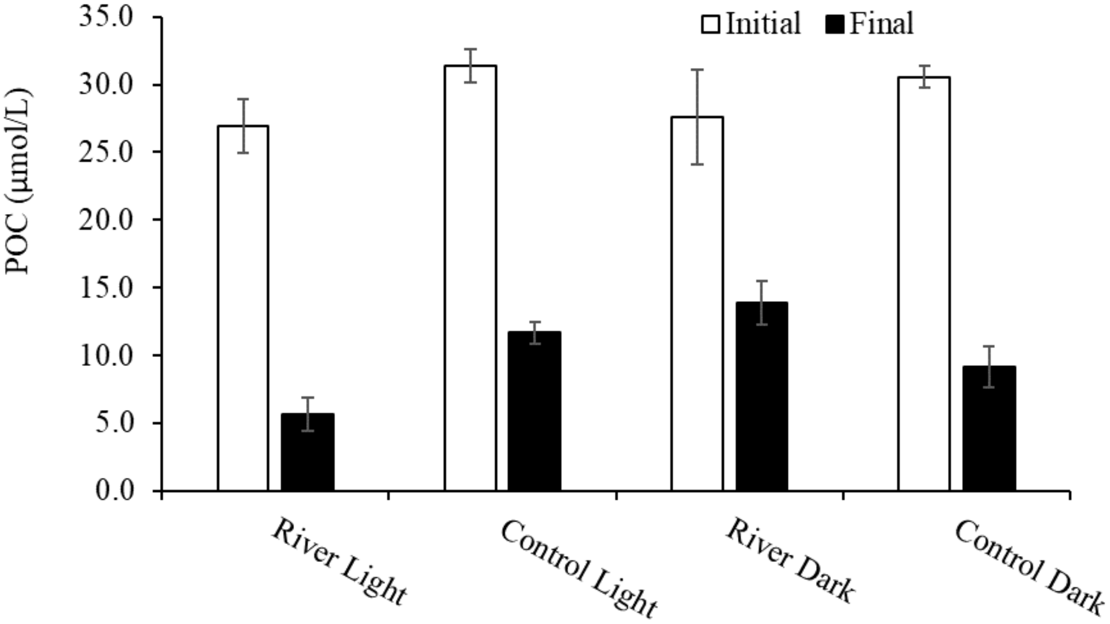


Figure 20: Initial and final concentrations of particulate organic carbon (POC) in the river water experiment. Spiked bottles (5% of Linthipe River water) and control bottles (central station epilimnetic water only)

## 3.4 Discussion

The current study has measured changes in carbon dioxide from incubation bottles in which river water and hypolimnetic water was mixed with Lake Malawi epilimnetic water. The objective was to simulate how the lake responds to inputs of organic carbon and nutrients from its tributaries and vertical mixing. Distinct $CO_2$ responses were observed in the two treatments. As expected vertical flux of hypolimnetic waters resulted in an increase in phytoplankton biomass and promoted net $CO_2$ uptake. More interesting is the observation that when Linthipe River water mixes with epilimnetic waters it results in net $CO_2$ production. These results highlight the role each source may play in the lake's metabolism. Even under light conditions, the addition of river water resulted in a respiration: gross photosynthesis ratio greater than 1.0. This is likely due to the high OC: DP ratio in river water, which promotes respiration more than it does photosynthesis. On the other hand, hypolimnetic water is characterized by high dissolved P and low DOC concentrations, and the introduction of this water to the euphotic zone has a greater influence on photosynthesis than respiration.

Accurate estimation of primary production and respiration from incubation bottles is very challenging. First all, extrapolation of observations based on short-term incubations to long-term-rates may result in errors. Secondly, making conclusions based on results obtained from small containers and scaling to the whole lake may fail to recognize the potential effect of spatial phytoplankton dynamic differences in the lake. Additionally, the introduction or production of bacteria and or settling of particulate organic material and particulate nutrients at the bottom of the incubation bottles may influence the ratio of respiration to primary production.

Phytoplankton dynamics have been studied previously in Lake Malawi and show increased primary productivity and biomass during the rainy season and the cool, mixing season when upwelling is at its highest (Patterson et al. 2000, Hamblin et al. 2003a). According to Bootsma (1993b) and Guildford et al. (2003), algal productivity in Lake Malawi is mostly controlled by phosphorus supply. Estimates of phosphorus loading into Lake Malawi indicate that 50% of the total P into the epilimnion is provided by vertical mixing while the remainder is supplied by river loading and atmospheric deposition (Bootsma and Hecky 1999). It is also observed that this loaded P is in different forms. For example, most of the phosphorus inputs into the epilimnion from the vertical exchange is in the dissolved form, SRP = 8.1 mmol P $m^{-2}$ $yr^{-1}$ and TDP = 7.7 – 22.4 mmol P $m^{-2}$ $yr^{-1}$. In contrast, riverine inputs of phosphorus into the epilimnion are in particulate form; PP = 4.5 – 7.0 mmol P $m^{-2}$ $yr^{-1}$ (Bootsma and Hecky 1999). Therefore, the influence of this loaded P on $CO_2$ dynamics in the lake will largely depend on the form of P that phytoplankton is able to utilize but also on the fate of the P when transported into the lake. Although soluble reactive phosphorus (SRP) is considered the available nutrient pool for phytoplankton (Cotner and Wetzel 1992, Auer et al. 1998) particulate phosphorus can also be transformed into the soluble form. The uncertainty is how fast the remineralization process of PP can occur once it is loaded into the lake. According to Bootsma and Hecky (1999), the residence time of phosphorus in the epilimnion is around 2.5 years which may provide enough time for the PP to remineralize to the soluble form. Our study was only for a period of one week in which case the dissolved P form would be low compared to vertical flux. It is therefore not surprising that results of the river experiment contradict the general norm of high primary productivity that is often observed during the rainy season in the lake. The trends in phytoplankton dynamics that we observe may be due to inputs of organic carbon and nutrients from several years back. Extensive measurements by Kingdon et al. (1999) of the thirteen major Lake Malawi tributaries revealed that most organic and nutrient loading occurs during the early part of the rainy season, December, and January. Relatively high DOC concentrations are also observed within that time period based on Ramlal et al. (2003) and Chapter 4 of this study. Chapter 2, observed that Lake Malawi is a net $CO_2$ sink and that $CO_2$ undersaturation is encountered during the rainy and cool, mixing season. It, therefore, implies that the heterotrophy observed in the incubation bottles may not have bracketed the potential period of P remineralization. In addition, CO2 fluxes were based on pCO2 measurements that were collected offshore and not close to river inlets.

Lake Malawi is permanently stratified, and so degradation of particulate material in the deep waters of the lake results in anoxia and an accumulation of dissolved nutrients. Vertical exchange of this nutrient-rich deep water due to upwelling, entrainment, and diffusion (Eccles 1962, Patterson and Kachinjika 1995, Hamblin et al. 2003a) therefore represent the major pathway of transporting nutrients to the epilimnion. While this exchange does not constitute a new nutrient flux to the whole lake, it is, in fact, an important source to the epilimnion and has been shown to be a major driver of the spatial and temporal dynamics of primary production (Bootsma and Hecky 1999). The uptake of $CO_2$ in the light incubation bottles in the hypolimnion spike experiment was matched by an increase in the POC and Chl *a* concentrations. While nutrient concentrations in Lake Malawi increase with depth, DOC shows a declining trend with depth and therefore DOC influence on the epilimnion during vertical exchange may be negligible. Since bacterial consumption of organic material in the hypolimnion also results in the production of dissolved inorganic carbon (DIC) along with dissolved phosphorus (DP), vertical exchange may also promote heterotrophy when the supply ratio of DIC: DP is high, as observed in the southeast arm of the Lake, where upwelling is most pronouned ( see Chapter 2).

The bottle incubations using hypolimnetic water result in an overall consumption of $CO_2$ but in situ $pCO_2$ measurements showed that upwelling resulted in degassing of $CO_2$ especially at the onset of the mixing season. The difference could be due to disparities in mixing ratios that may be experienced in the lake. Our experiments used a single mixing rate of 5% which could potentially be lower than what the lake experienced at the beginning of the mixing season.

# Chapter 4 - A Carbon Mass Balance for Lake Malawi

## Abstract

Carbon budgets are useful for understanding energy flow through aquatic systems, and for making comparisons among systems. In this study, measurements of inputs, outputs and internal dynamics of organic and inorganic carbon were used to construct a carbon mass balance for tropical Lake Malawi. In-lake primary production is the major source of organic carbon in the lake. Most of the organic carbon that is transported into and produced in the lake is recycled and respired within the lake with 4 - 8% export efficiency into the deep sediments and less than 1% lost through the outflowing Shire River. Riverine organic carbon inputs constitute about 60% of the total allochthonous inputs but most of this is in the particulate form. Although the POC and DOC concentrations in the lake are low, the total organic carbon pool is 11.5 times higher than allochthonous inputs indicating that internal organic carbon is mostly supported by autochthonous primary production. A comparison of POC in Linthipe River, which flows through one of the highly disturbed southern catchment between the current study and those conducted early 2000, indicate an overall reduction in erosion rates due to good agricultural practices.

Upward vertical DIC flux represents a major source of carbon to the epilimnion. Over 74% of the total epilimnetic inputs are accounted for by vertical exchange. Although this does not represent new input to the lake, it has implications on phytoplankton dynamics in the mixed zone. Our results further reveal that recycling rates of carbon are lower in the deep anoxic waters than the epilimnion. If carbon is selectively retained in the hypolimnion while P is efficiently recycled into the epilimnion, $CO_2$ fixation in the epilimnion will be enhanced leading to

autotrophy. The mass balance shows that, for the whole lake, total organic inputs, excluding the air-water $CO_2$ exchange are lower than the total outputs. This is only possible if an external source of $CO_2$ is available to account for the excess fixed carbon which agrees with results of C flux based on direct $pCO_2$ measurements.

## 4.1 Introduction

Lying at the southernmost end of the African Rift valley, Lake Malawi is one of the African Great lakes (Beadle 1981) and together with lakes Victoria and Tanganyika hold approximately 27% of the Earth's available surface freshwater (Bootsma and Hecky 2003). These lakes are a valuable resource to the riparian countries as they provide numerous benefits in addition to serving as biological databanks for the world at large. The available statistics indicate that Lake Malawi harbors the highest number of freshwater fish in the world, estimated to be between 700 and 1000 species (Ribbink 1991, Ribbink 1994, Turner 1996, Snoeks 2000). Over 90% of these fish species belong to the Cichlidae family and are only found in this lake. Most of these fish, breed in shallow areas and rocky habitats that are vulnerable to siltation and water level fluctuations. Although the quality of water from lakes Tanganyika and Malawi is relatively good, there have been substantial changes in land use within the catchments of these lakes. The increasing human population and poverty are exerting pressure on natural resources and accelerating environmental degradation through deforestation, biomass burning and marginal land clearing for agricultural purposes (Calder et al. 1995, Hudak and Wessman 2000). This is resulting in loss of wetlands which act as buffer zones and fish breeding grounds, and the acceleration of soil erosion, sedimentation, and nutrient loading into the lakes (Bootsma et al. 1996, Cohen et al. 1996, Hecky et al. 2003). Studies conducted by Rusuwa et al. (2006) revealed that habitats for rocky dwelling cichlids are deteriorating due to increased littoral sedimentation. There is evidence that increased sediment loads are accompanied by increased nutrient and carbon loads (Hecky et al. 2003, Ramlal et al. 2003).

Lake Malawi is meromictic, and as a result, the hypolimnion is anoxic and nutrient-rich (Hecky et al. 1996, Katsev et al. 2017). Vertical water exchange within the lake's water column is accomplished through entrainment during the cool season due to evaporative cooling, turbulent mixing (eddy diffusion) and upwelling (Bootsma and Hecky 1999, Hamblin et al. 2003a). Empirical measurements and model results reported by Hamblin et al. (2003) suggest that upwelling at the southern end of the lake is the primary mode by which hypolimnetic nutrients are introduced to the surface. Although this exchange does not represent a new flux to the lake, it has a strong influence on critical ecosystem processes including plankton and fish production in the epilimnion and is important to consider in the lake's nutrient budgets (Bootsma and Hecky 1999).

To determine the relative importance of atmospheric and terrestrial carbon sources on an annual basis, Dillon and Molot (1997a) suggest the need for mass balance studies. Additionally, Hecky et al. (1996) point out that knowledge of rates of vertical transport of nutrient species is critical for water quality modeling. The combined effects of various carbon budget components in Lake Malawi, including allochthonous loading, autochthonous production, atmospheric exchange, burial, and internal recycling have not been explored concurrently. Ramlal et al. (2003) investigated several important carbon pathways for the lake, but they were not able to construct a balanced carbon budget because they did not have data on inorganic carbon vertical exchange within the lake and the lake-atmosphere exchange. The aim of the current study is therefore to fill this gap by (1) updating estimates of the various inputs and outputs of carbon for the lake, (2) determining the carbon inventory in the lake and (3) developing a carbon budget, which can assist in understanding and conceptualizing the complex interaction between allochthonous and autochthonous inputs and their fate in the lake.

According to Andersson and Sobek (2006), carbon budgets can be accomplished through either an ecosystem model approach or by a mass balance approach. In an ecosystem model approach, carbon metabolism is estimated as the difference between primary production and respiration. Consequently, measurements of carbon flow rates between and within different organism groups (production, respiration, consumption) must be defined. This approach requires high-resolution observations and therefore a substantial amount of data is required which can be a big challenge for a large lake. On the other hand, the mass balance approach requires only data for inputs and outputs of carbon and so is most preferred. The current study used this approach.

## 4.2 Methods

The model considered here includes both particulate and dissolved forms of carbon for the whole lake and the epilimnion (Fig. 20). For the entire lake, a carbon mass balance is defined by the following relationship;

$$\boldsymbol{V\frac{dC}{dt} = D + R_{in} + G_{in} - B - R_{out} - G_{out} + P - R_{esp}} \tag{18}$$

Where *V* = volume of the lake, *C* = concentration of carbon (average over the lake), *D* = atmospheric deposition, $R_{in}$ = river input, $G_{in}$ = groundwater input, *B* = burial in the sedimentation, $R_{out}$ = river output, $G_{out}$ = groundwater output, P = primary production and $R_{esp}$ is respiration. Previous studies by Owen et al. (1990), determined that groundwater plays a minor role in the water budget of Lake Malawi and therefore terms for groundwater, $G_{in}$ and $G_{out}$ have been disregarded as potential inputs or outputs of carbon for the lake.

For the epilimnion, a mass balance is defined as;

$$\boldsymbol{V_e\frac{dC_e}{dt} = D + q_eR_{in} + F_m - S_e - R_{out} + P - R_{esp}} \tag{19}$$

Where $V_e$ = epilimnion volume, $C_e$ = concentration of carbon in the epilimnion, *D* = atmospheric deposition, $q_e$ = the fraction of river carbon that sinks directly into the epilimnion as opposed to flowing to deeper depths, $R_{in}$ and $R_{out}$ are carbon river inputs and outputs, $F_m$ = the upward vertical flux of DIC and DOC from metalimnion to epilimnion, $S_e$ = sinking rate out of the epilimnion into the metalimnion, P = primary production and $R_{esp}$ is respiration. The concentration of DOC in epilimnion is not different from that in metalimnion (Ramlal et al 2003; this study) and is even lower in the hypolimnion. Therefore, flux into the epilimnion will be negligible and has been disregarded from the budget. To construct the whole lake and epilimnion mass balance, carbon fluxes from atmospheric deposition, riverine inputs, and outputs, sedimentation, permanent burial, upward vertical exchange and air-water exchange were quantified (Fig. 21). The epilimnion boundary was set at a depth of 105 m according to estimates by Vollmer et al. (2002) and vertical fluxes were calculated using the same approach as Bootsma et al. (2003) based on silica (Si). Lake Malawi tributary rivers are sometimes cooler and therefore denser than surface lake water. Although the depth at which this river water flows after entering the lake is not important for the whole-lake budget, it is, in fact, important for the epilimnion budget (Rueda et al. 2007, Hararuk et al. 2018). Kingdon et al. (1999), McCullough (1999) and Bootsma et al. (2003) estimated proportions of river water that are directly introduced into epilimnion, metalimnion, and hypolimnion waters based on river and lake water density measurements. These proportions were used to calculate the amount of river organic carbon load to each depth strata.

To develop a carbon budget for Lake Malawi, a number of inputs and outputs are required. It was not possible to collect all parameters within the timelines of the study. Therefore, the previous carbon budget by Ramlal et al. (2003) was updated with some additional more recent flux variables collected in the present study. A summary table describing the variables and their source is provided in Table 6.

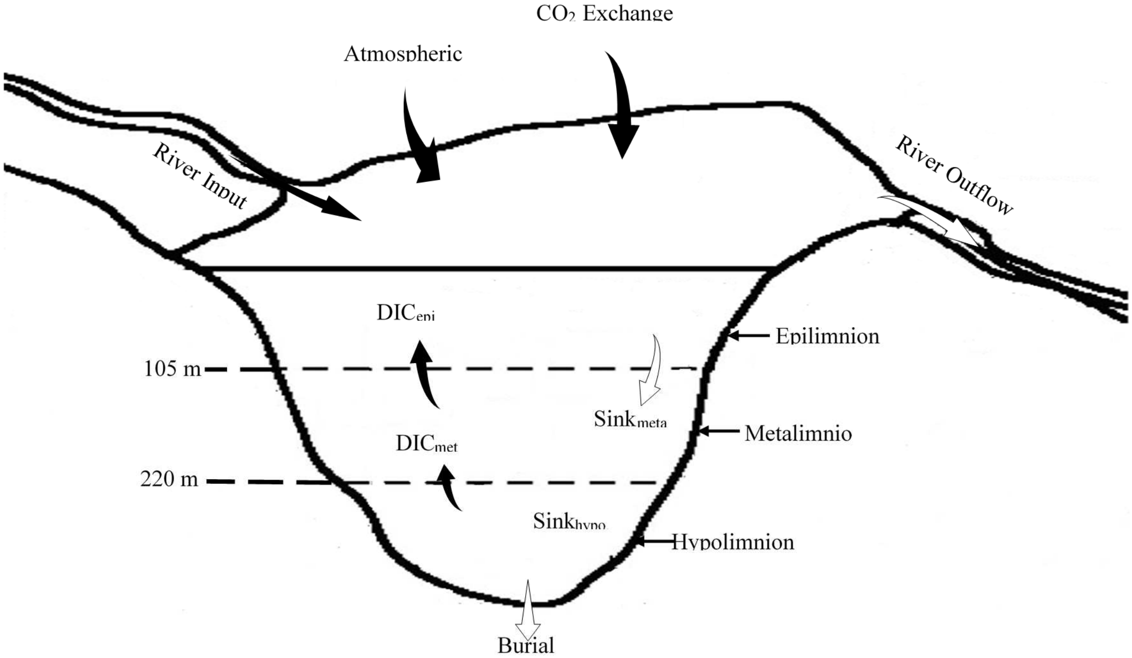


Figure 21: A generalized conceptual illustration of the carbon cycle in Lake Malawi

Table 6: A summary of the sources and sinks of organic (OC) and inorganic (DIC) carbon in Lake Malawi.

| Source or Sink | References | Estimate | Remarks |
|---|---|---|---|
| Atmospheric deposition | | | |
| OC annual deposition | Bootsma et al. (1999) | 260 - 608 mmol C $m^{-2}yr^{-1}$ | Senga Bay dry, |
| Whole lake OC deposition | Ramlal et al. (2003) | 0.77 – 1.79 x $10^{10}$ molC $yr^{-1}$ | wet deposition |
| Riverine input | | | |
| OC concentration | Kingdon et al. (1999); | 233 – 900 µmol $L^{-1}$ | Samples from |
| Areal OC yield | Hecky et al. (2003); | 298 – 1,547 mmol C $m^{-2}yr^{-1}$ | thirteen major |
| Annual OC riverine load | Ramlal et al. (2003) | 0.88 – 4.56 x $10^{10}$ molC $yr^{-1}$ | tributary rivers |
| Phytoplankton production – autochthonous | | | |
| Annual areal specific PP | Degnbol and Mapila (1982); | 19,770-25,500 mmol C $m^{2}yr^{-1}$ | Lake-wide |
| Surface lake area | Bootsma and Hecky (2003) | 2.95 x $10^{10}$ $m^{2}$ | sampling and |
| Annual phytoplankton production | Bootsma (1993b) | 59.2 – 66.4 x $10^{10}$ molC $yr^{-1}$ | $^{14}C$ method |
| River output | | | |
| Areal OC output | Hecky et al. (2003) | 25 – 29 mmol C $m^{-2}yr^{-1}$ | Shire River |
| Annual OC outflow | Ramlal et al. (2003) | 0.2 x $10^{10}$ molC $yr^{-1}$ | outflow |
| Atmospheric – water exchange | | | |
| Annual areal mean $CO_2$ flux | this study | -209 to -320 mmol C $m^{-2}yr^{-1}$ | Lake-wide |
| Annual $CO_2$ flux | this study | -0.62 to -0.94 x $10^{10}$ $molCyr^{-1}$ | $pCO_2$ data |
| Vertical mixing | | | |
| DIC Metalimnion – epilimnion | this study | 1,152 - 1,887 mmol C $m^{-2}yr^{-1}$ | $CO_2$ profiles |
| DIC Hypolimnion – metalimnion | this study | 533 - 793 mmol C $m^{-2}yr^{-1}$ | deep station |
| OC Sedimentation (100 m traps) | Bootsma and Hecky (1999) | 1,431-1,492 mmol C $m^{-2}yr^{-1}$ | Sediment traps |
| OC Sedimentation (180 m traps) | | 1,584-1,667 mmol C $m^{-2}yr^{-1}$ | three locations |
| OC Burial | H.A. Bootsma (unpubl.) | 1,453-2,813 mmol C $m^{-2}$ $yr^{-1}$ | Sediment cores |

### *4.2.1 Lake Sampling and chemical analysis*

Monthly water samples were collected from a deep station in the northern part of the lake, offshore of Nkhata Bay (11.5542$^{o}$S, 034.3134$^{o}$E; max. depth 400 m), central part of the lake (Station 928; 13.7131$^{o}$S, 034.6731$^{o}$E; max. depth 140 m) and the southern end of the lake (Maldeco; 14.3292$^{o}$S, 035.1599$^{o}$E; max. depth 20 m) in 2014 (Fig. 22). Between January 2014 and January 2015, temperature loggers were installed at Station 900 (13$^{o}$01.56'S, 34$^{o}$26.73'E; max. depth 184 m) at 5, 15, 40, 60, 80 and 100 m depths as part of the University of Minnesota, LLO cruise on Lake Malawi. At each station, water samples were collected from the surface at 10 – 20 m depth intervals using a Niskin bottle and analyzed for particulate carbon (PC), and chlorophyll *a* (Chl *a*). For particulate carbon, approximately, 1500 ml of water sample was filtered onto pre-combusted (500$^{o}$C for 2 hours) GF/F filter and dried in a desiccator. Dry filter samples were shipped to the UWM – School for Freshwater Science for analysis. The analysis was done on a Costech 4010 Elemental Analyzer System coupled with a Thermo Scientific CONFLO IV gas control module to a Thermo Scientific Delta-V Plus Isotope Ratio Mass Spectrometer. Sample runs were preceded with a blank and an acetanilide control to ensure instrument calibration. Acetanilide standards were run after every twenty-four samples to provide a standard curve which was used to convert the millivolt (mV) spikes in $CO_2$ for each sample to total POC mass. Together with known water sample volume filtered, POC concentration was calculated. The column insert containing quartz wool and chromium oxide was replaced after every twenty-four-sample run to avoid build-up of ash.

Chlorophyll *a* analysis was done by filtering between 1,000 and 2,000 ml of sample onto a GF/F filter under low pressure and low-light conditions. Filters were wrapped in aluminum foil and kept in a freezer if chlorophyll *a* extraction was not done on the same day. Chlorophyll *a* on

GF/F filters was extracted using a 10 ml mixture of acetone (27%), methanol (68%) and water (5%), stored in a freezer for 24h and fluorescence was measured on a calibrated Turner Series 10 fluorometer according to Stainton et al. (1977).

Samples for DOC analysis were filtered through 0.45 µm pore size membrane filters and the filtrate was preserved in phosphoric acid in dark bottles and kept in a fridge at 4$^{o}$C (Sharp et al. 2002, Griffith et al. 2012) until shipped to the University of Wisconsin-Milwaukee School for Freshwater Sciences for analysis. Analysis of samples was conducted on a Shimadzu Total Organic Carbon 5000 analyzer equipped with an ASI-5000 auto sampler using the high temperature combustion catalytic oxidation method. Exactly 25 ml of the preserved DOC samples were acidified with 2-3 drops of 1N HCl to attain a pH of 2 or less, allowing for the purging of all inorganic carbon prior to OC analysis.

A Seabird SBE19 CTD profiler was cast at each station to record, conductivity, pH, temperature and dissolved oxygen.

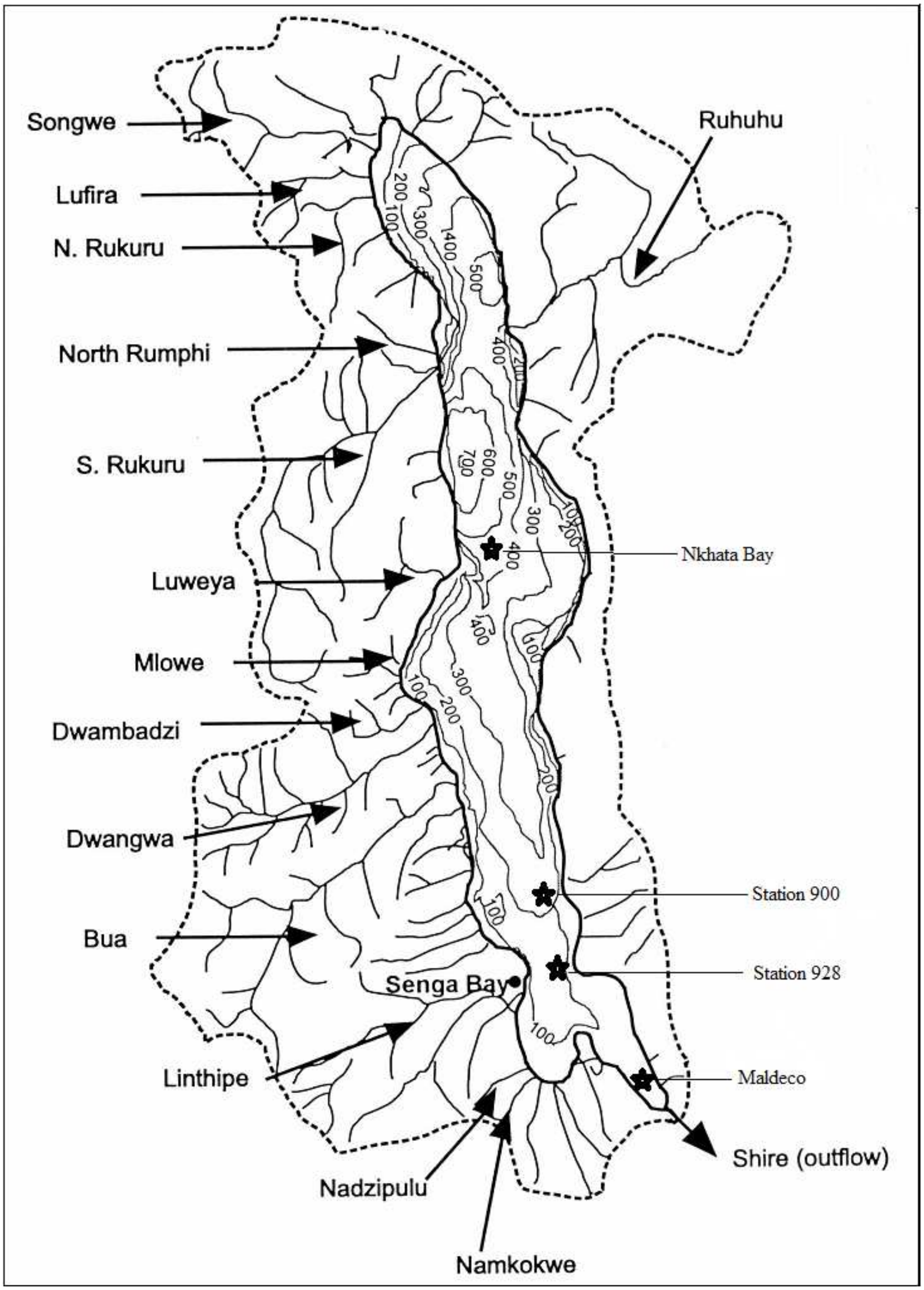


Figure 22: Map of Lake Malawi and its catchment showing 100 m depth contour intervals, the four sampling stations and major rivers into and out of the lake. The map has been reproduced after Kingdon et al. (1999)

### *4.2.2 DIC measurement*

The inorganic carbon system consists of pH, alkalinity, total dissolved inorganic carbon, carbonate, bicarbonate, and carbon dioxide. To describe the system, measurement of two of the above parameters are required, provided that data is available for the other acid/base species (Prieto and Millero 2002). The dissociation of carbon dioxide in water is shown below:

$$\boldsymbol{CO_{2(g)}} \ll - \gg [\boldsymbol{CO_2}]_{\boldsymbol{aq}} + \boldsymbol{H_2O} \ll - \gg \left[\boldsymbol{HCO_3^{-1}}\right] + \boldsymbol{H^+} \ll - \gg \left[\boldsymbol{CO_3^{-2}}\right] + \boldsymbol{2H^+} \qquad (20)$$

The calculation of the various carbon species requires dissociation constants for the carbonic acid which is dependent on water salinity. Since Lake Malawi has low salinity values (< 0.5 PSU), $K_1$ and $K_2$ were calculated as a function of temperature and salinity according to the relationship by Cai and Wang (1998), a modification of the relationships presented by Harned and Davis (1943) and Mook and Koene (1975):

$$\boldsymbol{K_1} = \frac{[\boldsymbol{HCO_3^{-1}}][\boldsymbol{H^+}]}{[\boldsymbol{CO_2}]} \qquad (21)$$

$$pK_1 = 3{,}404.71/T + 0.032786T - 14.8435 - 0.071692F_1(T)\,S^{1/2} + 0.0021487\,F_1(T) \qquad (22)$$

$$F_1(T) = 200.1/T + 0.3220$$

$$\boldsymbol{K_2} = \frac{[\boldsymbol{CO_3^{-2}}][\boldsymbol{H^+}]}{[\boldsymbol{HCO_3^{-1}}]} \qquad (23)$$

$$pK_2 = 2{,}902.39/T + 0.02379T - 6.4980 - 0.3191F_2(T)\,S^{1/2} + 0.0198\,S \qquad (24)$$

$$F_2(T) = -\,129.24/T + 1.4381$$

where T is the absolute temperature and S is salinity which can range between 0 and 40ppt. The ion product of water, $K_w$ was also used to determine $[H^+]$ and $[OH^-]$, (Stumm and Morgan 1996).

Water samples for $CO_2$ concentration measurement were collected using a Niskin water sampler. Water from the sampler was transferred to stoppered glass bottles and measured immediately in the field using the $CO_2$ system as described in Chapter 2. Partial pressures of carbon dioxide were converted to aqueous concentrations by correcting to ambient atmospheric pressure (*kPa*) and multiplying by Henry's solubility constant, $K_h$, (Weiss 1974):

$$[CO_2]\ (\mu mol\ L^{-1}) = pCO_2\ (\mu atm)\ x\ \frac{kPa}{101.325}\ x\ K_h \tag{25}$$

From equations 4 and 6 above, bicarbonate and carbonate concentration were calculated assuming constant alkalinity. DIC was estimated as below;

$$DIC = [CO_2]_{aq} + \left[HCO_3^{-1}\right] + \left[CO_3^{-2}\right] \tag{26}$$

### *4.2.3 Air-water $CO_2$ exchange*

The flux of $CO_2$ across the air-water interface was measured in the lake according to methods outlined in Chapter 2.

### *4.2.4 Vertical Exchange*

Vertical DIC flux between the metalimnion and epilimnion were estimated as below (Bootsma et al. 2003):

$$F_e = k_e \frac{V_m}{V_e}\ (c_m - c_e)\ x\ h_e \tag{27}$$

where $F_e$ is the flux (mmol $m^{-2}$ $yr^{-1}$) into the epilimnion, $k_e$ is the annual exchange coefficient rate between the metalimnion and epilimnion in units of $yr^{-1}$. $V_m$ and $V_e$ are respective volumes for the metalimnion and epilimnion, respectively while $c_m$ and $c_e$ are the corresponding volume-weighted mean DIC and SRP concentrations in the metalimnion and epilimnion (mol $L^{-1}$). $h_e$ is the depth of the epilimnion (Table 7).

For the metalimnion, vertical flux between hypolimnion and metalimnion was calculated as;

$$\boldsymbol{F_m = k_m \frac{V_h}{V_m} \ (c_h - c_m) \ x \ h_m} \qquad (28)$$

Where $F_\mathrm{m}$ is the flux (mmol $m^{-2}$ $yr^{-1}$) into the metalimnion, ($k_\mathrm{m}$) is the annual exchange coefficient rate between the hypolimnion and metalimnion provided in units of $yr^{-1}$, $V_{h,}$ and $V_m$ are the volumes for the hypolimnion and metalimnion, respectively (Table 7) while $c_h$ and $c_m$ are the volume-weighted mean DIC and SRP concentrations in the hypolimnion and metalimnion (mol $L^{-1}$). $h_m$ is the depth of the metalimnion (m).

Table 7. Equations and parameter values used to determine vertical fluxes and mass balance. Parameters from Vollmer et al. (2002) and Bootsma et al. (2003)

$F_m = k_e \frac{V_m}{V_e} \, (c_m - c_e) \; x \; h_e$; vertical flux the of DIC from metalimnion to epilimnion (mmol m$^{-2}$ yr$^{-1}$)

$F_h = k_m \frac{V_h}{V_m} \, (c_h - c_m) \; x \; h_m$; vertical flux of DIC from hypolimnion to metalimnion (mmol m$^{-2}$ yr$^{-1}$)

$k_e$ = epilimnion – metalimnion exchange coefficient; 0.27/yr

$k_m$ = metalimnion – hypolimnion exchange coefficient; 0.056/yr

$V_e$ = volume of the epilimnion (0 – 105 m = 2,754 km$^3$)

$V_m$ = volume of metalimnion (105 – 220 m = 2,310 km$^3$)

$V_h$ = volume of hypolimnion (>220 m = 2,711km$^3$)

$c_e$ = volume weighted average for DOC, PC or DIC concentration in the epilimnion (µmol C/L)

$c_m$ = volume weighted average DOC, PC or DIC concentration in the metalimnion (µmol C/L)

$c_h$ = volume weighted average DOC, PC or DIC concentration in the hypolimnion (µmol C/L)

$h_e$ = depth of the epilimnion (0 – 105 m)

$h_m$ = depth of metalimnion (105 – 220 m)

$h_h$ = depth of hypolimnion (>220 m)

$R_i$ = River inflow of OC (mmol m$^{-2}$ yr$^{-1}$)

$q_e$ = fraction of river inflow injected directly into epilimnion; 0.52

$q_m$ = fraction of river inflow injected directly into metalimnion; 0.16

$q_h$ = fraction of river inflow injected directly into hypolimnion; 0.32

### *4.2.5 Atmospheric deposition, river input, and output*

Extensive measurements of carbon and nutrient loading from atmospheric deposition (Bootsma et al. 1999) and the major tributary rivers (Kingdon et al. 1999, McCullough 1999) of Lake Malawi has been accomplished previously. The riverine measurements were augmented by monthly sampling of the Linthipe River between 2013 and 2015. A clean bucket, rinsed several times with river water was lowered from the bridge to collect a water sample. Immediately after sample collection, pH, temperature, conductivity, and $pCO_2$ were measured. Samples were stored in a cooler and transported to the Senga Bay laboratory for processing of POC, DOC, and Chl *a* and analyzed as described in Chapter 3.

### *4.2.6 Sedimentation and burial*

Extensive work on nutrients, sedimentation and organic carbon burial have been reported for Lake Malawi (Bootsma and Hecky 1999, Hecky et al. 1999). For an epilimnion budget, only measurements of sinking rates out of the epilimnion are required which were estimated using sediment traps that were moored at two locations in the lake (southern and central part of the lake). Traps were set at 100 m to capture epilimnetic sinking rates and in addition to epilimnetic sinking, traps were also moored at 180 m to capture metalimnetic sinking rates (Hecky et al. 1999). A single large cylindrical trap (200 cm tall x 30 cm diameter was deployed at each of the locations. Upon deployment, each trap was filled with water, followed by an addition of 500 ml of $7 gL^{-1}$ of KCL at the base of the trap to minimize mixing within the trap and 5 ml of chloroform (Bootsma et al. 2003). Traps were deployed for a period of four months.

For a whole lake budget, only burial rates are required and were estimated using sediment cores from several locations in the lake, i.e. the northern end, near the Songwe River delta and the central basin of the Dwangwa delta (Johnson et al. 2002). Data were analyzed at the Freshwater Institute, Winnipeg and organic carbon was estimated as “loss on ignition” assuming 50% of organic carbon (Bengtsson and Enell 1986). The $^{210}$Pb analysis and the constant rate of sedimentation (CRS) model were used to determine sediment chronology. For a complete methodology, refer to Hecky et al. (1999) and Johnson et al. (2002).

## 4.3 Results and Discussion

### *4.3.1 Atmospheric deposition*

Several studies have shown that the atmosphere is a significant source of carbon, phosphorus, and nitrogen to lakes and oceans (Scheider et al. 1979, Manny and Owens 1983, Cole et al. 1990, Paerl 1993, Bootsma et al. 1996, Tamatamah et al. 2005a). According to Bennett (1986), the increase in dissolved inorganic nitrogen concentration that has occurred in Lake Superior over the past century is the result of atmospheric N deposition. Atmospheric deposition within the African Great Lakes appears to be influenced by biomass burning, deforestation and agricultural activities (Andreae 1991, 1993, Bootsma et al. 1999, Downing et al. 1999). A comprehensive analysis of the chemical composition of dry and wet deposition over Lake Malawi has been conducted by Bootsma et al. (1999). DOC is regarded as the material that is less than 0.45 µm while POC is material that is retained on a 0.7 µm filter. Areal mean deposition rates of DOC and POC in Lake Malawi are estimated at 608 and 260 mmol C $m^{-2}$ $yr^{-1}$, respectively (Bootsma et al. 1999). The DOC: POC ratio for total atmospheric deposition is approximately 3:1. If the areal atmospheric flux rates are extrapolated to lake surface area, a total of $2.6 \times 10^{10}$ mol C $yr^{-1}$ is loaded into Lake Malawi. Dry deposition contributes approximately 84% probably because there are more days without rainfall in Malawi than there are for rain. A majority of the atmospheric organic carbon is comprised of DOC ($1.79 \times 10^{10}$ mol C $yr^{-1}$) representing 70% while POC contributed the remainder. The dataset shows that DOC in wet deposition contributes about 85% while DOC in dry deposition constitutes 67%. The contribution of DOC in wet deposition is comparable to that reported by Likens et al. (1983) for the northeastern United States and Pan et al. (2010) in China.

### *4.3.2 Riverine input and output*

The current study did not sample all the Lake Malawi tributary rivers but utilized previous observations from thirteen of the largest tributaries entering the lake, augmented with more recent measurements for the Linthipe River. The Linthipe River drains one of the most highly disturbed river catchments and has exceptionally high sediment and nutrient loads compared to other tributary rivers within the Lake Malawi catchment (McCullough 1999, Hecky et al. 2003). It has an estimated total catchment area of 8,560 $km^2$ and consists primarily of weathered loamy sandy soils. The Department of Water Services monitors daily river flows in most major rivers in Malawi. According to the dataset we acquired, during the 2014/15 rainy season, the Linthipe River discharged a total of $9.50 \times 10^9$ $m^3$ of water into the lake. Unlike DOC concentration which remained relatively constant during the high and low flow periods, POC concentration was extremely variable and correlated positively with discharge, with peak concentrations during the rainy season (Fig. 23). The volume weighted mean DOC and POC concentrations in the river were calculated for the full year as 274 and 989 μmol $L^{-1}$, respectively. Mean DOC concentration is comparable to what Ramlal et al. (2003) observed previously in the river but the mean POC observed by Ramlal et al. (2003) or the same river is high, 2,355 μmol $L^{-1}$. The DOC: POC ratio is 0.3. To determine potential causes for the relatively low POC concentrations observed in the present study compared to that of Ramlal et al. (2003), we examined Linthipe water discharge rates between the two sampling periods. The discharge rates are comparable. Year-to-year variabilities in nutrients and sediment loads have been reported previously for the Linthipe River. For example, Hecky et al. (2003) compared POC and runoff for the periods 1996/97 and 1997/98 rainy season and found POC concentrations that differed by 67% even though changes in runoff were only 9%. The authors attributed the difference due to changes in agricultural intensity within the catchment. The Government of Malawi, through the Ministry of Agriculture, Irrigation, and Water Development, is promoting conservation agriculture, through which farmers are encouraged to minimize soil disturbance by reducing soil tillage and yearly shifting of ridges (which makes soil loose) and maximizing soil cover using stalks from the previous harvest (Mloza-Banda and Nanthambwe 2010). This technology, among others, reduces soil erosion, improves soil water retention and soil fertility, and reduces weed infestation. In addition, the worldwide anti-smoking policies (Odermatt and Stutzer 2015) have reduced the amount of land devoted to tobacco growing, as well as the demand for fuelwood for tobacco curing. Therefore, the low POC concentration from Linthipe River encountered in the present study may be due to changes in agricultural activities and practices within the catchment (Sosola et al. 2011) and also due to normal inter-annual variability.

Based on previous measurements from the thirteen tributaries into Lake Malawi, Hecky et al. (2003) estimated the mean river DOC and POC concentration as 233±123 μmol $L^{-1}$ and 898±764 μmol $L^{-1}$, respectively. DOC concentrations are comparable to those in the Amazon River (Raymond and Bauer 2001), the Niger River (Lesack et al. 1984) and other African rivers reported by Martins and Probst (1991). However, they are lower than concentrations reported for some temperate rivers (Meybeck 1981). The mean DOC: POC ratio for all the thirteen tributary rivers for Lake Malawi is 0.7 but is spatially variable with the lowest ratios observed in the highly disturbed southern region catchment, where the mean is 0.19. By contrast, rivers in the central and northern parts of the lake’s watershed had DOC: POC ratios of 0.99 and 0.81, respectively. DOC: POC ratio for most temperate rivers is 3:1 but often close to 1:1 (Wetzel 2001) and the mean DOC: PC ratio for world rivers is 0.8 (Hedges et al. 1986). Annual mean areal DOC and POC yields for all thirteen rivers are 298 and 1,547 mmol C $yr^{-1}$, respectively. Extrapolating to the entire lake's surface area, total POC and DOC loading rates are 4.6 x $10^{10}$ mol C $yr^{-1}$ and 0.9 x $10^{10}$ mol C $yr^{-1}$, respectively, and a total riverine OC load of 5.4 x $10^{10}$ mol C $yr^{-1}$.

The Shire River constitutes the only outflow river from Lake Malawi. Annual mean areal DOC and POC outflow concentrations were estimated at 29 and 25 mmol C $m^{-2}$ $yr^{-1}$ with a total annual output of approximately 0.2±0.02 x $10^{10}$ mol C $yr^{-1}$. This loss rate from the lake is approximately 3% of the total allochthonous inputs i.e. the sum of riverine and atmospheric organic carbon inputs.

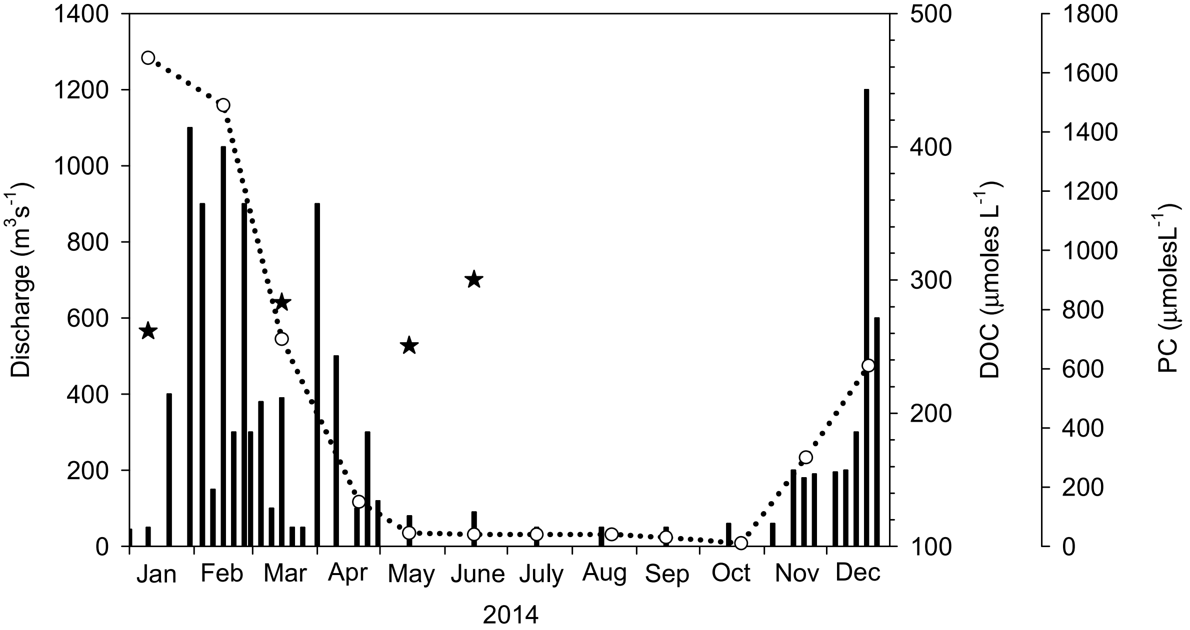


Figure 23: Seasonal variation of discharge (bar graphs), dissolved organic carbon (DOC) (filled stars) and particulate carbon (PC) (dotted line with open circles) in Linthipe River.

### *4.3.3 Air-water $CO_2$ exchange*

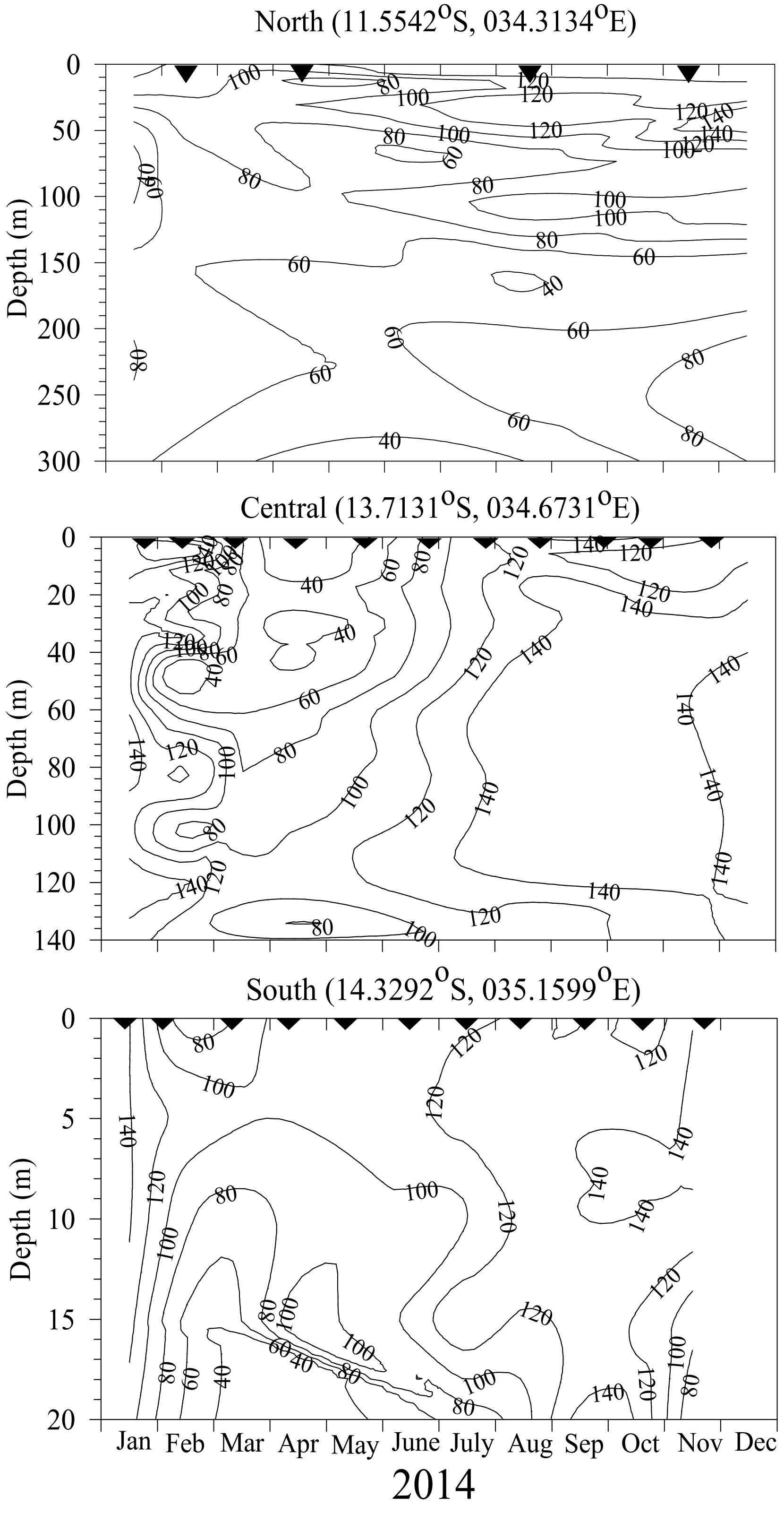
Lake Malawi is a net $CO_2$ sink with areal $CO_2$ flux across the air-water interface that fluctuate between -209 and -320 mmol C $m^{-2}$ $yr^{-1}$ (Chapter 2). When this annual net flux is extrapolated to the entire lake surface area, a total of 0.62 to 0.94 x $10^{10}$ mol C $yr^{-1}$ is absorbed by the lake.

### *4.3.4 Autochthonous Organic Carbon*

Profiles of DOC and POC were taken at three locations in the lake are provided in Figures 24 and 25. The concentration of DOC in the lake fluctuates between 40 and 160µmol $L^{-1}$ while POC varies from 3 to 40 µmol $L^{-1}$. The DOC: POC ratio in the lake varies between 4 and 13. Both DOC and POC concentrations varied with time and high concentrations were recorded between January and February, the period coinciding with rainfall in the lake. During this period, it is common to observe river plumes dispersing into the open waters of the lake. Concentrations of DOC in Lake Malawi are low but are comparable to those observed in Lake Superior (Urban et al. 2005). According to Urban et al. (2005), the low DOC concentrations observed in Lake Superior are attributed to low watershed to lake surface area ratio which makes Lake Superior less influenced by its catchment (Fig. 26). Nonetheless, DOC concentrations in Lake Baikal are in fact lower although the ratio of the watershed to lake surface area is high, estimated at about 17:1. Photochemical and biological degradation account for the low DOC in Lake Baikal (Yoshioka et al. 2002). The effect of UV degradation was also observed in North American temperate boreal lakes by Schindler et al. (1996).

DOC and POC concentrations were high and remained relatively high throughout the mixing season up until the stratified season (Fig. 24 and 25). According to Ramlal et al. (2003), the high POC values are attributed to high primary production in the mixed season while high

DOC concentrations are due to degradation of algal biomass that accumulates during the mixing season. Spatially, the southernmost region of Lake Malawi has high POC concentrations while lowest concentrations are observed in the northernmost station (Fig. 24). Annual mean POC and Chl *a* concentrations in the southernmost region were 23.4±7.1 μmol $L^{-1}$ and 1.95±0.67 μg $L^{-1}$, representing a C: Chl ratio of 12:1 while at the northern station, 16.5±8.4 μmol $L^{-1}$ and 0.3±0.21 μg $L^{-1}$ were recorded implying a C: Chl of 55:1. These results indicate high primary biomass at the southern end of the lake and are in agreement with those reported by Bootsma (1993b), Gondwe et al. (2011) and Hamblin et al. (2003a). High POC and Chl *a* values at the southern end of the lake reflect enhanced phytoplankton productivity in this area that is due to upwelling of nutrients, as there are no major rivers flowing into this part of the lake. Using the mean DOC and POC concentrations together with volumes for each depth strata, the inventory of organic carbon (POC + DOC) in Lake Malawi is estimated at 92 x $10^{10}$ mol C. Of this total, DOC contributes about 85% with an estimate of 78 x $10^{10}$ mol C while POC contributes 14 x $10^{10}$ mol C representing 15% (Table 8). Measurements of total OC pool by Ramlal et al. (2003) between 1997 and 1998 in the lake were 63 x $10^{10}$ mol C but ranged from 47 to 83 x $10^{10}$ mol C. The ratio of DOC: POC in Lake Malawi estimated at approximately 6:1. By comparison, Yoshioka et al. (2002) reported a DOC: POC ratio of 8:1 in Lake Baikal and Biddanda et al. (2001) reported a ratio of 10:1 for Lake Superior. Similarly, high ratios have been reported for the open ocean (Libes 1992). DOC is the main component of the organic carbon pool for most large lakes.


North (11.5542$^{O}$S, 034.3134$^{O}$E)

Central (13.7131$^{O}$S, 034.6731$^{O}$E)

South (14.3292$^{O}$S, 035.1599$^{O}$E)

Figure 24: Seasonal DOC profiles collected from the northern, central and southern station. Note the different depth ranges for each plot. Arrows indicate the date when a sample was collected.

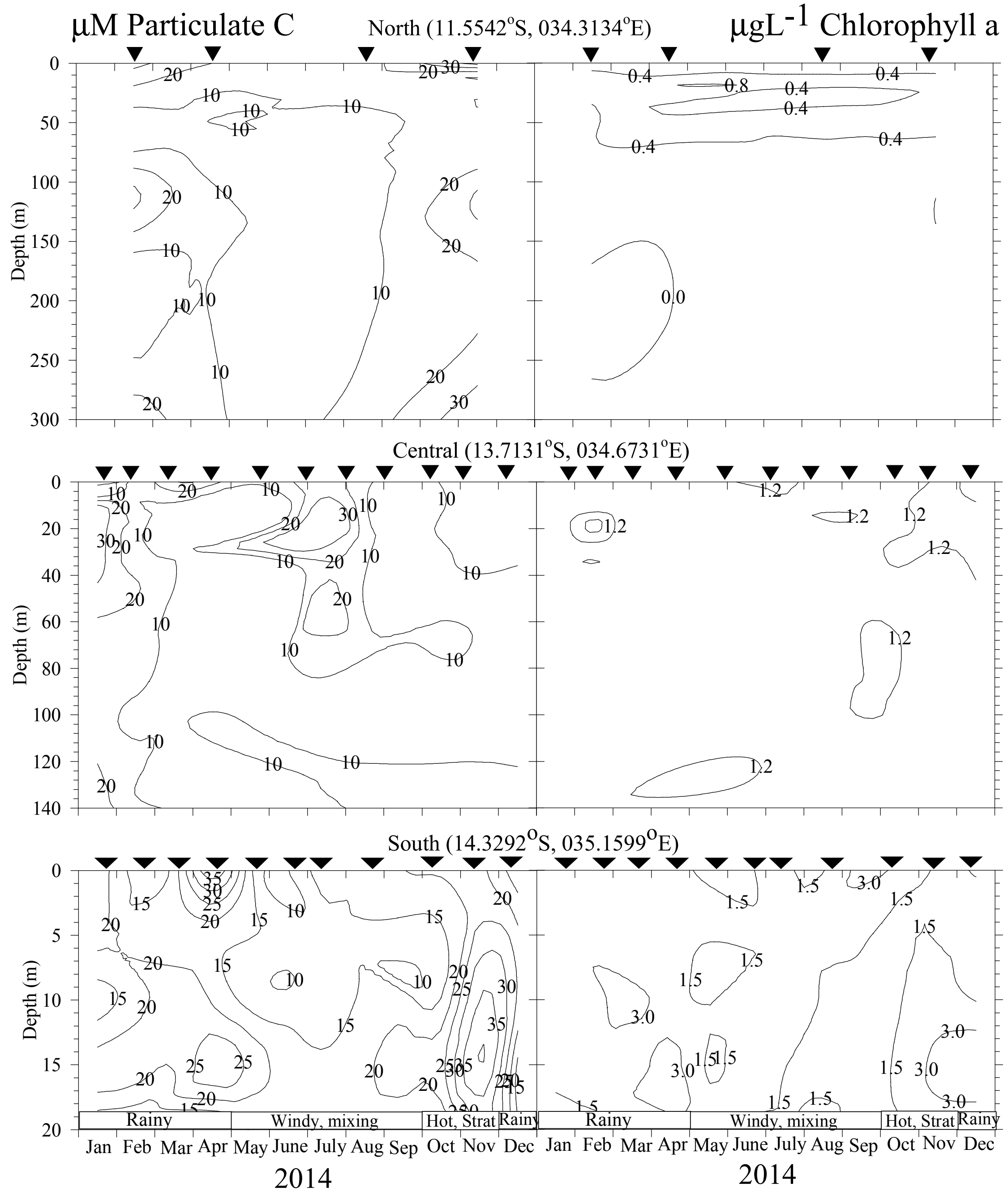


Figure 25: Seasonal profiles of particulate organic carbon and chlorophyll *a* collected from a station in the northern, central and southern regions of the lake. Arrows indicate the date when a sample was collected.

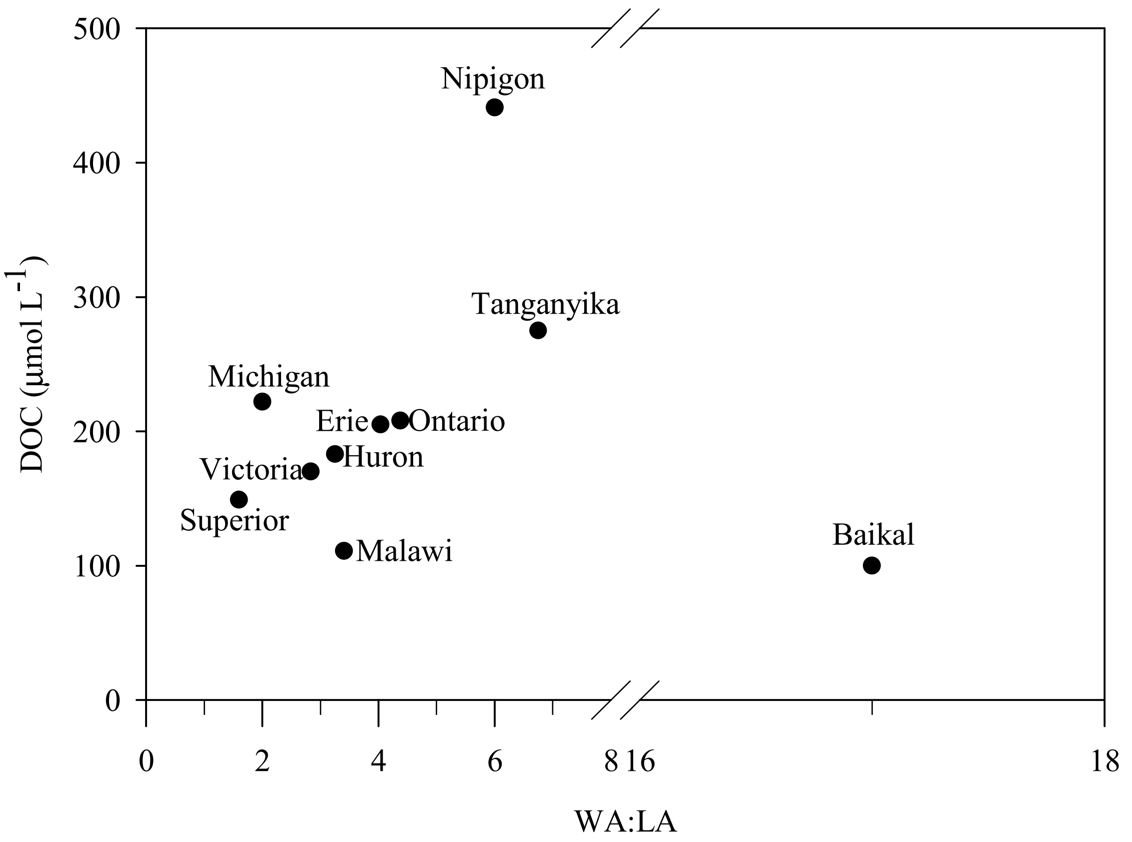


Figure 26: Mean dissolved organic carbon from some of the world's great lakes plotted against the ratio of watershed area to lake surface area (Laird and Scavia 1990, Hecky 1991, Kelly et al. 2001, Yoshioka et al. 2002).

Table 8: Volume – weighted mean annual DOC and POC concentration by depth strata and associated annual mean mass of carbon in Lake Malawi. Stratum volumes are based on Vollmer et al. (2002)

| Stratum | Volume ($km^3$) | DOC ($\mu mol\ L^{-1}$) | POC ($\mu mol\ L^{-1}$) | DOC (moles x $10^{10}$) | POC (moles x $10^{10}$) |
|---|---|---|---|---|---|
| Epilimnion (0 – 105m) | 2,754 | 111 | 17 | 30.6 | 4.8 |
| Metalimnion (105 – 220m) | 2,310 | 110 | 14 | 25.5 | 3.2 |
| Hypolimnion (> 220m) | 2,711 | 80 | 23 | 21.8 | 6.2 |
| **Total** | | | | **78.2** | **14.1** |

### *4.3.5 Vertical Exchange*

The concentration of dissolved inorganic carbon (DIC) and soluble reactive phosphorus (SRP) in each of the three layers from a deep station in the northern region and fluxes based on the vertical exchange coefficients determined by Vollmer et al. (2002) are provided in Fig. 27 and Table 9. In agreement with previous studies, anoxic conditions are observed at around 220 m which approximates the metalimnion-hypolimnion boundary. The mean temperature for waters deeper than 300m was estimated at 22.98 ± 0.01ºC. This is 0.23 ºC and 0.88 ºC higher than hypolimnion temperatures recorded in 2000 and 1940, respectively (Vollmer et al. (2005). This warming trend may have implications for lake mixing and nutrient dynamics, depending on how hypolimnetic temperature changes relative to epilimnetic temperature. In Lake Tanganyika, surface waters have warmed more than the hypolimnion, enhancing stability resulting in a 20% reduction in primary productivity and an overall reduction in fish yields of approximately 30% (O'Reilly et al. 2003, Verburg et al. 2003, Cohen et al. 2016). Long-term observations for the surface waters of Lake Malawi are required to confidently conclude whether the observed trend results in weakening or strengthening stratification in the lake. Similar to the observations of Katsev et al. (2017), dissolved inorganic carbon (DIC) levels increased with depth, from approximately 2.2 mmol $L^{-1}$ in the surface waters to 2.5 mmol $L^{-1}$ in the deep hypolimnetic waters. Concentrations of soluble reactive phosphorus were also highest in the epilimnion in agreement to previous observations (Bootsma and Hecky 1999). Profiles were collected on two dates in April and August 2015 and flux rates are reported as a range for those dates. The mean net flux of DIC and SRP from metalimnion to epilimnion was 1,520 and 13.4 mmol C $m^{-2}$ $yr^{-1}$, respectively while the mean flux from hypolimnion to metalimnion was 663 and 4.3 mmol C $m^{-2}$ $yr^{-1}$ for DIC and SRP, respectively (Table 9).

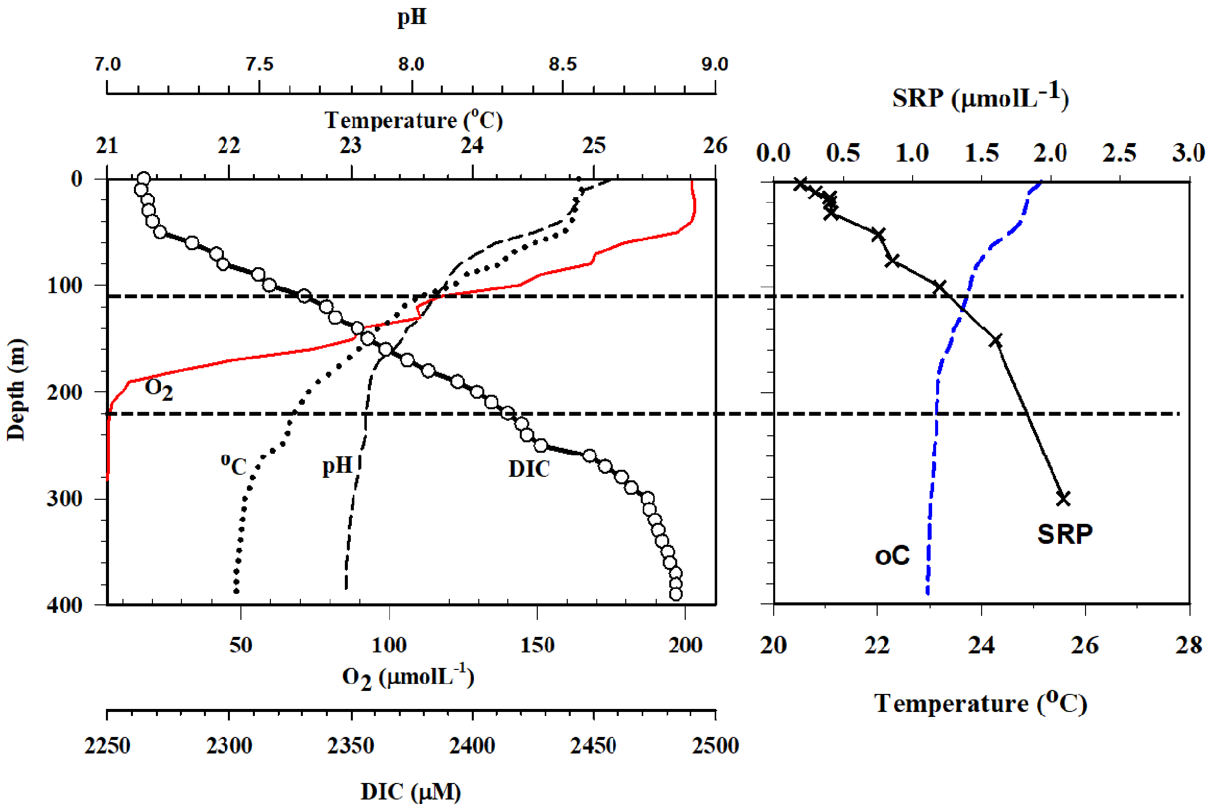


Figure 27: Temperature, dissolved inorganic carbon (DIC), dissolved oxygen (DO), pH and soluble reactive phosphorus (SRP) profiles measured at a northern station, Nkhata Bay on 29st April 2015.

Table 9: Volume weighted dissolved inorganic carbon (DIC) concentrations, vertical exchange coefficients (*k*) and volumes for each depth stratum, and annual DIC flux rates derived from these values. *k* values from Vollmer et al. (2002) and DIC flux rates represent annual exchange rates between a stratum and that underlying it. Flux rates have been normalized to lake surface area.

| Stratum | Volume ($km^3$) | *k* (1/yr) | DIC (μmol $L^{-1}$) | DIC (μmol $L^{-1}$) | DIC Flux (mmol $m^{-2}$ $yr^{-1}$) | DIC Flux (mmol $m^{-2}$ $yr^{-1}$) |
|---|---|---|---|---|---|---|
| Epilimnion (0 – 105m) | 2,754 | 0.270 | 2,269±17 | 0.49±0.25 | 1,520±520 | 13.4 |
| Metalimnion (105 – 220m) | 2,310 | 0.056 | 2,333±5 | 1.05±0.63 | 663±184 | 4.3 |
| Hypolimnion ( > 220m) | 2,711 | | 2,421±19 | 1.61±0.29 | | |

### *4.3.6 Autochthonous primary production*

Areal phytoplankton productivity rates in Lake Malawi have been estimated before and range between 240 and 270 g C $m^{-2}$ $yr^{-1}$, (Degnbol and Mapila 1982, Bootsma 1993b). Extrapolating the primary productivity rates to the entire lake surface area (29,500$km^2$), 58.3 - 66.4 x $10^{10}$ mol C $yr^{-1}$ is produced by photo-autotrophic production. The areal productivity rate observed in Lake Malawi is relatively high for a large lake, although the Lake Victoria production rate is almost 6 times higher. However, it is 1.5 times higher than that measured in lakes Ontario, Erie and Michigan. It is also two times that observed in lakes Baikal and Huron and nearly four times the rate from Lake Superior (Table 10). The low observed primary productivity in Lake Superior is due to low water column temperatures coupled with low P concentrations (Urban et al. 2005). Lake Superior experiences the lowest annual temperatures (mean 3.64°C) compared to the other Laurentian Great Lakes because of its size. Primary productivity rates are relatively higher in tropical lakes than temperate lakes. Kilham and Kilham (1990) and Alin and Johnson (2007) attribute the high primary productivity in tropical lakes as a result of high irradiance and warm water temperatures that persist throughout the year compared to temperate lakes. Kilham and Kilham (1990) refer to this phenomenon as the “endless summer” which results in an efficient breakdown and recycling of nutrients in the epilimnion resulting in high primary productivity (Bootsma 1993b, Spigel and Coulter 1996, Lewis 2010).

Table 10: Comparison of primary production rates for some large lakes of the world. Data from Bootsma (1993b), Hecky (2000) and Yoshida et al. (2003)

| Name of Lake | Annual Primary Production ($g\ C\ m^{-2}\ yr^{-1}$) |
|---|---|
| Victoria | 1,500 |
| Tanganyika | 290 |
| Malawi | 256 |
| Ontario | 170 |
| Erie (East) | 160 |
| Baikal | 113 |
| Huron | 100 |
| Superior | 65 |

### *4.3.7 Sedimentation*

Since flux rates out of the lake through the Shire River outflow are small, estimated at about 3%, there must be an additional major loss mechanism to balance the inputs. Sinking and burial constitute the major loss rates of particulate nutrients from the lake. For the water column, the important mechanism is sediment sinking. Sediment sinking from the epilimnion and metalimnion were estimated using sediment traps that were set at 100 m and 180 m, respectively (Bootsma and Hecky 1999). Sedimentation rates were higher at the south station than the central station and corroborate with earlier measurements of phytoplankton dynamics in the lake (Bootsma 1993b, Patterson and Kachinjika 1995). The estimated annual mean epilimnetic sedimentation rates were 1,462±43 mmol C $m^{-2}$ $yr^{-1}$ while metalimnetic mean estimates were 1,626±59 mmol C $m^{-2}$ $yr^{-1}$. Sedimentation accumulation rates show an increasing trend with the depth of traps with sedimentation rates at 180 m averaging approximately 10% greater than those at 100 m. This trend is surprising, but it emphasizes the mechanism of sediment focusing in the lake. This can only happen if there are direct inputs of organic material into the metalimnion that have not passed through the epilimnion. The sediment traps were set in relatively deep waters i.e. bottom depths of 200 m, 362 m, and 244 m. Considering the depth at which the traps were set relative to the bottom, the effect of sediment re-suspension may be unlikely and or minimal. We think that this could be due to lateral advection of sediments from shallow areas to deep waters that pass below the 100 m traps. Previous phytoplankton production measurements in the lake indicate that the shallow southern part of the lake exhibits high production rates (Bootsma 1993b). Since this shallow southern region of the lake is non-depositional (Johnson and Davis 1989), it is most probable that the organic material from this region is transported to the deeper central and northern waters during the windy season, May to September. This observation implies that the sedimentation rate of organic carbon and phosphorus is either underestimated for the epilimnion or overestimated for the metalimnion. At present, it is difficult to correct for sediment focusing and therefore a correction for the potential of under-sampling or over-sampling from the 100 m and 180 m traps has not been attempted. Rather than calculating a mean sedimentation rate for the lake, measurements from the two trap depths are reported as a range.

### *4.3.8 Organic carbon burial*

Burial rates are of interest only for the whole-lake budget and were collected using sediment core analysis. Two locations, northern and central part of the lake were considered. The sediment core from the Songwe River delta (SRdel), the northern part of the lake had a year record from 1908 to 1989 while that from the Dwangwa delta (Ddel), the central part, spanned between 1880 and 1991. Sediment cores had relatively comparable organic carbon burial between the period 1880 and 1960 with SRdel fluctuating between 1,619 and 3,639 mmol C $m^{-2}$ $yr^{-1}$ while at Ddel burial ranged between 1,659 and 3,087 mmol C $m^{-2}$ $yr^{-1}$. In contrast, since 1960, OC burial rates at the Dwangwa delta were on average 3 times higher than burial rates at the Songwe delta. A similar pattern was also observed for biogenic silica (BSi) within the same period by Hecky et al. (1999). The annual mean OC burial rate from the two locations was estimated as 2,666±850 mmol C $m^{-2}$ $yr^{-1}$. Alin and Johnson (2007) estimated the percentage depositional area of the lake basin to be 80% and so burial rates are calculated as 2,133±962 mmol C $m^{-2}$ $yr^{-1}$ and total annual net OC burial for the lake of $6.3\pm2.8 \times 10^{10}$ mol C $yr^{-1}$. Comparing this burial amount with the total organic carbon in the lake, ($R_{in} + D + P = 70.8\pm15.3 \times 10^{10}$ mol C $yr^{-1}$), we estimate an average burial efficiency of 8.7±2.1%. This burial efficiency is comparable to marine systems (Suess 1980) but is lower than that observed in the Laurentian Great Lakes (Thomsen et al. 2004, Li et al. 2012), Green Bay (Klump et al. 2009) and other temperate lakes (Dean and Gorham 1998, Cole et al. 2007). Organic carbon burial rates are lower in tropical Lake Malawi than in temperate lakes likely due to the perennial warm temperatures that promote high carbon remineralization rates (Alin and Johnson 2007, Katsev et al. 2017) in addition to the great depth which provides longer sinking and decomposing time for POC in the water column before it can reach the lake bottom.

### *4.3.9 A Carbon Mass Balance*

Sources and sinks of carbon in the lake are riverine, atmospheric deposition, air-water exchange, burial, respiration and autochthonous primary production. The carbon mass balance budget for the whole lake and the epilimnion are presented in Figure 28 and Table 11. For the epilimnion, an additional DIC input is provided by vertical flux from the underlying water strata. Autochthonous primary production constitutes the major OC source in the lake, contributing between 92 and 97% of the total organic carbon. A similar pattern was observed in Lake Superior, with primary production contributing between 87 and 89% of total organic carbon (Cotner et al. 2004). The low contribution from allochthonous inputs in Lake Superior was attributed to the low watershed to lake surface area ratio (WA: LA is about 1.6) which makes the lake less influenced by its catchment. It is apparent that most of the carbon entering or produced within the lake is recycled or respired within the basin with less than 1% being accounted for by the outflow through the Shire River. Annual average burial efficiency in Lake Malawi is estimated at 8.7±2.1%.

The high retention efficiency in Lake Malawi was also observed for silica by Bootsma et al. (2003) and described the lake as a "silica trap" because almost 99% of the silica was retained in the lake. This trend was attributed to the high hydraulic residence time and high phytoplankton growth rates probably diatoms within the lake. While riverine outputs in Lake Malawi are comparable to those from Lake Superior (ca. 1.3%), respiration constitutes the major loss of carbon in Lake Superior contributing 95 to 97% of the total outputs (Cotner et al. 2004).

Measurements of respiration rates in Lake Malawi are not available and, in their absence, the whole-lake carbon budget is not balanced. Since primary productivity rates and air-water $CO_2$ exchange in the lake are well quantified, respiration rates should approximate the difference between primary productivity (19,770-25,500 mmol C $m^{-2}$ $yr^{-1}$) and atmospheric $CO_2$ exchange (209-320 mmol C $m^{-2}$ $yr^{-1}$). The "P – $CO_{2exchange}$" is calculated 19,450-25,291 mmol C $m^{-2}$ $yr^{-1}$ (or 233-303 g C $m^{-2}$ $yr^{-1}$), where P is primary production and $CO_{2exchange}$ is the $CO_2$ flux at the air-water interface estimated using direct $pCO_2$ measurements. These respiration rates are within the range observed in a large tropical Lake Tanganyika, 130 to 766 g C $m^{-2}$ $yr^{-1}$ (Hecky et al. 1978, Sarvala et al. 1999). The ratio of primary production to respiration (P: R) in Lake Malawi is estimated at 1.01 – 1.02 which indicates somewhat close to equilibrium as NEP is closer than 1. In contrast, measurements of primary production and respiration in Lake Superior show that the lake is net heterotrophic with Russ et al. (2004) estimated P: R ratios of 0.4 – 0.83. Metabolism in Lake Superior, however, is spatially variable with the areas close to Duluth, Minnesota showing autotrophy, P: R of 1.7 due to a high loading of nutrients from urbanization (Russ et al. 2004).

Based on the mass balance in Table 11, total inputs (558-2,155 mmol C $m^{-2}$ $yr^{-1}$) excluding the air-water exchange for the whole lake are smaller than the outputs (1,478-2,872 mmol C $m^{-2}$ $yr^{-1}$) by about 687-919 mmol C $m^{-2}$ $yr^{-1}$. This implies that an external $CO_2$ source is required to fix this additional organic carbon. The deficit is comparable to the $CO_2$ flux we measured using direct $pCO_2$ measurements in the lake (209-320 mmol C $m^{-2}$ $yr^{-1}$). The difference could be because of underestimation of primary production as the $CO_2$ flux estimates were based on $pCO_2$ measurements collected offshore. This provides strong support for the conclusion that Lake Malawi is a net $CO_2$ sink and hence autotrophic considering that these estimates were made using independent approaches. However, inputs into the epilimnion are much higher than total outputs by an average of approximately 945 mmol C $m^{-2}$ $yr^{-1}$. Nevertheless, the lower end of inputs to the epilimnion of 1,152 mmol C $m^{-2}$ $yr^{-1}$ is fairly comparable to the mean output of

1,489 mmol C $m^{-2}$ $yr^{-1}$, the sedimentation rate that was determined in the lake from traps set at 100 m (Bootsma and Hecky 1999). The balance between inputs and outputs indicates that the estimated lower end vertical DIC flux of 1,152 mmol C $m^{-2}$ $yr^{-1}$ from the metalimnion to epilimnion in the current study, is a reasonable value. This vertical flux is about 74% of the total inputs into the epilimnion. Bootsma et al. (2003) observed that vertical flux of soluble reactive silica contributed about 72% of total epilimnetic inputs. This vertical DIC flux between the metalimnion and epilimnion (1,152 mmol C $m^{-2}$ $yr^{-1}$) represents 77% of the measured sinking rate (1,492 mmol C $m^{-2}$ $yr^{-1}$) implying that most of the carbon is recycled back to the epilimnion. On the other hand, the mean DIC flux (663±184 mmol C $m^{-2}$ $yr^{-1}$) from the hypolimnion to metalimnion (Fig. 8) is approximately 37% of the burial rate which indicates low recycling efficiency in the hypolimnion. The conclusion that recycling rates in the hypolimnion are low is in agreement with observations by Li et al. (2018) and corroborate Sobek et al. (2009)'s theory of low carbon recycling efficiency in anoxic waters. Autochthonous primary production is the major source of organic carbon in the lake. Although concentrations of DOC and POC are relatively low in the lake compared to other lakes, the carbon inventory is large, representing 11.5 times the annual OC load ($OC_{pool} / OC_{allochthonous} = 92 \times 10^{10} / 8 \times 10^{10}$).

### *4.3.10 Uncertainties in Carbon Mass Balance calculation*

As outlined in the methods section, most of the data used to calculate the mass balance are based on measurements from different time periods. The main fluxes used for the mass balance include 1) river loading/outflow, 2) atmospheric loading, 3) water column sedimentation, 4) permanent burial in sediment, 5) primary production and 6) vertical fluxes. Potential errors resulting from the use of flux rates measured at various temporal and spatial scales are discussed below.

Concentration of organic carbon loading (especially particulate carbon and phosphorus) from tributary rivers is strongly correlated to precipitation and watershed activities (Kingdon et al. 1999, Hecky et al. 2003). The year-to-year variation in total rainfall within the Lake Malawi watershed can be high as other years droughts are experienced while flooding is also experienced in some years. Thus, effect of rainfall on the total year-to-year river loading is going to vary but the long-term average may vary minimally. According to the current measurements, loading of organic carbon, especially particulate carbon in the 2014/15 rainy season has declined. This is attributed to good agricultural practices, the abandoning of most farms due to the low market of tobacco world-wide (Sosola et al. 2011). This implies that loading rates for organic carbon would either remain the same or change slightly resulting in minimal fluctuations in C:P ratios. Atmospheric deposition constitutes about 40% of the total allochthonous organic carbon inputs into the lake. Concentrations of nutrients from atmospheric deposition are dictated by activities in the catchment i.e. production of ash from biomass burning (Andreae 1993). With improved agricultural practices, it means that burning of forests and farmland to prepare for the next growing season will be reduced and hence inputs to the atmosphere will be reduced. Under moderate input conditions from both river loading and atmospheric deposition, our conclusion of the lake being a net $CO_2$ sink would not change as drivers of heterotrophy would have remained relatively the same. In addition, vertical exchange inputs of phosphorus (8 – 22 mmol P $m^{-2}$ $yr^{-1}$) into the epilimnion are approximately equal to allochthonous inputs (5.1 – 15.8 mmol P $m^{-2}$ $yr^{-1}$) and so if vertical mixing is a major mechanism by which P enters the epilimnion, the effect of riverine and atmospheric deposition is going to be dampened. Since the hypolimnion of Lake Malawi has a large nutrient inventory, and this storage increases with external nutrient input increase, the hypolimnetic nutrient concentrations will always be high and so will vertical flux inputs (Bootsma and Hecky 1999).

One of the challenges with calculating vertical flux is that the vertical exchange rates (*k*) used (Vollmer et al. 2002), are averaged over a long time period. In contrast, the dissolved inorganic carbon and nutrient profiles collected are for a single day and it is possible that these profiles may change from one year to the next. To ascertain the potential error in vertical flux estimates due to temporal variability in nutrient concentrations, we compared nutrient profiles from several studies conducted in the lake (Bootsma 1993b, Patterson and Kachinjika 1995, Bootsma and Hecky 1999, Hamblin et al. 1999, Guildford et al. 2003, Li 2014, Li et al. 2018). The nutrient profiles over time do not vary much and so we are confident that our vertical flux estimates represent the long-term average.

Another potential error in the estimation of mass balance could be the underestimation of the amount of carbon and phosphorus lost to sedimentation and burial in the sediments. The estimated sinking rate of organic carbon (1,431 - 1,489 mmol C $m^{-2}$ $yr^{-1}$) and of phosphorus (9.4 to 12.3 mmol $m^{-2}$ $yr^{-1}$) from the epilimnion based on traps set at 100 m are much lower than what was recorded at 180 m (Fig. 28). This may be due to the re-suspension and/or lateral scattering of epilimnetic sediments from the shallow non-depositional southern areas of the lake that result in the transport of a large amount of particulate organic carbon and phosphorus along the lake bottom. Although differences arise in sedimentation rates within the water column that does not affect the whole lake budget as total organic carbon and phosphorus inputs and outputs for the whole lake are closely balanced. Sediment traps and sediment cores were collected from a few points in the lake and extrapolated to the whole lake. If sampling underestimated sinking and burial rates in the lake, and corrections are made for that, it will make outputs to be higher than inputs and the budget more unbalanced. On the other hand, the two cores used to determine burial (Songwe and Dwangwa delta) had significant differences after 1960 and so it is not known which burial rate best represents the entire lake. A range rather than an average burial rate was therefore considered. Hecky et al. (1999) point out that sediment cores may have overestimated burial rates because sediment focusing was not accounted for. Nevertheless, this observation would require atmospheric $CO_2$ input to fix the excess observed buried carbon. Lake Malawi would still be autotrophic, a conclusion that was also reached in Chapter 2 using direct measurements of $pCO_2$.

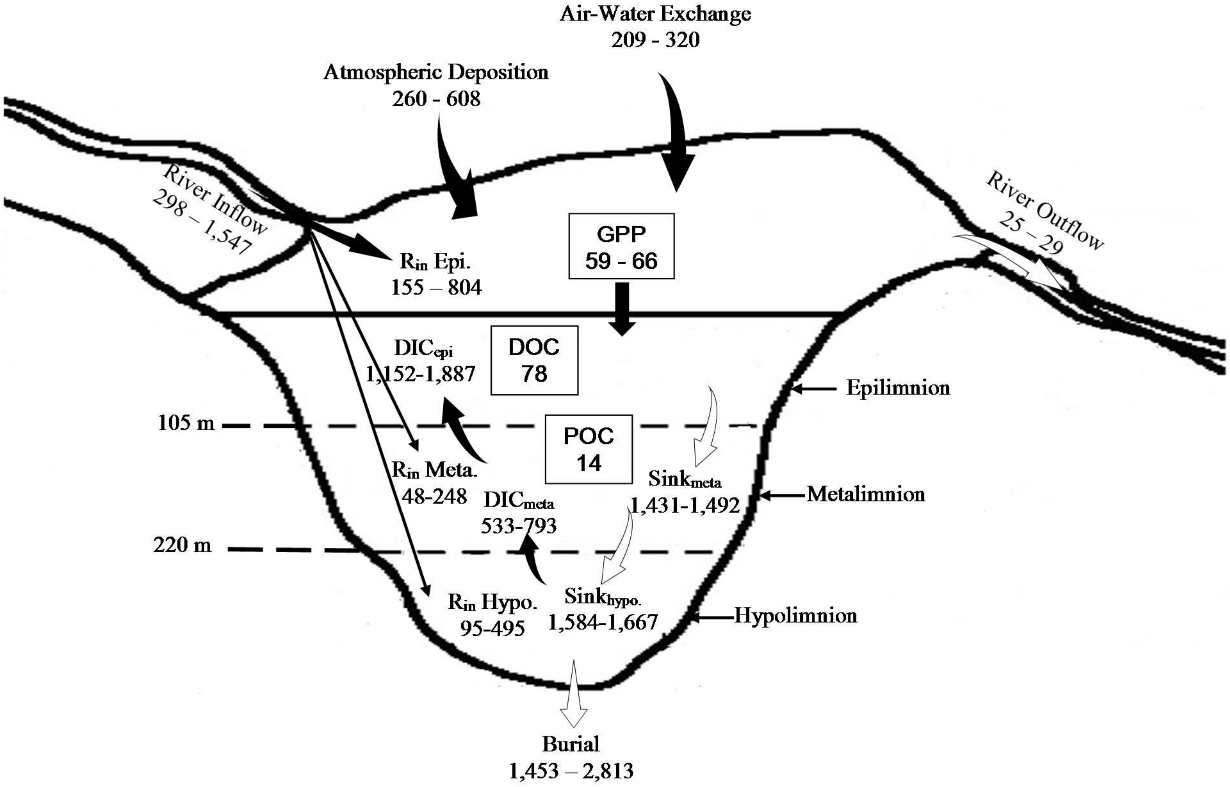


Figure 28: The carbon mass budget for Lake Malawi. Pools and fluxes are provided in rectangles (x $10^{10}$ mol C) and arrows (mmol C $m^{-2}$ $yr^{-1}$), respectively. $R_{in}$ represents river input and is provided for direct injection into each depth strata, based on proportions by Kingdon et al. (1999) and Bootsma et al. (2003). Sinking rates are provided for epilimnion to metalimnion ($Sink_{meta}$) and metalimnion to hypolimnion ($Sink_{hypo}$) based on traps that were set at 100 m and 180 m, respectively. Similarly, DIC vertical flux is provided for hypolimnion to metalimnion ($DIC_{meta}$) and metalimnion to epilimnion ($DIC_{epi}$).

Table 11: Carbon mass balance for Lake Malawi. All fluxes are mmol C $m^{-2}$ $yr^{-1}$ normalized to lake surface area of 2.95 x $10^{10}$ $m^2$. Epilimnion refers to the depth stratum from the surface to 105 m while metalimnion is 105 to 220 m. The whole lake carbon budget for Lake Superior by Cotner et al. (2004) is provided for comparison normalized to 8.21 x $10^{10}$ $m^2$.

| | | Whole Lake | Epilimnion | L. Superior |
|---|---|---|---|---|
| INPUTS | | | | |
| | Atmospheric | 260 – 608 | 260 – 608 | 162 – 416 |
| | River Inflow | 298 – 1,547 | 155 – 804 | 548 – 629 |
| | Vertical Mixing | | 1,152 – 1,887 | |
| | *Total Allochthonous Input* | *558 – 2,155* | *1,567 – 3,299* | *711 – 1,045* |
| | Primary Production | 19,770 – 25,500 | 19,770 – 25,500 | 5,380 – 8,323 |
| | **Total input** | **20,328 – 27,655** | **21,337 – 28,799** | **6,090 – 9,369** |
| OUTPUTS | | | | |
| | Sinking | | 1,431 – 1,492 | |
| | Burial | 1,453 – 2,813 | | 487 – 1,523 |
| | River Outflow | 25 – 29 | 25 – 29 | 18 – 102 |
| | *Sinking +Burial + Outflow* | *1,477 – 2,842* | *1456 – 1,521* | *568 – 1,624* |
| | Lake-atmospheric exchange | -209 to -320 | -209 to -320 | |
| | Respiration* | 19,450 – 25,291 | 19,450 – 25,291 | 13,195 – 39,586 |

* Calculated from the difference between primary production and lake-atmospheric $CO_2$ exchange. The assumption is that the balance between primary production and respiration (P – R) approximates the lake-atmospheric $CO_2$ exchange. therefore, P – $CO_2$ flux should equal respiration.

To determine the recycling efficiency of carbon and phosphorus in the lake, we determined and calculated the sinking, burial and vertical flux rates by water strata. Table 12 provides a summary of the fluxes by each category and the estimated C:P ratios. The dataset shows that recycling efficiency is higher for both carbon and phosphorus in the epilimnion. However, carbon recycling efficiency decrease with depth and the lowest was observed in the anoxic hypolimnion (35%). In contrast, phosphorus recycling rates were relatively higher than carbon in the hypolimnion (77%). This indicates a selective recycling of phosphorus relative to carbon. The C:P ratios of recycled carbon and phosphorus indicate an increased concentration of P relative to carbon. This is likely the result of anoxic conditions in the hypolimnion, which appear to impede carbon recycling rates (Sobek et al. 2009). The burial C:P ratio in Lake Malawi ranges between 250-578 (Hecky et al. 1999) indicating that P burial is much lower than carbon.

Table 12: Inputs and outputs of carbon and phosphorus between water strata, recycling efficiency, and the C:P ratio. According to Hecky et al. (1999), C:P ratio for the buried carbon and phosphorus fluctuates between 250-573:1

| Strata | Component | C (mmol/m$^2$/y | P (mmol/m$^2$/y | C:P Flux ratio |
|---|---|---|---|---|
| EPILIMNION | River input and phytoplankton fixation rates | 23,115 | 115 | 201 |
| | Sinking rates out of the epilimnion | 1,460 | 8.8 | 166 |
| | *Recycling efficiency (%)* | *94* | *92* | |
| METALIMNION | River inputs and sinking rates from the epilimnion | 1,610 | 13 | |
| | The vertical flux between metalimnion and epilimnion | 1,520 | 15 | |
| | Corrected flux from hypolimnion | 857 | 5.8 | 148 |
| | *Recycling efficiency (%)* | *56* | *39* | |
| HYPOLIMNION | River inputs and sinking rates from metalimnion | 1,900 | 12 | |
| | The flux between hypolimnion and metalimnion | 663 | 9.2 | 72 |
| | *Recycling efficiency (%)* | *35* | *77* | |

# Chapter 5 - Summary and Conclusion

## 5.1 Summary

1. On an annual basis, Lake Malawi is a net $CO_2$ sink and hence net autotrophic. The $CO_2$ drawdown in tropical Lake Malawi is controlled by phytoplankton production during the hot, wet season and cool, mixing season. By contrast, $CO_2$ evasion to the atmosphere was observed at the onset of cool, mixing season and the hot, stratified season. The areal $CO_2$ flux in Lake Malawi fluctuates between -209 and -320 mmol C $m^{-2}$ $yr^{-1}$ with a total annual flux of approximately $0.8 \times 10^{10}$ mol C $yr^{-1}$ from the atmosphere when extrapolated to the entire lake surface area.
2. As in previous studies of nutrient and phytoplankton dynamics, the dataset here reveals significant spatial and temporal changes in $pCO_2$ and $CO_2$ flux related to hydrodynamic and meteorological conditions in the lake. Spatially, the southernmost region of the lake was the most distinct. Although this region of the lake is the most nutrient-rich and hence most productive, it was $CO_2$ supersaturated with respect to the atmosphere at the beginning of the cool, mixing season due to the supply of DIC from the deep north-central area during upwelling. While upwelling also results in the flux of phosphorus into the epilimnion promoting photosynthesis, the high $pCO_2$ and positive $CO_2$ flux at the beginning of the mixing season imply that phytoplankton cannot immediately assimilate all the excess $CO_2$. Even though much of this $CO_2$ is lost to the atmosphere, the upwelled P is retained and likely transported northward. As a result, the more productive southern end of the lake is a

net $CO_2$ source while the less productive central and northern parts of the lake are $CO_2$ sinks. Seasonally, measurements could be divided into four periods: 1) December to April, the wet, hot season when almost the entire lake was $CO_2$ undersaturated with respect to the atmosphere and net $CO_2$ uptake was observed. 2) May to June, the onset of mixing season when the lake was $CO_2$ supersaturated with respect to the atmosphere and net $CO_2$ efflux was observed. 3) July to September, the cool, mixing season, when the lake was $CO_2$ undersaturated with respect to the atmosphere. 4) October to November, the hot, stratified season when surface waters showed supersaturation with respect to the atmosphere and $CO_2$ flux was from the lake to the atmosphere. Variation of both $pCO_2$ and lake-atmosphere $CO_2$ fluxes are generally in agreement with trends of phytoplankton biomass and photosynthesis in the lake, which appear to be regulated by river inflow and in-lake mixing. The observed spatio and temporal variability of $pCO_2$ highlights the need for high resolution datasets to accurately determine annual lake-atmosphere $CO_2$ flux.

3. Using the approach of Takahashi et al. (2002), it is evident that $pCO_2$ variability is chiefly controlled by biological processes while temperature plays a minor role. The highest seasonal $pCO_2$ amplitude was observed in the more southern region, where upwelling is strongest. The observation that the temperature effect in tropical Lake Malawi is low was expected considering that annual surface temperature fluctuates less than 25% (surface water temperatures fluctuate between 24 and 29°C).
4. Using bottle incubation experiments to determine the influence of carbon and nutrient flux into the epilimnion of Lake Malawi through river loading and vertical exchange, it is obvious that these input sources have opposing effects and based on the stoichiometry of C:P. Results from the vertical exchange experiment are in agreement with phytoplankton

dynamics that are dependent on hydrodynamics in the lake. However, the river experiment provided results that are different from what is observed in the field. The vertical exchange resulted in $CO_2$ consumption and higher phytoplankton biomass while river loading showed $CO_2$ supersaturation indicating that respiration is greater than photosynthesis. Given the uncertainty in what form of P is utilized by phytoplankton and considering the long residence time of P in the epilimnion, the results of the river experiment may not have bracketed the potential period for P remineralization in that occurs in the lake.

5. Based on the carbon mass balance, autochthonous primary production is the major source of organic carbon in Lake Malawi. Further, the budget shows that almost all organic carbon entering or produced with the lake is retained and recycled in the lake as outflow through the Shire River only accounts for less than 1%. Out of the total organic carbon load (allochthonous load + primary production), only 6% is buried in the sediments. This is relatively low, compared to a burial efficiency of 10% to 30% that is reported for most large, temperate lakes.
6. The mass balance provided here shows that internal cycling is an important source of carbon to the epilimnion and that carbon recycling rates in the metalimnion and epilimnion are much higher than in the hypolimnion. This observation complements earlier findings that carbon recycling rates under anoxic conditions may be low (Sobek et al. 2009) and this trend may promote autotrophy if P is selectively recycled into the mixed zone.

## 5.2 Conclusion

This is the first study to use direct measurements of $pCO_2$ to determine the spatial and temporal variability of $CO_2$ flux for any large tropical lake. The dataset provides evidence of a strong correlation between surface $pCO_2$ variability and hydrodynamic and meteorological conditions that ultimately control nutrients and phytoplankton dynamics in the lake. The observed variations in the lake-atmosphere $CO_2$ flux emphasize the need for comprehensive spatial and temporal data sets when estimating whole-lake metabolism. On an annual basis, Lake Malawi is a net $CO_2$ sink. The $CO_2$ drawdown in tropical Lake Malawi is controlled by phytoplankton production during the hot, wet and cool, mixing seasons while efflux to the atmosphere is driven by the physical resupply of DIC from deep waters to the epilimnion at the onset of the mixing season and the high respiration to photosynthesis ratio in the hot, stratified season. The high $pCO_2$ and positive $CO_2$ flux observed at the onset of the mixing season in the most productive southern part of the lake imply that, despite the increased availability of dissolved phosphorus due to upwelling, phytoplankton are overwhelmed with the DIC supply and cannot immediately assimilate all the excess $CO_2$.

The current study and previous measurements indicate that DOC concentrations in Lake Malawi are low, which is consistent with low watershed to lake surface area ratio and long residence time as described by others (Urban et al. 2005). Although DOC and POC concentrations in the lake are relatively low when compared to other lakes, the carbon inventory is large and most of this organic carbon is retained and recycled within the lake because organic carbon loss rates are low. From a biogeochemical perspective, the current study has provided important insights into the theory of autotrophy and heterotrophy for large tropical lakes and how meteorological conditions control algal dynamics. The observation that low-nutrient oligotrophic lakes tend to be supersaturated with $CO_2$ relative to the atmosphere (Cole et al. 1994) does not appear to be the case for tropical Lake Malawi. Observations from the current study may also apply to the other deep African Great Lakes as they are influenced by similar climatic forcing and also have anoxic or hypoxic hypolimnia. Net autotrophy in Lake Malawi appears to be due to a higher efficiency of P-recycling compared to carbon in the water column. However, further studies are needed to determine whether this may be due to biological processes (e.g. zooplankton nutrient recycling), physical properties (e.g. warm temperatures; meromixis), or chemical conditions (e.g. anoxic hypolimnion).

The carbon mass balance developed here has provided a framework for assessing carbon flows by quantifying and comparing various processes in the lake i.e. river loading, atmospheric deposition, vertical mixing and air-water flux. Autochthonous primary production is the major source of organic carbon in the lake. Although concentrations of DOC and POC are relatively low in the lake compared to other lakes, the carbon inventory is large, representing 11.5 times the annual OC load. Almost all organic carbon entering or produced with the lake is either respired as $CO_2$ and recycled in the lake as outflow through the Shire River only accounts for less than 1% and burial is about 8% of total inputs. Interestingly, the allochthonous organic carbon inputs are lower than the sum of river outflow and burial rates. This implies that additional carbon input must be provided to make up this difference, probably from the atmosphere. The difference between allochthonous inputs and the sum of river outflow and burial is negative which agrees with the direction of the $CO_2$ lake-atmospheric exchange based on the direct $pCO_2$ measurements. This provides strong support for the conclusion that Lake Malawi is a net $CO_2$ sink considering that these estimates were made using independent approaches.

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# CURRICULUM VITAE

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B.S. University of Malawi, Chancellor College, August 1997
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MS. Biology Department, May 2006 University of Wisconsin-Milwaukee, USA,
Thesis Title: Phytoplankton – zooplankton interactions in tropical Lake Malawi

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**Publications**

**Ngochera, M.J** and H. Bootsma. 2018. Carbon, nitrogen and phosphorus composition for seston and zooplankton in tropical Lake Malawi: Implications for zooplankton nutrient cycling. *In* GLOW 8 Advancing the Ecosystem Health Approach: Good Governance for Adaptation and Rehabilitation. DOI: 10.1080/14634988.2017.1280294

**Ngochera, M.J.** 2014. Southeast Arm of Lake Malawi: Limnology, pollution, siltation and habitat change. *In* S. Donda, M. Hara, M. Ngochera and E. Berge (Eds.). Fragmentation of resource management on the Southeast Arm of Lake Malawi: Dynamics around Fisheries. PLAAS. Lit. Berlin

**Ngochera, M. J**., and H. A. Bootsma. 2011. Temporal trends of phytoplankton and zooplankton stable isotope composition in tropical Lake Malawi. *J. Great Lakes Res*. **37**:45 - 53.

## Awards

1. Fulbright Junior Development Program Scholarship, UW-Milwaukee. 2003
2. Chancellor's Award, UW - Milwaukee. 2004
3. Clifford H. Mortimer award, UW-Milwaukee. 2005
4. National Research Council of Malawi (NRCM) research grant, $11,400. 2008
5. International Association of Great Lakes Research (IAGLR) award. 2010
6. International Foundation for Science (IFS) research grant award, $11,000. 2011
7. Teledyne equipment use award, HydroCO2 equipment. 2013
8. Distinguished Dissertator Fellowship (DDF) Award, UW – Milwaukee. 2017

## Professional Positions

Officer In – Charge, Monkey Bay Fisheries Research Station, Monkey Bay, Department of Fisheries, Malawi - January 2016 – to Present

Lead Scientist, Senga Bay Fisheries Research Center (SFRC), Salima, Department of Fisheries, Malawi - May 2008 to December 2015

Adjunct Professor, Mzuzu University, Department of Fisheries
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Teaching Assistant, Foundations of Biological Sciences 150/152 Laboratory, Biology Department, University of Wisconsin – Milwaukee, USA - August 2003 – May 2006