ESTIMATION OF CARBON DIOXIDE FLUX IN SHALLOW LAKES IN TURKEY

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ABSTRACT

ESTIMATION OF CARBON DIOXIDE FLUX IN SHALLOW LAKES IN TURKEY

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The role of Turkish shallow lakes as a sink or source of carbon from 44 shallow lakes sampled once from 2006 – 2012 over six degrees of latitude is analyzed in terms of spatial resolution. Two of the lakes (Eymir and Mogan) were sampled over the spring, summer, and fall seasons from 2006 – 2010 under dry and wet periods and analyzed for temporal resolution. An equation using pH, specific conductivity, wind speed, temperature, and acid neutralizing capacity (ANC) was used to determine CO_2 fluxes (Trolle et al., 2011). The influence of altitude, latitude, and environmental factors, including trophic status, was analyzed.

In the 44 lakes, an altitudinal gradient of CO_2 flux was observed, with higher fluxes at higher altitudes. Median rates of CO_2 emission were in 290 mg C m^{-2} d^{-1} in the northern highlands (NH), 352 mg C m^{-2} d^{-1} in the southern highlands (SH), -8 mg C m^{-2} d^{-1} in the northern lowlands (NL), and -21 mg C m^{-2} d^{-1} in the southern lowlands (SL). In Lakes Eymir and Mogan, a seasonal flux of CO_2 was observed, with higher emissions of CO_2 during summer in Lake Eymir and in spring in Lake Mogan, and less CO_2 emissions during fall. CO_2 fluxes were found to be strongly negatively correlated with pH for Lakes Eymir ($r = -0.87$, $P<0.001$) and Mogan ($r = -0.90$, $P<0.001$). A change from dry to wet period was observed, with an average increase of 138 mg C m^{-2} d^{-1} in Lake Eymir and 214 mg C m^{-2} d^{-1} in Lake Mogan. CO_2 flux was correlated with salinity in Lake Eymir ($r = -0.44$, $P<0.05$), and with water level in Lake Mogan ($r = 0.64$, $P <0.001$), which in turn was correlated with plant volume infested (PVI%) ($r = -0.65$, $P<-0.001$). Accordingly, it can be anticipated that the lakes' production, by macrophytes or phytoplankton, may vary CO_2 fluxes by fluctuating the pH of the lake.

Keywords: hydrology, altitudinal gradient, latitudinal gradient, trophic state

ÖZ

TÜRKİYE'DEKİ SIĞ GÖLLERDE KARBONDİOKSİT AKIŞININ BELİRLENMESİ

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Türkiye sığ göllerinin karbon kaynağı/yutağı olarak işlev görüp görmediğinin anlaşılabilmesi için 2006-2012 yılları arasında 6 enlemi kapsayan 44 sığ gölden alınan örnekler mekansal çözünürlüğe göre analiz edilmiştir. Ayrıca bu göllerden, Eymir ve Mogan, 2006-2010 yıllarının ilkbahar, yaz ve sonbahar mevsimlerinde ıslak ve kurak periyotları kapsayacak şekilde örneklenerek zamana bağlı değişimin anlaşılabilmesi için analiz edilmiştir. Karbondioksit akışının hesaplanmasında pH, özgül iletkenlik, rüzgar hızı, sıcaklık ve asit nötralize etme kapasitesi (ANC) kullanılarak elde edilen denklem kullanılmıştır (Trolle et al., 2011). Bu çalışma kapsamında, yükseklik, enlem ve trofik yapıyı içeren çevresel değişkenlerin de etkisi analiz edilmiştir.

Örneklenen 44 gölün analiz sonuçlarına göre en yüksek karbondioksit akışlarının yüksek rakımlarda olduğu rakımsal bir değişim gözlenmiştir. Karbondioksit salınımının medyan değerleri kuzeydeki yüksek rakımlı bölgelerde (NH) 290 mg C m^2 $gün^{-1}$, güneydeki yüksek rakımlı bölgelerde (SH) 352 mg C m^2 $gün^{-1}$, kuzey ova bölgelerinde (NL) -8 mg C m^2 $gün^{-1}$, güney ova bölgelerinde (SL) ise -21 mg C m^2 $gün^{-1}$ olarak hesaplanmıştır.

Eymir ve Mogan Gölleri'nde karbondioksit akışında mevsimsellik gözlenmekle birlikte, en yüksek salınım Eymir Gölü'nde yaz aylarında, Mogan Gölü'nde ise ilkbaharda ve en düşük salınım ise sonbahar mevsiminde gözlenmiştir. Eymir ($r = -0.87$, $P<0.001$) ve Mogan ($r = -0.90$, $P<0.001$) Gölleri'nde karbondioksit akışı pH değerleriyle negatif ilişkili olarak bulunmuştur.

Kurak dönemden ıslak döneme geçişte ise Eymir ve Mogan Gölleri'nin karbondioksit akışlarında ortalama olarak sırasıyla 138 mg C m^2 $gün^{-1}$ ve 214 mg C m^2 $gün^{-1}$ artış olduğu gözlenmiştir. Ayrıca, karbondioksit akışının Eymir Gölü'nde tuzlulukla ($r = -0.44$, $P<0.05$), Mogan Gölü'nde ise su seviyesi ($r = 0.64$, $P <0.001$) ve dolayısıyla suiçi bitki dolu hacim ($r = -0.65$, $P<-0.001$) ile ilişkili olduğu bulunmuştur.

Sonuç olarak bu çalışmada, suiçi bitkileri ve fitoplankton tarafından yapılan birincil üretimin, göl pH değerlerinde dalgalanmaya yol açarak karbondioksit akışının değişimine neden olabileceği görülmüştür.

Anahtar kelimeler: Hidroloji, rakımsal değişim, enlemsel değişim, trofik yapı

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CHAPTER 1

INTRODUCTION

1.1 The Role of Freshwaters in the Global Carbon Cycle

Recent attention has been given to the role of freshwaters in the global carbon (C) cycle. Though freshwaters have been termed a "passive conduit" of carbon dioxide (CO_2) from land to the ocean by the Intergovernmental Panel on Climate Change in 2007, significant studies now show that freshwater ecosystems are "active pipes", or crucial elements of the metabolism of the biosphere that exchange CO_2 with the atmosphere (Cole et al., 2007; Tranvik et al., 2009).

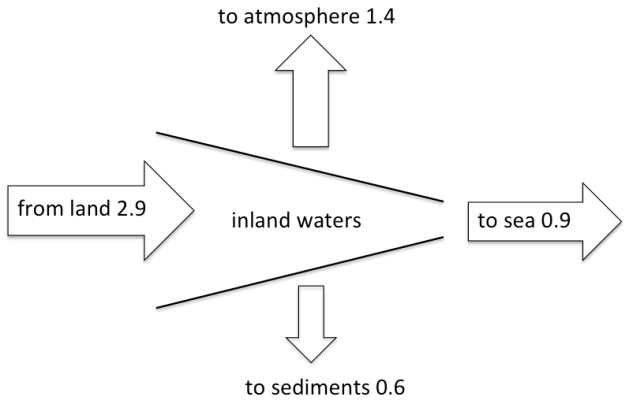

Figure 1.1: The latest view of the global movement of C from land to sea with values represented in Pg (10^{15} g). The figure shows that inland waters function actively in the global C cycle by storing carbon (0.6 Pg y^{-1}), emitting it to the atmosphere (1.4 Pg C y^{-1}), and transporting it to the sea (0.9 Pg C y^{-1}). The extra 2.0 Pg C y^{-1} entering the freshwaters denotes terrestrial net ecosystem production exported into inland waters. Taken from Tranvik et al. (2009).

Small lakes, which make up most of the area in the freshwater dominion (Downing et al., 2013), are typically shallow with plenty of light and nutrients and therefore are among the most productive systems on Earth (Wetzel, 2001). Even so, studies of small aquatic systems have been understated and future work is needed to emphasize their involvement in the global carbon cycle. Presently, most studies concerning CO_2 flux in freshwaters focus on the waters northern Europe and the United States.

1.2 Solubility of Carbon Dioxide in Water

The concentration of dissolved inorganic carbon (DIC) makes up alkalinity, and feeds into the photosynthesis process (Butler, 1992). The amount of DIC in each body of water depends on the equilibria established between atmospheric CO_2, the bicarbonate-carbonate system, external loadings, contributions from metabolic respiration, and utilization in photosynthesis (Wetzel, 2001), and typically ranges from 50 µmol to 10 mmol L^{-1} (Wetzel, 2001). Compared to the marine inorganic carbon pool of 2 mmol C L^{-1} , it is clear that the world's freshwaters are of considerable importance in the carbon cycle.

The dissolution of carbon dioxide in water is a slow reaction (a half-time of approximately 15 s) compared to the subsequent ionization of H_2CO_3.

$$H_2O + CO_2(aq) = H_2CO_3(aq)$$

Because they are uncharged species, the summation of $[CO_2]$ and $[H_2CO_3]$ are often written as $[CO_2]$ or $[H_2CO_3^*]$. H_2CO_3 is a weak acid and in basic waters, ionizes to yield hydrogen ions $[H^+]$, bicarbonate ions $[HCO_3^-]$, and carbonate ions $[CO_3^{2-}]$

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$$

The bicarbonate and carbonate ions also further dissociate to establish equilibrium.

$$HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$$

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$$

$$H_2CO_3 \rightleftharpoons H_2O + CO_2$$

These equilibria are the basis of the pH buffering action of alkaline waters. Unless the supply of carbonate or bicarbonate ions is depleted, the pH is able to remain essentially unchanged – if H^+ ions are added, they neutralize OH^- ions formed by the dissociation of HCO_3^- and CO_3^{2-}; nevertheless, more OH^- ions are formed immediately by the reaction of the carbonate with water.

1.3 Alkalinity and pH of Freshwaters

Bicarbonates, carbonates, and hydroxides are all components of alkalinity and combine with H^+ ions from the water and raise its pH. This function is known as alkalinity, or the buffering capacity of water, and it represents the acid neutralizing capacity (ANC) of an aqueous system (Stumm and Morgan, 1996). Highly alkaline waters are able to neutralize acidic or basic inputs; consequently, daily fluctuations of CO_2 concentrations in highly alkaline lakes do not cause large daily changes in pH (Addy et al., 2004).

In the waters of the world with high alkalinity, about 50% is contributed by dissolution of carbonates, and over 97% of global runoff has been classified as of the calcium carbonate type (Meybeck, 1993). Thus, the equation that will be used in this study for the conceptual definition of alkalinity is:

$$\text{Alkalinity} = [HCO_3^-] + [CO_3^{2-}] + [OH^-] - [H^+]$$

High alkalinity (> 20 mg L^{-1} $CaCO_3$) is normally found in lake water from sedimentary rock regions (besides sandstone), which contain high amounts of $CaCO_3$. Besides coming from the catchment, alkalinity can also be generated biologically (Schindler, 1986). The most common methods are exchange of base cations and redox reactions in hard water lakes, and reduction of sulfate and nitrate in soft water lakes (Schindler et al., 1986). Biological generation of alkalinity is more essential in seepage lakes or lakes with long hydrological residence times.

Since carbon dioxide is the most common form of acidity in water, the processes of photosynthesis, respiration, and decomposition all contribute to the change in pH in a body of water, which may even change diurnally, with the degree of change depending on the alkalinity. Higher rates of respiration and decomposition may lead to more extreme changes in pH (Wurts and Durborow, 1992).

Under times of intense photosynthesis, mainly in eutrophic lakes, the pH may undergo massive daily fluctuations, surpassing 10 in the late afternoon and falling below 8 at night (Wetzel, 2001). This high pH may be accompanied by bicarbonate (HCO_3^-) precipitation and subsequent CO_2 release:

$$Ca^{2+} + 2\ HCO_3^- \rightarrow CaCO_3 + CO_2$$

Respiration and decomposition can counteract this by producing CO_2, which dissolves in water as carbonic acid and lowers the pH. Eutrophic lakes tend to have higher alkalinity than oligotrophic lakes due to their high production and consequent release of $CaCO_3$ (Addy et al., 2004). Moreover, it has been observed that pCO_2 values are higher in lakes with low alkalinities (Lazzarino et al., 2009).

Table 1. Alkalinity categories for lakes and rivers as determined by the U.S. EPA, taken from URI Watershed Watch (2004). Alkalinity status indicates sensitivity to pH changes.

Alkalinity Status	**Concentration of $CaCO_3$ (mg L^{-1})**
Acidified	< 1 and pH < 5
Critical	< 2
Endangered	2 – 5
Highly Sensitive	5 – 10
Sensitive	10 – 20
Not Sensitive	> 20

The pH determines the distribution of the forms of inorganic carbon between free CO_2, bicarbonate, and carbonate. In prior carbon flux studies in lakes, pH has been the variable most correlated with pCO_2 (Trolle et al., 2011) and is frequently used in calculating partial pressures of CO_2 (Lazzarino et al., 2009; Trolle et al., 2011). The amount of dissolved bicarbonate and carbonate increases with increasing pH because of the ionization equilibria (pK). Free CO_2 dominates in water at pH 5 and under; between pH 7 and 9, HCO_3^- dominates. Above pH 9.5 CO_3^{2-} becomes quantitatively significant, and above a pH of 10.5 to 11, CO_2 + OH- → HCO_3^- is the dominant reaction.

1.4 Major Factors that Control the C Budget in Aquatic Ecosystems

Respiration, inflowing groundwater and surface waters, and atmospheric deposition support the input of CO_2 to freshwaters (Fig. 1.3) (Cole and Caraco, 1998). During the growing season, atmospheric invasion may be a significant source of carbon (Dillon and Molot, 1997). The amount of carbon dioxide in aquatic ecosystems depends on both biological and physical facets that regulate carbon absorption, sequestration, and release (Prentice et al., 2001).

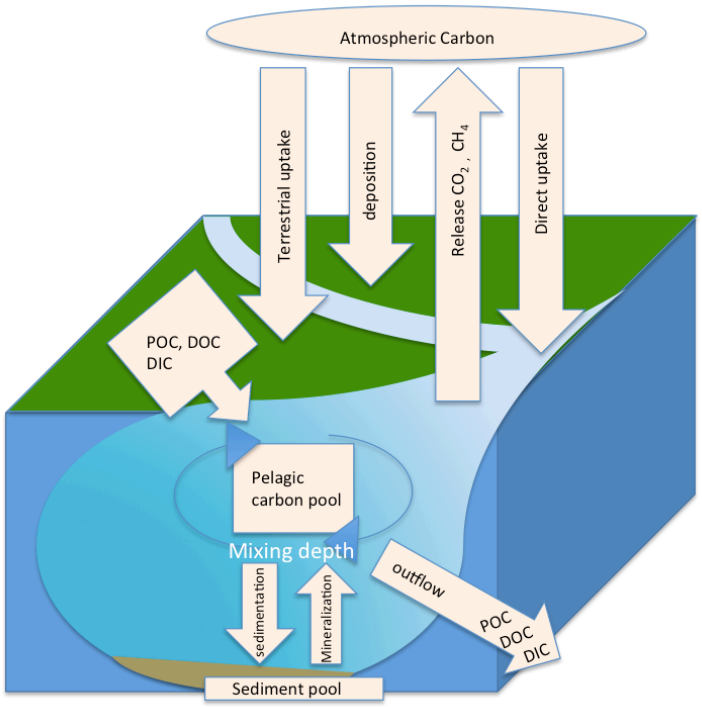

Figure 1.2: A depiction of the several pathways which carbon may enter and leave from lakes and other inland waters along with its possible fate within the lake or inland water itself.

1.4.1 Morphometry, Hydrology, and Catchment Characteristics

Geology, lake morphometry, catchment properties, and hydrology may influence a lake's temperature, physical mixing, nutrient concentrations, DOC, chlorophyll-*a* (Chl *a*), and transparency (Hanson et al., 2007; Nõges, 2009). These factors indirectly affect metabolism, which in turn affects the amount of carbon in the system (Staehr et al., 2011). Findings have shown that both gross primary production (GPP) and respiration (R) decrease with lake area and water depth (Staehr et al., 2011). Other findings show that lakes with a high terrestrial influence and a high inflow to evaporation ratio have high pCO_2 values.

Besides the lateral exchanges of carbon from the terrestrial environment, vertically imported carbon, especially groundwater, may also be important in determining the metabolic status in lakes. Groundwater is often rich in CO_2 deriving from soil respiration and weathering of carbonate rocks (Striegl and Michmerhuizen, 1998), and can thus contribute to a lake's super-saturated CO_2 levels (Kling et al., 1992; Striegl and Michmerhuizen, 1998). Studies show that lakes located low in the catchment generally receive higher groundwater input than lakes located high in the catchment (Cheng and Anderson, 1994) and thus may receive higher inputs of CO_2.

1.4.2 Photosynthesis and Respiration

Being the initial and end product of metabolism, carbon has been long used as a parameter to evaluate a lake's productivity. The concept is that the amount of CO_2 in the sediment from decomposition is about equal to the production of organic matter in the photic zone that settles to the hypolimnion.

The amount of carbon found in the sediment or water column may be due to factors other than metabolism, such as groundwater loading, physicochemical interactions, and flux with the atmosphere (Hanson et al., 2003), leading to complications in the accuracy of measuring productivity. Therefore, the imbalance between GPP and R, net ecosystem production (NEP) generally does not equal net C accumulation rate in ecosystems (Chapin et al., 2006; Lovett et al., 2013). Despite these drawbacks, measuring hypolimnetic CO_2 accumulation gives a practical estimate of the intensity of lake metabolism.

Community respiration rates are scaled as the two-thirds power of the gross primary production rates of aquatic ecosystems (Duarte and Agusti, 1998). This indicates that productivity has a stronger influence over whether a body of water will be a source or sink of carbon dioxide. Moreover, communities with high respiration rates tended to be associated with ecosystems with high rates of gross primary production (Duarte and Agusti, 1998).

1.5 Heterotrophy in Lakes and Allochthonous Carbon

A large number of scientific articles have exposed that net heterotrophy is more common than net autotrophy in aquatic ecosystems (Agusti et al., 2001; Chen et al., 2003; del Giorgio and Peters, 1994; Duarte and Agusti, 1998; Duarte and Prairie, 2005; Hanson et al., 2003; Jansson et al., 2000). Moreover, it has been noted that around 90% of aquatic ecosystems emit CO_2 to the atmosphere (Cole et al. 1994; Kling et al., 1992). Further studies show that lakes are frequently net sources of CO_2 to the atmosphere while simultaneously burying organic carbon in their sediments (Dillon and Molot, 1997; Duarte and Prairie, 2005; Kortelainen et al., 2006; Sobek, 2005).

Heterotrophy is usual in unproductive systems that receive laterally imported carbon from land or adjacent ecosystems (allochthonous carbon) in addition to their own primary production (del Giorgio and Peters, 1994). After entering aquatic ecosystems, allochthonous organic carbon undergoes chemical changes that make it more possible for bacterial degradation. This can raise respiration beyond the limits imposed by photosynthesis (Cole 1999; del Giorgio and Peters 1994).

1.6 Loss of Carbon from Freshwaters

Loss of carbon from inland waters occurs through mineralization, sediment organic carbon burial, emission to the atmosphere, and export to other bodies of water. Mineralization of organic carbon within lakes and subsequent CO_2 emission to the atmosphere is probably the most important carbon loss process (Algesten et al., 2003; Jonsson et al., 2001). Sediment organic carbon burial is also important, because lakes accumulate sediment from the watershed (von Wachenfeldt and Tranvik, 2008) and retain it efficiently. Eutrophic lakes show highest annual burial rates of carbon (von Wachenfeldt and Tranvik, 2008). Inland waters' loss of carbon by emission to the atmosphere is shown to be similar in magnitude to global terrestrial net ecosystem production (Tranvik et al., 2009). If a net annual loss of carbon gas from water to the atmosphere occurs, the water will be balanced with carbon from non-atmospheric sources in order for in-lake processes to be maintained (Striegl and Michmerhuizen, 1998).

1.7 Carbon Flux and Chemically Enhanced Diffusion

The amount of dissolved CO_2 and the flux of CO_2 across the lake surface are influenced by a group of interactions regarding respiration, photosynthesis, temperature, pH, and ANC (del Giorgio et al., 1999; Ojala et al., 2011). An influx of CO_2 into the water means that the water is undersaturated in CO_2, whereas efflux of CO_2 to the atmosphere shows super-saturated waters.

Some studies show that the net CO_2 emission is generally the result of the decomposition or preservation of allochthonous carbon (del Giorgio et al., 1999; Jansson et al., 2000). Thus, pCO_2 can be used as a proxy of lake net ecosystem metabolism (Sobek, 2005). What regulates the balance between CO_2 emission and carbon burial is not known, but climate change and temperature have been hypothesized to influence both processes (Kosten et al., 2010).

The carbon that enters the water from the atmosphere or vice versa must pass through a "stagnant boundary layer", a layer of about 300 µm in thickness at the surface of the water (Emerson, 1975). As wind velocity increases above 1.5 m sec^{-1} (Wetzel, 2001), the layer decreases in thickness allowing more gas exchange. Moreover, as wind speed increases, pCO_2 decreases and gas dissolution decreases.

At low pH levels, the flux of CO_2 is diffusive and rate limiting. However, at a high pH, there is very low CO_2 in the water because it shifts to carbonate and calcium carbonate, which can move to the sediment. In these under-saturated conditions, the flux of CO_2 from the atmosphere to the body of water is enhanced by the hydration reactions $CO_2 + OH^- = HCO_3^-$ and $CO_2 + H_2O = H_2CO_3$, which allow for a higher CO_2 concentration profile in the stagnant boundary layer (Bade and Cole, 2006; Emerson, 1975). This augmented flux, known as chemically enhanced diffusion (CED), has been well documented using a variety of gas transfer models and

assumptions (Bade and Cole, 2006; Emerson, 1975). CED can increase the mass transfer coefficient of CO_2 several fold depending on conditions of pH, wind speed, and temperature, and is especially important in eutrophic lakes since they have intense algal blooms, which can create a drawdown in CO_2 and an increase in pH.

1.7.1 CO_2 Flux and Trophic Status

Most lakes' surface waters are supersaturated with CO_2, thus resulting in an efflux to the atmosphere (Cole et al., 1994). Excess biotic generation of CO_2 is a major cause of CO_2 being released to the atmosphere whereas consumption of CO_2 by epilimnetic photosynthesis can enhance the flux of atmospheric CO_2 to the water (Emerson, 1975). Moreover, it has been shown that as trophic status decreases, the flux of CO_2 to the atmosphere generally increases (Trolle et al., 2011).

However, as shown in Kortelainen et al. (2006), CO_2 concentrations may be positively associated with lake trophic state. This is because as productivity increases, more algae grows and the lake's water can become murky. The density of large aquatic plants also increases with increased productivity, and the decomposition of algae and plants can use up oxygen. This study shows more CO_2 evasion from eutrophic lakes compared with oligotrophic lakes.

1.7.2 Seasonality in CO_2 Flux

Seasonality in CO_2 fluxes from the water may occur due to seasonal variation in metabolism (del Giorgio and Peters 1994). Studies have demonstrated this seasonal variation of CO_2 evasion to the atmosphere (Kling et al., 1992, Trolle et al., 2011). The seasonal dynamics of CO_2 flux from the water are largely driven by the trophic status of the lake and its interaction with ANC, which changes the pH and the equilibrium of the free CO_2 and bicarbonate relation (Trolle et al., 2011). Change in temperature with season also affects the amount of CO_2 able to be held in the body of water.

Studies have shown that most lakes are supersaturated in and emit CO_2 during the winter (Kortelainen et al., 2006; Trolle et al., 2011) due to respiration being dominant over production in the winter. Besides winter, samples during autumn overturn have been seen to carry the most CO_2 (Kortelainen et al., 2006). In most lakes, CO_2 concentrations reach their lowest values during the summer growing season at the time of maximum temperature and algal biomass (Cole et al., 1994), especially in highly eutrophic lakes due to their high production (Trolle et al., 2011).

On the contrary, some studies show that CO_2 emissions peak during the time of maximum temperatures, because heterotrophy increases with increasing temperature in these places (Findlay et al., 1991; Raymond et al., 1997). In a study carried out in the United States using large, coherent data sets, approximately 70% of lakes and reservoirs were supersaturated with respect to the atmosphere during the summer (McDonald et al., 2013).

1.7.3 Effects of Climate Change on CO_2 Flux

Understanding how climate change will affect the quantitative process of the carbon cycle is crucial for future predictions of carbon flux. The Mediterranean region is as hot-spot area in terms of climate change. This region is expected to have decreases in precipitation and increases in temperature, along with a higher chance of drought events (Giorgi and Lionello, 2008).

Besides the fact that warmer waters can not hold as much CO_2 gas as cooler waters, Increasing water temperatures also allow rates of respiration to increase at higher magnitudes than that of photosynthesis (López-Urrutia et al., 2006; Staehr and Sand-Jensen, 2007). Moreover, primary production can be limited by other factors such as nutrients and light, so carbon fixation may also decrease during light- and nutrient-limited periods of high temperature, and increases in carbon emission may result (López-Urrutia et al. 2006). Studies in experimental ponds have discovered that the P:R ratio decreases in response to warming, which may suggest that future warming will drive systems towards net heterotrophy and increased export of CO_2 to the atmosphere (López-Urrutia et al., 2006; Yvon-Durocher et al., 2012).

Mineralization also exhibits a strongly positive relationship with temperature, which suggests that warmer water temperatures lead to more mineralization and less organic carbon burial, signifying that an increase in temperature leads to a higher carbon emissions (Gudasz et al., 2010). In a different manner, however, global warming may provide a mode of burial of organic carbon. A recent mesocosm study (Kritzberg et al., 2014) showed that warming might enhance transfer of organic carbon to sediments.

In southern and western Turkey, climate models predict drought conditions with a >30% decrease in winter precipitation and enhanced summer evaporation (Lelieveld et al., 2012; Turunçoglu et al., 2013), which can lead to reduction in run-off waters, projected to be as large as 30-40% in Turkey (IPCC 2007). An altered precipitation regime may effect the hydraulic residence time, which can alter carbon sedimentation and mineralization (Algesten et al., 2003), and possibly change the lake's metabolism by varying the terrestrial inputs of nutrients and organic matter (Schallenberg and Burns, 1997).

Global warming may also increase the intensification in water color due to organic matter importation, also known as brownification, which has been occurring in a large number of surface waters in the Northern Hemisphere (Erlandsson et al., 2008). During brownification, reduced light may suppress phytoplankton production (del Giorgio and Peters, 1994). Heterotrophic respiration may be enhanced, since bacteria consume terrestrially derived DOC (Tranvik, 1988). Moreover, P:R has been reported to decrease with increasing DOC, with a concurrent increase of CO_2 flux to the atmosphere (Sobek et al., 2005).

1.7.4 CO_2 Flux and Latitudinal Gradient

Some research shows a latitudinal gradient pattern in lake autotrophy-heterotrophy (Alin and Johnson, 2007). Autotrophic lakes tend to be large and in low latitudes, whereas heterotrophic lakes tend to occur at higher latitudes. According to this proposition, lakes at higher latitudes exhibit lower production, higher evasion of carbon dioxide, and higher burial efficiency (Alin and Johnson, 2007). In a study done in Finland (Kortelainen et al., 2006), the CO_2 concentrations decreased with increasing latitude, with the summer months showing the strongest connections.

1.8 Water Level Fluctuations in Mediterranean Lakes

Due to the Mediterranean climate with seasonal fluctuations in precipitations, water levels in shallow Mediterranean lakes have natural both interannual and intra-annual fluxes (Coops et al., 2003). It has been observed that Turkish shallow lakes can have yearly water level fluctuations from 1 m to over 3 m (Beklioğlu et al., 2001). Precipitation regime and morphometry of the lake affect the magnitude of water level fluctuations (Beklioğlu et al., 2006).

Water level fluctuations due to wet and dry periods can change the clarity of the lake water by influencing macrophyte growth (Beklioğlu et al., 2001). High water levels can reduce light availability for submerged macrophytes, whereas low water levels may lead to stress for the plants via ice, waves, and dehydration (Coops et al., 2003). Since macrophyte-dominated waters may act as a CO_2 sink (Duarte and Agusti, 1998), water levels may influence the flux of CO_2 to and from an aquatic ecosystem.

Nutrient dynamics and trophic structure may also be altered due to changes in water levels (Beklioğlu et al., 2006; Beklioğlu and Tan, 2008). In the Mediterranean region, enhanced nutrient loading in wet periods may increase nutrient concentrations within the lake; however, drought periods may do the same due to evaporation and internal loading (Jeppesen et al. 2009; Özen et al., 2010). In addition to macrophyte dominated waters, high inputs of nutrients, especially TP, are strongly associated with net autotrophy of the lake and can thus cause it to function as a sink for CO_2 (Schindler et al., 1972; McConnaughey et al., 1994).

1.9 Aim of the Study

Following the CO_2 flux equation of Trolle et al. (2011), the CO_2 fluxes from 44 Turkish shallow lakes, spanning almost six degrees of latitude and a wide range of altitudes, have been calculated. Two of these lakes, Eymir and Mogan, have been analyzed with continuous lake data over a 4-year period and the effects of different hydrological periods have been examined, as well as to test whether seasonal variation of CO_2 flux from the water occurred. Our hypotheses are that CO_2 flux from the lake to the atmosphere will be less in eutrophic systems enriched with high phytoplankton (Chl *a*) growth as well as in macrophyte dominated clear water with low nutrients. Thus, we expect that with increasing amounts of primary production, the more the lake will act as a CO_2 sink, and the lower the CO_2 flux to the atmosphere will be, and that this can be modified through the impact of water level fluctuations (WLF) and salinity.

CHAPTER 2

MATERIALS AND METHODS

2.1 Study Sites

Long-term analyses of CO_2 fluxes from the water have been done on Lake Mogan and Lake Eymir, two interconnected shallow lakes 20 km south of Ankara, Turkey. The climate is semi-arid, with hot, dry summers and a wet season from late winter to spring.

Lake Mogan is large and shallow (drainage area: 925 km^2, surface area: 5.4-6 km^2, max: 3.5 m, mean: 2.1 m, 39° 47'N 32° 47'E). The inflows that mainly sustain the lake are Sukesen brook in the north, Gölcük and Yavrucak brooks in the west, and Çölovasi brook in the east. Lake Mogan's only outflow flows into Lake Eymir, through a canal and a wetland in the north (Levi et al., 2013).

Lake Eymir (drainage area: 971 km^2, surface area: 1.20-1.25 km^2, mean depth: 3.1 m; 39° 57'/N, 32° 53'/E) receives water from Lake Mogan as well as through a second inflow, Kışlakçı creek, which enters the lake from the north (Fig. 2.1) (Levi et al., 2013). A biomanipulation project in which tench and carp were removed from the lake was carried out in Lake Eymir during 2006 and 2007, which resulted in an improvement upon the lake quality (Özen et al., 2010): a twofold decrease in chlorophyll-*a*, a 1.5-fold decrease in suspended solids, and a 50% increase in annual Secchi depth were observed after biomanipulation.

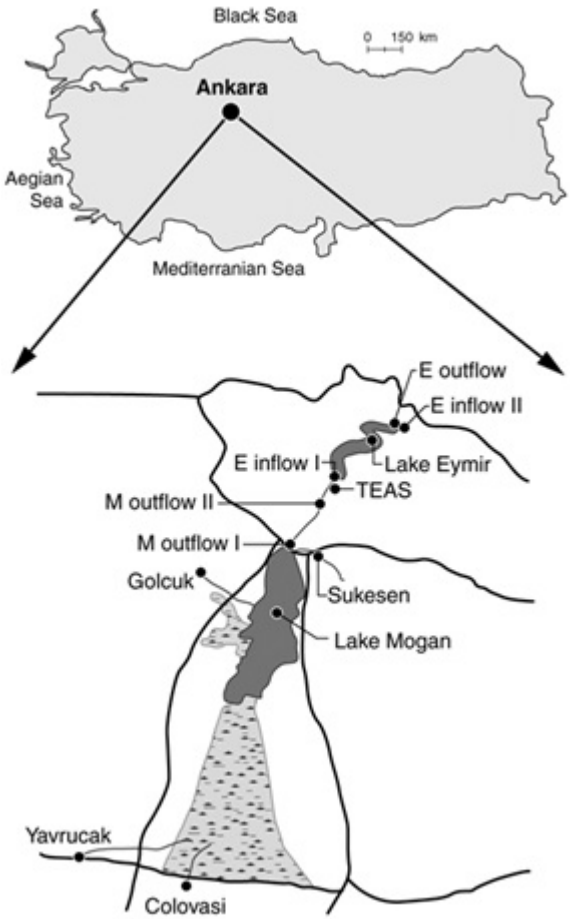

Figure 2.1: Position of Lake Eymir and Lake Mogan and sampling points.

In 2007 and 2008, Lakes Eymir and Mogan experienced lower water levels (with an average maximum depth of 3.7 m and 3.2 m, respectively). In 2009 and 2010, maximum water levels increased to an average of 4 m and 3.4 m, respectively (Table 2). Submerged macrophytes were high in 2007 and 2008, but became limited during the transition from dry to wet conditions.

Table 2. Characteristics of Lake Eymir and Mogan from dry (2007-2008) and wet (2009-2010) periods. Limnological data is based on averages of spring, summer, and fall months (March – November).

		Maximum depth (m)	TP (µg/l)	% PVI	Chl *a* (µg/l)	% Salinity
Eymir	**dry**	3.7	290	2	26	2.2
	wet	4	186	1	33	1.9
Mogan	**dry**	3.2	122	45	11	1.8
	wet	3.4	72.5	5	21	1.4

Including lakes Eymir and Mogan, 44 shallow lakes, covering around six degrees of latitude in total, were sampled once during the summers of 2006 to 2012 for physical, chemical, and biological properties along a latitudinal gradient from the north (41° 83'02"N, 27° 93'42"E) to the south (36° 69'54"N, 28° 83'43"E) of Turkey, (Fig. 2.2), and altitudes from 1 m to 1423 m. Sizes ranged from 0.1 to 635 ha, (Table 3) and all lakes were shallow excluding Abant and Büyük (which have maximum/mean depths of 17.4 m/4.8 m and 15.2 m/3.8 m, respectively).The lakes were meso-hypertrophic with total phosphorus (TP) concentrations ranging from ca. 15 to 632 µg L^{-1}, Chl-*a* from ca. 2 to 181 µg L^{-1}, and total nitrogen (TN) from 239 to 2340 µg L^{-1} (Table 3). Thirty-four of the lakes had submerged macrophytes and mean percent plant volume inhabited (PVI%) (*sensu* Lauridsen et al. 2003) of all lakes was approximately 20%.

Table 3. General Characteristics of the 44 Study Lakes

Variables	Range	Mean	Median
Altitude (m)	1-1423	697	930
Lake size (ha)	0.1-635	71.8	25
Salinity (‰)	0.05-14.5	1.1	0.24
Alkalinity (meq L^{-1})	0.5-24.3	4.4	2
Visibility index	0.05-1.0	0.3	0.3
Total Phosphorus (µg L^{-1})	15-632	138	88
Total Nitrogen (µg L^{-1})	239-2340	1133	1014
Chlorophyll *a* (µg L^{-1})	1.8-181	30	15.4
Plant Volume Infested (%)	0.0-79.9	20	7.2

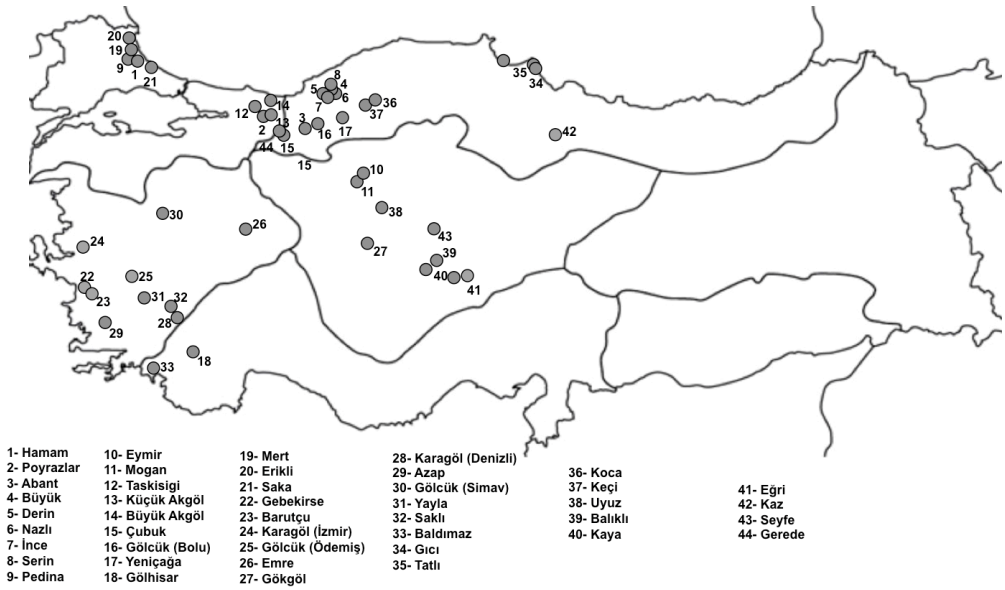

Figure 2.2: Map of 44 sampled lakes along a latitudinal gradient from the north (41° 83’02”N, 27° 93’42”E) to the south (36° 69’54”N, 28° 83’43”E) of Turkey.

The lakes have been classified into four categories based for further assessment based on their latitude and altitude into northern highlands (NH), northern lowlands (NL), southern highlands (SH), and southern lowlands (SL) lakes (Beklioğlu et al., submitted). The lakes located in the northern highlands have low agricultural influence and temperatures, and low Chl *a*. The lowland lakes have higher temperatures than those of the higlands as well as high agricultural influence and high nutrient and Chl *a* concentrations with cyanobacteria dominance. Macrophyte coverage is lower in the lowland lakes in comparison with the highland lakes. The southern lowland lakes are the most eutrophic and saline lakes (Beklioğlu et al., submitted).

2.2 Water Chemistry, Sampling, and Laboratory Analysis

Samples for various physical, chemical, and biological parameters of each of the 44 lakes, also known as "snapshot sampled lakes" were taken only once during the peak of the growing season by using the snapshot approach (Moss et al., 2003). Lakes Eymir and Mogan have been monitored for over 15 years; however years 2007 – 2010 were chosen for this study to analyze the effect of wet and dry periods on the carbon dioxide flux from the water. Years 2007 and 2008 were the driest years in the history of metrological records, whereas 2009 and 2010 were the wet years with high water levels and lower hydraulic residence times (Coppens et al., unpublished data)

To determine general chemical characteristics of all the lakes, water column samples from the deepest point of the lake were taken using a Ruttner Water sampler. In addition, Secchi depth (used to measure water transparency) was measured along with conductivity, pH, and dissolved oxygen (DO) using a YSI 556 MPS multi-probe field meter (YSI Incorporated, OH, USA). Water chemistry samples were sealed and

kept frozen until analysis. The acid hydrolysis method was used to determine TP (Mackereth et al., 1978). For TN, a Skalar Autoanalyzer (San++ Automated Wet Chemistry Analyzer, Skalar Analytical, B.V., Breda, The Netherlands) was employed. Chl *a* was measured spectrophotometrically after ethanol extraction (Jesperson and Christoffersen, 1987). The acid neutralizing capacities (ANCs) of the samples were measured using phenolphthalein and HCl (0.1 M) according to Henriksen (1982). Macrophytes were measured by plant coverage and percent volume infested (PVI%), which was calculated using the equation plant coverage × average plant height/water depth (*sensu* Canfield et al., 1984).

2.3 Calculation of CO_2 Flux

CO_2 flux from the water was calculated for each sampling date from pH and alkalinity, with the appropriate corrections for temperature and ionic strength following the CO_2 flux model used in Trolle et al. (2011). Negative CO_2 flux values represent flux from the atmosphere to the water. This model is based on a diffusion film model given in Stumm and Morgan (1996). Detailed equations for all parameters are given in the Appendix.

$$JCO_2 = k \cdot \beta \cdot ([CO_{2(aq)}] - K_H \cdot [pCO_{2(air)}])$$

Where:

$JCO_2 \left(\frac{\text{mol}}{cm^2 \cdot h}\right) =$ CO_2 flux through the water film

$k \left(\frac{cm}{h}\right) =$ transport coefficient

$\beta =$ chemical enhancement of diffusion (dimensionless)

$[CO_{2(aq)}] \left(\frac{mol}{l}\right) =$ concentration of dissolved CO_2 in well-mixed water phase

$K_H \left(\frac{mol}{l \cdot atm}\right)$ = Henry's law constant

$[pCO_{2(air)}]$ (atm) = partial pressure of CO_2 in the atmosphere; amount of CO_2 in water when in equilibrium with atmosphere and before chemical reaction with H_2O takes place

Transport coefficient *k*

The transfer of inorganic gases is independent of the nature of the gas and dependent on influencing factors of stagnant boundary layer (z_w), or the thickness of the stagnant boundary layer (Stumm and Morgan, 1996). z_w decreases with increasing turbulence, which could be due to wind speed (Stumm and Morgan, 1996).

The transport coefficient *k* is defined as the piston velocity, and can be thought of as the height of water that is equilibrated with the atmosphere per unit time for a given gas at a given temperature (Cole and Caraco, 1998). Most studies suggest that *k* increases predictably with increasing wind speed at winds ≥ 3 ms^{-1} (Wanninkhof, 1992; MacIntyre et al., 1995).

Conversely, both wind tunnel and tracer studies on whole systems show significant variation at wind speeds below 2 – 3 ms^{-1} (Cole and Caraco, 1998). At low wind speeds, *k* appears to be largely independent of wind since the relative influence of wind to the total turbulence in surface waters is less (Cole and Caraco, 1998) and other factors, such as convective cooling and chemical enhancement are thought to become increasingly important (Crusius and Wanninkhof, 2003).

Equations describing the relationship between the transport coefficient and wind speed have been established (Cole and Caraco, 1998; Crusius and Wanninkhof, 2003). Trolle et al. (2011) take an average of the following empirical relations:

$$k = 2.07 + 0.215 \cdot U^{1.7}$$

$$k = 0.72 \cdot U$$

$$k = 0.288 \cdot U^{2.2} + 0.168$$

Where U is the average wind speed (ms^{-1}) recorded at a standard height of 10 m. In this study, monthly average wind speeds are based on daily wind speed averages recorded at a standard height of 10 m (Turkish Meteorological Office, 2013).

The Chemical Enhancement of Diffusion, β

The chemical enhancement of diffusion, β occurs at high pH (when there is a direct reaction from CO_2 with OH^- to form HCO_3^-) and at low wind speeds when a thick stagnant boundary layer is present (Trolle et al., 2011). At pH = 8.2, 30 – 40% of the reaction is accounted for by direct combination of OH^- with CO_2 (Emerson, 1995). Trolle et al. (2012) use the following approach (Bade and Cole, 2006) to estimate β:

$$\beta = \frac{\tau}{(\tau - 1) + \frac{tanh\left(\frac{<r>\cdot\tau}{D}\right)^{0.5}\cdot z}{\left(\frac{<r>\cdot\tau}{D}\right)^{0.5}\cdot z}}$$

Where:

- $D\left(\frac{cm^2}{s}\right) =$ molecular diffusion coefficient for CO_2 in water, taken from Bade and Cole (2006)

- $z =$ thickness of the stagnant boundary layer, from Stumm and Morgan (1996)

$$z = \frac{D}{k_{CO_2}} \ (cm)$$

Where $k_{CO_2} =$ transport coefficient described above

- $\tau = \frac{[H^+]^2}{K_1 \cdot K_2 + K_1 \cdot [H^+]} + 1$

Where:

$[H^+] =$ hydrogen activity

$K_1 =$ dissociation constant = equilibrium constants for the reaction between $[CO_{2(aq)}]$ and HCO_3^- = the first apparent dissociation constant for carbonic acid, from Bade and Cole (2006)

$K_2 =$ dissociation constant = equilibrium constant for the reaction between HCO_3^- and CO_3^{2-} = second apparent dissociation constant for carbonic acid, from Bade and Cole (2006).

- $< r > = r_{CO_2} + r_{OH^-} \cdot [OH^-] =$ the combined rate of reaction terms describing hydration

Where:

r_{CO_2} (s^{-1}) = hydration rate constant in the reaction $[CO_2] + [H_2O] \rightleftharpoons [H^+] + [HCO_3^-]$. Johnson (1982) give the equation $r_{CO_2} = e^{1246.98 + \frac{-6.19 \cdot 10^4}{T} + -183.0 \cdot \ln(T)}$ where T is the temperature in Kelvin.

$r_{OH^-} =$ hydration rate constant in the reaction $[CO_2] + [OH^-] \rightleftharpoons [HCO_3^-]$. Johnson (1982) give the equation $r_{OH^-} \cdot K_w \left(\frac{mol}{dm^3 \cdot s}\right) = e^{-930.13 + 0.110 \cdot S^{0.5} + \frac{3.1 \cdot 10^4}{T} + 140.9 \cdot \ln(T)}$

Where T is the temperature in Kelvin and S is salinity in %. When calculating the enhanced CO_2 flux from water, salinity was accounted for using Snoeyink and Jenkins (1980), updated in Pawlowicz (2008).

Henry's Law Constant

At a constant temperature, the amount of a given gas that dissolves in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid. So, if the temperature and salinity in the liquid decrease, the solubility of the gas increases as the pressure of that gas increases. Wind speed has an influence on pCO_2, with more wind creating less atmospheric pCO_2.

Henry's law in arithmetic terms can be expressed as:

$$K_H = p/c$$

where K_H is a constant with the dimensions of partial pressure of the solute in the gas above the solution (p) divided by concentration of the solute (c). Henry's law constant depends on the solute, the solvent, and the temperature.

The formula for K_H is based on the tables in Butler (1991) and taken from Trolle et al. (2011).

Estimating $[CO_{2(aq)}]$ and $[CO_{2(atmo)}]$

Aqueous CO_2 concentration can be measured from pH and acid neutralizing capacity (ANC) (μeq L^{-1}) using previous methods (Kling et al., 1992; Cole et al., 1994).

$$H_2CO_3^* \leftrightarrow H^+ + HCO_3^- \quad K_1 = \frac{[HCO_3^-] \cdot [H^+]}{[H_2CO_3^*]}$$

where K_1 is the first acidity constant for the protolysis of $H_2CO_3^*$. By rearranging this equation, the concentration of dissolved CO_2 is estimated as

$$[CO_{2_{(aq)}}] \approx [H_2CO_3^*] = \frac{[HCO_3^-] \cdot [H^+]}{K_1} = \frac{[ANC] \cdot 10^{-pH}}{K_1}$$

By using this calculation, it is assumed that ANC is largely determined by HCO_3^-. At low values of ANC, non-carbonate ANC may be present and the calculated CO_2 concentrations may be overestimated (Cole et al., 1994). In this study, only lakes with a mean summer ANC greater than 1,000 μeq L^{-1} and a pH from 6.5 to 10.5 are used.

In accordance with Trolle et al. (2011), Table 4.3, p. 152 in Stumm and Morgan (1996) will be used for the temperature correction of K_1 and ionic strength will be corrected for K_1 using Table 2.1 from Butler (1991).

Atmospheric CO_2 ($CO_{2(atmo)}$)has been taken from monthly mean atmospheric carbon dioxide in situ measurements from measurements at Mauna Loa Observatory in Hawaii (Tans and Keeling). Data are reported as parts per million (ppm) of CO_2 in the air, after water vapor has been removed.

2.4 Possible Errors in Measurement

Since several different investigators have collected the samples, accurately measuring pH and alkalinity for the calculation of aqueous CO_2 is a challenging task (Herczeg and Hesslein, 1984), and thus, variation in the accuracy of the pH measurements may be the most likely cause of the observed differences between measured and calculated values of CO_2, (Raymond et al., 1997).

Moreover, alkalinity is difficult to accurately measure because it is susceptible to change between the time of collection and analysis. Thus it is rarely advised to retest the alkalinity if several days have passed since the bottle was first opened.

2.5 Statistical Analysis

R version 3.0.2 was used for all statistical analyses. Environmental variables were tested for normality using the Shapiro-Wilk normality test. Variables with non-normal distribution were transformed via log transformation or square root transformation.

Principle components analysis (PCA) was used to classify the 44 lakes according to variables including latitude, altitude, visibility index, salinity, temperature, TN, TP, and Chl *a*, pH, PVI%, and CO_2 flux, and was used for Lakes Eymir and Mogan using visibility index, PVI%, salinity, TP, Chl *a*, pH, and ANC and water level using pairwise Euclidean dissimilarities (Legendre and Legendre, 2012). Then, generalized linear models (GLM) were used to assess the effects of environmental variables on CO_2 flux. Collinear (Pearson $r>0.6$) predictors were excluded, and stepwise regression was performed in succession to find the best model.

CHAPTER 3

RESULTS

3.1 Carbon Dioxide Fluxes of Lakes Eymir and Mogan

In general, Lake Eymir released more CO_2 in all years than did Lake Mogan (Table 4). Both Lakes Eymir and Mogan showed the highest flux of CO_2 to the atmosphere in the summer of 2010. Both lakes showed seasonal variation, with Lake Eymir exhibiting the highest CO_2 evasion from the lake in summer, and Lake Mogan showing higher emissions during the spring months of 2007 – 2008, along with a continual increase under periods of high water level, which coincided with the low PVI%.

Table 4. CO_2 Flux from Lakes Eymir and Mogan, years 2007 – 2010. Values are expressed in mg C m^{-2} d^{-1}. Mean values include standard error of the mean.

Lakes	Range	Mean	Median
Eymir	-106 – 1757	250 ± 30	129
Mogan	-135 – 737	137 ± 26	81

Table 5. CO_2 Flux from Lakes Eymir and Mogan during the dry period 2007 – 2008. Values are expressed in mg C m^{-2} d^{-1}. Mean values include standard error of the mean.

Lakes	Range	Mean	Median
Eymir	-106 – 1077	185 ± 20	76
Mogan	-135 – 391	36 ± 7	-3.5

Table 6. CO_2 Flux from Lakes Eymir and Mogan during the wet period 2009 – 2010. Values are expressed in mg C m^{-2} d^{-1}. Mean values include standard error of the mean.

Lakes	Range	Mean	Median
Eymir	17 – 1757	323 ± 48	160
Mogan	-40 – 736	250 ± 31	156

In both lakes, the flux of CO_2 from lake to atmosphere was the highest in 2010, during the wet period. In the dry period, particularly Lake Mogan, functioned as a sink for atmospheric CO_2, specifically during fall.

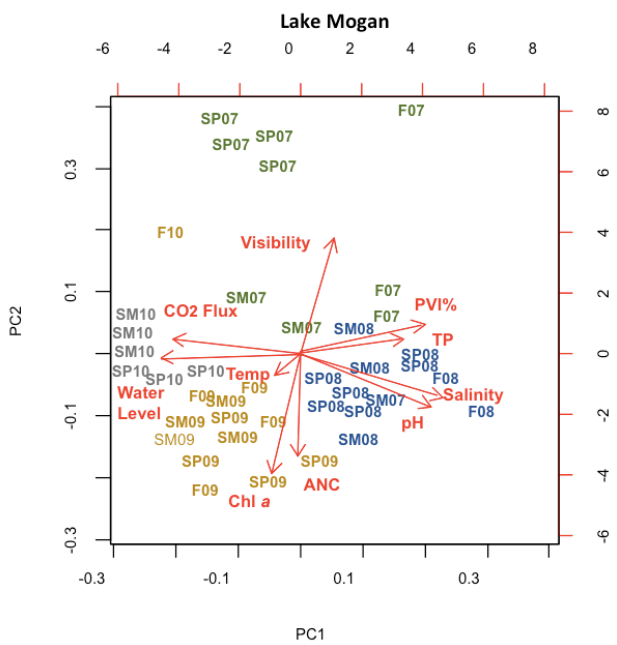

Figure 3.1: PCA Plot of Lake Mogan 2007 – 2009 color-coded according to year. SP07 = spring 2007, SP08 = spring 2008, SP09 = spring 2009, SP10 = spring 2010, SM07 = summer 2007, SM08 = summer 2008, SM09 = summer 2009, SM10 = summer 2010, F07 = fall 2007, F08 = fall 2008, F09 = fall 2009.

According to the PCA plot for Lake Mogan for years 2007 – 2010, the drier years are associated highly with low CO_2 flux to the atmosphere, visibility, PVI%, TP, pH, and salinity (Fig. 3.1). Salinity and pH are highly related, as are PVI% and TP. CO_2 flux to the atmosphere and water level are related and oppositely associated with PVI%, TP, salinity, and pH. The wet years are associated with CO_2 flux to the atmosphere, water level, Chl *a*, and ANC. Chl *a* shows less relationship with CO_2 flux to the atmosphere than PVI%, indicating that Lake Mogan's macrophyte communities are of more importance than its phytoplankton productivity.

The efflux was generally the highest from Lake Mogan during its low macrophyte period, PVI% (5%), while during its macrophyte dominated stage, which occurred with the low water level period, efflux was least. It is seen in the PCA plot that the wet years tend to assemble around water level and CO_2 flux to the atmosphere, and remain away from PVI%. When higher levels of PVI% were reached (45%) at low water levels, the lake functioned as a sink of atmospheric CO_2, especially during the summer and fall.

In Lake Mogan, CO_2 flux to the atmosphere was negatively correlated with pH ($r = -0.90$), TP ($r = -0.42$), salinity ($r = -0.65$), and PVI% ($r = -0.50$). A strong positive correlation of CO_2 flux to the atmosphere with water level ($r = 0.64$) was observed. Moreover, PVI% in Lake Mogan was positively correlated with TP ($r = 0.70$), salinity ($r = 0.59$), and pH ($r = 0.46$). It was negatively correlated with water level ($r = -0.65$).

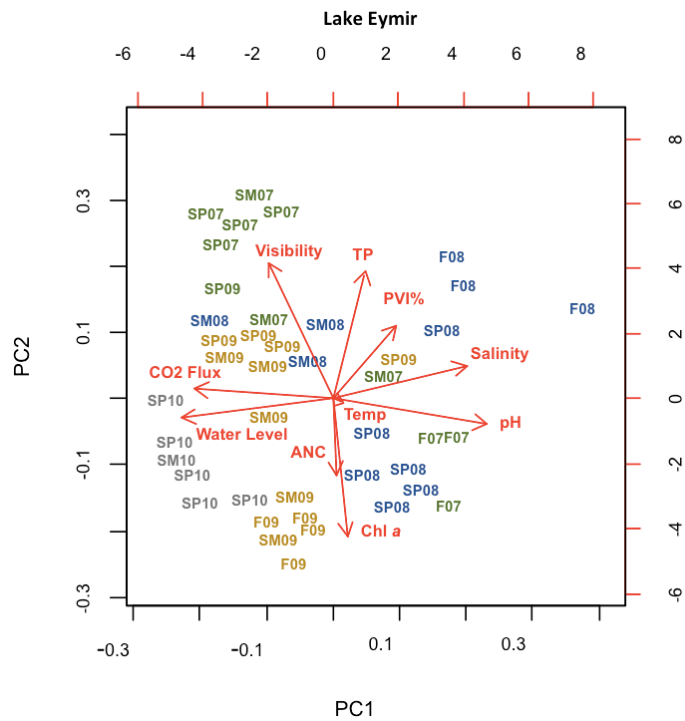

Figure 3.2: PCA Plot of Lake Eymir, color-coded according to year. SP07 = spring 2007, SP08 = spring 2008, SP09 = spring 2009, SP10 = spring 2010, SM07 = summer 2007, SM08 = summer 2008, SM09 = summer 2009, SM10 = summer 2010, F07 = fall 2007, F08 = fall 2008, F09 = fall 2009.

According to the PCA plot for Lake Eymir 2007 – 2010, the dry years correspond with visibility index, TP, PVI%, salinity, pH, and, unlike Lake Mogan, Chl *a* (Fig. 3.2). Like in Lake Mogan, CO_2 flux to the atmosphere and water levels are highly related, and in the opposite direction, salinity and pH are associated. PVI% has less importance in the matter of CO_2 flux to the atmosphere in Lake Eymir; moreover, Chl *a* does not seem to be directly related with CO_2 flux to the atmosphere. However; in 2009, Chl *a* was still a strong influencing factor, giving insight to why Lake Eymir decreased its CO_2 emission from 2008 to 2009 while Lake Mogan's emissions increased. The temperature vector in the PCA plot points at an opposite direction

from CO_2 flux; however, its magnitude is small. The wet years in Lake Eymir have some different characteristics than that of Mogan, with year 2009 in Lake Eymir associated with high Chl *a*, high CO_2 flux to the atmosphere (besides some samples in summer 2009 and fall 2009), water level, and visibility, and year 2010 associated with water level and high CO_2 flux to the atmosphere. The four years of data from Lake Eymir showed a decline from dry to wet years in TP, Chl *a*, ANC, and pH along with increases in CO_2 fluxes to the atmosphere. Lake Mogan shows a decline from dry to wet years in TP, and pH, and an increase in Chl *a* and ANC along with an increase in CO_2 flux to the atmosphere. Both Eymir and Mogan shifted from being a net sink of atmospheric CO_2 in the fall of 2007 and 2008 to a net source during the wet period (Fig. 3.5 and Fig. 3.6).

In Lake Eymir, CO_2 flux to the atmosphere was negatively correlated with pH (r = -0.87) and salinity (r = -0.44). A weak negative correlation was seen between CO_2 flux to the atmosphere and Chl *a* (r = -0.13) and CO_2 flux to the atmosphere and PVI% (-0.14). CO_2 flux to the atmosphere was positively correlated with water level (r = 0.60), alkalinity (r = 0.27), visibility (r = 0.29), and weakly correlated with temperature (r = 0.14). pH, in turn, was highly positively correlated with salinity (r = 0.60) and highly negatively correlated with water level (r = -0.71). There was only a slight positive correlation between pH and Chl *a* (r = 0.13) and PVI% (r = 0.19).

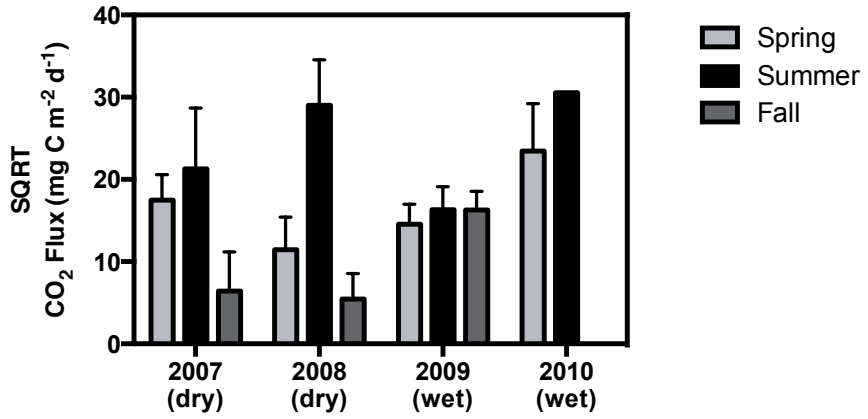

Figure 3.3: CO_2 flux from Lake Eymir years 2007 – 2010. CO_2 flux was measured for the spring, summer, and fall months (March – November).

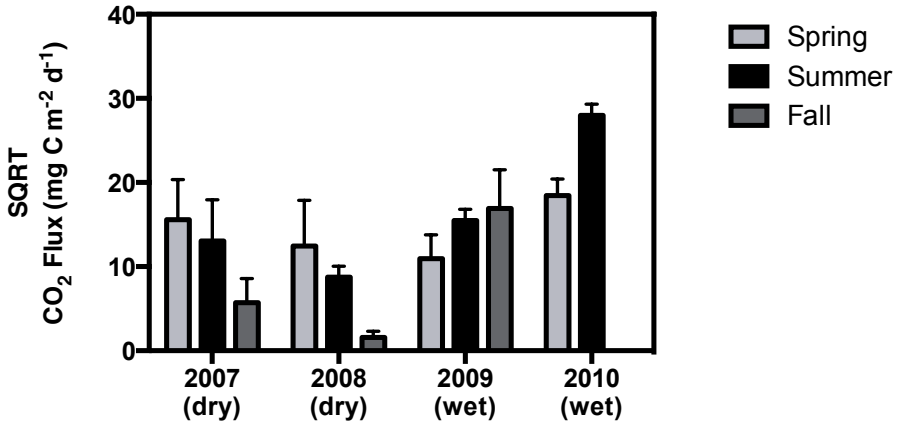

Figure 3.4: CO_2 flux from Lake Mogan years 2007 – 2010. CO_2 flux was measured for the spring, summer, and fall months (March – November).

In the dry years, Lakes Eymir and Mogan behave in different manners in regards to their CO_2 flux to the atmosphere. Lake Eymir emits CO_2 to the atmosphere during summer (Fig. 3.3), while Lake Mogan (Fig. 3.4) acted as sink in summer owing to its macrophyte dominated state, and it emitted more CO_2 during spring. During the wet

years, Lakes Eymir and Mogan behave in a similar style and are a source of CO_2 to the atmosphere.

During the dry period the seasonality in pH was apparent in Lakes Eymir and Mogan with a continuous increase from spring through fall. High pH tends to be a result of intense photosynthesis, and atmospheric uptake of CO_2. The highest pH during this period occurred in September and October, which coincided with the CO_2 sink. An opposite trend appeared when examining the pH of the wet period, with a gradual decrease from spring to fall and peak pH values during the spring, in March and April. In Lakes Eymir and Mogan, phytoplankton crop expressed in Chl *a* concentrations were low mostly during the wet period (only in 2010 in Lake Eymir), corresponding with an increase in CO_2 emissions from both lakes.

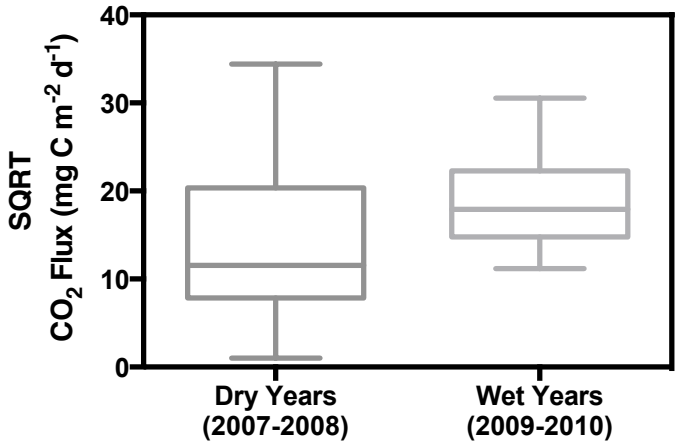

Figure 3.5. CO_2 flux from Lake Eymir years during the two hydrological periods, 2007 – 2008 (dry years) and 2009 – 2010 (wet years). CO_2 flux was measured for the spring, summer, and fall months (March – November).

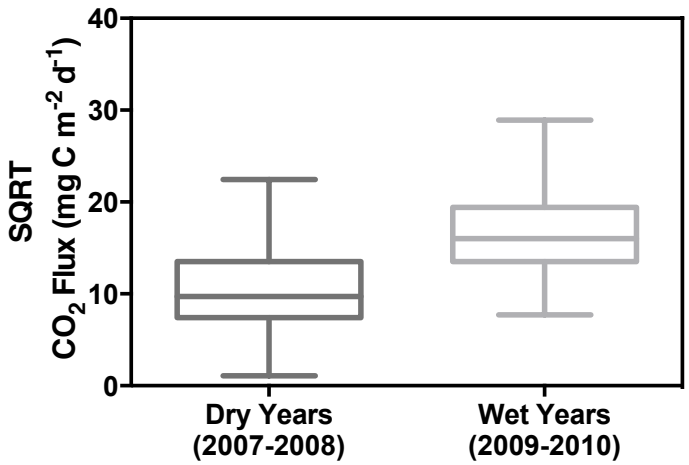

Figure 3.6. CO_2 flux from Lake Mogan years during the two hydrological periods, 2007 – 2008 (dry years) and 2009 – 2010 (wet years). CO_2 flux was measured for the spring, summer, and fall months (March – November).

Table 7. Generalized Linear Model of Multiple Regression for Lakes Eymir and Mogan. CO_2 flux values include the standard error of the mean.

Lake	Variables	CO_2 Flux	AIC
Lake Eymir	Water Level	17.79 ± 1.3 ***	297
	Chl *a*	-4.26 ± 1.8 **	280.3
	PVI%	0.96 ± 0.8	275.6
	TP	-6.17 ± 7.5	277
	Temperature	0.37 ± 0.2 *	280
***p<0.05 **p<0.01 ***p<0.001**			
Lake Mogan	Water Level	7.67 ± 1.5 ***	270.4
	Chl *a*	-3.60 ± 2.9	249.7
	Temperature	0.01 ± 0.1	248.1
	Visibility	-2.8 ± 21.2	248.2

Models were chosen for Lakes Eymir and Mogan using General Linearized Model of multiple regression (Table 7). Collinear (Pearson r>0.6) predictors for Lake Eymir included salinity and pH, salinity and water level, and visibility and Chl *a*. The variables chosen for the model were water level, Chl *a*, PVI%, ANC, TP, and temperature. Water level ($p < 0.001$), Chl *a* ($p < 0.01$), ANC ($p < 0.01$), and temperature ($p < 0.05$) showed significance in the model.

Collinear (Pearson $r > 0.6$) predictors for Lake Mogan included salinity and pH, water level and pH, PVI% and TP, salinity and water level, and water level and PVI%. Variables chosen for the model were water level, Chl *a*, ANC, temperature, and visibility. Significant variables were water level ($p < 0.001$), Chl *a* ($p < 0.05$), and ANC ($p < 0.05$).

3.2 Variables Influencing the Carbon Dioxide Flux of Lakes Eymir and Mogan

The relationship between CO_2 flux and some environmental variables is shown for Lake Eymir and Mogan in Fig. 3.7. At low visibilities, lower CO_2 flux to the atmosphere is observed in Lake Eymir. In both lakes at low salinity levels (<1.5%), higher CO_2 flux to the atmosphere is observed. In both lakes, pH levels affect the CO_2 flux, with pH <8.6, higher levels of CO_2 are observed evading the lake. At water levels <4m, less CO_2 is emitted, though the relationship is stronger in Lake Mogan. At low PVI%, higher CO2 flux is observed only in Lake Mogan (Fig. 3.7).

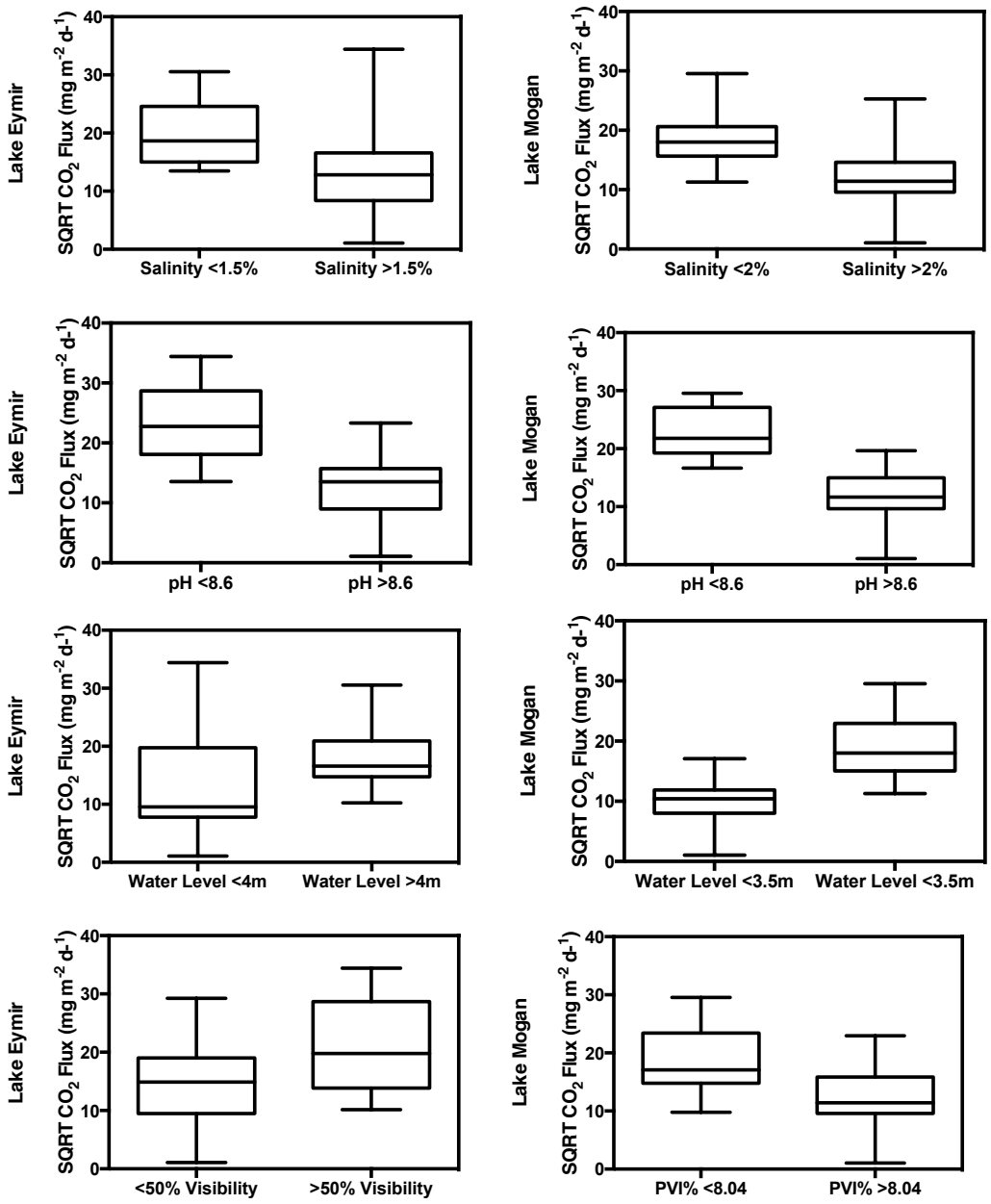

Figure 3.7 CO_2 flux from Lake Eymir and Mogan under several environmental conditions: visibility (only for Lake Eymir), salinity, pH, water level, and PVI% (only for Lake Mogan). Levels determined by piecewise regression.

3.3 Carbon Dioxide Fluxes of Snapshot Lakes

The PCA plot of the snapshot sampled lakes (Fig. 3.8) shows high CO_2 flux to the atmosphere to be related with altitude and ANC, and oppositely related to pH and salinity. Throughout the lakes, TP, TN, and Chl *a* are related. An aggregation of NH, NL, SH, and SL lakes is shown in the plot. NH and SH lakes are in the direction of high CO_2 flux to the atmosphere, with NH lakes being of higher altitude and the SH lakes being closer related to ANC. The lakes in the SH which have more of a relationship with Chl *a* are seen further from the CO_2 vector, showing less CO_2 flux to the atmosphere from these lakes. SL lakes are positioned entirely away from CO_2 flux, and are more aligned with vectors representing high productivity: Chl *a*, TP, and TN, as well as pH. Moreover, it can be seen that NH and SH lakes emit more CO_2 and NL and SL emit less (Fig. 3.9).

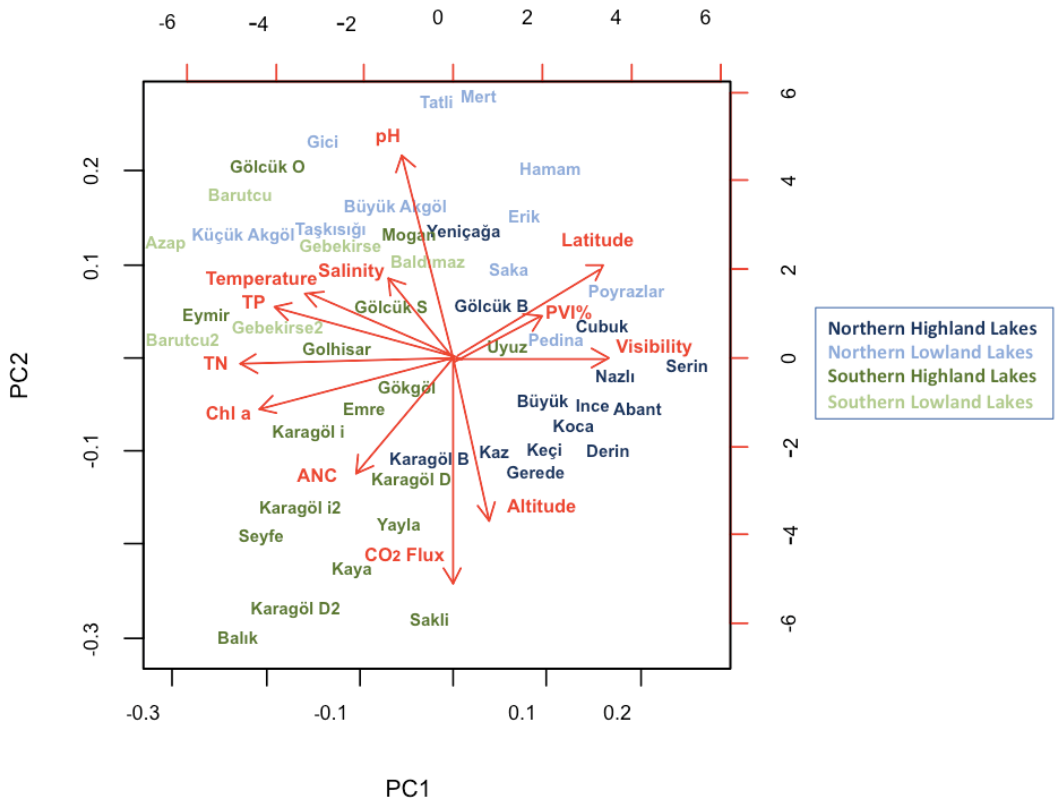

Figure 3.8. PCA Plot of snapshot sampled lakes shows groupings of lakes located in the northern highlands (NH), northern lowlands (NL) southern highlands (SH) and southern lowlands (SL).

In the 44 lakes dataset, CO_2 flux to the atmosphere was positively correlated with ANC (r = 0.52), altitude (r = 0.39), and Chl *a* (r = 0.22). In turn, ANC was positively correlated with Chl *a* (r = 0.35) and altitude (r = 0.23). Altitude was negatively correlated with pH (r = -0.35) and temperature (r = -0.36). Chl *a* was correlated with TP (r = 0.60), TN (r = 0.67), and temperature (r = 0.27).

Table 8. CO_2 Flux from the 44 snapshot lake dataset during the wet period. Values are expressed in mg C m^{-2} d^{-1}. Mean values include standard error of the mean.

Lakes	Range	Mean	Median
NH Lakes	-93 – 8596	1072 ± 381	290
NL Lakes	-89 – 823	95 ± 14	-9
SH Lakes	-70 – 20787	6480 ± 302	352
SL Lakes	-80 – 759	191 ± 29	-20

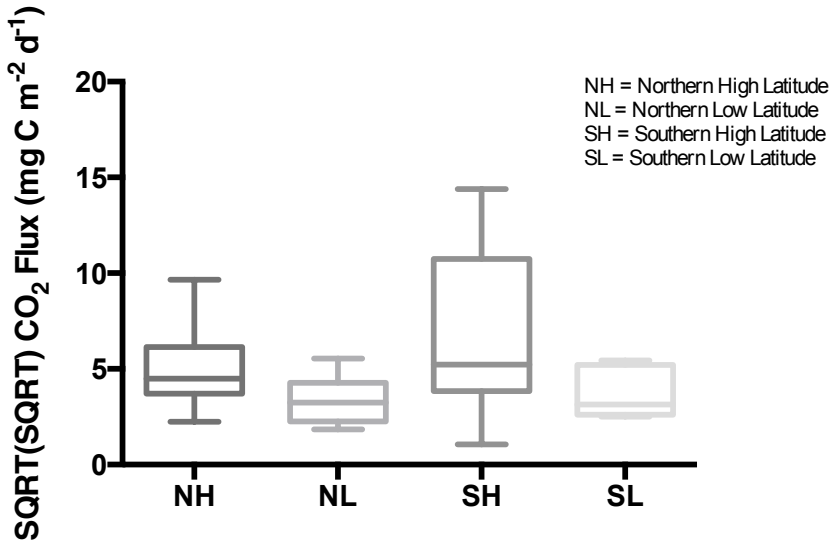

Figure 3.9: 44 snapshot sampled lakes categorized by their latitude and altitude and their CO_2 fluxes to the atmosphere. NH = northern highlands, NL = northern lowlands, SH = southern highlands, SL = southern lowlands.

Collinear (Pearson $r > 0.6$) predictors for the 44 snapshot lakes included TP, TN, and Chl *a*. Each were used in the General Linearized Model, but none yielded significant results and the best model was witnessed with altitude and ANC ($p < 0.05$, and $p < 0.001$, respectively) (Table 9).

Table 9. Generalized Linear Model of Multiple Regression for 44 Lakes. CO_2 flux values include the standard error of the mean.

	Variables	CO_2 Flux	AIC
Snapshot Lakes	Altitude	$4 \cdot 10^{-4} \pm 2 \cdot 10^{-4}$ *	118.2
	ANC	1.39 ± 0.4***	125.5

(* = p<0.05, ** = p<0.01, *** = p<0.001)

The snapshot lakes dataset showed relationships between CO_2 flux at high and low Secchi depths, with low depths (<1 m) related to less CO_2 emissions to the atmosphere. Low altitude lakes (0 – 36 m) also show less CO_2 emitted to the atmosphere in comparison with high altitude (784 – 1423) lakes, as well as low ANC (<2000 meq L^{-1}) values. Finally, pH is related to CO_2 flux, with pH < 8 emitting more CO_2 than higher pH values (Fig. 3.10).

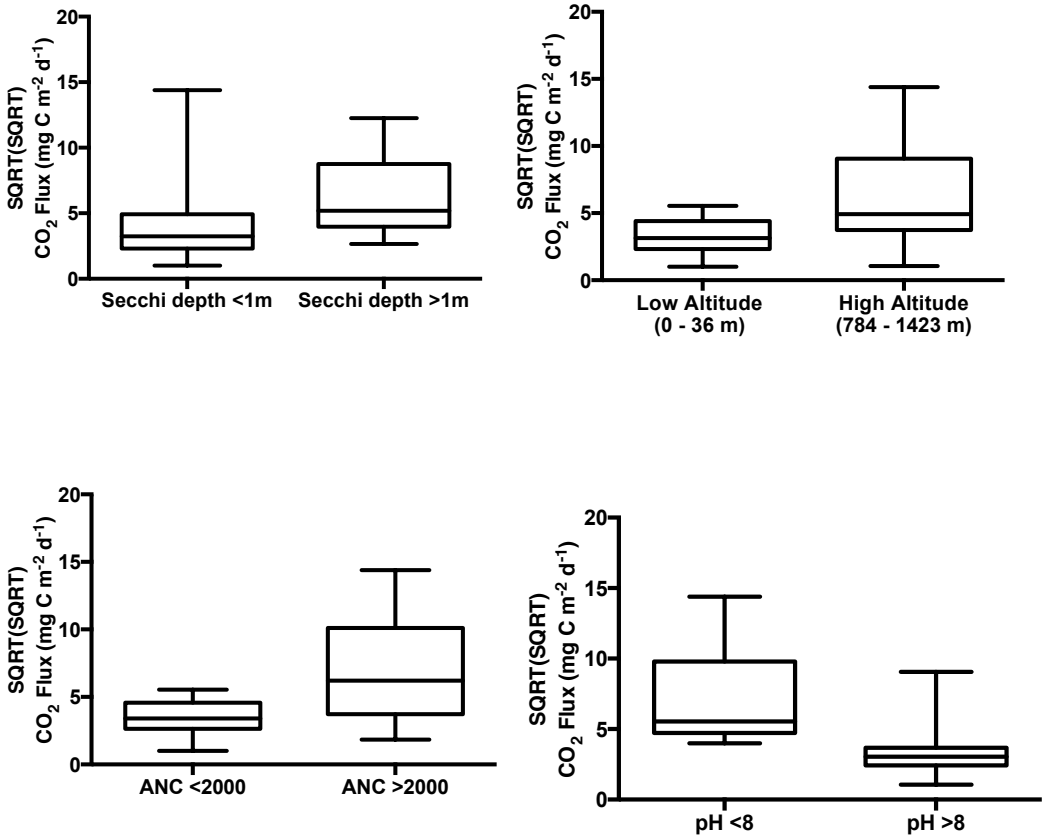

Figure 3.10 CO_2 flux from the 44 sampled lakes under conditions of high and low Secchi depth, altitude, ANC, and pH.

CHAPTER 4

DISCUSSION

4.1 Lakes Eymir and Mogan, 2007 – 2010

The hypothesis that lakes were sources of CO_2 to the atmosphere under productive conditions was shown to be accurate in Lakes Eymir and Mogan, along with the 44 snapshot sampled lakes. Lakes Eymir and Mogan emitted less CO_2 during the dry period in 2007 and 2008 (besides Lake Eymir in the summers of 2007 and 2008) and more CO_2 was emitted during the wet period in 2009 and 2010, especially in 2010. Water level fluctuations are assumed to bring upon this change in CO_2 flux, especially in Lake Mogan, which is more supported by lower water levels for its macrophyte communities, whereas Lake Eymir seems to be more controlled by levels of Chl *a*, and moreover, the pH of the lake. According to the results of the GLM, temperature was also seen as a significant factor in Lake Eymir, as temperature increases, the levels of CO_2 flux to the atmosphere also tend to increase.

Water level fluctuations are a distinctive characteristic of Mediterranean lakes, and can determine the structure of macrophytes, which are highly dependent on hydrology. A study conducted using five shallow lakes in Turkey showed the role of WLF as a significant driver of macrophyte growth (Beklioğlu et al., 2006). Water levels have effects on macrophyte growth dynamics (Özen, 2006), and the magnitudes of change in water level, as observed from years 2007 – 2008 and 2009 – 2010, showed decrease in macrophyte coverage from transitioning from a dry to a wet period.

The change in the amount of macrophytes is a plausible reason why Lake Mogan shifted from being a carbon sink to a carbon source from dry to wet periods. In the dry years, Lake Mogan had a stronger macrophyte presence, whereas in the wet years, macrophytes decreased in the system. Other studies have shown the role of macrophyte dominated systems acting as a CO_2 sink due to sequestration of CO_2 (Carignan et al., 2000; Duarte and Agusti, 1998), or showing lower pCO_2 values, if not complete sinks (Kosten et al., 2010).

Water levels showed significant relationships with CO_2 flux from both lakes. However, the relationship of CO_2 flux with PVI% was only significant in Lake Mogan, which had more macrophyte coverage than Lake Eymir. In Lake Eymir, the relationship of decreased water level and macrophyte development was weakened by eutrophication (Özen, et al., 2010).

Contrary to Lake Mogan, Lake Eymir does not function as a sink and emits more CO_2 in 2007 and 2008 than in 2009, especially in summer. The difference between Lake Eymir and Mogan in this regard lies in their different trophic structures. While Mogan is a macrophyte dominated lake, Lake Eymir is not; thus, its Chl *a* concentrations rather than its macrophyte content, comprise most of the lake's photosynthesis, which, at high levels can raise the pH of the waters, and thereby decreasing the amount of CO_2 emitted from the system. During periods of high photosynthesis, HCO_3^- is gradually depleted, and a direct chemical reaction with aqueous OH- and atmospheric CO_2 may occur to produce HCO_3^- (Jeppesen et al., 1998). In 2009, due to high levels of Chl *a*, the lake seemed to be less of a source, even though Lake Mogan acted as a source at this time because of low PVI%. Lake Eymir started to emit more CO_2 in 2010, when Chl *a* occurred at low levels, and decreases in pH were observed.

Moreover, the seasonality of CO_2 flux during the dry period differs between Lakes Eymir and Mogan. In Lake Eymir, CO_2 emissions increased more in summer, whereas Lake Mogan had highest emissions in spring. Lake Mogan may have high emissions in the spring because of less PVI%. In Eymir, the Chl *a* peaks in the fall may be a reason why the lake emitted less CO_2. Another explanation of higher CO_2 flux from the lakes in summer is increases in temperature promoting heterotrophy, or respiration, rather than photosynthesis. Studies have shown that peak CO_2 emissions may occur under periods of maximum temperatures since heterotrophy increases with increasing temperatures (Findlay et al., 1991; Raymond et al., 1997). Although many studies show lakes to be a sink during summer (Trolle et al., 2011), they may also be sources to the atmosphere due to the temperature-mediated respiration. Other studies have found supersaturation of CO_2 in respect to the atmosphere in summer, in periods of high temperatures (McDonald et al., 2013).

Substantial increases in salinity are seen in dry years in Lakes Eymir and Mogan, which is a characteristic of Mediterranean lakes in dry years (Beklioğlu et al., 2006). Although increased salinity was negatively correlated with CO_2 flux to the atmosphere, this was more likely to be due to the indirect effects of lower water levels and higher macrophytes.

Evidence shows positive relationships between photosynthesis to respiration (P:R) ratios and chlorophyll and total phosphorus (TP) concentration (del Giorgio and Peters, 1994; Hanson et al., 2003). Thus, at high TP levels, primary production and algal biomass are shown to increase (Hanson et al., 2003). In Lake Mogan, this relationship is seen and the lake acts as more of a sink at high TP and Chl *a* level.

In Lake Eymir, although high concentrations of TP were present, levels of Chl *a* did not always positively correspond as expected. This, along with its low PVI%, allowed

Lake Eymir to emit more CO_2 during the dry years in comparison to Lake Mogan. Even if there were high amounts of P, the Chl *a* concentrations may be low and the P:R ratio may favor R, especially if there are high amounts of dissolved organic carbon (DOC) in the lake (Hanson et al., 2003). DOC can be roughly examined by water color and visibility. Other reasons for a high TP – low Chl *a* environment with high levels of CO_2 emissions include the biomanipulation project carried out since 2006 by removal of carp in the lake allowed higher zooplankton to thrive, which increased the grazing pressure on the phytoplankton of the system, nitrogen limitation being insufficient for phytoplankton growth, and climate change and increased temperatures that may kill off phytoplankton or discourage their reproduction.

4.2 Snapshot Sampled Lakes

A recent study on the ecology of 44 Turkish shallow lakes (Beklioğlu et al., submitted), including the ones that are being used in this study, categorizes the types of lakes by their common characteristics along with their latitude and altitude. The groupings are: northern highland (NH), northern lowland (NL), southern highland (SH), and southern lowland (SL). It was found that, in general, NH lakes and SH lakes emit more CO_2 than NL and SL lakes.

The northern highland (NH) lakes, which have the lowest concentrations of nutrients and Chl *a*, and clear water conditions with high abundance of plants, are associated with CO_2 flux to the atmosphere. Since the lakes are less eutrophic than those in the lowlands, their P:R ratios may be less than 1, or in favor of respiration over production (del Georgio and Peters, 1994), which is further evidenced by low pH. Less production is seen in these lakes because of a top-down control of piscivorous

fish on planktivorous fish, and thus an increase in large-bodied zooplankton, which graze strongly on phytoplankton (Beklioğlu et al., submitted).

The northern lowland (NL) lakes tend to emit less CO_2 than the NH lakes. These lakes have higher temperatures than the NH lakes along with a higher agricultural impact and more nutrients. They are generally eutrophic lakes, high in Chl *a* and PVI%. These systems are thus highly productive and it is expected that they will act as CO_2 sinks. Their ecosystems are more dominated by omnivorous fish and small fish, which graze upon zooplankton. The NL lakes have higher nutrients, higher Chl *a* concentrations, higher phytoplankton biomass, and higher pH values than the NH lakes.

The southern highland (SH) lakes, like the NH lakes, are associated with high levels of CO_2 flux to the atmosphere. These lakes, in general, have lower pH values and less PVI%. These lakes also have high levels of Chl *a*; however, low visibility indices are also a common factor in these lakes, which may allow rates of heterotrophic respiration to surpass primary production (Cole et al., 2000; Kling et al., 1992b).

The southern lowland lakes, like the NL lakes, emit less CO_2 than the highland lakes. They have a high agricultural influence, and a similar ecosystem to the NL lakes, dominated by omnivorous and small fish. However, they are even more eutrophic than their northern counterparts, with higher levels of Chl *a* and phytoplankton biomass. They are also more saline, and because of their high internal loading, they are concentrated in nutrients (Özen et al., 2010). A higher phytoplankton yield may increase the amount of productivity in the system, making these lakes more likely to be a carbon sink.

High altitude lakes have been studied previously and have been shown to be sources of CO_2. While we conclude that the difference in high altitude lakes in comparison to low latitude lakes in terms of CO_2 emissions is due to the trophic structure of the lake, in that lakes with high trophic status tend to be sinks of CO_2 whereas lakes of low trophic status tend to emit CO_2, our study measured the CO_2 emission at one point in time in summer season and does not realize the effect of a seasonal effect on CO_2 flux. Other studies, however, have shown that lakes follow an altitudinal gradient with CO_2 flux. One study, carried out in Sweden, showed that CO_2 flux from higher altitude lakes are higher than the lower altitude lakes because of the capture of CO_2 in the snow and ice and its release during ice thaw, which may be in the spring and even summer months in very high altitude lakes, like those in northern Turkey (Karlsson, et al., 2013).

CHAPTER 5

CONCLUSION

Lake trophic status has an effect on the amount of CO_2 emitted from the system. This has been seen in snapshot sampled lakes in Turkey, as well as in two lakes which were sampled regularly over a period of four years. It was hypothesized that as trophic status increases, the lakes ability to act as a sink of CO_2 would also increase, due to their organisms' ability to sequester CO_2 during photosynthesis. This was witnessed in the Turkish shallow lakes in this study; however, the extent to which the trophic state can be estimated is limited.

Besides trophic status, there is other reasoning for the amount of CO_2 in a body of water, such as weathering, hydrological patterns, and atmospheric reactions (Lovett et al., 2013). The CO_2 flux equation used in this study gives an estimate of the amount of C being sequestered or emitted to/from the body of water based on the pH and ANC, variables determined by both biotic and abiotic features. We consider the biological influence on the system, and though previous studies in the literature have shown that heterotrophic aquatic communities are sources of CO_2 to the atmosphere and autotrophic communities act as CO_2 sinks, there are few direct demonstrations of relationships between net ecosystem production and CO_2 flux (Duarte and Prairie, 2005). It is advised to include other factors in the study of CO_2 flux, such as thermodynamics, hydrology, or anthropogenic effects (Duarte and Prairie, 2005).

Moreover, while eutrophic lakes show sequestration of carbon dioxide in this study over a four year period, these lakes may actual emit carbon dioxide in the long run through brownification and subsequent decreases in photosynthesis (del Giorgio & Peters, 1994). In eutrophic lakes, excess DOC may occur, which also can lead to more respiration in the system (Tranvik et al., 1988).

Further studies are necessary to help scientists clearly evaluate the role of lakes in the global carbon budget. Currently the movement of carbon through primary production, sediment burial, and gas exchange, among other processes, are inadequately known (Alin and Johnson, 2007). In order to gain a more comprehensive point of view, catchment studies should be enacted, because they will allow scientists to determine the sources and fates of carbon in lakes (Algesten et al., 2003), and scientists should be kept up to date on the most accurate estimations of the roles of freshwaters in the carbon cycle and identification of the mechanisms driving CO_2 concentrations.

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APPENDIX A

DETAILED EQUATIONS USED FOR CARBON FLUX

Table A1.

Parameter	Symbol	Unit	Parameter(s) within	Symbol	Unit(s)	Equation	Source
Ionic strength	I		Specific conductance	SC	mS/cm	I = 1.6*10^(-5)*SC	Snoeyink and Jenkins, 1980
Henry's constant	K_H	mol/l/atm	Temperature Ionic strength	T I	C	K_H = 10^(-((-0.0000895104895104852*T^2+0.0167664335664335*T+1.10825174825175)*(-0.165889312769593*I^3+0.146617178633051*I^2+0.046254736369491*I+1.00024410365369)))	Stumm and Morgan, 1996
First acidity equilibrium constant of CO_2	K_1	mol/l	Temperature Ionic strength	T I	C	K_1 = 10^(-((0.00012960372 9603717*T^2-0.0122074592074579*T+6.57551048951051)*(1.08632254302938*I^4-2.13619130941515*I^3+1.43095654709759*I^2-0.437780694071989*I+1.00000000002103)))	Stumm and Morgan, 1996
Transport coefficient	k	cm/h	Wind speed	w	m/s^2	k = ((2.07+0.215*w^(1.7))+ (0.72*w)+(0.228*w^(2.2)+0.168))/3	Cole and Caraco, 2008; Crusius and Wanninkhof 2003
Actual $CO_{2(aq)}$ concentration	$CO_{2(aq)}$	M	pH Acid neutralizing capacity First acidity constant of CO_2	pH ANC K_1	 meq/l mol/l	$CO_{2(aq)}$ = (10^(-pH)*(10^(-6)*ANC))/K_1	Stumm and Morgan, 1996
Saturated $CO_{2(aq)}$ concentration	$SCO_{2(aq)}$	M	Henry's constant Acid neutralizing capacity	K_H ANC	mol/l/atm meq/l	$SCO_{2(aq)}$ = K_H*(ANC*10^(-6))	Trolle et al., 2011
CO_2 flux	JCO_2	mol/cm^2/h	Transport coefficient Actual $CO_{2(aq)}$ Saturated $CO_{2(aq)}$	k $CO_{2(aq)}$ $SCO_{2(aq)}$	m/s^2 M M	JCO_2 = k*($CO_{2(aq)}$ - $SCO_{2(aq)}$)/1000	Stumm and Morgan, 1996

Table A1. (Continued)

CO_2 flux	JCO_2	mol/m^2/y	CO_2 flux	JCO_2	mol/cm^2/h	$JCO_2 = JCO_2$ *(100*100*24*365)	Stumm and Morgan, 1996
CO_2 flux	JCO_2	g C/m^2/y	CO_2 flux	JCO_2	mol/m^2/y	$JCO_2 = (JCO_2$ *12.0107)	Stumm and Morgan, 1996
CO_2 flux	JCO_2	mg C/m^2/d	CO_2 flux	JCO_2	g C/m^2/y	$JCO_2 = JCO_2$ *1000/365	Stumm and Morgan, 1996
Negative log of first acidity equilibrium constant of CO_2	pK_1	mol	Temperature	T	K	$pK_1 =$ 3403.71/T+(0.03279*T)-14.84	Stumm and Morgan, 1996
Negative log of second acidity equilibrium constant of CO_2	pK_2	mol	Temperature	T	K	$pK_2 =$ 2902.39/T+(0.02379*T)-6.5	Stumm and Morgan, 1996
Negative log of water ion product	pK_w	mol	Temperature	T	K	$pK_w =$ 4470.99/T+(0.01706*T)-6.09	Stumm and Morgan, 1996
Hydroxide ion concentration	OH	M	pH Negative log of water ion product	pH pK_w	mol	OH = 10^(pH-pK_w +3)	
First acidity equilibrium constant of CO_2 minus pH	r_1		Negative log of first acidity equilibrium constant of CO_2 pH	pK_1 pH	mol	$r_1 = 10$^(pK_1-pH)	Johnson, 1982
Second acidity equilibrium constant of CO_2 minus pH	r_2		pH Negative log of second acidity equilibrium constant of CO_2	pH pK_2	mol	$r_2 = 10$^(pH-pK_2)	Johnson, 1982
Bicarbonate	HCO_3	M	Acid neutralizing capacity Hydroxide ion concentration	ANC OH	meq/l M	$HCO_3 =$ (ANC*1000-OH)/(1+2* r_2)	Johnson, 1982
Carbonate	CO_3	M	Second acidity equilibrium constant of CO_2 minus pH Bicarbonate	r_2 HCO_3	M	$CO_3 = r_2$*HCO_3	Johnson, 1982
Carbon dioxide	CO_2	M	First acidity equilibrium constant of CO_2 minus pH Bicarbonate	r_1 HCO_3	M	$CO_2 = r_1$*HCO_3	Johnson, 1982
Total CO_2	TCO_2	M	Bicarbonate Carbonate Carbon dioxide	HCO_3 CO_3 CO_2	M M M	$TCO_2 = HCO_3 + CO_3 + CO_2$	Johnson, 1982

Table A1. (Continued)

First acidity equilibrium constant of CO_2	K_1	M	Negative log of first acidity equilibrium constant of CO_2	pK_1	mol	K_1 = 10^(-1*pK_1)	Stumm and Morgan, 1996
Second acidity equilibrium constant of CO_2	K_2	M	Negative log of second acidity equilibrium constant of CO_2	pK_2	mol	K_2 = 10^(-1*pK_2)	Stumm and Morgan, 1996
Molecular diffusion coefficient	D	cm^2/s	Temperature	T	K	D = 5019*EXP(-19.51/0.0083 1451/T)*10^(-5)	Jähne et al., 1987
Salinity	S	mg/l	Specific conductance	SC	mS/cm	S = SC*0.64*10^-3	Snoeyink and Jenkins, 1980
Rate constant for $[CO_2]$ + $[H_2O]$ → $[H^+]$ + $[HCO_3-]$	RCO_2	1/s	Salinity Temperature	S T	% K	RCO_2 =EXP(1246.98+0*(S)^0.5+(-6.19*10^4)/(T)+((-183)*LN(T)))	Johnson, 1982
Rate constant for $[CO_2]$ + [OH-] → $[HCO_3-]$ times rate constant for water	ROH_ K_w	mol/dm^3*s	Salinity Temperature	S T	% K	ROH_ K_w = EXP(-930.13+0.11*S^0.5+(10^4)*3.1/T+140.9*LN(T))	Johnson, 1982
Combined rate of reaction of hydration of CO_2	R		Rate constant for $[CO_2]$ + $[H_2O]$ → $[H^+]$ + $[HCO_3-]$ Rate constant for $[CO_2]$ + [OH-] → $[HCO_3-]$ times rate constant for water	RCO_2 ROH_ K_w	1/s $mol/(dm^3*s)$	R = RCO_2+ ROH_ K_w	Johnson, 1982
Hydrogen activity divided by first and second dissociation constants	T		Hydrogen ion concentration First acidity equilibrium constant of CO_2 Second acidity equilibrium constant of CO_2	aH K_1 K_2	M M M	T = 1+ aH^2*(K_1*K_2+ K_1* aH)^-1	Bade and Cole, 2006

Table A1. (Continued)

Precursor to chemical enhancement coefficient	Q		Combined rate of reaction of hydration of CO2 Hydrogen activity divided by first and second dissociation constants Molecular diffusion coefficient	R T D	 cm^2/s	Q = (R*T/D)^(0.5)	Bade and Cole, 2006
Thickness of stagnant boundary layer	z	cm	Molecular diffusion coefficient Transport coefficient	D k	cm^2/s cm/h	z = D/((k)/3600)	Stumm and Morgan, 1996
Chemical enhancement coefficient Chemical enhancement coefficient (cont.)	Beta Beta		Hydrogen activity divided by first and second dissociation constants Precursor to chemical enhancement coefficient Thickness of stagnant boundary layer	T Q z	 cm	Beta = T/((T-1)+TANH(Q*z)/(Q*z))	Bade and Cole, 2006
Enhanced CO_2 flux	JCO_2	mg $C/m^2/d$	Chemical enhancement coefficient CO_2 flux	Beta JCO_2	 mg $C/m^2/d$	JCO_2 = Beta*JCO_2	Stumm and Morgan, 1996