CARBON GAS CONCENTRATIONS AND FLUXES IN LAKE VESIJÄRVI - POSSIBLE EFFECTS OF ARTIFICIAL AERATION

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Lakes play an important role in both global and regional carbon cycling, especially, the role of lakes is pronounced in the boreal zone, where lakes cover up to 20% of the land area. Allochthonous carbon is discharged mainly from terrestrial processes, but also through anthropogenic eutrophication. The role of allochthonous carbon load in lacustrine ecosystems is important, which can have far-reaching effects on lacustrine biogeochemistry in general and especially on carbon cycling. Part of dissolved organic carbon is transformed to carbon dioxide ($CO_2$) and methane ($CH_4$) in biological processes that result in carbon gas concentrations in water that increase above atmospheric equilibrium, thus making boreal lakes serve as sources of the important greenhouse gases.

Lake Vesijärvi is renowned for its clear-water, but it has suffered eutrophication for a long history. The severely affected Enonselkä lake basin is the most eutrophic part since it surrounded mainly by urban area (28%) and forests (31%). To improve the water quality, large scale aeration in the autumn 2009 was started with the Mixoxoxygenators. Aeration is used to weaken thermal stratification and recharge oxygen by increasing vertical flow circulation within the water columns. This leads to most chemical concentrations become more homogenous with depth and concentrations of reduced forms decrease in the hypolimnion. The aeration units were operated on campaign basis in summer 2013.

One aim here was to investigate carbon gas concentrations and fluxes from the urban boreal lake basin, and examine the impacts of artificial aeration on greenhouse gases during the open water period in 2013. Besides $CO_2$ and $CH_4$ concentrations and fluxes, I measured also the water temperature and dissolved oxygen concentrations of the water columns for monitoring the efficiency of artificial aeration. All gas samples were analyzed at the Lammi Biological Station of University of Helsinki with gas chromatography using the head space technique. As background data I used the information on temperature and oxygen profiles collected from the measuring platform on Lake Vesijärvi, and a reference study on $CO_2$ and $CH_4$ concentrations and fluxes dating back to 2005 when there was no aeration going on.

In 2013, the studied lake basin was a source of $CO_2$ to the atmosphere during the open water period, although the lake basin showed uptake of $CO_2$ from the atmosphere for short times. The lake acted as a steady source of $CH_4$ to the atmosphere throughout the measuring period. The mean $CO_2$ flux was 34.1 mmol m$^{-2}$ d$^{-1}$, which was over 2.5 times higher than in the reference year 2005 when there was no aeration yet. During the campaigns, the $CO_2$ fluxes were higher from aerated than non-aerated water column and from the longer aerations as well. Therefore, aeration mixed stratified water columns and thus enhanced release of gases such as $CO_2$ from surface water to the atmosphere. The mean $CH_4$ flux was 0.2 mmol m$^{-2}$ d$^{-1}$. The $CH_4$ fluxes from the Enonselkä basin were slightly decreased in 2013. These decreased $CH_4$ fluxes in Enonselkä basin can be attributed to the limited $CH_4$ production and high rate of $CH_4$ oxidation in the oxygenated hypolimnion and surface of sediment. The daily $CH_4$ fluxes during the long time aerated operations decreased. The significance of aeration to carbon cycling processes depended on the residual $CH_4$ concentrations in the water column.
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1. Introduction

Carbon dioxide (CO\textsubscript{2}) and methane (CH\textsubscript{4}) are among the most important and abundant greenhouse gases (GHG) in the atmosphere. Global warming and climate change are mainly the results of GHG concentrations rising in the Earth’s atmosphere. The increase in atmospheric CO\textsubscript{2} is accelerating, and the 2013 average annual CO\textsubscript{2} concentration in the atmosphere is 396 ppm with the average annual increase of 2.1 ppm per year in the past decade (2003-2012) (http://co2now.org/). CH\textsubscript{4} is a highly potent GHG in the atmosphere; it has a Global Warming Potential (GWP) 25 times that of CO\textsubscript{2} on a 100 -year timescale (Forster et al. 2007). Moreover, globally 6-16% of CH\textsubscript{4} emissions are derived from lakes (Bastviken et al. 2004, Juutinen et al. 2009, Bastviken et al. 2010).

Freshwater ecosystems such as lakes, play an important role in both global and regional carbon cycling, even they share in total only ca. 3% (4.6 million km\textsuperscript{2}) of the Earth’s continental surface area (Downing et al. 2006). In the boreal zone, the role of lakes is especially pronounced, since lakes can locally cover up to 20% of the continental area (Huotari 2011). Therefore, it is worthy and meaningful to study carbon cycling within lacustrine ecosystems, and reveal their role as sources or sinks of CO\textsubscript{2} and CH\textsubscript{4}. Cole et al. (1994) manifested that most lakes worldwide are supersaturated with CO\textsubscript{2} and thus sources of atmospheric CO\textsubscript{2}. Besides, CH\textsubscript{4} concentrations in surface water of boreal lakes are usually higher than atmospheric equilibrium, especially during the spring and autumn turnover periods (Michmerhuizen et al. 1996, Riera et al. 1999). Therefore, the carbon gas fluxes of air-surface water interface are controlled by several factors such as seasonal stratification patterns of lakes, weather conditions, basin morphometry, landscape and regional hydrology, ecosystem process and perturbations.

1.1. Seasonal patterns in lakes

Dimictic mixing pattern and stratification are typical phenomena in deep boreal lakes during the open-water period. The dimictic lakes mean that lakes have two mixing periods, the spring and autumn turnovers, each year. The typical dimictic lake stratifies during the warm months and the water column is then thermally divided into three layers: the epilimnion, the metalimnion, and the hypolimnion. The epilimnion, the upper warm water layer is mixed well by wind whereas the
hypolimnion, the dense colder water at the bottom is little affected by wind action. Between the relatively isothermal epilimnion and the hypolimnion, there is an intermediate region of steep thermal gradient, the metalimnion. Thus, the cross section of a stratified lake is portrayed with dense cold water lying beneath lighter warm layers. The summer stratification affects gas and nutrient transfer in water column. Loss of stratification takes place when decreasing air temperatures and negative heat flux cools the surface waters, which then destroys the stratum of thermal discontinuity and initiates a circulation in the water column. As the entire water column is included in the circulation, the autumnal turnover starts. With the warming days of spring, the entire water column has a uniform temperature, and little thermal resistance to mixing. At this time, lake exposed even to weak winds, start to mix completely. Large lakes often circulate for a period of weeks, and wind can lengthen the both circulations (Cole 1983, Wetzel, 2001).

When observed continuously, higher latitude lakes are usually sources of CO$_2$ during the spring and autumn; however, the lakes can also have short periods when they are serving as sinks in summer (Riera et al. 1999, Huotari et al. 2009). The lake turnovers, mainly determined by weather conditions, contribute to gas exchange at the air-surface water interface, and circulate oxygen from the epilimnion to the hypoxic zone; meanwhile they also supply nutrients from the hypolimnion to the epilimnion. The carbon gas exchanges are also characterized by seasons. For instance, CO$_2$ fluxes in boreal lakes are higher in autumn than in spring, whereas CH$_4$ fluxes can be lower in autumn than in spring (López Bellido et al. 2009). The onset and duration of turnover period can result in high interannual variation in gas fluxes.

Weather conditions (temperature, precipitation, wind speed, solar radiation, etc.) can induce diverse changes in lacustrine carbon concentrations. Particularly sudden changes in weather patterns can result in increases in carbon gas fluxes, because surface waters show clear diel and day-to-day variations (Cole and Caraco 1998, Riera et al. 1999). Snowmelt and extreme rain events sustain a large portion of annual allochthonous carbon loading entering lake in a short period of time (Findlay and Sinsabaugh 2003). It is also demonstrated both in the field and in the laboratory that the rate of gas exchange can be affected and greatly enhanced by heavy rains (Ho et al. 2007). Moreover, strong wind can accelerate the loss of ice cover, and light wind is enough to initiate circulation of the water column and prolong the turnover period as well. Especially,
wind impinging on the surface of lake affects the carbon gas fluxes and thus, most correlative studies suggest that the magnitude of the gas exchange depends on the gas transfer velocity \((k)\), while the \(k\) increases predictably with increasing wind speed at winds \(\geq 3\ \text{m s}^{-1}\) (Cole and Caraco 1998, Wetzel 2001).

**1.2. Carbon loading and production of carbon gases**

Basic metabolic processes in lakes are photosynthesis and respiration, which correspondingly predominate the trophogenic processes in the epilimnion and the tropholytic processes in the hypolimnion. The lacustrine net production of \(\text{CO}_2\) is a result of photosynthetic incorporation of inorganic carbon and respiration of organic carbon in lake. In the pelagic zone most of the \(\text{CH}_4\) is produced through methanogenic decomposition of organic matter in the hypolimnion and the lake sediment zone, where the conditions are hypoxic and finally anoxic with the absence of alternative electron acceptors (\(\text{NO}_3^-\), \(\text{Fe}^{3+}\) and \(\text{SO}_4^{2-}\); cf. Capone and Kiene (1988)). \(\text{CH}_4\) can be biologically oxidized to \(\text{CO}_2\), resulting in spatial increase in \(\text{CO}_2\) concentrations. Anaerobic oxidation of \(\text{CH}_4\) is also possible but regarded as less important in lacustrine ecosystems (Schink 1997, Raghoebarsing et al. 2006). Through turbulent diffusion and lateral advection, \(\text{CO}_2\) can be transported in the water column and then across the air-water interface. In the pelagic \(\text{CH}_4\) fluxes are due to vertical diffusion and ebullition as well as lateral advection, whereas in the shallow areas fluxes can also be plant mediated (Cole 1983, Grinham et al. 2011).

Allochthonous carbon loading can widely affect lacustrine biogeochemistry and especially carbon cycling. Terrestrial ecosystems provide high productivity of organic carbon, and as a result, large amounts of organic carbon go into the adjacent waters mainly in the form of dissolved organic carbon (DOC) (Huotari 2011, Linnaluoma 2012). In lacustrine ecosystems in the boreal zone, the DOC magnitude derived from the surrounding catchments is always substantial (Ojala et al. 2011, López Bellido et al. 2011). Loading of allochthonous organic carbon is controlled by several factors including climate, hydrology, landscape morphometry, drainage ratio, as well as the land use of catchment (Linnaluoma 2012). Part of the DOC is processed in the lake, and mineralized to \(\text{CO}_2\) and \(\text{CH}_4\), whereas part is drained to further down
in the lake chain. By this way, gas saturation and the resulting emissions from lakes to the atmosphere increase (Ojala et al. 2011).

Anthropogenic allochthonous loading is derived from human activities, such as discharge of sewage water, storm water runoff, and industrial effluents. The excessive nutrients and organic matter have serious ecological effects by enhancing productivity in lakes (Wetzel 2001). Eutrophication can induce extra carbon gas emissions to the atmosphere, through the increased primary production and the following demineralization of organic compounds in the sediment, but simultaneously due to vigorous photosynthesis by algae, eutrophicated lakes can occasionally be subsaturated in terms of CO₂. The most directly influenced water bodies are those surrounded by or adjacent to densely populated areas, especially urban areas. Because there is a strong tendency of urbanization nowadays, as a consequence, there is potential to increased greenhouse gas fluxes, too.

CO₂ and CH₄ emissions from lakes to the atmosphere in the boreal zone have been intensively studied, especially in brown-water lakes. Among the few studies on clear-water lakes, truly urban lakes are rare. Lake Vesijärvi, a boreal urban clear-water lake, has been studied for its carbon gas fluxes in 2005 (López Bellido et al. 2011), i.e. at time without artificial aeration. Studies concerning carbon cycling but also aeration, are more common in small temperate lakes, Cowell et al. (1987) studied a hypereutrophic lake central Florida, and Martinez et al. (2013) a shallow eutrophic lake in southern California. In Finland, a study of carbon gases in artificially oxygenated eutrophic lake in winter time was carried out by Huttunen et al. (2001), whereas Forsius et al. (2010) studied a small humic lake under aeration.

2. Aims of study and hypothesis

This study concerns about the carbon gas concentrations in and fluxes from Lake Vesijärvi at the time the water columns were oxygenated by aeration in summer. I hypothesize that, due to artificial aeration, the atmospheric fluxes of CH₄ decreased, whereas the CO₂ fluxes increased. As a result of aeration, CH₄ is transported efficiently from hypolimnion and transformed to CO₂ through methanotrophic activity in the water column. Besides CO₂ and CH₄ concentrations and
fluxes, I will determine the possible influence of temperature and dissolved oxygen concentrations upon them. The hypolimnetic temperature and O\textsubscript{2} concentrations tend to increase when the water columns are mixed by artificial aeration. I will also look at weather patterns, i.e. wind speed and precipitation. All the measurements are throughout the open water period 2013. As a reference study I will use the data on CO\textsubscript{2} and CH\textsubscript{4} concentrations and fluxes dating back to 2005, when there was no aeration going on (López Bellido et al. 2011).

3. Material and methods

3.1. Study sites

The fluxes of CO\textsubscript{2} and CH\textsubscript{4} were studied in the open-water period 2013 in the pelagic regions of Lake Vesijärvi (61°4’58”N, 25°32’18”E), which is situated in southern Finland, and surrounded by the City of Lahti and the municipalities of Hollola and Asikkala (Figure 3 A). Lake Vesijärvi is a glacial drift lake, and a part of the River Kymijoki water course (Linnaluoma 2012). This irregularly shaped lake is made up of several basins connected by narrows and shoals. The four largest basins are Enonselkä, Kajaanselkä, Komonselkä and Laitialanselkä.

Lake Vesijärvi has a total area of 109 km\textsuperscript{2}, and by definition it is a large lake (the total area > 100 km\textsuperscript{2}). It is the 42nd largest lake in Finland, with the mean and maximum depths of 6 m and 42 m, respectively. The mean retention time of water is 5.4 years. The catchment area is 514 km\textsuperscript{2}, which is covered by forest (60%), arable land (23%), peat land (9%), and populated area (9%). The shoreline of Lake Vesijärvi is 180 km long, 45% of which is used for forestry, 33% for summer cottage (recreation) settlement, 13% for permanent settlement and the remaining 9% for agriculture (http://www.puhdasvesijarvi.fi/).

Lake Vesijärvi was a renowned for its clear-water, and thus named by its originally transparent water (‘vesi’ in Finnish language means ‘water’, ‘järvi’ means ‘lake’) (Kairesalo et al. 1999, Kairesalo & Vakkilainen 2004). Lake Vesijärvi and its surroundings benefitted human dwellings and various human activities, mainly agriculture, fishery, industry and transportation (Kairesalo & Vakkilainen 2004). The City of Lahti grew vigorously in the first half of the 20\textsuperscript{th} century and
the growth took its toll on Lake Vesijärvi. Thus, eutrophication appeared and was documented as early as 1928 as a consequence of increased industrial and sewage effluent discharges from the City of Lahti (Kairesalo et al. 1999, Kairesalo & Vakkilainen 2004). Such situation lasted until the middle of the 1970s. In the 1960s and 1970s, Lake Vesijärvi was one of the most eutrophic large lakes in Finland; especially the severely affected Enonselkä basin in the southern part of the lake and close to the City of Lahti, was in bad shape (Kairesalo & Vakkilainen 2004, Keto et al. 2012). The lake started to recover in 1976 when the sewage loading was diverted from the lake to a nearby river and the loading of phosphorus and nitrogen into the basin fell to 8% of the previous level. However, the recovery faded in the 1980s. Then to restore the lake, biomanipulation through mass removal of planktivorous and benthivorous fish was performed in 1989-1994. As a result, cyanobacteria blooms disappeared, water clarity increased and submerged macrophytes colonized larger areas (Kairesalo & Vakkilainen 2004).

The study was carried out in Enonselkä basin (Figure 1 B), which has a total area of 26 km² (61°04′N, 25°35′E). It is the southernmost basin of Lake Vesijärvi, and surrounded by the City of Lahti. The mean and maximum depths in the basin are 6.8 m and 33 m, respectively. The catchment area is 84 km², which is covered by urban areas (28%), forest (31%), arable land (7%) and peat land (1%). The retention time of water in the basin is 5.5 years (http://www.puhdasvesijarvi.fi/). The lake water is neutral (pH 7.5) and the concentration of dissolved organic carbon (DOC) is 6–7 mg L⁻¹. The total nitrogen concentration is moderate, but the total phosphorus concentration is high (total N, 740 µg L⁻¹; total P, 60 µg L⁻¹). The water colour is 30 mg Pt L⁻¹, and the chlorophyll a concentration in summer is around 8 µg L⁻¹ (Linnaluoma 2012). The Enonselkä basin was sampled from two pelagic sites equipped with the aeration units, i.e. Lankiluoto and Vasikkasaari (Figure 1). Lankiluoto is deep with a maximum depth of 31 m. Vasikkasaari has a maximum depth of 22 m.
Figure 1. Location of (A) Lake Vesijärvi in Finland (B) Enonselkä basin in Lake Vesijärvi (C) The red dots indicate the sampling sites: Lankiluoto (31 m) and Vasikkasaari (22 m) in Enonselkä basin.

3.2. Aeration in Lake Vesijärvi

During the early 2000s, Enonselkä basin was monitored, and the water quality development turned again to the unwanted direction. Especially the development of oxygen conditions was alarming. Large part of the hypolimnion became anoxic during the summer stratification period. As a consequence of anoxia, harmful substances like hydrogen sulphide (HS), methane (CH$_4$), ammonia (NH$_3$) appeared (Kauppinen 2013). To improve the water quality and reduce the internal phosphorus loading, a large scale aeration in the autumn 2009 was started with the Mixox-oxygenators. (Figure 2) Aeration is used to weaken or eliminate thermal stratification and density barriers by increasing circulation within the lake (Cowell et al. 1987). This results in
oxygenation of bottom waters and leads to general increases in rates of decomposition of organic matter in the sediment and water column, and decrease in the concentrations of reduced forms of iron, manganese, nitrogen, and sulphur.


Artificial aeration in Lake Vesijärvi was started firstly in Myllysäari location in the southern Enonselkä basin, where a Mixox MC 500 (Vesi-Eko Oy, Kuopio, Finland) was installed in winter 2007-2008. Another set of 8 units of Mixox MD 1100 were installed in the lake in 8 deep locations in autumn 2009 (Figure 3). Mixox pumps surface water to the bottom layers and creates a peaceful and very large-scale water cycle. One oxygenator influences an area of 50 to 500 ha, depending on the dimensions of the oxygenator. Mixox MD 1100 may pump about 680 000 m³ day⁻¹, whereas the pump power of Mixox MC 500 is about 15 000 m³ day⁻¹. However, Mixox-oxygenator does not add air or oxygen to upper water layer when it pumps, i.e. the device does not need much energy (Kauppinen 2013). Lankiluoto and Vasikkasaari in the Enonselkä basin are among the locations with the aeration equipment Mixox MD 1100 installed and they are the locations this thesis on urban limnology of a clear-water boreal lake is based on.
Figure 3. Locations of oxygenators (cycles with number), oxygenator's power stations (black solid points) and observation points/measurement stations (red points) in Lake Vesijärvi (NB: This figure does not show all the existing observation locations). The base map copyright Land Survey of Finland, permit No. 135/MML/12. Base map copied from (Kauppinen 2013).
The aeration equipment (Mixox-oxygenator) was on and operating in the both locations intermittently during the stratified period in 2013 (Table 1). The winter aeration in Vasikkasaari as well as in Lankiluoto started on 28 December 2012, and stopped on 19 April 2013. In both locations, the summer aeration was going on at the same time in July, August and September, with a malfunction break in July in Lankiluoto. In Lankiluoto the oxygenator was operating for a few days in June, whereas in Vasikkasaari it was off for the whole June. On 20 September at the time of autumn turnover, both aeration equipments were turned off. Approximately, the aeration equipment in Lankiluoto was on for 6 days in June, 6 days in July, 23 days in August, and 20 days in September. In Vasikkasaari the oxygenator was on for 0 day, 21 days, 23 days, and 20 days in June, July, August and September, respectively.

Table 1. Operation times of the aeration equipment in Vasikkasaari and Lankiluoto in 2013.

<table>
<thead>
<tr>
<th>Location</th>
<th>Winter 2012-2013</th>
<th>2013/6/1</th>
<th>2013/7</th>
<th>2013/8</th>
<th>2013/9</th>
</tr>
</thead>
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3.3. Sampling

All samplings were carried out between the end of April and the beginning of October 2013. Samples were once taken from the ice-covered lake before ice-out, on 24 April 2013. The ice-out took place on 2 May, and in the Enonselkä basin the open-water period lasted then to 5 December. The intensive samplings were carried out in June – August on campaign basis, i.e. there were three measuring periods, each lasting for two weeks. During the campaigns the aeration systems in Lankiluoto and Vasikkasaari were turned either off or on, depending on the
objective of the measurements. During the campaign each site was visited at maximum 3 times per week. Each time the water column was sampled for carbon gas concentrations (CO₂, CH₄), temperature, and oxygen concentrations.

At the both sites, samples were taken with a Limnos tube sampler (height 30 cm, total volume 2.1 L) at various depths throughout the water column. From the upper five meters, I took samples at 1- m interval, i.e. the samples were taken from depths of 0, 1, 2, 3, 4, and 5 m in both sites, and then at 5- m interval, i.e. samples of 10 m, 15 m, 20 m, 25 m, and 30 m in Lankiluoto, and 10 m, 15 m, 20 m in Vasikkasaari. The samples were always taken between 9:30 a.m. and 11:30 a.m. (solar time; Greenwich Mean Time +2h). Throughout the water column, the stratification pattern of water temperature (°C) and the profile of dissolved O₂ concentration (mg L⁻¹) was measured at 1-m interval down to the bottom using a temperature-compensated dissolved oxygen meter (YSI 58, Yellow Springs Instruments).

Estimation of carbon gas fluxes based on scanty samples during one open-water period limited testing of the validity of hypothesis. Fortunately, there is a measuring station in Lankiluoto (Figure 3) providing background monitoring data for measuring the water temperature and oxygen concentrations constantly (at depths of 10 m, 20 m and 30 m) during 2009 – 2013. Note that, there are other two monitoring stations located around Myllysaari and Enonselkä, but only the data/site most relevant to this thesis was adopted.

I used also the information on wind speed and wind direction, as well as precipitation. The wind and precipitation data were from the Lahti Laune weather station (60° 57' N, 25° 37' E, and elevation 84 m) run by the Finnish Meteorological Institute (FMI). Lahti Laune weather station is located in the City of Lahti, and it is the nearest weather station to Lake Vesijärvi, ca. 7.5 km and 8.5 km from Vasikkasaari and Lankiluoto, respectively. The wind data from Laune station were only used as background data and to confirm that application of gas transfer velocity deduced form Lake Kuivajärvi was correct (see section 3.4). Determinations of the relationship between gas transfer velocity and wind speed in lakes are often based on data form meteorological stations located on land, sometimes quite far away from the lake itself. However, it cannot be assumed that the same wind conditions will prevail over the water because of the
vastly different drag coefficients between different ecosystems (Kwan and Taylor 1994, Markfort et al. 2010).

3.4. Carbon gas measurements

Dissolved gas samples of CH₄ and CO₂ (volume 30 mL) were taken from the Limnos sampler throughout the water column. Water samples from each depth were drawn into 60 mL polypropylene syringes (Terumo), which could be closed with three-way stopcocks (Luer-lock, Codan, Steritex) after removing any gas bubbles. The syringes were invariably stored in crushed ice filled cool-box until analysis on the same day at the Lammi Biological Station of University of Helsinki using gas chromatograph (GC) and head-space technique. In the laboratory, the syringes were placed in a water bath at a temperature of 20 °C for 5-10 min. Then 30 mL of nitrogen gas was added into the syringes, and mixed with the water samples. Samples from the gas phases were injected into vacuumed 12 mL Labco Exetainer® vials (Labco Limited, High Wycombe, Buckinghamshire, UK), which were placed in Gilson 222 XL autosampler (Gilson Inc., Middleton, Wisconsin, USA). Samples were then transferred to the GC through a 1 mL Valco 10-port valve (VICI Valco Instruments Co. Inc., Houston, USA). Analyses were carried out with an Agilent 6890 N (Agilent Technologies, Santa Clara, California, USA) GC equipped with a flame ionization detector (FIC) (temperature 210 °C) and a thermal conductivity detector (TCD) (temperature 120 °C, oven 40 °C, PlotQ capillary column, flow rate 12 mL min⁻¹, helium gas as a carrier gas). The GC was calibrated with CO₂ using concentrations of 4010 ppm and 15200 ppm, and with CH₄ using concentration of 503 ppm, and in addition, using air with CO₂ concentration of 393 ppm and CH₄ concentration of 1.74 ppm (Oy AGA Ab, Finland).

The concentrations of carbon gases in the water (C; μmol L⁻¹) were determined from solubility of CO₂ and CH₄ as a function of temperature and applying the appropriate Henry’s law constant (Kᵢ; mol L⁻¹atm⁻¹):

\[ C = x_g \ p_{atm} \ K_H, \]  

(1)
where $\chi_g$ is the mole fraction of CH$_4$ and CO$_2$ in water samples (given by the detector output), and $p_{atm}$ is the atmospheric pressure ($= 1$ atm).

The equilibrium concentration of carbon gas was calculated with the equation (1). The atmospheric CO$_2$ and CH$_4$ concentrations are 393.84 ppm (http://co2now.org/) and 2 ppm, respectively.

3.5. Calculation of carbon gas fluxes

Briefly, the carbon gas flux, between the lake surface-water layer and the overlying atmosphere, depends on two main factors: the concentration gradient between the water and the air ($C_s - C_{eq}$), and the gas transfer velocity ($k$) for a given gas at a given temperature (Cole and Caraco 1998). The boundary layer method according to Cole and Caraco (1998) is as follow:

$$F_g = k (C_s - C_{eq}),$$

(2)

where $C_s$ is the concentration of carbon gas (CH$_4$ or CO$_2$) in the surface-water and $C_{eq}$ is the concentration of carbon gas in equilibrium with the air.

In my study, for the atmospheric CH$_4$ concentrations and the gas transfer velocity ($k$), I used information and an empirical parameterization from Lake Kuivajärvi (61°50’ N, 24°17’ E) in Hyytiälä. Lake Kuivajärvi is a humic lake in southern Finland with a maximum depth of 13.2 m, and a surface and catchment area of 0.638 km$^2$ and 9.35 km$^2$, respectively. The gas transfer velocity in Lake Kuivajärvi was 6.5 cm h$^{-1}$ at low winds (<1 m s$^{-1}$) from which it increased to 10 cm h$^{-1}$ at stronger winds (~ 4 m s$^{-1}$). Since Lake Vesijärvi and Enonselkä basins are much bigger than Lake Kuivajärvi, with generally higher wind speeds, I adopted the value of 10 cm h$^{-1}$ for $k$ in my calculation (Heiskanen J.et al. 2014).
4. Results

4.1. Air temperature

The mean air temperatures for the measuring period from May – October and the summer period from June – August were 13.1 and 16.5 °C, respectively. Thus, these mean temperatures were close to the mean values of the past two years (2011 & 2012). The air temperature followed the seasonal change, which led to the temperature increase in May and June and decrease since late August. However, the monthly mean air temperature differed between 2013 and the previous years. The study year had a relatively higher air temperature in May and June, but relatively lower mean temperature in July. The monthly air temperature was 13.3, 17.1, 16.9, 15.5, 10.6, and 5.2 °C in May - October, respectively. In addition, the largest monthly temperature difference was 13, 12.8, 8.6, 9.3, 10.6, 14.1 °C in May – October, respectively. The highest mean and maximum daily air temperatures were 24.4 and 30.8 °C registered on the same day, on 26 June (Figure 4). During autumn, the first sub-zero daily mean air temperature was registered on 19 October. During each aeration period (see Table 1), the corresponding mean air temperature was 18.2 (n = 6), 16.6 (n = 21), 16.3 (n = 17) and 12.7 (n = 25) °C in June, July, August and September, respectively.

4.2. Precipitation

According to the observations from Laune weather station, precipitation in May - October 2013 was 433.4 mm (Figure 4). The study year was rainier than usually since the precipitation was higher than the long-term (2000-2012) mean precipitation of 381.9 mm, and in 2013 the annual precipitation was the fourth highest in the past decade. The highest precipitation (556.5 mm) was recorded in 2004.
The monthly precipitation was 31.1, 85.7, 57.7, 117.6, 48.7, and 92.6 mm in May to October, respectively. August was thus the rainiest month, but also June and October had a relatively high precipitation (Figure 4). The major rain events occurred on 14 August, 27 June, 1 October, 18 July and 1 September with the daily precipitation of 54 mm, 28.4 mm, 23.5 mm, 19 mm and 16.9 mm (Figure 4).

4.3. Wind direction distribution

The dominant wind direction was always inconstant (Figure 5). Wind from southeast was dominant in July and from south-west in August and October. In June, wind from northwest was the prevailing wind blowing on the lake. Wind from northeast occurred more often in May. Thus, most of the time the fetch in Lake Vesijärvi was consistent.
Figure 5. Wind direction and speed (m s\(^{-1}\)) distribution in May to October 2013 in Laune weather station. N.B. different scale for wind speed in October.

In May to October the average wind speed was 1.1 m s\(^{-1}\). Winds were < 3 m s\(^{-1}\) over 93% of the time. The windiest months were May, July and October (Figure 5). On 2 May, the day of the ice break-up, the maximum wind speed recorded was 6.2 m s\(^{-1}\), and the high wind started at 7 a.m. in the morning and lasted until 3 p.m. in the afternoon. Beyond that, it was windier in mid-June, when the highest wind speed was 5.2 m s\(^{-1}\), recorded on 15 June. This was also the highest wind speed during the open water period 2013. However, between May and October, the most dominant feature of the wind profile was the light breeze or gentle breeze. In pelagic zone light breeze results in small wavelets, and crests have a glassy appearance and they do not break. Gentle breeze can create larger wavelets, when crests begin to break and foam of glassy appearance shows up.

4.4. Thermal stratification

In 2013 the open-water period lasted from 2 May to 5 December in the Enonselkä basin. One week before the ice out, i.e. on 24 April, the temperature beneath the ice cover varied from 2.9 to
3.3 °C (Figures 6 & 7). Most probably the lake basin attained the state of spring turnover already before the ice breakup. The temperatures in the entire water column were ca. 4 °C at the beginning of May, and with the help of wind the spring turnover lasted till early May when the temperature stratification started to appear. At the beginning, the epilimnetic temperature followed the increase in air temperature and a weak thermal stratification developed. The thermal discontinuity in the water columns developed to more and clearer one and finally by the early June the water columns were clearly stratified. After that the thermocline gradually sank deeper and in mid-August the metalimnion was located between ca. 6 - 13 m depth.

![Figure 6. Temperature (°C) stratification in Lankiuloto in 2013. Blue shades indicate the days when the artificial aeration was in operation.](image-url)
Figure 7. Temperature (°C) stratification in Vasikkasaari in 2013. Blue shades indicate the days when the artificial aeration was in operation.

During the open-water period the epilimnetic temperature varied from ca. 3 to 21 °C; the maximum surface water temperatures of 20.7 °C and 20.8 °C in Lankiluoto and Vasikkasaari were registered on 26 June and 8 July, respectively. In hypolimnion the temperature ranged from 3.3 to 14.7 °C, i.e. the temperature difference was 11.4 °C. The monthly mean water temperatures in June, July and August throughout the hypolimnion were 7.2 °C (n=112), 8.8 °C (n=64) and 13.7 °C (n=80) in Lankiluoto and 7.5 °C (n=70), 9.8 °C (n=40) and 14.3 °C (n=50) in Vasikkasaari. During stratification (ca. June - August), there was one long aeration period in Lankiluoto in August, whereas Vasikkasaari was aerated both in July and August. Both locations showed a clear temperature effect of aeration, i.e. the thermal stratification eroded as a result of aeration (Figures 6 & 7). The hypolimnetic temperature was usually higher in Vasikkasaari than in Lankiluoto, especially in July, probably due to successful aeration in Vasikkasaari, whereas in Lankiluoto the aeration equipment was malfunctioning. The stratification in Enonselkä basin began to break up in the end of July and in mid-July in Lankiluoto and Vasikkasaari, respectively. Finally, by the end of September, the water columns were homogeneous at ca. 12 °C, thus the basin was in a state of complete autumn turnover.
4.5. Oxygen conditions

In the study year, the mean oxygen concentrations in the water column were 6.7 mg L\(^{-1}\), in Lankiluoto (n= 540, SE 0.13) and Vasikkasaari (n=324, SE 0.14). There was a slight difference in epilimnetic oxygen concentration which varied from 4.0 to 11.55 mg L\(^{-1}\) in Lankiluoto and from 3.8 to 10.8 mg L\(^{-1}\) in Vasikkasaari. The mean hypolimnetic oxygen concentration was 5.7 mg L\(^{-1}\) in both Lankiluoto (n=324) and Vasikkasaari (n=162), i.e. in general the sampling locations had similar oxygen conditions (Figures 8 & 9).

Similar to temperature, from early June onwards the water column started to stratify also in terms of oxygen concentration. As a consequence of stratification, oxygen in the hypolimnion was rapidly depleted in Lankiluoto by the end of July and in Vasikkasaari by mid-July, which times were consistent with the starting time of artificial aeration in each water column. The range in decline was from ca. 6 to ≤1 mg L\(^{-1}\) in Lankiluoto and from ca. 9 to ≤1 mg L\(^{-1}\) in Vasikkasaari. The lowest concentration of oxygen in both locations was 0.8 mg L\(^{-1}\), measured close to the bottom in both locations. Thus, the hypolimnion was hypoxic and anoxic from mid-July to the end of August and from mid-July to late August in Lankiluoto and Vasikkasaari, respectively.

However, in summer 2013 anoxia in the Enonselkä basin lasted only for a short time. As a result of aeration, the hypolimnetic oxygen concentrations in both water columns showed an increasing trend. In Vasikkasaari the 3 week aeration was not started until 12 July and thus, the oxygen concentration declined till mid-July. In Lankiluoto the long-time aeration started on 6 August and the oxygen depletion lasted until that (Figures 8 & 9). As a consequence, the oxygen concentration rose up in Vasikkasaari earlier than in Lankiluoto. The concentration increased from 3 to 10.2 mg L\(^{-1}\) with a daily increasing slope of 0.08 in Vasikkasaari, and from 1.55 to 9.8 mg L\(^{-1}\) with a daily increasing slope of 0.12 in Lankiluoto.
**Figure 8.** Oxygen concentration (mg L$^{-1}$) in Lankiluoto in 2013. Blue shades indicate the days with artificial aeration on.

**Figure 9.** Oxygen concentration (mg L$^{-1}$) in Vasikkasaari in 2013. Blue shades indicate the days with artificial aeration on.
4.6. CO₂ concentrations

During thermal stratification there was also stratification pattern in CO₂ concentrations starting in mid-June in both measuring locations (Figures 10 & 11). In general, the concentrations in Lankiluoto varied from 3.1 to 389.4 µM (mean = 86.8 ± 5.8), whereas in Vasikkasaari the concentrations range was from 3 to 263.9 µM (mean = 73.6 ± 5.8). In both locations, the mean hypolimnetic concentration was approximately 4-fold higher than the epilimnetic one (Table 2), i.e. the CO₂ concentrations were always much higher in hypolimnion than in epilimnion during the open-water period, in particular during the summer months. In the hypolimnion, the high CO₂ concentrations emerged concomitantly with the development of hypoxia. The highest concentrations were recorded on 11 July at the depth of 20 m in Lankiluoto and 26 June at the depth of 20 m in Vasikkasaari. There was a negative correlation (r = -0.9) between the hypolimnetic concentrations of O₂ and CO₂.

Table 2. Carbon gas concentrations (µM) and fluxes of CO₂ and CH₄ (mmol m⁻² d⁻¹) in Lankiluoto (blue) and Vasikkasaari (light blue) in 2013. Values in bold are daily means ± SE and values in parenthesis indicate the range.

<table>
<thead>
<tr>
<th></th>
<th>Location</th>
<th>Gas concentrations (µM)</th>
<th>Gas fluxes (mmol m⁻² d⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Surface (0-30 cm)</td>
<td>Epilimnion (0-5 m)</td>
</tr>
<tr>
<td>CO₂</td>
<td>Lankiluoto</td>
<td>36.5 ± 9.8 (4.2 – 191.8)</td>
<td>36.7 ± 3.4 (3.1 – 215.7)</td>
</tr>
<tr>
<td></td>
<td>Vasikkasaari</td>
<td>25.6 ± 3.4 (3.4 – 54.8)</td>
<td>34.1 ± 2.6 (3 – 135.5)</td>
</tr>
<tr>
<td>CH₄</td>
<td>Lankiluoto</td>
<td>0.1 ± 0.01 (0.05 – 0.3)</td>
<td>0.10 ± 0.007 (0.03 – 0.7)</td>
</tr>
<tr>
<td></td>
<td>Vasikkasaari</td>
<td>0.1 ± 0.01 (0.02 – 0.2)</td>
<td>0.1 ± 0.003 (0.02 – 0.2)</td>
</tr>
</tbody>
</table>
Before ice-out, the aquatic CO₂ concentration in the surface water of Lankiluoto was ca. 50 µM, but the concentration immediately increased to over 100 µM under the ice cover, whereas close to the bottom the concentration was 191.5 µM (Figure 10). Straight after ice-out, the surface CO₂ concentration started to increase, but from May onwards, the CO₂ concentration declined in the surface water as well as deeper down till the depth of ca. 16 m and was below 50 µM. In this part of the water column also chlorophyll a was high indicating vigorous photosynthesis. (Appendix I). In the hypolimnion the CO₂ concentration was over 100 µM. In Vasikkasaari (Figure 11), the CO₂ concentrations beneath the ice cover varied more than in Lankiluoto, i.e. between 21.6 and 242.4 µM. Similarly to Lankiluoto, the concentration in Vasikkasaari declined in May. In early June the water column was fairly well homogenized in terms of CO₂.

In Lankiluoto, a peak of CO₂ concentration appeared in the metalimnion and hypolimnion right after mid-June; the highest concentration 207.3 µM was registered on 24 June. As a consequence of the short aeration (on 22 – 26 June), CO₂ concentration in the surface and metalimnion increased, whereas the hypolimnetic CO₂ concentration dropped to an average of 28.7 µM on 26 June. From the beginning of July, CO₂ started to accumulate again in the hypolimnion, and the maximum CO₂ concentration of 398.4 µM was observed on 11 July at 20 m. A similar pattern in CO₂ concentration was observed in Vasikkasaari, but the maximum concentration close to bottom was only ca. 260 µM.

Due to the long-time aeration in Lankiluoto in August, the hypolimnnetic concentration slowly declined from the middle of August from 213.9 µM (n=4) to 193.2 µM (n=12). However, in Vasikkasaari the long-time aeration started already on 11 July, and the hypolimnetic CO₂ concentration decreased during a longer time period. Before and after the aeration, the mean hypolimnetic concentrations in Vasikkasaari were 229.5 µM (n=6) and 162.7 µM (n=21). After aeration, in July, concentration was 177.4 µM (n=9) and in August, 151.6 µM (n=12). When the sampling ceased on 1 October, the water column concentration of CO₂ was almost homogeneous at ca. 40 µM and ca. 34 µM in Lankiluoto and Vasikkasaari, respectively. Thus, the concentrations indicated that the water column was completely mixed in both locations.
Figure 10. Carbon dioxide (CO$_2$) concentration (µM) in Lankiluo in 2013. Blue shades indicate the days with artificial aeration in operation.

Figure 11. Carbon dioxide (CO$_2$) concentration (µM) in Vasikkasaari in 2013. Blue shades indicate the days with artificial aeration in operation.
In 2013 the average annual concentration of CO$_2$ in the atmosphere was 396.5 ppm (ca. 17.2 µM) ([http://co2now.org/](http://co2now.org/)). In Lankiluoto and Vasikkasaari, CO$_2$ concentration at the depth of 0-30 cm varied from 4.2 to 191.8 µM and from 3.4 to 54.8 µM, respectively. On average, the concentrations in Lankiluoto and Vasikkasaari were 2.1 (range 0.3 – 12), and 1.5 (range 0.2 – 3.1) times higher than that of the atmospheric equilibrium and for the most of the summer time - with only few exceptions - the surface water CO$_2$ concentrations were above the atmospheric equilibrium. In Lankiluoto, concentrations below the equilibrium were recorded on 29 July (4.2 µM) and 7 August (4.4 µM). In Vasikkasaari concentrations lower than the equilibrium were observed on 24 April (21.6 µM), 4 June (4.6 µM), 24 June (9.3 µM), 29 July (6 µM) and 7 August (3.4 µM). Concentrations below the equilibrium were recorded at the time of high chlorophyll $a$ concentration.

### 4.7. CH$_4$ concentrations

In 2013, the CH$_4$ concentrations were low in Enonselkä basin, and only occasionally higher concentrations emerged within 5 m above the bottom at the time of hypoxia and anoxia (Figures 8, 9, 12 & 13). The CH$_4$ concentrations in Lankiluoto were in general higher than in Vasikkasaari, and showed more daily variations all the time. In Lankiluoto, the CH$_4$ concentrations varied from 6.8 to 913.7 nM (mean = 126.7 nM ±8.5), and in Vasikkasaari from 28.2 to 649.6 nM (mean = 100.7 nM ±5). The hypolimnetic concentrations were approximately 1.5-fold higher than the epilimnetic ones (Table 2). During the open water period, the highest hypolimnetic CH$_4$ concentrations were recorded on 11 July (863.4 nM) in Lankiluoto and on 20 August (649.6 nM) in Vasikkasaari. The hypolimnetic concentrations of CH$_4$ correlated negatively ($r = -0.7$) with O$_2$ concentrations. Additionally, the CO$_2$ and CH$_4$ concentrations throughout the water columns were weakly positively correlated ($r = 0.4$).

In Lankiluoto, the hypolimnetic CH$_4$ concentrations before ice-out were high due to the oxygen depletion; at the 30 m depth the maximum concentration was 913.7 nM (Figure 12). Right after the ice out, the hypolimnetic CH$_4$ decreased and in terms of CH$_4$, the water column beneath the epilimnion was homogeneous till the end May. At the beginning of June, a peak of CH$_4$ concentration was observed at the depth of 1 m in Lankiluoto. In mid-June and early July the
hypolimnetic CH\(_4\) concentration grew transiently. In August when the aeration was in use, the hypolimnetic concentration increased to approx. 500 nM. During each break in aeration, the concentration in the hypolimnion decreased (Figure 12). Throughout the open water period, the concentrations in the epilimnion and metalimnion did not vary distinctly, and the mean concentrations in June, July and August were 113.0, 109.0 and 87.9 nM, respectively. During the autumn turnover, the concentration of CH\(_4\) throughout the water column was 160.9 nM (Figure 12).

![Figure 12](image)

**Figure 12.** Methane (CH\(_4\)) concentration (nM) in Lankiluoto in 2013. Blue shades indicate the days with artificial aeration on the lake.

In Vasikkasaari, CH\(_4\) concentrations in the epilimnion were low ranging from 28.2 to 208.4 nM (mean = 90.9 ± 3.5 nM). CH\(_4\) accumulated in the hypolimnion until August. Thus, the concentrations in Vasikkasaari increased only in August when the aeration was in use. The highest concentration of 649.6 nM was registered on 20 August. When the sampling ceased on 1 October, the water column mean concentration of CH\(_4\) was 86.9 nM (Figure 13).
**Figure 13.** Methane (CH$_4$) concentration (nM) in Vasikkasaari in 2013. Blue shades indicate the days with artificial aeration on the lake.

The surface water (0 – 30 cm) concentrations varied from 50 to 268.8 nM in Lankiluoto and from 28.2 to 164.9 nM in Vasikkasaari. In Lankiluoto the highest and the lowest surface water concentrations were observed, respectively, on 4 June and 21 August. In Vasikkasaari, the highest CH$_4$ concentration was recorded on 15 July during windy days, and the lowest CH$_4$ concentration was recorded on 22 August at the end of the aeration operation. Besides these extreme values, CH$_4$ concentrations in the surface water showed very little variation. On 1 October, the CH$_4$ concentration in surface water in Lankiluoto was twice of that in Vasikkasaari. The CH$_4$ concentrations in the surface water were clearly higher than the atmospheric equilibrium concentration (2 ppm ≈ 3 nM), and the surface water was thus supersaturated with CH$_4$. On average, the concentrations were ca. 30 times higher than that of the equilibrium. However, there was very little variation in surface water values.

### 4.8. Gas fluxes

In Lankiluoto, the CO$_2$ fluxes varied from -27.3 to 422 mmol m$^{-2}$ d$^{-1}$ (mean = 46.5±23.3 mmol m$^{-2}$ d$^{-1}$) and the CH$_4$ fluxes varied from 0.1 to 0.6 mmol m$^{-2}$ d$^{-1}$ (mean = 0.2±0.03 mmol m$^{-2}$ d$^{-1}$).
In Vasikkasaari, the respective ranges of fluxes were 29.4 to 89.1 mmol m$^{-2}$ d$^{-1}$ (mean = 20.2±8.2 mmol m$^{-2}$ d$^{-1}$) for CO$_2$, and 0.06 to 0.4 mmol m$^{-2}$ d$^{-1}$ (mean = 0.2±0.02 mmol m$^{-2}$ d$^{-1}$) for CH$_4$. Thus, Enonselkä basin was constantly an atmospheric source of CH$_4$, whereas in CO$_2$ the flux was occasionally towards the lake and thus for short periods in summer, the lake acted as a sink of CO$_2$. (Figure 14)

In Lankiluoto the highest peaks in effluxes of CO$_2$ and CH$_4$ were observed since 4 June and they lasted for about a week at the beginning of stratification (Figure 14 A), and the corresponding proportions of the peak fluxes were 67% in the total CO$_2$ flux and 23% in the total CH$_4$ flux during the open-water period. After the peak, CO$_2$ flux decreased steadily until 7 August. The CO$_2$ flux was close to zero or towards the lake from 11 July until the beginning of August. Contrary to CO$_2$, CH$_4$ flux did not show any trend but fluctuated during the sampling period. There was a contradictory pattern between CO$_2$ and CH$_4$ fluxes on 20-24 June, 11-15 July, and in the end of July and August, i.e. when the oxygenators were operating. Thus, the short-time aerations induced diverse trends in the CO$_2$ and CH$_4$ fluxes, whereas the long-time aeration in Lankiluoto in August increased the CO$_2$ fluxes but the CH$_4$ fluxes decreased. Both carbon gas fluxes showed a smaller peak when the stratification began to erode.

In Vasikkasaari (Figure 14 B), CO$_2$ as well as CH$_4$ fluxes fluctuated throughout the summer months, but always in a contradictory way. Similar to Lankiluoto, higher fluxes were observed in June. Also, CO$_2$ and CH$_4$ fluxes tended to reverse when the aeration unit was in operation.

In both measuring points, CO$_2$ fluxes showed rather similar trends regardless of the status of the artificial aeration, whether it was on or off. For CH$_4$ fluxes, the long-time aerations induced similar decreasing trends in both locations.
Figure 14. Fluxes of carbon dioxide (CO$_2$) and methane (CH$_4$) (mmol m$^{-2}$ d$^{-1}$) in Lankiluoto (A) and Vasikkasaari (B) in 2013. Line segments in yellow indicate the days with artificial aeration in operation. Please note that positive values indicate fluxes from the lake to the atmosphere and negative fluxes towards the lake. Light blue bars denote the time of ice cover period. N.B. different scale for different location.
5. Discussion

Dissolved CO₂ concentration and the resulting CO₂ flux to the atmosphere is primarily sustained by decomposition of organic matter through respiration, and largely associated with the allochthonous DOC input. CO₂ can be produced through aerobic or anaerobic degradation (Cole, 1983). Significant input of DOC renders the lake heterotrophic and can affect CO₂ production in water column. (Cole et al. 2000, Huttunen et al. 2003, Huotari 2011, Linnaluoma 2012). The allochthonous carbon load can greatly vary from lake to lake depending on factors such as lake characteristics and human activities. The Enonselkä lake basin is known to be net heterotrophic (Linnaluoma 2012). As a result of urbanization, the hypolimnetic CO₂ concentrations in the Enonselkä basin have been clearly higher than they should be in this kind of boreal lake (López Bellido et al. 2011). The same kind of high CO₂ concentrations throughout the years without and with aeration indicate that Enonselkä basin is always abundant with organic carbon compounds, and thus, the eutrophic condition of the lake cannot be easily regulated by the artificial aeration.

The production of CO₂ in the bottom waters and sediment resulted in accumulation of gases in the hypolimnion (Huttunen et al. 2001), in 2013 the hypolimnetic CO₂ concentrations were sometimes very high, which contributed to the higher average CO₂ concentrations of the Enonselkä lake basin. In this study year, under oxic condition, CH₄ oxidation is also a significant pathway of CO₂ production (López Bellido et al. 2011, Huttunen et al. 2001, 2003). The most obvious CO₂ concentration gradient in the water column appeared between 10 – 15 m under the water surface, indicating the location of the oxic-anoxic boundary layer (López Bellido et al. 2011). The surface concentrations of carbon gases markedly increased at the time of autumn turnover. These findings are in good agreement with previous studies in lakes showing that there is a general seasonal pattern in carbon gas concentrations during the open water period (Michmerhuizen et al. 1996, Riera et al. 1999, Linnaluoma 2012, Miettinen et al. 2014).

In 2013 the Enonselkä lake basin was a source of CO₂ throughout the open-water period, although the surface water concentration was occasionally lower than the atmospheric equilibrium (Figure 14 A). The action as a carbon sink rarely happened in the non-aeration year 2005. However, it seems to be common that boreal lakes act as a sink of CO₂ for short times.
The seasonal flux of CO\textsubscript{2} in Lankiluoto, integrated over the measuring period, was over 2.5 times higher than in 2005, when the summer was warm and with average precipitation (López Bellido et al. 2011). Higher CO\textsubscript{2} fluxes are often recorded in rainy years (Huotari et al. 2009, Einola et al. 2011). These observations could be one explanation for the higher fluxes of CO\textsubscript{2} in 2013. Moreover, there were unexpected peak fluxes of CO\textsubscript{2}, which emerged in June, especially in Lankiluoto. The peak fluxes were up to 67\% of the integrated seasonal flux from Lankiluoto and 23\% from Vasikkasaari. A negative correlation between CO\textsubscript{2} and chlorophyll \(a\) imply that photosynthesis can regulate the CO\textsubscript{2} concentration in the epilimnion through CO\textsubscript{2} consumption (cf. Miettinen et al. 2014). However, in the study year, chlorophyll \(a\) concentration after May was normal or even lower than usually (Appendix I). In that way, the unexpected CO\textsubscript{2} effluxes in June could at least partly be explained with modest amount of photosynthesis but vigorous catabolic processes. In autumn, the timing of CO\textsubscript{2} release to the atmosphere is in agreement with the time of increased surface CO\textsubscript{2} concentration due to turnover.

In spite of the increased seasonal CO\textsubscript{2} fluxes, between these peak fluxes, CO\textsubscript{2} fluxes were close to zero or towards the lake in mid summer 2013, and the lowest CO\textsubscript{2} fluxes were registered in the end July and early August. In 2005 the lake basin showed a steady increase in CO\textsubscript{2} fluxes throughout the summer (López Bellido et al. 2011). The different trend in CO\textsubscript{2} fluxes in July between the two years can be attributed to the efficient mixing of the water columns. The artificial aeration led CO\textsubscript{2} concentrations to be more homogeneous throughout the water column.

The general trends of CO\textsubscript{2} fluxes from both study locations were quite consistent with each other (Figure 14), but during the campaign, the CO\textsubscript{2} fluxes were higher from the aerated water column than from the non-aerated water column. Also, more CO\textsubscript{2} was released during longer aervations. Therefore, the aeration enhanced mixing of the stratified water columns and thus increased CO\textsubscript{2} fluxes (Cowell et al. 1987, Huttunen et al. 2001).

The bottom water is oxygenated due to the artificial aeration, leading to homogeneous O\textsubscript{2} concentration throughout the treated water columns (Cowell et al. 1987). The efficiency of aeration was well presented in dissolved oxygen concentrations and distribution also in Lake
Vesijärvi. For instance, the O$_2$ concentrations at 10 m were similar at the beginning of June in both the reference year (López Bellido et al. 2011) and the study year (Figures 8 & 9), whereas in hypolimnion, dissolved oxygen was rapidly depleted in 2005 but only decreased slightly in 2013. Till the end of June, the bottom water layer was anoxic in 2005, but in 2013 the concentration at that time of the year was ca. 6 mg L$^{-1}$ throughout the water column. Even the period of hypoxia and anoxia was shortened: the hypolimnion was anoxic (DO ≤ 1 mg L$^{-1}$) and hypoxic (DO ≤ 2 mg L$^{-1}$) for 98 days (17 June – 24 September) in 2009, 41 days (14 July – 23 August) in 2012 and 63 days (15 July – 15 September) in 2013. Particularly, the hypolimnion suffered from anoxia for approximately 30 days in 2005, i.e. from mid-July to mid-August (López Bellido et al. 2011), whereas in both 2012 and 2013, the Enonselkä basin was completely anoxic only for 14 days (Figure 15). Prevention of oxygen depletion in the hypolimnion due to the aeration was also observed by Huttunen et al. (2001).

The amount of dissolved oxygen increases when water temperature decreases and pressure increases. However, dissolved oxygen in the whole water column in summer 2013 was similar to previous summers until August (Figure 15) even though the water temperatures were apparently lower (Figure 16). The situation implies that more oxygen was consumed for the CO$_2$ production during summer.
In the oxygenated water columns, CH$_4$ concentrations were low throughout the study period, and the concentrations were fairly close to those in lakes classified as clear-water lakes (Juutinen et al. 2009). The CH$_4$ concentrations in Enonselkä basin were close to those in Lake Ormajärvi,
which is a smaller, shallow (surface area 6.53 km², maximum and mean depth 30 m and 10.7 m, respectively) clear-water lake stratifying in summer (Ojala et al. 2011). The mean hypolimnetic CH₄ concentrations in Lake Vesijärvi were on average 0.12 µM, which was approx. 1/100 of that from the Enonselkä basin in summer 2005 with prolonged hypoxia/anoxia and no aeration in operation (López Bellido et al. 2011). In contrast with CO₂, there was no sharp CH₄ gradient in the water columns in the Enonselkä basin during this open water period and the CH₄ concentrations did not increase concomitantly with the stratification in summer months. Artificial aeration plays a significant role in limiting methanogenesis in the hypolimnion and anaerobic sediment surface (Cowell et al. 1987, Huttunen et al. 2001). Only one distinct but unexpected high CH₄ concentration, similar to CO₂, was observed in the surface water of Lankiluoto between the end of May and beginning of June, which was then reflected in the gas flux to the atmosphere (Figures 12 & 14 A).

Water temperature and dissolved oxygen are of considerable significance for controlling the CH₄ concentration above the sediment (Liikanen 2002, Huttunen et al. 2003), thus in 2013, CH₄ release was restrained by the lower hypolimnmonic temperature and oxic condition. CH₄ can be transported up via turbulent diffusion, ebullition, or the transportation can be plant-mediated, which is only of importance in shallow, littoral areas. CH₄ escapes from sediment with bubbling through the water column, and the ebullition rate is closely tied to the production of CH₄ (Kiene 1991, Huttunen et al. 2003, Linnaluoma 2012). Unfortunately, the bubbling of CH₄ was not measured in this study, but from earlier echo sounding campaigns for fishery purposes it is known that there is bubble formation in the profundal sediment, but the bubbles disappear before reaching the surface water (Anne Ojala, personal communication). CH₄ diffusion can be markedly affected by biological oxidation which thus regulates the flux of CH₄ from lakes to the atmosphere.

Consumption of CH₄ through methanotrophic oxidation is prevailing in presence of dissolved oxygen, and the extent can be up to 90% of the CH₄ produced; furthermore CH₄ oxidation is also possible in the stratified and anaerobic conditions, yet the importance of this process is difficult to evaluate (Kiene 1991). In spite of apparent CH₄ oxidation, some CH₄ escaped methanotrophic oxidation because the lake basin was supersaturated with CH₄. The Enonselkä basin acted as a
steady source of CH₄ to the atmosphere throughout the measuring period in 2013 with the mean CH₄ flux of 0.2 mmol m⁻² d⁻¹. The CH₄ fluxes clearly decreased during the long time aeration in 2013. These decreased CH₄ fluxes in Enonselkä basin can be attributed to the limited CH₄ production under oxygenation and high rate of CH₄ oxidation (Kiene 1991).

Artificial aeration can result in marked changes in thermodynamic properties of a lake, for instance, by eliminating the thermal stratification and increasing water temperature in the hypolimnion during summer-autumn season (Cowell et al. 1987, Forsius et al. 2010). In terms of flow dynamics, the warmer upper part of water column is circulated into the cool hypolimnion by artificial vertical mixing force. In the study year, the Enonselkä lake basin started its thermal stratification with an indistinct thermocline which then gradually sank deeper. The stratified period shortened in 2013 (Figures 6 & 7) and was different in comparison to the year 2005 without aeration when the stratification was steeper and lasted longer. (Figure 1 A) (López Bellido et al. 2011).

In the Enonselkä basin, the hypolimnetic temperature increased distinctly already in 2010 which was the second year after the aeration equipment was installed, and the hypolimnetic temperature remained high in 2011 and 2012 (Figure 16). Yet, the water temperatures in both thermocline and hypolimnion were continuously lower in May – August 2013 than during the corresponding periods in 2009 – 2012 (Fig 15). In 2013, the monthly mean of hypolimnetic temperature in May–August was 4.8 °C, 6.6 °C, 8.4 °C, and 13.4 °C, respectively, whereas, for instance in 2012, the corresponding monthly means were 7.8 °C, 11.4 °C, 15.1 °C and 16.9 °C, and in 2009 were 7.7 °C, 9.7 °C, 11.4 °C and 12.2 °C. Thus, the hypolimnetic water temperature in the end of July 2013 was ca. 7 °C lower than in 2012. When comparing with the reference year 2005 when the aeration was not in use, the mean hypolimnetic temperature between May and October 2013 was still ca. 3 °C lower than in 2005 (López Bellido et al. 2011).
Lakes stratify in winter as well, but the temperature distribution in water column is reversed of that during summer stratification (Wetzel. 2001). Similar to summer aeration, artificial aeration during winter weakens the thermal discontinuity in the whole water column (Huttunen et al. 2001). In the Enonselkä lake basin, winter aeration started on 28 December and lasted until 19

Figure 16. Water temperatures (°C) in Lankiluoto at the depths of 10, 20, and 30 m in 2009-2013. Recordings for this figure adopted from the thermistor chain in Lankiluoto.
April in winter 2012 – 2013, which was 40 days longer than in the winter 2011 – 2012. However, the water column in winter 2012-2013 had a thermal pattern comparable to winter 2011-2012 (Pauliina Salmi, personal communication). And actually, the water in Enonselkä basin was the coolest in winter 2011-2012. Therefore, the seasonal stratification pattern in winter was not the cause of the low water temperature later in 2013. The lower mean water temperature in Enonselkä basin could have been due to groundwater input, since the input can be significant (Linnaluoma 2012). Precipitation in summer 2013 was higher than usually making the extra supply of groundwater a possible explanation, but unfortunately I do not have any data on inflow of groundwater. The most plausible explanation for the cool water in 2013 is in warm spring and in the resulting rapid stratification. This highlights the importance of weather and thus climatic drivers for lacustrine carbon gas fluxes.

6. Conclusion

As a result of efficient aeration, the water temperature and dissolved oxygen concentration in the hypolimnion increased, and these changes were very well in agreement with the aeration times. Stratification was eliminated and hypoxic/anoxic period was shortened, due to the mixed and oxygenated water column, which then affected the production and spatial as well as temporal distribution of carbon gases. In particular, the hypolimnetic CH$_4$ concentrations in the lake basin were lower all the time than they were in summer 2005, and decreased to the level which is typical of boreal lakes.

Fluxes of CO$_2$ and CH$_4$ revealed that the Enonselkä lake basin of Lake Vesijärvi was a source of carbon gases during the open water period 2013, although the CO$_2$ fluxes showed also negative values occasionally. The averaged seasonal CO$_2$ flux was higher in the aeration year than in the non-aeration year, whereas the flux of CH$_4$ remained the same as before. When the artificial aeration units were operating, there was contradictory pattern between CO$_2$ and CH$_4$ fluxes; the CO$_2$ fluxes increased while CH$_4$ fluxes decreased, which means that the hypothesis was supported but only on the condition of long time of aeration. The unexpected flux peaks of CO$_2$ and CH$_4$ in June contributed markedly to the total seasonal emission; the cause of the flux peaks remained unknown.
I can conclude that in terms of greenhouse gas emissions, the artificial aeration was successful, but for the desired outcome, the aeration – e.g. timing and duration of operation - needs to be carefully planned.

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8. References


Appendix I. Chlorophyll $a$ concentration (µg L$^{-1}$) in Lankiluoto at the depths of 10, 20, and 30 m in 2009-2013. Recordings for this figure adopted from the automatic monitoring in Lankiluoto.