Summer greenhouse gas fluxes in different types of hemiboreal lakes

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Abstract

Lakes are considered important regulators of atmospheric greenhouse gases (GHG). We estimated late summer open water GHG fluxes in nine hemiboreal lakes in Estonia classified under different lake types according to the European Water Framework Directive (WFD). We also used the WFD typology to provide an improved estimate of the total GHG emission from all Estonian lakes with a gross surface area of 2204 km^2 representing 45,227 km^2 of hemiboreal landscapes (the territory of Estonia). The results demonstrate largely variable CO_2 fluxes among the lake types with most active emissions from Alkalitrophic (Alk), Stratified Alkalitrophic (StratAlk), Dark Soft and with predominant binding in Coastal, Very Large, and Light Soft lakes. The CO_2 fluxes correlated strongly with dissolved CO_2 saturation (DCO_2) values at the surface. Highest CH_4 emissions were measured from the Coastal lake type, followed by Light Soft, StratAlk and Alk types; Coastal, Light Soft and StratAlk were emitting CH_4 partly as bubbles. The only emitter of N_2O was the Alk type. We measured weak binding of N_2O in Dark Soft and Coastal lakes, while in all other studied lake types, the N_2O fluxes were too small to be quantified. Diversely from the common viewpoint of lakes as net sources of both CO_2 and CH_4, it turns out from our results that at least in late summer, Estonian lakes are net sinks of both CO_2 alone and the sum of CO_2 and CH_4. This is mainly caused by the predominant CO_2 sink function of Lake Peipsi forming ¾ of the total lake area and showing negative net emissions even after considering the Global Warming Potential (GWP) of other GHGs. Still, by converting CH_4 data into CO_2 equivalents, the combined emission of all Estonian lakes (8 T C day^{-1}) is turned strongly positive: 2720 T CO_2 equivalents per day.

Keywords

Estonian GHG emission, CO_2, CH_4, N_2O, EU Water Framework Directive lake types, floating chamber FTIR measurement

1. Introduction

In the world fighting against climate warming, there are still many open questions about greenhouse gas (GHG) emissions from natural sources. One of the less explored areas among others is the emission of the three important GHGs – carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O) – from lakes. There are around 117 million lakes on the globe and even though they represent only a tiny fraction of the Earth's nonglaciated land area (Verpoorter et al., 2014), they are an important part of global carbon (C) and nitrogen (N) cycles. Lakes receive C and N from terrestrial ecosystems and fix these elements also from the atmosphere. Both elements are sequestered and/or released from lakes at various rates and in various forms depending on multiple lake characteristics and processes that ultimately determine the GHG balance (Galloway et al., 2003; Tranvik et al., 2009; Kortelainen et al., 2013; Wang et al., 2021). GHGs have various sources and sinks within lakes: CO_2 is received from the catchment under the form of dissolved or particulate inorganic carbon, from atmosphere, and it is released in the course of organic matter decomposition through within-lake pelagic and benthic respiration (Del Giorgio et al., 1999). Depending on the partial pressure in the lake's surface layer, CO_2 may either outgas from the lake or be absorbed from the atmosphere through the water-air interface. Water carbonate and humic substance concentrations are important in predicting the dissolved CO_2 (DCO_2) levels in lakes (Karlsson et al., 2007; Marcé et al., 2015; Khan et al., 2022). Diversely, CH_4 is mostly created within lakes and never absorbed from the atmosphere, as this gas is almost always supersaturated in lakes relative to the atmosphere (Bastviken et al., 2004). The major part of CH_4 is produced by methanogenic microbes in the anoxic zone of organic-rich sediments (Bastviken et al., 2004). Still, as the surface layer of lakes is often supersaturated with CH_4, it has been hypothesized that efficient source processes should also exist in the oxic pelagic zone (Bogard et al., 2014). The surface CH_4 pool, however, may also be supplied by an advective transport from the shallow water macrophyte beds which support considerably high rates of conventional benthic methanogenesis due to their very high production and burial rates of organic matter (Juutinen et al., 2003; Kankaala et al., 2005). In addition to diffusional flux from the sediments, CH_4 supersaturation in sediments may lead to bubble formation and subsequent release, which is especially frequent under shallow water column due to low hydrostatic pressure, and it may also be released to the atmosphere through the stems of vascular plants (Whiting and Chanton, 1996; Bastviken et al., 2004). The third aforementioned gas, N_2O, is created in lakes mostly during microbial nitrification or ammonification as a by-product and in denitrification as an intermediate product (Knowles, 1982). Consequently, its source may be either ammonia excreted or degraded from organic matter or nitrates acquired from the atmosphere or catchment runoff, the latter also via groundwater.

All the three gases are also quickly consumed in lakes – CO_2 is fixed by various guilds of autotrophs all over the water column (Lapierre et al., 2017) while CH_4 is actively consumed by either anoxic or oxic methanotrophs in redoxclines or the oxic zone, respectively (Bodelier and Steenbergh, 2014). Methane captured in bubbles or released through plant stems, nevertheless, escapes methanotrophy (Langenegger et al., 2019). For N_2O, the only known sink is the last step of denitrification pathway, which in case of classical denitrification takes place in reduced environment in the absence of oxygen and at depleted nitrates (Chapuis-Lardy et al., 2007, Richardson et al., 2009). However, recent research has found that an aerobic N_2O reduction may be widespread in soils and oceans, carried out by non-denitrifying microbes possessing a previously unknown type of N_2O reductase gene and commonly lacking enzymes for the preceding steps in the denitrification reaction chain (Sanford et al., 2012; Rees et al., 2021).

While lakes are increasingly viewed as hotspots for CO_2 and CH_4 emissions, their contribution to N_2O emissions is considered negligible compared to terrestrial ecosystems (Tranvik et al., 2009). Even more, certain types of lakes may at least periodically be important consumers of N_2O (Webb et al., 2019) and may have historically been so even more before the era of intense agricultural use of nitrogen fertilizers. The conditions potentially favouring N_2O reduction – abundant labile organic matter coupled with the temporary shortage of oxidised nitrogen – can be easily met in these waterbodies (Knowles, 1982).

The global estimates of GHG emissions from lakes build on the extrapolation of average rates of emissions related to lake size or other widely measured characteristics and the density distributions of lakes along the gradients of these characteristics (Downing, 2009). The best global estimates to date have taken account of both the size of the lakes and some available predictor variables for productivity such as nutrients and surface water chlorophyll *a* (Chl *a*) content (DelSontro et al., 2018). However, there is a range of other potentially important predictors of lake GHG fluxes like depth, spatial coverage of macrophytes, the stability of stratification, water pH, concentrations of dissolved salts, organic and inorganic carbon, and volcanism, to name a few (Bastviken et al., 2004; Kankaala et al., 2013; Andrade et al., 2016, 2019a; Davidson et al., 2018). Data on these predictors, while lacking at the global scale, may however be available at a regional scale. Several studies have revealed patterns related to environmental gradients and/or some categorization of waterbodies (e.g. lakes and ditches in Netherlands; ponds, reservoirs, and lakes in Canada) (Schrier-Uijl et al., 2011; Tadonléké et al., 2011; DelSontro et al., 2016). For instance, trophic state, alkalinity, humic substances, stratification, and temperature have all emerged as good predictors for pelagic emissions in boreal and/or temperate lakes in North America and Europe (Schrier-Uijl et al., 2011; Marcé et al., 2015; Weyhenmeyer et al., 2015; Yang et al., 2015; DelSontro et al., 2016; Webb et al., 2019). Some studies from Sweden and Finland have further provided regional estimates for lakes based on water chemistry and/or some physical characteristics like lake size and water retention time (Kortelainen et al., 2006; Kankaala et al., 2013; Weyhenmeyer et al., 2015). Tank et al. (2009) estimated the CO_2 fluxes of the Mackenzie River Delta area lakes (Canadian Arctic) based on three lake types describing the degree of isolation of lakes from the watershed. However, we are not aware, for regional extrapolations, of any utilization of elaborate composite categorizations (typologies) which are adjusted for monitoring purposes and group lakes based on combination of several factors, despite such systems are widely used for the management of anthropogenic disturbances and are in many cases very finely tuned (Moss et al., 2003; Nõges et al., 2007). National or regional lake typologies based on water chemistry and morphometric features (*e.g.* as the one established by the European Union Water Framework Directive (WFD)) would allow to improve the estimates of aquatic GHG emissions. Knowing the conditions in different lake types and the type-specific areal net GHG emissions enables (1) to raise strong hypotheses in order to find out the biogeochemical processes responsible for the emissions in particular lakes; (2) to design type-specific mitigation measures based on these processes; (3) to prioritise the management measures depending on the areal proportion of different lake types in a region, e.g., it may be easier to manage large emissions from lakes with a small area than vice versa.

The aims of the present study were (1) to create the first inventory of lake type specific summer GHG fluxes in the pelagic zone of hemiboreal Estonian lakes according to the WFD lake types (Table 1), (2) to study the connections between GHG emissions and lake physico-chemical and biological parameters, and (3) to compile a regional assessment of GHG emissions from lakes considering the areal distribution of lakes between the different lake types. We mapped GHG fluxes of nine lakes representing the different type classes and hypothesised largely variable type specific GHG emissions. We further extrapolated from our results an estimate of late summer GHG fluxes from all Estonian lakes with a gross surface area of 2204 km^2.

2. Study area characterization

2.1 Lake typology

All studied lakes (Fig. 1, A – I) were chosen to be typical representatives of the eight Estonian lake types according to the WFD typology, which is based on lake area, alkalinity, conductivity, chloride content, thermal stratification, and colour (Table 1). The two largest lakes in Estonia, Peipsi (Peipus, 3555 km^2, the fifth largest lake in Europe) and Võrtsjärv (270 km^2), form individual types referred to as V-Large and Large (Fig. 1, A – B). They were allocated to separate lake types in the WFD compliant lake typology (ME, 2020) because strong wind induced mixing makes them incomparable with smaller lakes in the region, whereas stronger sediment resuspension in the shallower Võrtsjärv causes higher turbidity and light limitation clearly distinguishing it from the deeper Peipsi.

The remaining 2534 small lakes are grouped into six types (Ott, 2006; ME, 2020). For our study purposes, we created a ninth lake type – the stratified alkalitrophic lakes (StratAlk) – to account for the potential differences in GHG emissions. To make the text easier to follow, the nine lakes in this study are further referred to by their abbreviated type names (Table 1 and Fig. 2).

A general overview of the most important lake parameters is given in Table 2. All lakes were rather shallow with a mean depth below 10 m. Measurements in all lakes were carried out within a 2-month period from July to September 2014 (Table 3), and measurements of CO_2 and CH_4 fluxes above the lakes with all supportive physicochemical measurements were made once or twice during the same period.

2.2 Alkalitrophic lakes (Alk)

The study lake, Äntu Sinijärv, is a source lake fed by karstic ground waters and represents highly alkalitrophic (>240 HCO_3^- mg L^{-1}) lakes in Estonia (Fig. 1C). Lakes of this type are characteristic of the Pandivere Upland area (only a few elsewhere) and with a total area of ca 200 ha they make up only 0.09% of the total area of lakes in Estonia (EDR – *environmental data register of Estonia*). With a mean light attenuation coefficient (K_d) of 0.16 ± 0.02 m^{-1} for the photosynthetically active spectral region measured in 1995–96, Äntu Sinijärv was the most transparent lake in Estonia (Nõges and Nõges, 1998; Nõges, 2000).

2.3 Stratified alkalitrophic lakes (StratAlk)

In the WFD compliant lake typology (ME 2020), these lakes are categorised under stratified lakes with medium alkalinity (StratMedAlk). Considering the different character of many dimictic stratified lakes with high alkalinity (>240 HCO_3^- mg L^{-1}), mainly located in South-East Estonia, we created a new type and selected Lake Karijärv (Fig. 1D) as the representative for those 114 lakes. Karijärv is a highly alkalitrophic stratified light-coloured eutrophic system in generally good ecological state. During the thermal stratification from June to September, anoxia is formed at the bottom despite rather high water transparency in the epilimnion (Secchi depth ca 4 m).

2.4 Non-stratified lakes with medium alkalinity (MedAlk)

This is the most abundant type of small lakes in Estonia, comprising approximately 1/5 of the total number and 4% of the total area of lakes in this country. Lakes under this type are relatively shallow, with medium water retention times and may exhibit only episodic thermal stratification. Most of the lakes are eutrophic or hypertrophic. Lake Ülemiste, selected as the study site (Fig. 1G), provides drinking water for Estonian capital city Tallinn (0.43 mln people).

2.5 Stratified lakes with medium alkalinity (StratMedAlk)

The 201 lakes of this type, represented in our study by Lake Saadjärv (Fig. 1H), form 2.3% of the total lake area making it the second most abundant small lake type in Estonia. Being deeper, these lakes provide more diverse habitats than the non-stratified lakes but are also more sensitive to human impacts due to the potential build-up of bottom anoxia, leading to sediment phosphorus release and thus a positive feedback to eutrophication (Ott, 2010).

2.6 Dark-coloured soft-water lakes (DarkSoft)

By area, about 1.5% of Estonian lakes are dark-coloured soft-water lakes (890 lakes). These lakes are shallow and acidic containing large amounts of humic matter that contributes to radiative heating in summer (Ott, 2010). Strong light attenuation (up to 11 m^{-1}) restricts the euphotic layer and limits photosynthesis (Reinart et al., 2000). In our study, this lake type is represented by Valguta Mustjärv, a very shallow 20-ha lake that has partly recovered from a heavy nutrient loading in the 1980s (Fig. 1E).

2.7 Light-coloured soft-water lakes (LightSoft)

The study of Ott and Kõiv (1999) shows that the 310 light-coloured soft-water lakes comprise a little more that 0.8% of all Estonian lakes by area. Those lakes have originally been oligotrophic or semi-dystrophic, mainly characterised by low productivity, small catchment area implying slow water exchange, low buffering capacity, and weak stress tolerance (Ott, 2010). Because of high water transparency, these lakes do not develop stable stratification. If impacted, *e.g.* by eutrophication, the ecosystems of light-coloured soft-water lakes become strongly destabilized, characterised by frequent algal blooms and onset of stratification. In the current study, this lake type is represented by Lake Erastvere (Fig. 1F).

2.8 Coastal lakes (Coastal)

The 221 coastal lakes constitute approximately 1.6% of the total lake area in Estonia. Their functioning depends strongly on the irregular marine water inflow, which creates highly variable conditions and unstable biota. Estonian coastal lakes are shallow with high pH, transparent water (to the bottom) and high water temperature in summer. The main primary producers are charophytes and not phytoplankton. Since those lakes are shallow and clear-water, there is no temperature stratification. In our study, this category is represented by Lake Mullutu Suurlaht (Fig. 1I).

3. Methods

3.1 Greenhouse gas flux experiments

The gas flux was measured on two days (with the exception of Large) within the summer stratification period, from July to September 2014 (Table 3) *in situ* using floating chamber combined with a computer-operated portable Fourier transform infrared (FTIR) spectrometer Gasmet Dx-4030 (Gasmet Technologies Oy), also described in Rõõm *et al*. (2014). Measurements took place at one precise location of each lake (Table 3), chosen to represent the open-water area. The deepest area of the lake was chosen except for Large and V-Large. In Large, the measurement site was located close to the long-term monitoring point which, according to Nõges and Tuvikene (2012), is representative for 90% of the lake area. In V-Large, measurements were made at a station in the Mustvee bay, approximately 1 km from the western shore. This station represents the characteristic depth for the open-water area and is located at the downwind side of the open lake areas for most of the time.

Transparent rectangular polycarbonate floating chamber with a volume of 31 L was used for this study. The chamber was surrounded by an isolation foam tube to achieve chamber buoyancy. Foam frames were equipped with stabilizing weights (around 6 kg) to withstand wave action during windy conditions common especially in large lakes. The chamber and FTIR spectrometer were connected with teflon tubes and the air was pumped through the 0.4-L sample cell of the spectrometer with a constant speed of 2 L min^{-1}. Rotation of the air was found to be sufficient and no fans were added to the chamber. The temperature in the chamber did not differ more than ±5 °C from the ambient air temperature, guaranteeing a less than 2% concentration difference in the chamber caused by temperature. The spectrometer was calibrated with pure gaseous nitrogen (AGA, 5.0 N_2) for the baseline correction once before every measuring day and, if needed, repeatedly during the day. The results (average of 10 measured spectra per minute) were collected automatically within 1-min interval for at least 3 min for achieving the gas concentrations of ambient air and for at least 8 min from the chamber above the water. For each site, according to the consistency of the measured results, two or more consecutive measurements were performed (following the method described by Tremblay et al., 2005). The minimal time span spent on a single experimental site typically ranged between 45 to 60 min. The concentrations of CO_2, CH_4, and N_2O as well as water vapour were automatically calculated for each measured spectrum by applying the calibration datasets of IR-spectra (in FTIR gas analyser database) and background calibration spectra. According to the manual, the detection limit of the spectrometer Gasmet Dx-4030 for N_2O is 0.02 ppm, for CH_4 0.06 ppm, and for CO_2 11 ppm, and the linearity deviation is <2% of the measuring range. Typical volumetric concentrations of the three gases in ambient air (Table 3) were, accordingly, 0.28-0.31, 1.73-2.11, and 369–382 ppm.

3.2 Measurement of environmental variables

3.2.1 Manual measurement and sampling

The set of variables measured at each floating chamber sampling occasion (Table 3) included air pressure, local wind speed and direction, temperatures in the open air and floating chamber, temperature profile of 0.5 m resolution down from the water surface layer (10–15 cm) to the sediment top layer (at 2–3 cm depth), water and sediment pH, concentration of dissolved oxygen (DO) in water as well as the depth of the water column. Air pressure was measured automatically by Gasmet Dx-4030. Air temperature, local wind speed and direction were measured 1 m above the water surface with a HD2303.0 anemometer (DeltaOhm S.r.L.) by averaging the results of 5 equally distributed 1-min measurements within a period of at least 30 min. Temperature in the floating chamber was measured with a thermometer DM-9231A (Transfer Multisort Elektronik Sp. z o.o.). For field measurements of DO, pH and temperature in water and sediments we used a handheld multiparametric sonde (YSI ProPlus).

Water samples for laboratory analyses of dissolved organic carbon (DOC), phosphates (PO_4-P), nitrates (NO_3-N), sulphates, chlorides, silicium, ammonium (NH_4-N), total phosphorus (TP) and nitrogen (TN), carbonate alkalinity (HCO_3^-), Chl *a*, and phytoplankton were taken from all studied lakes once during the sensor deployment period. DOC concentration was measured in Whatman GF/F filtrate according to Toming et al. (2013). Total phosphorus (TP) was determined with C. Zeiss spectrophotometer, according to Estonian national standard EVS-EN 1189, total nitrogen (TN) with Bran + Luebbe autoanalyser, according to EVS-EN ISO 13395. HCO_3^- was determined colorimetrically using 0.02% methyl orange test. For Chl *a*, 0.1–1 L of water was passed through Whatman GF/F glass microfiber filter and concentrations were measured spectrophotometrically in 96% ethanol extracts at a wavelength of 665 nm (Edler, 1979). The phytoplankton was fixed with Lugol's solution and maintained in darkness until microscopic analysis. Phytoplankton cells were counted and measured with an inverted microscope (Ceti Versus, Kontich-Antwerp, Belgium) at 100× or 400× magnification using Utermöhl (1958) technique. Samples were counted until at least 400 counting units (filaments, cells, colonies), which gives a counting error of ±10% for the total biomass.

3.2.2 Sensor deployments and monitoring stations

All lakes were equipped with a high frequency monitoring platform or small lake buoy (OMC-7012 data-buoy) for a 6 to 12 full days period to register changes of water temperature, DO, and DCO_2 in every 10 to 30 min over the study period. Before sensor deployment, water temperature (T, °C), DO, and electrical conductivity profiles were measured with handheld multiparametric sonde (YSI ProPlus) to determine the location of the metalimnion from water temperature profile according to Wetzel (2001). Continuous monitoring of DO concentration and water temperature was performed by an automated station equipped with a multiparametric sonde (Yellow Springs Instruments (YSI) 66,002–4) at one-meter depth. Additional sensors for DO/temperature (Ponsel OPTOD) and for dissolved CO_2 partial pressure (pCO_2) (AMT Analysenmesstechnik GmbH) were deployed at up to four depths. In all lakes, the upper sensors were placed at 0.5 m depth and the position of other sensors was decided depending on stratification to adequately characterize all different layers. In the deepest lake (StratMedalk), a chain of 12 HOBO Pendant temperature loggers was used reaching from 0.5 to 20 m depth. Detailed information on high frequency data collection is given in Laas et al., 2016.

Automated stations were placed near the GHG flux measurement points. In DarkSoft, we could not capture parallel data on CO_2 and GHG fluxes because of malfunctioning of devices. Thus, for this lake, we chose close dates with similar weather conditions and used the recordings of DCO_2 from these days for the comparison of fluxes with DCO_2. In MedAlk, parallel measurements of both gases at all depths succeeded for one full day only. In StratMedAlk with a maximum depth of 25 m we could measure temperature down to 20 m and CO_2 only down to 10 m depth due to the limited length of the cables. The lake was stratified with the largest drop in pH (0.4-0.5 units) and DO (5.3-6.6 mg L^{-1}) between 6 and 7 m on July 19th and between 8 and 9 m on July 26th. Below oxycline, DO remained relatively stable and fluctuated by less than 2 mg L^{-1} in every 5 m depth interval while pH decreased towards bottom by ≤ 0.2 units per 5 m. Temperature drop was the largest (~8ºC) between 8 and 15 m depth and only 0.4 ºC between 15 and 20 m. For those reasons we assume that the limited length of sensor cables did not affect our conclusions.

3.3 Theory and calculation methods

3.3.1 Greenhouse gas flux calculations

Temperature and air pressure corrections were made automatically by Gasmet Dx-4030 software. Gas fluxes were calculated from linear regression of the gas concentrations in the chamber headspace versus time according to Eq. (1):

$$Flux = \frac{Slope * V}{S} \quad (1)$$

where *Flux* denotes GHG flux in ppm(v) C m^{-2} day^{-1}, *Slope* – slope of the GHG concentration in the chamber headspace versus time in ppm(v) day^{-1}, *V* – volume of air trapped in the chamber (m^3), and *S* – surface area of the floating chamber (m^2). The fluxes were rejected if the Pearson determination coefficient (R^2) was below 0.9 for CO_2, below 0.85 for CH_4, and below 0.6 for N_2O. Since the concentrations of CH_4 and N_2O were about 10–1000 times smaller than those of CO_2, we found, similarly to Tremblay et al. (2005), that the less strict R^2 value would be justified. When the flux is approaching zero, the difference between measurements will be close to the precision of the instrument which results in higher share of random fluctuation in data and lower R^2. Exception was made for the repeatedly measured similar low efflux concentrations of CO_2 in case of highly persistent CH_4 efflux with an R^2 higher than 0.95.

In case of ebullition, the additional *Slope* for ebullition was calculated directly from visible concentration ‘‘jumps’’ on the plots versus total time of floating experiments at a particular measuring site (Fig.3), i.e. in case of a single ebullition event for two or more floating chamber experiments at a particular measuring site, the time for ebullitive flux *Slope* calculation was gained as a sum of all ‘‘on-water’’ experiment times. To avoid considering the ebullition due to the possible disturbance created by setting up the experiment, all plots with ebullition occurring during the first three minutes of floating were rejected and remeasured.

3.3.2 Calculation of dissolved CO_2 values

All CO_2 sensors had a fixed measuring depth, therefore we could do the depth correction for each measurement time interval once for all. We assumed a constant atmospheric pCO_2 of 400 μatm (http://co2now.org/), which was taken as the equilibrium value for the air-water interface for the calculations of dissolved CO_2 saturation (DCO_2) values (Laas et al., 2016) as during the 24 h period CO_2 concentrations in air are changing. For the comparison with the flux measurement, the exact DCO_2 values were calculated according to measured air CO_2 concentrations (Table 3).

3.3.3 Estimation of GHG emissions of the Estonian lakes

We used our collected data to estimate the daily summer GHG emissions of the studied lakes. We extrapolated our results further by combining the experimental data from our study with the typology of Estonian lakes (Ott, 2006; ME, 2020) to present a rough estimate of GHG emissions of all Estonian lakes. We assumed that lake type is affecting the summer emission of GHG from the open water area. The typology utilizes physical and chemical parameters which all display large variation in the study area: carbonate content of water (DIC), water humic substance (DOC) content, the presence of summer stratification, size, depth, and connection with the brackish water Baltic Sea. While macrophytes are not used as a classificator in the typology, the extent of macrophyte coverage is nevertheless largely predicted by the lake type in the study area (Alahuhta et al., 2018), mostly because of being related to depth and water optical parameters. Carbonates, humic substances, stratification, and macrophytes have all been shown to affect lake GHG emissions (e.g. Tank et al., 2009; Weyhenmeyer et al., 2015; Yang et al., 2015; Andrade et al., 2019b; Webb et al., 2019; Andrade et al., 2020, 2021). Accordingly, our assumption is well supported by published evidence.

Pelagic GHG emission of a whole lake was calculated by multiplying the average GHG emissions in mg m^{-2} day^{-1} by the lake surface area. To compare the warming effect on climate of these three GHGs, it is reasonable to convert all the emissions into CO 2 equivalents (denoted in tables 4–5 as CO 2e) by weighing the amount of the different gases with their Global Warming Potential (GWP). We used the GWP coefficient of 1 for CO_2, 28 for CH_4, and 265 for N_2O based on the lifetime of 100 years without feedback (Myhre et al., 2013).

To estimate the GHG emissions from all 2536 Estonian lakes, average type specific emissions of CO_2 and CH_4 in mg m^{-2} day^{-1} were multiplied by the total area of lakes belonging to that type. We decided to leave N_2O out from the final balance, as we considered the precision of our instrument insufficient for measuring prevailing very small fluxes in the lakes. The environmental data register of Estonia (*EDR*) was used for calculating the type specific total areas of lakes. For the lakes with unidentified type in the EDR (1345 of total 2536), if possible, we assigned a type by using known physico-chemical parameters (Information System of Environmental Monitoring) in combination with soil and landscape type published in Estonian Geoportal (GP). In special cases, the Estonian name of the lake was used as a hint for the lake type, *e.g.* lakes with names including '*allik-*' (spring), '*laugas-*' or '*lauka-*' (marsh pool), and '*-laht*' or '*lahe-*' (bay) in certain landscape areas were designated to Alk, DarkSoft, and Coastal type, respectively. The remaining area of lakes with unidentified type (1.7% of total lake area and 14% of the pooled area of small lakes, *i.e.*, excluding Large and V-Large), was divided among types proportionally with the areal division of the small lakes with known types excluding Coastal. The area of Narva Reservoir (106 km^2) was added to Lake Peipsi (V-Large) since it is fed by waters from this lake whereas only the Estonian parts of both water bodies (shared with Russia) were added to the calculations.

3.4 Statistical analysis

The fluxes of CO_2 and CH_4 were compared with physical, chemical, and biological variables (DCO_2, DO, pH, water temperature, lake size, mean and maximum depth, depth at sampling site, metalimnion depth, TP, TN, N:P ratio, Chl *a*, DOC, HCO_3^-, Kd, Secchi depth, phytoplankton biomass, air temperature and pressure, wind speed) by means of pairwise linear (Pearson) correlation. As

Coastal deviated in water salinity and specific conductance from all the other lakes by about an order of magnitude, we used Spearman rank correlation to study the relationships of these two variables and their water column gradients with the fluxes of CO_2 and CH_4.

4. Results

4.1 Environmental parameters

The maximum depth of the studied lakes ranged from 1 to 25 m with three lakes being more than 10 m deep (Table 2). During our field campaign, the three deepest lakes displayed stable stratification with anoxic hypolimnion while Alk, albeit shallow, showed well developed thermal stratification with fully oxygenated hypolimnion. The depth profiles of temperature, salinity, pH, DCO_2, and DO are presented on Fig. 4. TP levels were indicative to rather high eutrophication in all lakes except Alk, while the opposite was true for TN (Table 2), and all inorganic nutrients NO_3-N, NH_4-N, and PO_4-P remained below 1 mg L^{-1} in most of the lakes (see Table S1 for more detail). The hypolimnia of LightSoft and StratAlk were also rich in reduced nitrogen (Table S1). Water sulphates content varied from 2 mg L^{-1} to 32 mg L^{-1} with the exception of Coastal, which had sulphates level as high as 266 mg L^{-1} at the time of our experiments (Table S1).

4.2 Fluxes of CO_2, CH_4, and N_2O

Based on the R^2 of flux calculations (linear regression of the gas concentrations in the chamber headspace versus time), we omitted two nonlinear declines of N_2O from DarkSoft and StratAlk with R^2<0.6, where the readings of N_2O in the chamber air decreased by 0.04-0.05 ppm(v) during the first 5 minutes of chamber incubation and levelled off subsequently. For the rest of the measurements with low R^2 values, the change in N_2O concentrations was less than 0.04 ppm(v) during the incubation time. We consider this to be too close to the detection limit of our instrument for quantitative conclusions, and we interpret these measurements hereafter as very small fluxes that we cannot confirm to differ from zero (Fig. 5).

Our results demonstrate a broad variety of CO_2 fluxes among the lakes (Figs 5 and 6, Table 4) with the most active emissions from Alk, StratAlk, and DarkSoft and with negative fluxes in Coastal, V-Large, and LightSoft. As expected, the fluxes correlated strongly with surface DCO_2 values in lakes (Table S2). The strong correlation with Secchi depth must be taken cautiously since among the two most transparent waterbodies, Alk was the most active CO_2 emitter and Coastal the most active binder.

By CH_4 emissions, Coastal was the most active, followed by LightSoft, StratAlk, and Alk (Figs 5 and 6, Table 4). The first three lake types were also emitting bubbles with the same order of activity. CH_4 fluxes displayed strong correlation with CO_2 saturation differences between the lakes' surface and metalimnion (Table S2). CH_4 emissions also correlated with the salinity and/or specific conductance depth gradients (increases towards bottom) in water (Table S2). Both CO_2 and CH_4 fluxes correlated weakly with pH and TN; in case of CO_2, both correlations were negative.

We observed measurable N_2O emission only in Alk (Fig. 5, Table 4). It is worth mentioning that Alk displayed very high NO_3-N levels (3.13 mg L^{-1} compared to 0.03 ± 0.04 mg L^{-1} in other lakes) as well as the lowest TP content (9 µg L^{-1} against 91 ± 68 µg L^{-1}) and the highest N/P mass ratio (38 against 12 ± 6). A weak uptake of N_2O was recorded in Coastal and DarkSoft lake types (Fig. 5, Table 4). In all the other cases, N_2O fluxes were negligible.

4.3 Total GHG fluxes of Estonian lakes

Regarding summer GHG fluxes, Estonian lakes were net sinks of CO_2, and a negative net balance was observed also for the sum of CO_2 and CH_4 (Table 5). The main reason here is the areal dominance of the V-Large Lake Peipsi which individually remained a net sink even after considering the GWP coefficients. Still, after converting the CH_4 emissions from the small lakes into CO_2 equivalents (CO_{2e}), the net GHG emission from Estonian lakes turned strongly positive.

We included the N_2O emissions in the regional balance calculations only for the three lake types for which we had reliable quantitative estimates. Considering the N_2O fluxes, the GHG balance increased by 11% for Alk lakes and decreased by 10% and 0.6% for DarkSoft and Coastal lakes, respectively (Table 5).

5. Discussion

5.1 General patterns

We found largely variable GHG emissions in lakes located in close vicinity in a spatially confined area (Estonia) but belonging to different lake types *sensu* WFD lake typology. The average (± standard deviation) CO_2 emission of 1070 ± 2275 mg m^{-2} d^{-1} in our study is comparable with the previous recordings from lakes of boreal and temperate regions (Huttunen et al., 2003; Schrier-Ujil et al., 2011; Tadonleke et al., 2011). However, the lakes larger than 1 km^2 in our study had notably lower emission rates compared to Swedish and Norwegian lakes sized between 1 and 100 km^2 (Yang et al., 2015) and the Finnish large lakes with size > 100 km^2 (Rantakari and Kortelainen, 2005). Our average CH_4 emission of 114 ± 207 mg m^{-2} d^{-1} was notably high, likely because of the very high emissions from LightSoft and Coastal lakes, as our median CH_4 emission of 33 mg m^{-2} d^{-1} is in good accordance with other studies from the boreal region (Huttunen et al., 2003; Rasilo et al., 2015; Yang et al., 2015). Our measured N_2O range is comparable with the other studies from the region (Huttunen et al., 2003; Yang et al., 2015).

The well-known fact is that CH_4 is mostly released by sediments. Judging upon the CO_2 profiles (Fig. 4), lake sediments were likely also an important CO_2 source in our study in summer (Laas et al., 2016; Rantakari and Kortelainen, 2005), with the exception of Alk where the main source of high CO_2 is predominant calcareous ground water feeding (Laas et al., 2016). Lakes highest in carbonates (Alk, StratAlk) or DOC (DarkSoft) were the strongest emitters of CO_2. As expected, the correlation between DCO_2 in the surface layer and CO_2 fluxes was very strong (Table S2), suggesting DCO_2 as a very good predictor for the flux. Laas et al. (2016) has demonstrated clear negative correlation between the gradient of DCO_2 and the trophic state of the lake. Thus, DCO_2 and the associated emission of CO_2 in the studied lakes were likely affected by an interaction of many factors: the carbonate content of water (e.g. Li et al., 2021), sediment and water column catabolic activity (e.g. Jonsson et al., 2003), phytoplankton and macrophyte photosynthesis (Rõõm et al., 2014; Andrade et al., 2021; Trolle et al., 2012), and the aeration of water by mixing (Laas et al., 2016; Andrade et al., 2019b). The logical sequence of fluxes activity according to the trophic state and carbonate content in our studied lake types would be as Alk – StratAlk – StartMedAlk – MedAlk – LightSoft. In other four lake types, CO_2 fluxes seem to be triggered by other characteristics, for example by high water column turbulence in Large and V-Large lake types or by high concentrations of organic carbon in DarkSoft and Coastal.

With the exception of Coastal, shallow unstratified lakes were rather low CH_4 emitters compared to stratified lakes. One possible explanation might be better oxygenation of sediment surface in several large and shallow unstratified lakes (Fig. 4). This does not always imply more efficient methanotrophy. Notably, as methanotrophy has been shown to require certain undersaturation of oxygen (Thottathil et al., 2019) and is often limited by substrate (Duc et al., 2010), one important factor reducing methane emissions in these well-oxygenated lakes may have been the competition of aerobic sediment respiration with methanogenesis for the organic matter in surface sediments. The observed positive correlation between the DCO_2 difference between the surface and metalimnion and the emissions of CH_4 could result from the organic carbon content in sediments affecting both variables. Opposite to CO_2, CH_4 emissions were slightly positively related to TN content in water. All major CH_4-emitting lake types – Coastal, LightSoft, and StratAlk – are nutrient- and organic-rich with fast metabolism, likely to build up sediment layers with high organic matter content. This is in accordance with the previous studies relating the increased CH_4 emission to eutrophication (Huttunen et al., 2003; Bastviken et al., 2004).

The lack of measurable N_2O emission in most lakes in our study is likely following the seasonal dynamics of N cycling. Lake water N_2O concentrations in late summer may be at their lowest due to (1) the high primary production and (2) the strongest stratification at this time. Nitrification and denitrification are considered the main sources for N_2O in lakes (Seitzinger and Kroeze, 1998). Both in unstratified lakes and in the epilimnia of stratified lakes, the late summer N availability may be insufficient for either nitrification or denitrification to occur as phytoplankton outcompetes bacteria for nitrous substrates (Webb et al., 2019). Indeed, we saw very low nitrate levels in the mixed layers of all lakes except the strongly P limited Alk lake type, suggesting N limitation as a reason for the possible N_2O undersaturation. Thermal stratification of lakes has also proven to be an important factor in their N_2O metabolism. In the start of summer stratification in dimictic lakes, there may be enough oxygen and nitrates available to curb the N_2O reduction, which is the most oxygen-sensitive step of denitrification (Richardson et al., 2009), leading to the build-up of N_2O in the hypolimnion. As the stratification continues, oxygen will be gradually used up and the bottom water becomes increasingly reduced. By late summer, near-bottom anoxia may have lasted long enough to deplete the nitrate pool and favour N_2O reduction. Indeed, many studies have found a strong seasonal gradient in summer N_2O saturation in lakes and reservoirs with the N_2O peak in June and the lowest and often negative flux values occurring in late summer (Knowles et al., 1981; Jacinthe et al., 2012; Beaulieu et al., 2014; McCarthy et al., 2016).

5.2 Individual features of lakes

The studied Alk lake was intense CO_2 and moderate CH_4 emitter. As described in Laas et al. (2016), the main feature that makes Alk distinct is the predominant ground water feeding of this lake type while the watershed is located in carbonate-rich karstic area. Carbonate-rich ground water (> 300 mg L^{-1} of HCO_3^-, Information System of Environmental Monitoring) releases CO_2 via intense calcite precipitation (Marcé et al., 2015; Laas et al., 2016) that forms the most likely source of the outstanding CO_2 emissions in Alk which were comparable to the average emission of 6703 mg m^{-2} d^{-1} from an 1- year-old reservoir in the boreal Canada (Tadonleke et al., 2011) and surpassed 3- to- 30-fold the average emissions measured for the other 15 lakes and 7 – 35 years old reservoirs in that study, as well as the other reports for boreal lakes (Huttunen et al., 2003; Yang et al., 2015). The low TP water of the lake is highly transparent revealing almost no planktonic life forms in the water column (Table 2), and most of the DCO_2 gradient is caused by diffusional efflux. These lakes behave as "CO_2-chimneys" and contribute to the Estonian net CO_2 emissions equally to the other emitting lake types despite of a magnitude smaller net area. In our study, the diffuse CH_4 emission in Alk varied from moderate to high. The most probable source is the constantly undisturbed sediment, as the lake is small and sheltered from winds, and the water column is very stable. Also, the abundant *Chara* community covering most of the bottom may have reinforced CH_4 diffusional efflux to the water column. Notable N_2O emission distinguishes Alk from the other studied lakes. This feature may be related to the water NO_3-N levels that were by at least one order of magnitude higher than in the other lakes. In fact, midsummer undersaturation of N_2O has been observed in lakes with water NO_3-N content below 1 mg L^{-1} (Jacinthe et al., 2012), a threshold which was surpassed only by Alk in our study. Nitrate content of water has been shown to predict N_2O emissions also in several other studies (McCrackin and Elser, 2010; Webb et al., 2019). Even more, well oxygenated lakes as Alk have been turned out to be net N_2O sources even at low nitrate levels as such lakes may lack a relevant functional sink for N_2O (Salk and Ostrom, 2019). Due to the apparent P limitation, also the NH_4-N concentration in the water is relatively high. Thus, the N_2O emitted from Alk may have been produced both by aerobic nitrification in the whole water column or by denitrification at the sediment chemocline.

The watershed of the studied StratAlk lake includes mainly sandy and loamy areas. The lake has springs but also an inflowing groundwater fed stream. Because of higher phosphorus content and phytoplankton activity, the lake is more eutrophic than Alk (hypertrophic for TP). Still, the content of carbonates is only slightly smaller compared to Alk and the CO_2 emission levels are clearly distinct from StratMedAlk to which type these lakes are usually categorised. As for Alk, the most likely source may have been calcite precipitation (Marcé et al., 2015). Stable stratification most likely prevented the release of CO_2 from the anoxic hypolimnion (Andrade et al., 2020). At the same time, more active photosynthesis in the epilimnion, indicated by Chl *a*, pH, and O_2 saturation profiles, may have been the cause for lower DCO_2 and CO_2 emissions in StratAlk compared to Alk despite the comparable water carbonate levels in these lakes. In StratAlk, the CH_4 emission was the third highest. Clear evidence of ebullition was observed and measured during the second experiment while the diffusional flux of CH_4 was moderate. Interestingly, the bottom layer was fully depleted of NO_3-N indicating the most prominent denitrification in the hypolimnion among the stratified lakes in our study. The extent to which such depletion may affect the emission of N_2O from the lake probably depends on the conditions in the epilimnion and/or the chemocline mixing rates (Heiskanen et al., 2014). While it seems that the flux of N_2O from the epilimnion to depleted hypolimnion can turn a lake into a net sink for N_2O, in other cases, despite the undersaturation in the hypolimnion, the epilimnion may still act as a N_2O source (Knowles et al., 1981; Webb et al., 2019; but see Mengis et al., 1997). In the present case, no epilimnetic N_2O production could be expected as the epilimnion of StratAlk was depleted of both NO_3^- and NH_4^+. Moreover, the sharp initial decline in N_2O concentrations recorded during our chamber measurements may indicate a fast uptake of N_2O by this lake, but higher precision methods would be needed to confirm this hypothesis.

Both CO_2 and CH_4 fluxes of studied MedAlk lake were slightly positive and higher on the second measurement with higher wind speed. The mean values of 108 and 11.7 ppm m^{-2} d^{-1} for CO_2 and CH_4 fluxes, respectively, remained below average compared with the other studies from the Nordic region. For example, average CO_2 and CH_4 emissions of 771.3 and 31.9 ppm m^{-2} d^{-1}, respectively, were recorded for oligotrophic and mesotrophic Norwegian and Swedish lakes with surface area of 1 – 100 km^2 (Yang et al., 2015), and 767 and 33.3 ppm m^{-2} d^{-1} of CO_2 and CH_4, respectively, for eutrophic Finnish lakes and reservoirs (Huttunen et al., 2003). High nutrient content supports high phytoplankton biomass and Chl *a*, but the photosynthetic activity seems to be still the minor component of the CO_2 flux balance compared to respiration, and as a result, the net flux remains positive. The low CH_4 emission may be related to the large and shallow bathymetry of the lake which apparently causes the low stability of the water column: DO dropped at the sediment surface during our first sampling at the wind speed of 5.1 m s^{-1}, while at the second sampling with the higher wind speed of 10.3 m s^{-1}, high DO zone reached the muddy surface sediment layer (Fig. 4). Thus, the oxygenation of the sediment may enable high CH_4 consumption during its diffusion from sediments (Thottathil et al., 2019), as well as suppress methanogenesis in the upper sediment layer consisting the highest quality organic matter (Jarrell, 1985; Yang et al., 2017).

In the deep and stratified StratMedAlk, the nutrient content and phytoplankton biomass are considerably lower compared to MedAlk, while DO is below the saturation level even in the surface layer. Although CO_2 emission stayed below the average values measured in Scandinavian studies (Huttunen et al., 2003; Yang et al., 2015), it still exceeded the emissions from MedAlk despite similar alkalinity and DOC. The emission of CH_4 resembled closely the Scandinavian lakes (Huttunen et al., 2003; Yang et al., 2015). Low DO and Chl *a* indicate strong heterotrophy in epilimnion as a possible source of CO_2. Based on the measured DCO_2 gradient and the absence of DO below thermocline we can assume substantial storage of both CO_2 and CH_4 in the hypolimnion (Fig. 4). As the lake is relatively large, wind-induced fluctuations in the depth of thermocline and related leakage of CO_2 and CH_4 from hypolimnion may thus also be possible (Huotari et al., 2011; Heiskanen et al., 2014).

The DarkSoft lake was the second highest CO_2 emitter of the study whereas the CH_4 emission was the second lowest. With its hypertrophic nature, it is not the most common dystrophic lake, but still quite representative for the post-soviet landscapes of Estonia (Ott and Kõiv, 1999). Compared to the other lakes, the pH was remarkably variable during the measurements suggesting that the lack of stabilising carbonate buffer was influencing the results, and at windy conditions pH stayed moderate while in windless conditions the high respiration activity increased the acidity of the surface water layer quite rapidly due to its very low carbonate content. Here, the phytoplankton biomass is strongly light-limited in the dark brown water (Table 2), and the low DO levels give evidence of strong heterotrophy (Cremona et al., 2016). Hence, the decomposition of high concentrations of DOC, primarily the humic components in allochthonous organic matter, is apparently the main contributor to the CO_2 flux. This kind of lakes form the second type of "CO_2-chimneys" in our study, where high fluxes are caused by high organic C respiration rates (Cole et al., 1994; Jonsson et al., 2003). Low CH_4 emission may be explained by water column methanotrophic activity observed also in other humic boreal lakes (van Grinsven et al., 2021). Furthermore, as DarkSoft is one of the two lakes with measurable N_2O uptake in our study, the simultaneous consumption of CH_4 and N_2O may indicate active anaerobic CH_4 oxidation. This process would take advantage of the abundant humic substances, which can promote the extracellular electron transfer and thus couple the anaerobic oxidation of CH_4 with the reduction of N_2O (Valenzuela et al., 2020).

The hypertrophic and low carbonate content LightSoft system was the second highest CH_4 source with a very high proportion of ebullitive flux, and at least a part-time CO_2 sink. Very high cyanobacterial biomass, Chl *a* level, and DO supersaturation above the metalimnion during the first measurement campaign, suggested that the CO_2 uptake can be likely attributed to high photosynthetic activity. The small CO_2 release at the second measurement episode could be explained by strong winds (up to 10 m s^{-1}) on 25–26 August 2014 causing deepening of the thermocline and bringing up less oxygenated water (but still not considerably alleviating the lack of CO_2 in the epilimnion). The hypertrophic lake sediment was evidently the strong bubbling source of CH_4, whereas the wind might have increased the emissions during the second measurement.

The Large type (Võrtsjärv) was characterised by notably small fluxes of both CO_2 and CH_4. As demonstrated by Rõõm et al. (2014), the lake may also become a weak CO_2 sink in summer. The shallowness and the large area opened to the wind balancing the partial pressures of gases between the atmosphere and water, as well as the good balance between gross primary production and respiration (Laas et al., 2012) results in a net CO_2 flux close to zero (Cremona et al. 2016). Also, the low CH_4 emission despite organic-rich sediment is likely due to the well oxygenated sediment surface enabling high methanotrophy. In large lakes, wave action could induce the lateral transport of GHG from the open littoral zone to the pelagic area (Hofmann et al., 2010), and this lake is characterized by rather extensive zone of submerged macrophytes (18 % of the lake area); however, this likely does not influence its pelagic GHG balance substantially, as CO_2 and CH_4 emissions from this zone are similar to the pelagic area (Rõõm et al., 2014).

The V-Large type (Peipsi) is also characterised by a large open area but since the lake is deeper, it is less turbid compared to Large. Still, the whole water column is nearly saturated with DO. Similarly to the Large, the V-Large acts as a weak CO_2 sink and CH_4 source, whereas the photosynthetic activity is likely exceeding the total community respiration. The weak CH_4 emission may be related to the sandy organic-poor sediment and good oxidising conditions. The lower emissions of CO_2 in both Large and V-Large compared to the Finnish large lakes may rise from the latter being mostly oligotrophic (Rantakari and Kortelainen, 2005), as lower trophic state predicts lower CO_2 emissions (Trolle et al., 2012).

The Coastal system was the strongest CH_4 source and at the same time, the strongest CO_2 sink among the studied lake types. By its GHG emissions, it reminded more a subtropical macrophyte lake than a boreal lake (*e.g.* Colina et al., 2021). The lake is very shallow, fully saturated with DO and transparent to the bottom. Dense *Chara* cover on the bottom is characteristic of lakes with low TP and high TN. The lake is connected to the sea by Nasva River. Depending on the tide and currents, the lake's salinity differed almost by a factor of two between the measurement campaigns and is generally more similar to that of the Baltic Sea than of all the other lakes in our study. In the Coastal type, CO_2 is concentrated in bottom waters, although the lake is typically shallow with a short water retention time. One reason for this gradient may be active methanotrophy inside the *Chara* stands (Kuivila et al., 1988; Liebner et al., 2011). Since both Chl *a* and total phytoplankton biomass were moderate and the bottom concentration of DCO_2 was clearly the highest among shallow unstratified lakes, the strong CO_2 uptake could be explained by intense photosynthesis by *Chara* (Laas et al., 2016). The highest CH_4 emissions, both by diffusion and ebullition, gave evidence of a high sediment decomposition rate in the warm environment (Duc et al., 2010; DelSontro et al., 2016), while the diffusion could be amplified by *Chara* similarly to the Alk type. Our finding does not fully agree with DelSontro et al (2016) who found that temperature increases CH_4 emissions only at high TP. Regarding N_2O uptake in this lake, higher water sulphate concentrations may facilitate sulphur cycling in the sediment and the growth of heterotrophic or autotrophic sulphur-oxidizing bacteria that can utilize N_2O as electron acceptor in the bottom redoxcline (Shao et al., 2010). Abundant CH_4 may support nitrate/nitrite-dependent anaerobic methane oxidation, competing for oxidised N species in the sediments (Ettwig et al., 2010; Cui et al., 2015).

5.3 Estimated GHG balance for all Estonian lakes

The estimated emissions of CO_2 and CH_4 from the open water area of all Estonian lakes in summer period were -69 and 36 T day^{-1}, which equals to -19 and 27 T C (tons of carbon) day^{-1}, respectively (Table 5). Accounting for the higher GWP of CH_4, the climate impact of the total emission of both gases equalled to 2720 T CO_2 equivalents per day (Table 5). Interestingly, the two largest lakes are strongly underrepresented in their climate impact compared to their areal share: while the largest Lake Peipsi (V-Large) with the areal share of 76% contributed to CO_2 exchange by a negative flux with the magnitude of 49% of all the CO_2 exchange, its contribution to climate impact, while still negative, formed only 2% of all the fluxes. The second largest, Lake Võrtsjärv (Large) with the areal share of 12% contributed 6% to the CO_2 exchange and 8% to the climate impact of emissions. One factor behind the disproportionately small climate impact was the low 7% contribution of both large lakes to the CH_4 efflux.

The most intriguing in the GHG balance of Estonian lakes is the ability of V-Large (Peipsi) to bind CO_2 in late summer. This is strikingly different from the estimates by Rantakari and Kortelainen (2005) for the Finnish large lakes (mean summer emission 337.7 ppm m^{-2} d^{-1} in lakes sized 100 – 4400 km^2, compared to -79.8 ppm m^{-2} d^{-1} in Lake Peipsi). It suggests that the annual net emission of Peipsi might also be negative since the period of autumn CO_2 emission typically caused by die-off of the planktonic community had still not begun in mid-September and high CO_2 uptake could be expected again in early spring just after an emission peak typical at the ice break-up (Rõõm et al., 2014). While being only a small CO_2 sink per m^2, due to its large surface area, Lake Peipsi had still a huge influence on the total net flux from Estonian lakes, turning the total daily CO_2 emission negative. By the CO_2 sink function, Peipsi was followed by the Coastal type having 48 times smaller total net area compared to Peipsi but only 6 times smaller total CO_2 uptake.

Among the CO_2 net sources, the high areal emission from the Alk type was counterbalanced by the small quantity of these lakes, and the most intense emitters at the country level were small marsh pools (DarkSoft) followed by stratified alkalitrophic lakes (StratAlk), the second rarest type by number of lakes but with a large surface area. Considering CH_4 emissions, the Coastal type was a real outlier both per square metre and at the country level, showing values of the same magnitude as the CO_2 fluxes of most other lake types. The next largest CH_4 sources at the country level were LightSoft and StratAlk, both forming a small share of the total lake area but still considerably influencing the total flux. On the other hand, the considerable contributions of the Large and V-Large to the country budget of lakes could be attributed to their large surface areas.

Despite of excluding N_2O from the GHG balance of all Estonian lakes, the fluxes below our detection limit may still have an important regional effect due to the high GWP of N_2O. For instance, a close-to-zero flux of ±0.12 ppm (N_2O) m^{-2} d^{-1}, too small to be confirmed by our method, would affect the total exchange of GHG of V-Large by ±92 T (CO_2 equivalent) day^{-1}. Thus, more precise quantification of the N_2O fluxes, especially from large lakes, would improve the accuracy of the regional estimates.

Similar to most of the regional studies, we have based our estimate on the pelagic zone measurements without accounting for the littoral zone, which may emit large amounts of GHG depending on the type and amount of vegetation and sediment characteristics (Kankaala et al., 2005; Rõõm et al., 2014). In our study region, helophytes have been shown to support high GHG emissions (Rõõm et al., 2014) and may add to the pelagic GHG balance assessed by us, making our present estimate more conservative.

Both the measurements in boreal lakes globally (Vachon et al., 2017) and the earlier measurements by our group (Rõõm et al., 2014 and unpublished data) reveal strong CO_2 emissions during early spring and late autumn due to the release of winter under-ice and summer hypolimnic accumulations, respectively. Therefore, the annual CO_2 emissions from many lake types could be even higher than the summer estimates in the present study. This release, especially the autumn release, is larger from deeper waterbodies (Ducharme-Riel et al., 2015). It has been estimated to account on average for about 24 % of the annual flux in some Canadian lakes, and 29 – 46 % in large Finnish lakes in different years (Rantakari and Kortelainen, 2005; Ducharme-Riel et al., 2015). However, these releases may not suffice to counterbalance the cessation of gas exchange with atmosphere during ice cover: median efflux values from large Finnish lakes show that daily summer estimates can be on average two times higher than the daily annual estimates where seasonal differences are accounted for (from data presented by Rantakari and Kortelainen, 2005). Since the strong spring CO_2 emission is followed by the most active uptake during the period of fast planktonic biomass burst in most of the boreal lakes, and from the fact that the largest Lake Peipsi was still a carbon sink in late summer, prediction of the net annual CO_2 balance of Estonian lakes would require data of finer seasonal resolution than presently available. It is probable that on an annual basis, uptake would balance the emissions and turn the net CO_2 flux if not negative, then at least only moderately positive. In the case of CH_4, the strong positive temperature dependence of fluxes has been demonstrated (Kelly et al., 1981, Schulz et al., 1997, Yvon-Durocher et al., 2011, Rõõm et al., 2014), and, therefore, the average annual daily emission of CH_4 from the most important emitter, Coastal lake type, can only be smaller compared to midsummer emissions. For stratified lakes, the autumn overturn is an important part of the yearly CH_4 cycle (Kankaala et al., 2006; Fernández et al., 2014), thus potentially increasing the annual balance for these lake types. However, due to winter methanotrophy, the annual daily emission may still be notably lower compared to the daily efflux at the summer stratification period (Kankaala et al., 2006). While N_2O has been observed to build up under ice (Cavaliere and Baulch, 2018), no significant release fluxes are expected at ice melt in spring based on measurements from the Finnish lakes (Huttunen et al., 2003).

6. Conclusions

The studied lakes, representing all lake types in Estonia and most lake types in the whole hemiboreal region, showed a large variety of their GHG fluxes. The strongest CO_2 sources were lakes with predominantly allochthonous supplies of either mineral (carbonate rock) or organic (peat) carbon – the alkalitrophic lake with spring water supply (Alk) and the dystrophic lake with high humic substance content (DarkSoft), followed by stratified alkalitrophic and medium alkalinity lakes (StratAlk and StratMedAlk). Three of nine types (Coastal, LightSoft, and V-Large) acted as net CO_2 sinks. The fluxes correlated strongly with surface DCO_2 values in lakes. Highest CH_4 emissions were measured in the Coastal lake type, followed by LightSoft, StratAlk, and Alk, most of them also emitting bubbles of CH_4. The Alk type was also the only late summer N_2O emitter, while Coastal and DarkSoft lakes were acting as small sinks for N_2O. In other lakes, N_2O fluxes remained close to the detection limit.

The results of our analysis suggest a predominant sink effect of Estonian lakes for CO_2 in summer. However, the summer efflux of carbon in GHG was 8 T C day^{-1}, and the greenhouse effect of this emission, 2720 T CO_2 equivalents per day, remains positive due to the high GWP of methane.

More detailed seasonal and spatial sampling, incorporation of littoral helophyte zones, and higher precision measurements for N_2O would be the first scientific improvements required to decrease the uncertainty of the regional estimate for Estonian lakes. Given the high GWP of this gas, precise N_2O emission estimates for large lakes are advisable to adequately assess its greenhouse effect in the region.

In this study, methanogenic lakes added the most to the regional climate warming effect. Notably the Coastal lake type, despite its small areal share (1.6% of the regional lake area), was the key emitter of GHG (62 % of total CH_4 emission). On the other hand, the two largest lakes with the joint areal share of 1945 km^2 (88% of the regional lake area) showed very small climate impact and even a cooling effect in case of Lake Peipsi. For climate mitigation efforts in Estonia, one important target would be to protect the largest lakes from further eutrophication to maintain their low methane and nitrous oxide emissions.

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Figure Legends

Figure 1. Lakes included in the present study and representing all the EU WFD lake types (and one additional type, StratAlk) in the study area, Estonia. Abbreviated WFD type names are indicated in brackets. A – Lake Peipsi (V-Large) and the portative monitoring buoy; B – Võrtsjärv (Large) with the stationary monitoring buoy; C – Transparent water of Äntu Sinijärv (Alk) with the reflection of the sky on the surface and our measurement sensors under the water; D – Lake Karijärv (StratAlk); E – Valguta Mustjärv (DarkSoft): almost no reflection of the sky even in a sunny day due to the blackish water; F – Lake Erastvere (LightSoft); G – Lake Ülemiste (MedAlk) with the portative monitoring buoy; H – Lake Saadjärv (StratMedAlk) on a windless day; I – Lake Mullutu Suurlaht (Coastal) with the FTIR gas analyser. Photos A-C, E, G-I by Eva-Ingrid Rõõm, photos D and F by Henn Timm.

Figure 2. Location of the studied lakes in Estonia.

Figure 3. Example of simultaneous occurrence of diffusive and ebullitive GHG fluxes at StratAlk on July 30th, 2014. All concentrations are presented in volumetric parts per million units. Empty red and green circles represent the floating chamber aeration before the experiment and filled circles – measurements during the floating experiment. Dashed trendlines show data used for CO_2 (green) and CH_4 (red) diffusive flux calculation. Concentration ‘‘jump’’ between blue circles (vertical arrow) against whole ‘‘on-water’’ experiment time (horizontal arrow) is used as a Slope for CH_4 ebullitive flux calculation (see Eq. (1)).

Figure 4. Measured physical and chemical parameters of the studied lakes during GHG flux evaluations with floating chamber method. The deepest measured value is taken 2-4 cm below sediment surface (except for DCO_2 measured with buoy). For a better overview,

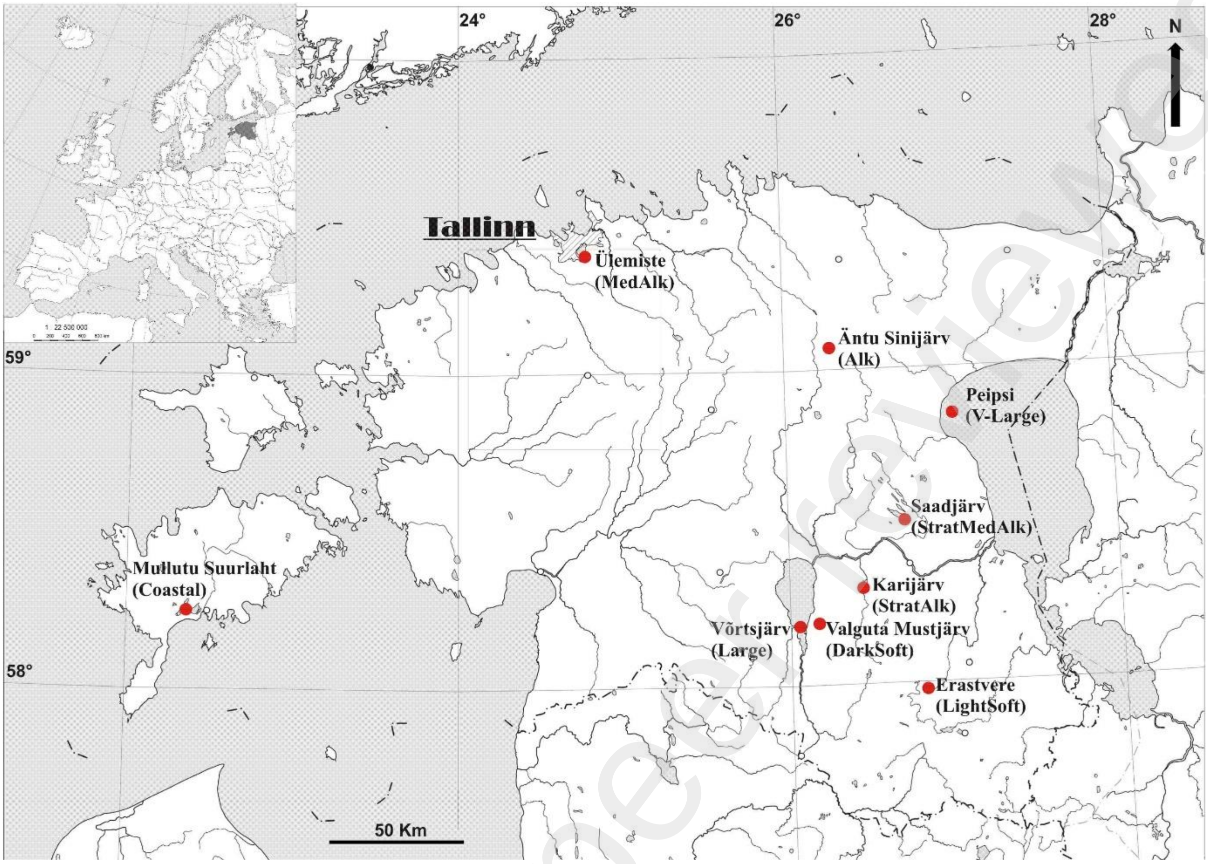
some points (marked with black) are labelled with measured values. Note the differences in x-axis scaling in case of DCO_2 (marked with different green colours).

Figure 5. Results of the floating chamber flux measurements. A – summaries of CO_2 (green) CH_4 diffusive fluxes (red) and the ebullitive flux of CH_4 (blue) on the left scale; B - diffusive CH_4 flux presented with higher resolution on the right scale; C - measured N_2O fluxes. White columns denote very small fluxes which numeric value cannot be reliably confirmed by our method. Diagonally cut columns indicate that values exceed the scales. Column labels show the average flux values for CO_2 and ebullitive CH_4 (A), diffusive CH_4 (B), and N_2O (C). Error bars show the standard deviation (in section A separately for CO_2 and CH_4 ebullitive flux). Lakes are denoted by type as described in Table 1.

Figure 6. Distribution of lake types according to average CO_2 and CH_4 fluxes in ppm m^{-2} day^{-1}.

Figure 1

Figure 2



24°
26°
28°
N
Tallinn
Ülemiste
(MedAlk)
Äntu Sinijärv
(Alk)
Peipsi
(V-Large)
Saadjärv
(StratMedAlk)
Karijärv
(StratAlk)
Võrtsjärv
(Large)
Valguta Mustjärv
(DarkSoft)
Erastvere
(LightSoft)
Mullutu Suurlaht
(Coastal)
59°
58°
50 Km

Figure 3

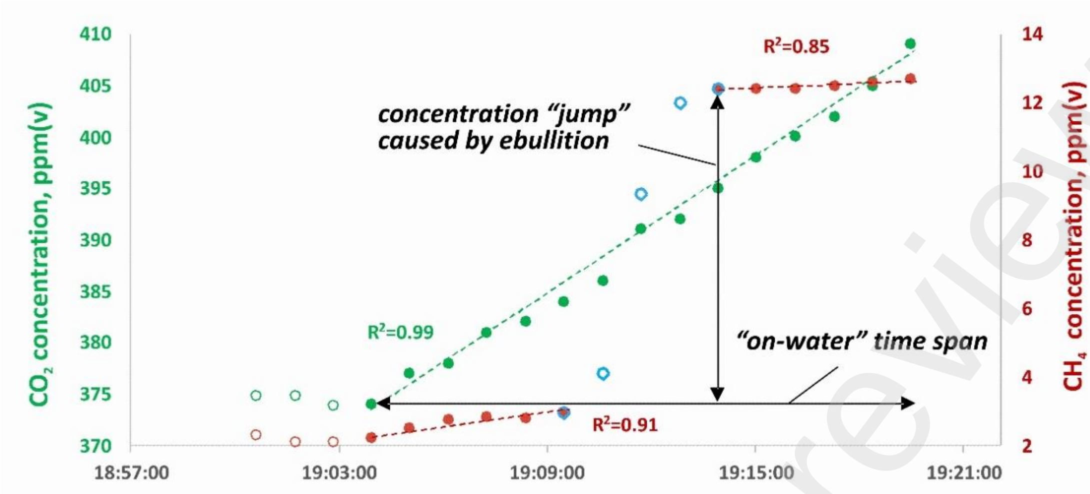

410
405
400
395
390
385
380
375
370
CO2 concentration, ppm(v)
14
12
10
8
6
4
2
CH4 concentration, ppm(v)
R²=0.85
concentration "jump"
caused by ebullition
R²=0.99
"on-water" time span
R²=0.91
18:57:00
19:03:00
19:09:00
19:15:00
19:21:00

Figure 4

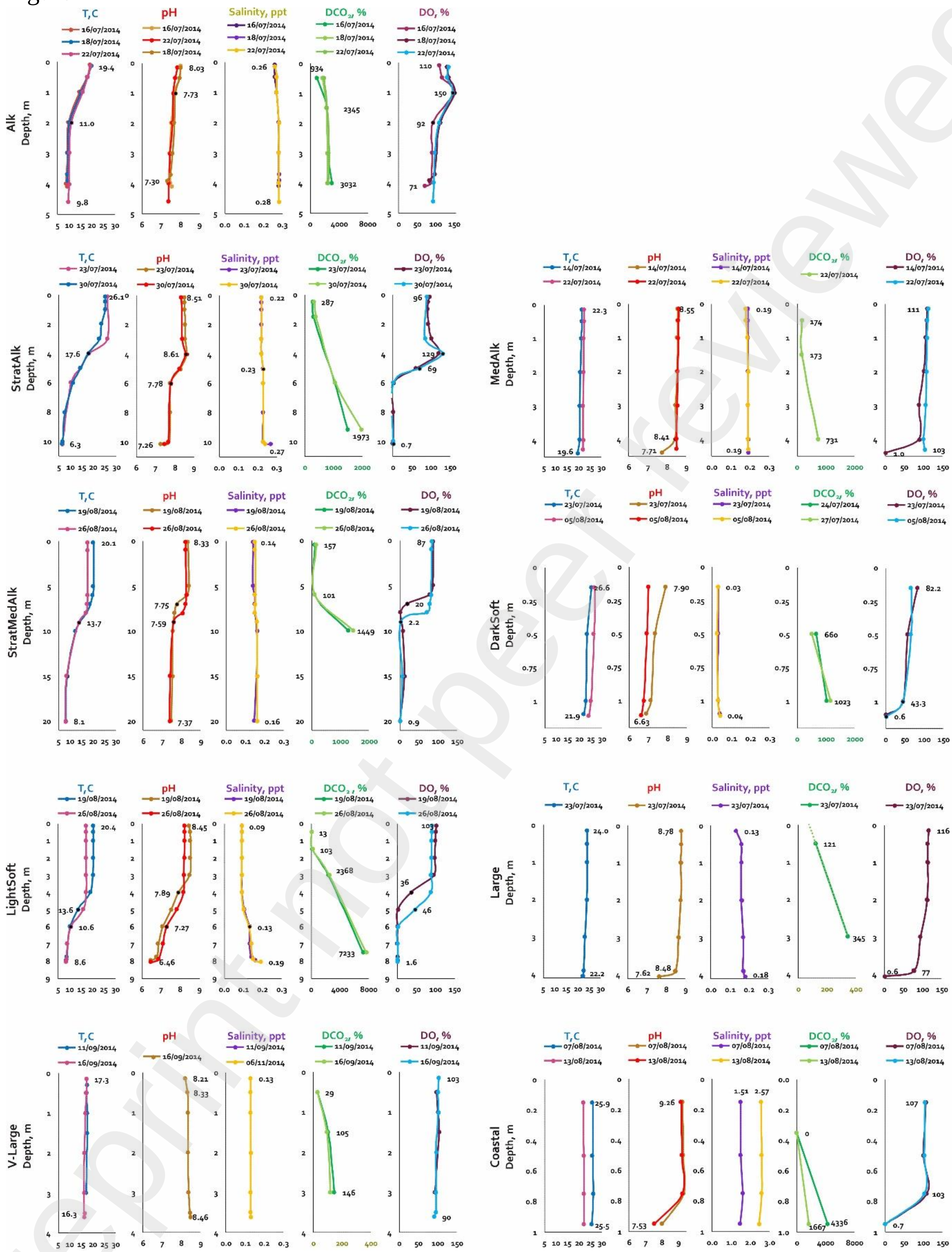

T,C
pH
Salinity, ppt
DO, %
Alk
Depth, m
StratAlk
MedAlk
StratMedAlk
DarkSoft
LightSoft
Large
V-Large
Coastal

Figure 5

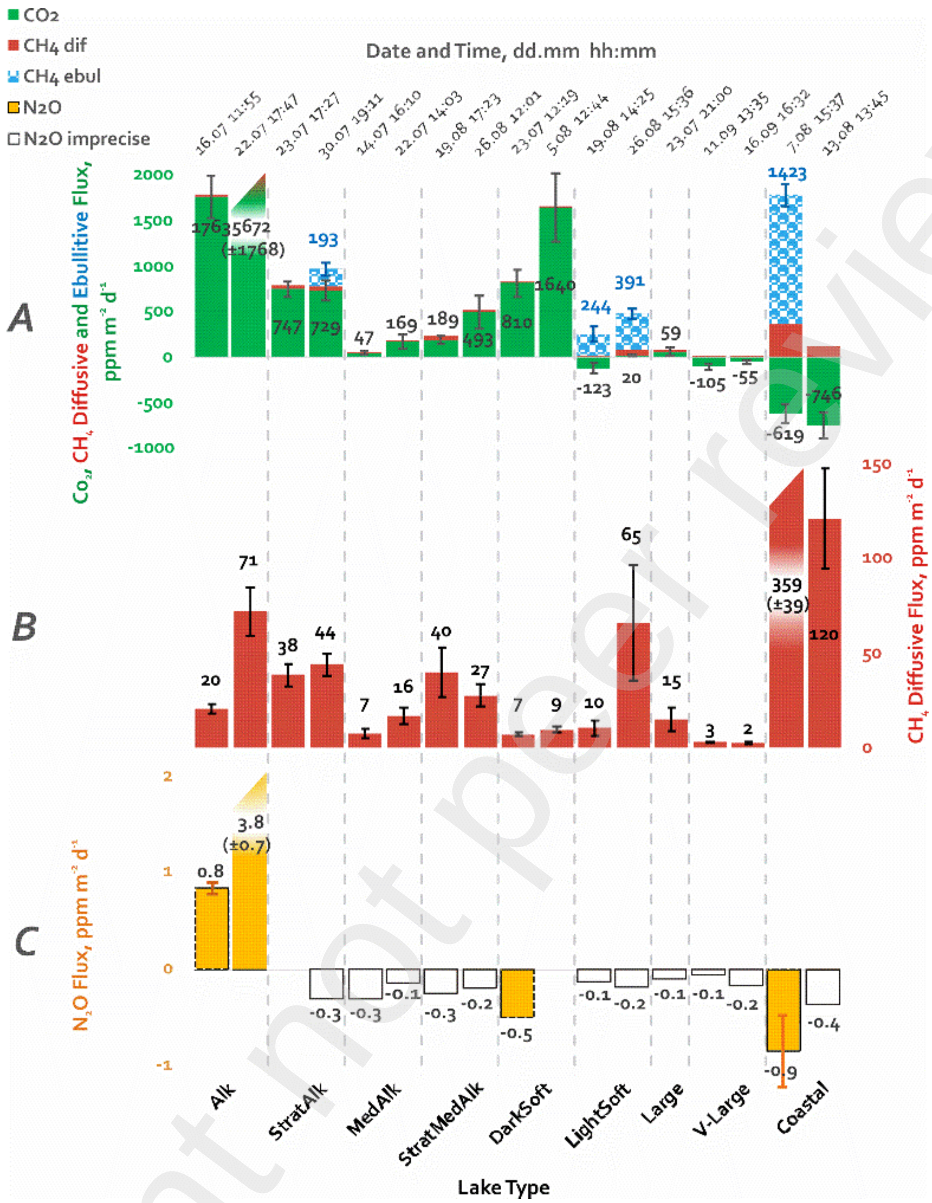

CO2
CH4 dif
CH4 ebul
N2O
N2O imprecise
Date and Time, dd.mm hh:mm
Co2, CH4 Diffusive and Ebullitive Flux, ppm m-2 d-1
CH4 Diffusive Flux, ppm m-2 d-1
N2O Flux, ppm m-2 d-1
A
B
C
Alk
StratAlk
MedAlk
StratMedAlk
DarkSoft
LightSoft
Large
V-Large
Coastal
Lake Type

Figure 6

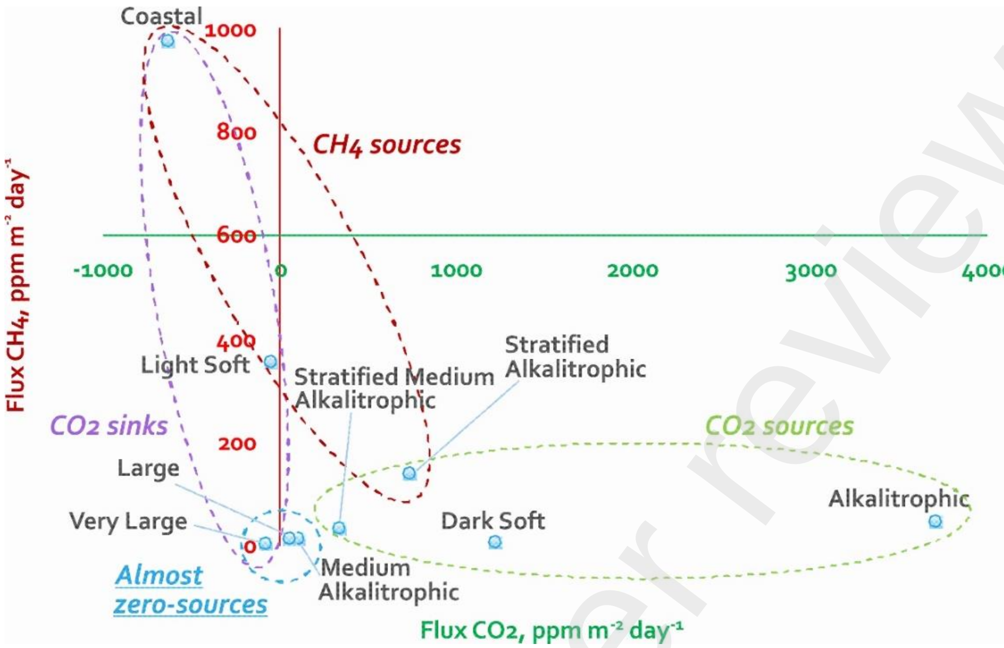

Coastal
1000
800
CH4 sources
600
-1000
0
1000
2000
3000
4000
400
Light Soft
Stratified Medium
Alkalitrophic
Stratified
Alkalitrophic
CO2 sinks
200
CO2 sources
Large
Alkalitrophic
Very Large
Dark Soft
0
Almost
zero-sources
Medium
Alkalitrophic
Flux CO2, ppm m-2 day-1
Flux CH4, ppm m-2 day-1

Table 1. Estonian lake types according to the European Water Framework Directive

Type name	Abbreviation	Area km^2	Alkalinity HCO_3^- mg L^{-1}	Conductivity µS cm^{-1}	Cl^- mg L^{-1}	Thermal stratification	Colour Pt/Co scale	Representative in the current study
Alkalitrophic	Alk	<10	>240	> 400	<25	Non-stratified	N/A	Äntu Sinijärv
Alkalitrophic, Stratified [a]	StratAlk	<10	>240	> 400	<25	Stratified	N/A	Karijärv
Non-stratified, medium alkalinity	MedAlk	<10	80–240	165–400	<25	Non-stratified	N/A	Ülemiste
Stratified, medium alkalinity	StratMedAlk	<10	80–240	165–400	<25	Stratified	N/A	Saadjärv
Dark-coloured soft-water lakes	DarkSoft	<10	<80	<165	<25	Non-stratified	≥100°	Valguta Mustjärv
Light-coloured soft-water lakes	LightSoft	<10	<80	<165	<25	Non-stratified	<100°	Erastvere
Lake Võrtsjärv	Large	100–300	80–240	165–400	<25	Non-stratified	<100°	Võrtsjärv
Lake Peipsi	V-Large	>1000	80–240	165–400	<25	Non-stratified	<100°	Peipsi

Coastal lakes	Coastal	>25	Non-stratified	Mullutu Suurlaht

[a] - Additional subtype separated from stratified medium alkalinity lakes

*Table 2. General description of the study lakes. ^{OM} - average values of our measurements, ^{DB}- long-term average values from the database of the Centre for Limnology, Estonia. TP — total phosphorous, TN — total nitrogen, Chl a — chlorophyll a, DOC — dissolved organic carbon, HCO^{-}_{3}— alkalinity, K_d— vertical light-attenuation coefficient. # - most samples of Phytoplankton are integrated, with the exception of Saadjärv and Erastvere, where the surface water / three layers (surface/metalimnion/bottom) average samples were used. * - In case of Lake Peipsi (Peipus), only an areal share of 10489 km^2 is in Estonia. Phytoplankton taxonomic groups: Bac stands for diatoms, Chryso – chrysophytes, Crypto – cryptophytes, Cy – cyanobacteria, Chloro – chlorophytes, Dino – dinoflagellates.*

Variable	**Alk (Äntu Sinijärv)**	**StratAlk (Karijärv)**	**Medalk (Ülemiste)**	**StratMedalk (Saadjärv)**	**DarkSoft (Valguta Mustjärv)**	**LightSoft (Erastvere)**	**Large (Võrtsjärv)**	**V-Large (Peipsi)***	**Coastal (Mullutu Suurlaht)**
Trophic status^{DB}	Alkalitrophic	Eutrophic	Eutrophic	Mesotrophic	Hypertrophic	Hypertrophic	Eutrophic	Eutrophic	Eutrophic
Mixing regime^{DB}	Polymictic	Dimictic	Polymictic	Dimictic	Polymictic	Dimictic	Polymictic	Polymictic	Polymictic
Area (ha)^{DB}	2.1	84	944	724.5	20.4	16.3	27000	261100	412.7
Mean depth (m)^{DB}	6	5.7	2.5	8	<1	3.5	2.8	8.3	<1
Max depth (m)^{DB}	8	14.5	4.2	25	1	9.7	6	12.9	1.7
TP (μg L^{-1})^{OM}	9	126	48	22	242	137	48	47	60
TN (μg L^{-1})^{OM}	3450	654	723	414	670	1126	910	375	1000
Chl *a* (μg L^{-1})^{OM}	1	13.5	24.7	5.62	23.19	125.64	35.71	13.4	9.04
DOC (mg L^{-1})^{OM}	4.72	11.9	13.7	9.9	35.2	12.3	11.8	12.3	18.1

HCO_3^- ($mg\ L^{-1}$) OM	293	266	201	150	31	99	211	170	109
K_d (m^{-1})DB	0.25	-	3.5	0.42	10.34	2.96	2.76	1.6	0.58
Total Biomass of Phytoplankton (g/m^3) OM #	0.77	3.02	25.07	5.19/ 3.41	1.12	23.60/ 11.85	8.34	7.38	8.67
Dominant families of PhytoplanktonOM	*Bac, Chryso, Crypto*	*Cy, Dino, Chryso*	*Cy, Bac, Chloro*	*Bac, Cy, Chloro*	*Chryso, Cy, Chloro*	*Cy, Chloro, Dino*	*Cy, Bac, Chloro, Dino*	*Cy, Bac, Chloro*	*Dino, Cy, Chloro*
Secchi depth (m) OM	8 (bottom)	4.1	0.55	4.9	0.15	1.25	0.55	2.9	1.7 (bottom)
Water residence time (y)DB	7	1	0.33	0.13	0.33	0.5	1	2	0.2
Watershed size (km^2)DB	1,37	11.1	98.8	28.4	1.34	5.2	3116	47800	238

Table 3. Dates of experiments and weather conditions during measurements. MSt – data range (and average) of daily mean meteorological variables during measurements from the closest meteorological station to the lake, Local – data from the measuring site. Lakes are denoted by type as described in Table 1.

Lake	**Sampling point coordinates**	**Period of buoy measurement**	**Dates of flux experiments**	**CO_2 air, ppm**	**CH_4 air, ppm**	**N_2O air, ppm**	**Wind speed, m s^{-2} MSt**	**Air temperature, °C MSt**	**Air temperature, °C Local**	**Wind speed, m s^{-2} Local**	**Depth, m Local**	**Air pressure, mBar Local**
Alk	N 59°03’50.6’’ E 26°14’27.0’’	15.07-22.07.2014	16.07; 22.07	372	1.86	0.30	1.2-3.4 (2.4)	17.4-19.8 (18.7)	24.2	2.6	4.4	1008.5
StratAlk	N 58°18’01.2’’ E 26°25’00.5’’	23.07-05.08.2014	23.07; 30.07	373	2.07	0.28	2.5-3.4 (2.9)	22.6-24.7 (23.7)	26.9	2.5	10.2	1014.5
MedAlk	N 59°24’45.3’’ E 24°46’34.3’’	16.07-23.07.2014	14.07; 22.07	374	1.92	0.30	1.6-2.1 (1.9)	20.1-22.2 (21.2)	22.3	7.7	4.4	1016
StratMedAlk	N 58°32’14.8’’ E 26°38’42.2’’	18.08-27.08.2014	19.08; 26.08	369	1.73	0.31	1.7-4.1 (2.6)	13.0-14.3 (13.5)	17.4	7.2	21.2	996
DarkSoft	N 58°12’27.4’’ E 26°08’38.0’’	23.07-05.08.2014	23.07; 5.08	375	1.91	0.30	2.5-3.4 (2.9)	22.6-24.7 (23.7)	27.5	1.9	1.1	1017
LightSoft	N 57°58’45.8’’ E 26°46’57.7’’	19.08-29.08.2014	19.08; 26.08	369	1.85	0.30	1.4-4.4 (2.8)	12.4-15.7 (13.9)	17.1	6.8	7.9	993

Large	N 58°12'43.0'' E 26°06'12.5''	23.07-05.08.2014	23.07	367	2.11	0.29	2.5-3.4 (2.9)	22.6-24.7 (23.7)	27.7	0.4	4.1	985
V-Large	N 58°50'27.2'' E 26°58'20.6''	09.09-16.09.2014	11.09; 16.09	382	1.81	0.31	0.6-2.8 (1.3)	9.9-16.6 (13.8)	17.1	2.0	3.6	1025.5
Coastal	N 58°14'30.7'' E 22°22'00.6''	07.08-14.08.2014	7.08; 13.08	372	1.97	0.29	1.9-7.0 (4.5)	17.1-21.9 (20.4)	22.5	7.6	1.0	1011.5

*Table 4. Estimates of daily summer CH_4, CO_2 and N_2O emissions of the studied lakes based on average fluxes recorded on the days of observation. For N_2O, values close to detection limits are given in brackets. Lakes are denoted by type as described in Table 1. * - CO_2 equivalent calculated by applying the 100 years coefficients of Global Warming Potential (GWP) with no feedback: 1 for CO_2, 28 for CH_4, and 265 for N_2O (Myhre et al., 2013).*

Lake	Flux of CO_2, ppm m^{-2} d^{-1}	Flux of CH_4, ppm m^{-2} d^{-1}	Flux of N_2O, ppm m^{-2} d^{-1}	Flux of CO_2, mg m^{-2} d^{-1}	Flux of CH_4, mg m^{-2} d^{-1}	Flux of N_2O, mg m^{-2} d^{-1}	CO_2 flux per lake, kg day^{-1}	CH_4 flux per lake, kg day^{-1}	N_2O flux per lake, kg day^{-1}	Total CO_2+CH_4 flux, mol GHG $lake^{-1}$ day^{-1}	Total CO_2+CH_4 flux, kg C $lake^{-1}$ day^{-1}	Total CO_2+CH_4 flux, mol CO_{2e}* $lake^{-1}$ day^{-1}	Total CO_2+CH_4 flux, T CO_{2e}* $lake^{-1}$ day^{-1}	Total CO_2+CH_4+N_2O flux, T CO_{2e}* $lake^{-1}$ day^{-1}
Alk	3717.8	45.9	2.32	6600	29.7	4.12	139	0.6	0.1	3188	38	4237	0.2	0.2
StratAlk	737.8	137.3	*(-0.32)*	1310	88.8		1100	75		29653	356	155259	6.8	
MedAlk	108.2	11.7	*(-0.23)*	192	7.6		1813	72		45645	548	165983	7.3	
StratMedAlk	340.8	33.4	*(-0.23)*	605	21.6		4384	157		109379	1314	372969	16.4	
DarkSoft	1225.4	8.0	-0.53	2175	5.2	-0.95	444	1.1	-0.2	10150	122	11925	0.5	0.5
LightSoft	-51.5	355.1	*(-0.15)*	-91	229.8		-15	37		1996	24	65030	2.9	
Large	59.3	14.7	*(-0.11)*	105	9.5		28434	2561		805720	9677	5115633	225.1	
V-Large	-79.8	2.3	*(-0.12)*	-142	1.5		-370071	3965		-8161746	-98028	-1488676	-65.5	

Coastal	-631.9	972.4	-0.62	-1122	629.3	-1.10	-4630	2597	-4.5	56681	681	4427657	194.9	193.7

Table 5. Estimation of daily summer greenhouse gas (GHG) emissions from all Estonian lakes based on measured GHG emissions and division of the total lake area between types. The N_2O emissions were excluded from the estimate of the total emission due to their marginal importance and lack of reliable quantitative data for most lake types.

Type	% of total lake area in Estonia by type	Total area of lakes by type, ha	Number of lakes by type	Mean area of lakes by type, ha	Total CO_2 emission by type, T day^{-1}	Total CO_2 emission by type, T C day^{-1}	Total CH_4 emission by type, T day^{-1}	Total CH_4 emission by type, T C day^{-1}	Total N_2O emission by type, T day^{-1}	Total CO_{2e} emission[a] by type, N_2O excluded, T day^{-1}	Total CO_{2e} emission[a] by type, N_2O included, T day^{-1}
Alk	0.1	213	94	2.3	14	4	0.06	0.05	0.01	19	21
StratAlk	1.5	3362	114	29.5	44	12	3.0	2.3		273	
MedAlk	4.3	9536	539	17.7	18	5	0.7	0.5		74	
StratMedAlk	2.3	5025	201	25.0	30	8	1.1	0.8		114	
DarkSoft	1.5	3404	890	3.8	74	20	0.2	0.2	-0.03	88	79
LightSoft	0.8	1742	310	5.6	-2	-1	4.0	3		306	
Large	12.2	26919	1	26919	28	8	2.6	2		224	
V-Large	75.7	167588	2	83794	-238	-65	2.5	1.9		-42	
Coastal	1.6	3524	221	16.0	-40	-11	22.2	16.7	-0.04	1664	1654
Total	**100**	**220354**	**2536**		**-69**	**-19**	**36**	**27**		**2720**	

[a] - GHG fluxes weighed by Global Warming Potential coefficients for 100 years without feedback: 1 for CO_2, 28 for CH4, and 265 for N_2O (Myhre et al., 2013)

Appendix A (Tables S1 – S2)

Supplement 1

*Table S1. Chloride, sulphate, and inorganic nutrient concentrations (mg L^{-1}) in studied lakes. * - indicates values below detection limit.*

Lake	Date	Sampling depth	Chlorides	Sulphates	Si	NO_3-N	NH_4-N	PO_4-P
Alk	22/07/2014	integrated water column	12.4	17.7	2.56	3.13	0.067	0.006
StratAlk	26/08/2014	surface	5.44	13.1	2.5	0.012	0.006	0.008
	26/08/2014	metalimnion	5.17	13.3	2.53	0.005	0.007	0.005
	26/08/2014	bottom	5.3	6.77	5.28	*	0.55	0.263
MedAlk	22/07/2014	integrated water column	8.09	31.9	0.763	*	0.028	0.005
StratMedAlk	26/08/2014	surface	10.2	22.8	0.8	*	0.015	0.011
	26/08/2014	metalimnion	19.3	24.3	1.34	*	0.025	0.005
	26/08/2014	bottom	8.35	22.3	2.77	0.124	0.036	0.005
DarkSoft	22/07/2014	integrated water column	3.18	5.21	1.56	0.127	0.013	0.184
LightSoft	26/08/2014	surface	14	2	0.189	*	0.003	0.003
	26/08/2014	metalimnion	14.1	1.93	0.192	*	0.006	0.005

	26/08/2014	bottom	15.8	10.9	0.685	0.027	0.542	0.2
Large	22/07/2014	integrated water column	7.2	12	3.3	*	*	0.011
V-Large	16/09/2014	integrated water column	5.46	12.55	0.456	0.004	0.018	0.015
Coastal	12/08/2014	integrated water column	very high	266	6.52	0.012	0.088	0.005

Supplement 2

Table S2. Correlations between the GHG fluxes in lakes and lake parameters. Spearman correlation coefficients are presented for relationships including salinity or specific conductance and Pearson correlation coefficients for all the other relationships. Only results with p≤0.15 are presented, results with p≤0.05 are marked in bold.

	Fluxes, ppm					
	CO_2		**CH_4 Diffusional**		**CH_4 Total**	
	R	**p**	**R**	**p**	**R**	**p**
DCO_2 Surface, %	**0.99**	**<0.001**				
ΔDCO_2 Surface *vs* Metalimnion, %			**0.79**	**0.01**	**0.91**	**0.001**
pH Surface	-0.60	0.09	0.63	0.07	0.63	0.07
pH Metalimnion	-0.55	0.13	0.59	0.10	0.54	0.13
Δt_{water} Surface *vs*_Metalimnion, ºC	0.58	0.11				
ΔSalinity Surface_Metalimnion, ppt					-0.85	0.07
ΔSalinity Surface_Bottom, ppt					**-0.88**	**0.04**
ΔSpecific Conductance Surface_Bottom, µS cm^{-1}					-0.85	0.07
Total Nitrogen (µg L^{-1})	-0.56	0.12			0.596	0.09

Total Biomass of Phytoplankton (g/m^3) Surface	-0.52	0.15
Secchi Depth (m)	**0.71**	**0.03**