ANU LIIKANEN

Greenhouse Gas and Nutrient Dynamics in Lake Sediment and Water Column in Changing Environment

Doctoral dissertation

To be presented by permission of the Faculty of Natural and Environmental Sciences of the University of Kuopio for public examination in Auditorium L21, Snellmanin talo, University of Kuopio, on Friday 1st November 2002, at 12 noon

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ABSTRACT

Introduction Greenhouse gases, carbon dioxide (CO₂), methane (CH₄), and nitrous oxide (N₂O), are produced in various microbial processes in soils, sediments and water. These gases are essential in the atmosphere to prevent the heat escaping from the earth’s surface. However, anthropogenic activity has increased the concentrations of greenhouse gases in the atmosphere thus contributing to global warming. In this study the dynamics of CO₂, CH₄, and N₂O and the cycling of nutrients, ammonium (NH₄⁺), nitrate (NO₃⁻) and phosphorus (P) were studied in mid-boreal, hyper-eutrophic Lake Kevätön, Finland. Spatial (littoral, shallow and deep profundal areas) and temporal (winter, summer and autumn) variation, the effects of temperature, the availability of O₂, NO₃⁻, NH₄⁺ and SO₄²⁻ on sediment gas and nutrient dynamics were studied in a laboratory microcosm (a continuous water flow system) developed for the study. The dynamics of CH₄ and O₂ in the water column were studied both in situ and utilizing laboratory experiments.

Methane Significant amounts of CH₄ were released from eutrophic lake sediments especially in summer and autumn from the deep profundal and littoral sediments with the anoxic overlying water. Eububtion was an important mechanism in transporting CH₄ directly from the sediment to the atmosphere. When O₂ existed on the sediment surface or in the water column, CH₄ was effectively oxidized resulting in negligible emissions. Some CH₄ oxidation was determined also in winter in anaerobic or microaerobic conditions. High CH₄ emissions can furthermore occur during spring overturn when CH₄ stored under the ice is released after the ice-melt, since at that time the CH₄ oxidation of the water column was negligible.

Nitrous oxide Lake sediments were not significant sources of N₂O due to the limited availability of NO₃⁻. Some N₂O was released with oxic flow from the shallow profundal sediments. The sediments producing N₂O were different from those favourable to CH₄ production.

Nutrients The profundal sediments with high release rate of CH₄ released also large amounts of NH₄⁺ and P. In the deep profundal sediments high mineralization of organic matter (sum of CO₂ and CH₄) regenerated plenty of nutrients, which were released from the sediments into the overlying water in anoxic conditions. The ebullition of CH₄ had an important role in transporting NH₄⁺ and P from the sediments into the overlying water.

Changing environment Lake anoxia, which increases in the course of eutrophication, increases the liberation of CH₄ and that of the important nutrients NH₄⁺ and P. However, carbon mineralization rate (CO₂ + CH₄) was not affected by O₂ availability. Predicted increase in temperature would increase the release of CH₄, CO₂, NH₄⁺ and P from sediments. Currently, the availability of NO₃⁻ and NH₄⁺ in freshwaters is increasing while that of SO₄²⁻ is decreasing. A risen NO₃⁻ level highly increases N₂O release in comparison to CH₄ release. Increasing NH₄⁺ level has minor effects on sediment gas dynamics. Decreasing SO₄²⁻ availability may increase CH₄ emissions from sediments with a low organic matter content. Thus, various anthropogenic activities can significantly change the greenhouse gas balance of a boreal lake ecosystem.

Universal Decimal Classification: 556.55, 504.45
CAB Thesaurus: greenhouse gases; cycling; nutrients; carbon dioxide; methane; nitrous oxide; nitrogen; phosphorus; sediment; lakes; eutrophication; oxygen; mineralization; ammonium; nitrate; sulfate; temperature
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TIHVISTELMÄ (abstract in Finnish)


Dityppioksidit Dityppioksidin tuotto järvisedimentsissä oli vähäistä, sillä nitraatin saatavuus rajotti dentrifikaatiota. Dityppioksidia muodostui hieman matalan veden alueen sedimenteissä hapellisissä oloissa. Dityppioksidia syntyi siis sedimenteissä, joissa ei muodostunut metaania.


ACKNOWLEDGEMENTS

The present study was carried out in the Department of Environmental Sciences, University of Kuopio, in the Laboratory of Environmental Microbiology, Division of Environmental Health, National Public Health Institute, Kuopio and in the Research Department of North Savo Regional Environment Centre during the years 1998-2002. I thank the Heads of the Department of Environmental Sciences, Professors Pentti Kalliokoski and Taisto Raunemaa; the Head of the Division of Environmental Health, Professor Jouko Tuomisto, M.D.; the Head of the Laboratory of Environmental Microbiology, Docent Aino Nevalainen, Ph.D.; and the Head of Research, Docent Kristina Servomaa, Ph.D., in the Environment Centre for allowing me to work in their units and for providing excellent facilities. The study was financed by the Academy of Finland and Finnish Graduate School in Environmental Science and Technology (EnSTe).

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There are many important people who took part in this study and I am extremely grateful to them for their contributions. First of all I thank all of my co-authors in the publications, particularly Heikki Tanskanen for helping me with the microcosm and Tero Väisänen for consulting help in sediment sampling and with minielectrodes. I am also grateful to other colleagues in the biogeochemistry research group in the Universities of Kuopio and Joensuu. Special thanks to Jari Huttunen for sharing a room and being innovative and good company and to Hannu Nykänen for his never-ending willingness to help. I thank all of the laboratory assistants in National Public Health Institute, Department of Environmental Sciences, North Savo and North Ostrobothnia Regional Environment Centres for doing a large part of the hard work. Päivi, Irma, Tarja, Pirjo and Henna kindly liberated me from the gas-chromatographs. I am grateful to the personnel of North Savo Regional Environment Centre, particularly to the technical assistants for sharing the sampling equipment and giving a helping hand in the field and to Taina Hammar for providing information on Lake Kevätönn. The Tihonen family, living next to Lake Kevätönn, deserve special acknowledgements, they kindly provided their backyard, sauna building, boat and shoreline of Lake Kevätönn for our research.
Finally, I owe my warmest thanks to my family, relatives and friends. During this work I was fortunate to get to know new people, which are now very close friends. These new friends and the good old fellows offered me relaxing, enjoyable moments, thank you for cheering me up. I thank my relatives for empathizing in both the highlights and low points of my life. My deepest and dearest thanks are given to my family, to my mother, father, sister, brother and grandparents, they have trusted in me and have offered me an unquestioning support. Loving thanks to Juha and Isa for delighting my everyday life.

Dedicated to my mother and father, Pirjo and Markku Liikanen.

Kuopio, September 2002

Anu Liikanen
# Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>methane</td>
</tr>
<tr>
<td>CO</td>
<td>carbon monoxide</td>
</tr>
<tr>
<td>CO₂</td>
<td>carbon dioxide</td>
</tr>
<tr>
<td>DIC</td>
<td>dissolved inorganic carbon</td>
</tr>
<tr>
<td>ECD</td>
<td>electron capture detector</td>
</tr>
<tr>
<td>FID</td>
<td>flame ionisation detector</td>
</tr>
<tr>
<td>GC</td>
<td>gas chromatograph</td>
</tr>
<tr>
<td>GWP</td>
<td>global warming potential</td>
</tr>
<tr>
<td>HPO₄²⁻</td>
<td>hydroxyphosphate ion</td>
</tr>
<tr>
<td>H₃PO₄</td>
<td>dihydroxyphosphate ion</td>
</tr>
<tr>
<td>IPCC</td>
<td>Intergovernmental Panel on Climate Change</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>ammonium ion</td>
</tr>
<tr>
<td>NO</td>
<td>nitric oxide</td>
</tr>
<tr>
<td>NO₂⁻</td>
<td>nitrite ion</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>nitrate ion</td>
</tr>
<tr>
<td>N₂O</td>
<td>nitrous oxide</td>
</tr>
<tr>
<td>NPOC</td>
<td>non purgeable organic carbon</td>
</tr>
<tr>
<td>NPP</td>
<td>net primary production</td>
</tr>
<tr>
<td>NVOC</td>
<td>non volatile organic carbon</td>
</tr>
<tr>
<td>PO₄³⁻</td>
<td>phosphate ion</td>
</tr>
<tr>
<td>S₂⁻</td>
<td>sulhide ion</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>sulphate ion</td>
</tr>
<tr>
<td>SOC</td>
<td>sediment oxygen consumption</td>
</tr>
<tr>
<td>SRP</td>
<td>soluble reactive phosphorus</td>
</tr>
<tr>
<td>TCD</td>
<td>thermal conductivity detector</td>
</tr>
</tbody>
</table>
ORIGINAL PUBLICATIONS

This thesis is based on the following publications, referred to by the Roman numerals I-VI.


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ORIGINAL PUBLICATIONS
1 INTRODUCTION

1.1 Finnish lakes -widely affected by anthropogenic activities

Finnish landscape was shaped by the last Scandinavian continental ice sheet, which started to melt 11 500 years ago. The melting generated a lot of wetlands and lakes, which were isolated during the retreat of the shorelines of the Baltic (Saarmisto, 2000). There are currently 188 000 lakes (with a surface area of more than 500 m²) in Finland, which cover approximately 10% of the total surface area of Finland (Raatikainen and Kuusisto, 1990). Lakes in Finland are typically shallow and have long shorelines (Matinvesi et al., 1990).

For humans, lakes have provided recreation, fishing, drinking water, irrigation, transportation, energy and a dumping site for wastewaters (Lakso and Alasaarela, 1990). Therefore settlements, agriculture and industry have developed extensively to the surroundings of lakes e.g. in southern and Middle Finland. Intense human activities in the vicinity of lakes and their catchments affect lake ecosystems diversely. Especially in cool, boreal regions, where the lakes are in stable and stagnant conditions under ice for long periods (Fig. 1), the lake ecosystems are vulnerable to changes. Eutrophication, the excess availability of nutrients, nitrogen (N) and phosphorus (P), leached from the catchments (e.g. from agriculture or wastewaters) enhances the primary production and causes algal blooms in lakes. This increases the amount of oxygen (O₂) consuming degradable organic matter in lakes, which can cause lake anoxia to develop (Smith et al., 1999; Wetzel, 2001). In Finland, approximately 9% of the lakes are eutrophic as for their P availability (Mannio et al., 2000). Lakes are also susceptible to acidification (Forsius et al., 1990). The concentrations of acid anions, sulphate (SO₄²⁻) and nitrate (NO₃⁻), in lakes have increased due to the atmospheric deposition of nitric and sulphuric acids from industry and energy production as well as from N load from agriculture and wastewaters (Henriksen et al., 1997). Currently, the SO₄²⁻ concentrations are decreasing whereas the NO₃⁻ concentrations are still increasing in aquatic ecosystems (Stoddard et al., 1999). The critical load of sulphur is exceeded nowadays in 9% of Finnish lakes (Henriksen et al., 1997). Also global climate change may have diverse effects on freshwater ecosystems in boreal regions. Increased precipitation may increase nutrient inputs and the risen air and water temperatures stimulate primary production, eutrophication and O₂ depletion and change the duration of ice-free season and stratification periods (Carpenter et al., 1992; Schindler, 2001). All these changes may affect the biogeochemical cycles of elements and the production and consumption of important greenhouse gases and nutrients within a lake ecosystem.
Figure 1. Seasonal variation of A) O₂ and temperature, B) nutrients, and C) greenhouse gases in hypolimnion of dimictic, hypereutrophic, mid-boreal Lake Kevojärvi, Finland. Temperature, O₂, and nutrient concentrations are determined 1 m and gas concentrations 0.5 m above the sediment surface at the deep profundal (9-m depth). Shaded areas represent the duration of ice-cover.
1.2 Greenhouse gas dynamics in lakes and their atmospheric impact

Carbon dioxide (CO₂), methane (CH₄), and nitrous oxide (N₂O) are important greenhouse gases, which occur naturally in the atmosphere. They are required to prevent the heat from escaping from the earth’s surface. Particularly, during the last decades human activities have increased the concentrations of these gases in the atmosphere, which according to predictions will lead to the warming of the climate (IPCC, 2001). Greenhouse gases are produced naturally in soils, sediments and waters in various microbiological processes. In boreal regions, the gas dynamics are extensively studied in peatland ecosystems (Crill et al., 1991; Laiho et al., 1996). In Finland, the Finnish Research Programme on Climate Change (SILMU) in 1990-1995 clarified greenhouse gas dynamics in terrestrial ecosystems including natural, drained, forested and agricultural peat soils and forest ecosystems (Roos, 1996), yet neglected the gas balances of aquatic ecosystems. However, due to an abundance of lakes in boreal region, knowledge of gas dynamics in aquatic ecosystems is required when evaluating regional gas budgets. This thesis is a part of a research consortium ‘Radiatively Important Trace Gas Fluxes in Boreal Lakes’ launched in 1998. In the following sections, microbial processes responsible for the production and consumption of important greenhouse gases, CO₂, CH₄, and N₂O will be discussed.

**Carbon dioxide** Carbon dioxide is formed in aerobic and anaerobic degradation of organic matter. In lakes, the organic matter produced in the water column (autochthonous) or leached from the catchment (allochthonous) settles and is mostly remineralized in sediments; some of the settling organic matter is already decomposed in the water column. Organic matter is predominantly degraded by microbial processes, which provide maximum energy yield. Thermodynamic energy yield from the oxidation reactions with various electron acceptors decreases in the order of O₂ > NO₃⁻ > Mn⁴⁺ > Fe³⁺ > SO₄²⁻ > CO₂ (Capone and Kiene, 1988). The electron acceptors that diffuse into the sediment from the overlying water are consumed in sediments in the order of their energy yield capacity. This results in vertical zonation of various mineralization processes (Fig. 2) (Conrad, 1996). The occurrence and ratio of oxidised and reduced compounds regulate sediment redox potentials, which can be used as an indicator of the most dominant degradation process. Carbon dioxide is also produced in anoxic fermentation processes and in ‘acetoclastic’ methanogenesis, which uses acetate as a substrate (see below) (Fig. 2). Carbon dioxide can also be reduced to CH₄ in methanogenesis (see below) or to acetate in homoacetogenesis in anaerobic sediments (Schultz and Conrad, 1996; Lay et al., 1998). In the water column, CO₂ can be fixed back to biomass in primary production.
Figure 2. Biogeochemical processes in sediments; carbon degradation, nutrient regeneration and greenhouse gas production. Redox potentials are from the review of Kimura (2000).

Carbon dioxide, a water-soluble gas, is transported into sediment and water column, and from water into the atmosphere by the means of advection and diffusion. Carbon dioxide can also evolve from sediments in bubbles (Chanton and Whiting, 1995). Lakes can be either net sources or sinks of atmospheric CO₂ depending on the surface water CO₂ concentration in respect of atmospheric equilibrium (water CO₂ concentration in equilibrium with the atmosphere is 15 μM at 20°C). Surface water CO₂ concentration is mainly regulated by respiration and primary production. Northern lakes, which receive a lot of allochthonous organic matter (Kortelainen, 1993) are generally heterotrophic i.e. the respiration in lakes exceeds the amount of CO₂ fixed in primary production (Cole, 1999). They are a net source of CO₂ (Cole et al., 1994; Kelly et al., 2001). On the other hand, in highly productive lakes intense primary production fixes more CO₂ than is released from decomposition, thus carbon is accumulated in sediments (Kling et al., 1992; Schindler et
Carbon dioxide exchange has a strong diurnal and seasonal variation within a lake, and a lake can act both as a sink and a source of CO₂ depending on the time and the season (Anderson et al., 1999; Kelly et al., 2001). The variation in CO₂ exchange is regulated mainly by radiation and photosynthetic activity. During daytime lakes are sinks, and in the dark, sources of CO₂. In boreal region, lakes serve typically as sources of CO₂ in spring and autumn, and as sinks in summer.

**Methane** The concentrations of electron acceptors other than O₂ available to oxidize organic matter are generally low in natural, unpolluted, freshwater sediments. In fact, also O₂ is present in the surface sediment layers, which are merely some millimetres thick (Sweerts, 1990). Most of organic matter, up to 87%, is degraded in various fermentation processes and methanogenesis to CH₄ and CO₂ in anoxic sediments (Capone and Kiene, 1988). However, if inorganic electron acceptors, NO₃⁻ or SO₄²⁻, are present in polluted freshwaters, more energy yielding respiring bacteria (Fig. 2) will outcompete CH₄ producing bacteria i.e. methanogens for the substrates thus suppressing the production of CH₄ (Capone and Kiene, 1988). Methanogens only utilize a limited number of small organic molecules in energy production. Methane can be produced by reduction of CO₂ to CH₄, in which H₂, formate, alcohols or CO are used as electron donors i.e. as reductants (Boone, 1991). In freshwater sediments, most of the CH₄ is produced by the reduction of the methyl group of acetate (Woltemate et al., 1984; Whiticar et al., 1986; Jones, 1991). Methanogens also reduce methyl group from methanol, dimethyl sulphide, mono-, di-, and trimethylamines (Jones, 1991). These methylated ‘noncompetitive substrates’ are used especially in marine sediments where sulphate reducing bacteria, abundant in SO₄²⁻ rich marine sediments, compete with methanogens for H₂ and other low molecular weight substrates, such as acetate and formate (Capone and Kiene, 1988; Kiene, 1991).

Methane produced in anoxic sediments diffuses along concentration gradient upwards and is susceptible to oxidation by CH₄ oxidizing bacteria, aerobically by the methanotrophs in sediment surface (Kuivila et al., 1988, Frenzel et al., 1990; Sweerts et al., 1996,) and in the water column (Rudd et al., 1974; Michmerhuizen et al., 1996; Utsumi et al., 1998) or anaerobically even in the freshwater sediments (Panganiban et al., 1979; Zehnder and Brock, 1980). Methanotrophs are aerobic bacteria, which use CH₄ as a sole carbon and energy source. In freshwaters, CH₄ oxidation is most active in the vicinity of the oxic and anoxic interface, where both O₂ and CH₄ are available (Kiene, 1991). In sediments and the hypolimnion, the concentrations of CH₄ are generally high at micro and millimolar range and methanotrophs there have a low affinity for CH₄. In addition to CH₄, methanotrophs are capable of oxidizing also NH₄⁺, which thereby may interfere CH₄ oxidation (Hanson and Hanson, 1996). Methanotrophs also compete with NH₄⁺ oxidising bacteria for O₂, which may limit the CH₄ oxidation activity. The oxidation of CH₄ is known to occur also
in anaerobic conditions, generally in $\text{SO}_4^{2-}$ rich environments such as marine sediments (e.g. Martens and Berner, 1977; Barnes and Goldberg, 1976; Devol and Ahmed, 1981). In oceans, the anaerobic $\text{CH}_4$ oxidation is thought to involve $\text{CH}_4$ oxidizing archaea bacteria in consortium with sulphate reducing bacteria (Hoehler et al., 1994; Boetius et al., 2000; Pancost et al., 2000; Schouten et al., 2001). Microaerophilic (Rudd and Hamilton, 1975; Rudd et al., 1976) and anaerobic $\text{CH}_4$ oxidation (Panganiban et al., 1979; Zehnder and Brock, 1980) has been reported to occur also in freshwaters. Rudd et al. (1976) found that microaerophilic conditions would even support $\text{CH}_4$ oxidation in lake water if there is shortage of mineral nitrogen for the growth of methane oxidizing bacteria. The reason is that microaerophilic conditions allowed biological $N_2$ fixation by the methanotrophs (Davis et al., 1964). Nitrogen fixation requires low $O_2$ conditions, because $O_2$ inhibits the activity of the nitrogenase enzyme, the key enzyme in biological $N_2$ fixation. However, the mechanism for anaerobic oxidation in freshwaters with a low availability of $\text{SO}_4^{2-}$ and limited number of sulphate reducing bacteria is unknown.

Generally freshwater lakes are sources of $\text{CH}_4$ (Kiene, 1991; Table 1) especially in anoxic conditions (Fig. 1C). Emissions of $\text{CH}_4$ are high from eutrophic lakes with anoxic hypolimnions, whereas the $\text{CH}_4$ emissions from oligotrophic lakes with a good $O_2$ status can be negligible (Table 1) due to low $\text{CH}_4$ production and effective $\text{CH}_4$ oxidation in surface sediments and water column. Methane is transported in lakes by diffusion, advection, ebullition or through plants (Chanton and Whiting, 1995). Since diffusion rates are low, dissolved $\text{CH}_4$ is transported from anoxic sediments and hypolimnion to surface waters by advection especially during overturn periods. From surface waters dissolved $\text{CH}_4$ is diffused into the atmosphere when the $\text{CH}_4$ concentration in surface waters exceeds the concentration (2.7 nM at 20°C) equilibrium with the atmosphere. However, $\text{CH}_4$ is poorly soluble in water and evolves easily from sediments in bubbles, which are released directly into the atmosphere without being subjected to significant oxidation (Strayer and Tiedje, 1978). Especially in eutrophic lakes, where degradation and $\text{CH}_4$ production is high, ebullition can be a significant source of $\text{CH}_4$ (Casper et al., 2000; Nakamura et al., 1999; Takita and Sakamoto, 1993). Aquatic macrophytes (vascular plants) are important in conducting $\text{CH}_4$ in their aerenchyma directly from the anoxic sediments into the atmosphere (Dacey and Klug, 1979). Plants also provide fresh, easily decomposable organic matter in root exudates into the sediments thus promoting methanogenesis. At the same time, plants provide $O_2$ for root respiration, which increases $\text{CH}_4$ oxidation in their vicinity (Chanton and Whiting, 1995).
Table 1. Published fluxes of CH$_{4}$ and CO$_{2}$ (dissolved inorganic carbon = DIC) from sediment to water in various lakes. Averages and/or minimum and maximum are presented.

<table>
<thead>
<tr>
<th>Lake</th>
<th>Site characteristics</th>
<th>Flux mg CH$_{4}$ m$^{-2}$ d$^{-1}$</th>
<th>Flux mg CO$_{2}$ m$^{-2}$ d$^{-1}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>hypereutrophic:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L. Kevätn, Finland</td>
<td>littoral</td>
<td>49, 0.5–243</td>
<td>890, 410–1550</td>
<td>11</td>
</tr>
<tr>
<td>L. Kevätn, Finland</td>
<td>profundal</td>
<td>44, 0.2–184</td>
<td>1030, 510–1860</td>
<td>11</td>
</tr>
<tr>
<td>Green Bay, L. Michigan, USA</td>
<td>profundal</td>
<td>10–17</td>
<td></td>
<td>4</td>
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<tr>
<td>Frain's Lake, MI, USA</td>
<td>profundal</td>
<td>40–300</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>L. Wintergreen, MI, USA</td>
<td>profundal</td>
<td>500$^a$, 1070$^b$</td>
<td></td>
<td>19</td>
</tr>
<tr>
<td>eutrophic:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blelham Tarn, UK</td>
<td>profundal</td>
<td>330</td>
<td>1850</td>
<td>8</td>
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<tr>
<td>L. Constance, Germany</td>
<td>littoral</td>
<td>0.3–1520</td>
<td>3, 22</td>
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<tr>
<td></td>
<td>profundal</td>
<td>0.6$^a$, 7.7$^d$</td>
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<tr>
<td>L. Müggelsee, Germany</td>
<td>eroded littoral</td>
<td>27</td>
<td>16</td>
<td></td>
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<tr>
<td></td>
<td>deposited littoral</td>
<td>190</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>profundal</td>
<td>13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>L. Dagow, Germany</td>
<td>profundal</td>
<td>&lt;176</td>
<td>5</td>
<td></td>
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<tr>
<td>Loosdrecht lakes, The Netherlands</td>
<td>profundal</td>
<td>3–105</td>
<td>18</td>
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</tr>
<tr>
<td>L. Vechten, The Netherlands</td>
<td>littoral</td>
<td>1.6–6.4</td>
<td>21</td>
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<tr>
<td></td>
<td>profundal</td>
<td>0–150</td>
<td></td>
<td></td>
</tr>
<tr>
<td>L. Sempach, Switzerland</td>
<td>littoral</td>
<td>22</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>profundal</td>
<td>50</td>
<td></td>
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</tr>
<tr>
<td>Lake 227, ON, Canada</td>
<td>profundal</td>
<td>16–160</td>
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<td>L. Washington, WA, USA</td>
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<td>4.2</td>
<td>67–160</td>
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<tr>
<td>L. Mendota, WI, USA</td>
<td>profundal</td>
<td>570</td>
<td>6</td>
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<td>L. Erie, OH, USA</td>
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<td>13–120</td>
<td>35–300</td>
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<tr>
<td>Third Sister Lake, MI, USA</td>
<td>profundal</td>
<td>74–79</td>
<td>9</td>
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<tr>
<td>oligotrophic:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L. Stechlin, Germany</td>
<td>profundal</td>
<td>&lt;40</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Lake 18, NT, Canada</td>
<td>profundal</td>
<td>11</td>
<td>96</td>
<td>14</td>
</tr>
<tr>
<td>3 Shield lakes, ON, Canada</td>
<td>profundal</td>
<td>130–1100</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>L. Taupo, New Zealand</td>
<td>profundal</td>
<td>3.2–21</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>acidotrophic:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L. Fuchskule, Germany</td>
<td>profundal</td>
<td>&lt;59</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Lake 3025, ON, Canada</td>
<td>littoral</td>
<td>480–1890</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>L. Orta, Italy</td>
<td>profundal</td>
<td>27</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

Hamilton Harb., L. Ontario, Canada: profundal 0–370, 88–650 15

Nitrous oxide

Nitrous oxide is mainly produced in denitrification, where N₂O is produced as an intermediate in the reduction of NO₃⁻ to N₂ (NO₃⁻ → NO₂⁻ → NO → N₂O → N₂) (Firestone and Davidson, 1989). In anoxic conditions heterotrophic, denitrifying bacteria oxidise organic matter with NO₃⁻, whereas in oxic conditions O₂ is used as an electron acceptor. Denitrification can proceed in the absence of O₂ when substrates, NO₃⁻ and organic matter are present. The reduction of N₂O to N₂ is the most sensitive reaction step and is inhibited by O₂, NO₃⁻, sulphide, or low pH, under which conditions the ratio of N₂O to N₂ in denitrification increases (Knowles, 1981). Nitrous oxide is also a by-product of nitrification, the oxidation of NH₄⁺ to NO₂⁻ and NO₃⁻ (Firestone and Davidson, 1989). In nitrification N₂O is formed at low O₂ levels when NO₂⁻ is reduced to N₂O by ammonium oxidizing bacteria (Firestone and Davidson, 1989). In comparison to denitrifying bacteria, nitrifying bacteria require O₂ but do not need organic carbon for living. However, nitrifiers are dependent on organic matter mineralization, which liberates NH₄⁺ for their energy production and CO₂ for their C source.

In freshwaters, sediments serve as important sites for denitrification (Chan and Campbell, 1980), nitrification (Hall, 1986) and N₂O production (Mengis et al., 1996). Sediments with a high mineralization rate produce a lot of NH₄⁺ for nitrification. However, nitrification is generally limited by the availability of O₂. Anoxic sediments with an abundant supply of organic carbon provide a good environment for heterotrophic denitrification (Seitzinger, 1988). Denitrification in sediments is limited by a low availability of NO₃⁻ and is generally closely coupled to nitrification, which produces NO₃⁻ (Knowles, 1979; Jensen et al., 1993 and 1994; Blackburn et al., 1994). Therefore, denitrification and nitrification are segregated in sediments (Fig. 2). In oxic surface sediments, nitrification generates NO₃⁻, which is diffused deeper into the anoxic sediments and consumed by denitrification. A major source of NO₃⁻ in sediments is the NO₃⁻ produced in the sediments via nitrification but not the NO₃⁻ diffusing from the overlying water (Chan and Campbell, 1980; Gardner et al., 1987; Jensen et al., 1993 and 1994). Most of the NO₃⁻ used in sediments is reduced to N₂, and the production of N₂O is low with the ratio of N₂O to N₂ being generally < 5% (Seitzinger, 1988). However, N₂O production may increase as a result of eutrophication or acidification due to the inhibition of N₂O reduction by NO₃⁻ and H₂S (Seitzinger, 1988). In the water column, nitrification produces N₂O in the oxic surface waters (Elkins et al., 1978; Priscu et al., 1996) and denitrification can either produce (Yoh et al., 1983; Mengis et al., 1997) or consume N₂O (Mengis et al., 1997) depending on the O₂ availability.

Lakes are known to be either sinks or sources of N₂O depending mainly on O₂ and NO₃⁻ availability and the level of eutrophication (Elkins et al., 1978; Kaplan et al., 1978; Knowles et al., 1981; Lemon and Lemon, 1981). Concentration of N₂O equilibrium with
the atmosphere is 9 nM (at 20°C), above that concentration lakes emit N_2O. Generally natural, lakes have low N_2O fluxes (Mengis et al., 1997). However, anthropogenic inputs of nitrogen significantly increase N_2O emissions from freshwaters (Kaplan et al., 1978; Kroeze and Seitzinger, 1998).

1.3 Interaction between gas and nutrient dynamics

Human activities such as land use, fertiliser application and wastewaters discharge, have increased eutrophication of lake ecosystems (Smith et al., 1999). Primary production in lakes is generally limited by the availability of phosphorus (P) and nitrogen (N), and is therefore enhanced by the external nutrient load. Phosphorus is generally considered as the most limiting nutrient, since cyanobacteria, abundant in freshwaters, are capable of fixing N_2 from the atmosphere when N availability limits their growth (Hellström, 1996; Hendzel et al., 1994). Nutrient loading and the associated higher rates of primary production enhances the production of organic matter and sedimentation (Boström et al., 1988). The elevated amount of organic matter in sediments increases decomposition, O_2 consumption, and the production of carbon gases, CO_2 and CH_4. Mineralization also liberates nutrients from the organic matter back into the water column where they can be used again in primary production (Sinke et al., 1990). This internal loading of nutrients is an essential mechanism in maintaining long-term eutrophication of lakes.

Nitrogen Elevated sediment organic matter content (van Luijn et al., 1999) and high content of N in organic matter (Fenchel et al., 1998) increase the release of N from sediments. Nitrogen is liberated from the sediments as particulate N, dissolved organic N, NH_4^+, NO_3^-, NO_2^-, N_2O, or N_2 as a result of organic matter mineralization, nitrification and denitrification (Keeney, 1973). The proportion of various N compounds released from the sediments is dependent on O_2 availability and the amount of organic matter (Keeney, 1973; van Luijn et al., 1999). The mineralization of organic matter produces NH_4^+ (ammonification) liberating organic N bound in proteins and nucleic acids to NH_4^+ (Fig. 2). Under anoxic conditions, N_2O is released into the overlying water (Fig. 1B), whereas in the presence of O_2 some of the NH_4^+ is oxidised in nitrification to NO_3^-. Nitrate is either diffused upwards to the overlying water or downwards to more reduced sediments, where it is reduced in denitrification to N_2O and/or N_2 (Fig. 2). Liberation of gases, N_2O and N_2, is significant in controlling eutrophication by removing nitrogen from a lake ecosystem into the atmosphere (Seitzinger, 1988). The dissolved organic N, NH_4^+ and NO_3^-, which can be used in primary production, are, on the other hand, of most importance in maintaining eutrophication.
**Phosphorus** Phosphorus can be released from sediment as dissolved P compounds (organic P and inorganic orthophosphate, $\text{H}_2\text{PO}_4^-$, $\text{HPO}_4^{2-}$, $\text{PO}_4^{3-}$) or in resuspended particles (in organic matter or absorbed to minerals) (Boström et al., 1988; Reddy et al., 1996). The most essential is the release of inorganic dissolved phosphorus (soluble reactive P = SRP), which can be used by primary producers. It has been established that more P is liberated from the sediments under anoxic conditions (Boström et al., 1988). Several biological and chemical mechanisms are responsible for P release under anoxic conditions. The initial step is the mineralization of organic matter, which releases dissolved $\text{PO}_4^{3-}$ into the sediment pore water after hydrolysis of the phosphate-ester bond. Mineralization also consumes $\text{O}_2$ and the lower redox conditions supports the existence of $\text{PO}_4^{3-}$ in a dissolved form. Under oxic conditions, $\text{PO}_4^{3-}$ is precipitated (a chemical process) to (hydroxy)phosphates with oxidized iron ($\text{Fe}^{3+}$) and manganese ($\text{Mn}^{4+}$) ions (Fig. 2). The capacity of oxic surface sediments to block $\text{PO}_4^{3-}$ loss depends on the availability of $\text{Fe}^{3+}$ and $\text{Mn}^{4+}$. Phosphate can also be released from oxic sediments, if the binding capacity of these ions is exceeded (Jensen et al., 1992). In the absence of $\text{O}_2$ or $\text{NO}_3^-$, $\text{Fe}^{3+}$ and $\text{Mn}^{4+}$ are used as electron acceptors. After their reduction $\text{PO}_4^{3-}$ is liberated from the hydroxyprecipitate (Fig. 2). Previously, the reduction of $\text{Fe}^{3+}$ in sediments was thought to be a chemical process (Mortimer, 1941 and 1942), but it has since then been established that reduction can be microbially driven (Lazzaretti et al., 1992; Eckerrot and Pettersson, 1993; de Montigny and Prairie, 1993).

Released P can also originate from bacteria rather than precipitated hydroxides (e.g. Gächter et al., 1988). Under oxic conditions, bacteria can act as a sink of P by taking up P and storing phosphates intracellularly. Bacteria liberate $\text{PO}_4^{3-}$ from polyphosphates to cytoplasm under anoxic conditions. It then can diffuse from the cells into the water (Gächter et al., 1988; de Montigny and Prairie, 1993). Phosphates are also released when bacterial cells are lysed (de Montigny and Prairie, 1993). Cell lysis can be abundant when strictly aerobic bacteria are killed by the absence of $\text{O}_2$ (Boström et al., 1988). Phosphorus can be mobilized physically and chemically via desorption, ligand exchange mechanism and dissolution of P containing precipitates (e.g. hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, and variscite $\text{AlPO}_4\cdot2\text{H}_2\text{O}$) (Boström et al., 1988; Kairesalo, 1995). However, $\text{PO}_4^{3-}$ precipitated with $\text{Ca}^{2+}$ and $\text{Al}^{3+}$ is less easily affected by changes in $\text{O}_2$ and redox conditions (Moore and Reddy, 1994).

**Transportation of nutrients** Mobilised nutrients, N and P, are diffused or advected from sediments (Reddy et al., 1996). The diffusion rate of nutrients from or into sediments is determined by Fick’s law of diffusion and is driven by the concentration gradient of nutrients across the sediment-water interface. Diffusion alone is not effective in
transferring nutrients to the epilimnion for primary producers. Most nutrient transfer from sediments occurs by advective processes such as wind-induced turbulence, bioturbation, and gas convection, which result in mixing the sediment pore water and particles into the lake water (Boström et al., 1988). Under stagnant anoxic conditions especially during ice-covered periods, there is no wind-induced turbulence, and much zoobenthos cannot live under anoxic conditions. Then gas convection, mainly bubbling of CH₄, can be more significant in transferring nutrients from sediments into the water. In eutrophic lakes, high decomposition rate in sediments simultaneously produces both CH₄ and nutrients resulting in the release of nutrients from the sediments.

1.4 Objectives

The objectives of the studies in this thesis were to integrate the various microbial processes producing and consuming greenhouse gases (CO₂, CH₄, and N₂O) and nutrients in boreal, freshwater lakes. The processes associated to the gas and nutrient dynamics in boreal lakes are highly affected by anthropogenic activities such as eutrophication and atmospheric deposition. Detailed objectives were as follows:

- Develop novel microcosm methodologies for sediment gas and nutrient studies (I), so that the biogeochemical processes that lead to fluxes of gases and nutrients can be studied simultaneously.
- Identify and measure seasonal and spatial variation in sediment gas and nutrient dynamics (II) with an emphasis on a wide range of oxygen (O₂) availability and temperature in laboratory studies (III).
- Describe sediment gas dynamics in changing environment conditions: a) under decreasing O₂ content (I-V), b) increasing NH₄⁺ (V) and NO₃⁻ (IV) availability, d) with changing SO₄²⁻ availability (IV) and e) with rising temperature (II).
- Establish the interaction between lake sediment gas and nutrient release and its contribution to internal loading and eutrophication (I-III).
- Study the importance of water column CH₄ oxidation and its contribution to lake anoxia (VI).
- Evaluate the greenhouse gas release from lake sediments and the relative importance of CO₂, CH₄, and N₂O.
2 MATERIALS AND METHODS

2.1 The study lake, Lake Kevätöön

Experiments were conducted with sediment and water samples from a mid-boreal Lake Kevätöön (63°6'N, 27°37'E, Finland) (Fig. 3). Lake Kevätöön is a small, hyper-eutrophic lake, which was initially eutrophied by sewage in 1930-1975. Presently agriculture and internal loading are the most significant sources of nutrients to the water column. The lake is a typical boreal lake, ice-covered and dimictic with two stratification periods (from a few days to weeks in summer, and 4-5 months in winter) (Fig. 1). There were three study sites in the lake (Fig. 3); a middle infralittoral at a depth of 1.5 m (growing Phragmites australis and Nuphar lutea), a shallow profundal at a depth of 4 m, and a deep profundal at a depth of 9 m. The littoral (depth 0–1.5 m), shallow profundal (depth 1.5–6 m), and deep profundal (depth 6–9 m) zones cover 30, 67, and 3%, respectively, of the total surface area of the lake.

Figure 3. Study sites on Lake Kevätöön: the infralittoral (1.5 m, in studies I-II), shallow profundal (4 m, in studies I-VI), and deep profundal (9 m, in studies I, II, IV, and VI). Total P and N and chlorophyll-a concentrations are averages in the water column of the deep profundal site in 1998.
2.2 Sediment gas and nutrient dynamics

2.2.1 Microcosm studies with intact sediment cores

Sediment gas and nutrient dynamics were studied with intact sediment cores under controlled conditions in a laboratory microcosm using a continuous water flow technique (I-V). Spatial and seasonal variation in sediment gas and nutrient production potentials within the lake (I, II) were examined. By changing the composition of the test waters utilized in the experiments, the effects of O$_2$ concentration (I-V), temperature (III), and availability of NO$_3^-$ (IV), NH$_4^+$ (V), and SO$_4^{2-}$ (IV) on the sediment gas and nutrient dynamics were evaluated (see Table 2 for details).

Table 2. Studies conducted with intact sediment cores in a laboratory microcosm using a continuous water flow technique.

<table>
<thead>
<tr>
<th>Time</th>
<th>Site depth$^a$ (m)</th>
<th>No of cores$^b$</th>
<th>T ($^\circ$C)</th>
<th>Incubation time and test water O$_2$ status</th>
<th>Experimental setup</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>June 1998</td>
<td>1.5, 4, 9</td>
<td>9</td>
<td>15</td>
<td>14 d oxic, 14 d anoxic</td>
<td>Kuopio water works</td>
</tr>
<tr>
<td>Aug. 1998</td>
<td>1.5, 4, 9</td>
<td>9</td>
<td>15</td>
<td>14 d oxic, 14 d anoxic</td>
<td>Kuopio water works</td>
</tr>
<tr>
<td>Apr. 1998</td>
<td>1.5, 4, 9</td>
<td>9</td>
<td>15</td>
<td>14 d anoxic, 14 d oxic</td>
<td>Kuopio water works</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aug. 1998</td>
<td>4</td>
<td>3</td>
<td>28 d oxic,</td>
<td>Kuopio water works</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6, 11, 16, 23</td>
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<td>6, 11, 16, 23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>June 1999</td>
<td>9</td>
<td>10</td>
<td>15</td>
<td>28 d oxic</td>
<td>0, 30, 100, 300 or 2000 μM SO$_4^{2-}$</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>10</td>
<td>15</td>
<td>28 d anoxic</td>
<td>0, 30, 100, 300 or 2000 μM SO$_4^{2-}$</td>
</tr>
<tr>
<td>July 1999</td>
<td>4</td>
<td>2</td>
<td>15</td>
<td>21 d anoxic, 10 d oxic</td>
<td>0 μM SO$_4^{2-}$/NO$_3^-$</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>8</td>
<td>15</td>
<td>21 d anoxic, 10 d oxic</td>
<td>30, 100, 300 or 2000 μM NO$_3^-$</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>8</td>
<td>15</td>
<td>21 d anoxic</td>
<td>30, 100, 300 or 2000 μM SO$_4^{2-}$</td>
</tr>
<tr>
<td>Feb. 2000</td>
<td>4</td>
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<td>23</td>
<td>23 d anoxic</td>
<td>0 μM NH$_4^+$</td>
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<tr>
<td></td>
<td>4</td>
<td>10</td>
<td>23</td>
<td>3 d anoxic, 4 d oxic, 13 d oxic and NH$_4^+$</td>
<td>0, 50, 500, 5000 or 15000 μM NH$_4^+$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3 d anoxic and NH$_4^+$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ 1.5 m = infralittoral, 4 m = shallow profundal, and 9 m = deep profundal; $^b$ studies I-III were conducted with triplicate and studies IV-V with duplicated cores; $^c$ see papers I-III for composition of water from Kuopio water works, and paper IV-V for composition of artificial water.
Sediment cores were collected by utilizing a Limnos sediment sampler in the profundal and a piston core sampler in the infralittoral. Sediment and control cores (without sediment) were incubated under oxic (8.5–10.5 mg O$_2$ l$^{-1}$) or anoxic (< 1 mg O$_2$ l$^{-1}$, deoxygenated with N$_2$) water, which was pumped continuously from reservoirs over the sediment cores at a flow rate of 50 ml h$^{-1}$. The outflowing water from the sediment and the control cores were sampled for gas and nutrient analyses. Dissolved fluxes of gases and nutrients were then calculated from the concentration differences between outflowing water from sediment and control cores (no sediment). In the experiments IV and V, the control cores were not used (10 control cores would have been required in the installation). Instead, samples were taken from the inflowing and outflowing water and the fluxes were calculated from their concentration differences. The incubation core system was constructed so that the gas evolved from the sediments by diffusion and ebullition could be determined separately (I).

Dissolved fluxes of the greenhouse gases, CO$_2$, CH$_4$, and N$_2$O, were determined during the experiments 3-5 times a week. Dissolved gas concentrations in the water were determined using a headspace equilibration technique (Mc Auliffe, 1971; Jones and Simon, 1980). The water (20-30 ml) was equilibrated in syringes with added nitrogen (30-40 ml) and the headspace gas concentrations were determined with two gas chromatographs (GC) equipped with a flame ionization detector (FID) for CH$_4$, a thermal conductivity detector (TCD) for CO$_2$ and CH$_4$ (> 1000 ppm CH$_4$), and an electron capture detector (ECD) for N$_2$O (see details Nykänen et al., 1995). The dissolved gas concentrations in the water were then calculated from the headspace gas concentrations according to Henry’s law using the values from Lide and Fredikse (1995). Bubble gases were collected and analysed when 3-10 ml of the gas was accumulated in the gas traps.

Sediment oxygen consumption, SOC, dissolved fluxes of total phosphorus (P), ammonium (NH$_4^+$), combined nitrate and nitrite (NO$_2^-+NO_3^-$), sulphate (SO$_4^{2-}$) and non volatile/purgeable organic carbon (NVOC / NPOC) were determined once at the end of the incubations. Dissolved O$_2$ concentration was determined with an O$_2$ electrode. Phosphorus was determined according to the standard SFS 3026 (SFS Standardization 1986). Combined NO$_2^-+NO_3^-$ was determined according to the standard SFS-EN ISO 13395 (SFS Standardization 1997) or analyzed with an ion chromatograph (IV, V). Ammonium was determined according to the standard SFS 3032 (SFS Standardization 1976) (I-III), according to with Fawcett and Scott (1960) (IV) or was analyzed with an ion chromatograph (V). Sulphate was determined with an ion chromatograph and organic carbon with a Shimadzu TOC-5000 Analyzer. At the end of the incubations, sediment
redox-potential, overlying water O₂ concentration and pH were measured with electrodes, and the profiles of dissolved O₂ (II, III, IV) concentration and redox potential (II, IV) in the sediment water interface were measured with mini-size electrodes.

2.2.2 Sediment CH₄ production and oxidation potentials

Sediment CH₄ production and oxidation potentials (VI) were measured in vitro with sediment slurry incubations (Saarnio et al., 1997). Samples for the potential studies were taken from the shallow and deep profundal sediments of Lake Kevätönn with a Limnos sampler in winter and summer 1999 (VI). The potentials were determined from layers of 0-1, 1-2, 2-3, 3-4, and 4-10 cm, and in addition from layers of 10-15 and 15-20 cm in summer.

Sediment CH₄ production potential was determined in 120 ml flasks with 15 ml of sediment under anaerobic headspace. Anoxic conditions were created by flushing the headspace with nitrogen. The flasks were incubated in the dark at 22°C for 7 days under 42 kPa N₂ overpressure. Headspace samples of 20 ml were drawn for CH₄ analyses at the beginning and at the end of the incubations. The CH₄ production potential was calculated from the increase in CH₄ concentration during the incubation.

Methane oxidation potential was studied in 600 ml flasks with 30 ml of sediment-water (1:1) slurry under aerobic headspace with 10 000 ppm CH₄. The flasks were shaken in a dark at 22°C for 2-6 days under 17 kPa air overpressure. Gas samples of 25 ml for the CH₄ analyses were taken from the headspace 3-5 times during the incubation. The CH₄ oxidation potentials were calculated from the maximal decrease in the CH₄ concentration with time.

2.3 Water column carbon dynamics

2.3.1 Primary production

In situ net primary production (NPP) of phytoplankton was determined using a ¹⁴C technique over a 24-h period (Keskitalo and Salonen, 1994). NPP was determined every second week from June to September 1998 in the epilimnion of the deep (0-4 m) and shallow (0-2 m) profundals.
2.3.2 Methane oxidation

*Methane oxidation kinetics and potential CH₄ oxidation* Kinetics of water column CH₄ oxidation were studied in the laboratory in June 1999 (VI) with water from 1 m above the sediment from the shallow and deep profundal of Lake Kevätöns. Water column CH₄ oxidation potentials were studied in the laboratory in July 1999 (VI) with samples from the shallow profundal from the depth of 1, 2, and 3.5 m and from the deep profundal from the depth of 1, 3, 5, 7, and 8.5 m. Incubations were performed in 600 ml flasks with 200 ml of water under aerobic headspace and conducted similarly as for the CH₄ oxidation potential experiments with sediments (see 2.2.2). In the kinetic studies, the headspace CH₄ concentrations were 3, 10, 100, 1000, 10 000, and 50 000 ppm CH₄ corresponding to 0.005, 0.015, 0.15, 1.5, 15, and 75 μM CH₄ in the water. Methane oxidation potentials at various CH₄ concentrations were calculated from the decrease in the headspace CH₄ concentration with time. Since the maximum oxidation rate was achieved with 10 000–25 000 ppm CH₄, the CH₄ oxidation potential experiments were then conducted at 10 000 ppm CH₄ in the headspace.

*In situ CH₄ dynamics* Methane dynamics in the water column *in situ* were studied in the deep profundal in 1999–2000 (Aug. 1999, Feb., May, June, July, Aug. and Oct. 2000) (VI). The study was conducted as a hanging-bottle experiment similar to Michmerhuizen et al. (1996). Water samples were taken with a peristaltic water pump from depths of 1, 2, 3, 4, 5, 6, 7, and 8–8.5 m directly into the incubation flasks by overfilling them (without a headspace). Immediately after the filling, two of the flasks were sampled and another two were sealed with septa, tied onto a rope and suspended into the lake, to the depth where they were originally sampled. After 24 h, another two flasks were retrieved and sampled. Water samples for CH₄ analyses were taken with syringes from the bottom of the flasks, and the temperature, dissolved O₂ and water pH were determined with electrodes. Water CH₄ concentration was determined with headspace equilibration technique (see 2.2.1). The difference between the initial and final CH₄ concentrations showed net oxidation (a negative change) or production (a positive change) of CH₄. *In situ* O₂ consumption in hypolimnion was calculated similarly. Since the incubations showed net O₂ change including both production of O₂ in primary production and consumption of O₂ in aerobic respiration, the epilimnetic O₂ consumption could not be determined.
3 RESULTS AND DISCUSSION

3.1 Spatial and seasonal variation in lake gas and nutrient dynamics

3.1.1 Sediments

*Spatial variation* Littoral and profundal sediments had distinct gas and nutrient release potentials (I, II). The deep profundal sediments with the highest carbon content had the greatest potential to release carbon gases, CO$_2$ and CH$_4$, and nutrients, NH$_4^+$ and P. Fluxes of CH$_4$, NH$_4^+$ and P were low from the shallow profundal sediments whereas the release of N$_2$O was the highest among the sediments. The littoral sediments released CO$_2$ and CH$_4$ at high rates but only negligible amounts of nutrients.

Eutrophic lake sediments had high capacity to produce CO$_2$ and CH$_4$, their contribution to the total global warming potential (GWP) of the sediment gas release was almost 100%, 3-77% for CH$_4$ and 22-92% for CO$_2$ (Fig. 4). The highest CH$_4$ fluxes were retrieved from the deep profundal and infralittoral, and the lowest from the shallow profundal sediments (II). The CO$_2$ fluxes were the highest from the deep profundal sediments (II). In the deep profundal sediments, accumulated organic matter from the other parts of the lake contributed to the high mineralization and carbon gas (CH$_4$ and CO$_2$) production, whereas in the littoral, plant derived organic matter fuelled the CH$_4$ production. The CH$_4$ and CO$_2$ release rates from the sediments of Lake Kevätönn were within the range of the previously measured from the eutrophic lake sediments (Table 1). In previous studies, eutrophic lakes have shown the greatest CH$_4$ production either in the profundal (Casper, 1996; Jones and Simon, 1981; Adams and Baudo, 2001) or in the littoral (Bosse et al., 1993; Thebrath et al., 1993; Rolletschek, 1997), whereas in oligotrophic lakes, the littoral have shown greater CH$_4$ emissions and C mineralization than the profundal (den Hayer and Kalff, 1998; Casper, 1996; Thebrath et al., 1993). The evaluation of littoral CH$_4$ production is difficult. Littoral consists of various zones (Wetzel, 2001) and CH$_4$ production can vary greatly between the zones. In this study only one of the littoral zones, the middle infralittoral segment without macrophytes, was studied. Recently, higher CH$_4$ emissions have been measured from the upperlittoral zones growing macrophytes (Juutinen et al., 2001). Thus this study might underestimate the littoral CH$_4$ production in Lake Kevätönn. However, on the whole lake scale, the littoral, which comprises 30% of the Lake Kevätönn surface, was the most important source of CH$_4$ (II) Also the large area (67%) of the shallow profundal with moderate CH$_4$ release rates contributed significantly to the lake CH$_4$ budget. The deep profundal with merely a 3% coverage was of less importance as for the lake CH$_4$ budget despite its high CH$_4$ production capacity. Lake CO$_2$ budgets from the sediment CO$_2$ fluxes were not evaluated as the lake CO$_2$ dynamics are greatly controlled.
also by degradation processes and primary production in the water column and the leaching from the catchments.

![Figure 4. Total GWP's (100 yr time horizon) of the gases (CH₄, CO₂, N₂O) released from A) littoral, B) shallow profundal and C) deep profundal sediments under oxic and anoxic conditions. Calculated from the results of the study II according to IPCC (2001).](image)

The sediments were minor sources of N₂O and its contribution to the total GWP of the sedimentary gases was negligible (Fig. 4) (I-III). Some N₂O emission potentials, up to 930 µg m⁻² d⁻¹, were measured from the core incubations of shallow profundal sediments (II). Although fluxes of N₂O from the lake sediments are generally small (Seitzinger, 1988), extremely high emissions have been measured from highly eutrophic river sediments (Garcia-Ruiz et al., 1998 and 1999). The sediments producing N₂O differed from the sediments most favourable to CH₄ production (II). N₂O was produced only with the oxic flow from the sediments, which had shown a low CH₄ efflux under the anoxic flow. In those sediments, CH₄ oxidation did not consume all of the O₂ thus leaving O₂ for the NH₄⁺ oxidation. The production of N₂O in sediments was obviously limited by the availability of NO₃⁻ produced in nitrification as observed also in previous studies (Knowles, 1979; Jensen et al., 1993 and 1994; Blackburn et al., 1994). The shallow profundal with the highest N₂O release rate and coverage was the most important source of the N₂O in Lake Kevätönn.
In the profundal, nutrient release was closely associated with mineralization and carbon gas production (I–III). Mineralization liberated P and NH$_4^+$ from the organic matter to the sediment pore water and under anoxic conditions the nutrients were further released into the overlying water (Sinke et al., 1990). The ebulition of CH$_4$ was significant in transporting the nutrients from the sediments into the water by causing turbulence and resuspension of sediment particles and nutrient rich pore water (II). Saarijärvi and Lappalainen (2001) evaluated that gas ebulition induced 20% of total internal nutrient loading in eutrophic Lake Postilampi, Finland. The littoral sediments did not serve as a storage for nutrients as did the profundal sediments. Although carbon was mineralised at the same rate in the littoral as in the profundal, hardly any P, NH$_4^+$ or NO$_2^-+NO_3^-$ was released from the sediments (II). When examining the lake as a whole, the shallow profundal with the largest coverage and moderate nutrient release rates was the most important source of nutrients, being responsible for about 80% of the P and mineral N (NH$_4^+ + NO_2^- + NO_3^-$) release in Lake Kevätön.

**Seasonal variation** Sediment gas and nutrient release exhibited high seasonal variation (II). The sediments had a greater potential to release gases and nutrients in summer and autumn than in winter, probably due to a greater supply of fresh organic matter from primary production during open water period (II). Also temperature and availability of O$_2$, which vary highly in boreal lakes (Fig. 1A) were important in regulating gas and nutrient release (III). Temperature increased the release of CO$_2$, CH$_4$, NH$_4^+$, and P from the sediments, whereas the release of N$_2$O and NO$_2^-+NO_3^-$ was optimal at 16°C (III). The availability of O$_2$ increased NO$_2^-+NO_3^-$ and N$_2$O fluxes and reduced fluxes of CH$_4$, NH$_4^+$, and P, but did not affect the CO$_2$ release and the total C mineralization rate considerably (II, III).

The release rates of gases CH$_4$ and CO$_2$, and nutrients NH$_4^+$ and P, are likely to be the highest during summer stratification (II), when the conditions for the release are the most favourable i.e. the supply of fresh organic matter is the most abundant, temperatures are the highest and the availability of O$_2$ is low (Fig. 1A). In summer, despite the O$_2$ availability in the overlying water, the sediments had potential to release CH$_4$, NH$_4^+$ and P probably due to high mineralization rates (II). However, high release rates of CH$_4$, NH$_4^+$, and P in summer seem to increase the hypolimnetic concentrations only moderately, probably due to the short duration of stratification and anoxic conditions in summer (Fig. 1B and C). During autumn overturn, with fresh organic matter in sediments and hypolimnion well oxygenated, the release of CH$_4$, NH$_4^+$ and P is not likely to occur, but instead the conditions are favourable for the production of NO$_2^-+NO_3^-$ and N$_2$O. From the oxic autumn sediments, negligible release of CH$_4$ and P, yet some liberation of NH$_4^+$ and N$_2$O were determined (II). These material fluxes are reflected by the chemical
composition of hypolimnion during oxic overturn periods i.e. the NO$_3^-\text{+NO}_3$ and N$_2$O concentrations were high, and the amounts of CH$_4$ and NH$_4^+$ (Fig. 1B and C) in situ negligible. In winter the low supply of fresh organic matter, and low temperatures i.e. from 3 to 6 °C, are factors, which are likely to result in low mineralization and release rate of carbon gases, NH$_4^+$ and P. In winter, during a long anoxic period lasting up to 5 months, however, microbial processes in sediments produce a lot of CH$_4$, NH$_4^+$ and P, which accumulate in the hypolimnion (Fig. 1B and C).

3.1.2 Water column

Oxidation of CH$_4$ in the water column was a significant factor in reducing CH$_4$ emissions into the atmosphere (VI). In the deep profundal of Lake Kevätön, CH$_4$ oxidation in water column in situ (VI) was higher than the measured CH$_4$ release from the anoxic intact sediment cores (II), and the CH$_4$ oxidation potential of the entire water column was greater than the CH$_4$ production potential of the sediments (VI). Utsumi et al. (1998) estimated that up to 94% of the dissolved CH$_4$ can be oxidized in the water column.

As for the seasonal variation in the water column, CH$_4$ oxidation was high and controlled mainly by the availability of CH$_4$ (VI). In situ, the CH$_4$ oxidation rate increased linearly with the water CH$_4$ concentration. The highest CH$_4$ oxidation rates in situ were measured in the hypolimnion during summer and winter stratification periods when the CH$_4$ concentrations were the highest. In comparison, the epilimnion showed negligible CH$_4$ oxidation during the stratifications as a result of a low CH$_4$ content. The depth-integrated CH$_4$ oxidation in the entire water column was most significant during the stratification periods. The CH$_4$ concentrations and oxidation rates were low throughout the water column during spring and autumn turnovers. In autumn, the water column consumed some CH$_4$ but in spring, just after the ice-melt, the overall water column showed net production of CH$_4$. Also Striegeler and Michelmerhizen (1998) measured low CH$_4$ oxidation rates during spring overturn. After the break-up of the ice-cover, CH$_4$ stored under the ice (Fig. 1C) is likely to be released into the atmosphere without being subjected to significant CH$_4$ oxidation (VI).

The content of O$_2$ also affected the kinetics of CH$_4$ oxidation in the water (VI). The oxidation of CH$_4$ proceeded at a higher rate with high O$_2$ (30-380 µM) concentrations than with low (<30 µM) O$_2$ concentrations. In summer, when the O$_2$ deficiency lasted only for a short period, microbes were not adapted to oxidize CH$_4$ at low O$_2$ concentrations. However, in winter, when the hypolimnion had been anoxic for weeks, significant CH$_4$ oxidation was observed at low O$_2$ concentrations indicating that the microbial population

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was adapted to anaerobic or microaerobic conditions (VI). The amount of CH$_4$ consumed from the water in winter would have required over 6 times the amount of O$_2$ present in the water. Thus, other electron acceptors must have been involved in the oxidation of CH$_4$. Anaerobic CH$_4$ oxidation has been previously observed in freshwaters, yet the mechanism for this kind of oxidation is unknown (Panganiban et al., 1979; Zehnder and Brock, 1980).

3.2 Sediment gas and nutrient dynamics in changing environment

3.2.1 Depletion in oxygen content

The depletion of O$_2$ occurs during stratification in hypolimnion of eutrophic lakes (Fig. 1A) as a result of a large amount of O$_2$ consuming organic matter. A significant finding was that the depletion of O$_2$ from the overlying water did not change the carbon mineralization rates in sediments (II, IV), but decreased the sediment redox potential and changed degradation pathways towards the anaerobic processes as seen in the enhanced release of CH$_4$ (I-IV). Anaerobic processes are important in the water logged sediments since only a few millimetres of the surface sediments are oxic even with the presence of O$_2$ in the overlying water (II-IV). Availability of O$_2$ evidently increases mineralization in surface sediments, but this increase does not considerably account for the total mineralization rate of the entire sediment profile. The results of this study agree with the conclusions of Wellsbury et al. (1996) and Sweerts et al. (1991) on the importance of anaerobic C mineralization in freshwater sediments. Furthermore, the bacterial growth in lake water column has been similar in oxic and anoxic conditions (Bastviken et al., 2001).

The depletion of O$_2$ significantly increased the sediment CH$_4$ release (I-IV). In anoxic conditions, contribution of CH$_4$ to the total GWP of the sedimentary gases was up to 77% (Fig. 4). When O$_2$ is present at the sediment surface, methanogenesis is inhibited and a part of the CH$_4$ diffused from deeper anoxic sediments is oxidized. With oxic overlying water sediment CH$_4$ release can be negligible (Frenzel et al., 1990; Sweerts et al., 1996), like it was from the shallow profundal sediments of Lake Kevätön (II, III). In the shallow profundal sediments, the CH$_4$ oxidation potential was similar to the sediment CH$_4$ production potential (VI). However, the deep profundal sediments released some CH$_4$ also with the oxic flow (II), and their CH$_4$ production potential was higher than the oxidation potential (VI). The oxidation of CH$_4$ at sediment surface (I-V) and in hypolimnion (VI) is important in contributing to lake anoxia. It was estimated that in summer stratification up to 50% of the O$_2$ consumed in the hypolimnion of Lake Kevätön was used in CH$_4$ oxidation (VI). Methane oxidation has been reported to account to between ~10 to 64% of the total sediment O$_2$ consumption (Kuivila et al., 1998, Frenzel et al., 1990, Sweerts et al., 1996). Especially in eutrophic sediments with a high organic matter content, the
production of CH$_4$ is high and its oxidation greatly contributes to lake anoxia. Furthermore, when CH$_4$ is produced at high rates, it easily evolves from the sediments as bubbles. Methane in bubbles is not susceptible to oxidation and is therefore released into the atmosphere (Chanton and Whiting, 1995). Ebullition supports high CH$_4$ emissions from Lake Kevätönn during summer stratification (Huttunen et al., 1999), even though the CH$_4$ oxidation potential in the water column is high (VI).

Opposite to CH$_4$ release, shortage of O$_2$ at sediment water interface reduced the release of N$_2$O from the sediments (I-V). As described earlier, the N$_2$O production in sediments was dependent on nitrification, which fuels denitrification by producing NO$_3^-$ and NO$_2^-$. Since the emissions of N$_2$O with the oxic flow were low compared to the CH$_4$ release rates with an anoxic flow, the O$_2$ depletion highly increased total global warming potential (GWP) of the gases produced in the sediments (Fig. 4) (III-V).

Since the mineralization rate in the sediments was not affected by the O$_2$ content of the overlying water, it could be expected that the regeneration rate of nutrients NH$_4^+$ and P from the sediment organic matter was similar in sediments under oxic and anoxic water. However, the depletion of O$_2$ increased the release of both NH$_4^+$ and P from the sediment (I-IV). In anoxic conditions, NH$_4^+$ is not susceptible to oxidation in nitrification, and is released into the overlying water. It seems that in sediments the CH$_4$ oxidizing bacteria can compete successfully with the nitrifying bacteria for O$_2$ (II; III; V; Sweerts et al., 1991; van Luijn et al., 1999). Therefore, CH$_4$ oxidation in sediments favour the release of NH$_4^+$ from sediments. In anoxic conditions, P is in a dissolved form and is therefore released when regenerated from organic compounds (Søndergaard et al., 1990). Furthermore, P previously precipitated to iron(hydr)oxyphosphate in oxic conditions, is released from the precipitate, when Fe$^{3+}$ is reduced to Fe$^{2+}$ (Holdren and Armstrong, 1980) and P can also be released from bacterial cells (de Montigny and Prairie, 1993). In anoxic sediments with plenty of CH$_4$, NH$_4^+$ and P in the pore water, the ebullition of CH$_4$ was a significant factor in transporting the nutrients from sediments into the water column (II).

3.2.2 Increasing temperature

Temperature increased the mineralization of organic matter and the release of CO$_2$, CH$_4$, NH$_4^+$, and P from the sediments (III). In boreal regions, the air temperature is predicted to increase by 1-3°C from year 1860 to 2050 (Mitchell et al., 1995). The same temperature increase in hypolimnion could increase the CO$_2$ production by 13-66% and the CH$_4$ release from anoxic sediments by 13-39% (III). This elevation potential in carbon gas production in future would be possible in Lake Kevätönn since the current assimilation of
carbon in primary production, on average 590 mg C m\(^{-2}\) d\(^{-1}\) (II), exceeds the sediment carbon mineralization rate of 340 mg C m\(^{-2}\) d\(^{-1}\) measured at high temperatures (the shallow profundal) (III). Due to the increase in the carbon gas emissions also the total GWP of the sediment gases will increase with rising temperatures especially in anoxic conditions, which promote the release of CH\(_4\) (III). Warming of 1-3\(^{\circ}\)C could increase the release of NH\(_4^+\) by 14-42% from anoxic sediments and the release of P by 9-57% (III). The high sedimentation rate of nutrients in Lake Kevätöön (H. Tanskanen, personal communication) would fuel the predicted increase in nutrient release. As a result of the increase in nutrient release and the associated increase in primary production and sedimentation, the CH\(_4\) emissions would increase more than predicted merely due to the temperature increase. Furthermore, higher CH\(_4\) production rates would increase ebullition, which would enhances the release of nutrients.

3.2.3 Nitrogen load

*Nitrate* Increase in the availability of NO\(_3^-\) did not enhance mineralization in the sediments, but changed the degradation pathways by decreasing the release of CH\(_4\) (IV). Addition of NO\(_3^-\) to overlying water increased redox potentials in the sediments. Redox potential of 200 mV, which is reported to be the lowest potential allowing the presence of NO\(_3^-\) (Fig. 2), was observed at sediment surface without NO\(_3^-\) addition and down to a depth of 3 cm when 2000 \(\mu\)M NO\(_3^-\) was added. This indicates that after NO\(_3^-\) load there is NO\(_3^-\) in deeper sediments allowing denitrification there. Denitrifying bacteria, which are able to out-compete the methanogens for organic substrates, suppressed CH\(_4\) production in the sediments (Capone and Kiene, 1988). In the shallow profundal sediments with a low organic C content, even a small concentration of NO\(_3^-\) in the overlying water reduced the release of CH\(_4\) (IV). The CH\(_4\) fluxes decreased with the increasing NO\(_3^-\) concentration up to the highest concentration of NO\(_3^-\) tested (2000 \(\mu\)M NO\(_3^-\)). With 2000 \(\mu\)M NO\(_3^-\) in anoxic overlying water, the CH\(_4\) release was similar to the CH\(_4\) release with the oxic flow. We have also found that in the eulittoral sediments of Lake Kevätöön with a high organic C content, the NO\(_3^-\) fertilization reduced the CH\(_4\) release only to some degree (Liikanen et al., 2002). Therefore, the extent to which the denitrifying bacteria were able to out-compete the methanogens depended on the availability of both NO\(_3^-\) and organic carbon.

The addition of NO\(_3^-\) increased the release of N\(_2\)O from the sediments (IV) thus indicating that the N\(_2\)O production in denitrification was greatly limited by the availability of NO\(_3^-\). Excess NO\(_3^-\) obviously increased denitrification rate and may also have inhibited the last step of denitrification, the reduction of N\(_2\)O to N\(_2\), which increases the N\(_2\)O release (Knowles, 1981). The NO\(_3^-\) concentrations are generally low, below 10 \(\mu\)M (Henriksen et al., 1997) in freshwater environments, and therefore NO\(_3^-\) is a factor generally limiting
denitrification (Seitzinger, 1988). It was established that the N₂O fluxes from the sediments increased linearly with NO₃⁻ concentration under anoxic water. The highest N₂O emission of 31 000 µg m⁻² d⁻¹ measured with 2000 µM NO₃⁻ was higher than the N₂O fluxes measured from boreal, organic agricultural soils (Regina et al., 1996; Nykänen et al., 1995). Even higher N₂O emissions i.e. up to 61 440 µg m⁻² d⁻¹ were detected from the eulittoral sediments of Kevätöen fertilized with 3 g NO₃⁻-N m⁻² (Liikanen et al., 2002). These fluxes are similar to the highest N₂O fluxes previously measured from ecosystems with a high NO₃⁻ availability, such as organic agricultural soils (Granli and Böckmann, 1994) and rivers (Garcia-Ruiz et al., 1998 and 1999; McMahon and Dennehy, 1999). Thus, in polluted freshwaters, where NO₃⁻ can occur in concentrations up to 700 µM (Wetzel, 2001), N₂O emissions can be significant.

The effect of NO₃⁻ on the total global warming potential (GWP) of the sedimentary greenhouse gases depends on the loading rate. High loads of NO₃⁻, more than 100 µM NO₃⁻, e.g. from agriculture or wastewaters drastically increased the total GWP of the gases produced in the sediments. This is a result of increased N₂O release, whose warming capacity cannot be compensated by the decrease in the CH₄ release caused by NO₃⁻. The maximum total GWP of the released gases, 7130 mg CO₂ eqv m⁻² d⁻¹, was observed with the highest availability of NO₃⁻, then the contribution of N₂O was 87% (IV). However, with the slightly increased NO₃⁻ availability, below 30 µM, the total GWP of the gases decreased since the decrease in the CH₄ release compensates the N₂O release.

**Ammonium** The increased availability of NH₄⁺ did not affect the sediment gas dynamics (V). Ammonium did not decrease the CH₄ oxidation. In freshwaters with a high availability of CH₄ and a low O₂ content, methanotrophs out-compete NH₄⁺ oxidizing bacteria (nitrifiers) for O₂ (II; III; V; Sweerts et al., 1991; Roy and Knowles, 1994; van Luij et al. 1999) due to having a higher affinity for O₂ than nitrifiers (Megraw and Knowles, 1987). The addition of NH₄⁺ did not enhance the N₂O production in sediments (V), probably since the nitrification in sediments was limited by O₂ rather than NH₄⁺. In nitrifying sediments, N₂O could have been produced either in nitrification or denitrification. However, the highest NH₄⁺ addition of 15 000 µM NH₄⁺ increased nitrification. The increased nitrification activity decreased the availability of O₂ at sediment-water interface and accumulation of NO₃⁻ and N₂O, which were evidently effectively reduced to N₂ in denitrification (V). Thereby, extremely high NH₄⁺ load may accelerate the development of anoxia, reduce N₂O release and enhance CH₄ production.
3.2.4 Sulphate load

Increased availability of $\text{SO}_4^{2-}$, which in freshwaters can originate from acid deposition, did not considerably affect carbon mineralization, but changed the degradation pathways (IV). The addition of $\text{SO}_4^{2-}$ decreased the CH$_4$ release in the shallow profundal sediments with a low organic C content, but did not affect the CH$_4$ release from the highly organic deep profundal sediments. In the shallow profundal sediment, $\text{SO}_4^{2-}$ reduced the CH$_4$ release less than that of NO$_3^-$ and O$_2$. The highest inhibition of CH$_4$ release was achieved at a concentration of 300 $\mu$M $\text{SO}_4^{2-}$ in the overlying water. Thus, sulfate-reducing bacteria were able to partly out-compete methanogens in the shallow profundal with a low organic carbon content. However, in the deep profundal sediments, the high availability of organic substrates evidently allowed activity of methanogenic bacteria even though they were to compete their substrates with sulphate reducers. Therefore, as with denitrifying bacteria, the extent to which the sulphate reducers were able to out-compete the methanogens depended on the amount of organic substrates and $\text{SO}_4^{2-}$ available. Previously, methanogenesis has been reported to be inhibited by $\text{SO}_4^{2-}$ at concentrations from 60 to 500 $\mu$M (Winfrey and Zeikus, 1977; Jones et al., 1982; Lovley and Klug, 1983).

Currently in Finland and Europe, freshwater $\text{SO}_4^{2-}$ concentrations are decreasing due to the reduction in acid deposition (Stoddard et al., 1999). This decrease in $\text{SO}_4^{2-}$ availability can therefore increase the CH$_4$ release and the total GWP of the sedimentary gases especially in the sediments with a low organic C content. However, in highly organic sediments, the changes in water $\text{SO}_4^{2-}$ concentration have probably no impact on the sediment CH$_4$ dynamics. It can therefore be concluded that the future changes in the $\text{SO}_4^{2-}$ availability will effect the total GWP of sedimentary gases less than the changes in the NO$_3^-$ load or O$_2$ depletion.
4 CONCLUSIONS

*Methane and carbon dioxide* Eutrophic lake sediments had a high capacity for producing CO₂ and CH₄ as high primary production provides great amounts of degradable organic matter. Carbon mineralization, i.e. production of CO₂ and CH₄, was highest in the littoral sediment where plants produced fresh organic material and in the deep profundal sediments which received organic matter (accumulation area) from other parts of the lake. In small and shallow boreal lakes with long shore lines, the littoral zone with high CH₄ emission rates can be a major source of atmospheric CH₄. In contrast, the deep profundal zone, if its coverage is small, does not contribute significantly to the total CH₄ emissions from lakes. From the littoral and deep profundal sediments with high CH₄ production, CH₄ was transported in bubbles to the atmosphere.

Low O₂ availability did not affect the carbon mineralization rate, but did change the degradation pathways towards the anaerobic processes as seen in the enhanced release of CH₄. In anoxic conditions, CH₄ accounted for up to 77% of the total global warming potential (GWP) of the gases (CO₂, CH₄, N₂O) released from the sediments. In oxic conditions, CO₂ contributed up to 92%, of the total GWP. With a good O₂ supply, CH₄ was effectively oxidized in the uppermost sediment layers and in water column resulting in minor CH₄ emissions. Both sediments and water column possessed a high potential to oxidize CH₄. In sediments, the CH₄ oxidation potential was close to the sediment CH₄ production potential and the CH₄ oxidation potential integrated for the whole water column was much higher than the production potential of the sediments. Some CH₄ was also oxidized in anaerobic or microaerobic conditions in the water column in winter. However, high amounts of CH₄ did accumulate under the ice during winter, thus being released to the atmosphere after the ice-melt, since in spring CH₄ oxidation in the water column was negligible.

The predicted increase of 1-3°C in temperature in boreal regions may increase sediment CO₂ production by up to ~70% and release of CH₄ from anoxic sediments by up to ~50%. The enhanced mineralization with warming will increase sediment O₂ consumption and development of anoxia would further favour the release of CH₄. Changes in NO₃⁻ and SO₄²⁻ availabilities did not affect the carbon mineralization rate in the sediments of Lake Kevätön, but changed the degradation pathways (Table 3). Increased NO₃⁻ and SO₄²⁻ availability decreased the release of CH₄ from the sediment with a low organic matter content. The availability of NH₄⁺ did not affect sediment CH₄ dynamics.

*Nitrous oxide* When there was no external nitrogen load, the sediments were minor sources of N₂O since a low availability of NO₃⁻ limited their N₂O production, and the
proportion of N₂O out of the total GWP of the sedimentary gases was negligible. In sediments, production of N₂O is closely coupled to nitrification, which produces NO₃⁻ for denitrification. Nitrification in sediments was limited by the low O₂ availability whereas NH₄⁺ was always present in excess. Therefore, some production of N₂O occurred only with a good O₂ availability when NO₃⁻ was generated. The sediments producing N₂O differed from those producing CH₄. In sediments with a high CH₄ production, intense CH₄ oxidation in surface sediments consumed O₂ and thus suppressed nitrification and N₂O production.

The optimum temperature for N₂O production was 16°C, at higher temperatures decreased O₂ availability limited nitrification and N₂O production. External NO₃⁻ input increased significantly the N₂O release (Table 3), which then could contribute up to ~90% of the total GWP of the released gases. Extremely high availability of NH₄⁺ increased nitrification and associated O₂ consumption, decreased sediment O₂ availability and accumulation of NO₃⁻ and N₂O, which were evidently reduced to N₂ in denitrification.

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↑ = increasing trend, ↓ = decreasing trend, n.m. = not measured.

Table 3. Effects of temperature and some important water chemical characteristics associated with environmental changes and release of gases and nutrients from sediments.

**Nutrients** Profundal sediments with a high organic matter content were important reservoirs of nutrients. Mineralization in sediments regenerated nutrients, NH₄⁺ and P, which were released in anoxic conditions into the water column. The sediments with high mineralization and nutrient regeneration rates produced also CH₄ at high rates. Methane had particular importance in the release of nutrients: CH₄ produced deeper in anoxic sediments is oxidized at sediment surface contributing to anoxic conditions and presence of nutrients in a dissolved form, and the ebullition of CH₄ created turbulence in sediments.
enhancing the transportation of nutrients from sediments into the water column. The predicted increase of 1-3°C in temperature may increase the release of NH₄⁺ by up to ~40% and the release of P by up to ~60%.

This study established some regulating factors of the processes responsible for greenhouse gas and nutrient dynamics in a small eutrophic lake. These mechanisms need to be studied in other aquatic ecosystems with different characteristics, including various littoral zones, rivers, estuaries and great lakes as well as in man-made water ecosystems, such as water reservoirs and wastewater lagoons, which receive high amounts of allochthonous organic material and nutrients. More basic research has to be done for example to understand the observed anaerobic or microaerobic CH₄ oxidation which can have major global importance in CH₄ dynamics in freshwater ecosystems.
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