Fluxes of methane and nitrous oxide from an Indian mangrove

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Fluxes of greenhouse gases, CH$_4$ and N$_2$O, were measured from a mangrove ecosystem of the Cauvery delta (Muthupet) in South India. CH$_4$ emissions were in the range between 18.99 and 37.53 mg/sq. m/d, with an average of 25.21 mg/sq. m/d, whereas N$_2$O emission ranged between 0.41 and 0.80 mg/sq. m/d (average of 0.62 mg/sq. m/d). The emission of CH$_4$ and N$_2$O correlated positively with the number of pneumatophores. In addition to the flux measurements, different parts of the roots of *Avicennia marina* were quantified for CH$_4$ concentration. Invariably in all the seasons, measured CH$_4$ concentrations were high in the cable roots, with gradual decrease through the pneumatophores below water level and the above water level. This clearly indicates the transport of CH$_4$ through the roots. We were able to establish that CH$_4$ was released passively through the mangrove pneumatophores and is also a source to the atmosphere. We present some additional information on transport mechanisms of CH$_4$ through the pneumatophores and bubble release from the mangrove ecosystems.

Keywords: Mangroves, methane, nitrous oxide, pneumatophores.

Methane (CH$_4$) and nitrous oxide (N$_2$O) are atmospheric trace gases and contribute about 15 (CH$_4$) and 6% (N$_2$O) to the greenhouse effect. Both N$_2$O and CH$_4$ have a long atmospheric residence time of about 114 and 12 years respectively, and since they are key compounds in the chemical reaction cycles of the troposphere and the stratosphere, their potential to directly or indirectly influence global climate is high. Although atmospheric loading of N$_2$O is lower than CH$_4$, globally, the former is 310 times a more potent greenhouse gas (GHG) than CO$_2$ on a 100 yr timescale, while CH$_4$ is only 21 times more potent. During 1990–99, CH$_4$ and N$_2$O concentrations increased by 0.007 and 0.008 ppb/yr respectively. In recent years, although the slope of increase for CH$_4$ has slowed down, its concentration has doubled during the last 100 years. The current tropospheric concentration of N$_2$O is 317 ppb and that of CH$_4$ is 1.75 ppm.

Among the biogenic sources of CH$_4$ and N$_2$O, ecosystems in which anoxic conditions prevail are of particular significance, because under such conditions CH$_4$ and N$_2$O are produced as intermediate and end-products in microbial processes (methanogenesis, denitrification). Such emission has been observed in a number of natural wetlands that are considered to contribute between 22 and 40% to global source strength of CH$_4$ and N$_2$O respectively. Mangroves occupy the intertidal zone of tropical and subtropical regions of the world, contributing to the biogenic sources of GHGs. They act as a buffer zone between land and sea as they prevent erosion, reduce currents, attenuate waves and encourage sediment deposition and accretion. These ecosystems are characterized by a high rate of nutrient turnover and are therefore considered highly productive sources of organic matter. Due to tidal flooding, anoxic conditions prevail at least periodically in the soil of mangrove ecosystems. Under these conditions denitrification and methanogenesis may significantly contribute to nutrient turnover. From these features it may be concluded that anoxic wetlands are potential sources of CH$_4$ and N$_2$O since at a high rate of nutrient turnover, small leaks in nutrient cycles may result in high rates of emission of these GHGs. However, despite the proposed possibility of measurable methane or nitrogen oxides as sources of GHGs, detailed information on the contribution of mangrove wetlands to the overall source strength of natural wetlands for GHGs is scarce.

Materials and methods

Study site and vegetation

Muthupet mangrove is located at 10°20’N and 79°32’E of South India, covering an area of 68.03 sq. km, the majority of which is covered by mangrove creeks. Five rivers

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flow into these mangroves, among which the Koraiyar is quantitatively the most important (Figure 1). These rivers are highly seasonal and freshwater input into the system is directly dependent on rainfall. The rivers feed a network of mangrove creeks, which run into an extensive lagoon (Mullicapallam lagoon), pass through Palk Strait and finally join the Bay of Bengal. These mangroves are subjected to a variety of anthropogenic inputs, including aquaculture (shrimp-farming effluent), and more diffuse and seasonal agricultural run-off. The system is typically characterized by a neap tidal range of ∼0.4 m and a spring range of ∼1 m. We sampled the mangrove system spatially at 15 locations that were selected based on inflow of rivers, run-off from agricultural sources and aquaculture outlets to the Bay of Bengal (Figure 1). The dominant species found is *Avicennia marina*, which is high salinity-tolerant. *Avicennia* has a highly differentiated root system with cable roots running parallel to the sediment surface and pneumatophores projecting from the cable roots upwards and connecting it to the atmosphere. Our measurements therefore included the enclosure of these pneumatophores (numbers were enumerated during sampling) within the static chamber to determine the flux of CH$_4$ and N$_2$O through the pneumatophores, as described below.

*Dissolved CH$_4$ in surface water*

Temporal and spatial measurements of dissolved CH$_4$ were made in 15 locations from March 2002 to March 2003 (five seasons). Serum bottles of 100 ml capacity were filled with surface water and 0.1 ml of saturated mercuric chloride (HgCl$_2$) was added to inhibit phytoplankton activity. The bottles were sealed and transported to the laboratory for analysis of dissolved CH$_4$. Exactly 50 ml of the surface water was subsequently transferred into 100 ml sealed bottles, which were pre-flushed with N$_2$. The bottles were hand-equilibrated for 10 min and the gas taken from the headspace was analysed under the gas chromatograph conditions, as described in detail below. For dissolved CH$_4$ measurements the headspace mixing ratios were converted to concentrations using a primary standard (14.2 ppmv CH$_4$ in N$_2$, National Physical Laboratory (NPL), New Delhi), which was run prior and between analyses.

*Flux measurements (static chamber)*

Seasonal measurements of CH$_4$ eflux at the sediment–water interface were made during the wet (September and December 2002) and dry (March 2002, June 2002 and March 2003) seasons at Forest Camp in the Muthupet mangrove covering the pneumatophores of *A. marina* as was done in previous studies. Additionally, water-level fluctuations due to tides and air temperature were measured in parallel. Methane emission was calculated from the linear increase of mixing ratio with time, taking into account the actual volumes of the chamber.

*Gas bubbles and aerenchyma*

Gas bubbles entrapped in the sediments were collected using an inverted glass funnel (20 cm dia) fitted with a silicone rubber septum in its stem between 10 and 20 m
from the location where the static chamber was placed\textsuperscript{15,19}. Gas samples were also collected from the aerichyma of the cable roots (CR), and from the pneumatophores, which were submerged (below water level: BWL) and those that were exposed (above water level: AWL). Gas samples from at least five pneumatophores were drawn using a 1 ml syringe and were transferred to 5 ml Venoject-tubes. The cable root, located between 20 and 25 cm from the sediment surface, was sampled by excavating the sediment along the root (pneumatophore) zone until it was exposed. Care was taken at all times (during excavation) to retain about 3–5 cm of standing water to avoid artifacts.

Gas analysis

Methane measurements were carried out using standard procedure\textsuperscript{15}. Pure methane (99.95%) and a secondary standard with a concentration of 1195 ± 2.6 ppm, CH\textsubscript{4} in nitrogen (Bhoruka Gases, Bangalore) were used for the analysis of CH\textsubscript{4} in gas bubbles and in the aerichyma of cable roots and pneumatophores respectively.

Nitrous-oxide measurements were carried out in the HP-GC 5890 fitted with an Electron Capture Detector and a Poropak-Q column (mesh: 80/100). The column, injector and detector temperatures were 60, 100 and 250°C, respectively. The carrier was nitrogen at a flow rate of about 20 ml/min. For flux measurements, the gas chromatograph was calibrated using a secondary standard 5.78 ± 0.35 ppm, N\textsubscript{2}O in nitrogen (NPL).

Gas samples were taken using pressure-lock syringes (Dynatech, Baton Rouge, USA) from the sampling tubes for gas chromatographic analysis. Linearity check of the gas chromatograph was made on a regular basis by injecting various volumes (0.1 to 1.0 ml) of the appropriate standards for CH\textsubscript{4} and N\textsubscript{2}O.

Results

Fluxes of CH\textsubscript{4} and N\textsubscript{2}O for five different seasons (Figure 2) indicate a distinct seasonal variability, with peak emissions during monsoon (December 2002) and the least in September for both trace gases. CH\textsubscript{4} flux ranged between 18.69 ± 0.92 and 37.47 ± 0.52 mg/sq. m/d, with a mean of 25.10 ± 0.80 mg/sq. m/d. For N\textsubscript{2}O, the flux varied from 0.43 ± 0.02 to 0.81 ± 0.066 mg/sq. m/d, with an average of 0.63 ± 0.030 mg/sq. m/d. We observed a strong positive correlation ($r^2 = 0.82$) between the fluxes of CH\textsubscript{4} and N\textsubscript{2}O in this study. In addition we also determined the effect of pneumatophores on the exchange of gases from the sediment to the atmosphere, by correlating emission with the number of pneumatophores (Figure 3). A strong positive correlation between the number of pneumatophores and trace gases (CH\textsubscript{4}, $r^2 = 0.96$ and N\textsubscript{2}O, $r^2 = 0.81$) was observed in the present study.

There was a strong CH\textsubscript{4} gradient from soil through roots to the atmosphere (Figure 4) during all the seasons.
ference in gas concentration (mol/l) between the air to water phases on either side of the interface. Various empirical relationships have been derived for estimating k. Another relationship for estuaries (using data from the Hudson River estuary), takes into account non-wind speed-driven turbulence due to interaction with the seafloor. For this reason, all three methods were included here to aid comparison with similar studies, although the model developed by Clark is probably the most applicable to Muthupet mangrove. Muthupet mangrove functions as a significant CH₄ source and measurement of dissolved CH₄ in the surface water indicated distinct seasonal dynamics. The mean dissolved CH₄ concentration for all seasons and spatially was 225 ± 41.0 nmol/l, ranging from 182.75 ± 3.2 nmol/l in September 2002 to 267.69 ± 2.65 nmol/l in December 2002 (Figure 5). There was a decrease in estuarine CH₄ concentration with increasing salinity during all the seasons and a strong negative correlation ($r^2 = -0.8$) was observed (Figure 6). Dissolved O₂ concentration correlated weak negative correlation with dissolved CH₄ concentration ($r^2 = -0.55$), implying increased CH₄ fluxes at low O₂ concentrations, although not very obvious during our study period. We also did not observe any distinct changes in CH₄ concentration due to seasonal variations in dissolved nutrients – NO₃, NO₂ and PO₄ (with the exception of NH₄, which showed positive correlation; $r^2 = 0.76$); probably due to the fact that the mangrove ecosystems are in general a low-nutrient environment, especially with reference to their dissolved concentrations (Table 1).

Discussion

The present work combined both CH₄ and N₂O emission measurements from the Indian mangrove ecosystems. The highest emissions were observed just after the monsoon season (December), which could have resulted from anthropogenic inputs from the seasonal rivers. The present results seem to be in accordance with earlier studies conducted by Purvaja et al. on CH₄ emission from similar mangrove ecosystem in South India (Pichavaram). Table 2 compares the results of this study with similar CH₄ flux data for tropical coastal systems. We have observed an average flux of 9.2 g CH₄/sq. m/yr, as also reported by Purvaja et al. for the Pichavaram mangrove (10.0 g CH₄/sq. m/yr). Kreuzwieser et al. conducted similar measurements of trace gases from Australian mangroves and observed comparatively low fluxes, 0.18–3.07 g CH₄/sq. m/yr and 0.02–0.12 g N₂O/sq. m/yr. The higher flux of CH₄ (from the Australian mangroves) in the current study is due to anthropogenic additions from land-based sources. CH₄ emission in the Vembanad Lake (highly impacted by coconut husk decomposition) was about 1690 g/sq. m/yr, more than two orders of magnitude higher than what was observed in the present study due to high anoxic stress. N₂O emission rates from Muthupet mangrove varied between 0.41 and 0.77 μmol/sq. m/h. Similar values for N₂O emissions were recently reported from Australian mangroves and other tropical ecosystems. Corredor et al. reported highest N₂O emission rates from mangroves of Puerto Rico and attributed this to the availability of nitrogenous substrates.

The increase in CH₄ and N₂O concentration with the number of pneumatophores substantiated the fact that vegetation also plays a major role in the transport of gases to the atmosphere. Schutz et al. and Singh and Singh studied the role of wetland plants as pathways for
Table 1. Environmental factors and nutrients from surface-water samples (n = 15) of the Muthupet mangrove

<table>
<thead>
<tr>
<th>Season</th>
<th>pH</th>
<th>EC (μS/cm)</th>
<th>Salinity</th>
<th>Dissolved oxygen (mg/l)</th>
<th>NH₄ (μmol/l)</th>
<th>NO₃ (μmol/l)</th>
<th>NO₂ (μmol/l)</th>
<th>PO₄ (μmol/l)</th>
<th>SO₄ (μmol/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jan-02</td>
<td>7.4 ± 0.1</td>
<td>45.8 ± 12</td>
<td>22.9 ± 6</td>
<td>25.2 ± 6.1</td>
<td>9.4 ± 2.8</td>
<td>34.21 ± 14.3</td>
<td>3.31 ± 0.8</td>
<td>3.02 ± 0.8</td>
<td>0.87 ± 0.6</td>
</tr>
<tr>
<td>Sep-02</td>
<td>7.4 ± 0.1</td>
<td>28.6 ± 27</td>
<td>14.1 ± 7</td>
<td>22.9 ± 6.6</td>
<td>8.59 ± 2.3</td>
<td>64.58 ± 33.3</td>
<td>7.28 ± 4.2</td>
<td>1.74 ± 1.1</td>
<td>0.81 ± 0.2</td>
</tr>
<tr>
<td>Dec-02</td>
<td>7.2 ± 0.1</td>
<td>7.0 ± 2.6</td>
<td>3.5 ± 1.3</td>
<td>19.6 ± 6.9</td>
<td>12.8 ± 3.6</td>
<td>78.45 ± 11.7</td>
<td>5.06 ± 2.4</td>
<td>0.76 ± 0.4</td>
<td>0.45 ± 0.2</td>
</tr>
<tr>
<td>Mar-03</td>
<td>7.0 ± 0.2</td>
<td>7.1 ± 0.8</td>
<td>3.6 ± 0.4</td>
<td>22.5 ± 6.8</td>
<td>10.6 ± 1.7</td>
<td>32.22 ± 18</td>
<td>4.23 ± 1.8</td>
<td>2.59 ± 1.0</td>
<td>2.90 ± 0.3</td>
</tr>
<tr>
<td>Average</td>
<td>7.3 ± 0.2</td>
<td>22.2 ± 18.8</td>
<td>11.0 ± 9.4</td>
<td>22.6 ± 2.8</td>
<td>10.3 ± 1.8</td>
<td>52.37 ± 22.84</td>
<td>4.97 ± 1.7</td>
<td>2.02 ± 1.0</td>
<td>1.26 ± 1.11</td>
</tr>
</tbody>
</table>

Figure 6. Correlation of dissolved CH₄ concentration with salinity.

Gas transport from the root zone into the atmosphere, whereas Kreuzwieser et al. demonstrated clearly the role of Australian mangrove vegetation as a transport path for CH₄ and N₂O emission via their aerenchyma. It has been further strengthened by the recent findings of Purvaja et al. from the Pichavaram mangrove.

Methane concentration in gas bubbles was high (Figure 4), reaching values comparable with those reported from freshwater wetlands and rice fields. The concentra-
Table 2. Methane emission from mangroves and wetlands (updated from Purvaja et al.11)

<table>
<thead>
<tr>
<th>Ecosystem/site</th>
<th>Latitude</th>
<th>Flux (mg CH₄/ sq. m/d)</th>
<th>Flux (g CH₄/ sq. m/yr)</th>
<th>Notes and references</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mangrove (Avicennia), Muthupet, South India</td>
<td>10°N</td>
<td>18.9–37.5</td>
<td>9.2</td>
<td>Chamber method; flux through pneumatophores; the present study</td>
</tr>
<tr>
<td>Mangrove (Avicennia), Pichavaram, South India</td>
<td>11°N</td>
<td>7.4–63.7</td>
<td>10</td>
<td>Chamber method; flux through pneumatophores; 15</td>
</tr>
<tr>
<td>Pulicat Lake, South India (in press)</td>
<td>13°N</td>
<td>18.48–25.36</td>
<td>8</td>
<td>Chamber method; sediment–water fluxes; 36</td>
</tr>
<tr>
<td>Mangroves (Rhzophora), Queensland, Australia</td>
<td>27°S</td>
<td>0.02–0.35</td>
<td>–</td>
<td>Chamber method; flux through pneumatophores; 23</td>
</tr>
<tr>
<td>Coastal South Kalimantan, Indonesia</td>
<td>–</td>
<td>3.28–5.21</td>
<td>1.2–1.9</td>
<td>Chamber method; 37</td>
</tr>
<tr>
<td>Verbanad Lake, South India</td>
<td>9°N</td>
<td>223.2–4632</td>
<td>1690</td>
<td>Chamber method; sediment water fluxes; 24</td>
</tr>
<tr>
<td>Ranong Mangroves, Thailand</td>
<td>9.5°N</td>
<td>0.19–0.52</td>
<td>–</td>
<td>Chamber method; sediment water fluxes; 38</td>
</tr>
<tr>
<td>Mangroves (Braquiera), Hainan</td>
<td>18°N</td>
<td>0.12–0.39</td>
<td>–</td>
<td>Chamber method; water surface and soil; 39</td>
</tr>
<tr>
<td>Mangrove, Sunderban</td>
<td>22°N</td>
<td>–16–32</td>
<td>43</td>
<td>Gradient, micrometeorological measurement; 40</td>
</tr>
<tr>
<td>Mangrove (Avicennia), Puerto Rico</td>
<td>18°N</td>
<td>4–42</td>
<td>n.a.</td>
<td>Chamber method; gradient from pristine to polluted; 41</td>
</tr>
<tr>
<td>Hudson Bay Lowlands, coastal marshes</td>
<td>50°–58°N</td>
<td>84.3</td>
<td>8</td>
<td>Chamber method; coastal marshes; 42</td>
</tr>
<tr>
<td>Hudson Bay Lowlands, open fens</td>
<td>50°–58°N</td>
<td>78.6</td>
<td>6.7</td>
<td>Chamber method; coastal marshes; 42</td>
</tr>
</tbody>
</table>

n.a.: not available.

Table 3. Comparison of nitrous oxide emissions from mangrove ecosystems world-wide using closed chamber

<table>
<thead>
<tr>
<th>Ecosystem/site</th>
<th>Latitude</th>
<th>N₂O flux (µmol/sq. m/h)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mangrove (Avicennia), Muthupet, South India</td>
<td>10°N</td>
<td>0.41–0.77</td>
<td>This study</td>
</tr>
<tr>
<td>Mangroves, Queensland, Australia</td>
<td>27°S</td>
<td>–0.045–0.32</td>
<td>23</td>
</tr>
<tr>
<td>Red mangrove fringe, South West Coast of Puerto Rico</td>
<td>17°N</td>
<td>0.05</td>
<td>43</td>
</tr>
<tr>
<td>Red mangroves, Puerto Rico</td>
<td>17°N</td>
<td>0.54</td>
<td>44</td>
</tr>
<tr>
<td>Mangroves, Puerto Rico</td>
<td>17°N</td>
<td>0.12–7.8</td>
<td>25</td>
</tr>
</tbody>
</table>

Conclusion

In summary, the present results support the view that mangroves act as sources of atmospheric CH₄ and N₂O. In addition, vegetation plays an important role as transport path for CH₄ and N₂O emissions, as previously observed for herbaceous species in other wetland ecosystems33–35. Therefore, in order to extrapolate CH₄ emissions from mangrove to global levels, composition, distribution of vegetation and quantity of different root types should also be taken into account.

RESEARCH ARTICLES


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