CHAPTER 5

pCO₂ AND DISSOLVED CH₄ IN MANGROVE SURROUNDING WATERS OF THE SUNDARBANS AND PICHAVARAM

Mangrove ecosystems found along the tropical and sub tropical coastal margins are one of the most productive ecosystems of the world (Odum and Heald 1975, Alongi et al 2001). They are characterized by high turnover rates of organic matter and nutrient cycling between marine and terrestrial ecosystems (Nedwell et al 1994). They are located in estuarine zones at the land ocean interface and characterized by strong physicochemical gradients, enhanced biological activity and intense sedimentation and resuspension (Abril and Borges 2004). pCO₂ and dissolved CH₄ in the open ocean waters are usually slightly saturated or close to saturation (200 - 390 µatm for pCO₂ and 2 - 3 nmol l⁻¹ for CH₄) whereas those in the coastal zone can be orders of magnitude higher (Wang et al 2000, Amouroux et al 2002, Middelburg et al 2002). Many studies indicate that most of the C produced in mangrove systems is stored in sediments due to limited export of plant litter and therefore these systems act as a sink for C (Robertson et al 1992, Kristensen et al 1995, Alongi et al 1998). In contrast other studies report that nutrient outwelling from mangroves can exceed riverine fluxes (Dittmar and Lara 2001b). Mangrove litter under anoxic condition of the sediment and at high temperatures could be a strong source of atmospheric CH₄ (Purvaja and Ramesh 2001). Therefore very little is known about the sediment accumulation, mineralization and burial of OC in mangrove forests (Alongi et al 2001).
The surface area of mangrove ecosystems worldwide is declining by 2 % yr\(^{-1}\) resulting in major changes in the coastal C cycle (Duarte et al 2005). Land use change would also affect the C stocks in woods and soils. Anthropogenic processes, responsible for the conversion of a productive estuary to a heterotrophic one (Frankignoulle et al 1998, Mukhopadhyay et al 2002a), further complicates the uncertainty of the estimation of unaccounted sinks. This may result in blooming of phytoplankton and may change the efficiency of the biological pump. Again, river runoff can also cause the considerable dilution of coastal water, which can change the solubility pump. Despite the important role played by mangroves in C cycling relatively little is known about it (Biswas et al 2004).

In this study an attempt has been made to understand a part of C cycle in terms of concentrations of pCO\(_2\) and CH\(_4\) and their fluxes in mangrove surrounding waters of anthropogenically impacted mangrove forests. For this purpose comparison of trace gas measurements were made from the largest mangrove in the world, the Sundarbans and another ecologically important estuary in South India the Pichavaram mangroves (Chapter 1, Table 1.3). The former is characterized by high tidal range with strong bi-directional currents. The main river channels are funnel-shaped with extensive tidal-flats, colonized by mangroves. It is a tide dominated allochthonous type of mangrove ecosystem. The latter is a river dominated allochthonous type of mangrove ecosystem. It is characterized by rapid deposition of terrigenous material and delta expands seaward. Mangroves dominate in the region of abundant delta with the absence of mangrove vegetation on the active delta found nearby. These two mangrove ecosystems found on the east coast of India will be discussed in the following sections.
5.1 pCO₂ AND DISSOLVED CH₄ CONCENTRATIONS IN THE JHARKALI MANGROVE SURROUNDING WATERS OF THE SUNDARBANS

The Sundarbans mangrove ecosystem is located in the north eastern coast of Bay of Bengal and is the largest deltaic system on earth. East to west it spans a length of 140 km and extends approximately 52 - 70 km from the sea level far north (Biswas et al 2004). Such a vast area could not be covered and only a part of the mangrove ecosystem, that is the Jharkali area was included in the sampling survey. Other results published on CH₄ and CO₂ in the Sundarbans have dealt only with the variations between different fixed locations (Biswas et al 2007) as well as diurnal and seasonal variations (Biswas et al 2004). However this is the first study that has attempted to measure CO₂ on a continuous basis along the Sundarbans mangrove creek. CH₄ and other parameters were also measured along the creek. This study attempts to understand the spatial variability in the distribution of CO₂ and CH₄ in the Sundarbans. Table 5.1 gives the concentrations of trace gases and other physicochemical parameters that were collected during the sampling survey conducted in December 2006 in the Jharkali mangroves of the Sundarbans.

A transect covering an area of ~40 km was sampled and samples were collected from inside creeks towards the sea. The width of the mangrove creeks along which samples were collected ranged from 10 - 15 m, unlike the Andaman mangroves where width of the creek was more narrow (4 - 5 m). The mangroves that fringed the creeks that were sampled were less dense compared to those that were sampled in Andaman. The Sundarbans mangroves are a tide dominated estuary with high tidal ranges. The mean highest high water level and mean lowest low water level are 5.94 and 0.94 m respectively (Selvam 2003). The gentle slope of the coast along with the high
Tidal amplitude results in penetration of coastal waters up to 110 m inland and in some areas the effect of the tides is felt 300 km inland (Selvam 2003). The salinity variation observed along the surveyed length was low, signifying the influence of upstream freshwaters over a large distance. In order to comprehend the area covered and the small salinity variation observed, all the figures in the forthcoming sections show variation with salinity and insets show the same values with distances covered.

**Table 5.1** Average ± SD and range of pCO$_2$, dissolved CH$_4$ along with their respective saturation percentages and other physicochemical parameters in Jharkali mangroves of the Sundarbans in December 2006

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Parameters (units)</th>
<th>Average ± SD (n=25)</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>pCO$_2$ (µatm)</td>
<td>411 ± 39.7</td>
<td>353 - 476</td>
</tr>
<tr>
<td>2</td>
<td>CO$_2$ (saturation %)</td>
<td>109 ± 10.5</td>
<td>93 - 126</td>
</tr>
<tr>
<td>3</td>
<td>CH$_4$ (nmol l$^{-1}$)</td>
<td>13.3 ± 6.5</td>
<td>5.8 - 30.9</td>
</tr>
<tr>
<td>4</td>
<td>CH$_4$ (saturation %)</td>
<td>607 ± 300.6</td>
<td>267 - 1425</td>
</tr>
<tr>
<td>5</td>
<td>Dissolved O$_2$ (saturation %)</td>
<td>101 ± 5.3</td>
<td>95 - 120</td>
</tr>
<tr>
<td>6</td>
<td>Excess CO$_2$ (µmol kg$^{-1}$)</td>
<td>0.98 ± 1.2</td>
<td>(-0.9) - 3.0</td>
</tr>
<tr>
<td>7</td>
<td>Apparent O$_2$ utilization (µmol kg$^{-1}$)</td>
<td>(-3.4) ± 14.1</td>
<td>(-54.3) - 13.6</td>
</tr>
<tr>
<td>8</td>
<td>Salinity</td>
<td>16.9 ± 0.98</td>
<td>15.2 - 18.3</td>
</tr>
<tr>
<td>9</td>
<td>pH</td>
<td>8.05 ± 0.1</td>
<td>7.84 - 8.27</td>
</tr>
<tr>
<td>10</td>
<td>Water Temperature (°C)</td>
<td>24.8 ± 0.4</td>
<td>24.2 - 25.7</td>
</tr>
<tr>
<td>11</td>
<td>TA (mmol kg$^{-1}$)</td>
<td>2.15 ± 0.08</td>
<td>1.82 - 2.27</td>
</tr>
<tr>
<td>12</td>
<td>DIC (mmol kg$^{-1}$)</td>
<td>2.07 ± 0.06</td>
<td>1.91 - 2.17</td>
</tr>
<tr>
<td>13</td>
<td>POC (µmol l$^{-1}$)</td>
<td>26.7 ± 9.3</td>
<td>8.8 - 47.9</td>
</tr>
<tr>
<td>14</td>
<td>Wind Speed (m s$^{-1}$)</td>
<td>2.6 ± 2.1</td>
<td>0.1 - 9.6</td>
</tr>
</tbody>
</table>
5.1.1 \( pCO_2 \)

\( pCO_2 \) was measured \textit{in situ} in the Jharkali mangroves of the Sundarbans along with other physicochemical parameters. Only spatial measurements could be accomplished due to time constraints. Moreover, since the study on these mangroves was carried out only once the seasonal or diurnal variations of trace gases could not be included in this study. Average \( pCO_2 \) concentrations in the Jharkali mangroves observed in December 2006 was 411 ± 39.7 µatm and ranged from 353 - 476 µatm (109 \% saturation). \( pCO_2 \) was measured \textit{in situ} using the equilibrator technique attached to a NDIR analyser as described in section 3.6.1.5 (Figure 5.1).

![Figure 5.1](image)

**Figure 5.1** The distribution of \( pCO_2 \) with salinity in Jharkali mangroves of the Sundarbans in December 2006. Inset shows its spatial distribution along the transect.

In this Figure 5.1 \( pCO_2 \) concentrations are plotted as a function of salinity. The inset in the figure shows the same concentrations (raw values as obtained during \textit{in situ} analysis), plotted against the transect locations from the starting point of sampling towards the sea. These raw values were
obtained through the NDIR analyser. It measures pCO₂ from the headspace after equilibration at every second and the output is given as values averaged every minute (Section 3.6.1.5). The x axis in the inset does not show the exact distance but is only an approximation and represents the number of points that were measured along the transect. It was observed that there was a gradual increase in pCO₂ along the creek as samples were collected from inside the creek towards the sea. Also pCO₂ was marginally lesser at the lower salinity zone and increased at higher salinities. It was found that pCO₂ remained supersaturated with respect to the atmosphere over the entire spatial survey except over a small area.

5.1.2 Dissolved CH₄

Dissolved CH₄ concentrations at Jharkali mangroves (Sundarbans) were supersaturated with respect to the atmosphere throughout the creek (Figure 5.2).

![Figure 5.2 The distribution of dissolved CH₄ with salinity in Jharkali mangroves of the Sundarbans in December 2006. Inset shows the spatial distribution of dissolved CH₄ along the transect](image)
Concentrations ranged from 5.8 - 30.9 nmol l\(^{-1}\) with an average of 13.3 ± 6.5 nmol l\(^{-1}\). Saturation percentages ranged from 267 - 1425 % with respect to atmospheric equilibrium. Though CH\(_4\) was supersaturated with respect to the atmosphere throughout the sampled creek there was no discernable trend in dissolved CH\(_4\) concentrations. However the location that showed the highest concentration in the sampled creek also had higher salinity.

5.2 FACTORS INFLUENCING pCO\(_2\) AND DISSOLVED CH\(_4\) IN JHARKALI MANGROVE SURROUNDING WATERS

A number of factors affect the concentration of trace gases CO\(_2\) and CH\(_4\) dissolved in the Sundarbans mangrove surrounding waters. The following is an account of only some of the important ones. The Sundarbans mangrove ecosystem is the largest mangrove deltaic system in the world and covers a vast surface area (4,264 km\(^2\) of mangrove forests) governed by a number of geophysical and biogeochemical processes. It is therefore beyond the scope of the present study to evaluate all the processes that may govern the concentrations and fluxes of these gases in the mangrove creeks. The following factors therefore represent the possible causes for pCO\(_2\) and dissolved CH\(_4\) supersaturations observed and their distribution in the mangrove creek. This was derived from measurements made in one such mangrove creek of the Sundarbans, the Jhakali creek.

5.2.1 Salinity

Salinity is known to affect trace gases and most authors have reported an inverse trend of pCO\(_2\) (Abril and Borges 2004, Barnes et al 2006) and CH\(_4\) (Jayakumar et al 2001, Middelburg et al 2002, Abril and Iversen 2002) with salinity. In the other locations studied in this thesis such as in Pichavaram (section 5.4.1) and in Andaman mangroves (chapter 4,
a similar inverse trend with salinity was observed. Concentrations of pCO$_2$ were marginally higher at higher salinities (~18.5) than at lower salinities. Correlation of salinity with pCO$_2$ observed in the Jharkali mangrove waters was $r^2 = -0.64$. However the variation in salinity measured during the sampling survey in the Sundarbans was lesser than 4. Thus it cannot be concluded that in this system pCO$_2$ increases at higher salinities. This small decrease in salinity in spite of the distances covered during the sampling survey indicates the influence of upstream freshwaters.

Nutrient and C dynamics in the creek are significantly influenced by porewater input from the upper forest sediment layer (Lara and Dittmar 1999). Tidal range and flooding frequency determine direction and quantity of nutrient and organic matter exchange between mangroves and ocean (Dittmar and Lara 2001b). Macrotidal regions also enable strong out welling of nutrients to the adjacent coastal areas (Dittmar and Lara 2001a). Dittmar and Lara (2001b) observed that in the nutrient-rich water at low tide is not immediately exported from the mangroves, but transported back at the beginning of flood tide. The macrotidal Sundarbans estuary is also governed by tides and the slight increase in pCO$_2$ with salinity and lack of any discernable trend in CH$_4$ concentrations (correlation with salinity $r^2 = 0.07$) could be explained by tidal mechanism within the estuary. During the flood tide, CO$_2$ and CH$_4$ rich waters from the mangroves mixes with the undersaturated coastal waters and are carried back into the mangrove creeks. At ebb tide a comparatively well mixed water body leaves the mangrove. Therefore in the Jharkali mangrove waters enriched with pCO$_2$ and dissolved CH$_4$ produced within the mangroves is not directly exported. It first returns to the forest and there, mixes with estuarine water.
5.2.2 Dissolved O$_2$

Dissolved O$_2$ varied inversely with pCO$_2$ and saturation percentages of O$_2$ in the Jharkali mangrove waters were $101 \pm 5.3\%$ and ranged from (95 - 120 %). Dissolved O$_2$ was generally supersaturated with respect to the atmosphere in the lower salinity zones while understaturation was observed in samples with higher salinity (Figure 5.3). There was a general decrease in dissolved O$_2$ along the sampled mangrove creek towards the sea (inset of Figure 5.3). Locations with undersaturation of dissolved O$_2$ coincided with those with higher pCO$_2$. This negative correlation ($r^2 = -0.6$) of dissolved O$_2$ and pCO$_2$ suggested a heterotrophic association.

pCO$_2$ concentrations were generally marginally supersaturated with respect to the atmospheric equilibrium over the majority of the system, although it was undersaturated over a small area (Figure 5.1). This CO$_2$ undersaturation corresponded to a peak in observed dissolved O$_2$ (120 % saturated, Figure 5.2). The sampling area was comprised of a series of large water bodies (10 km$^2$) interlinked by waterways of about 100 - 200 metres wide. Figure 5.1 shows the variation of pCO$_2$ with salinity where the range of salinity over the entire sampled area was small (15.2 - 18.3). The distance covered during the sampling survey of ~ 40 km and salinity increased gradually towards the sea. However salinity variation for the entire length sampled was less than 4 and this shows the influence of upstream freshwaters in these mangroves.

Waters adjacent to mangroves (salinities ~ 15 to 16) generally showed lower CO$_2$ saturations (stations 0 - 100). Undersaturation of CO$_2$ is a possible reflection of the hydrological mixing regime (as explained in section 5.2.1) because salinity was also notably lower in the area of CO$_2$ undersaturation (~15) compared with salinities of about 18 in areas of highest CO$_2$ supersaturation (450 - 475 µatm). Inverse relationships between pCO$_2$
and dissolved O$_2$ were observed ($r^2 = -0.6$). Overall the system was net heterotrophic. Absence of any relation between CH$_4$ and O$_2$ ($r^2 = 0.04$) is because the oxygenated waters (average O$_2$ saturation 101 %) of the Jharkali do not favour CH$_4$ producing methanogens which thrive in anoxic conditions (Casper 1992).

![Figure 5.3](image)

**Figure 5.3** The distribution of dissolved O$_2$ with salinity in Jharkali mangroves of the Sundarbans in December 2006. The same data are shown in the inset along the transect

### 5.2.3 Particulate Organic Carbon

Concentrations of POC were generally high and ranged from 8.8 - 47.9 µmol l$^{-1}$ and average concentrations were 26.7 ± 9.3 µmol l$^{-1}$. As seen in Figure 5.4 lower POC concentrations were observed at lower salinities and higher concentrations at higher salinities. In general there was an increase in POC from inside the creek towards the sea (Inset of Figure 5.4). Higher POC coincided with locations with high pCO$_2$. 

Figure 5.4 The distribution of POC with salinity in Jharkali mangroves of the Sundarbans in December 2006. Inset shows the same values along the transect.

Higher pCO₂ coincided with higher concentrations of POC. Though correlation between pCO₂ and POC was minimal ($r^2 = 0.3$), in general higher concentrations of POC were seen in sites which recorded higher pCO₂. This further supports the theory of heterotrophic respiration being the main cause for pCO₂ supersaturations. Therefore in the case of the Jharkali mangroves we find that the major source of CO₂ and CH₄ distribution is the tidal mechanism within the estuary. CO₂ in this case is also produced in the waters as a result of heterotrophic respiration. The high suspended matter with high POC in these waters fuels this heterotrophic respiration.

The observed range of pCO₂ and dissolved CH₄ at Jharkali was somewhat lower than those published so far for mangroves and also when compared with those from the Andaman Islands. This is possibly due to the differences in mangrove densities of the sampled locations in both sites. The
mangrove creeks in Jharkali that were sampled were fringed by short trees and the area sampled was a main distributary and water depth in this region was high (~15 m). CH$_4$ is mainly produced in the mangrove sediments and dissolved CH$_4$ in mangrove surrounding waters is primarily due seepage from porewater (Barnes et al 2006). This explains the higher dissolved CH$_4$ concentrations in the Andaman mangrove creek waters where depths are lower enhancing porewater contribution. TSM was higher in the Andaman mangrove waters which leads to higher pCO$_2$ due to heterotrophic respiration (Chapter 4, section 4.5.4).

5.3 \textbf{pCO$_2$ AND DISSOLVED CH$_4$ IN WATER SURROUNDING PICHAVARAM MANGROVES}

The Pichavaram mangroves cover an area of 13 km$^2$ and have numerous creeks. Dense growth of mangroves covers less than 5 km$^2$ and rest of the 8 km$^2$ have moderately dense and open mangroves (FSI 2005). Twenty four samples were collected along one such creek which leads into the main channel where it joins the Bay of Bengal at the mouth of the estuary (Figure 2.4). The creeks are fringed by mangroves on either side. Selvam et al (2003) have reported that Rhizophora and Avicennia sp. dominate the Pichavaram mangroves with Rhizophora fringing the creeks and Avicennia behind this zone. The mangroves are also sparse towards the sea with mostly exposed tidal flats seen near the mouth. The creek from which samples were collected extended ~ 5 km from inside to the mouth. The width of the creek ranged from 3 - 4 m in the creeks to 8 - 10 m near the mouth. The bar mouth at the estuary mouth is not wide and freshwater discharges are low and extremely seasonal. The tidal ranges at Pichavaram are low (range 0.03 - 0.67 m) (Selvam 2003) when compared to the Andaman and Sundarban mangroves. The observations made during the sampling survey in Pichavaram are given in table 5.2.
Table 5.2 Average ± SD and range of pCO$_2$, dissolved CH$_4$ along with their respective saturation percentages and other physicochemical parameters in the Pichavaram mangroves in April 2007

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Parameters (units)</th>
<th>Average ± SD (n = 24)</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>pCO$_2$ (µatm)</td>
<td>1233 ± 566.9</td>
<td>535 - 2359</td>
</tr>
<tr>
<td>2</td>
<td>CO$_2$ (saturation %)</td>
<td>321 ± 226.1</td>
<td>118 - 968</td>
</tr>
<tr>
<td>3</td>
<td>CH$_4$ (nmol l$^{-1}$)</td>
<td>67.2 ± 79.3</td>
<td>6.1 - 332.6</td>
</tr>
<tr>
<td>4</td>
<td>CH$_4$ (saturation %)</td>
<td>4160 ± 5028.6</td>
<td>388 - 22143</td>
</tr>
<tr>
<td>5</td>
<td>Dissolved O$_2$ (saturation %)</td>
<td>73 ± 14.8</td>
<td>45 - 91</td>
</tr>
<tr>
<td>6</td>
<td>Excess CO$_2$ (µmol kg$^{-1}$)</td>
<td>27.9 ± 26.6</td>
<td>3.7 - 102.6</td>
</tr>
<tr>
<td>7</td>
<td>Apparent O$_2$ utilization (µmol kg$^{-1}$)</td>
<td>65.8 ± 38.6</td>
<td>20.3 - 146.8</td>
</tr>
<tr>
<td>8</td>
<td>Salinity</td>
<td>20.4 ± 6.9</td>
<td>7.5 - 27.6</td>
</tr>
<tr>
<td>9</td>
<td>pH</td>
<td>8.28 ± 0.15</td>
<td>7.95 - 8.66</td>
</tr>
<tr>
<td>10</td>
<td>Water Temperature (°C)</td>
<td>32.5 ± 0.8</td>
<td>30.8 - 34.9</td>
</tr>
<tr>
<td>11</td>
<td>TA (mmol kg$^{-1}$)</td>
<td>2.97 ± 0.37</td>
<td>2.56 - 3.62</td>
</tr>
<tr>
<td>12</td>
<td>DIC (mmol kg$^{-1}$)</td>
<td>2.77 ± 0.45</td>
<td>2.28 - 3.58</td>
</tr>
<tr>
<td>13</td>
<td>Wind Speed (m s$^{-1}$)</td>
<td>3.9 ± 1.0</td>
<td>1.3 - 5.2</td>
</tr>
</tbody>
</table>

5.3.1 pCO$_2$

The concentrations of both pCO$_2$ and dissolved CH$_4$ were supersaturated with respect to the atmosphere. Maximum pCO$_2$ (2359 µatm) and dissolved CH$_4$ (332.6 nmol l$^{-1}$) concentrations were observed at the lower salinity end (7 - 15). Strong negative correlations of pCO$_2$ with dissolved O$_2$ ($r^2 = -0.8$) and negative correlations with salinity ($r^2 = -0.6$) were observed (Figure 5.5).
Figure 5.5  Variation of pCO$_2$ and salinity in Pichavaram mangroves in April 2007

5.3.2  Dissolved CH$_4$

Dissolved CH$_4$ concentrations ranged from 6.1 to 332.6 nmol l$^{-1}$ with an average value of 67 ± 79.3 nmol l$^{-1}$ (Figure 5.6).

Figure 5.6  Variation of dissolved CH$_4$ and salinity in Pichavaram mangroves in April 2007
Dissolved CH$_4$ was therefore supersaturated with respect to the atmosphere throughout the creek and saturation percentages ranged from 388 to 22143 % (average 4160 ± 5028.6 %). CH$_4$ concentrations showed strong negative correlation ($r^2 = -0.7$) with salinity. Dissolved CH$_4$ also showed negative correlation with dissolved O$_2$ ($r^2 = -0.5$).

5.4 FACTORS CONTROLLING pCO$_2$ AND DISSOLVED CH$_4$ IN PICHAVARAM MANGROVE SURROUNDING WATERS

A number of biogeochemical processes control the concentrations of these trace gases in the water column of the Pichavaram mangroves. The following sections deal with some of the important factors that could explain the concentrations and distribution of trace gases in the mangrove surrounding waters of Pichavaram. These factors are thought to be important in mangroves and past studies in an assortment of estuarine regions have used similar approaches to interpret the temporal and spatial variations in concentrations.

5.4.1 Salinity

Average salinity in the Pichavaram mangroves during April 2007 was 20.4 ± 6.9 (range 7.5 - 27.6). Salinity gradually increased from within the creek towards the sea with the last few locations near the mouth of the estuary showing salinity values close to seawater salinity. Figure 5.7 shows the variation of salinity along the creek. In general the annual rainfall received by the Pichavaram mangroves is 1310 mm and most of the precipitation falls during the northeast monsoon season from October to November (annual average number of rainy days is 56). Thus in this mangrove areas the dry season is long, extending from February to September and corresponding to it, the average salinity of the Pichavaram mangrove surrounding waters is also high during the dry season, ranging from 35 to 45 (Selvam 2003). However when the sampling survey was conducted in April 2007 for the present study,
higher rainfall than previous years was recorded in Pichavaram. 295 mm was recorded during the South west monsoon (March to May 2007) in Cuddalore district where Pichavaram is located (Indian Meteorological Department website 2007). This resulted in the increase in freshwater discharge in the Vellar estuary and resultant lower salinities recorded during the study. A clear salinity pattern (Figure 5.7) is thus observed by lower salinities (~ 7) in the creek end and highest salinity was recorded (27.6) at the estuary mouth.

Although statistical relationships with salinity were negative they were weak for pCO₂ (0.54) and stronger for CH₄ (0.67). The spatial variation of trace gases (Figure 5.5 and 5.6) with salinity indicates that the main source of CO₂ and CH₄ in Pichavaram waters is from the mangroves creeks. The pCO₂ and dissolved CH₄ concentrations gradually increase from inside the creek towards the mouth of the estuary.

![Figure 5.7](image)

**Figure 5.7** Variation of salinity along the mangrove creek sampled in Pichavaram during April 2007

The stronger negative relationship observed for salinity versus CH₄ (Figure 5.6) is consistent with a number of studies which indicate CH₄ is
produced in the sediments (Allen et al 2007) and porewaters of mangroves. The sharp CH$_4$ gradient shown in this profile also demonstrates that bottom sediments are probably a significant source of CH$_4$ for shelf waters (Bange et al 1998).

This is also consistent with the hypothesis of inhibition of methanogenesis by SO$_4^{2-}$ (Lovley et al 1982, Magenheimer et al 1996). The decreasing dissolved CH$_4$ levels as sampled from brackish to freshwater maybe attributed to variations in CH$_4$ production with the mangrove sediment as salinity (and along with it SO$_4^{2-}$) varied. CH$_4$ consumption as SO$_4^{2-}$ vary could also account for this trend. Reeburgh (1982) showed that in marine sediments (with high SO$_4^{2-}$) anaerobic oxidation of CH$_4$ can effectively consume nearly all the CH$_4$ produced deeper in the sediments, while anaerobic oxidation does not occur in freshwater (with low SO$_4^{2-}$) sediments. Thus as salinity (along with it SO$_4^{2-}$) increases down the creek towards the sea, the combination of decreased methanogenesis and increased anaerobic oxidation of CH$_4$ would allow less CH$_4$ to be released from the sediment into the creek waters.

5.4.2 Dissolved O$_2$

Average dissolved O$_2$ at Pichavaram was $73 \pm 14.8$ (range 45 - 91 %). It remained undersaturated with respect to the atmosphere throughout the creek (Figure 5.8). Thus these waters are a sink for O$_2$ and or O$_2$ is utilised for the processes that occur in the water column. The strong negative correlation ($r^2 = -0.8$) between pCO$_2$ and dissolved O$_2$ indicated heterotrophic dominance in waters surrounding Pichavaram mangroves.
Figure 5.8  Distribution of dissolved O$_2$ as a function of salinity in the Pichavaram mangroves in April 2007

In contrast to dissolved CH$_4$ the source / sink mechanism for CO$_2$ in mangroves surrounding waters is quite complex. It includes fixation of atmospheric CO$_2$ by mangroves and marine algae and bacteria. Higher pCO$_2$ was observed in the creek and its concentration decreased towards the estuary mouth. This is due to the release of CO$_2$ from mangrove sediments and porewaters into the water column (Bouillon et al 2007a). Although these data still indicate that CO$_2$ is produced at low salinities (Figure 5.5) the overall relationship is weaker than that observed for CH$_4$. The high correlation of CO$_2$ and O$_2$ also indicate that most of the observed CO$_2$ in the water column is produced in the water column by heterotrophic respiration.

Despite low O$_2$ saturation percentages it does not support the production of CH$_4$ through methanogenesis in these waters as methanogens require a complete absence of O$_2$ to thrive and produce CH$_4$ (Rudd and Taylor 1980, Kuivila et al 1988, Casper 1992). Also the correlation of O$_2$ with CO$_2$ ($r^2 = -0.8$) is higher than that with CH$_4$ ($r^2 = -0.5$) indicating that similar processes control the simultaneous increase and decrease of CO$_2$ and O$_2$. Thus
most of the CH$_4$ observed in the mangrove creeks of Pichavaram were produced in the sediment and released into the surrounding waters by diffusion into the water column. Plants are also known to transport CH$_4$ from the sediments to the water column (Lekphet et al 2003) and produce exudates that act as substrates for the production of these gases (Purvaja et al 2004).

5.4.3 DIC and TA

The inorganic C pool (TA and DIC) were measured in Pichavaram mangrove waters (Figure 5.9). Average TA concentrations ranged from 2.56 - 3.62 mmol kg$^{-1}$ (average 2.97 ± 0.37 mmol kg$^{-1}$). Highest concentrations were observed at low salinities and correlation with salinity was high ($r^2 = -0.9$). DIC showed similar inverse trend with salinity ($r^2 = -0.9$). High concentrations were observed in the creek waters where salinity was lower and lowest concentrations towards the sea. DIC ranged from 2.28 - 3.58 mmol kg$^{-1}$ (average 2.77 ± 0.45 mmol kg$^{-1}$).

Figure 5.9 Variation of TA and DIC with salinity in Pichavaram in April 2007
Variations in pCO$_2$ and CH$_4$ concentrations were similar, being lowest at the estuary mouth and increasing in the creeks towards the estuary mouth (Figures 5.5 and 5.6). The inorganic C pool showed similar dynamics as those of trace gases, that is, highest TA and DIC in the creek and lowest at the mouth of the estuary (Figure 5.9). The high metabolic activity in mangrove sediments creates elevated porewater concentrations of TA, DIC, DOC, and other metabolites (Marchand et al 2006, Bouillon et al 2007b). During ebb, porewaters can migrate into the water column and increase the concentrations of these solutes (Ovalle et al 1990, Borges et al 2003, Barnes et al 2006). The inorganic C data presented here are again consistent with a strong influence of porewaters, which typically have high TA, high DIC and pCO$_2$ (Bouillon et al 2007b). Ovalle et al (1990) explain the high porewater TA by SO$_4^{2-}$ reduction that along with aerobic respiration, account for almost all the diagenetic C degradation in mangroves. Generally, SO$_4^{2-}$ reduction is the major diagenetic pathway in mangroves (Alongi et al 1998), but in some cases aerobic degradation predominates (Alongi et al 2001), and in one Thai mangrove, iron reduction was reported as the dominant process (Kristensen et al 2000).

The relative variation of TA and DIC follows a well established stoichiometry that is specific to the biogeochemical process controlling these variables (Borges et al 2003). They report that in the waters of Gaderu creek (Godavari mangroves of India) the slopes of TA and DIC indicate that aerobic respiration also strongly contributes to the TA and DIC dynamics. In the Pichavaram mangrove waters also as in the case of the Godavari mangrove system, CO$_2$ is thought to be the result of heterotrophic respiration in the water column. The latter reported finding is consistent with the previous findings where negative correlations of CO$_2$ and dissolved O$_2$ strongly suggested heterotrophic respiration to be the main cause for the observed high pCO$_2$ in this region.
5.5 SUMMARY

Waters surrounding the largest mangrove ecosystem in the world, the Sundarbans and those from anthropogenically impacted Pichavaram showed supersaturations of pCO\(_2\) and dissolved CH\(_4\). Concentrations of these trace gases were an order of magnitude higher in Pichavaram when compared to the Sundarbans. The spatial transect studies at both sites revealed that the concentrations of pCO\(_2\) and dissolved CH\(_4\) and their distribution along the creeks were different. The factors governing the production and distribution of pCO\(_2\) and dissolved CH\(_4\) in the Sundarbans were based on the tides that govern this region. pCO\(_2\) and dissolved CH\(_4\) produced in the Jharkali mangroves is not directly exported but first returns to the forest with the incoming tide and there is mixed with estuarine water. pCO\(_2\) showed negative correlations with dissolved O\(_2\) reiterating the heterotrophic nature of the Jharkali water. Also POC in the waters fuelled heterotrophic respiration resulting in slightly higher concentrations in the lower end of the estuary.

In the Pichavaram mangroves correlation of pCO\(_2\) with salinity suggests that its release from porewaters and stronger correlations with O\(_2\) suggest heterotrophic respiration in the water column. The higher dissolved O\(_2\) concentrations in the water column do not support methanogenesis and so dissolved CH\(_4\) in Pichavaram is mainly produced in the sediment. Therefore the production and distribution of dissolved CH\(_4\) is mainly governed by its release from porewaters. The inorganic C data presented here are again consistent with a strong influence of porewaters, which typically have high TA, high DIC and pCO\(_2\). Dissolved CH\(_4\) concentrations decreased towards the estuary mouth and its strong correlation with salinity was due to inhibition of methanogenesis by SO\(_4^{2-}\) in seawater.

Thus data presented in this chapter emphasize the differences in trace gas production and distribution from two mangrove systems in India. It
also highlights the importance of direct measurements from each mangrove system individually as the factors governing each system are different. An in-depth study of these systems in the future would reveal the seasonal and temporal variations in trace gas production and distribution. Though these values represent data collected over a single season they demonstrate the importance of mangrove systems in terms of trace gas production and climate change at a global scale.