Seasonal Variations in the Concentrations of Three Greenhouse Gases (CH4, CO2 and N2O) in a Shallow Coastal Area Affected by Inputs of Organic Matter and Nutrients

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CH₄, CO₂ and N₂O are greenhouse gases with relatively long atmospheric lifetimes. Increasing atmospheric concentrations of these gases due to human activity, and their influence in global warming have stimulated the development of specific programs to study in depth their global budgets and the potential regulating effect of the oceans.

The role of the oceans and the coastal zones is still not clear today, and there are sources that are not yet identified due to the poor database, the uncertainties in estimates of coastal fluxes, the lack of continuous monitoring and the neglect of seasonal variations.

More data are available in the case of CO₂ exchanges between aquatic systems and the atmosphere, as this gas can be measured with IR techniques. N₂O and CH₄ determination is more complicated, as this requires chromatographic techniques, and therefore less is known about their distribution in aquatic systems.
<table>
<thead>
<tr>
<th>Gas</th>
<th>Atmospheric concentration (ppm)</th>
<th>Annual increase</th>
<th>Lifetime (years)</th>
<th>Greenhouse effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>356</td>
<td>+0.4%</td>
<td>150</td>
<td>1</td>
</tr>
<tr>
<td>CH₄</td>
<td>1.74</td>
<td>+0.6%</td>
<td>10</td>
<td>23</td>
</tr>
<tr>
<td>N₂O</td>
<td>0.31</td>
<td>+0.25%</td>
<td>150</td>
<td>270</td>
</tr>
</tbody>
</table>

Source: Figueruelo, 2001
1. To characterise the seasonal variations of dissolved CH$_4$, CO$_2$ and N$_2$O in a shallow coastal system affected by inputs of organic matter and nutrients.

2. To study the influence of the tide in the concentration of these biogases.

3. To estimate the emissions into the atmosphere in order to define the general behaviour of the system.
STUDY AREA

Tidal creek in a salt marsh area of the Bay of Cádiz.
Semidiurnal mesotides
Average tidal range: 0.98-3.20 m
Length: 12 km
Average depth: 3 m

It receives large amounts of organic matter and nutrients due to the presence of three aquaculture plants, that discharge their wastewater into the inlet.

INCREASE BENTHIC METABOLISM

INCREASE CH₄, CO₂, N₂O PRODUCTION
Measurements of dissolved CH$_4$, CO$_2$ and N$_2$O were performed during 10 samplings, at one fix station.

13-hours cycles: 1 sample / hour

Samples (50 mL) were kept, after adding HgCl$_2$, in dark until analysis (máx. 2 weeks)
GAS CROMATOGRAPHY

1. EXTRACTION OF THE GASES FROM THE WATER SAMPLE

   HEADSPACE METHOD: Helium atmosphere

2. ANALYSIS OF THE GAS PHASE AFTER EQUILIBRIUM

3. CALCULATION OF DISSOLVED GASES CONCENTRATION

   SOLUBILITY EQUATIONS
   CH₄: Wiesenburg and Guinasso, 1979
   CO₂ y N₂O: Weiss and Price, 1980

   MASS BALANCE: Initial concentration of the gases in the water phase
**METHODOLOGY**

**GAS CROMATOGRAPH**

GC VARIAN 3600 CX  
Simultaneously determine the concentration of CH₄, CO₂ and N₂O  
DETECTORS:  
- Thermal Conductivity Detector (TCD)  
- Flame Ionisation Detector (FID)  
- Electron Capture Detector (ECD)  
Provided with a valve that allows the injection, with a same sample flow, into 2 different chromatographic columns, which are connected to different detectors.
RESULTS

TIPICAL VARIATIONS OF SALINITY AND TEMPERATURE IN THE SYSTEM

13/02/2004-20/02/2004
There are considerably variations in the concentration of dissolved gases during a tidal cycle.

Maximum concentrations correspond to low tide (minimum of salinity)
GASES EVOLUTION DURING A TIDAL CYCLE

Changes in salinity do not seem to be responsible for the variations of dissolved CH₄, CO₂ and N₂O during tidal cycles.

Maximum concentrations during low tide (higher values of salinity)

IMPORTANCE OF DIAGENETIC PROCESSES
RESULTS

METHANE CONCENTRATIONS DURING SEVERAL TIDAL CYCLES IN THE DIFFERENT SEASONS

11.4-45.3 nM  23.2-56.7 nM  13.3-33.1 nM  12.9-29.3 nM

MAXIMUM VALUES IN JULY AND SEPTEMBER
LOWEST VALUES IN MAY
RESULTS

CARBON DIOXIDE CONCENTRATIONS DURING SEVERAL TIDAL CYCLES IN THE DIFFERENT SEASONS

**46.4-85.0 µM**

**57.7-70.0 µM**

**38.4-78.8 µM**

**40.1-71.75 µM**

**36.2-93.0 µM**

**57.4-114.6 µM**

**59.37-108.4 µM**

**28.8-102.2 µM**

MAXIMUM VALUES IN JULY AND SEPTEMBER

MINIMUM VALUES IN FEBRUARY AND MAY
RESULTS

NITROUS OXIDE CONCENTRATIONS DURING SEVERAL TIDAL CYCLES IN THE DIFFERENT SEASONS

MAXIMUM VALUES IN JULY
MINIMUM VALUES IN MAY
SATURATION VALUES

\[ \text{Sat} = 100 \times \frac{C_w}{C_a} \]

% SAT > 100 \rightarrow TRANSFER TO THE ATMOSPHERE

\( C_w \) = Concentration of dissolved gas

\( C_a \) = Expected equilibrium water concentration

<table>
<thead>
<tr>
<th>Date</th>
<th>Saturation (%CH(_4))</th>
<th>Saturation (%CO(_2))</th>
<th>Saturation (%N(_2)O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>19/02/04</td>
<td>488-1894</td>
<td>349-627</td>
<td>246-459</td>
</tr>
<tr>
<td>01/03/04</td>
<td>935-2201</td>
<td>399-499</td>
<td>282-434</td>
</tr>
<tr>
<td>04/05/04</td>
<td>598-1483</td>
<td>313-639</td>
<td>220-422</td>
</tr>
<tr>
<td>19/05/04</td>
<td>589-1313</td>
<td>329-576</td>
<td>218-380</td>
</tr>
<tr>
<td>01/07/04</td>
<td>893-2625</td>
<td>350-910</td>
<td>225-626</td>
</tr>
<tr>
<td>12/07/04</td>
<td>1767-3258</td>
<td>558-1124</td>
<td>381-814</td>
</tr>
<tr>
<td>07/09/04</td>
<td>1784-3012</td>
<td>573-1070</td>
<td>308-612</td>
</tr>
<tr>
<td>15/09/04</td>
<td>1104-3781</td>
<td>263-955</td>
<td>191-546</td>
</tr>
</tbody>
</table>
ESTIMATION OF THE FLUXES ACROSS AIR-WATER INTERFACE

\[ F = k_g \left( C_W - \alpha C_a \right) \]

(Ca \rightarrow \text{Azores Meteorological Station (NOAA website)}

\( \alpha \rightarrow \text{CO}_2 \text{ and N}_2\text{O (Weiss and Price, 1980)} \)

\( \text{CH}_4 \rightarrow \text{(Wiesenbourg and Guinasso, 1979)} \)

\( K_g \rightarrow \text{Carini et al., 1996} \)

<table>
<thead>
<tr>
<th>Date</th>
<th>( F_{\text{CH}_4} ) (( \mu \text{mol m}^{-2} \text{ d}^{-1} ))</th>
<th>( F_{\text{CO}_2} ) (( \text{mmol m}^{-2} \text{ d}^{-1} ))</th>
<th>( F_{\text{N}_2\text{O}} ) (( \mu \text{mol m}^{-2} \text{ d}^{-1} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>19/02/04</td>
<td>41.3</td>
<td>85.4</td>
<td>33.0</td>
</tr>
<tr>
<td>01/03/04</td>
<td>57.6</td>
<td>81.1</td>
<td>36.3</td>
</tr>
<tr>
<td>04/05/04</td>
<td>33.9</td>
<td>76.7</td>
<td>30.1</td>
</tr>
<tr>
<td>19/05/04</td>
<td>30.7</td>
<td>74.9</td>
<td>25.8</td>
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<tr>
<td>01/07/04</td>
<td>50.5</td>
<td>85.6</td>
<td>35.7</td>
</tr>
<tr>
<td>12/07/04</td>
<td>77.4</td>
<td>118.8</td>
<td>51.2</td>
</tr>
<tr>
<td>07/09/04</td>
<td>71.9</td>
<td>104.4</td>
<td>37.8</td>
</tr>
<tr>
<td>15/09/04</td>
<td>67.2</td>
<td>86.1</td>
<td>29.2</td>
</tr>
</tbody>
</table>
BENTHIC FLUXES MEASURED IN THE SYSTEM

<table>
<thead>
<tr>
<th>Date</th>
<th>$F_{CH4}$ (µmol m$^{-2}$ d$^{-1}$)</th>
<th>$F_{CO2}$ (mmol m$^{-2}$ d$^{-1}$)</th>
<th>$F_{N2O}$ (µmol m$^{-2}$ d$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>06/04-07/04</td>
<td>21.7 ± 8.4</td>
<td>30.7 ±11.6</td>
<td>23.5 ± 7.3</td>
</tr>
<tr>
<td>01/05-02/05</td>
<td>10.8 ± 3.7</td>
<td>4.4 ± 0.6</td>
<td>5.0 ± 2.8</td>
</tr>
</tbody>
</table>

Sediments are a source of CH$_4$, CO$_2$ and N$_2$O to the water column.

Benthic fluxes were significantly higher in the summer.

Spatial variability related with the closeness to the wastewater discharges.

REMINERALITATION OF ORGANIC MATTER IN THE SEDIMENT CONTROLS THE CONCENTRATION OF CH$_4$, CO$_2$ AND N$_2$O IN THE WATER COLUMN
1. There is a clear link between the hydrodynamics of the area and the variability of dissolved CH$_4$, CO$_2$ and N$_2$O.

2. The concentrations of dissolved gases in the water column depend mainly on organic matter mineralization processes, and therefore, can be affected by the inputs of organic matter and nutrients coming from the aquaculture plants.

3. The system was in all cases supersaturated with respect to the atmosphere, reaching values higher than 3800%, 1100% and 800%, for CH$_4$, CO$_2$ and N$_2$O, respectively. Maximum saturations were found in July and September, when benthic metabolism is more intense.

4. The tide creek under study acts, during all year, as a source of these gases into the atmosphere.