Air-Sea Fluxes of CH\textsubscript{4} and CO\textsubscript{2} from the Penlee Point Atmospheric Observatory (PPAO)

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Outline

1. Variability in eddy covariance CH$_4$ and CO$_2$ fluxes from Penlee Point Atmospheric Observatory

2. Inter-comparison between Picarro G2311f and Los Gatos Research FGGA sensors for measuring CH$_4$ and CO$_2$ fluxes
Penlee Point Atmospheric Observatory (est. 2014)

http://www.westernchannelobservatory.org.uk/penlee/
<table>
<thead>
<tr>
<th>Observations</th>
<th>Instrumentation/Methods</th>
<th>Period</th>
</tr>
</thead>
<tbody>
<tr>
<td>Meteorology</td>
<td>Gill Metpak Pro</td>
<td>May 2014 –</td>
</tr>
<tr>
<td>Momentum/Heat Flux</td>
<td>Gill WMP/R3 w/ EC</td>
<td>May 2014 –</td>
</tr>
<tr>
<td>CO₂/CH₄ Flux</td>
<td>Picarro G2311-f w/ EC</td>
<td>May 2014 – Oct 2015</td>
</tr>
<tr>
<td>CO₂/CH₄ Flux</td>
<td>Los Gatos Research FGGA w/ EC</td>
<td>Sep 2015 –</td>
</tr>
<tr>
<td>Total Aerosol Number Flux</td>
<td>TSI 3025 ultrafine CPC (&gt;3 nm) w/ EC</td>
<td>Feb 2015 –</td>
</tr>
<tr>
<td>Aerosol Size Distributed Flux</td>
<td>CLASP (0.2–18 micron) w/ EC</td>
<td>Feb 2015 –</td>
</tr>
<tr>
<td>Aerosol Chemistry</td>
<td>IC &amp; ICPMS</td>
<td>Jan 2015 –</td>
</tr>
<tr>
<td>SO₂</td>
<td>TS Pulsed Fluorescence 43i</td>
<td>May 2014 –</td>
</tr>
<tr>
<td>O₃</td>
<td>2B UV Absorption 205</td>
<td>May 2014 –</td>
</tr>
<tr>
<td>NO₂/CH₂O/CHOCHO/IO..</td>
<td>MAX-DOAS</td>
<td>Apr 2015 – Mar 2016</td>
</tr>
<tr>
<td>NO/NO₂</td>
<td>EnviroTechnology T200</td>
<td>Apr – June 2015</td>
</tr>
<tr>
<td>CO</td>
<td>EnviroTechnology T300U</td>
<td>Apr – June 2015</td>
</tr>
<tr>
<td>CINO₂</td>
<td>CIMS</td>
<td>Apr – June 2015</td>
</tr>
<tr>
<td>N₂O₅/NO₃</td>
<td>Heated Cavity</td>
<td>Apr – June 2015</td>
</tr>
</tbody>
</table>

**CO₂ and CH₄**: Closed path sensors with eddy covariance (EC) technique
Site Validation for EC Flux Measurements

Two wind sectors for air-sea fluxes:

SW (open water) and NE (Plymouth Sound)

$C_{D10n}$ within 20% of open ocean estimates when $\geq 18$ m AMSL
- Majority of flux footprint over water 20 m deep
- No obvious tidal dependence when mast raised

Further Sanity Checks: Cospectra and Diel Variability

Cospectra of CO$_2$ and CH$_4$ consistent with theoretical Kaimal fits for atmospheric turbulent transport

Higher mast (≥ 18 m AMSL):
- Weaker diurnal cycle
- Better agreement with expected air-sea CO$_2$ flux
- Significantly reduced local impact (grass/algae)

CO₂ air-to-sea flux increases with wind speed and shows strong temporal variability.
First Report of Eddy Covariance CH$_4$ Flux Measurements from a Marine System

<table>
<thead>
<tr>
<th>Mast Height</th>
<th>Period</th>
<th>Mean Flux (SE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 m AMSL</td>
<td>May-June 2014</td>
<td>0.016 (0.002)</td>
</tr>
<tr>
<td>27 m AMSL</td>
<td>June-July 2014</td>
<td>0.025 (0.004)</td>
</tr>
<tr>
<td>18 m AMSL</td>
<td>Apr-June 2015</td>
<td>0.030 (0.002)</td>
</tr>
</tbody>
</table>

Fluxes from open water sector (SW)
Units = mmole m$^{-2}$ d$^{-1}$; + = sea-to-air emission

Greater flux at higher mast height suggests the source of CH$_4$ is seawater, not foreshore

Estimated open ocean CH4 emission: typically <0.01 mmole m$^{-2}$ d$^{-1}$

Tidal (semi-diurnal) dependence in CH$_4$ flux

Greater CH$_4$ flux during rising tide, likely because the tide influences the extent of estuary outflow within the flux footprint

Analyzer Intercomparison: Picarro (physically dried) vs. Los Gatos Research (‘numerically dried’)

Shaded periods: air-water fluxes

Reasonable Agreement in Mean Cospectra

- High frequency flux loss $\leq 10\%$ for both analyzers
- LGR cospectra noisier at high frequencies
- Numerical water vapor correction in LGR only noticeable at low frequencies
Eddy Covariance Hourly Flux Detection Limits

Most of uncertainty in CH$_4$ covariance flux driven by natural variability in CH$_4$ mixing ratio, rather than instrument noise.

Hourly flux certainty (estimated following Blomquist et al. 2010) comparable to sea-to-air flux.

Picarro has significantly better precision and so lower flux detection limits than LGR

<table>
<thead>
<tr>
<th>CO₂</th>
<th>Precision (10 Hz) [ppm]</th>
<th>Flux Detection Limit [mmol m⁻² d⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Picarro G2311-f</td>
<td>0.15</td>
<td>2</td>
</tr>
<tr>
<td>LGR FGGA</td>
<td>1.4</td>
<td>8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CH₄</th>
<th>Precision (10 Hz) [ppb]</th>
<th>Flux Detection Limit (mmol m⁻² d⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Picarro G2311-f</td>
<td>1.1</td>
<td>0.02</td>
</tr>
<tr>
<td>LGR FGGA</td>
<td>5.5</td>
<td>0.05</td>
</tr>
</tbody>
</table>

*Estimated open ocean CH₄ emission: typically <0.01 mmole m⁻² d⁻¹*
What does this mean for direct flux measurements globally?

Estimated global air-sea CO$_2$ flux maps from NOAA (Park et al. 2010)

Gray squares: above hourly detection limit of Picarro (~40% of global oceans)

Longer averaging necessary in regions of lower flux or if using LGR
Summary

• Penlee Point Atmospheric Observatory suitable for eddy covariance measurements of fluxes between atmosphere and coastal seas

• CO₂ and CH₄ fluxes highly variable temporally (CH₄ flux appears to be tidal dependent)

• Picarro better precision (lower flux detection limit) than LGR

Publications from Penlee Point Atmospheric Observatory

• Air-sea CO₂ and CH₄ fluxes (Yang et al. Atmos. Chem. Phys, 16, 5745–5761, 2016)


• SO₂ emission from ships and DMS (Yang et al. Atmos. Chem. Phys, 16, 4771–4783, 2016) – See poster
Looking Forward...

- Seasonal variability in CO$_2$ and CH$_4$ fluxes
- Measurements of waterside CO$_2$ and CH$_4$ concentrations in EC flux footprints ➔ transfer velocities
- Impacts of surfactants on gas exchange?
- Aerosol fluxes (total and size-distributed number)
- Other gases (organics, ozone, ammonia)

Interested in collaborating?
Acknowledgment

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