Gas gradient in top 10 meters of coastal upwelling biases sea-to-air flux estimates

Nitrous oxide observations off Peru

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Coastal upwelling regions are often strong emitters of nitrous oxide ($\text{N}_2\text{O}$) and other trace gases

[Nevison et al. 2004, Naqvi et al. 2010]

$\text{N}_2\text{O}$ supersaturation of surface water off Peru, Dec. 2012

Damian Arévalo-Martínez et al., Session 043: Nitrous oxide in the eastern tropical South Pacific Ocean
Our motivating hypothesis to look for gas gradients in the top meters of the ocean:

Emissions from coastal upwelling systems may be overestimated, when using gas exchange bulk formulae.

Substantially more N$_2$O outgassing than supply from below found in Canary Upwelling. Surface production seems unlikely as sole explanation [Kock et al., 2012].

The flux equation indicates two possible sources of error:

$$F = -k_W \cdot (c - c_{sat})$$

Surface slicks reducing transfer velocity

A. Loginova et al.; poster #125, distribution of slicks in the Peruvian upwelling

Incorrect estimate of surface concentration due to vertical gas gradient.
[e.g. Soloviev et al. 2002, Calleja et al. 2013]
Checking gas gradient hypothesis using \( \text{N}_2\text{O} \) as observable

During Meteor M91 SOPRAN cruise, Dec. 2012:
An integrated biogeochemical study of the upwelling off Peru.

- CTD-\( \text{O}_2 \)
  - Currents
- Microstructure
- 11 biogeochemistry working groups
- Underway 5m chemistry, (e.g. \( \text{N}_2\text{O} \))
- Resolved concentration profiles at stations (e.g. \( \text{N}_2\text{O} \))
- Surface Microlayer
- Tropospheric chemistry

24h-stations, during which

- 4 \( \text{N}_2\text{O} \) profiles of top 10m away from ship influence could be performed.
Sampling $N_2O$ near the ocean surface

Submersible pump

0.1 – 1 m depth

1 – 10 m depth

Niskin plus MicroCat
$N_2O$ gradients exist at sites of elevated $N_2O$ concentrations.
N$_2$O gradients exist at sites of elevated N$_2$O concentrations

Emission overestimation

<table>
<thead>
<tr>
<th>Emission overestimation</th>
<th>5m-conc.</th>
<th>10m-conc.</th>
<th>100m</th>
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<tr>
<td>5m-conc.</td>
<td>20 %</td>
<td>25 %</td>
<td>60 %</td>
</tr>
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<td>5 %</td>
<td>30 %</td>
<td>60 %</td>
<td></td>
</tr>
<tr>
<td>40 %</td>
<td></td>
<td></td>
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5000m
3000m
150m
100m
... where shallow stratification is not completely eroded at night

Density profiles day vs. night

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5000m 3000m 150m 100m
Is this more than a random finding?

**N₂O concentration at 5m**

Top 10 m stratification is strong in most of the area; Seems roughly correlated to high N₂O concentrations.
Is this more than a random finding?

**N₂O concentration at 5m**

**Stratification of top 10m vs. local time**

- High N₂O (>15 nmol/kg)
- Low N₂O (<15 nmol/kg)

Suggests: Stratification not completely eroded at night = high N₂O
Is this more than a random finding?

The 4 profiles suggest: high $N_2O$ = stronger $N_2O$ gradients
Is this more than a random finding?

**N₂O concentration at 5m**

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<td>C₅m / C₁₀m</td>
<td>99%</td>
</tr>
<tr>
<td>C₁m / C₅m</td>
<td>?</td>
</tr>
</tbody>
</table>

(Our profiles)

(100 %) (97/87 %) (76 %)
Is this more than a random finding?

N₂O concentration at 5m

\[
\begin{array}{c}
\text{N}_2\text{O at 5m} \\
\text{N}_2\text{O at 10m}
\end{array}
\]

(CTD)

\[
\frac{C_{5\text{m}}}{C_{10\text{m}}} \quad 99 \%
\]

\[
\frac{C_{1\text{m}}}{C_{5\text{m}}} \quad ?
\]

(Our profiles)

\[
\frac{2}{3} \text{ of the survey area}
\]

\[
\log_{10} \text{ conc (5 m) / conc (10 m)}
\]

\[
\begin{array}{c}
< 15 \\
15 - 60 \\
> 60
\end{array}
\]

nmol/kg
Summary

Gas gradient in top 10m exists, seemingly throughout large parts of the coastal upwelling off Peru.

Associated with a strong shallow stratification not eroded at night.

Effect: emission estimates biased, strongest bias where emission estimates most affected.

Open questions

Quantification of total bias for emission estimates off Peru.

Is there such phenomenon in other coastal upwelling systems?

Need more high resolution profiles.
References


