Air-Sea Exchange of Acetone and the Impacts on the Remote Troposphere

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Chemistry in the middle of nowhere

- **Atmospheric Tomography Mission (ATom):** The heavily instrumented DC-8 deploys a comprehensive suite of scientific payload measuring a variety of gases and aerosols, profiling constantly from 0.2 to 13 km.
- In this work we focus on the Pacific during ATom-1 period (29 Jul – 23 Aug 2016)
- Oxygenated volatile organic compounds (OVOCs): greatly affect the HOx chemistry and hence the chemical lifetime of CH4 (greenhouse gas) and man-made pollutants.
- Observational and modeling studies suggest ocean plays a key role in the budget of trace gases in the remote MBL (Carpenter et al Chem Rev 2015; and refs therein).

![Diagram showing the cycle of OVOCs]
CH$_3$COCH$_3$ overview

- CH$_3$COCH$_3$ is emitted from anthropogenic and natural sources, also produced from the photooxidation of a wide range of VOC precursors.$^1$

- CH$_3$COCH$_3$ oxidation forms peroxyacetyl nitrate (PAN), a key NO$_x$ reservoir especially in remote regions.$^1$

- Ocean could be either a source or a sink for CH$_3$COCH$_3$.$^2$

- Ocean biogeochemistry affects the production and removal of CH$_3$COCH$_3$ in the seawater.$^3$

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$^1$ Singh et al Nature 1995; etc
$^2$ Fischer et al GRL 2012; etc
$^3$ Carpenter et al Chem Rev 2015; etc
CH$_3$COCH$_3$ affects oxidative capacity

- CH$_3$COCH$_3$ is a net source for HO$_x$ radicals; plays an important role in the middle-upper FT (Neumaier et al GRL 2014; etc).
- Observation-based box model: during ATom-1, CH$_3$COCH$_3$ and CH$_3$CHO together contribute to 30-40% HO$_x$ production in the remote free troposphere over Pacific.

Note: anthropogenic, biomass burning, cloud influence all filtered out, unless otherwise noted. Average ± standard deviation.

→ CESM2, FSDC (GEOS-5)
1 deg grid resolution (f09_f09)
HTAP + FINN1.5 + MEGAN
lightning NO$_x$
Air-sea exchange for trace gases

Ocean biogeochemistry

- **Production**: Biologically mediated production and the photodegradation of dissolved organic matters.\(^1\)

- **Removal**: \(^{14}\)C-labeled experiments: bacteria are utilizing acetone as either energy or carbon source;\(^2\) perhaps some phytoplankton too.\(^3\)

- Fischer et al (GRL 2012) studied air-sea exchange of CH\(_3\)COCH\(_3\), assuming constant seawater concentration of 15 nM, while measurements span vastly from 3 to 55 nM.\(^4\)

- In this work: seawater CH\(_3\)COCH\(_3\) is scaled to chlorophyll a (MODIS), mainly based on Beale et al JGR 2013 (Atlantic).

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\(^1\) Nemecekmarshall et al Environ Microbiol 1995; Sinha et al ACP 2007; de Bruyn et al J Photochem Photobiol 2011;  
\(^2\) Dixon et al GRL 2011;  \(^3\) Beale et al JGR 2013;  
Comparison: ship-based observations

- It appears the parameterization underestimates seawater acetone in the northern Pacific. Perhaps annual variation of Chl a? Or CH$_3$COCH$_3$ produced / removed differently?
- Modeled oceanic flux: quite good agreement with measurements!
Comparison: airborne measurements

- CH$_3$COCH$_3$ measured using NCAR TOGA (Eric Apel; Rebecca Hornbrook). LOD: 20 pptv
- Anthropogenic (indicators: CO, NO$_x$, NO$_y$/NO$_x$), biomass burning (indicators: HCN, CH$_3$CN), cloud influence all filtered out.
- **August 2016**: 36% and 44% CH$_3$COCH$_3$ in the tropical Pacific MBL from vegetation emissions and BVOC oxidation.
Budget: 2016 August only

- Burden (and lifetime) comparable to Khan et al and Fischer et al: 3.5 Tg (18 days), 5.6 Tg (25 days).

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<th>Global (Tg / mo)</th>
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Summary

• With the air-sea exchange module, CAM-Chem predicted CH$_3$COCH$_3$ in the remote troposphere over Pacific are greatly improved.

• The air-sea exchange module for CESM greatly improves CH$_3$CHO and CH$_3$ONO$_2$ as well (results not shown).

• Future plan: couple with the ocean biogeochemistry model.

THANK YOU

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