Oxygenated Compounds in the Tropical Atmosphere of the ICOS site of La Réunion Island
Significant impact on the atmospheric oxidative capacity & climate

- CH$_3$OH, CH$_3$CHO, CH$_3$COCH$_3$ : most abundant OVOCs, esp. in marine atmosphere

Poor knowledge of sources due to paucity of observations

- CH$_3$OH and HCOOH are exceptions thanks to satellite observations (IASI/MetOp), used to tie down estimates of their emissions over land (Stavrakou et al. ACP, 2011, Wells et al. ACP, 2014, Stavrakou et al. 2012)
New photochemical source of CH$_3$OH through CH$_3$O$_2$+OH: explanation for persistent model underestimations in remote tropical oceans?

Very large, unexplained model underestimation of observed CH$_3$CHO in remote Tropics at surface and FT (Millet et al. ACP 2010)

Key difficulty: ocean/atmosphere exchanges of OVOCs (and precursors)

Observed CH$_3$CHO incompatible with observed PAN (Millet et al. ACP 2010)
Objective of OCTAVE

Improve our appraisal of global budget of key OVOCs and their role in tropical regions, relying on an integrated approach combining in situ measurements, satellite retrievals and modelling.
OCTAVE in the blink of an eye

WP1 (BIRA-IASB, CNRS)
Local (O)VOC measurements at Reunion Island
- T1.1 PTR-MS
- T1.2 FTIR
- T1.3 Campaign-based HCHO and GC-MS

WP2 (BIRA-IASB, CNRS)
Analysis of local measurements
- T2.1 (O)VOC source apportionment
- T2.2 Interpretation with Meso-NH model
- T2.3 Intercomparison of local measurements

WP3 (ULB, BIRA-IASB)
IASI retrievals of (O)VOCs
- T3.1 Neural network retrieval methodology
- T3.2 Evaluation of retrieved (O)VOC total columns
- T3.3 Decadal IASI record for methanol and other (O)VOCs

WP4 (BIRA-IASB, CNRS, ULB)
Global modelling evaluation of OVOC budget and impacts
- T4.1 Model developments
- T4.2 Global budget evaluation of acetaldehyde and acetone
- T4.3 Revisiting the global methanol budget

WP5 (BIRA-IASB, ULB, CNRS)
Management, outreach to the scientific community and to a broader public, interaction with follow-up committee
Local measurements at Reunion

- PTR-MS measurements (BIRA-IASB)
- FTIR measurements (BIRA-IASB)
- Campaign-based HCHO measurements and GC-MS (O)VOC measurements (LAMP, CNRS-LACy)
PTR-MS measurements

- *in situ* technique, fast & sensitive, online
- well suited for long-term VOC monitoring
- no unambiguous detection of isomeric and isobaric VOCs
- 2-year continuous measurements → seasonal evolution of the contribution of VOC sources to the local air masses
- Simultaneous GC-MS (BIOMAIDO 2018)

<table>
<thead>
<tr>
<th>Compound</th>
<th>m/z</th>
<th>Compound</th>
<th>m/z</th>
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<tr>
<td>methanol</td>
<td>33</td>
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<td>acetonitrile</td>
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<td>monoterpenes</td>
<td>137</td>
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<tr>
<td></td>
<td></td>
<td>+ HCHO, acetic acid, PAN</td>
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</tbody>
</table>
FTIR measurements

BIRA-IASB operates FTIR instruments at La Réunion
- St-Denis, since 2002
- Maida, since March 2013

- FTIR at Maida (automated, remotely controlled)
- CH$_3$OH, HCOOH, CO, HCHO, and C$_2$H$_2$: total columns (+error+avk)
- PAN, C$_2$H$_4$ and CH$_3$COCH$_3$: challenging, but less contaminated spectra by water vapour at Maida & signal-to-noise ratio is much improved

Vigouroux et al ACP 2012
Analysis of local measurements

✓ **Multivariate statistical analysis**
  - EPA Unmix 6.0: # source types, profiles, relative contributions, used for VOC source apportionment from PTR-MS data

✓ **Backtrajectory calculations**
  - **FLEXPART**: large-scale transport @ 15 km (ECMWF), select air masses of marine origin, infer marine (O)VOC concentration/seasonal cycle
  - Calculate concentrations for each set of trajectories → linearize transport btw surface and Maïdo
  - 4D least-squares method (Brioude et al JGR 2011) → best estimates of surface fluxes of CH$_3$OH

- **AROME** forecasts at 2.5x2.5 km
- **Meso-NH** model at 500 m (case study)
IASI retrievals of (O)VOCs

Retrieval algorithms for the (O)VOCs:
- CH$_3$OH, C$_2$H$_2$, C$_2$H$_4$, HCOOH (previously detected) or PAN (challenging)

New method based on NN: gain in sensitivity, uncertainty estimates, computationally efficient, optimized retrievals over land/oceans

Evaluation against ground-based observations & previous satellite retrievals

Decadal record (2008-2018) for CH$_3$OH, HCOOH, C$_2$H$_2$, C$_2$H$_4$ (& PAN)
Global modelling evaluation of OVOC budget and impacts

- IMAGESv2 global CTM
- Adjoint-based inversion scheme
- Used to infer CH$_3$OH and HCOOH fluxes over land based on IASI
- Method will be improved and extended
Our «best» knowledge on OVOC budget

Sources
- Global source: 147 Tg/yr
- Lifetime = 1 month
- Biogenic flux: 32 Tg/yr (range: 20-172), first study accounting for oceanic flux

Millet et al GRL 2012

Sinks
- Global source: 213 Tg/yr
- Lifetime ~1 day
- Compared to Singh et al JGR 2004:
  - x2.5 lower ocean flux
  - x4 higher secondary production
Key questions

- Can we explain the elevated CH$_3$CHO levels over remote tropical ocean? Are there unknown oceanic or biogenic CH$_3$CHO precursors?
- What are the contributions of CH$_3$CHO, CH$_3$COCH$_3$ and other OVOCs to PAN formation?
- Can we confirm and better constrain the importance of the CH$_3$O$_2$+OH reaction as major remote source of CH$_3$OH?
- Can we better constrain the biosphere/atmosphere and ocean/atmosphere exchanges of CH$_3$CHO, CH$_3$OH, CH$_3$COCH$_3$?
- What is the overall impact of OVOCs on atmospheric oxidants (esp. OH)?
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Thanks for your attention.