# Oxygenated volatile organic Compounds in the Tropical Atmosphere: Variability and Exchanges (OCTAVE)


## SUMMARY

### Context

Oxygenated Volatile Organic Compounds (OVOCs) have a significant impact on the atmospheric oxidative capacity and climate. Methanol, acetaldehyde and acetone are among the most abundant OVOCs, especially in the marine atmosphere where they make up 37-63% of the total non-methane volatile organic carbon. Their sources include terrestrial vegetation, oceans, the oxidation of VOCs, biomass burning and anthropogenic emissions. However, large discrepancies in OVOC budget estimates still exist, mostly due to incomplete representation of photochemical OVOC production, and uncertainties in terrestrial emissions and ocean/atmosphere exchanges of OVOCs and their precursors.

The paucity of OVOC observations in tropical regions strongly contributes to those uncertainties. Although ocean/atmosphere exchanges of OVOCs are significant, their magnitude and direction remain poorly constrained. Very large, yet unexplained model underestimations of observed acetaldehyde concentrations have been reported at remote tropical locations, which might imply the existence of so far unknown sources of acetaldehyde or its precursors. Also, for methanol, a large photochemical source has been recently identified, the $CH_3O_2 + OH$ reaction, of magnitude comparable to the combined terrestrial emissions. Although this source might provide a long-needed explanation for persistent model underestimations over remote tropical oceans, its precise magnitude and its implications for global budget assessments remain unclear. For acetone as well, models fail to predict their observed seasonal variability. A better understanding of OVOC sources and sinks is required to quantify their impact on atmospheric oxidants, on the lifetime of methane and consequently on climate.

### Objectives

OCTAVE aims to provide an improved assessment of the budget and role of OVOCs in tropical regions, relying on an integrated approach combining in situ measurements, satellite retrievals and models. The specific objectives are:

- To generate a 2-year dataset of atmospheric measurements of OVOCs (methanol, acetaldehyde and acetone) and related compounds by proton-transfer-reaction mass spectrometry (PTR-MS) and remote sensing infrared spectroscopy (FTIR) at the high-altitude site of the Maïdo observatory (2155 m above sea level) on Reunion Island, in the Indian Ocean.

- To identify and quantify OVOC sources contributing to the measurements at Reunion Island, with the help of multivariate statistical analysis, back-trajectory calculations and 3-dimensional modelling.
- To apply an innovative methodology based on artificial neural networks (ANNI) to generate improved and better characterized global distributions of the column abundances of methanol and other VOCs using multi-annual remote sensing data from the IASI sensor on the MetOp satellite.
- To perform an updated model evaluation of the budget of OVOCs, based on spaceborne data (for $CH_3OH$), and a wide collection of aircraft, ship-based and ground-based measurements, including those obtained at Reunion. The latter will be used to evaluate OVOC sources and sinks in the area, with the help of high-resolution chemistry-transport models, like WRF-Chem.

**Main conclusions**

- The photochemical formation of acetone and formic acid in biomass burning plumes has been identified based on PTR-MS data collected at Maïdo and back-trajectory calculations. The production of acetone was found consistent with the emission ratios of known precursors. A substantial missing source of formic acid in biomass burning plumes is suggested from the analysis.
- The artificial neural network applied to the IASI data is operational and ensures the retrieval of 8 (O)VOCs throughout the entire operational time series of IASI/Metop-A, -B, and -C (i.e., since 2007). It proved to be sensitive, flexible, and robust for the retrieval of weak infrared absorbers. The retrieval of acetic acid and acetone represents a step beyond what was envisioned in the initial OCTAVE proposal. Altogether, this suite of IASI products constitutes an extensive and unique decadal dataset of global (O)VOCs column abundance from a single satellite sounder, which is of high value for tackling scientific questions in link with the atmospheric composition.
- Cross-evaluation of IASI, FTIR and aircraft in situ data indicate significant biases between the different datasets, for reasons yet unclear. IASI appears to underestimate the high columns; the magnitude of the bias is moderate against FTIR data, and much more pronounced against aircraft-based columns.
- The high-resolution WRF-Chem model was found to be appropriate for simulating long-lived compounds over Reunion Island, even at low resolution (12.5 km), but it is very dependent on the quality of the lateral boundary conditions.
- The derivation of methanol emissions by inverse modeling based on IASI data leads to enhanced emissions over semi-arid areas, similar to previous work. The magnitude of the emission update inferred by the inversion is very dependent on the bias-correction applied to the data. No single optimization succeeds in reproducing all measurement techniques (satellite, aircraft, in situ) simultaneously.

**Recommendations**

- Despite encouraging results of IASI OVOC evaluation against FTIR data, further efforts are needed to tackle IASI underestimations of high columns. A more thorough collocation of the IASI measurements might be required. The scarcity or absence of FTIR data for PAN, acetone and acetic acid hampers a complete validation of these IASI products.
- Evaluation using models and aircraft data has been attempted but led to unclear conclusions. For methanol, inconsistency between aircraft, FTIR and IASI datasets highlights the need for dedicated intercomparison campaigns, which could be conducted within the ACTRIS European research infrastructure.
- In order to improve comparisons with models and independent measurements, the production of averaging kernels by the ANNI retrieval framework should be developed.
- Retrieval of other OVOCs identified recently in the IASI spectra (e.g. glycolaldehyde) should be attempted.
- Use of mesoscale chemistry models (Meso-NH or WRF-Chem) is advised to further exploit the Maïdo dataset generated within OCTAVE. They would allow a detailed source apportionment of VOCs recorded at Maïdo and potentially identify the role of the ocean.
- High-resolution anthropogenic emissions ($\sim 1 \times 1 km^2$) are required to simulate reactive species on Reunion Island and more specifically at Maïdo observatory. To respond to the lack of such emission data for Reunion Island, FLEXPART-AROME back-trajectories and the Maïdo measurements can be used to derive emissions of specific compounds (e.g., benzene). To that aim, FLEXPART-AROME should be driven by meteorological data from Meso-NH.

**Keywords**

- Oxygenated volatile organic compounds
- Biosphere/atmosphere/ocean exchanges
- IASI satellite VOCs
- Oxidizing capacity
- Emissions
- In situ measurements and ground-based remote sensing