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# Link of glyoxal-to-formaldehyde ratio ($R_{GF}$) to meteorology

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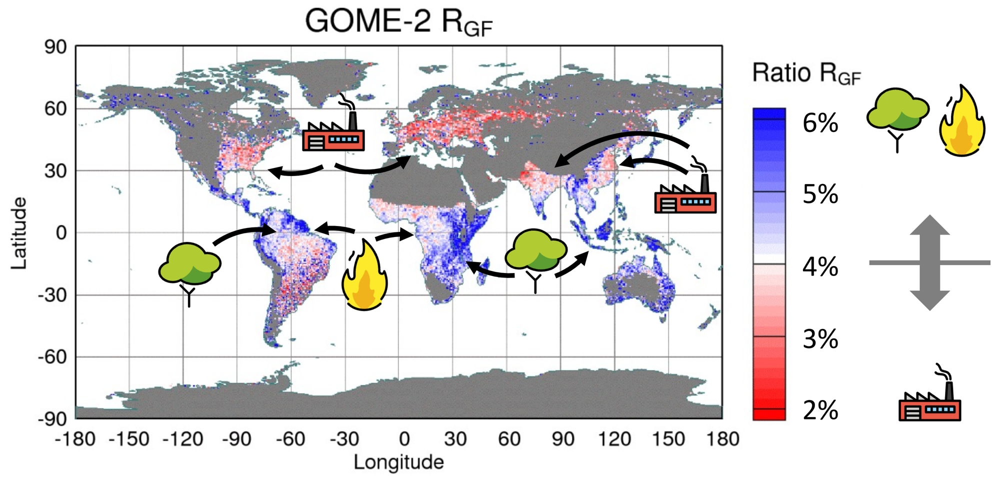
## 1. Motivation

- Volatile organic compounds (VOCs) serve as fuel for summer smog formation[1]
- Formaldehyde (HCHO) and glyoxal (CHOCHO) important intermediate products in oxidation chain of VOCs[2, 3]

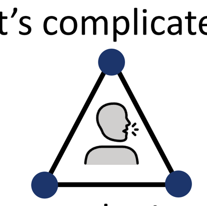



Global map of mean $R_{GF}$ from GOME-2 instrument from the years 2007 and 2008. Highlighted are the regions and their expected source types. An $R_{GF}$ above 4% correlates with biogenic and pyrogenic source regions and an $R_{GF}$ below 4% correlates with anthropogenic source regions. Figure adapted from [3].

- Similar sources (primary emissions, secondary formation from VOCs, $CH_4$ oxidation) and identical sinks (photolysis, OH oxidation, deposition)[3]

➡ Use their ratio ($R_{GF}$) as a proxy for VOC source identification of air masses

- Conflicting observations and ongoing debate in the literature since 2010[4]




The positions/findings in the literature can be grouped into three categories: a) same behaviour as in [3], i.e. $R_{GF}$ > 4% for pyrogenic/biogenic and $R_{GF}$ < 4% for anthropogenic sources b) reversed behaviour to [3] c) mixed signals. Studies with mixed signals try to extend the concept of $R_{GF}$.

## 2. Measurement setup

- Multi-year ground-based data set at four sites in different environments[4]
- Multi-Axis Differential Optical Absorption Spectroscopy (MAX-DOAS) instruments
  - Comparing differential absorption cross-sections with differential absorption
  - Retrieve differential slant column density (dSCD) from low elevation (1-3°)
- Retrieve { CHOCHO in vis / HCHO in UV } wavelengths

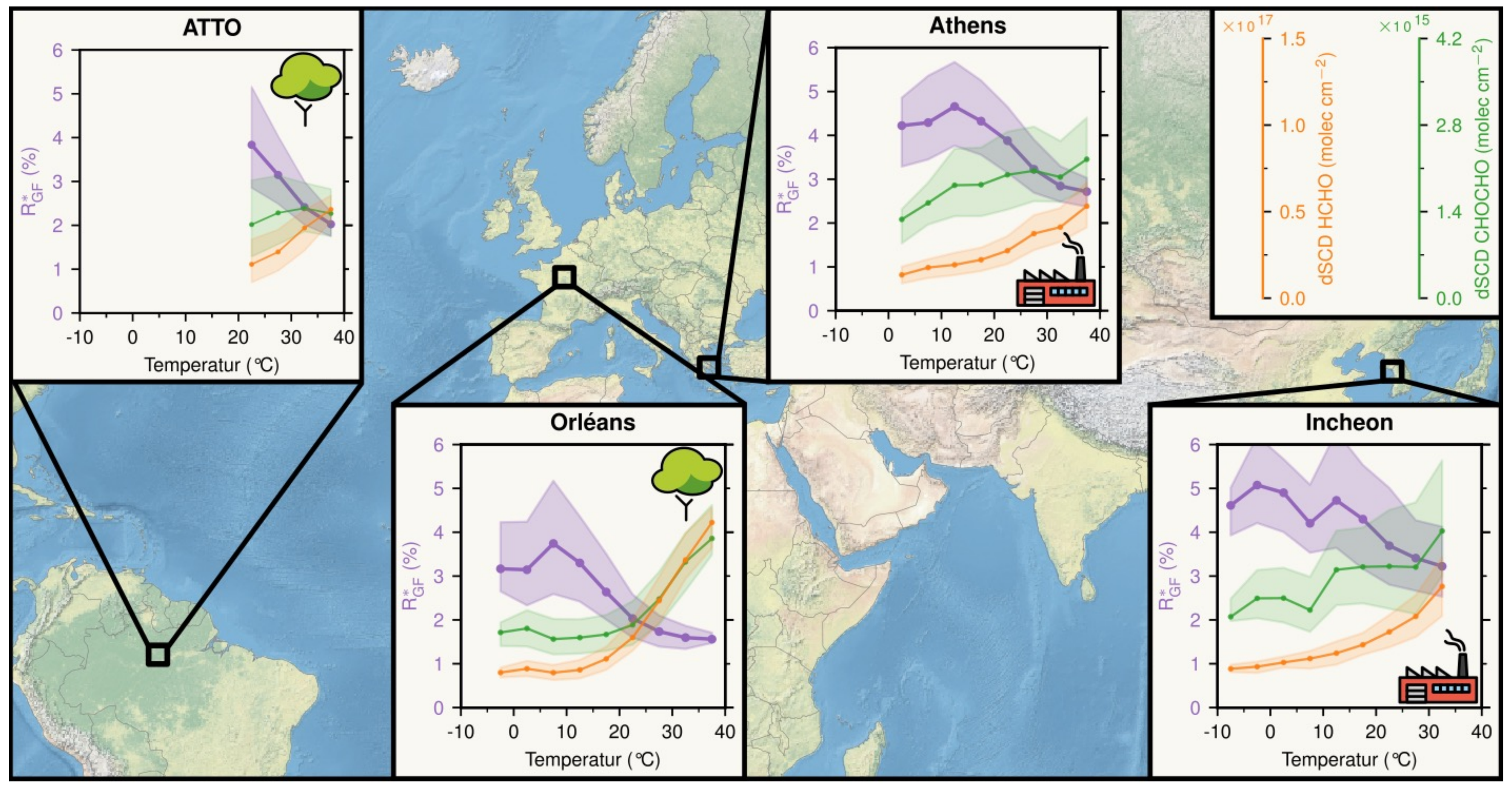
$$R^*_{GF} = \frac{dSCD^{CHOCHO}_{vis}}{dSCD^{HCHO}_{UV}} \cdot \frac{dSCD^{O_4}_{UV}}{dSCD^{O_4}_{vis}}$$

Correction factor for different effective light path lengths in UV/vis

- Meteorological variables from hourly ERA5 interpolated to measurement times

The backside of the telescope of the MAX-DOAS instrument on a tripod from Orléans.

## 3. Temperature response




Map data: Natural Earth

OpenMoji

Map showing the four sites and the local temperature response of CHOCHO, HCHO, and $R_{GF}$. Athens and Incheon are characterised as anthropogenic environments, whereas Orléans and ATTO are characterised as biogenic environments.

- Comparable absolute levels of HCHO and CHOCHO
- Temperature response of HCHO is consistently stronger than that of CHOCHO
  - $R_{GF}$ decreases with temperature across all sites
- The same processes govern both species, yet they respond differently:
  a) Biogenic precursor emissions
  b) Secondary formation rates
  c) Direct (primary) emissions

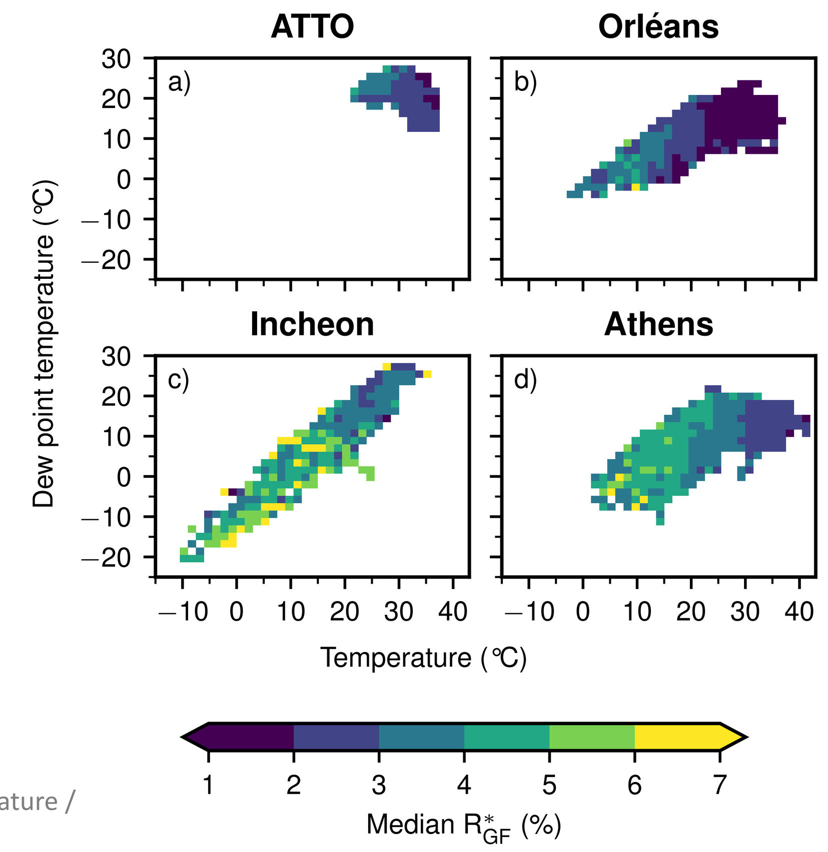
  } Different importance between species? Same importance for HCHO across sites?

## 4. Water content vs temperature

- water solubility of CHOCHO higher than HCHO[5]
  - Multiphase chemistry more important for CHOCHO
  - Does $R_{GF}$ respond to different water content?

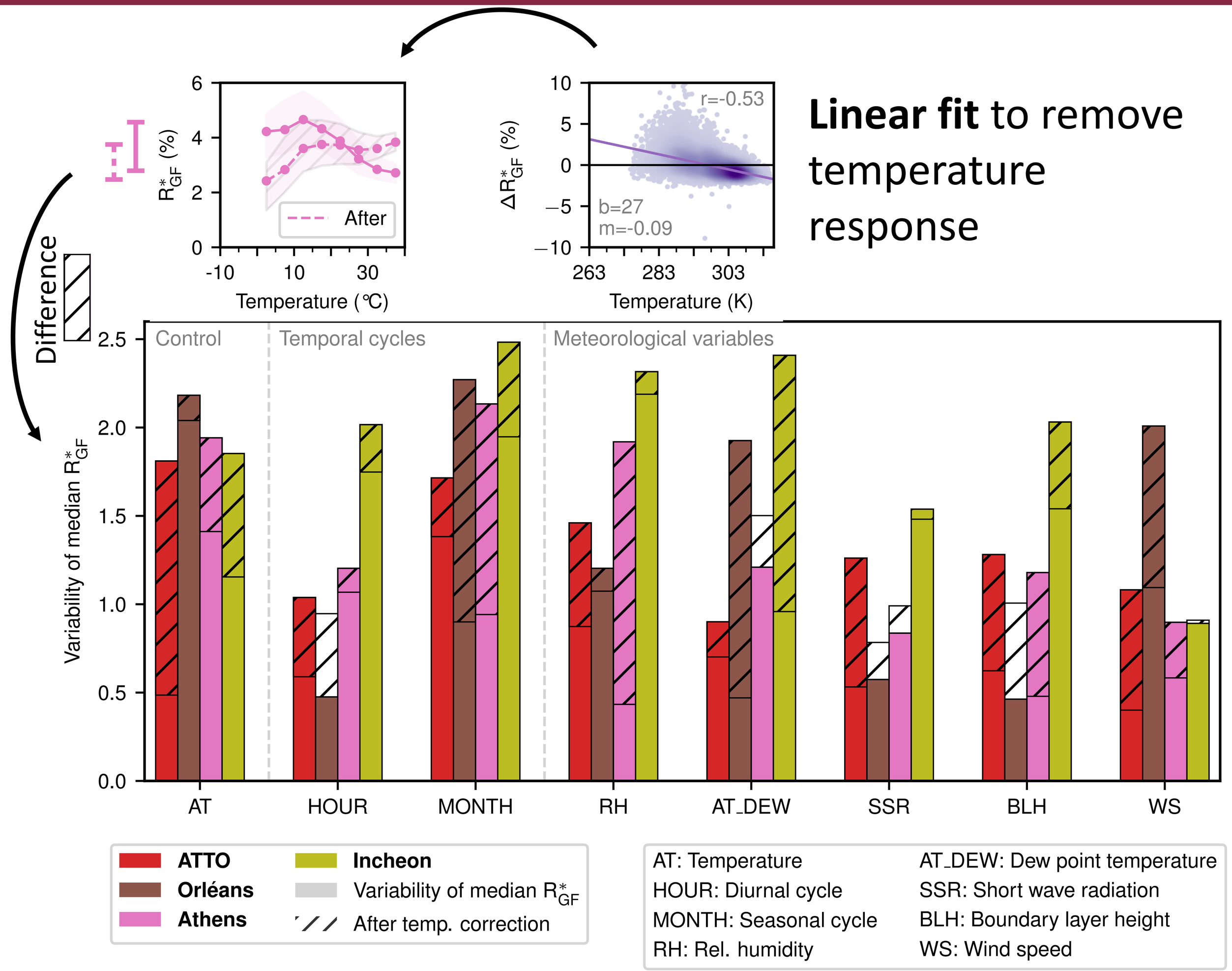
water content ⟷ dew point temperature

- No clear response to changing water content at the same temperature visible
- Temperature effect more pronounced in comparison




Heatmap showing the median $R_{GF}$ on a temperature / dew point temperature grid for each station.

## 5. Remaining variability




Full response of other variables

Visualisation showing the variability of $R_{GF}$ (max – min median of $R_{GF}$) over the whole variable range and how much the variability changes after accounting for the temperature response.

- Variables are strongly intercorrelated → Difficult to isolate individual drivers
- Investigating residual variability after temperature correction
  - Diurnal cycle preserved ⟷ seasonal cycle reduced (outside tropics)
  - Apparent correlations with other meteorological variables vanish after correction
    - Exception Incheon: sensitivity to RH, SSR, BLH remains
    - Possible local influence?

## 6. Conclusions

1. Stronger temperature response of HCHO than CHOCHO drives $R_{GF}$ consistent temperature response
2. No clear response to water content is visible
3. Accounting for temperature response reduces variability of $R_{GF}$ significantly for most variables

Reduced: seasonal cycle, RH, AT_DEW, SSR, BLH, WS
Preserved: diurnal cycle, RH, SSR, BLH in Incheon

## 7. Selected references

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