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The complexity of biogenic boreal emissions through the lens of hydroxyl radical (OH) reactivity

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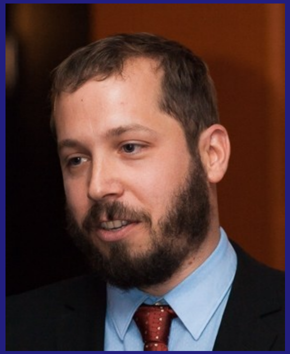

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Motivation

- **Unexplained hydroxyl radical (OH) reactivity** observed in **forested environments** (Di Carlo et al., 2004), including **the boreal forest** (Sinha et al., 2010; Nölscher et al., 2012)
- Reasons for unexplained reactivity unclear:
  - **unkown primary emissions** of reactive compounds (Nölscher et al., 2013) or
  - **secondary (oxidation) compounds** (Kim et al., 2011)

This study

- **Total OH reactivity of Emissions (TOHRE)** and its unexplained (or missing) fraction from
  - **seedlings** of three different boreal forest tree species (Praplan et al., 2020), in pots placed outside, in 2017,
    - Downy **birch** *(Betula pubescens)*
    - Norway **spruce** *(Picea abies)*
    - Scots **pine** *(Pinus sylvestris)*

  - and two trees (birch and spruce) for **in situ** conditions (SMEAR II, Hyytiälä, Finland) in 2019.

Methods

- **Dynamic branch enclosures** (Hakola et al., 2006)
  - 6-litre enclosure made of Teflon®
  - flow *f* through the enclosure (ca. 4 l min^{-1})
- **Comparative Reactivity Method** (CRM; Sinha et al. 2008; Praplan et al., 2017)
  - Measures **total OH reactivity** (R_{exp})
- **Gas Chromatography – Mass Spectrometry** (GC-MS; Hellén et al. 2017, 2018):
  - terpenes, 2-methyl-3-butenol (MBO), and $C_{5\text{-}10}$ aldehydes (2017 and 2019)
  - alcohols and volatile organic acids (2017 only)

OH Reactivity of the Emissions

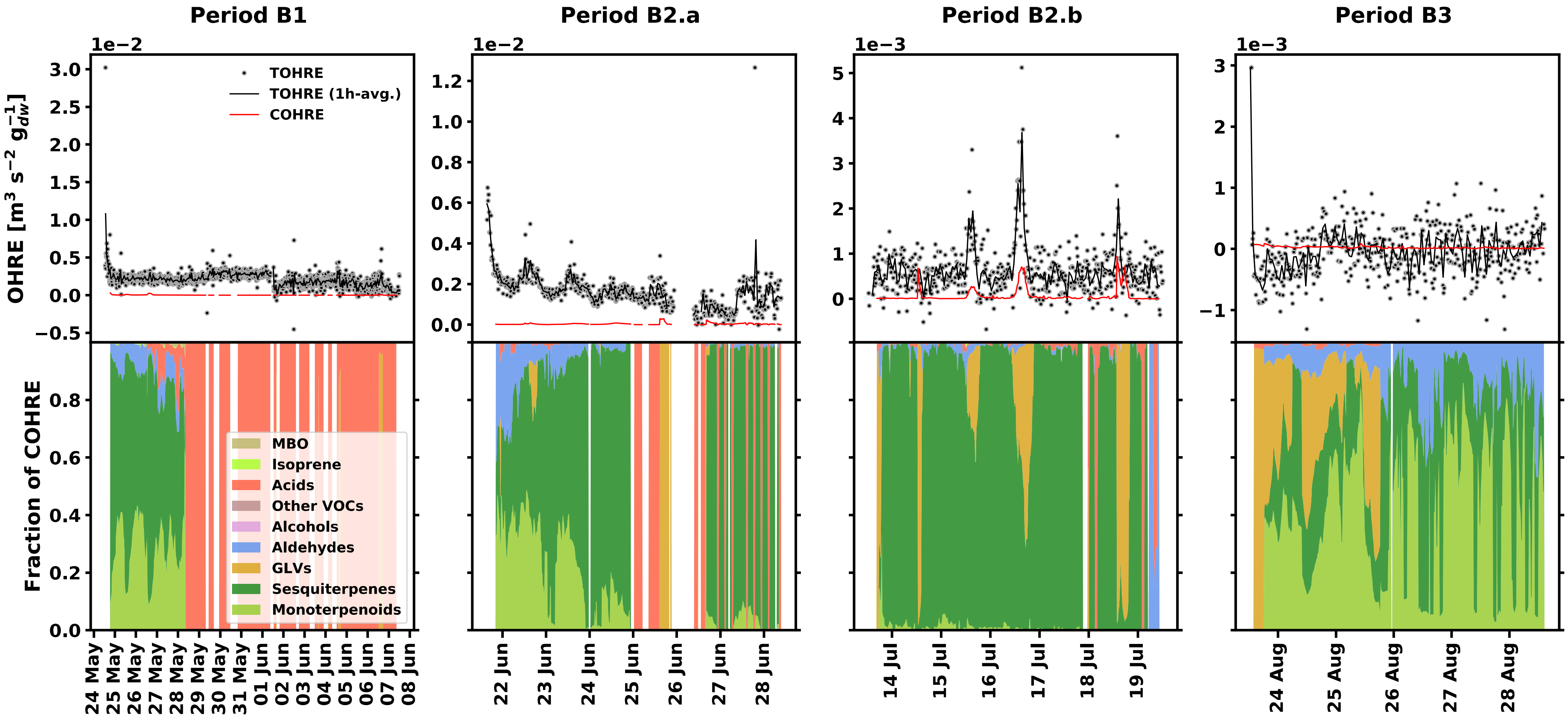
- **Total OH Reactivity of the Emissions (TOHRE, measured)**
  from R_{exp}, f, and the dry weight of the biomass (leaves or needles), m_{dw}:

$$\mathbf{TOHRE} = \boldsymbol{R_{exp} \cdot f / m_{dw}}$$

- **Calculated OH Reactivity of the Emissions (COHRE)**
  from emisions (E_i) of single compounds (i) and their reaction rate with OH ($k_{OH,i}$):

$$\mathbf{COHRE} = \Sigma\, \boldsymbol{E_i \cdot k_{\mathrm{OH},i}}$$

Results 1a: Birch (seedling)



- TOHRE generally higher than COHRE
- TOHRE and COHRE follow each other qualitatively most of the time
- Composition of the emission changes, but important contribution from sesquiterpenes
- Large fraction of organic acids in the emissions are due to missing measurement of other compounds.

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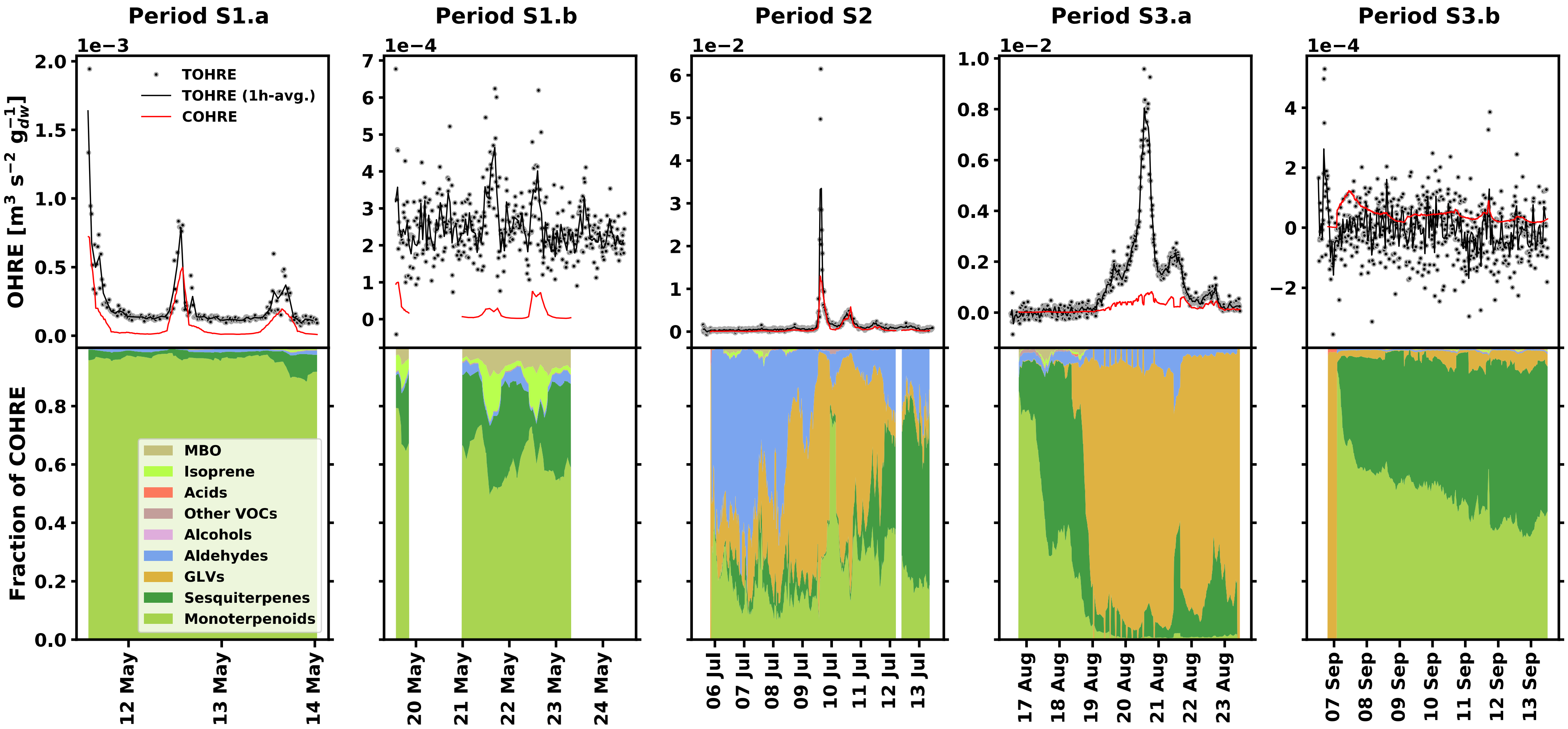
Results 1b: Spruce (seedling)



- TOHRE generally higher than COHRE
- TOHRE and COHRE follow each other qualitatively most of the time
- Vary large difference between TOHRE and COHRE, when the fraction of GLVs is up to 90% (stress?)

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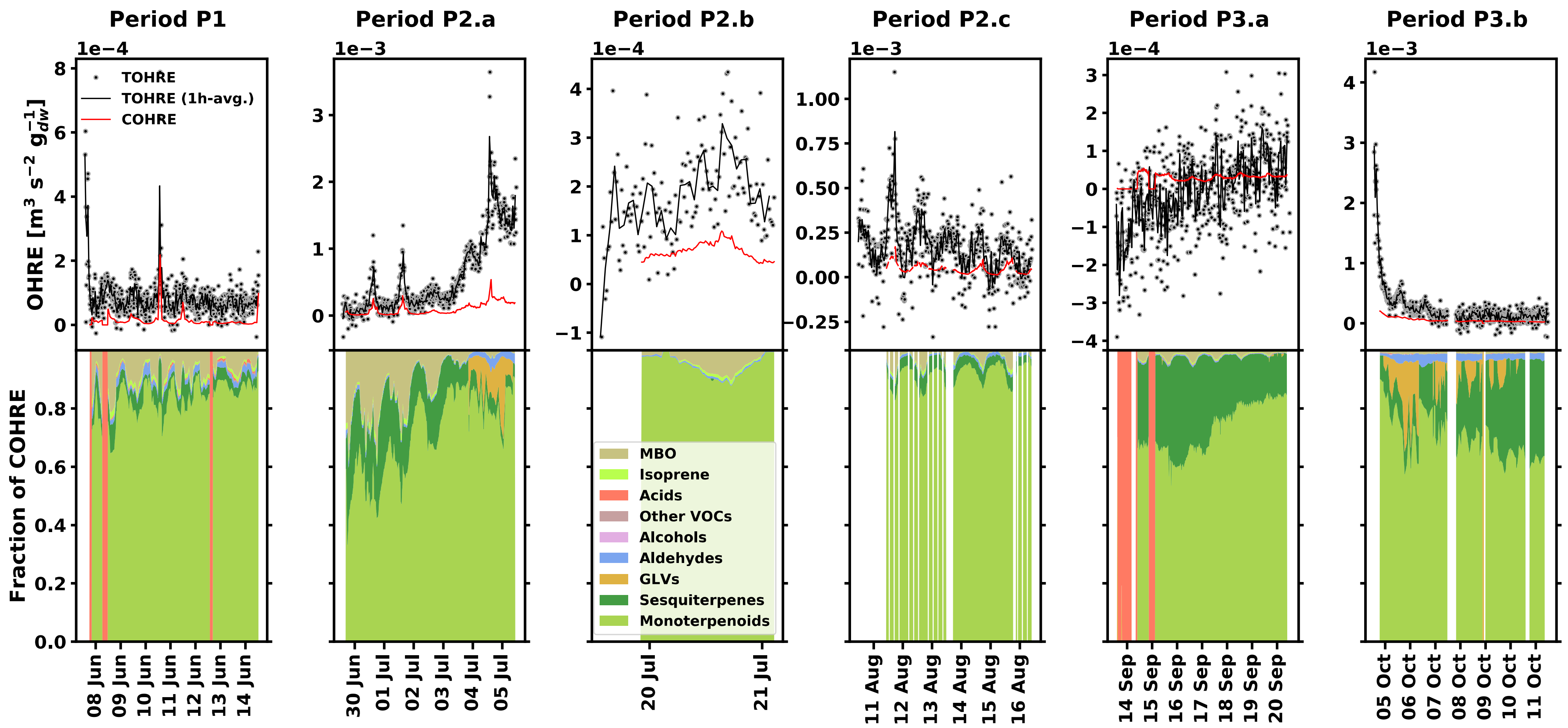
Results 1c: Pine (seedling)



- TOHRE generally higher than COHRE
- TOHRE and COHRE follow each other qualitatively most of the time
- Large difference between TOHRE and COHRE, when the fraction of GLVs increases (stress?)
- Increase of monoterpenoid emissions also observed during stress period

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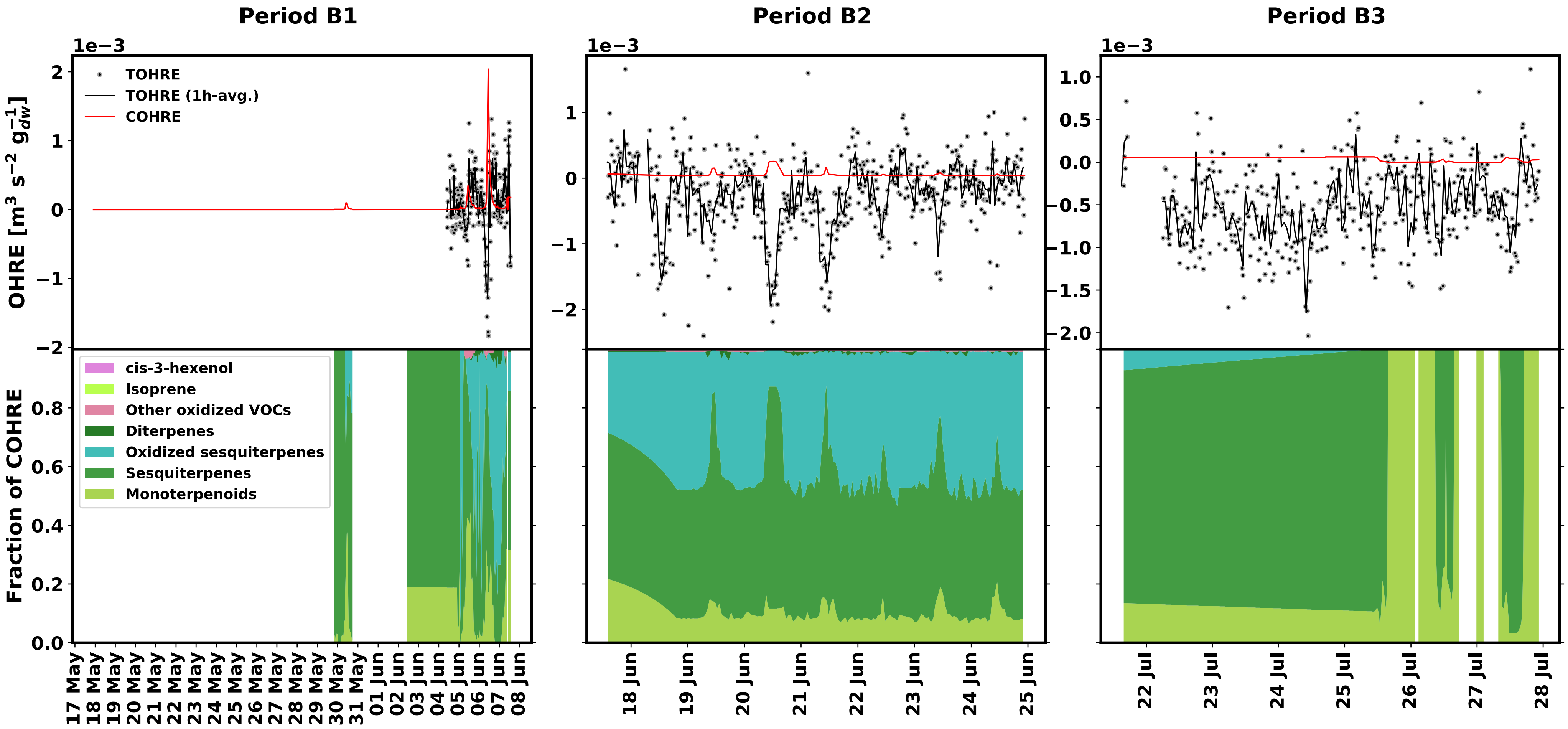
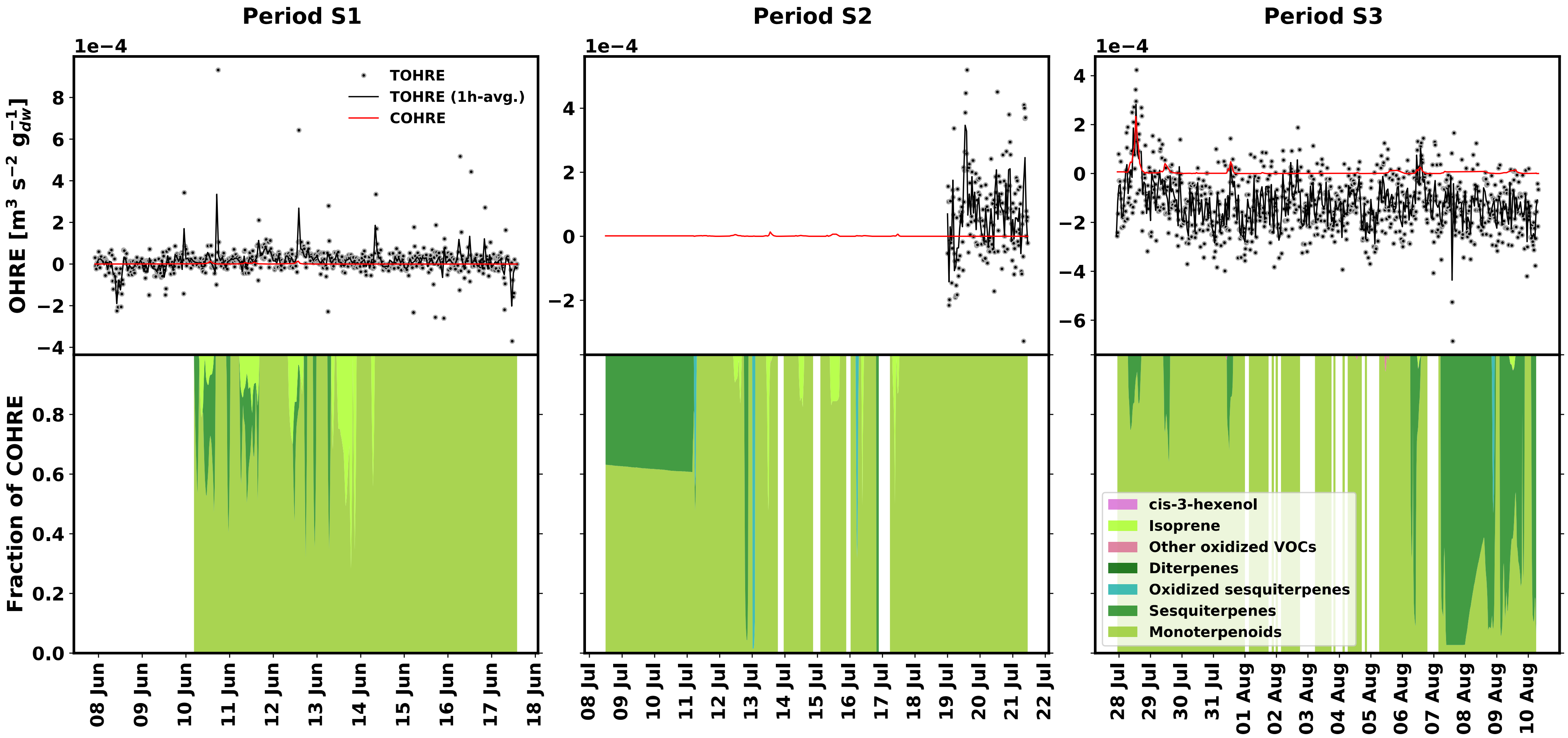
Results 2a: Birch (in situ)



- Low TOHRE values
- Important fraction of oxidised sesquiterpenes (only measured in 2019)
- Sesquiterpenes and oxidised sesquiterpenes are mainly responsible for OHRE

Results 2b: Spruce (in situ)



- Low TOHRE values
- Mostly monoterpene emissions
- Isoprene and sesquiterpenes responsible for only a small fraction of the OHRE

Conclusions

- **TOHRE is generally higher than COHRE**, especially for seedlings
- **TOHRE and COHRE follow each other qualitatively** most of the time
- TOHRE in general **higher for seedlings**
  - due to **stress?** (larger fraction of stress-related Green Leaf Volatiles – GLVs – observed)
- **TOHRE of birch** is on average **higher than for spruce and pine**
  - Important fraction of **oxidised sesquiterpenes observed in birch emissions** (measured only in 2019, could possibly explain missing reactivity in 2017)

Outlook

- Verify **reproducibility** of the results
  - for upscaling
- Investigate **non-hydrocarbon compounds**
  - in particular during **stress periods**

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