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

Arnaud P. Praplan¹, Simon Schallhart¹, Toni Tykkä¹, Jaana Bäck², Heidi Hellén¹

¹Finnish Meteorological Institute, P.O. Box 503, 00101 Helsinki, Finland
²Institute for Atmospheric and Earth System Research/Forest Sciences, Faculty of Agriculture and Forestry, P.O. Box 27, 00014 University of Helsinki, Finland

EGU2020: Sharing Geoscience Online
#shareEGU20

BG3.3/SSS9.13
EGU2020-13057
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:
  - unknown 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$_{5-10}$ 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 $R_{\text{exp}}$, $f$, and the dry weight of the biomass (leaves or needles), $m_{\text{dw}}$:

  $$\text{TOHRE} = \frac{R_{\text{exp}} \cdot f}{m_{\text{dw}}}$$

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

  $$\text{COHRE} = \sum E_i \cdot k_{\text{OH},i}$$
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.
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?)
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
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

A.P. Praplan (EGU2020-13057)
#shareEGU20 – BG3.3/SSS9.13
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**
References

- Nölscher et al. (2013), Biogeosciences, 10, 4241–4257.
- Praplan et al. (2017), Atmos. Env., 169, 150–161.
- Sinha et al. (2008), Atmos. Chem. Phys., 8, 2213–2227.