Total OH reactivity at Cape Corsica during summer 2013

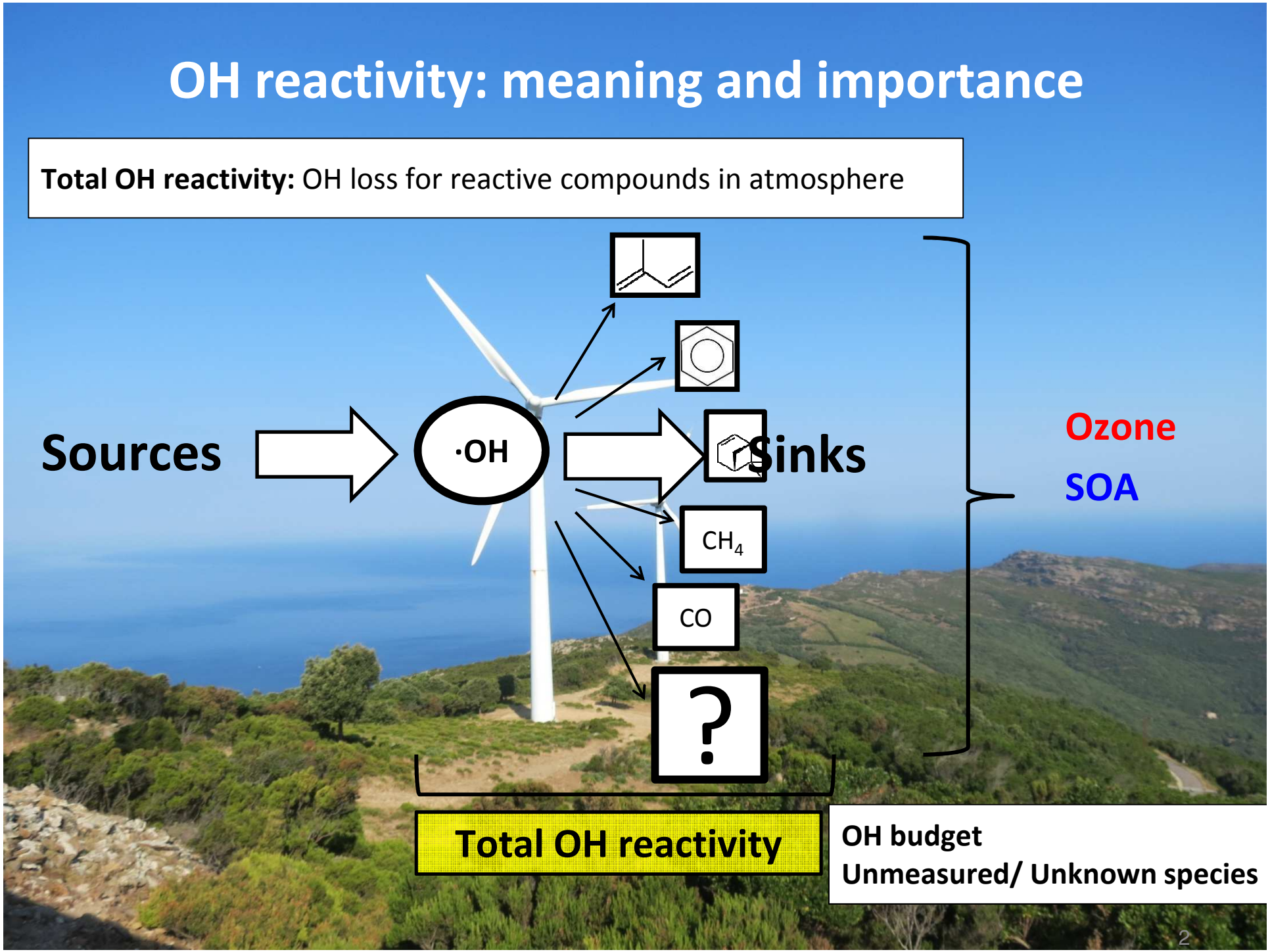
Nora Zannoni,

Valerie Gros, Roland Sarda-Esteve,

Sebastien Dusanter, Vincent Michoud, Vinayak Sinha

OH reactivity: meaning and importance

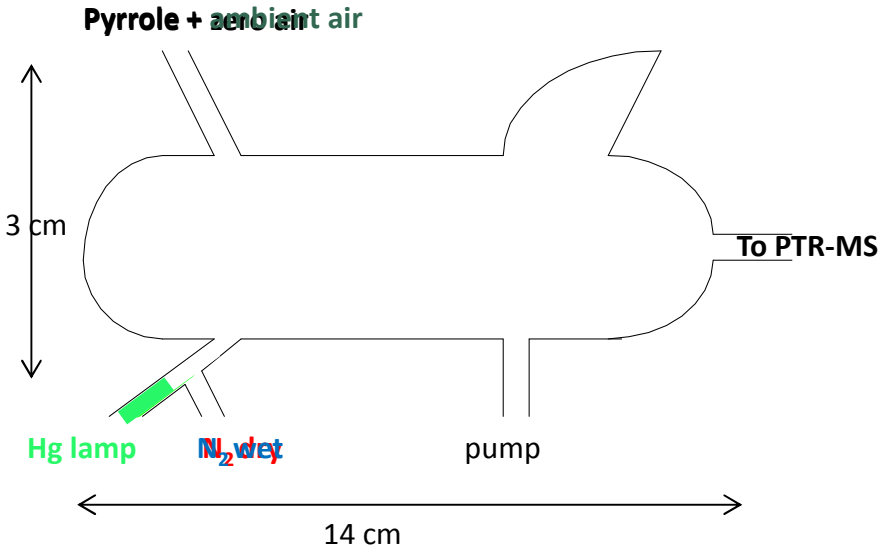
Total OH reactivity: OH loss for reactive compounds in atmosphere



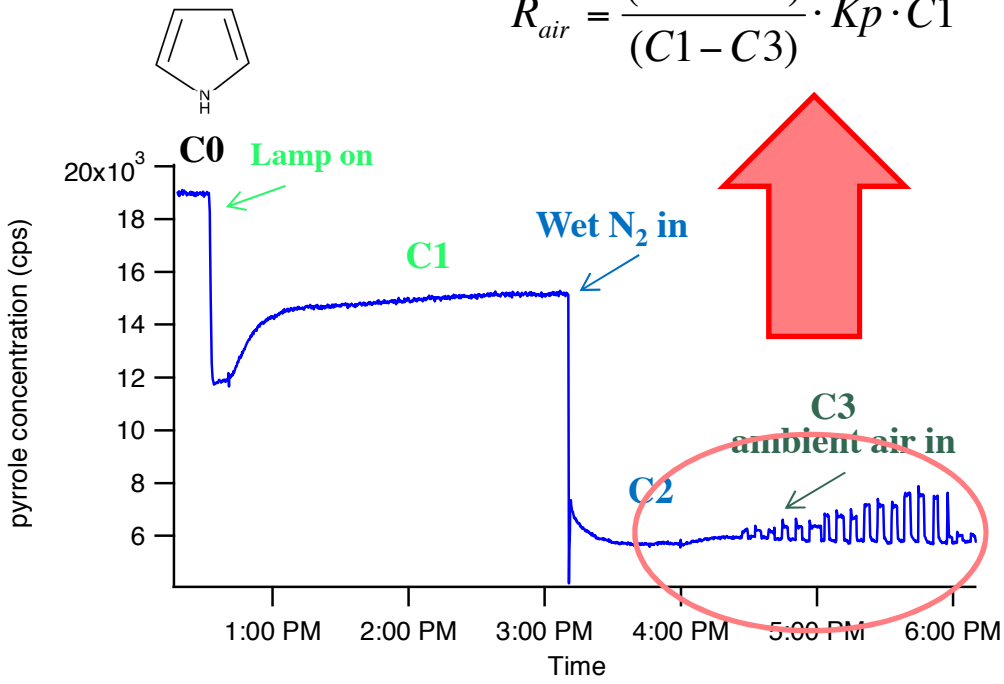
Measuring the Total OH reactivity: The Comparative Reactivity Method (CRM)

(Sinha et al., 2008)

- Glass reactor + PTR-MS
- OH produced in situ
- Pyrrole (m/z 68) reference compound
- Competition between pyrrole and ambient reactive compounds



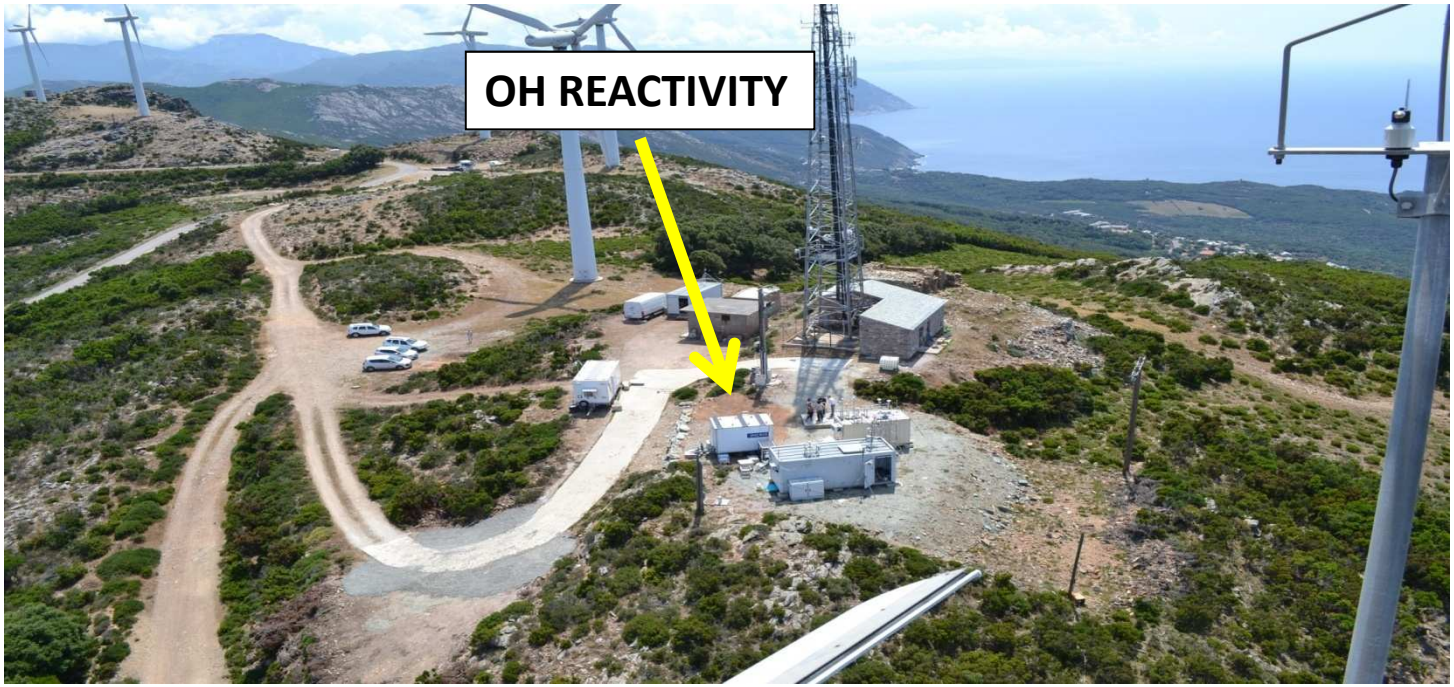
$$R_{air} = \frac{(C3 - C2)}{(C1 - C3)} \cdot Kp \cdot C1$$

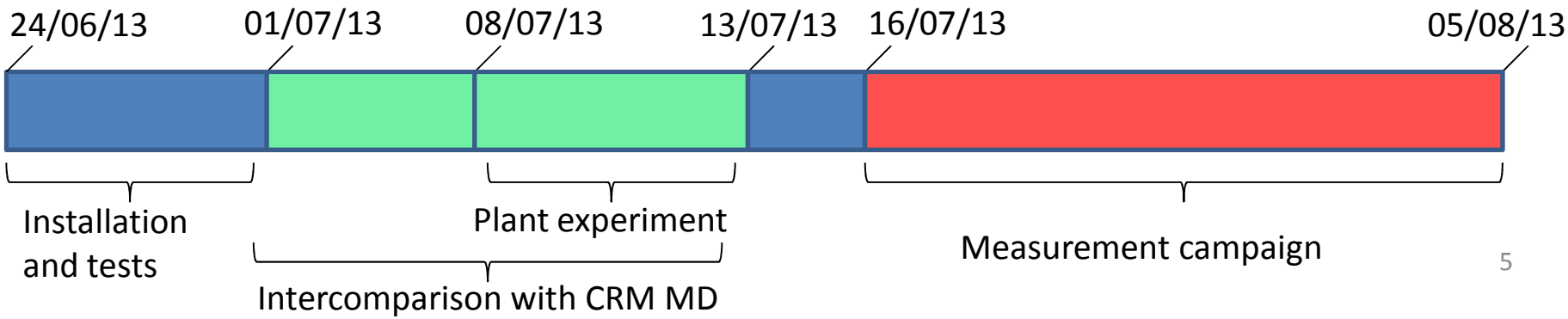


Site of study

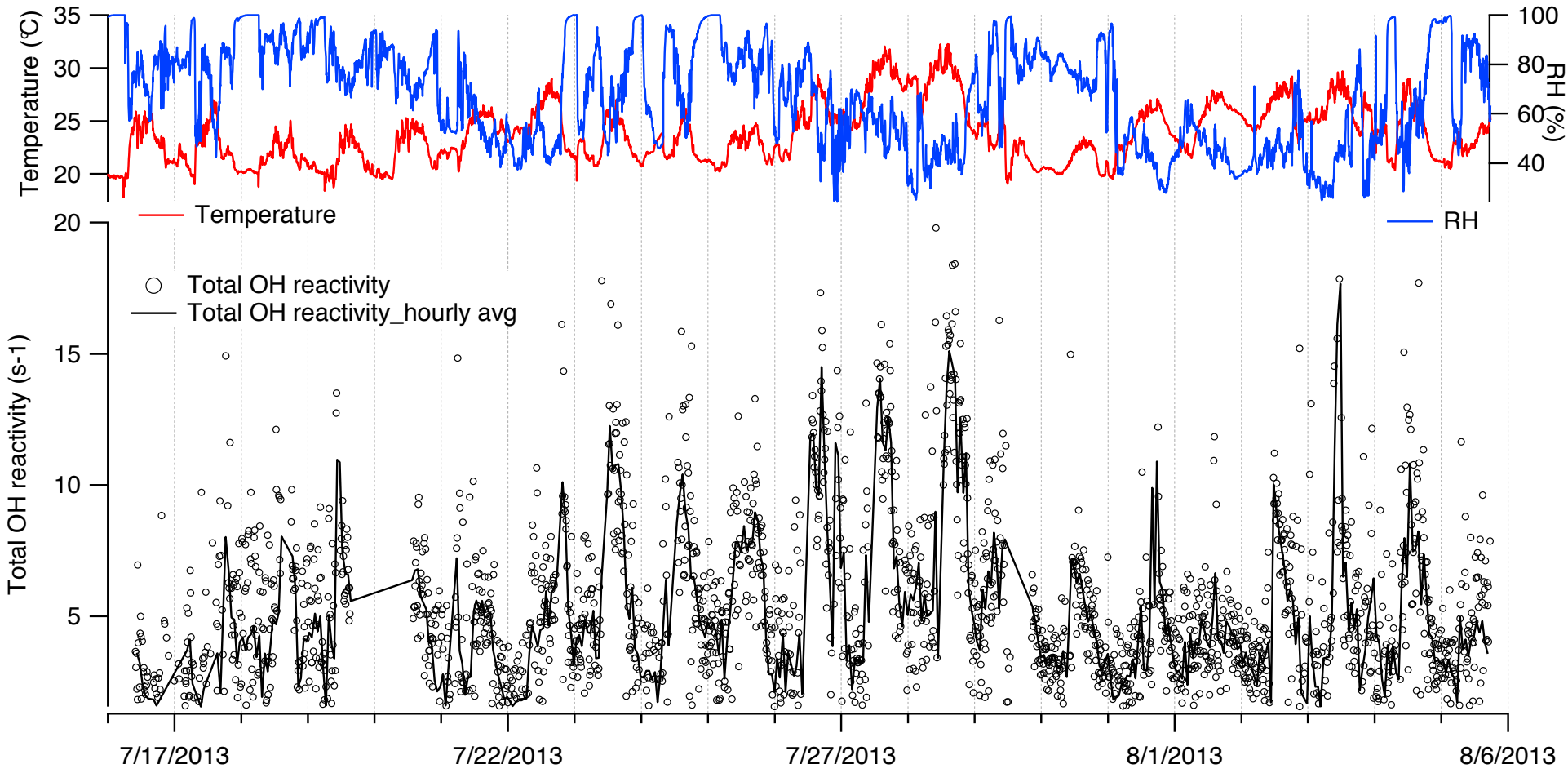
Cape Corsica monitoring station (42.97°N, 9.38°E, alt 533 m)

Goal: (i) Measure reactivity of air masses enriched in anthropogenic compounds and their oxidation products;
(ii) Use missing reactivity as a tool for chemical closure





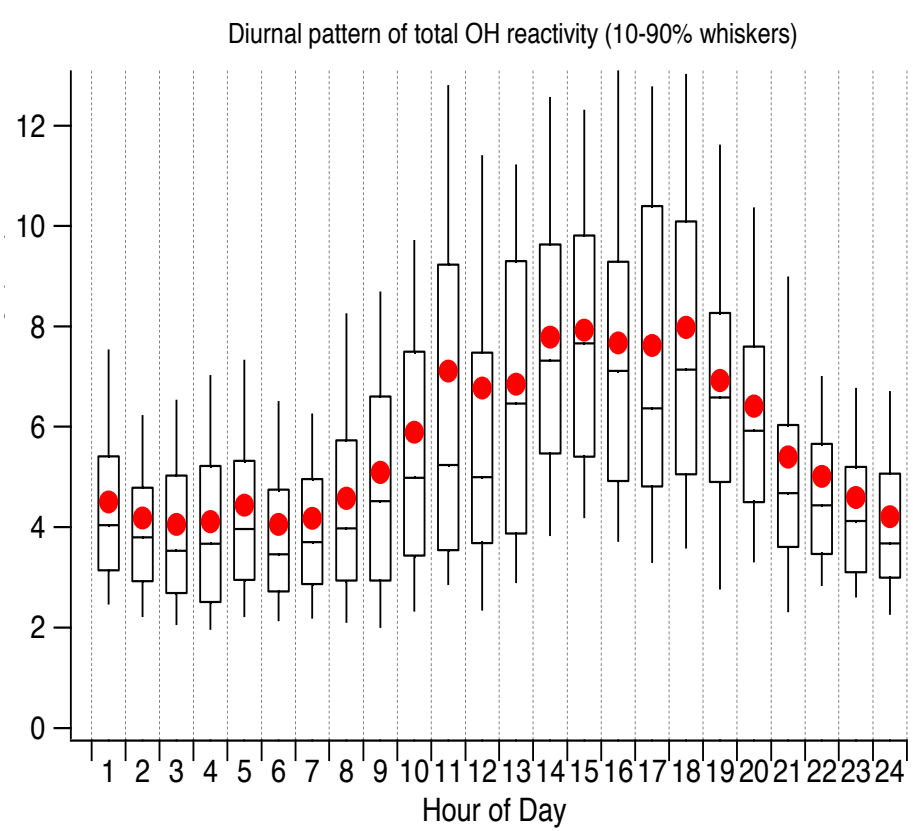
Total OH reactivity

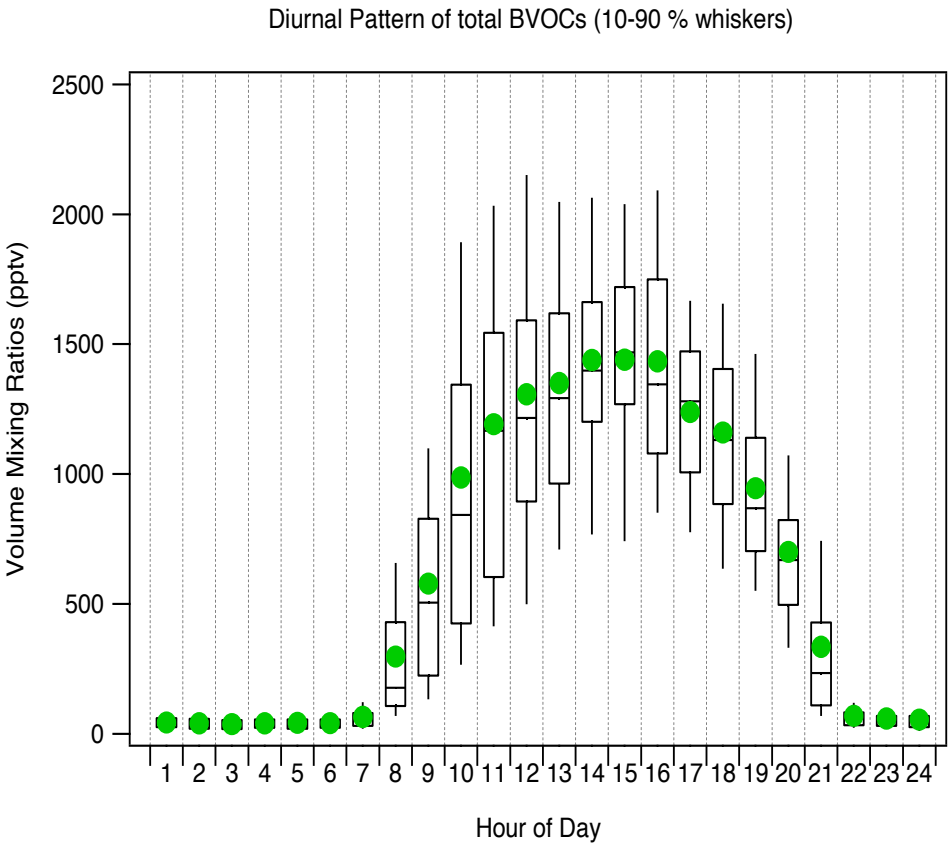


- Total OH reactivity ranges between CRM LOD up to 20 s^{-1}
- On average 5 s^{-1} during the whole campaign
- Diurnal profile
- Peaks when temperature increases

Zannoni et al., *in preparation +* poster

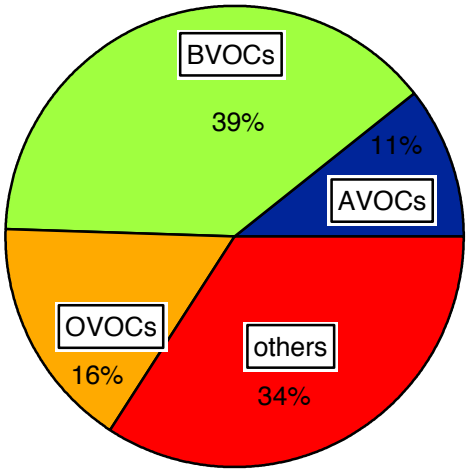
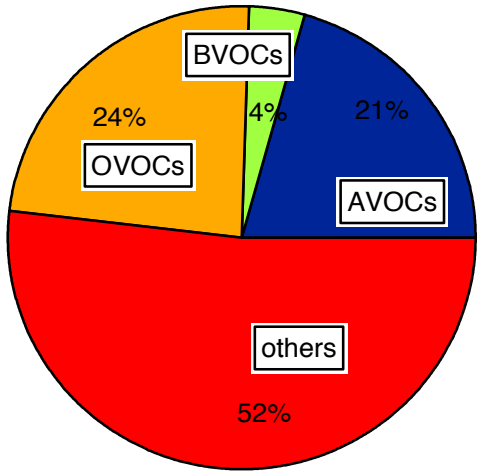
Diurnal pattern





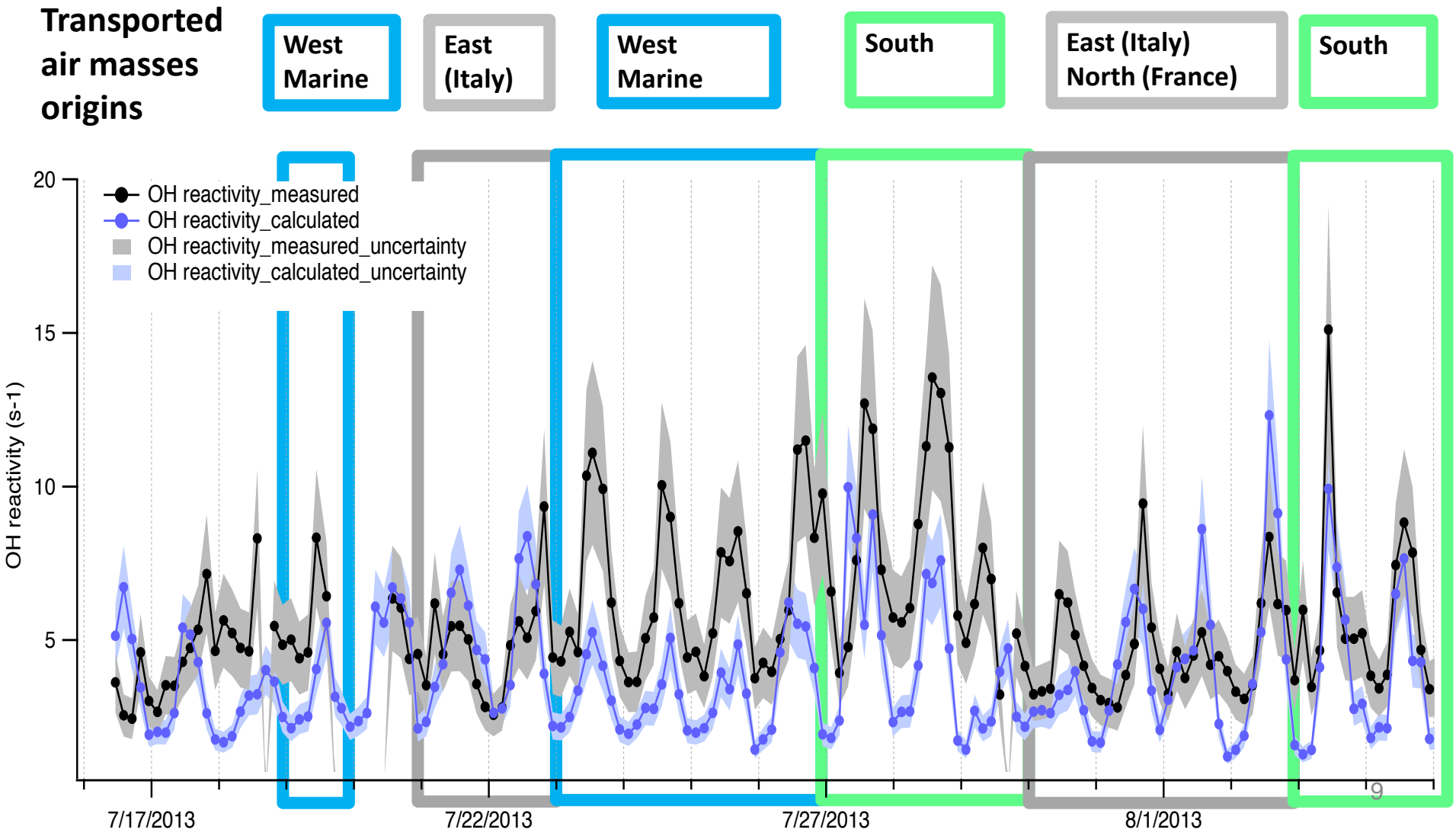
Diurnal pattern of total OH reactivity well resembles the one of total BVOCs

Ancillary gas phase measurements

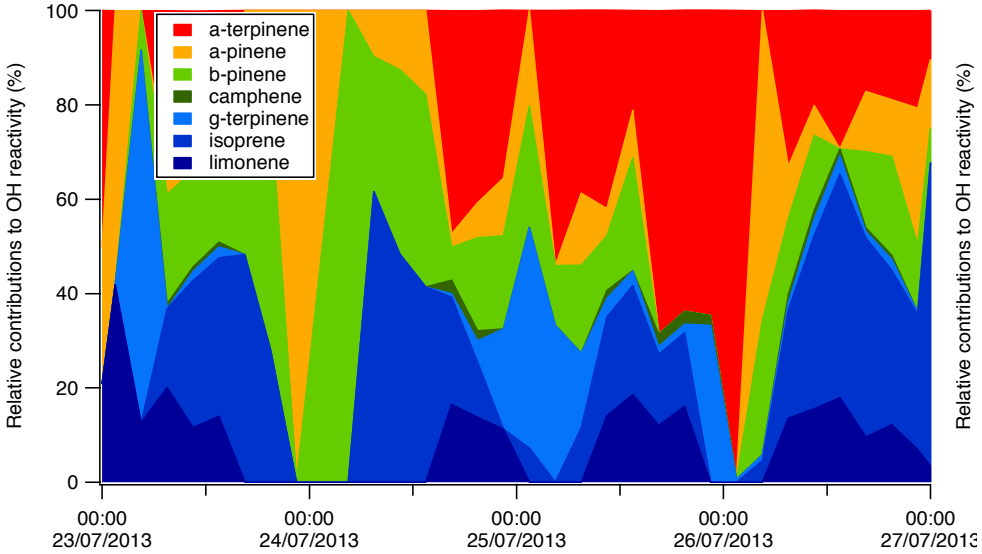
Species group	Species name
AVOCs (44)	Daytime OH reactivity speciation  Nighttime OH reactivity speciation  nonane, hexane, propene, s-2- uene, ,
BVOCs (	phene.
OVOCs (	one, propionic acid, ethyl vinyl ketone, butiric acid, nopinone, pinonaldehyde, methacrolein, methyl vinyl ketone, formaldehyde, methanol.
Others (3)	NO, NO_2, CO.

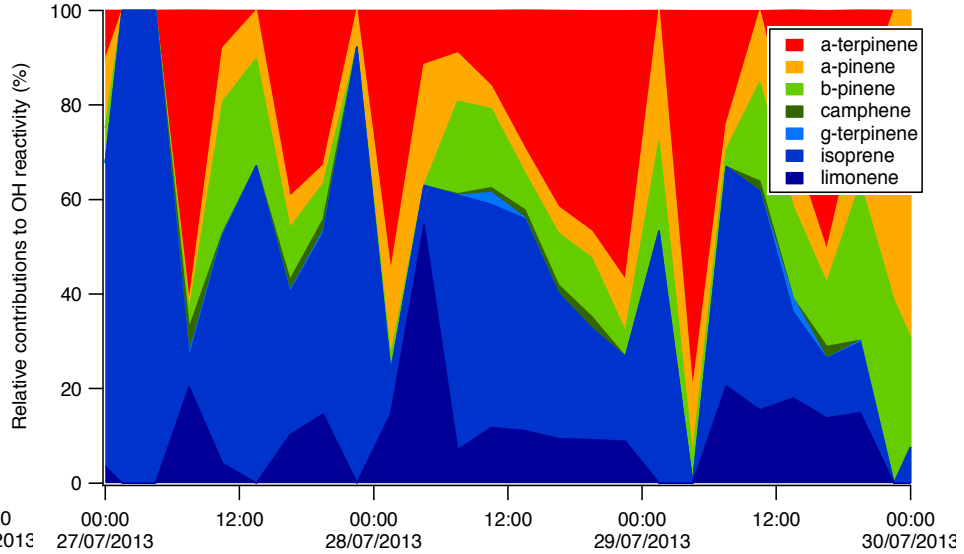
$$R = \sum_i k_{i+OH} \cdot X_i$$

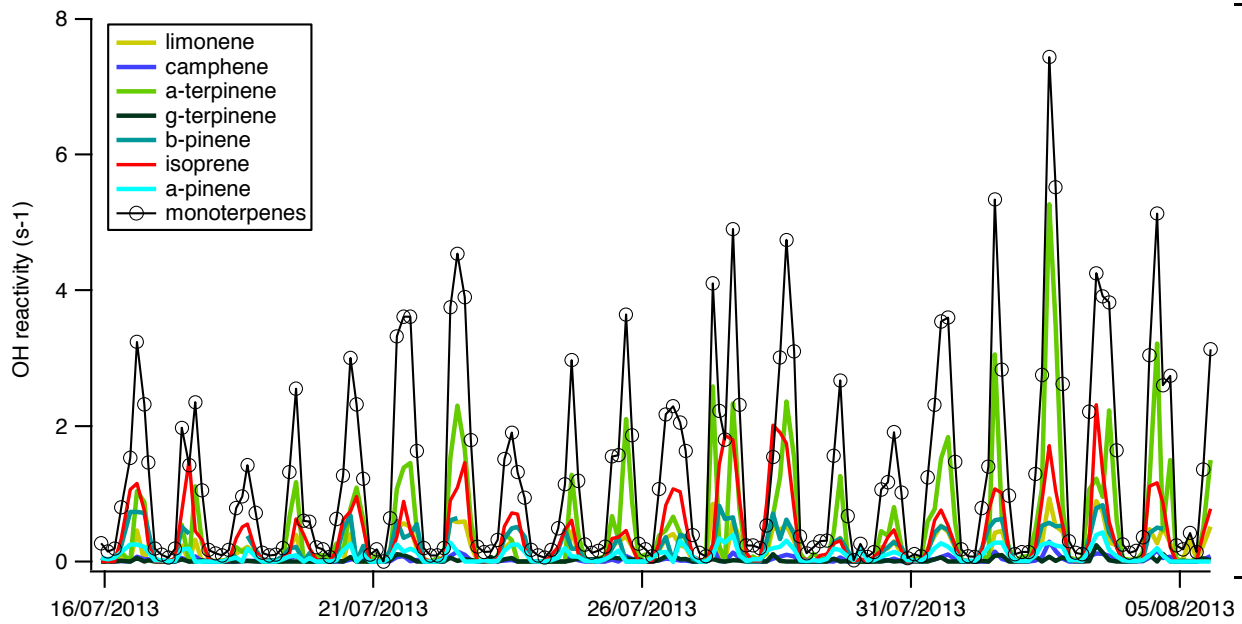
Measured vs calculated reactivity



BVOC's relative and absolute reactivity

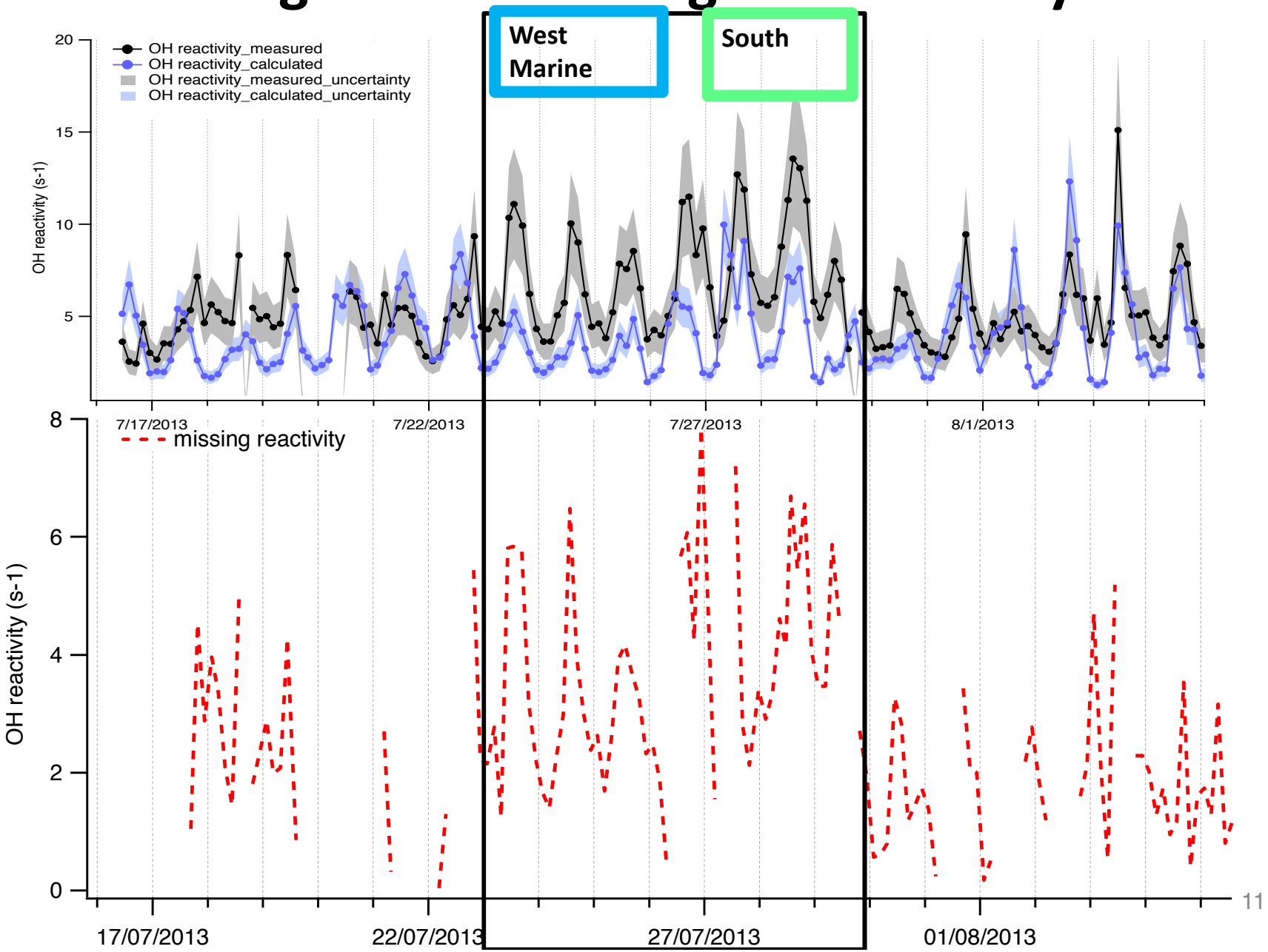






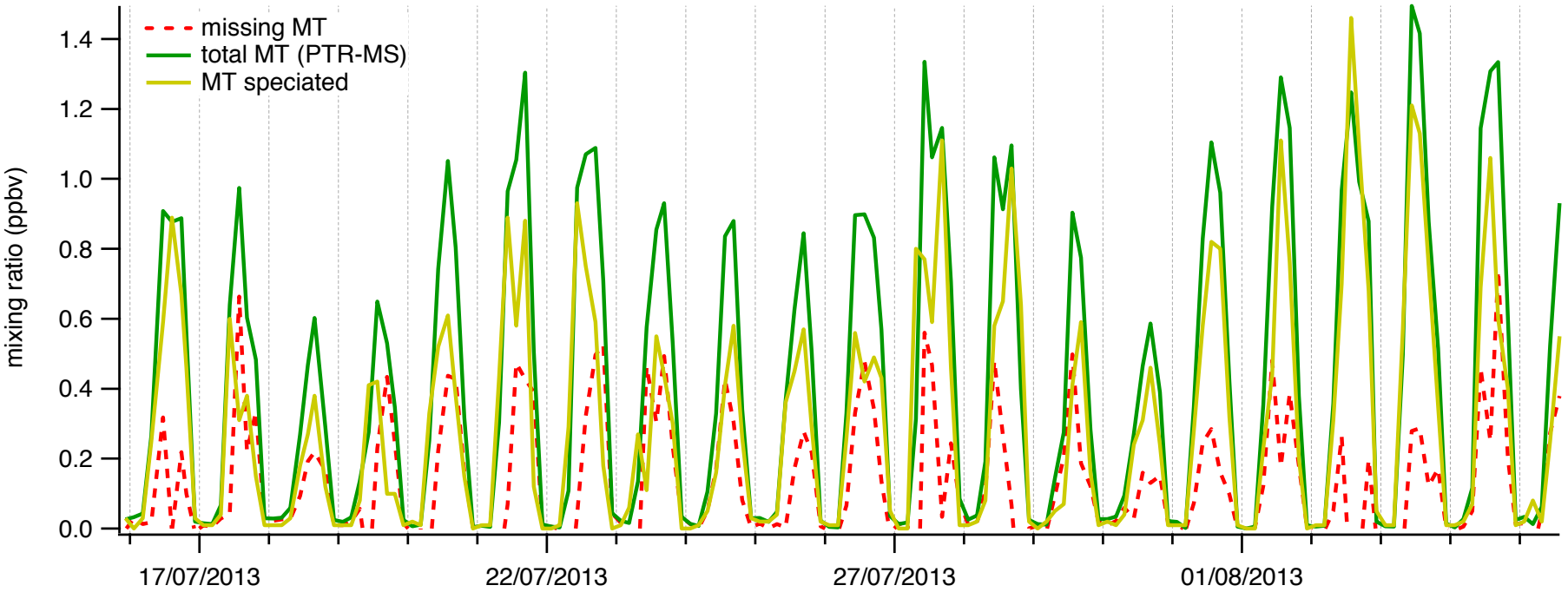
BVOC	Day (%)	Night (%)
a-pinene	7.69	20.73
b-pinene	16.49	16.05
limonene	12.03	11.36
camphene	1.48	3.05
a-terpinene	31.08	31.33
g-terpinene	1.28	5.04
isoprene	29.96	12.45

Significant missing OH reactivity



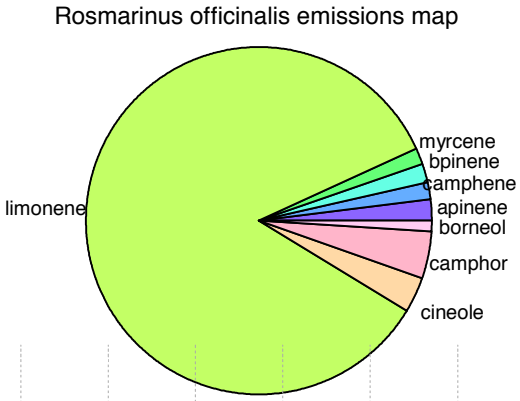
What can explain the missing OH reactivity?

Missing monoterpenes?

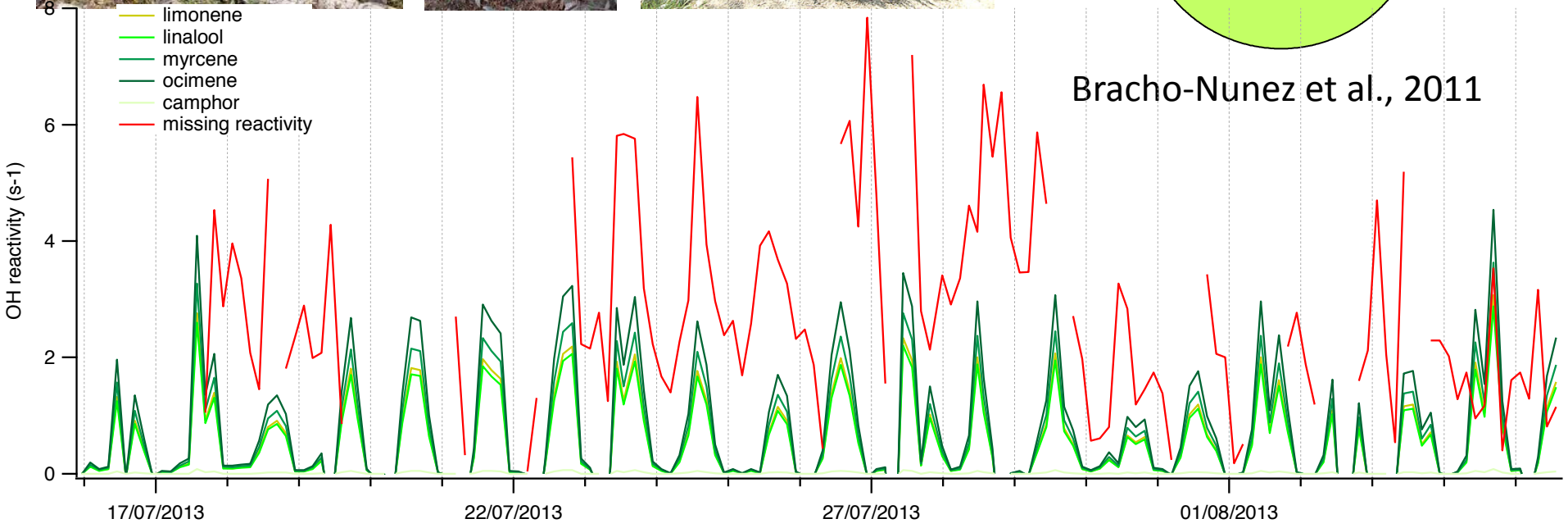


What can explain the missing OH reactivity?

Hypothetical influence of unmeasured monoterpenes expected for the Mediterranean shrubland based on the missing monoterpenes concentration



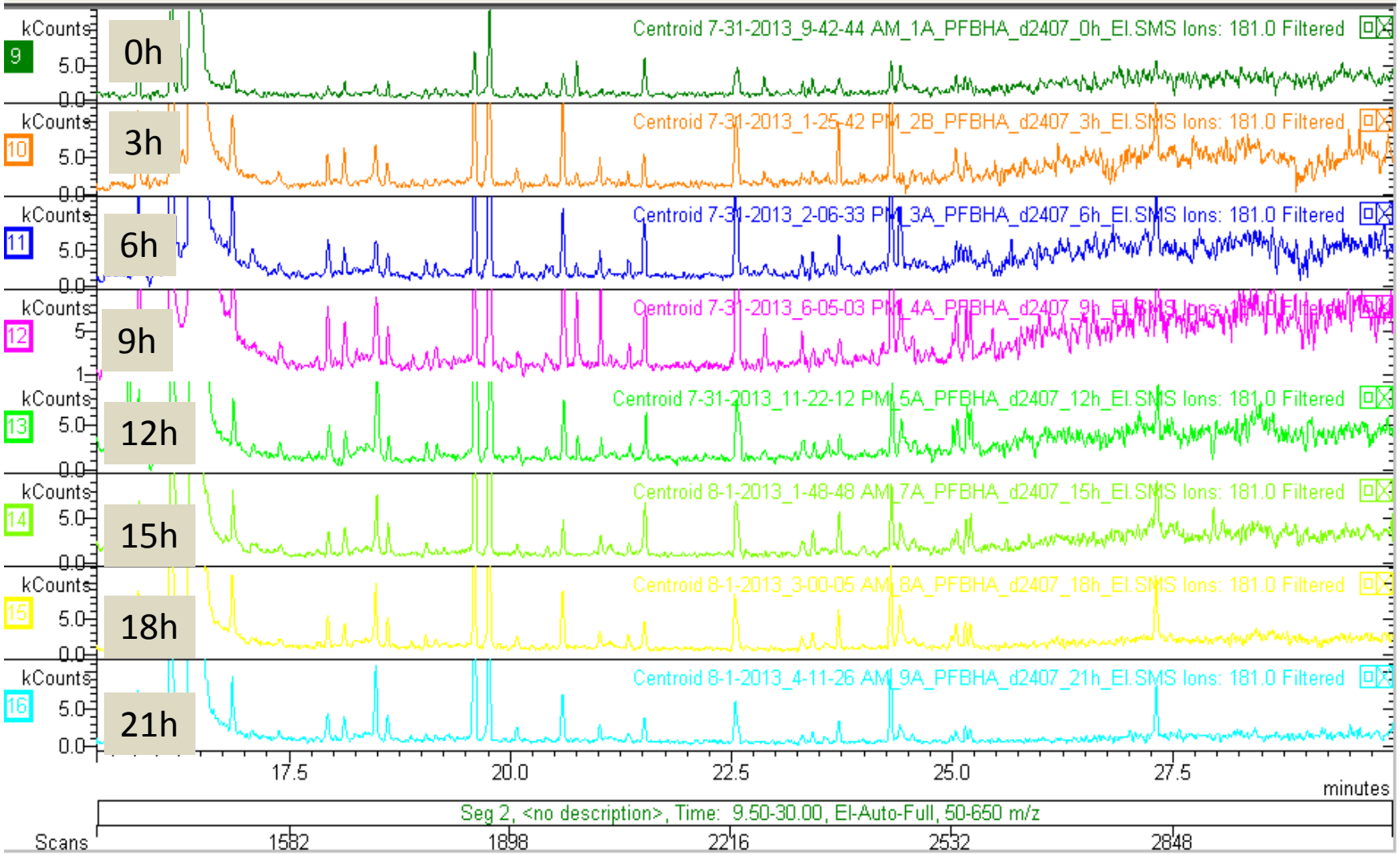
Bracho-Nunez et al., 2011



…In part yes!

What can also explain the missing OH reactivity?

Chromatogram 24/07/13 mono and multifunctional carbonyls



Unmeasured OVOC's? Probably also!

Courtesy of Agnes Borbon

Take home message(s):

- Total OH reactivity varied between LOD-20 s^{-1}

- Main influences from BVOC's

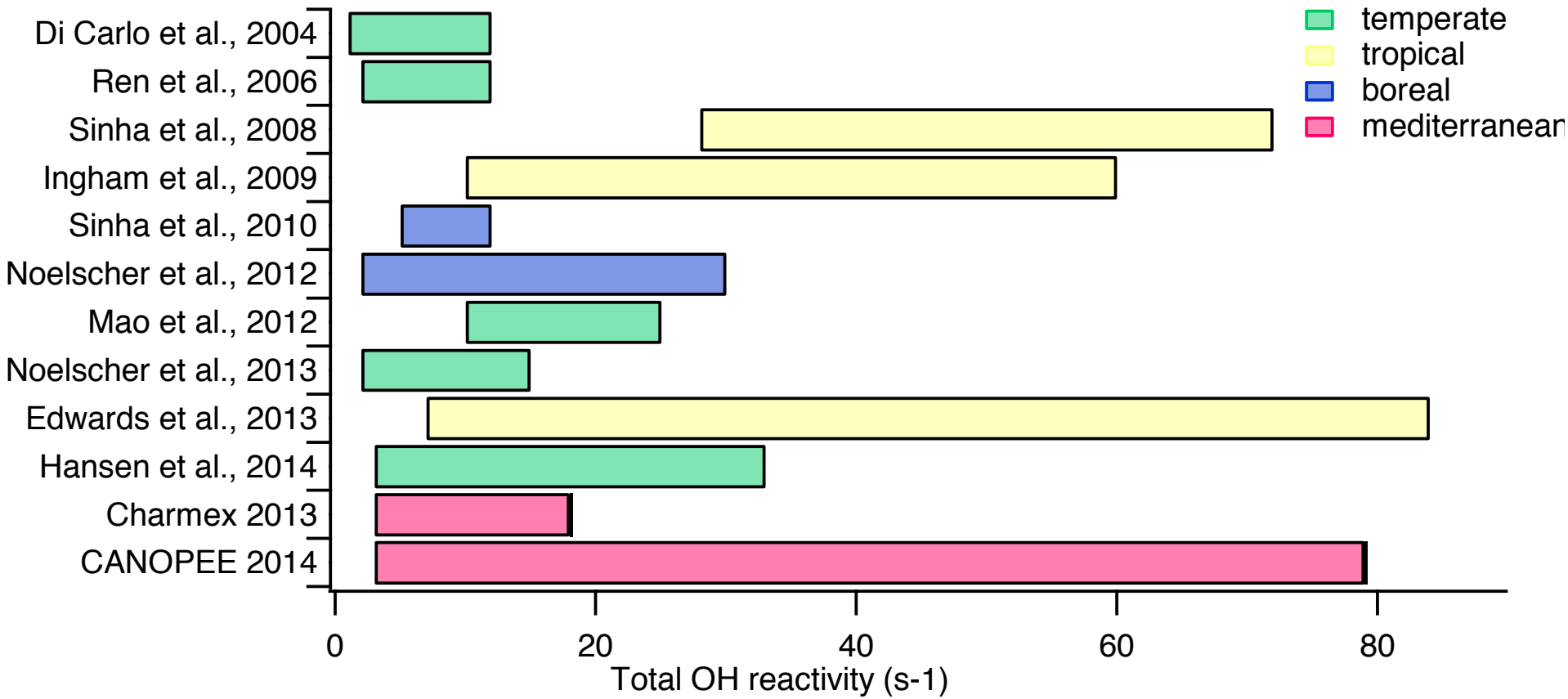
- Significant missing reactivity during 23-31/07:

    -missing MT
    -OVOC's

-Research question not completely answered: few anthropogenic events and low loadings of anthropogenic pollutants

-Further investigate the west marine period for OVOC's

OH reactivity in biogenic environments:



- High OH reactivity measured in the Mediterranean basin (even at a site not supposed to be "forested")
- Cape Corsica site very complex: budget not constrained, highest influence by BVOC's…

…what about the OH reactivity at other remote and continental Mediterranean sites?

Acknowledgments:

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LISA: Agnes Borbon

...and you for your attention!

ANY QUESTION?