“Production of Secondary Organic Aerosol from Multiphase Terpene Photooxidation”

Shepson Group
Purdue Climate Change Research Center

Project Hypotheses

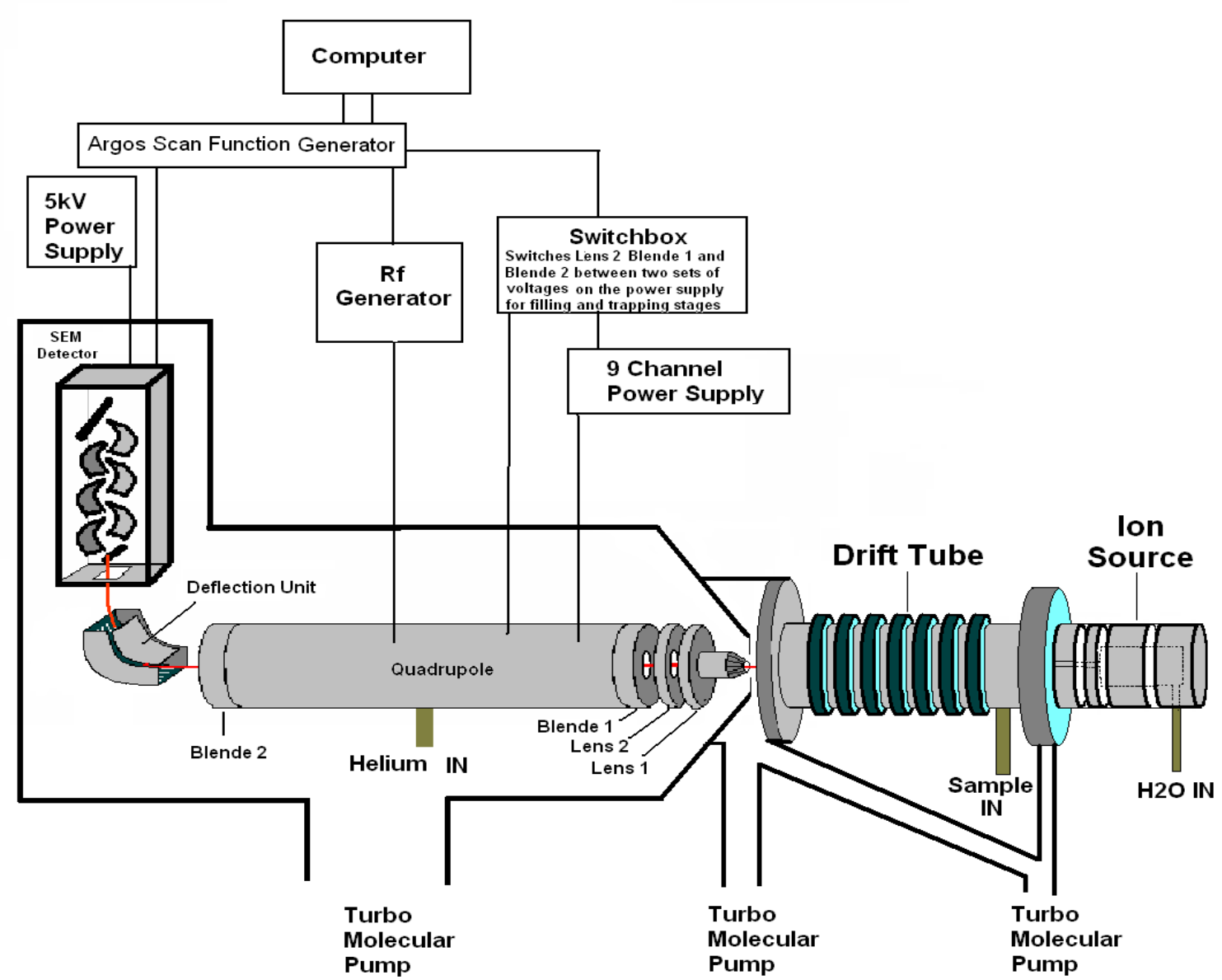
•PTRLIT can be used to vastly improve our ability to identify and quantify the photooxidation products of BVOCs that are important aerosol precursors.

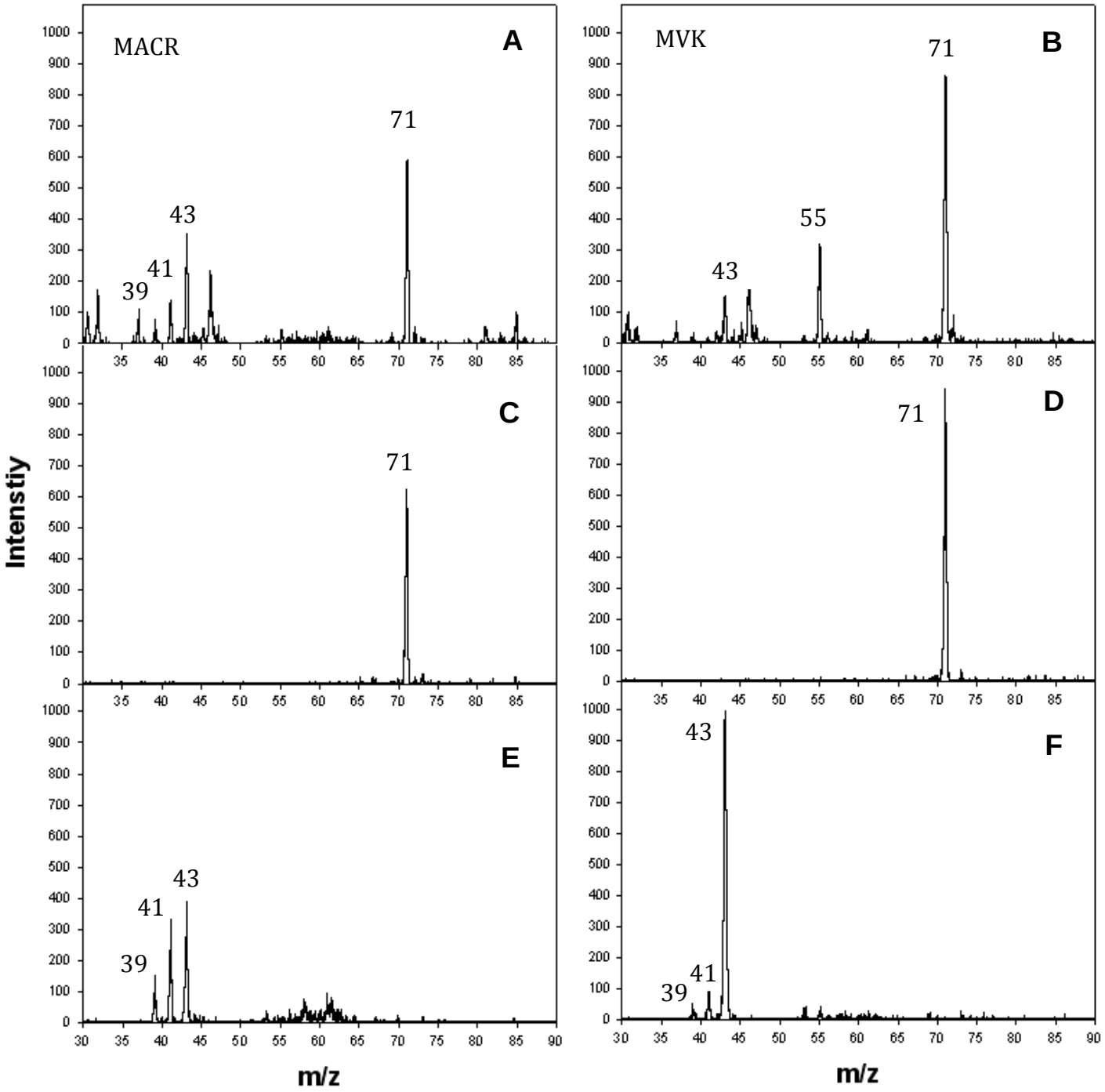
•DESI can be used in conjunction with smog chamber-based studies of BVOC/NOx irradiations to investigate the nature of oxidation products that are important SOA precursors.

•Aerosol can age both as a result of polymerization chemistry, but also because of aerosol-phase photochemistry, and this processing influences the distribution of species between the gas and aerosol phase.

•We can quantitatively assess the contribution of α- and β-pinene to ambient SOA production in forest environments through simultaneous measurement of their oxidation products and aerosol growth.

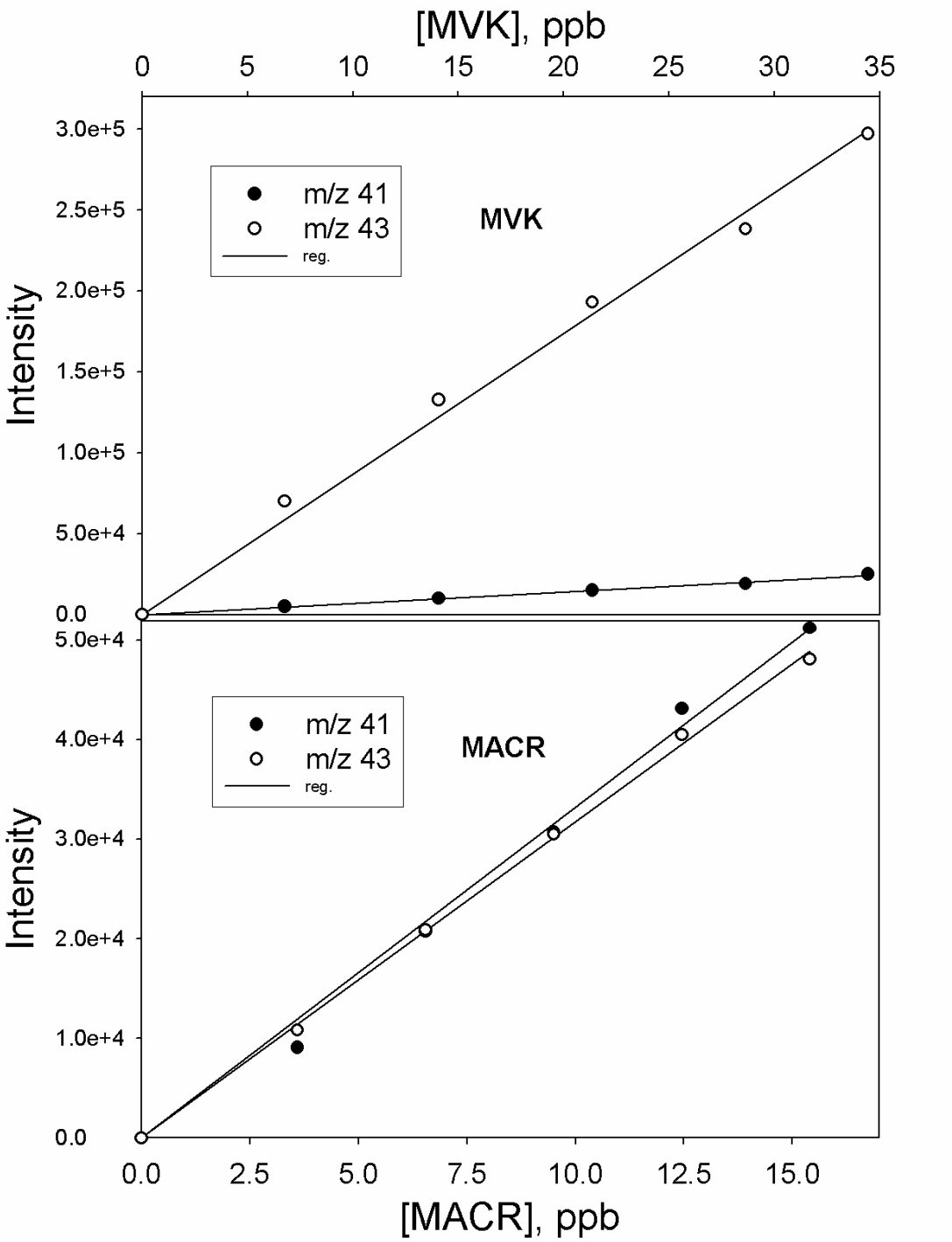
Proton Transfer Reaction Linear Ion Trap (PTR-LIT)



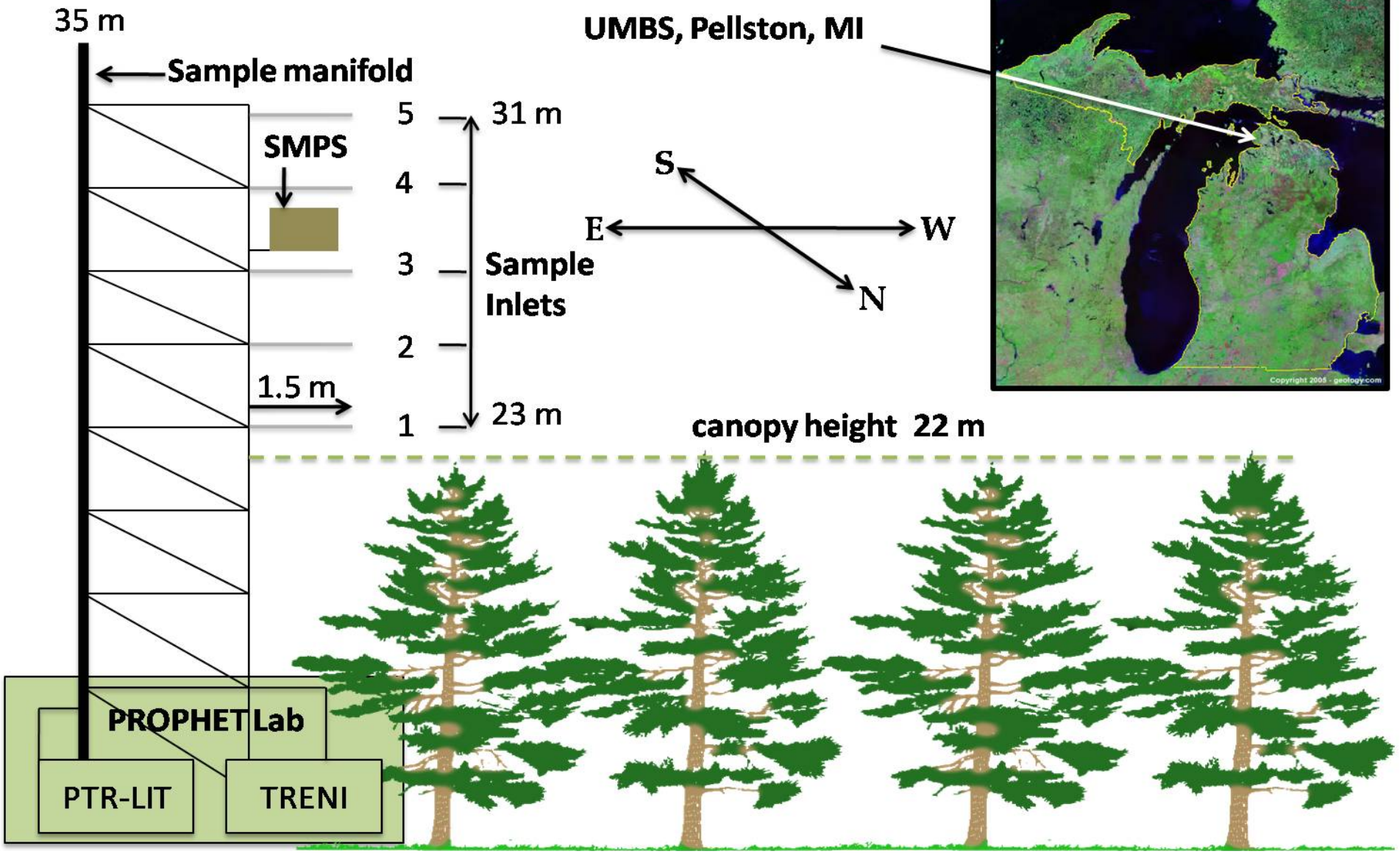


Lab Studies

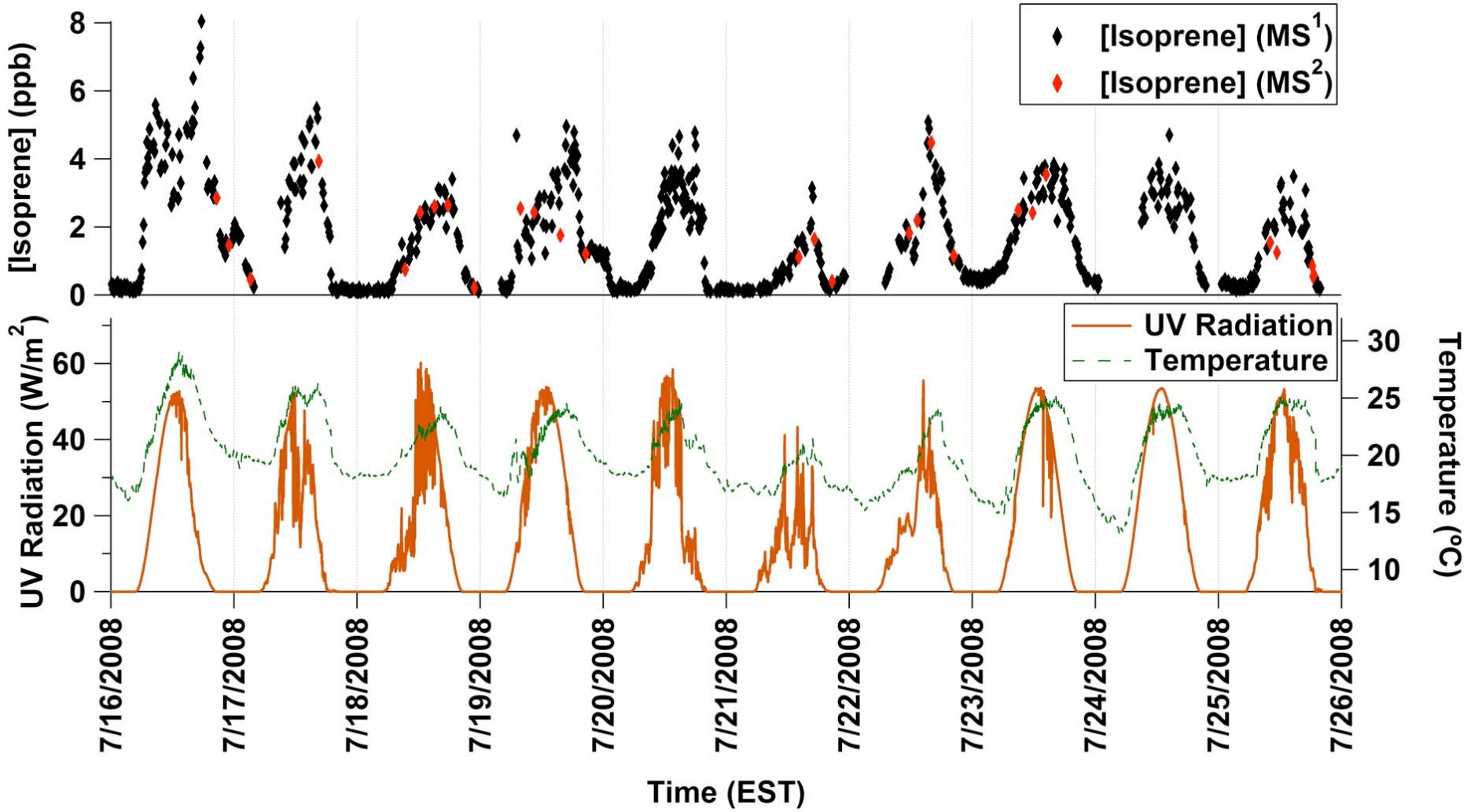
Mielke et al., *Anal. Chem.*, 2008

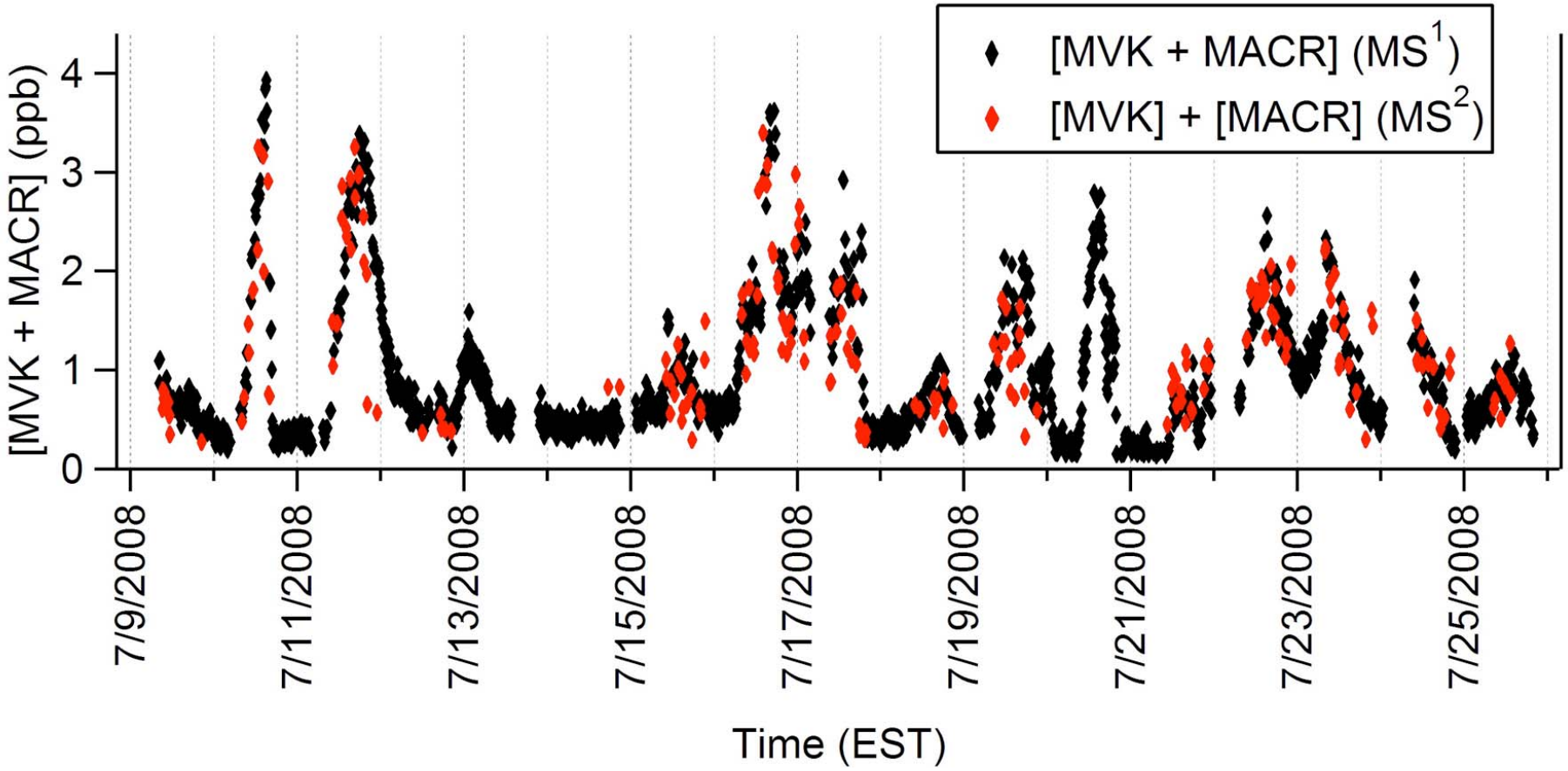

[MVK], ppb
0
5
10
15
20
25
30
35
3.0e+5
2.5e+5
2.0e+5
1.5e+5
1.0e+5
5.0e+4
0.0
Intensity
m/z 41
m/z 43
reg.
MVK
5.0e+4
4.0e+4
3.0e+4
2.0e+4
1.0e+4
0.0
Intensity
m/z 41
m/z 43
reg.
MACR
0.0
2.5
5.0
7.5
10.0
12.5
15.0
[MACR], ppb

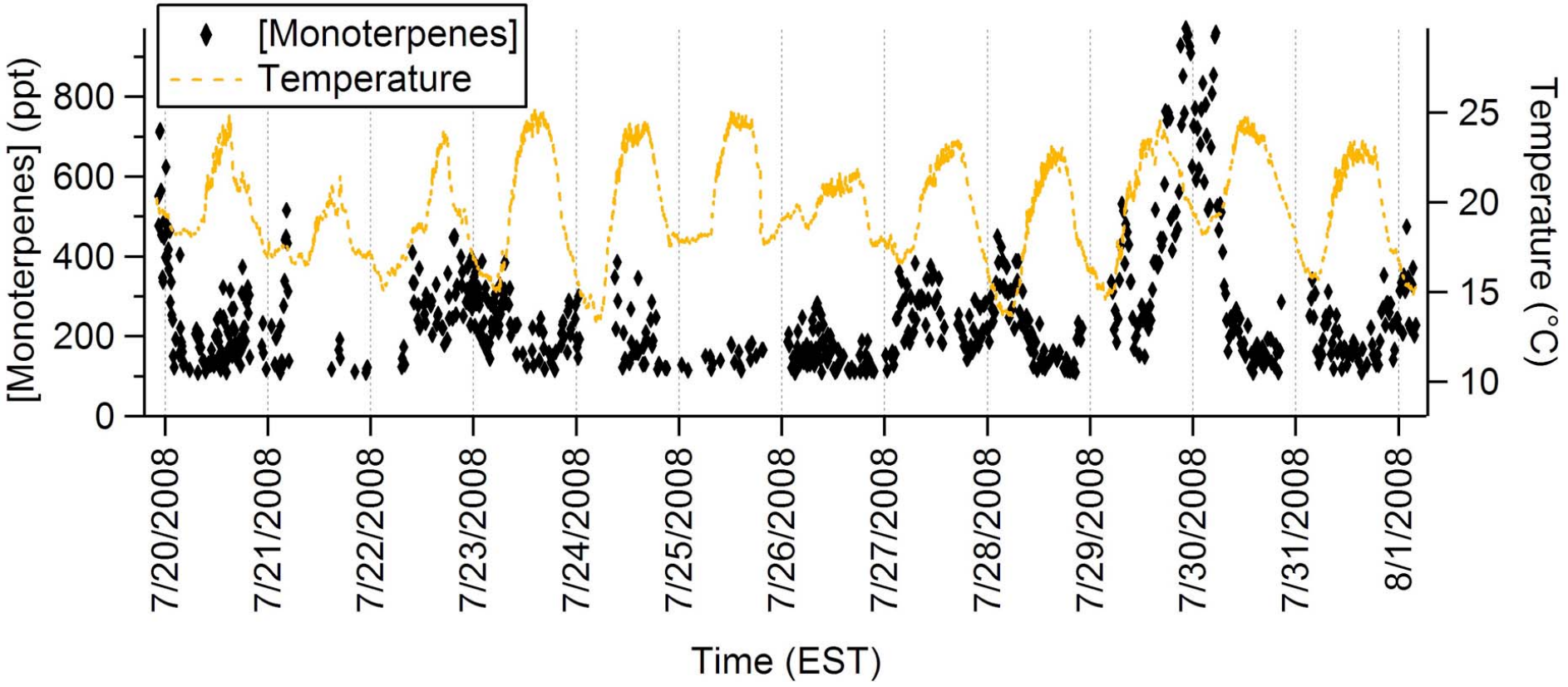
But, does it work in the real world?

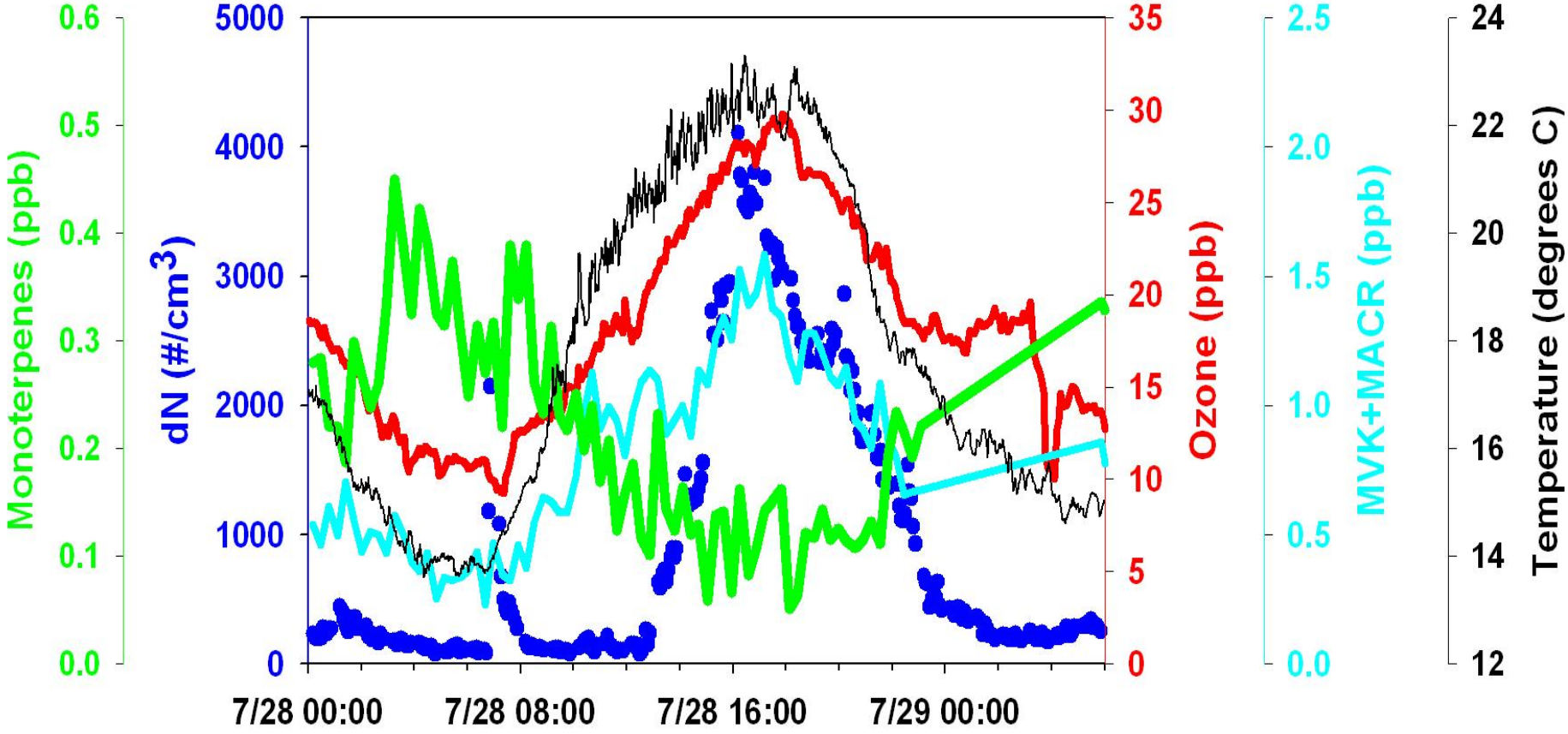


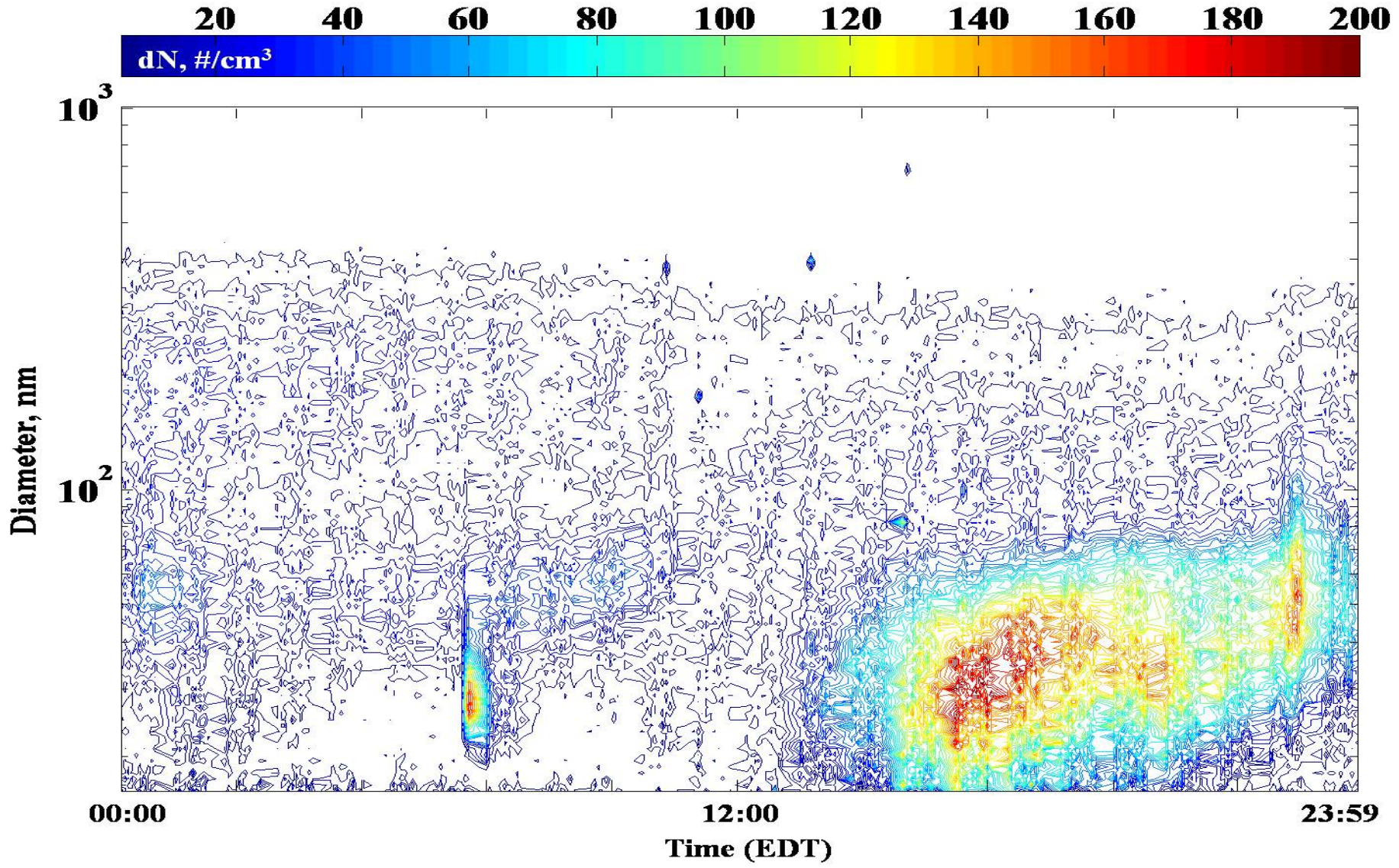
Mielke et al., *Anal. Chem.*, 2010

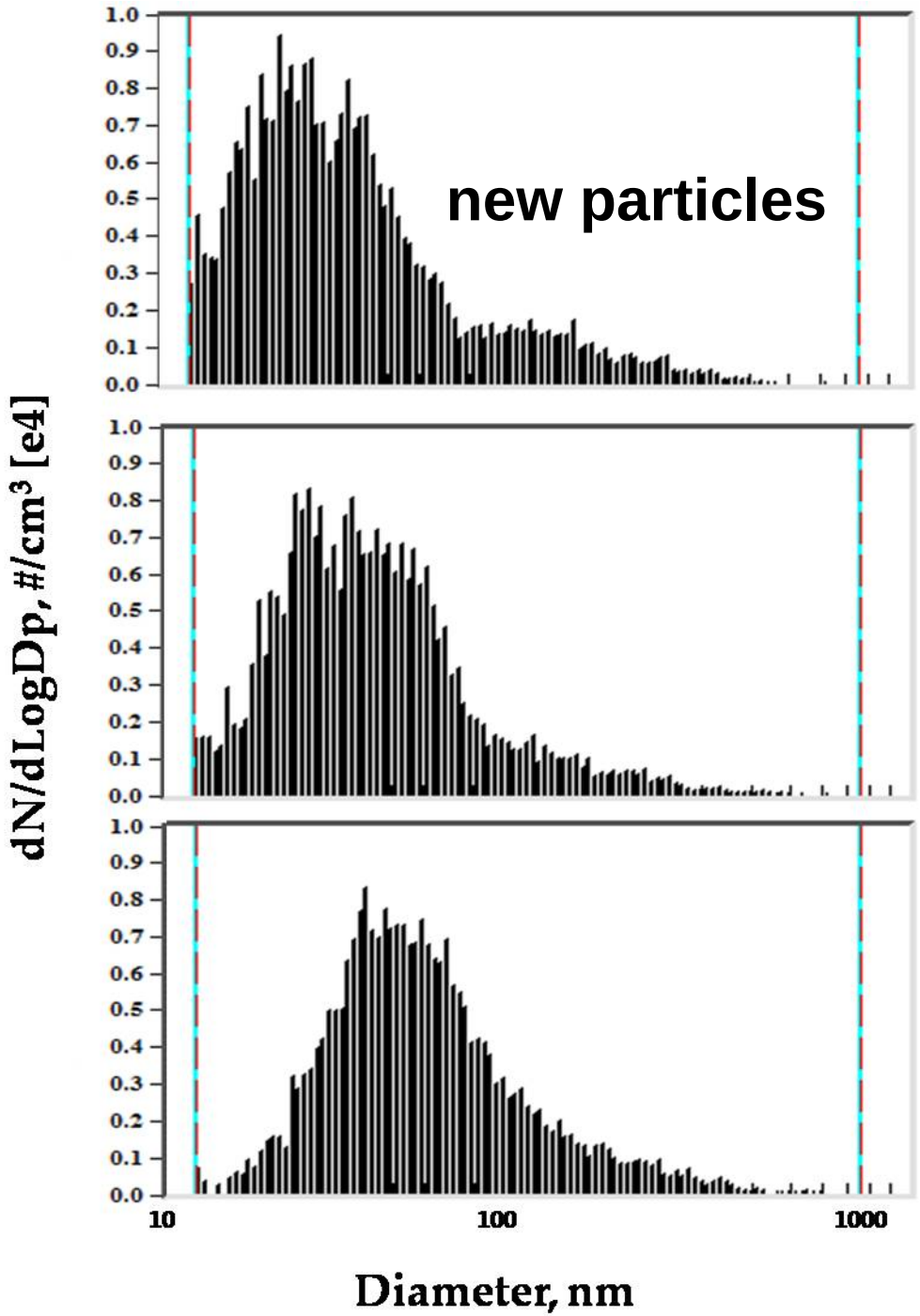



[MVK + MACR] (MS1)
[MVK] + [MACR] (MS2)
[MVK + MACR] (ppb)
0
1
2
3
4
7/9/2008
7/11/2008
7/13/2008
7/15/2008
7/17/2008
7/19/2008
7/21/2008
7/23/2008
7/25/2008
Time (EST)


[Monoterpenes]
Temperature
[Monoterpenes] (ppt)
0
200
400
600
800
Temperature (°C)
10
15
20
25
7/20/2008
7/21/2008
7/22/2008
7/23/2008
7/24/2008
7/25/2008
7/26/2008
7/27/2008
7/28/2008
7/29/2008
7/30/2008
7/31/2008
8/1/2008
Time (EST)


Monoterpenes (ppb)
0.6
0.5
0.4
0.3
0.2
0.1
0.0
dN (#/cm3)
5000
4000
3000
2000
1000
0
Ozone (ppb)
35
30
25
20
15
10
5
0
MVK+MACR (ppb)
2.5
2.0
1.5
1.0
0.5
0.0
Temperature (degrees C)
24
22
20
18
16
14
12
7/28 00:00
7/28 08:00
7/28 16:00
7/29 00:00


20
40
60
80
100
120
140
160
180
200
dN, #/cm3
10^3
10^2
Diameter, nm
00:00
12:00
23:59
Time (EDT)



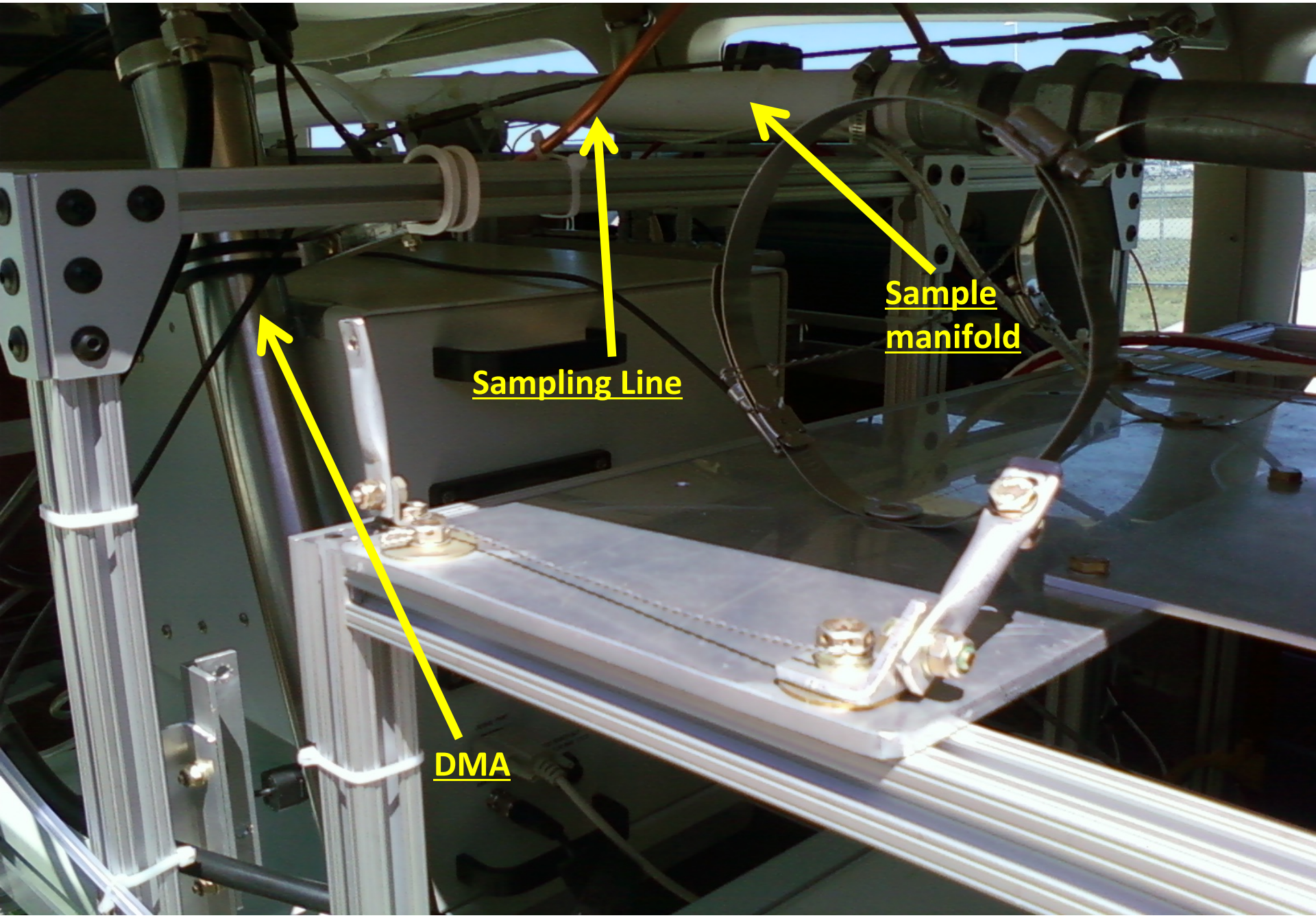
Hypothesis:

New particles are produced from BVOC oxidation in the near-canopy environment.

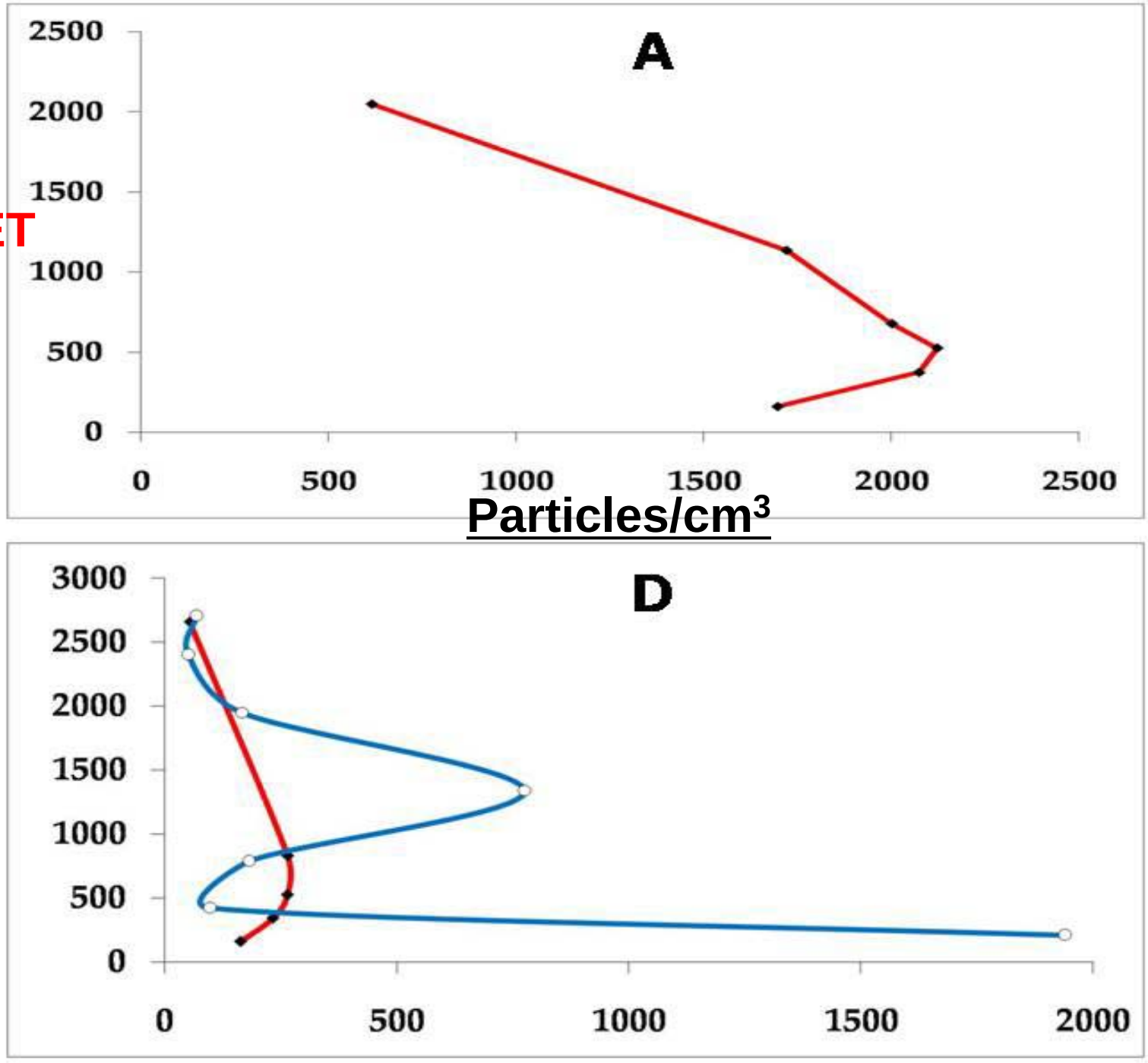
If so, we will see a vertical gradient of Aitken nuclei

Airborne Laboratory for Atmospheric Research (ALAR)

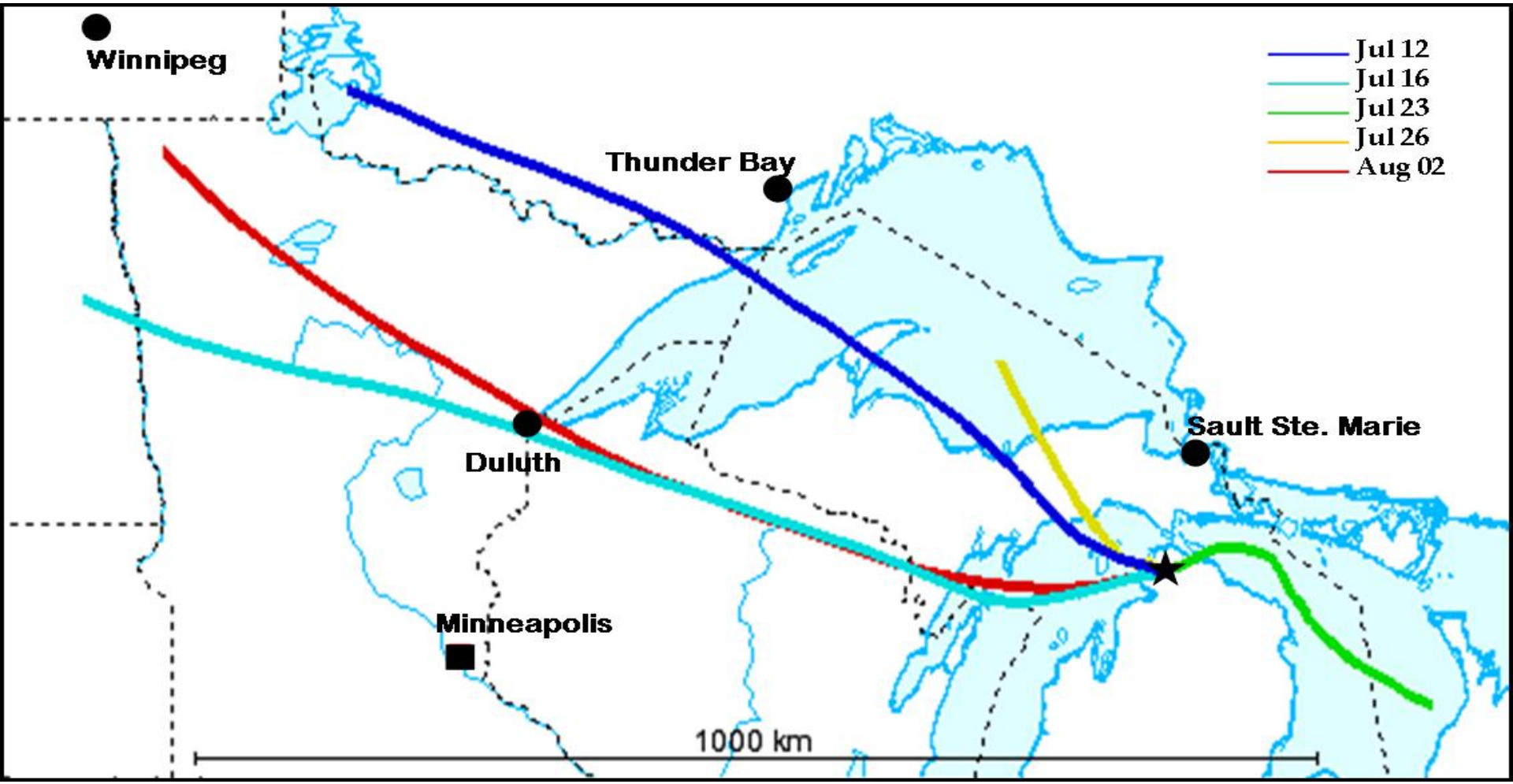
http://www.purdue.edu/climate

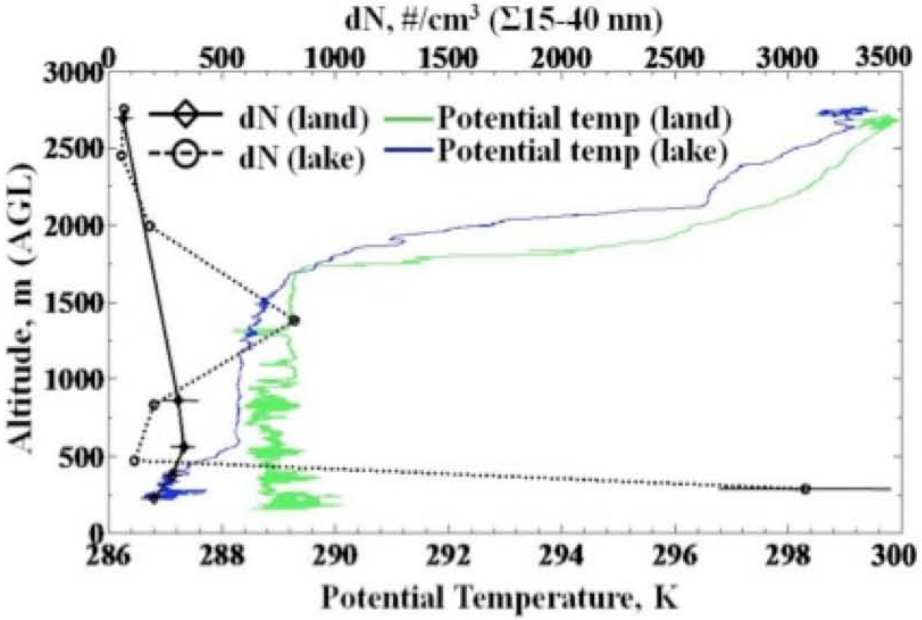

Sample manifold
Sampling Line
DMA

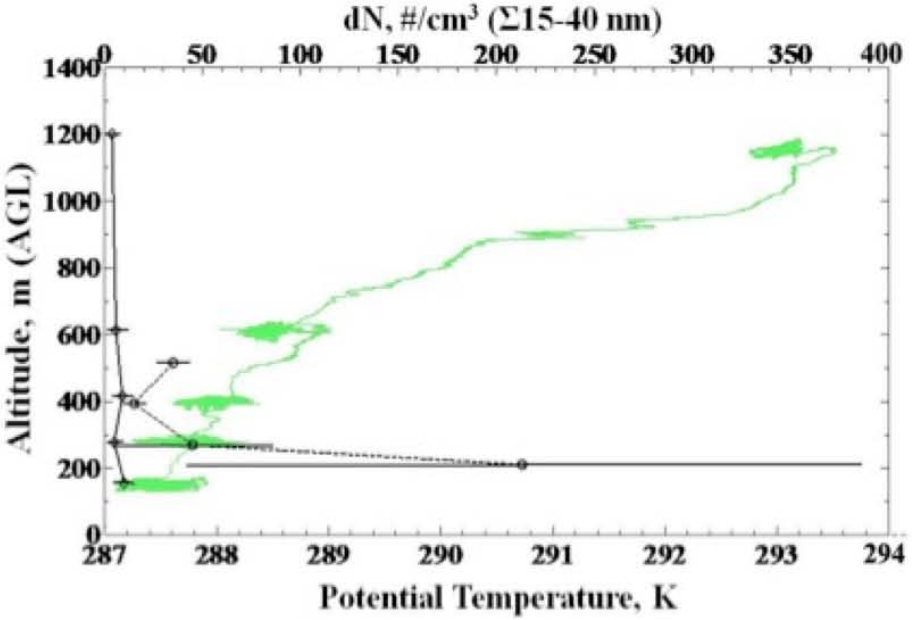
Profile over PROPHET

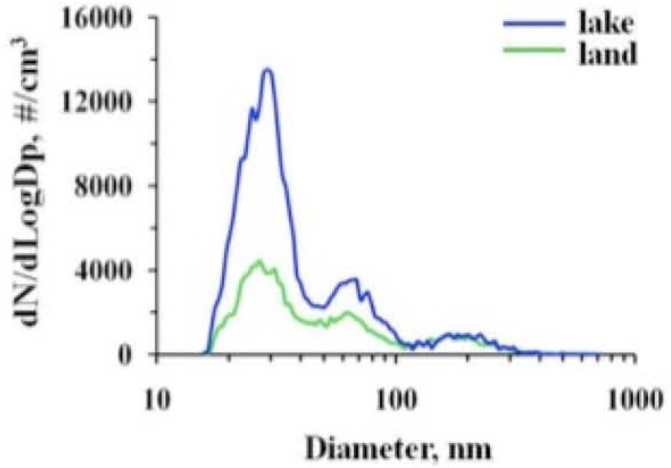


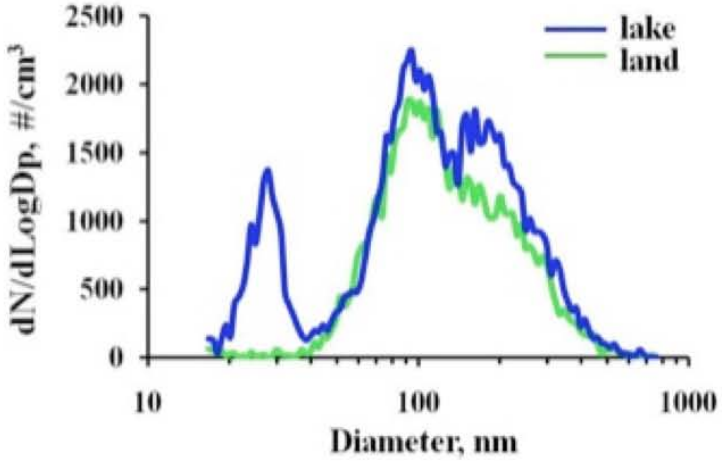
HYSPLIT Back Trajectories




dN, #/cm3 (Σ15-40 nm)
0
500
1000
1500
2000
2500
3000
3500
dN (land)
dN (lake)
Potential temp (land)
Potential temp (lake)
Altitude, m (AGL)
0
500
1000
1500
2000
2500
3000
286
288
290
292
294
296
298
300
Potential Temperature, K

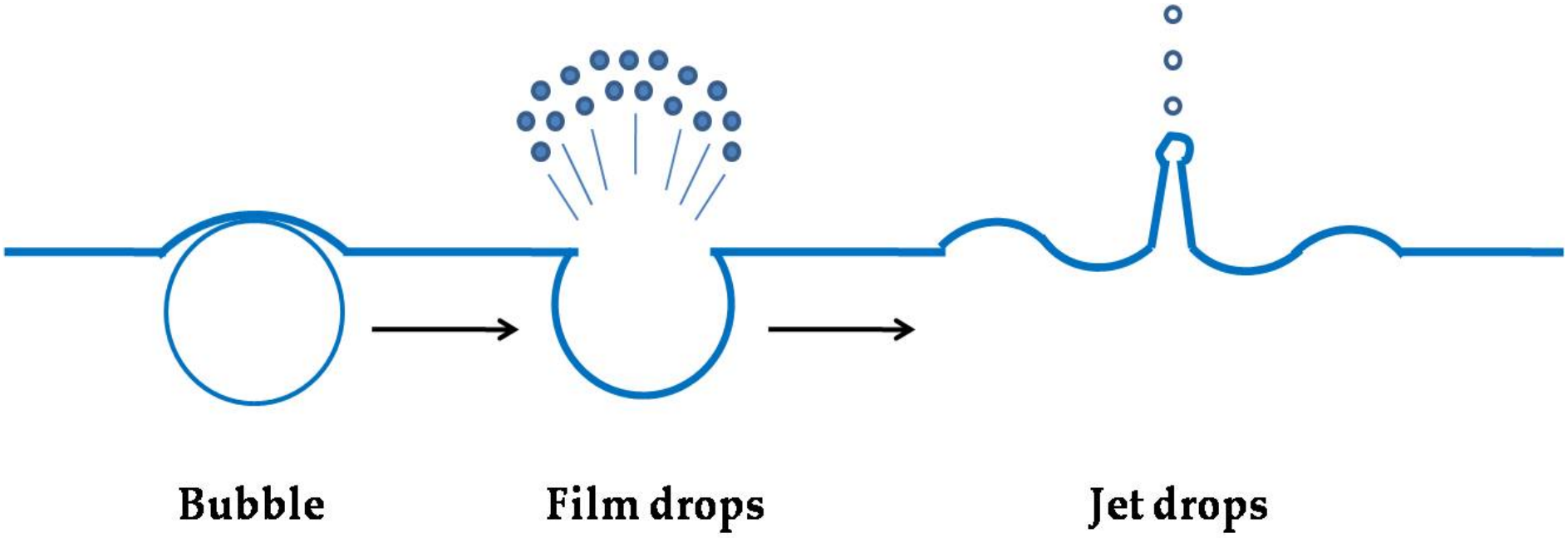

dN, #/cm3 (Σ15-40 nm)
0
50
100
150
200
250
300
350
400
Altitude, m (AGL)
0
200
400
600
800
1000
1200
1400
287
288
289
290
291
292
293
294
Potential Temperature, K


lake
land
dN/dLogDp, #/cm3
0
4000
8000
12000
16000
10
100
1000
Diameter, nm

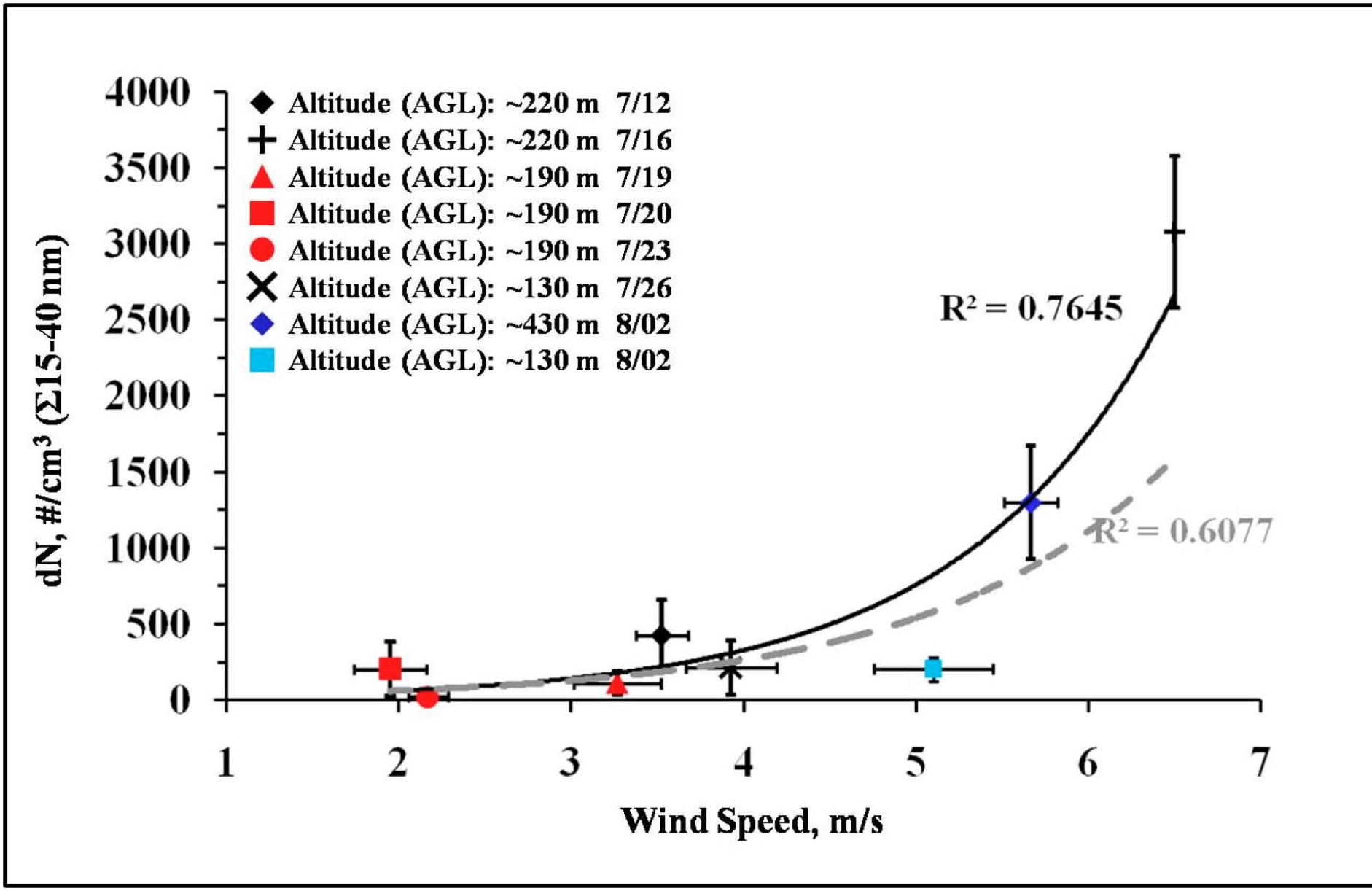

lake
land
dN/dLogDp, #/cm3
0
500
1000
1500
2000
2500
10
100
1000
Diameter, nm

Hypothesis:

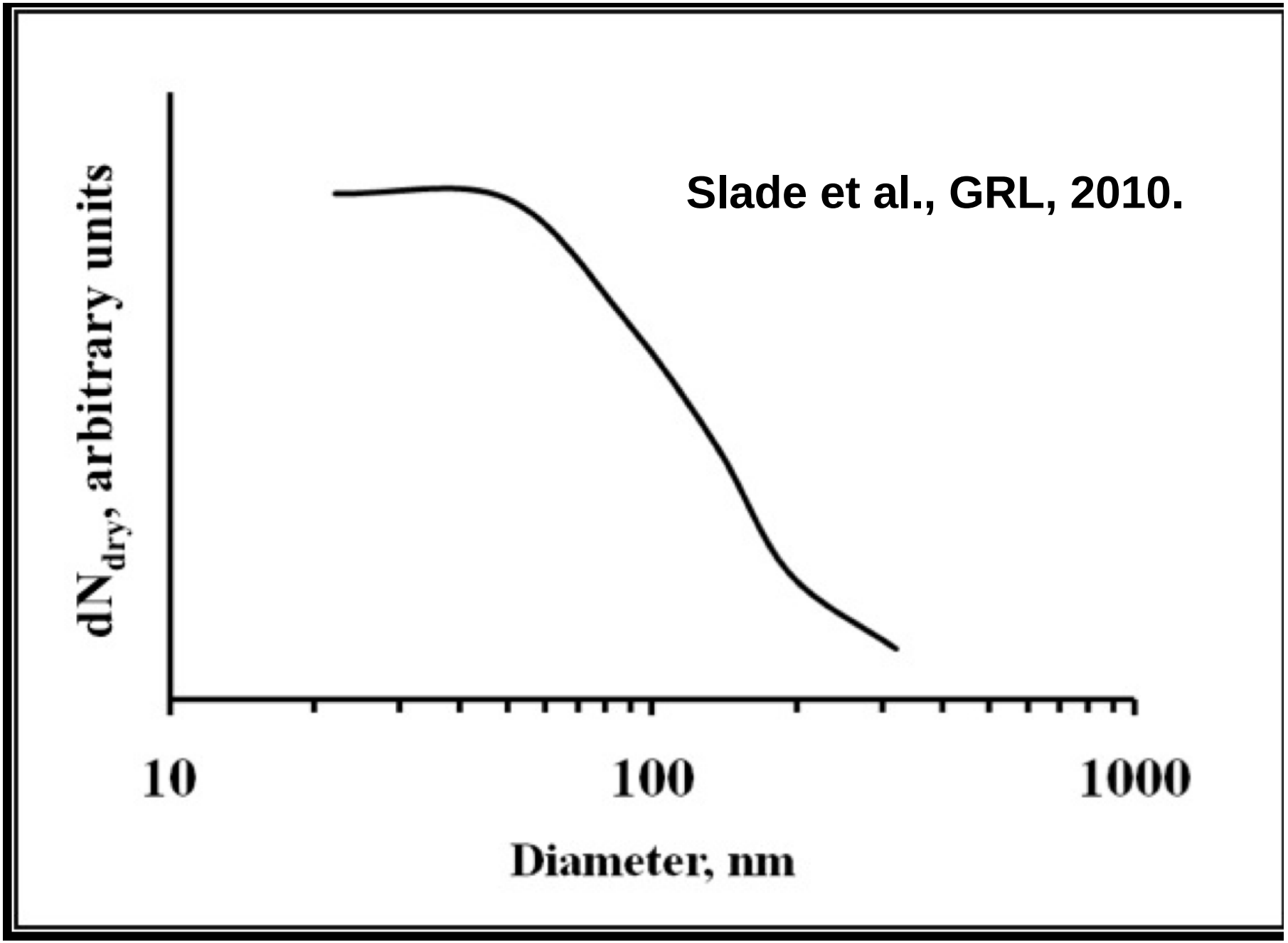
New particles are formed from evaporation of droplets from bubble bursting from breaking waves, leaving the non-volatile matter as a particle



If so, the aerosol concentration above the lake should increase exponentially with wind speed (wave height).


Altitude (AGL): ~220 m 7/12
Altitude (AGL): ~220 m 7/16
Altitude (AGL): ~190 m 7/19
Altitude (AGL): ~190 m 7/20
Altitude (AGL): ~190 m 7/23
Altitude (AGL): ~130 m 7/26
Altitude (AGL): ~430 m 8/02
Altitude (AGL): ~130 m 8/02
R² = 0.7645
R² = 0.6077
dN, #/cm³ (Σ15-40 nm)
4000
3500
3000
2500
2000
1500
1000
500
0
1
2
3
4
5
6
7
Wind Speed, m/s

Calculated aerosol size distribution from lake water analysis

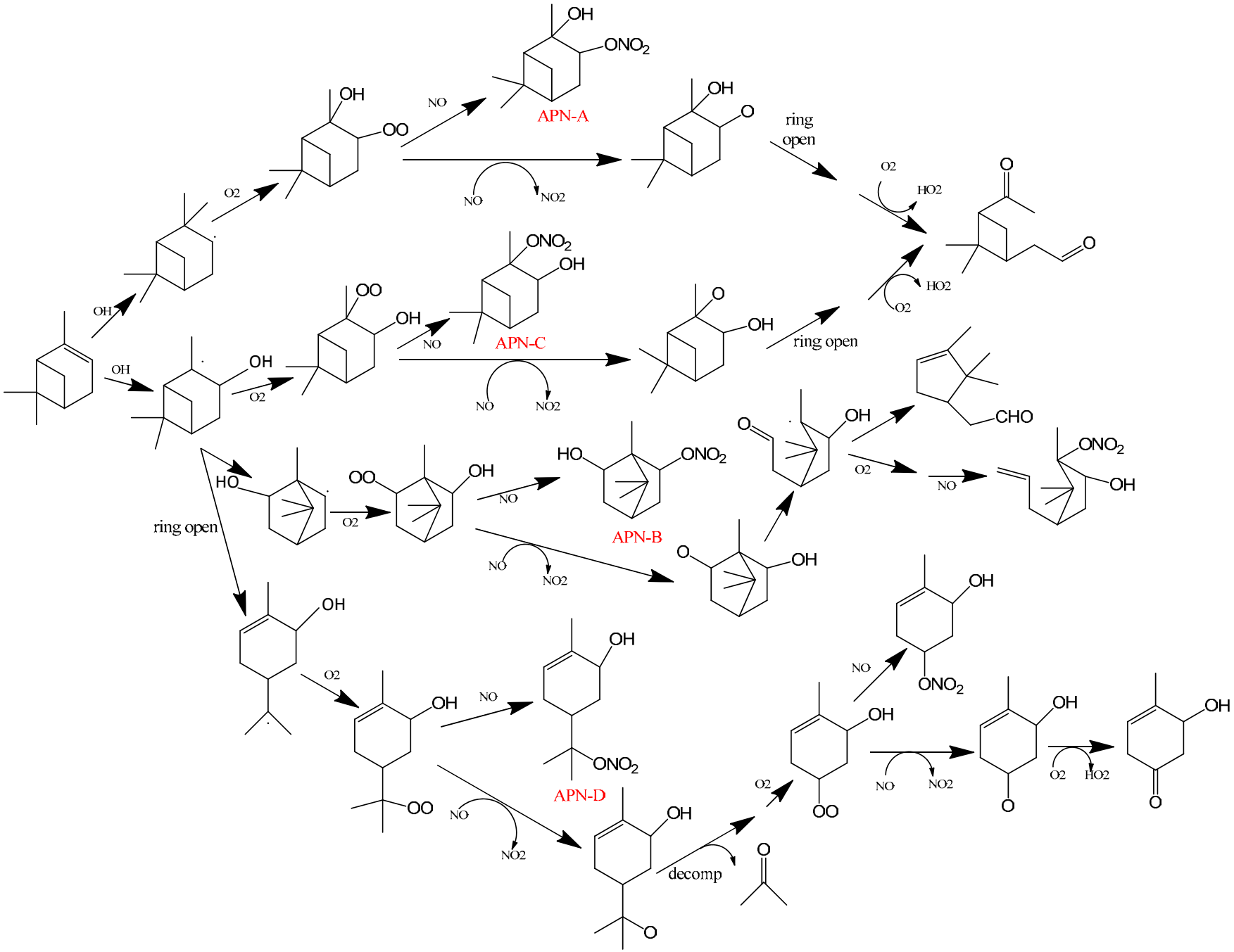


Hypothesis

Organic nitrate production from OH, O_3 and NO_3 oxidation of BVOCs can contribute significantly to SOA.

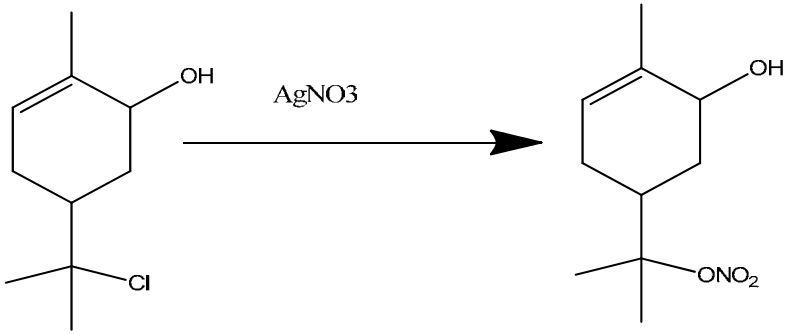

"BOB"
+ OH, NO
ONO2
OH

Schematic of the OH-initiated oxidation of a-pinene in the presence of NO_x.

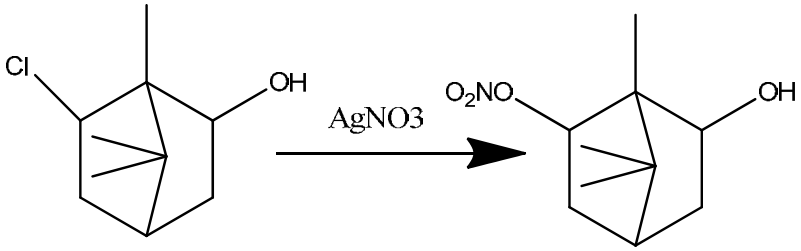


Synthesis procedure:

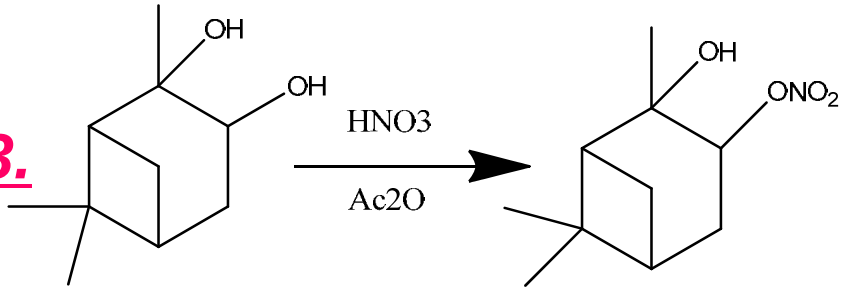
1.



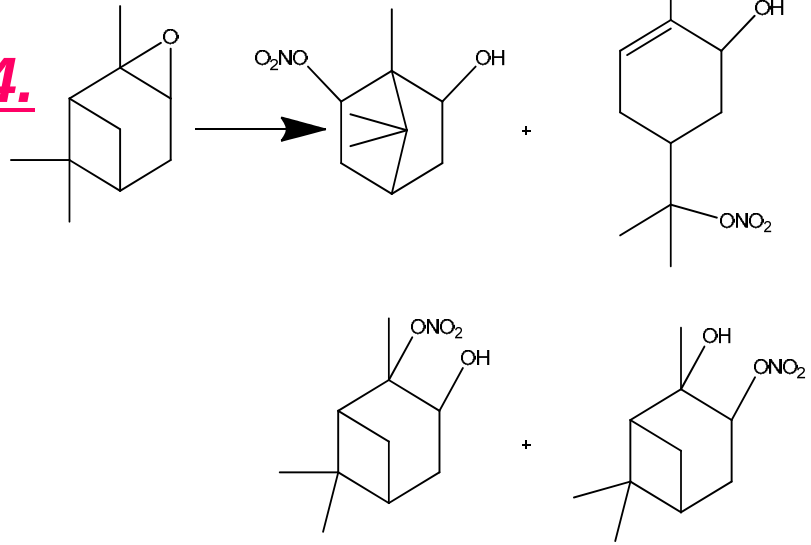
2.

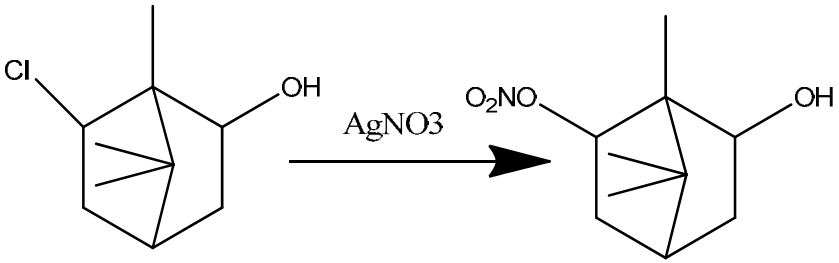


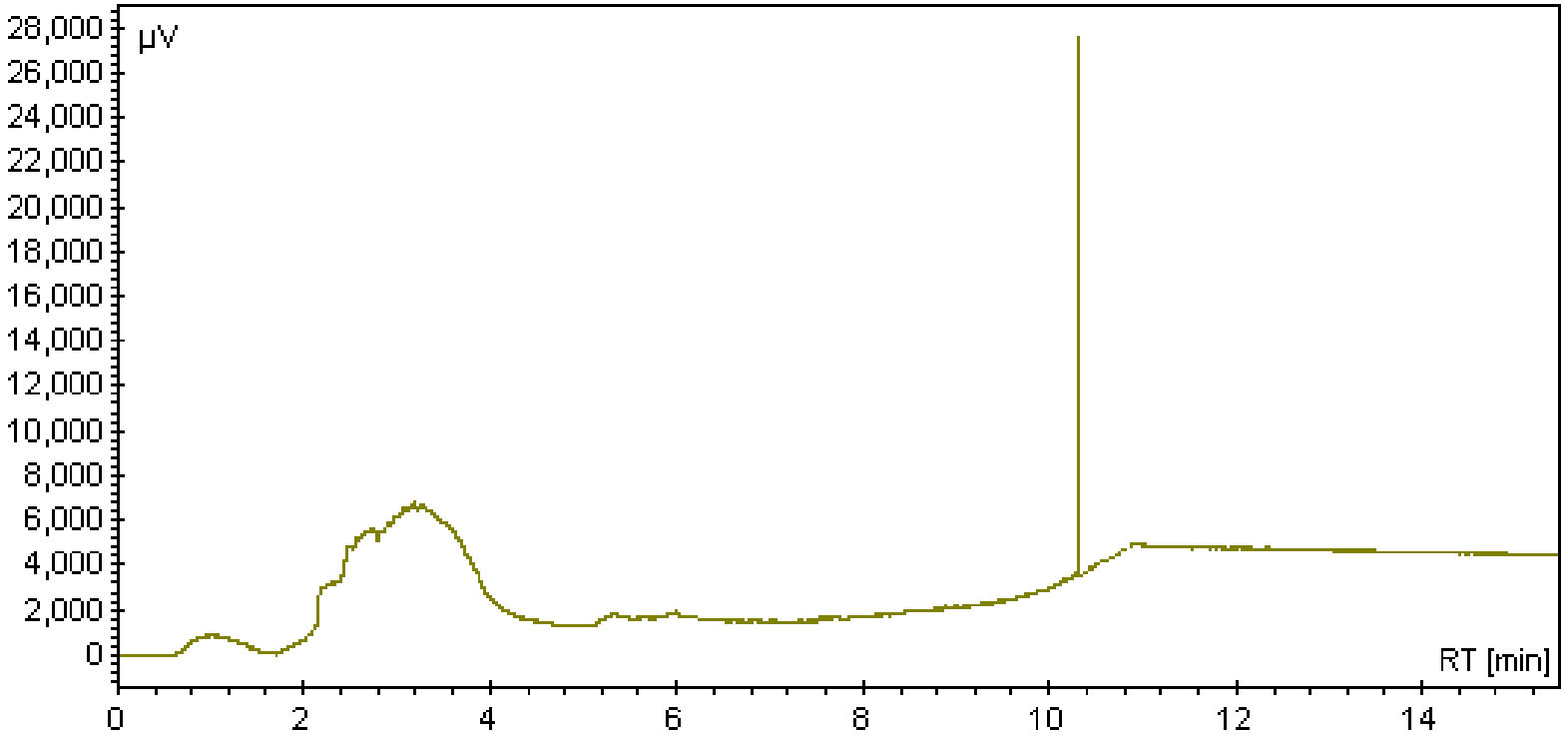
3.



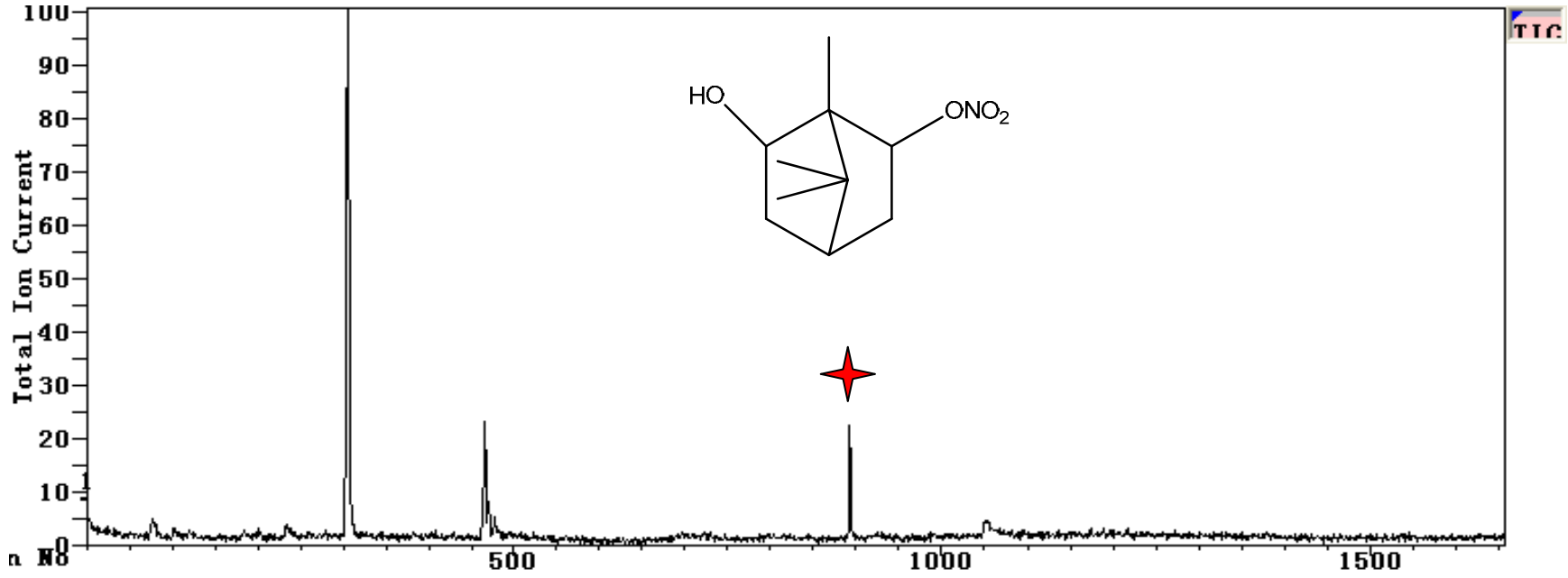
4.

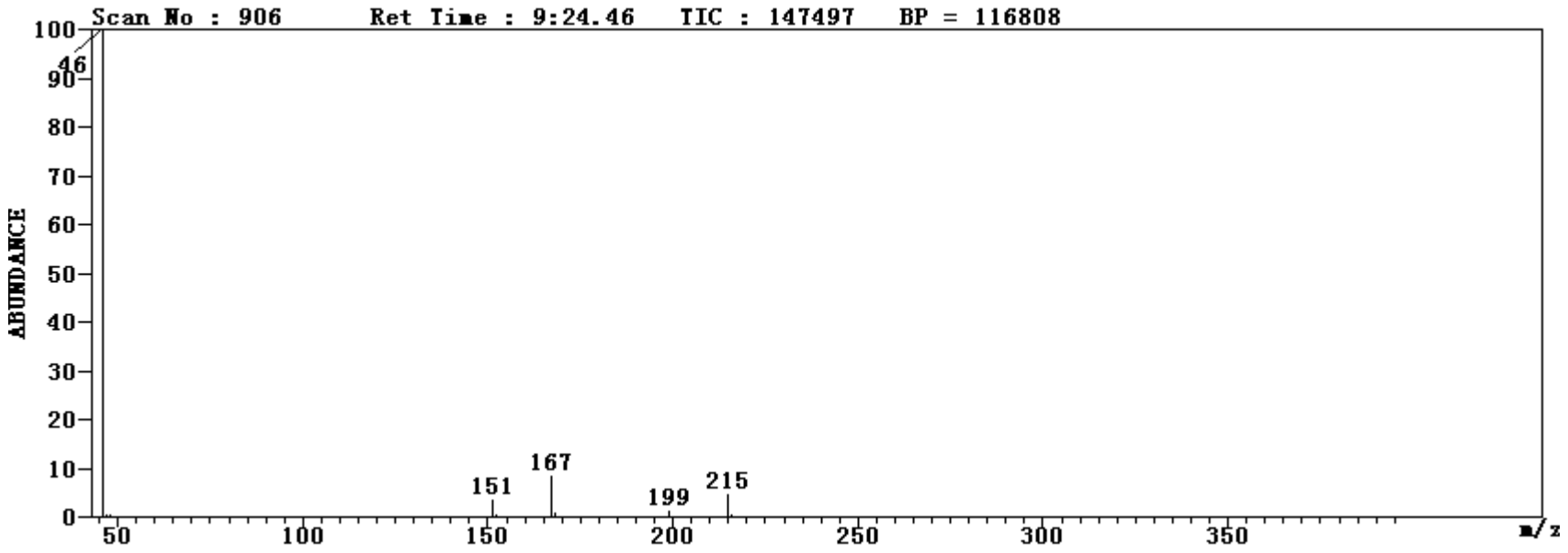


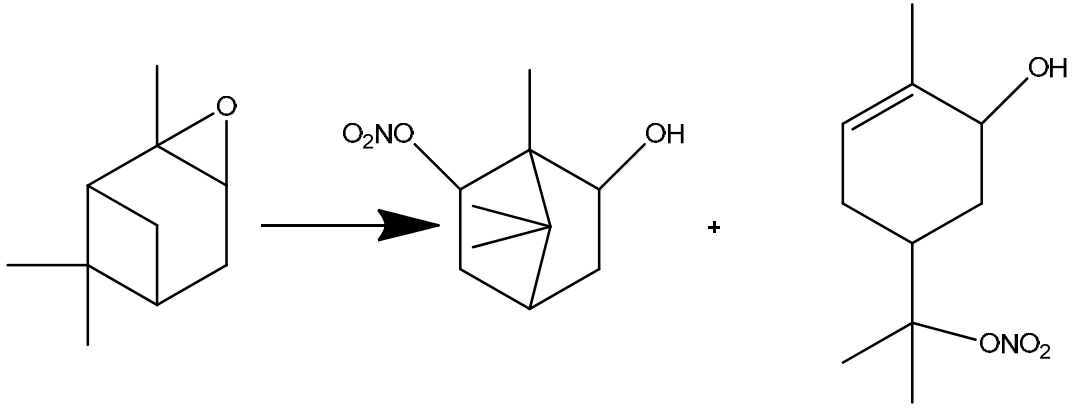

Cl
OH
AgNO3
O2NO
OH

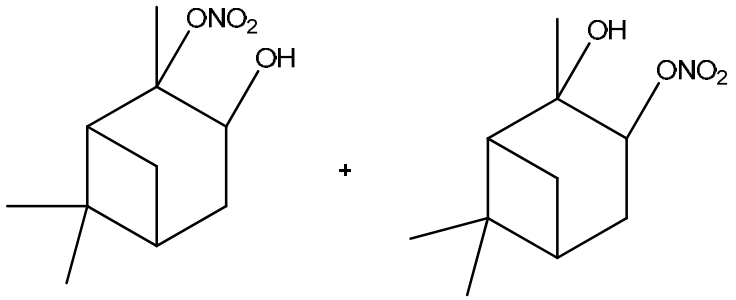

µV
28,000
26,000
24,000
22,000
20,000
18,000
16,000
14,000
12,000
10,000
8,000
6,000
4,000
2,000
0
RT [min]
0
2
4
6
8
10
12
14

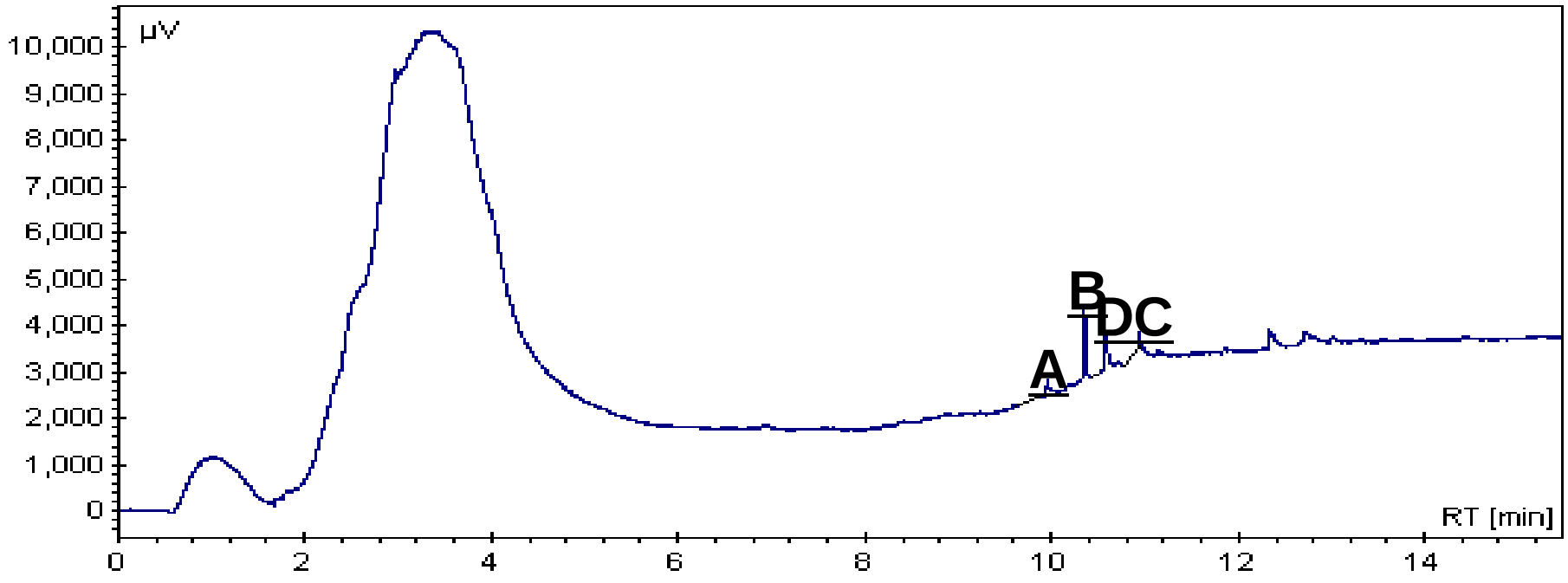
Purified a-pinene nitrate

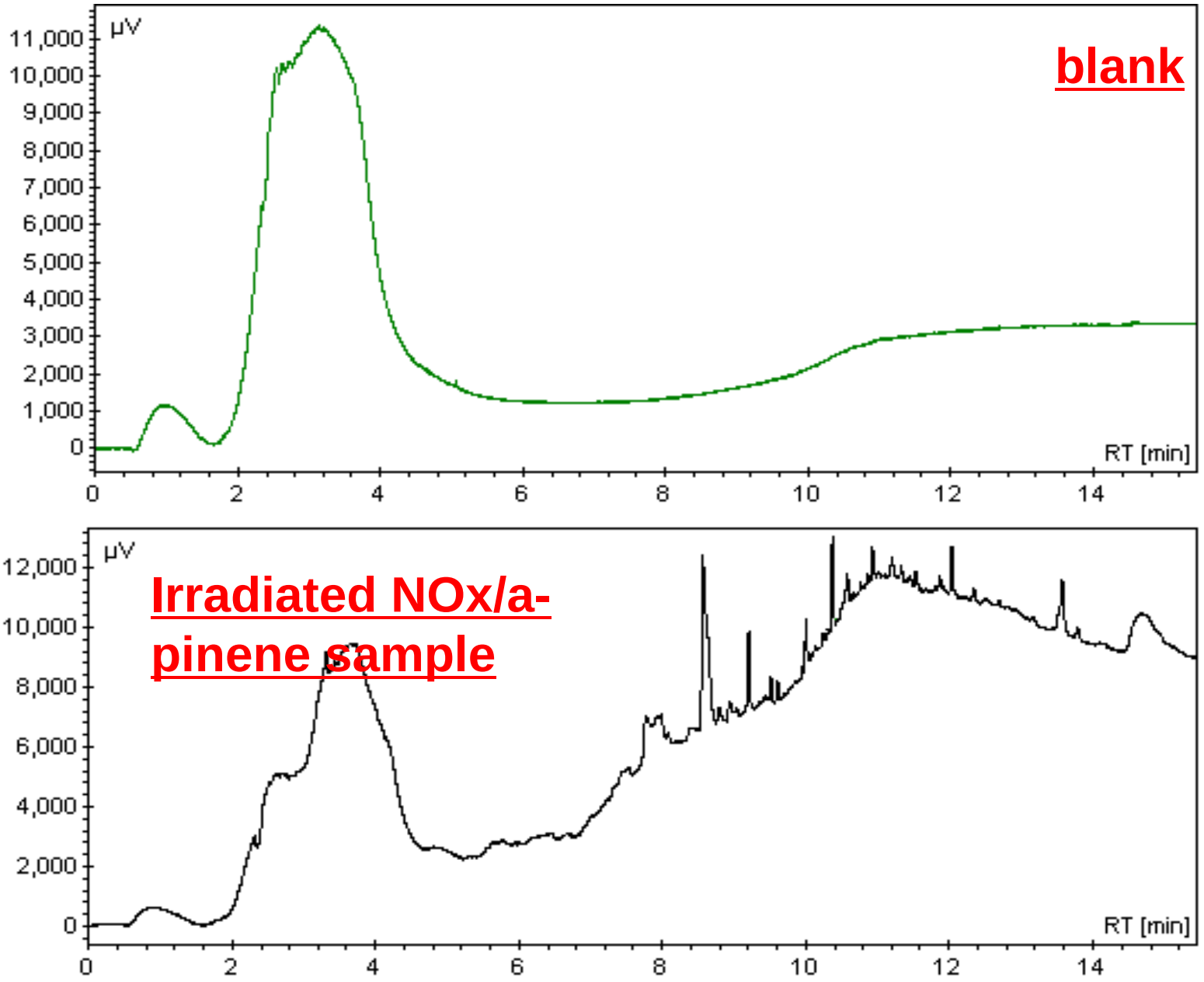


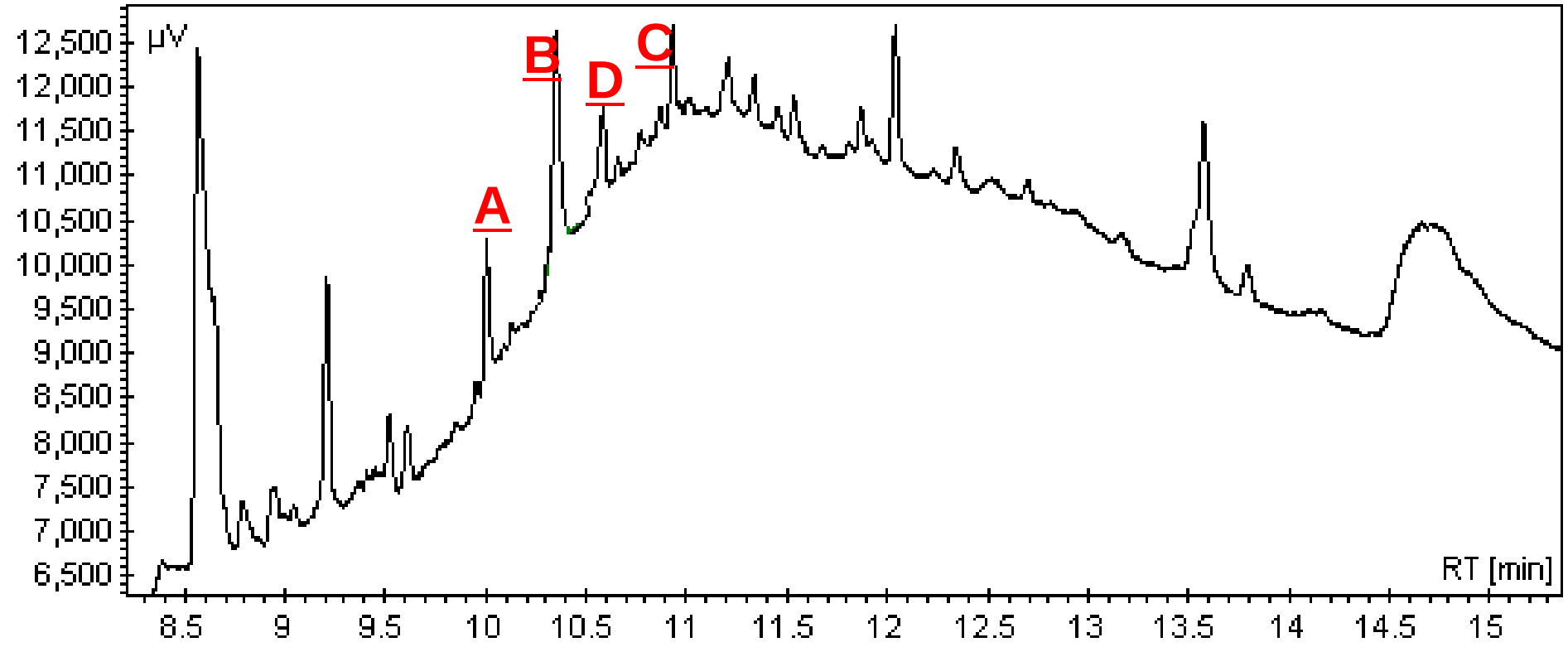



O
O2NO
OH
+
OH
ONO2

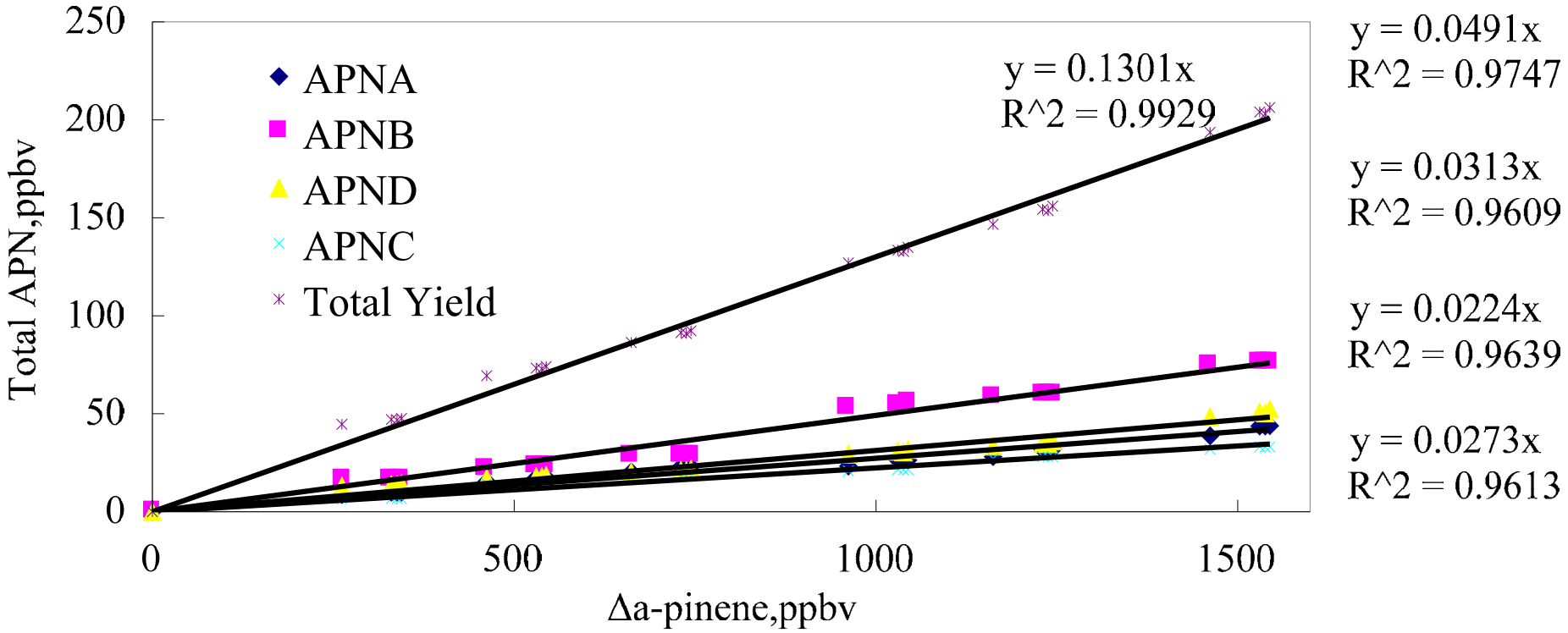

ONO2
OH
+
OH
ONO2


µV
10,000
9,000
8,000
7,000
6,000
5,000
4,000
3,000
2,000
1,000
0
A
B
DC
RT [min]
0
2
4
6
8
10
12
14


blank
µV
11,000
10,000
9,000
8,000
7,000
6,000
5,000
4,000
3,000
2,000
1,000
0
RT [min]
0
2
4
6
8
10
12
14
Irradiated NOx/a-pinene sample
µV
12,000
10,000
8,000
6,000
4,000
2,000
0
RT [min]
0
2
4
6
8
10
12
14


µV
12,500
12,000
11,500
11,000
10,500
10,000
9,500
9,000
8,500
8,000
7,500
7,000
6,500
A
B
D
C
RT [min]
8.5
9
9.5
10
10.5
11
11.5
12
12.5
13
13.5
14
14.5
15

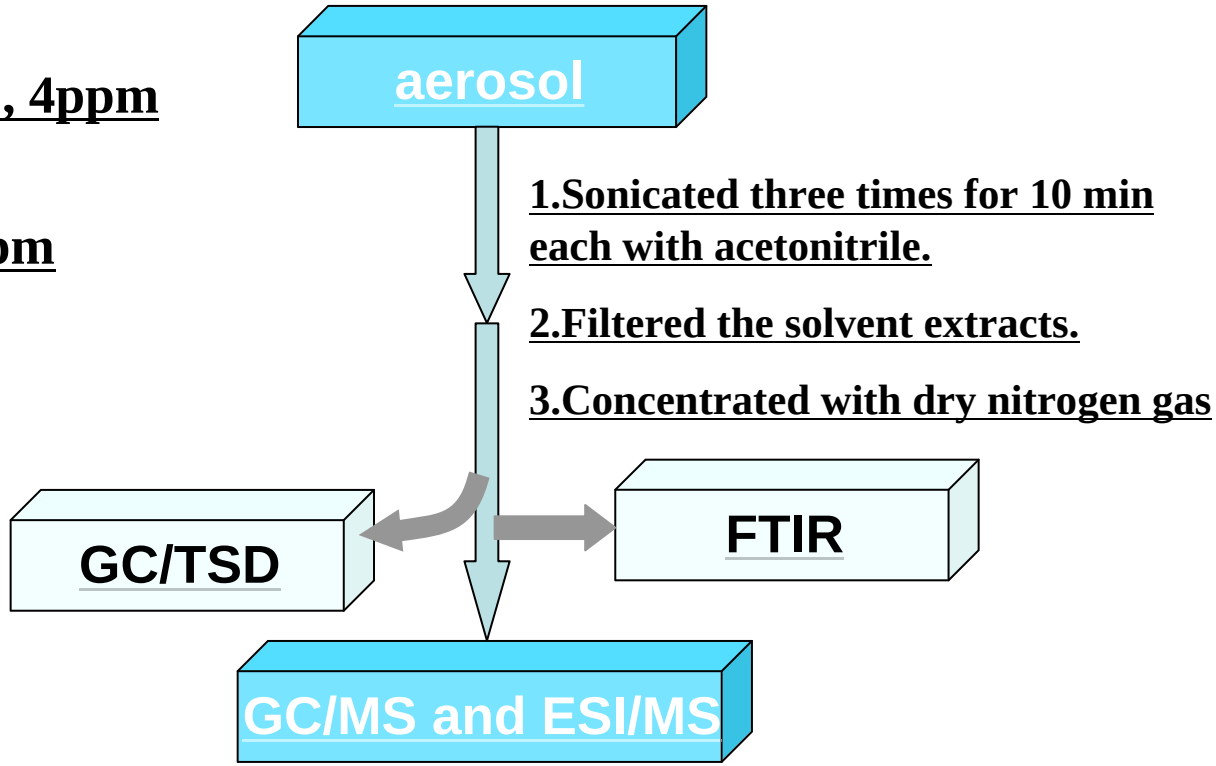
Total and speciated APN yields

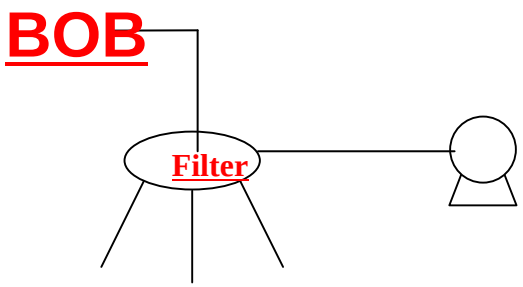


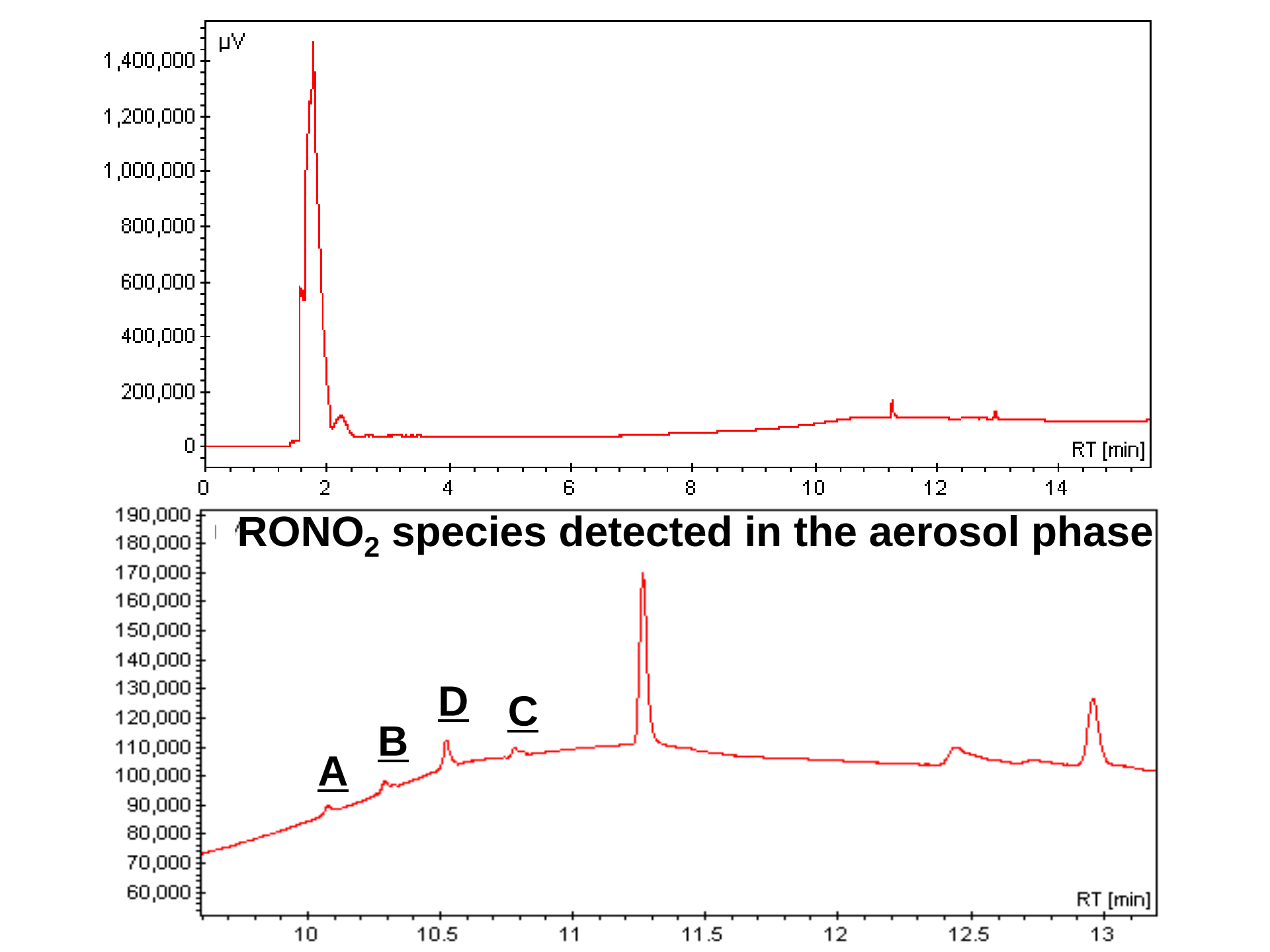
13% $RONO_2$ yield, but this is just from the four that we synthesized.

Next step

- **Chamber experiment with seed, measure the uptake coefficient into the aerosol**
  - **Isopropyl nitrite(IPN), 4ppm**
  - **a-pinene, 200ppb-2ppm**
  - **Seed, $(NH_4)_2SO_4$**
  - **NO, 200ppb-2ppm**






μV
1,400,000
1,200,000
1,000,000
800,000
600,000
400,000
200,000
0
RT [min]
0
2
4
6
8
10
12
14
RONO2 species detected in the aerosol phase
190,000
180,000
170,000
160,000
150,000
140,000
130,000
120,000
110,000
100,000
90,000
80,000
70,000
60,000
A
B
D
C
RT [min]
10
10.5
11
11.5
12
12.5
13

Examination of successional change of a midwest forest, from predominately deciduous to predominately coniferous.

- Across the upper Midwest, aspen and birch in the canopy are dying and being replaced by pine, oak, and maple.
- This is prompting a major successional transition, altering microclimate and increasing species and structural complexity of the forest canopy.
- These changes will have a profound effect on the region's carbon cycle.

Experimental treatment

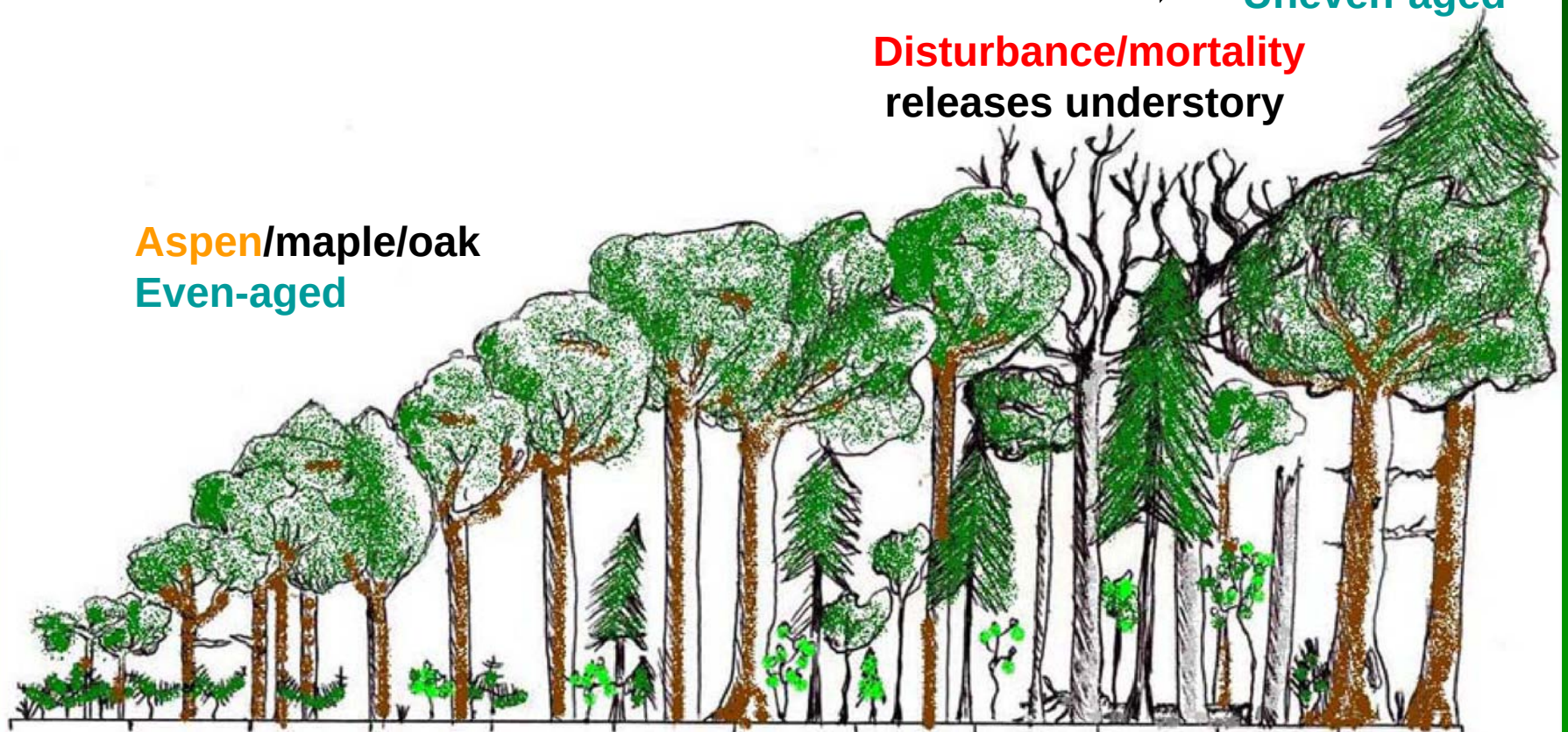
Accelerated succession
via experimental disturbance

Insects
Pathogens
Natural senescence

Pine/maple/oak
Uneven-aged

Disturbance/mortality
releases understory

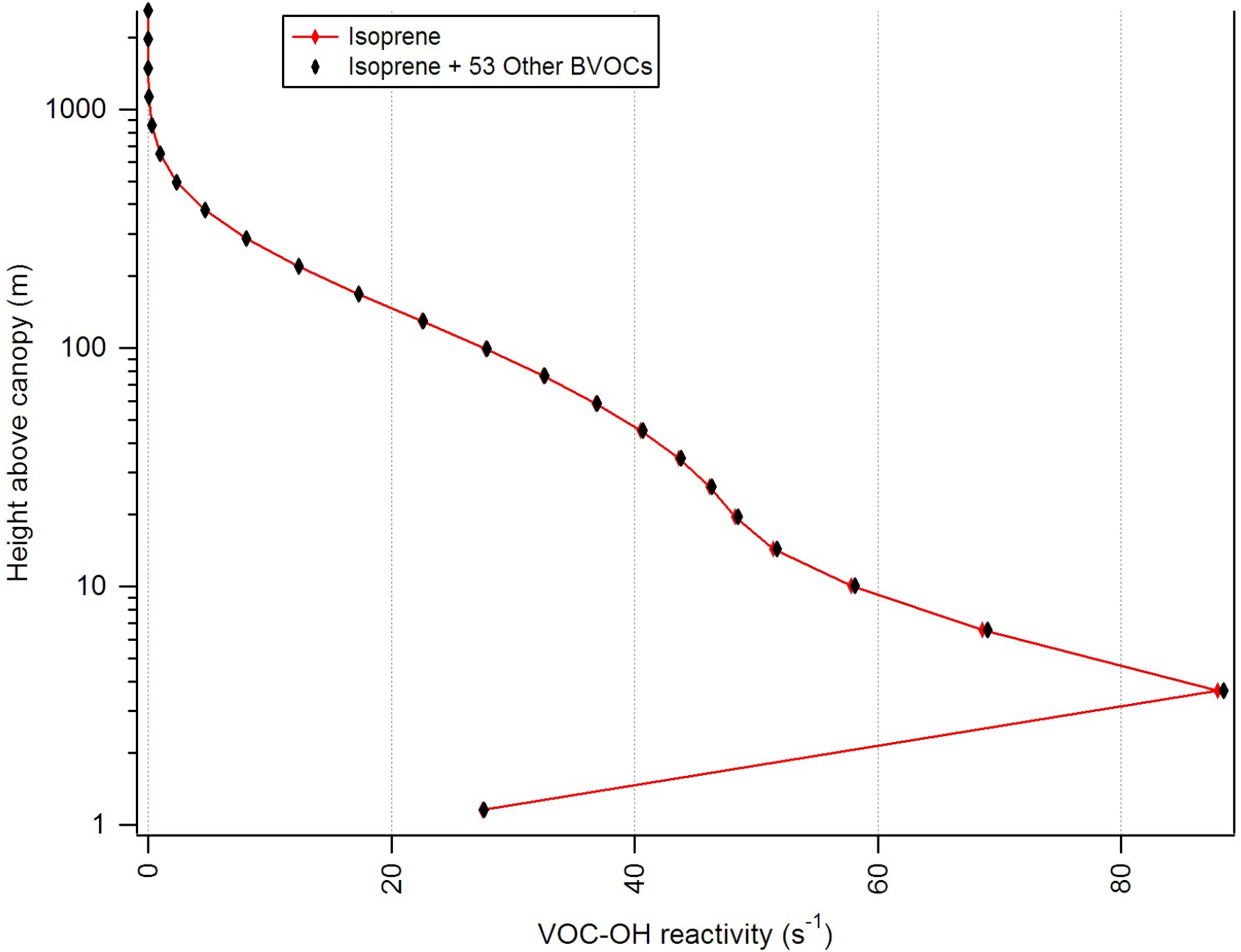
Aspen/maple/oak
Even-aged



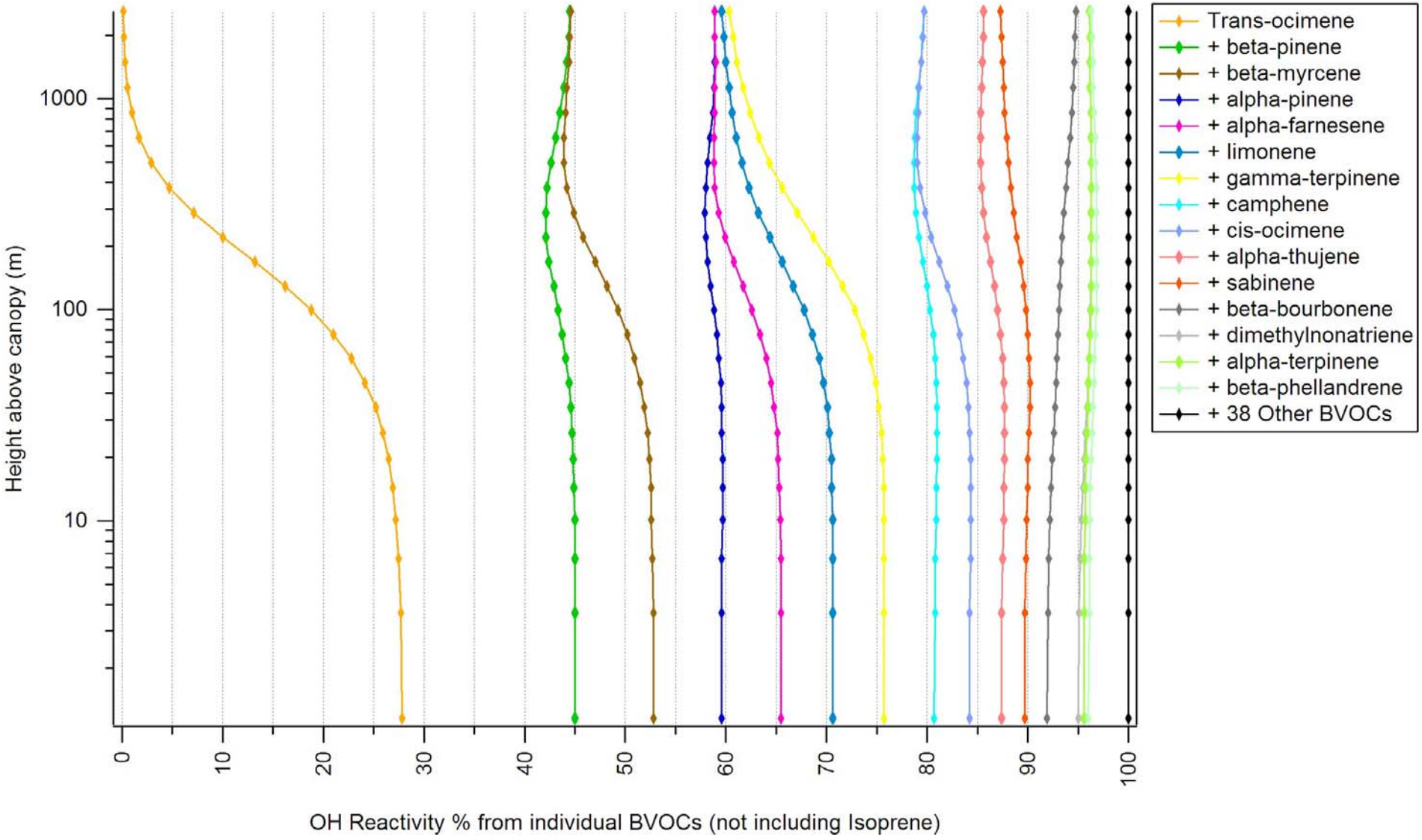
1st task is understanding the state of the forest in terms of BVOC contributions to various important processes

We are doing this using measured individual fluxes (Helmig group) and a simple 1D model that uses constant OH and O3 (from measurements), calculated NO_3, and measured or estimated aerosol and $RONO_2$ yields.

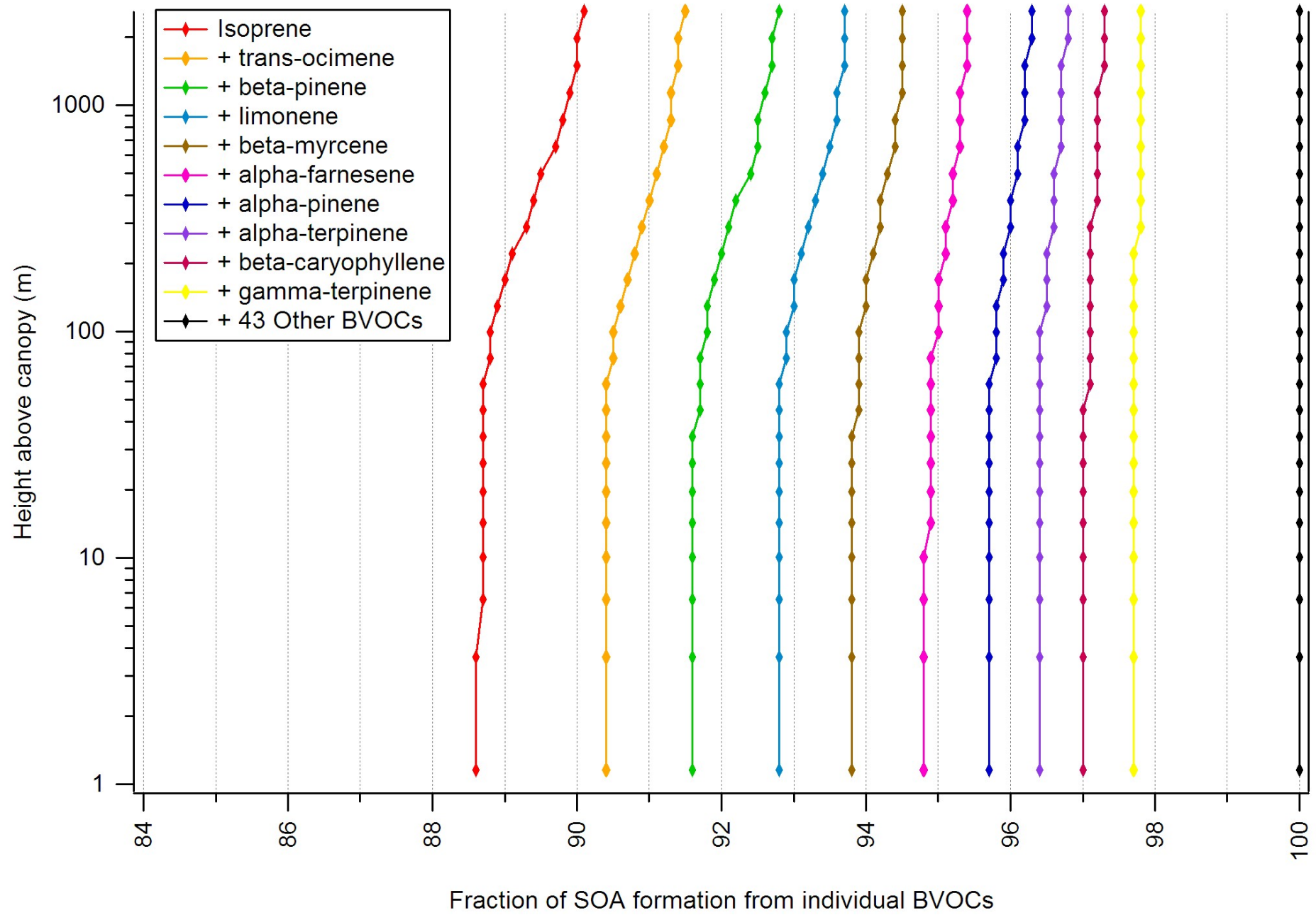
Current OH-reactivity (i.e. $k_{OH} \cdot [VOC]$)

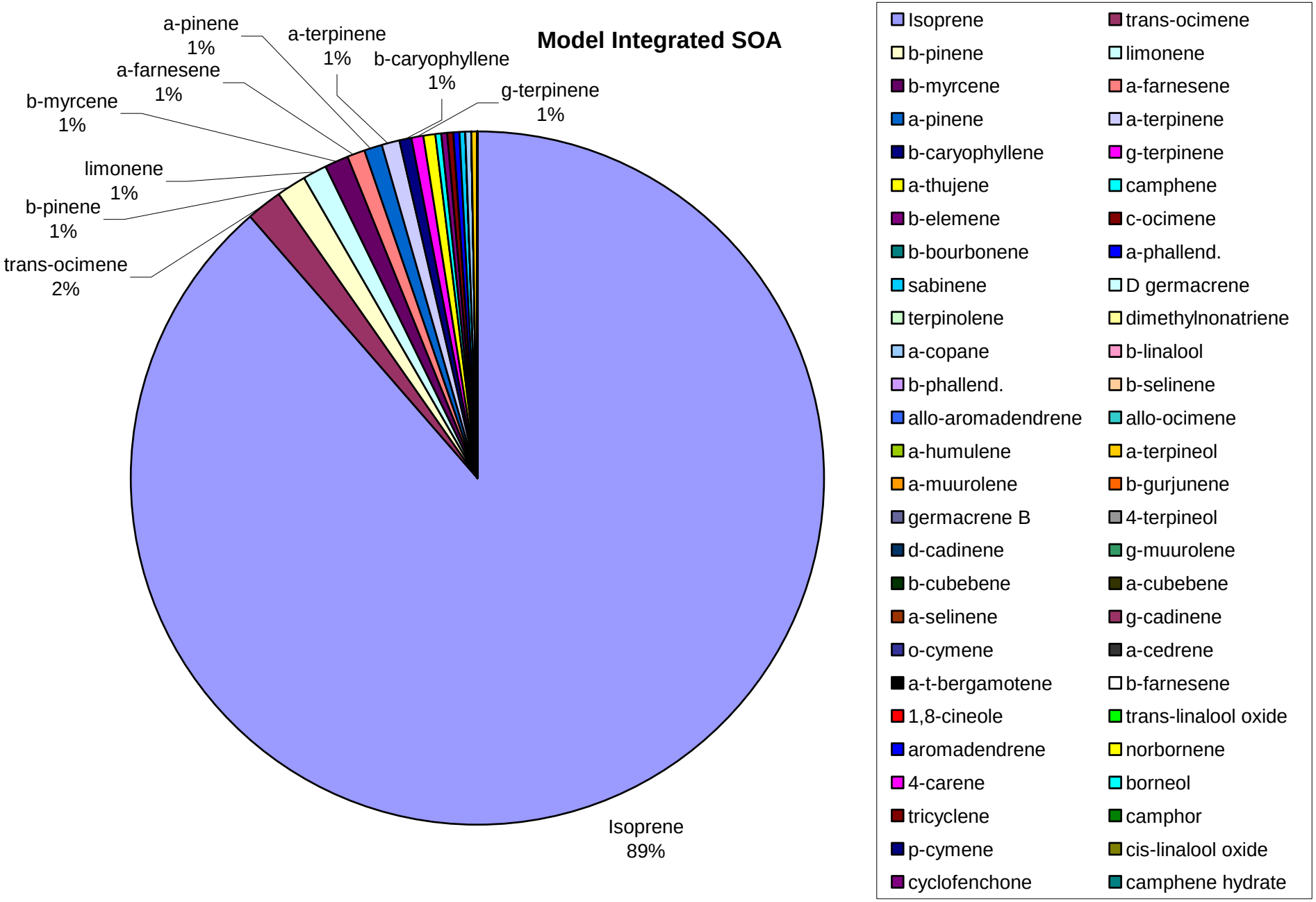


Relative reactivities of the terpenes



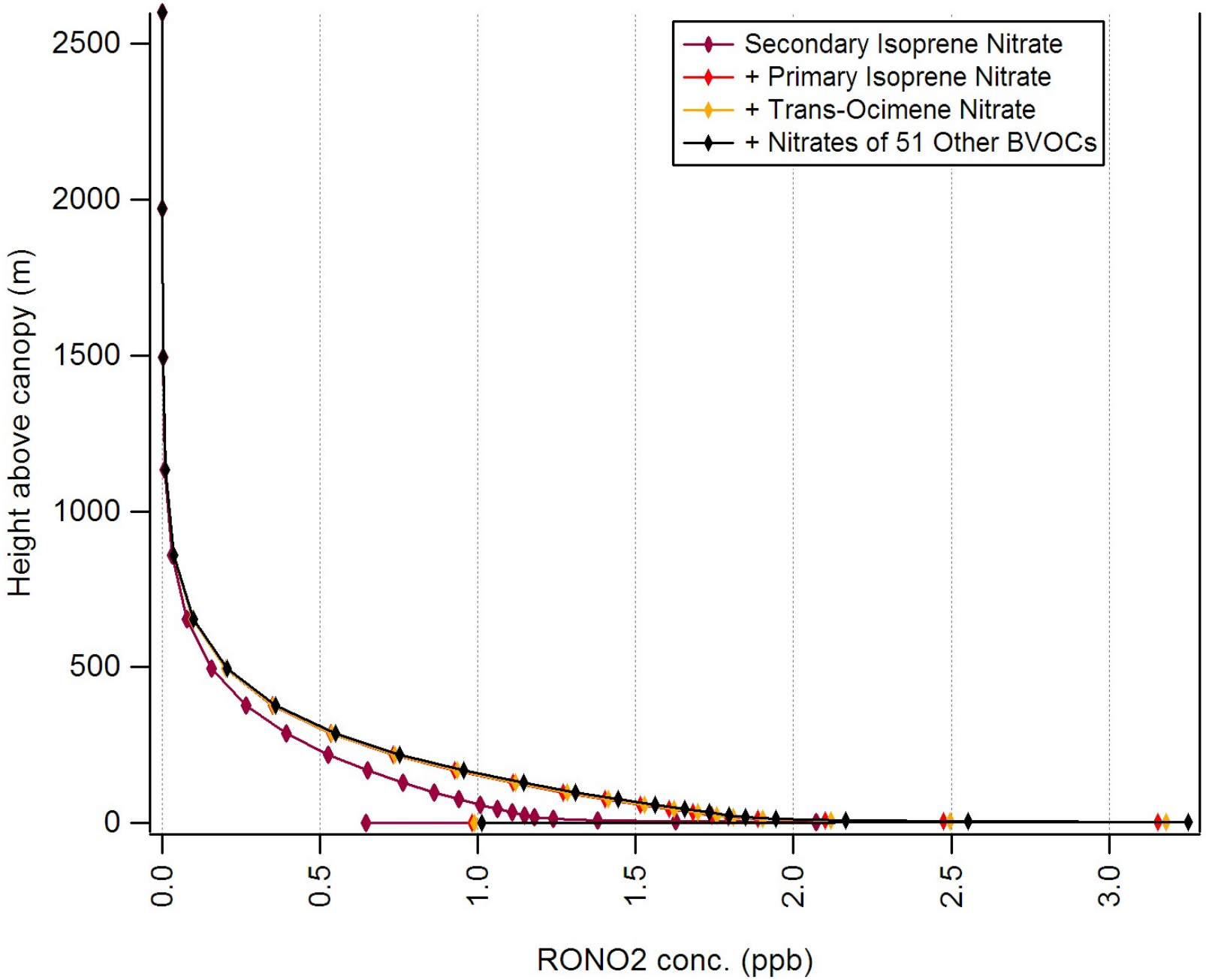
Relative SOA produced from each VOC

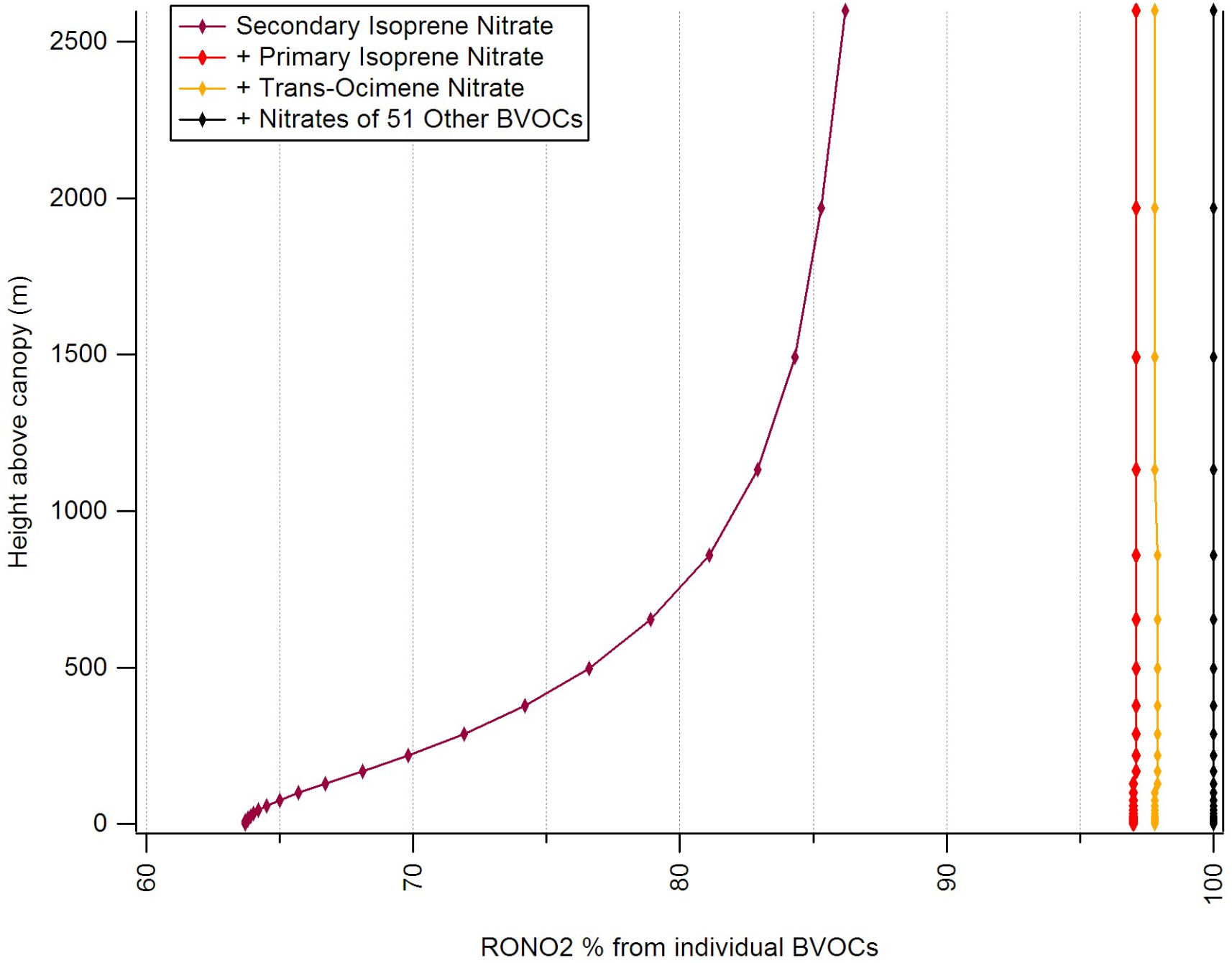


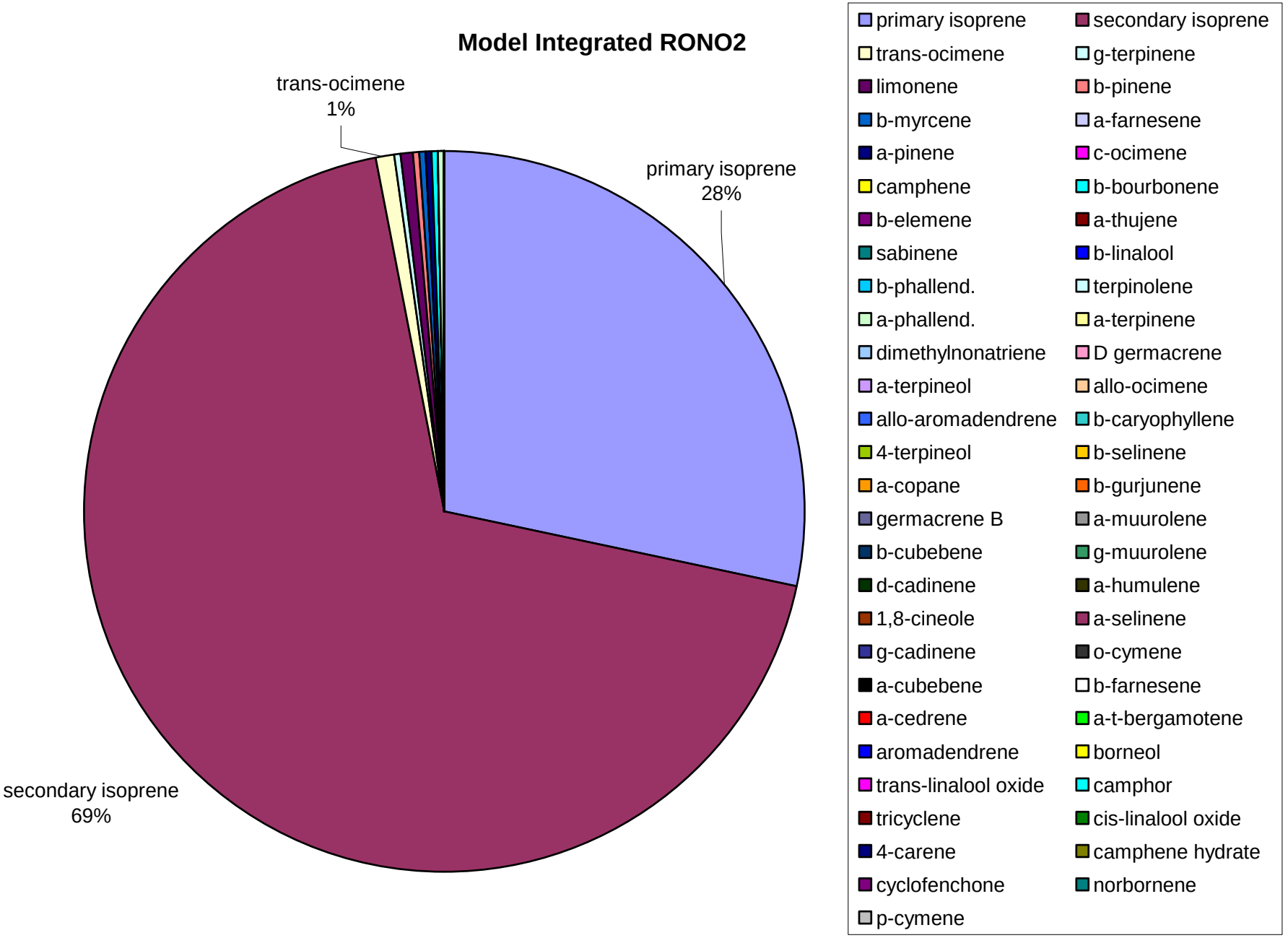


Integrating over the BL yields the total contribution

So, what species contribute to that SOA? $RONO_2$?




Secondary Isoprene Nitrate
+ Primary Isoprene Nitrate
+ Trans-Ocimene Nitrate
+ Nitrates of 51 Other BVOCs
Height above canopy (m)
0
500
1000
1500
2000
2500
60
70
80
90
100
RONO2 % from individual BVOCs



Integrated over the BL

Conclusions

- **The PTRLIT works great for isobaric species, but not so well for terpenes/sesquiterpenes and their isomeric oxidation products**

- **Aerosols from breaking waves can influence local climate (e.g. cloud cover) in the vicinity of freshwater lakes**

- **Work from many groups indicates that $RONO_2$ species likely contribute significantly to ambient SOA**

- **$RONO_2$ are likely highly reactive in the aerosol phase, and thus their fate needs to be studied**

Thank you, EPA, for your support!
Input?