Supplement material

Table 1s(a). List of compounds contributing to > 95% of SOA mass yield at 258K. The names of compounds are given in MCM format. The PRAM compounds are highlighted in red.

Molecular Weight (g/mol)	Species name	Contribution (%)
174.194	C810OOH	0.186
261.229	C920PAN	9.348
190.194	C812OOH	0.258
130.099	H1C23C4CHO	0.201
204.22	C98OOH	2.881
178.14	C621OOH	0.19
172.221	C96OOH	1.322
235.191	C813NO3	0.358
188.221	C97OOH	3.07
174.194	C811OOH	0.292
216.231	C108OOH	5.666
204.22	C921OOH	0.302
191.139	C614NO3	2.488
200.232	C107OOH	5.936
162.141	C614OOH	1.638
174.151	C717OOH	3.432
247.202	C811PAN	10.111
200.232	C109OOH	4.752
188.221	C920OOH	0.294
203.192	C810NO3	0.215
206.193	C813OOH	0.251
233.219	C98NO3	4.528
184.232	PINONIC	4.404
245.229	C108NO3	8.968
220.22	C922OOH	0.296
203.149	C717NO3	11.294
203.192	C811NO3	0.555
170.206	C89CO2H	0.276
198	C10H14O4	0.169

214	C10H14O5	0.183
230	C10H14O6	0.548
246	C10H14O7	0.875
262	C10H14O8	0.646
278	C10H14O9	0.927
294	C10H14O10	0.521
310	C10H14O11	0.322
200	C10H16O4	1.385
216	C10H16O5	1.228
232	C10H16O6	1.134
248	C10H16O7	1.122
264	C10H16O8	1.112
280	C10H16O9	0.843
296	C10H16O10	0.579
312	C10H16O11	0.244
277	C10H15O8N1	0.192
293	C10H15O9N1	0.24
309	C10H15O10N1	0.24
325	C10H15O11N1	0.333
341	C10H15O12N1	0.207
430	C20H30O10	0.161
446	C20H30O11	0.223
462	C20H30O12	0.178

Table 1s(b). List of compounds contributing to > 95% of SOA mass yield at 293K. The names of compounds are given in MCM format.

Molecular Weight (g/mol)	**SPECIES NAMES**	**Contribution (%)**
261.229	C920PAN	4.099
190.194	C812OOH	2.728
204.22	C98OOH	7.438
178.14	C621OOH	1.034
235.191	C813NO3	3.101

188.221	C97OOH	3.025
174.194	C811OOH	1.351
186.205	PINIC	0.773
216.231	C108OOH	6.242
204.22	C921OOH	1.682
164.113	C516OOH	1.441
162.141	C614OOH	1.595
174.151	C717OOH	0.534
200.232	HOPINONIC	0.7
247.202	C811PAN	4.574
188.221	C920OOH	0.791
206.193	C813OOH	2.638
233.219	C98NO3	3.811
245.229	C108NO3	1.488
220.22	C922OOH	1.644
246	C10H14O7	1.17
262	C10H14O8	1.262
278	C10H14O9	2.855
294	C10H14O10	3.633
310	C10H14O11	6.187
326	C10H14O12	2.409
200	C10H16O4	1.654
248	C10H16O7	0.674
264	C10H16O8	1.97
280	C10H16O9	2.347
296	C10H16O10	3.194
312	C10H16O11	2.771
328	C10H16O12	2.195
344	C10H16O13	0.566
325	C10H15O11N1	0.797
341	C10H15O12N1	1.2
357	C10H15O13N1	1.93
373	C10H15O14N1	0.898
446	C20H30O11	0.586

462	C20H30O12	0.701
478	C20H30O13	1.1
494	C20H30O14	1.39
510	C20H30O15	0.792
448	C19H28O12	0.623
464	C19H28O13	0.815
480	C19H28O14	0.756
496	C19H28O15	0.452

Table 1s(c). List of compounds contributing to > 95% of SOA mass yield at 313K. The names of compounds are given in MCM format.

Molecular Weight (g/mol)	SPECIES NAMES	Contribution (%)
190.194	C812OOH	6.952
204.22	C98OOH	1.423
178.14	C621OOH	1.927
235.191	C813NO3	6.827
204.22	C921OOH	3.033
164.113	C516OOH	3.853
206.193	C813OOH	7.457
220.22	C922OOH	3.255
278	C10H14O9	1.004
294	C10H14O10	0.695
310	C10H14O11	18.28
326	C10H14O12	6.04
280	C10H16O9	0.602
296	C10H16O10	0.899
312	C10H16O11	5.621
328	C10H16O12	6.555
344	C10H16O13	1.506
357	C10H15O13N1	4.631
373	C10H15O14N1	1.949
494	C20H30O14	3.151

510	C20H30O15	2.571
526	C20H30O16	0.54
464	C19H28O13	1.197
480	C19H28O14	1.774
496	C19H28O15	1.647
512	C19H28O16	0.548
450	C18H26O13	0.559
466	C18H26O14	0.789
482	C18H26O15	0.599

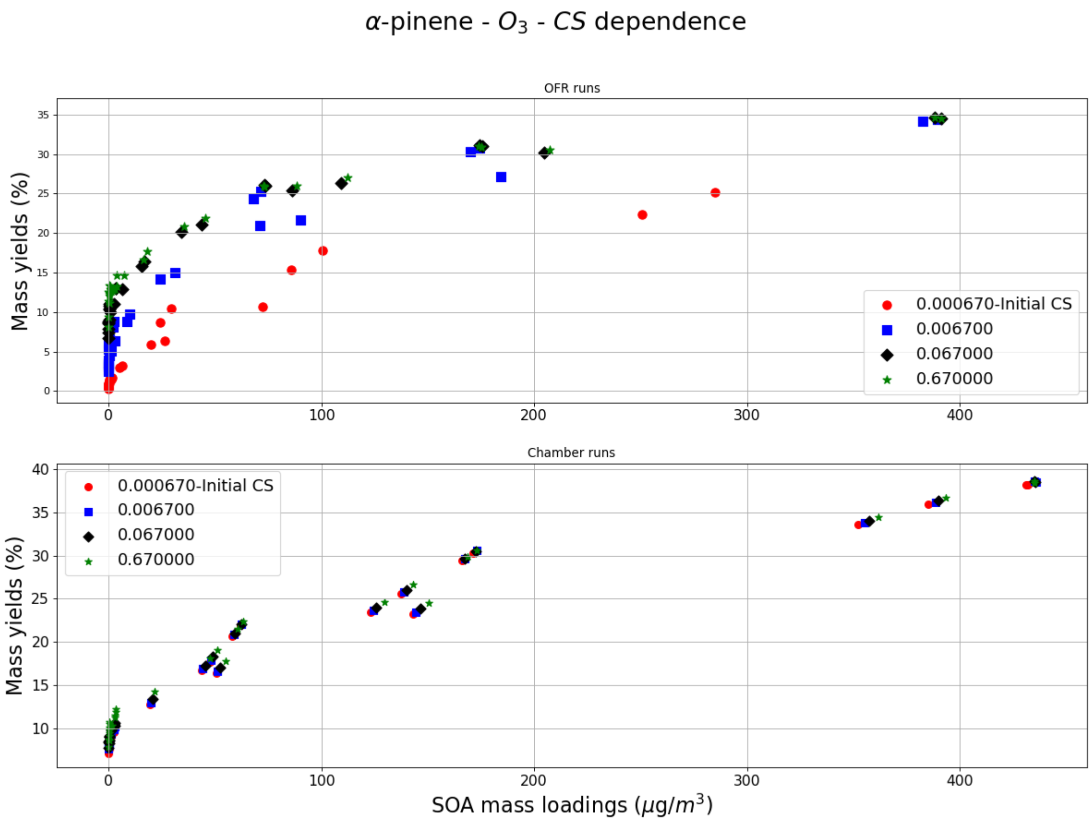

Figure S1. SOA mass yields for α-pinene oxidation using O_3 for different CS values. For the OFR runs the yields level off above a CS value of 0.067 s^{-1} , while chamber simulation show negligible variation with CS . Hence 0.067 s^{-1} is selected as CS for the OFR simulations while chamber simulations are run with 0.00067 s^{-1}.

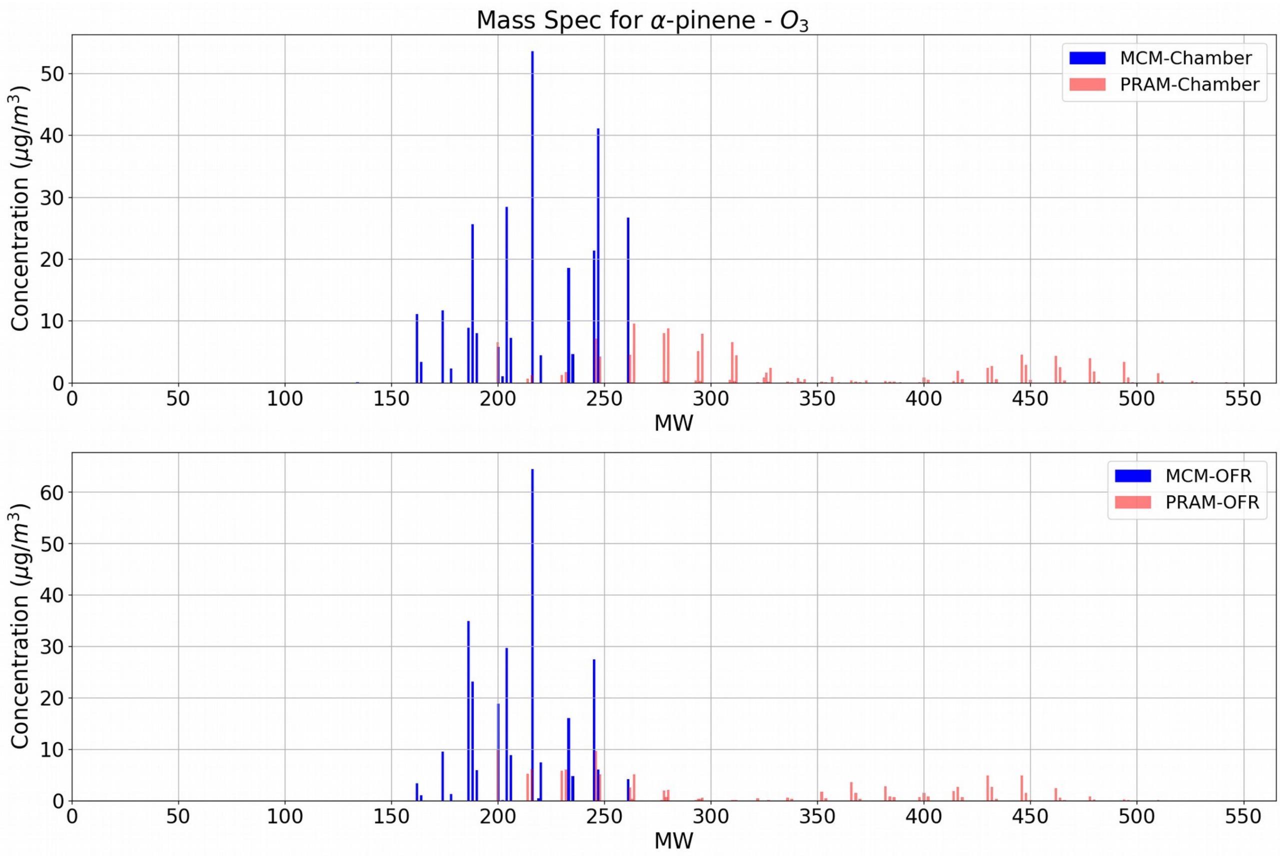

Figure S2. Mass spectra of SOA formed from α-pinene ozonolysis in the particle phase. The upper panel indicates spectra from chamber simulations while the lower panel represents the spectra from OFR simulations.

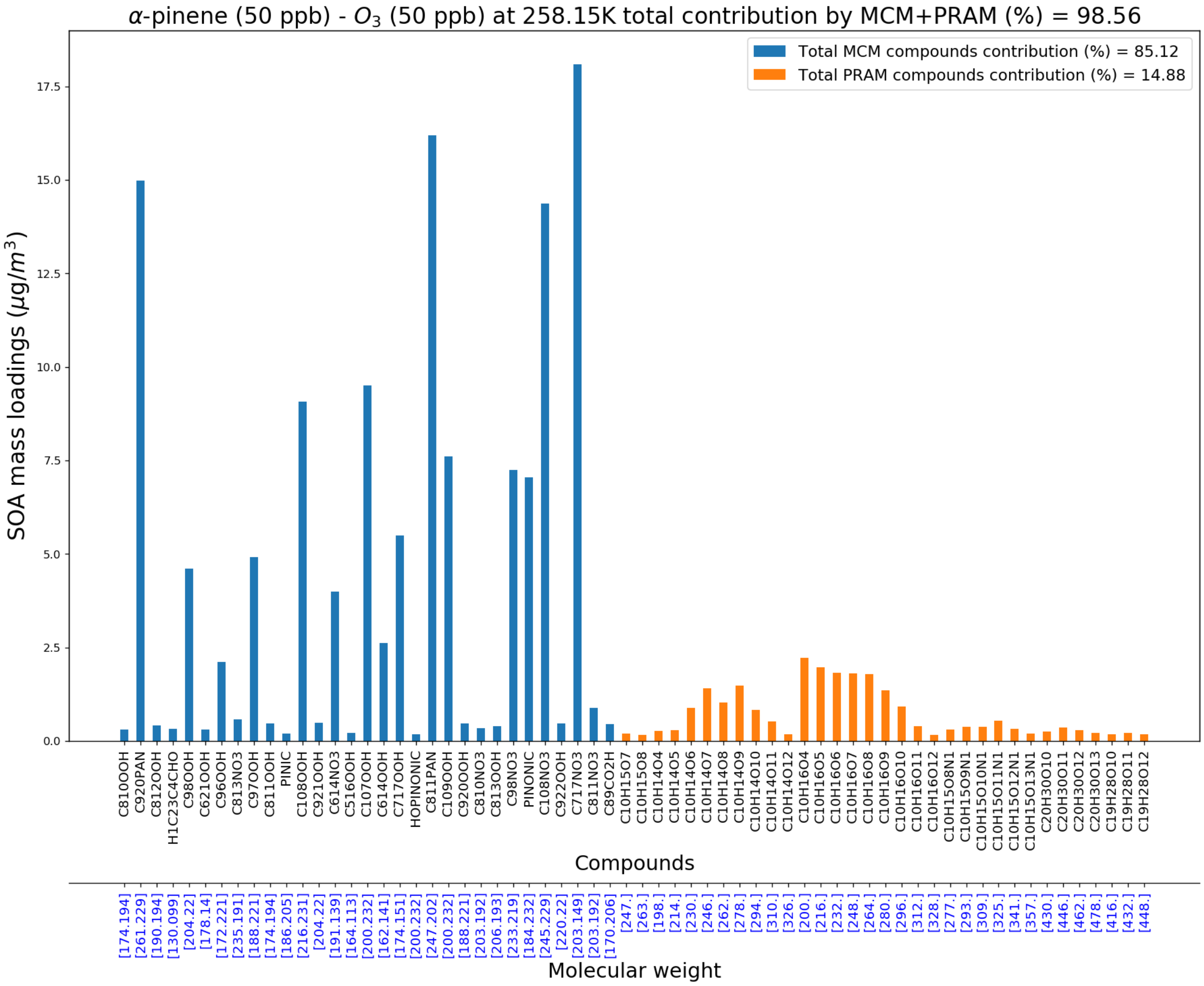

Figure S3(a). MCM and PRAM compounds contributing to > 95% of SOA mass at 258 K and 50ppb O_3 and α-pinene concentrations. It can be noted that a large fraction of the PRAM species that contribute to the SOA mass at 258 K are not classified as HOM (i.e. contain at least 6 oxygen atoms), and many of them will not be detected in the gas-phase using the present state-of-the-art Chemical Ionization-Atmospheric Pressure Interface TOF (CI-APi-TOF) technique.

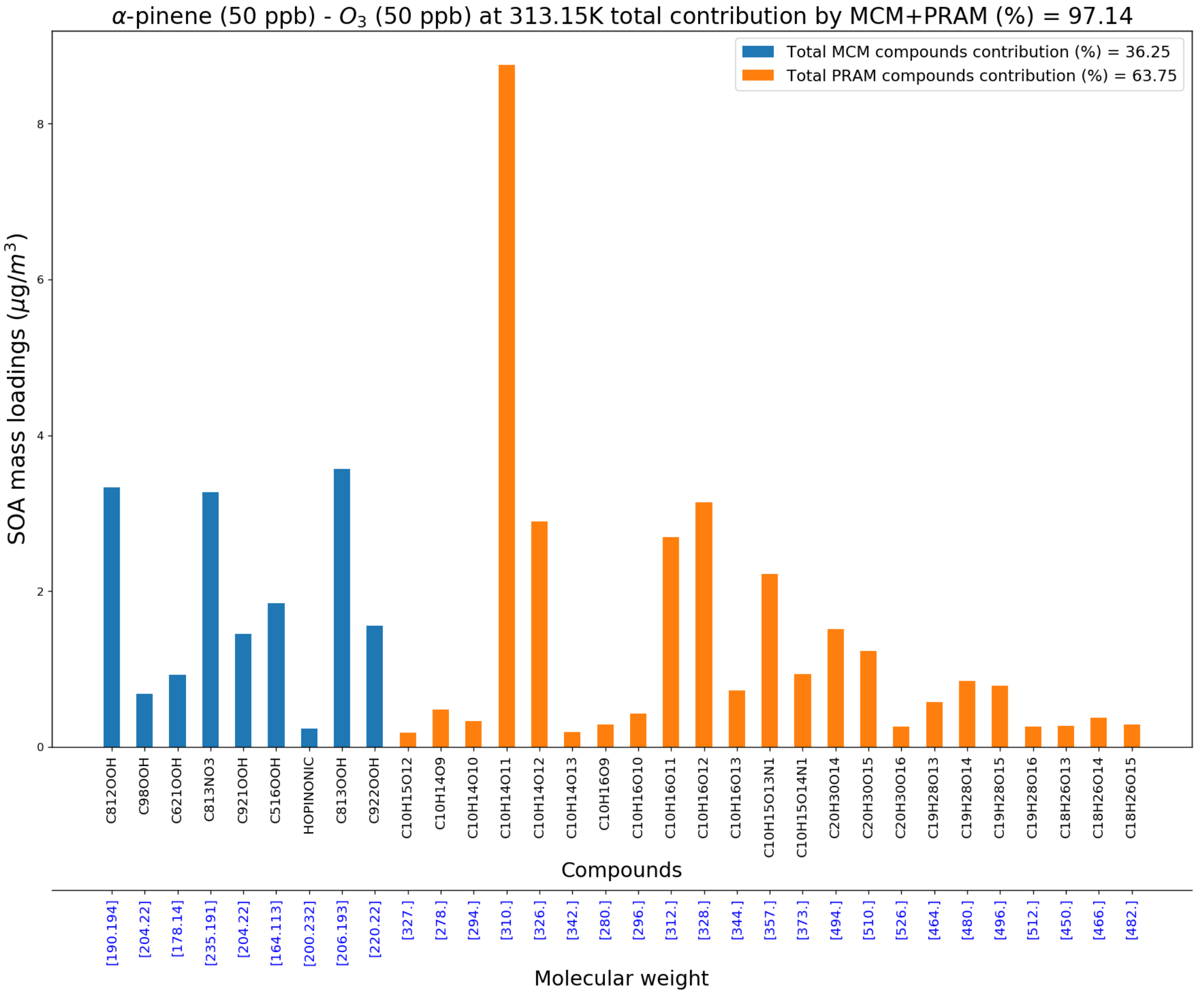

Figure S3(b). MCM and PRAM compounds contributing to > 95% of SOA mass at 313.15 K and 50ppb O_3 and α-pinene concentrations.

The importance of using the MCM+PRAM scheme is illustrated in Fig. 4 which shows the relative contribution by PRAM and MCM compounds for the oxidation of α -pinene, β-pinene and limonene by OH (upper panel) and O_3 (lower panel) for their respective maximum SOA mass yields for both chamber and flow tube setup simulations. The present PRAM mechanism does not include the peroxy radical autooxidation products from β-pinene ozonolysis, products from oxidation of isoprene and β-caryophyllene and the products from NO_3 oxidation of BVOCs. Therefore, they are excluded from Fig.4.

The impact of PRAM compounds contribution to limonene ozonolysis, irrespective of chamber or flow tube setup is considered. It is evident from Fig. 9 (lower panel), which shows that upon using the standalone MCM mechanism underpredicts the SOA mass yields with PRAM compounds contributing ~ 80% and 60% respectively. For α-pinene ozonolysis, the standalone MCM scheme under-predicts the modelled mass yields by approximately 25 % and 22.5 % respectively.

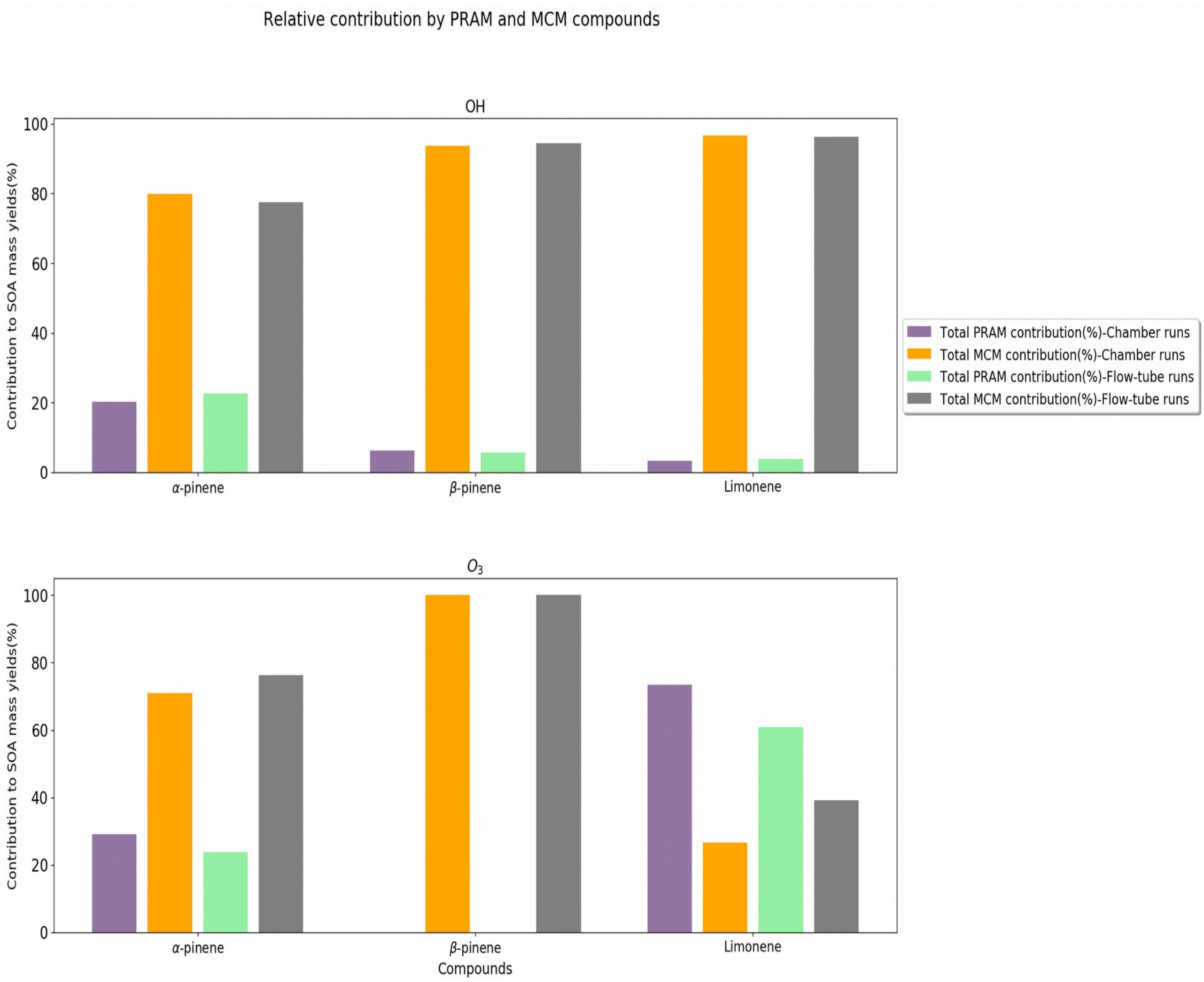

Figure 4. Relative contribution of HOM and MCM compounds for selected maximum mass yields of α- pinene, β-pinene and limonene oxidation by OH (upper panel) and O_3 (lower panel) at 293.15 K.