Seasonal perspectives of the Oxidation State and Sources of OA in Cape Corsica

First results of 15-month continuous observations with ACSM

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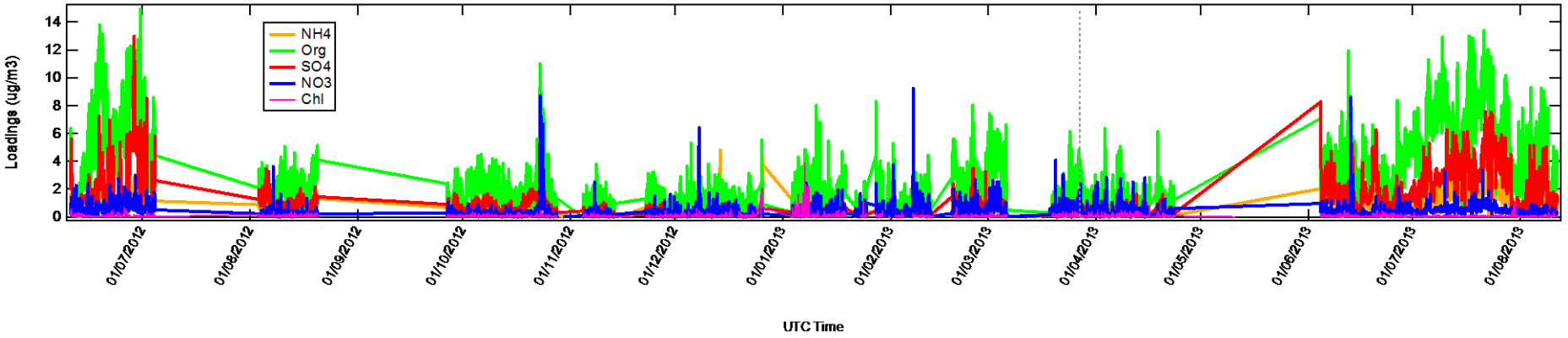
The Cape Corsica monitoring station

Oxidation State of OA/ First results from long term ACSM observations

June 2012 **August 2013**



f44 (%) = *m/z* 44 / total Org signal

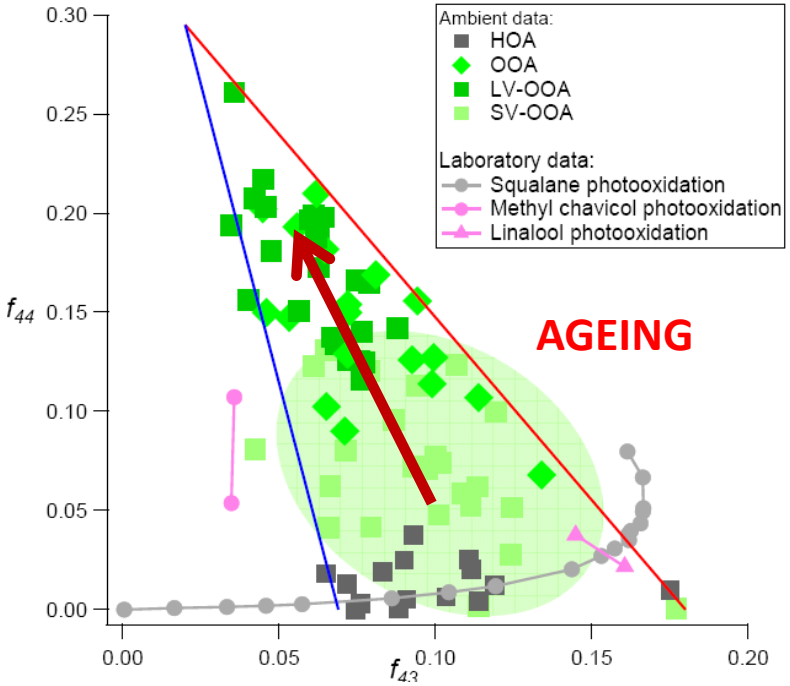
→ **Mostly CO_2^+ (acid and/or acid derived – ester – species)**

f43 (%) = *m/z* 43 / total Org signal

→ **Mostly $C_2H_3O^+$ for OOA (non acid oygenates for OOA)**

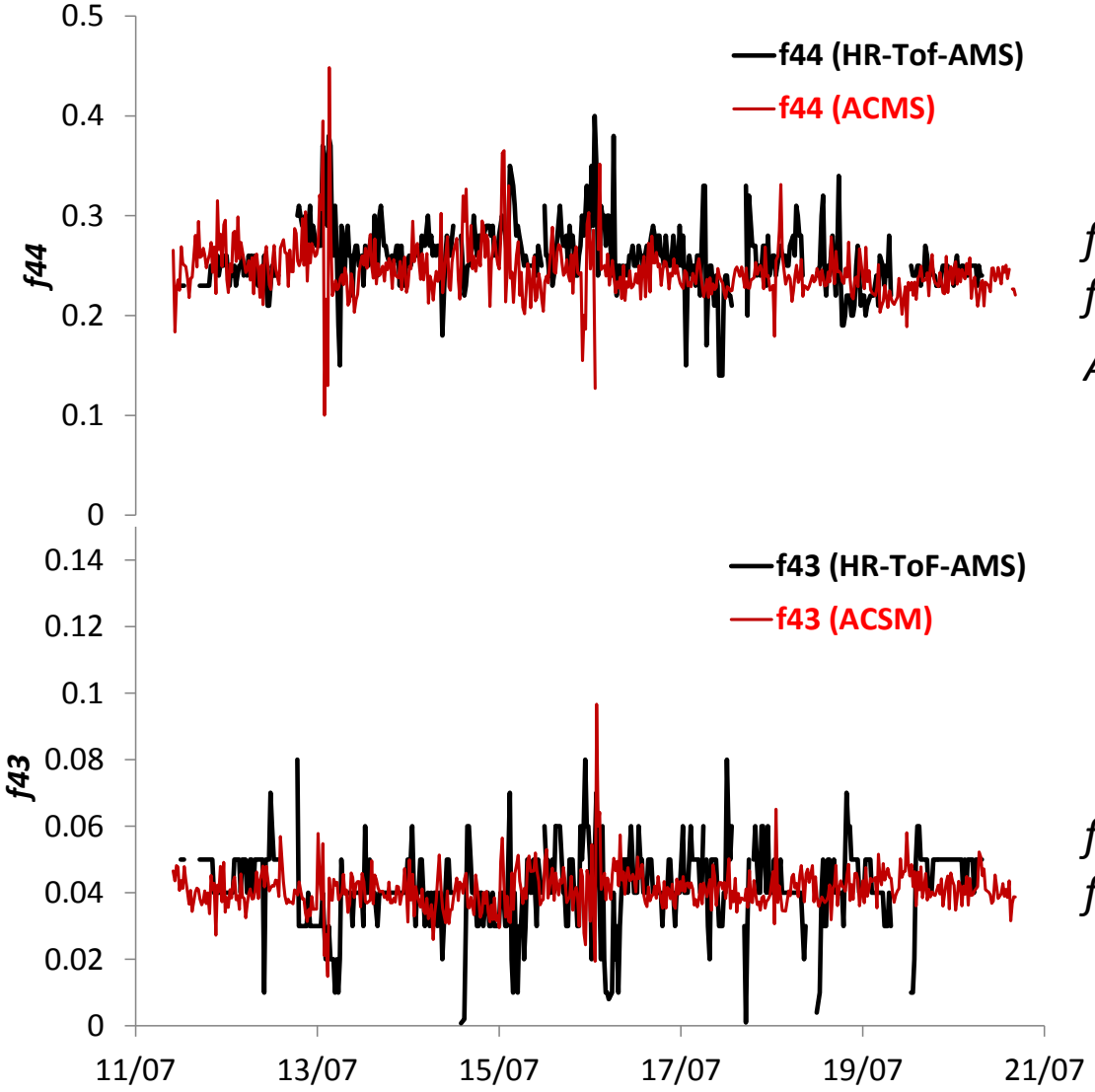
→ **Mostly $C_3H_7^+$ for HOA**

Triangle plot from *Ng et al.* (ACP, 2010)



Comparison of f43 and f44 between ACSM and HR-ToF-AMS

Cape Corsica (11-21 July 2013)



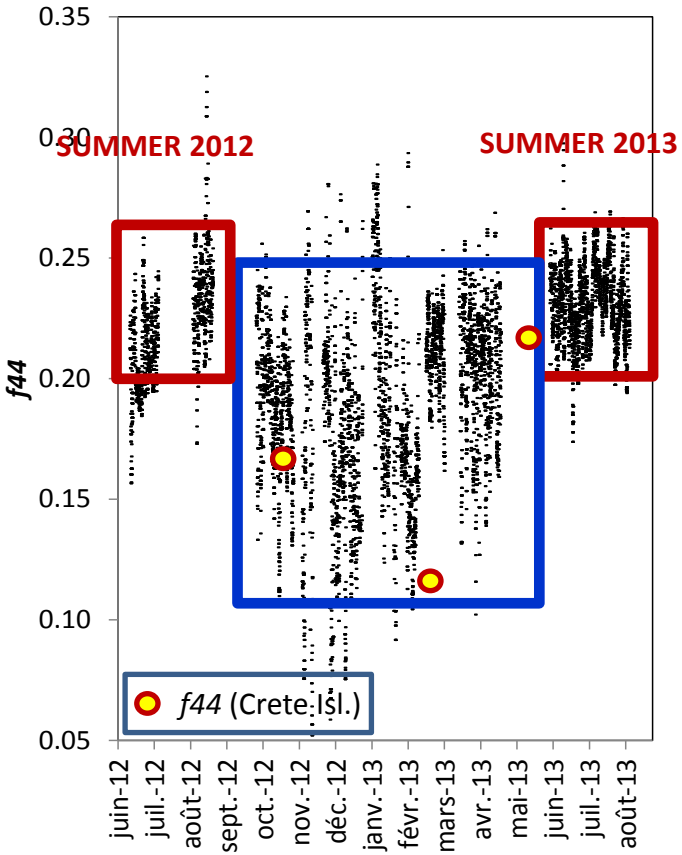
f44 (ACSM) = 0.245±0.029
f44 (HR-ToF-AMS) = 0.258±0.033

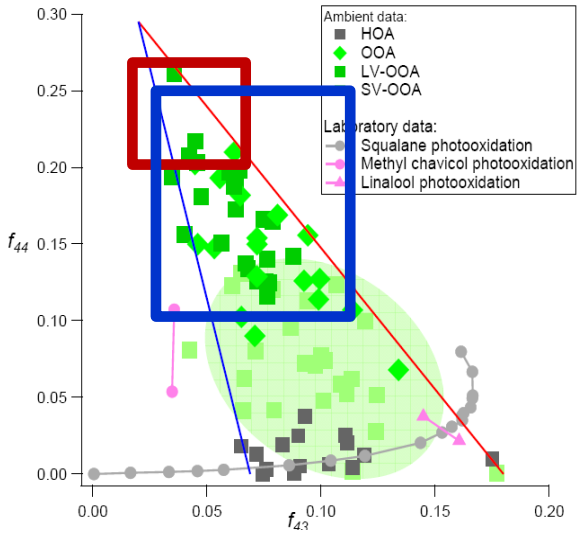
About 4% difference

f43 (ACSM) = 0.041±0.006
f43 (HR-ToF-AMS) = 0.041±0.012

HR-ToF-AMS data courtesy of N. Marchand and L. Dewit (LCP); ANR-SAFMED project

Seasonal variation of *f44* (June 2012 – August 2013)





Triangle plot from *Ng et al. (ACP, 2010)*

DURING SUMMER (June to Aug.):

→ Very High values during summer (among the highest reported in litterature for AMS data). Probably no significant amount of SV-OOA

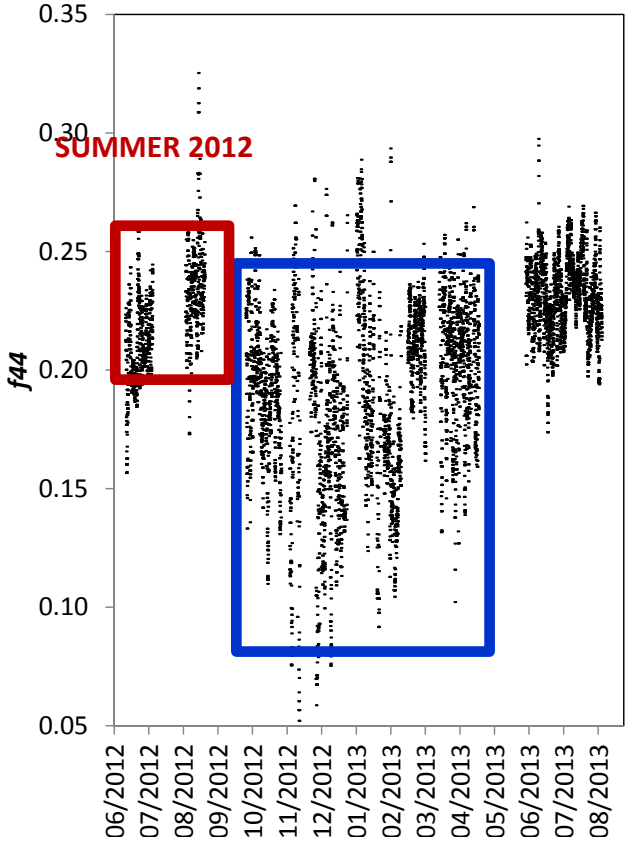
→ Poor variability (mostly between 0.2 & 0.3) / OA oxidation state is likely to be quite similar (although OA is more variable)

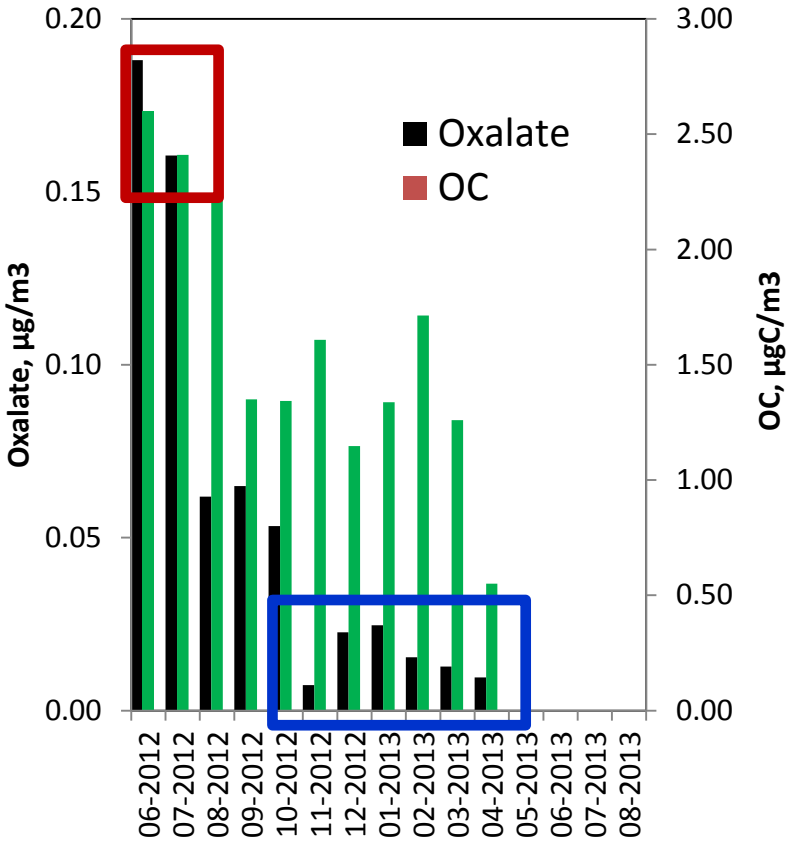
DURING WINTER (From Nov. To Feb.) :

→ Lower *f44* but still in the range of 0.15 (still important oxidation, LV-OOA)

→ Very High variability suggesting fast transport of poorly oxydized OA

Comparison between *f44* and oxalate

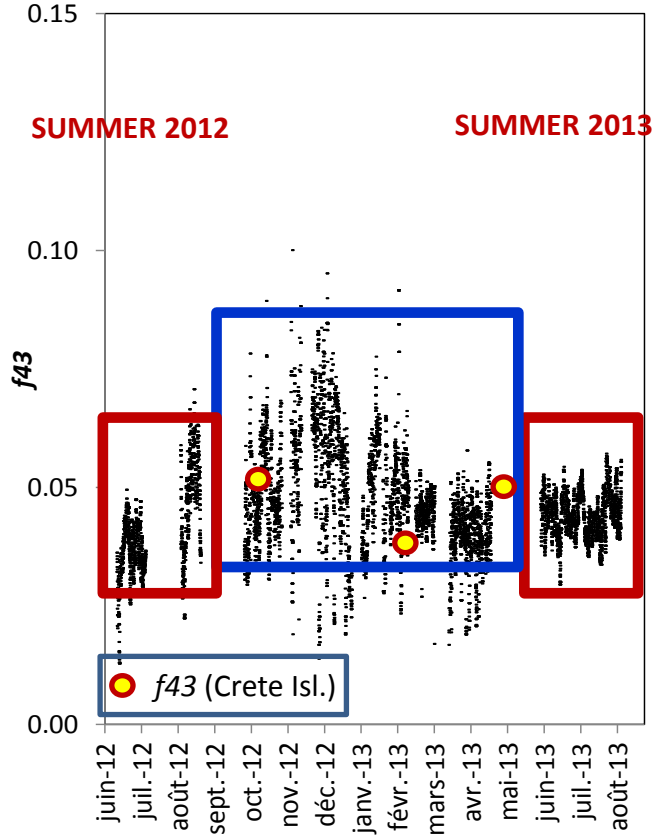


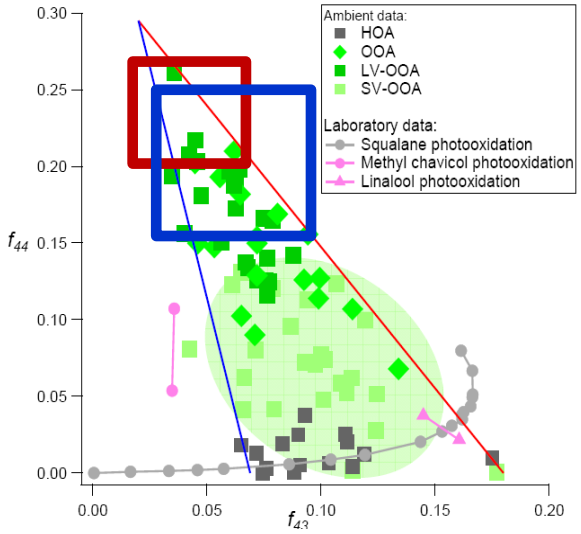


[Oxalate]/[OC] ~ 7% during summer
[Oxalate]/[OC] ~ 2% during winter

Some similarities between f44 seasonal pattern and the fraction of oxalate in OA

Seasonal variation of *f43* (June 2012 – August 2013)





Triangle plot from *Ng et al.* (ACP, 2010)

DURING SUMMER (June to Aug.):

→ Very Low values during summer (among the lowest reported in litterature for AMS data). Probably no significant amount of SV-OOA

→ Poor variability (mostly between 0.03 & 0.7) / OA oxidation state is likely to be quite similar (although OA is more variable)

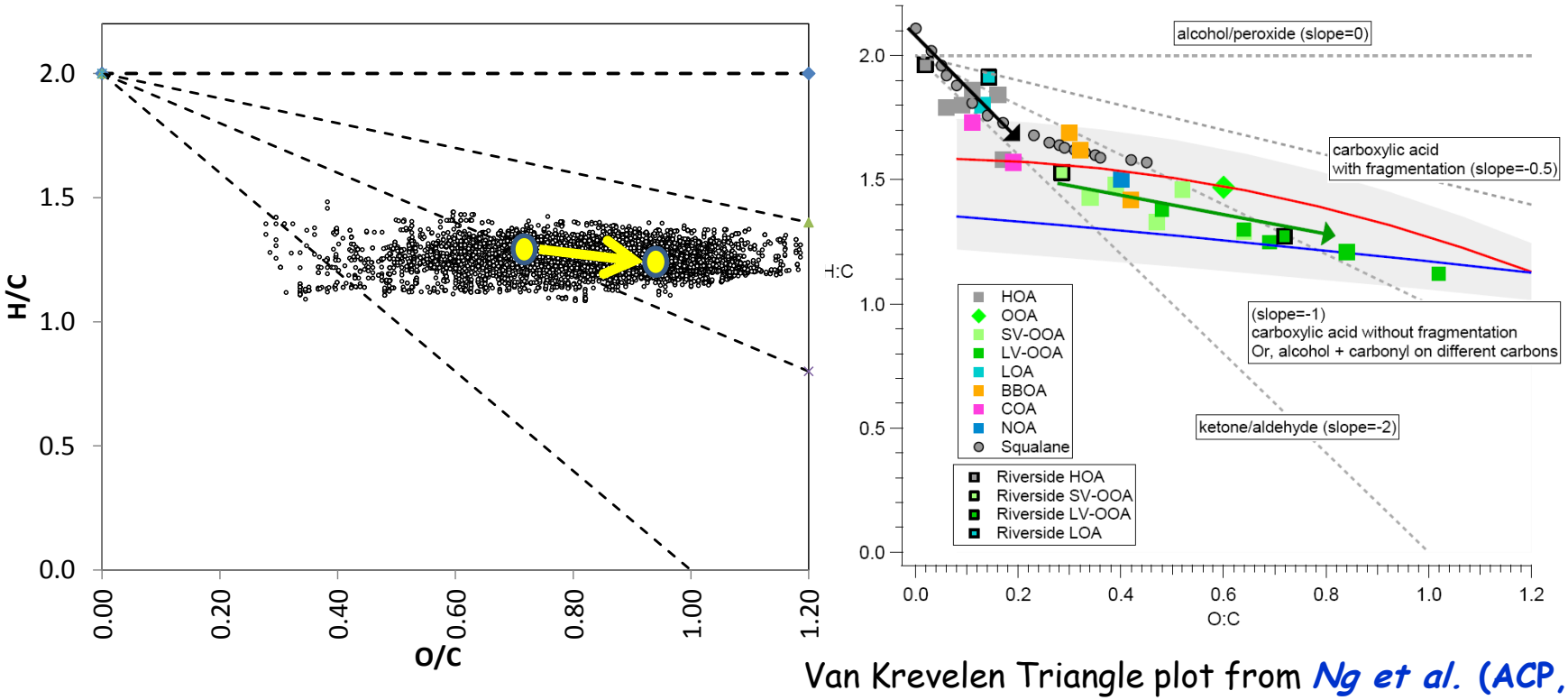
DURING WINTER (From Nov. To Feb.) :

→ Higher *f43* but in the range of 0.5-0.7 (still important oxidation, LV-OOA)

→ Very High variability suggesting fast transport of poorly oxydized OA

H/C versus O/C: Fragmention of OA ?

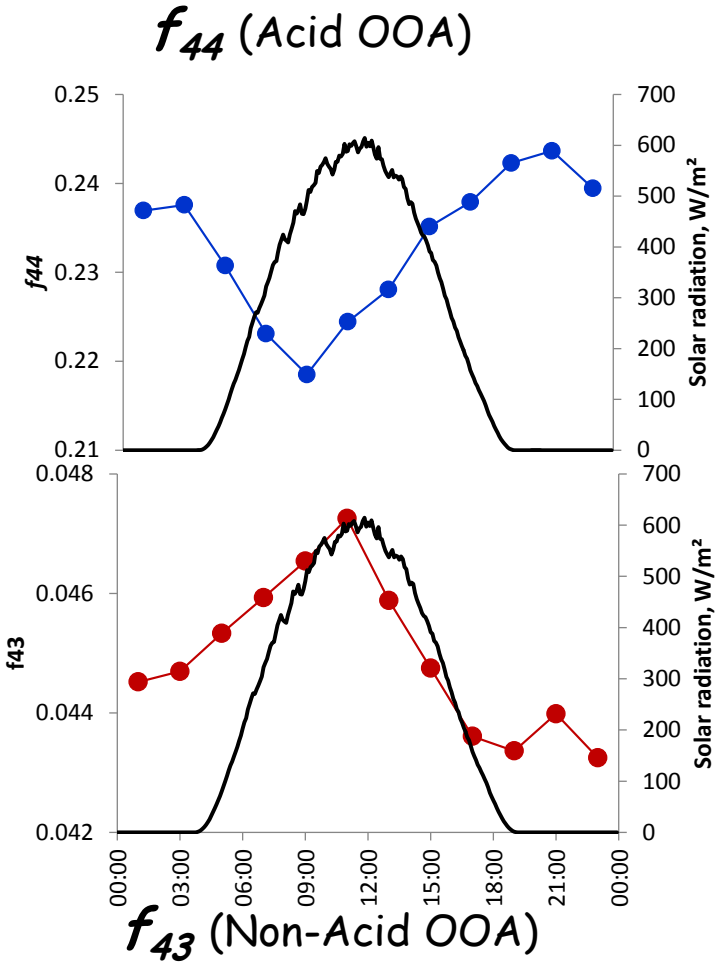
Aiken et al. (Environ. Sci. Technol., 2008)
$O/C = 0.0382\ xf44 + 0.0794$
Ng et al. (Atmos. Chem. Phys., 2011)
$H/C = 1.01 + 6.07\ xf43 - 16.01\ xf43^2$

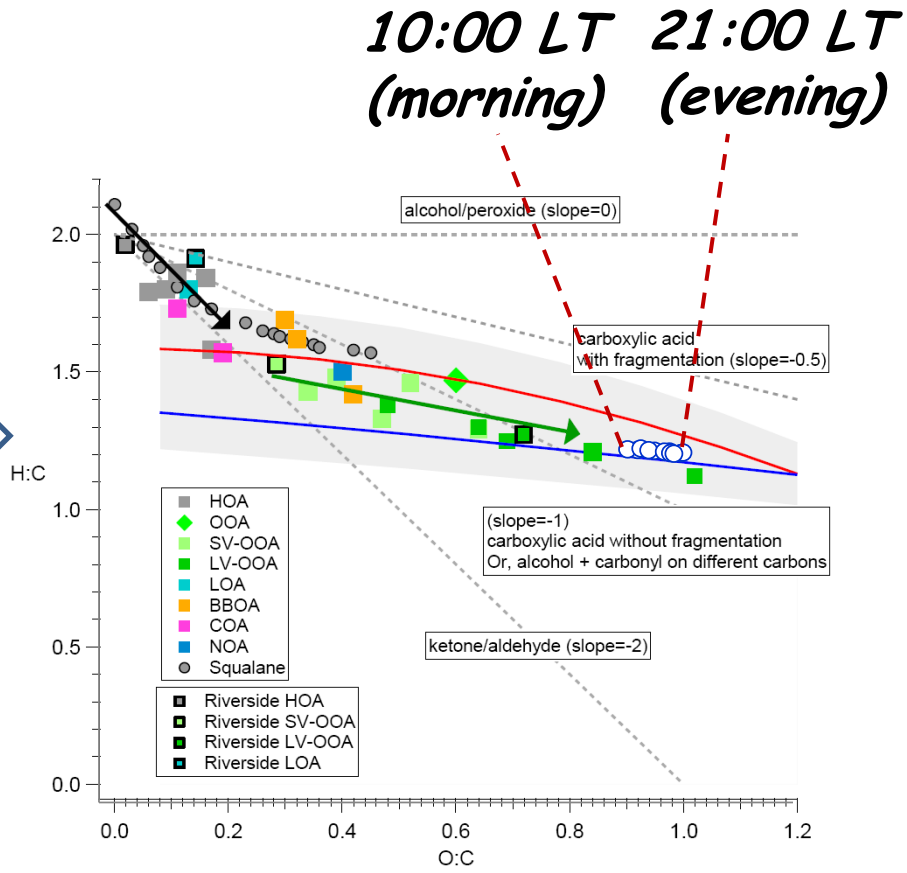


Van Krevelen Triangle plot from *Ng et al.* (ACP, 2011)

→ Already highly oxidized OA during winter (carboxylic acids and/or alcohol+carbonyl) towards fragmentation with carboxylic acides during summer

Diurnal variations of *f43* & *f44*





⇒ Photochemically-induced formation/destruction of non-acid OOA (f_{43})

⇒ Photochemically-induced formation of acid OOA (f_{44}). Possibly with fragmentation

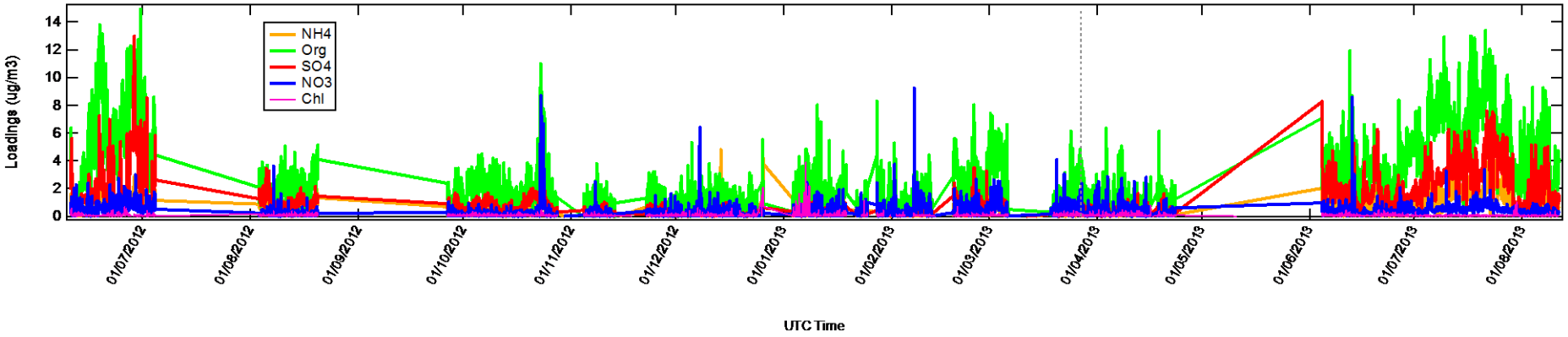
However,

Diurnal variability remain rather small (~8% amplitude of *f44*; ~4% amplitude of *f43*)

Source apportionment of OA/ First results from long term ACSM observations

June 2012

August 2013



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SoFi - Source Finder

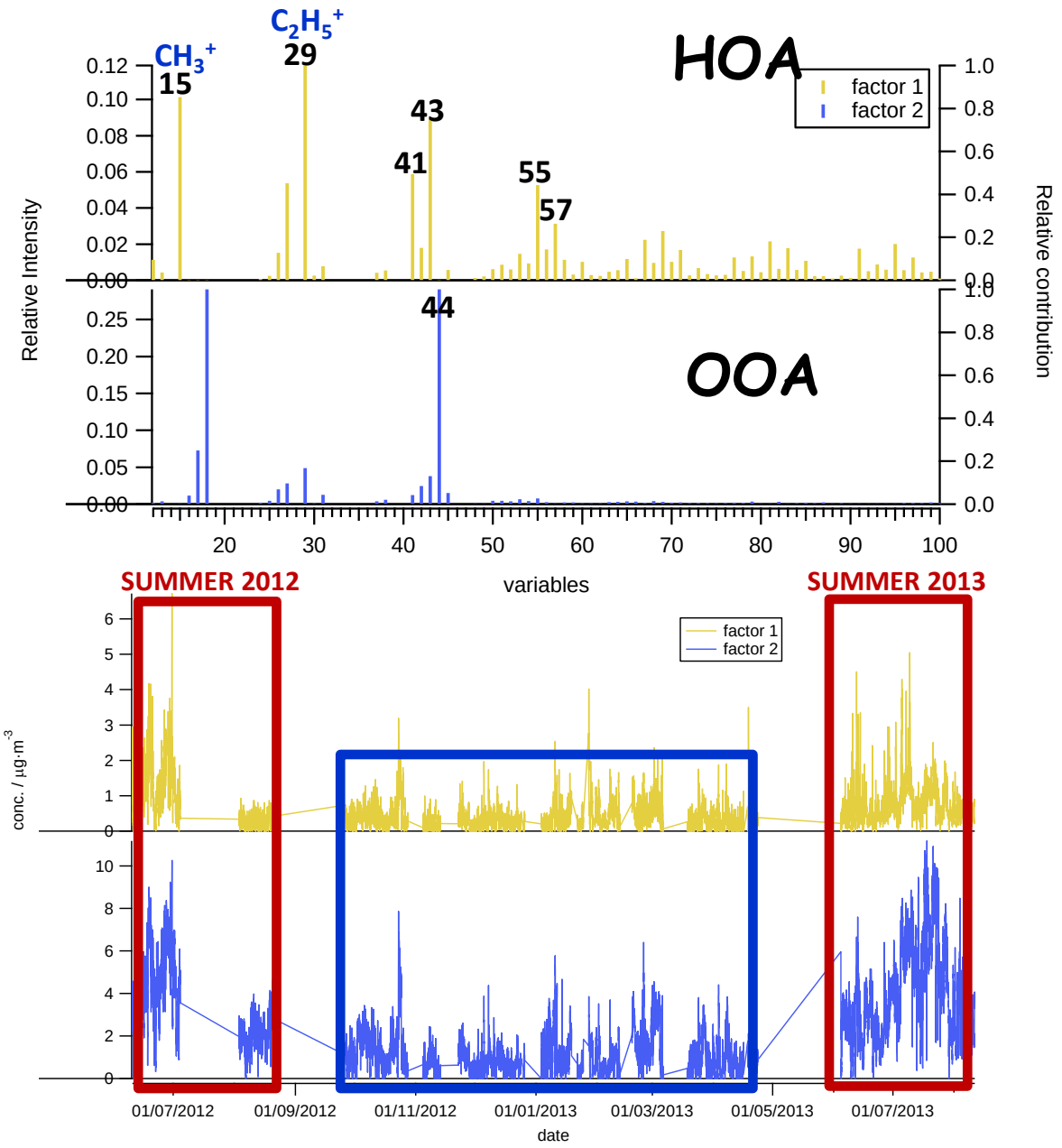
LABOR FÜR ATMOSPHÄREN-CHEMIE

PMF with 2 & 3 factors

ME-2 with 2, 3, 4 factors
Fix factors = HOA, MSA

Comparison

Results from PMF (2 factors) – 14 months (june 2012 – Aug. 2013)



Similar spectra compared to PMF (2 factors) restricted to during summer 2013

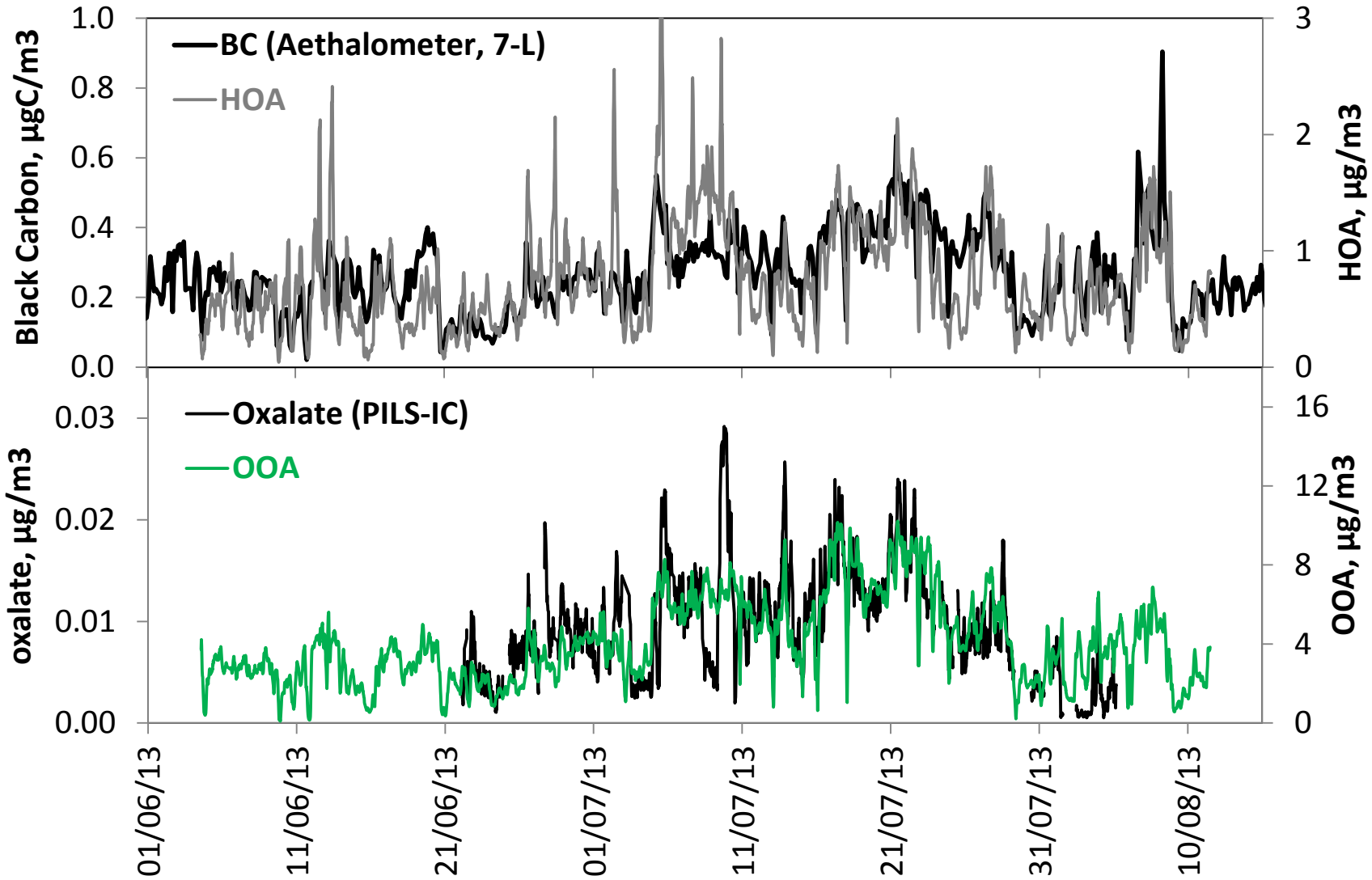
BUT

Slightly lower contribution of m/z 15 & 29 for the summer period (compare to m/z 41 and 45)

Is it something from the real world ?
(or PMF artefact)

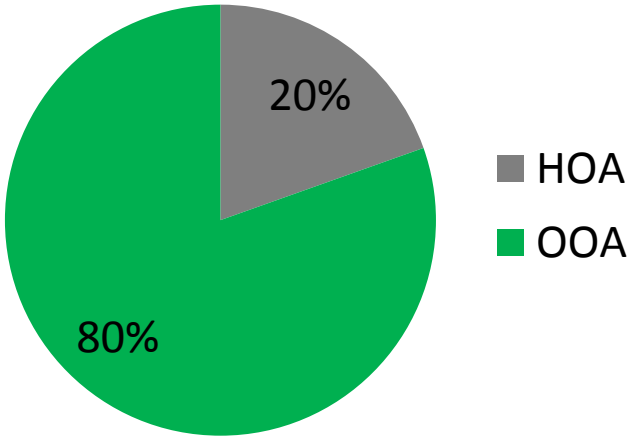
Comparison with tracers

Summer 2013 (June → August 2013)



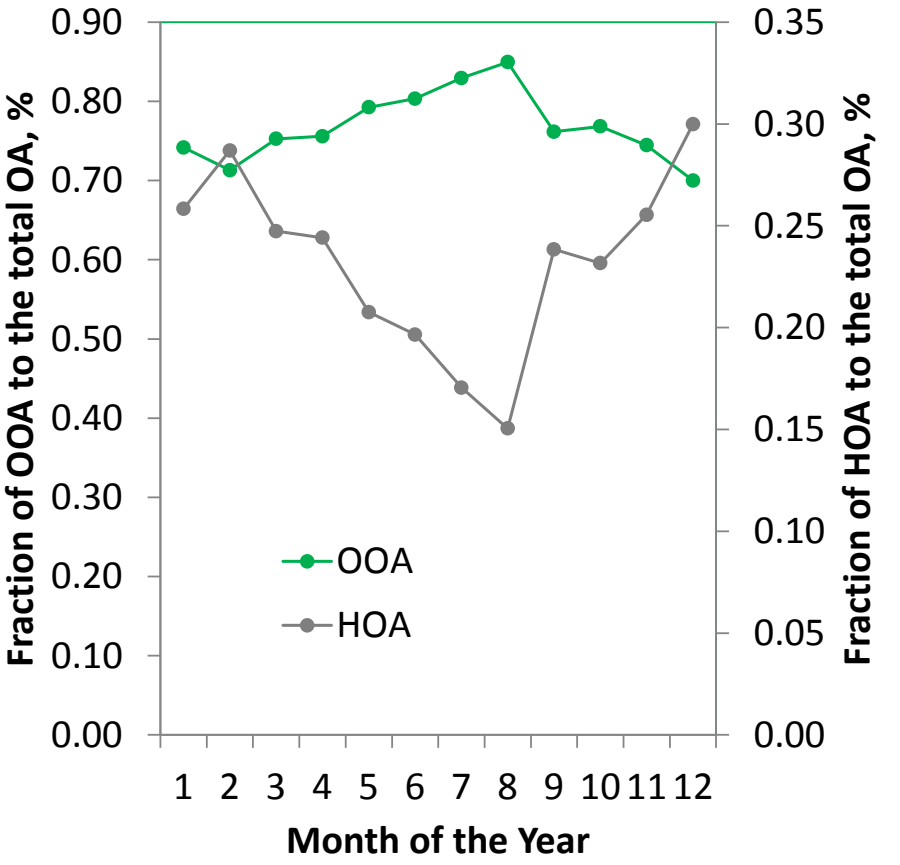
Results from PMF (2 factors)

On a yearly average



With observable seasonal variation*

*(results from 15-month observations)



OOA

70% of OA during winter months

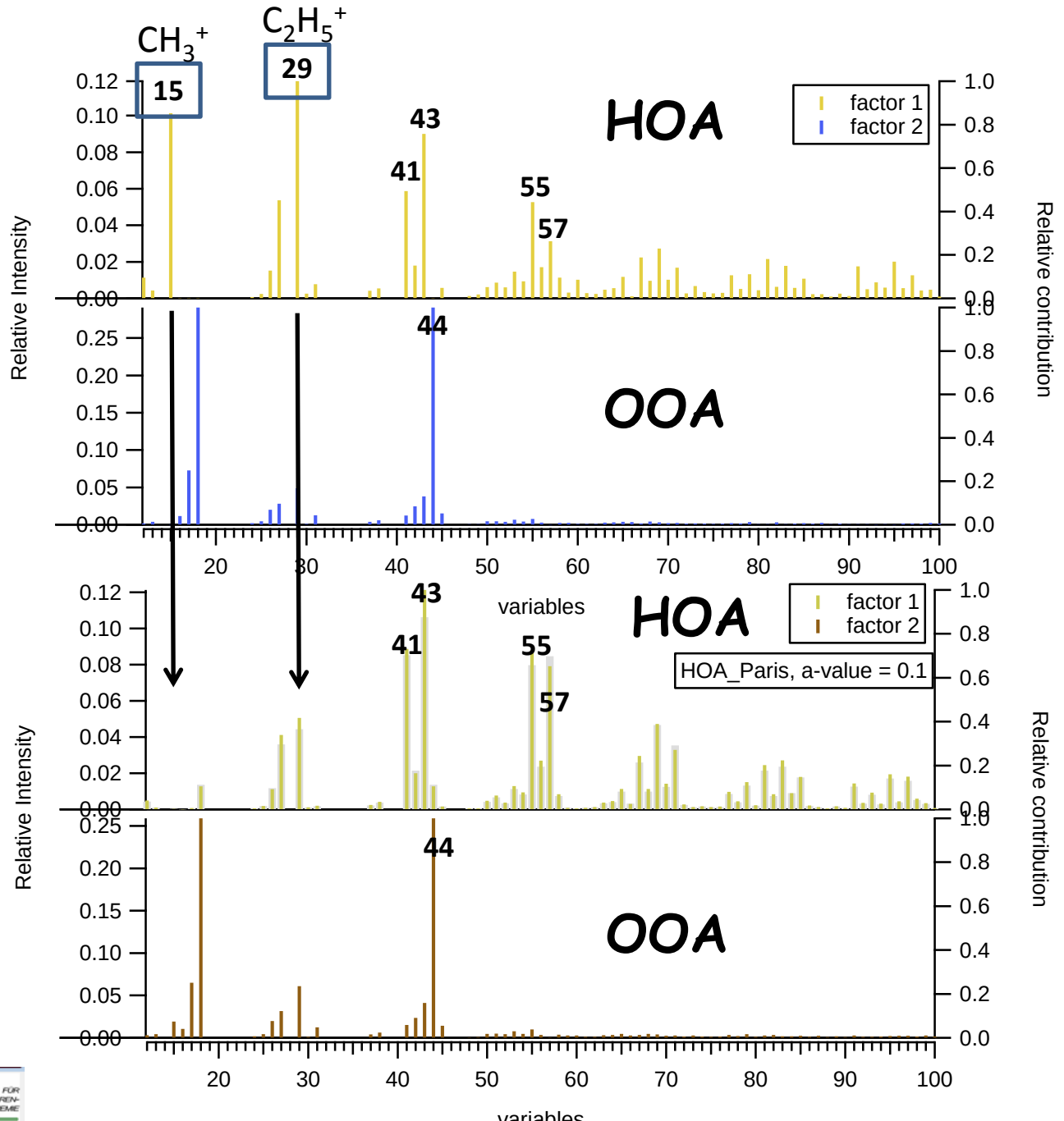
85% of OA during summer months

Fraction of OOA is high along the year; Even higher during summer

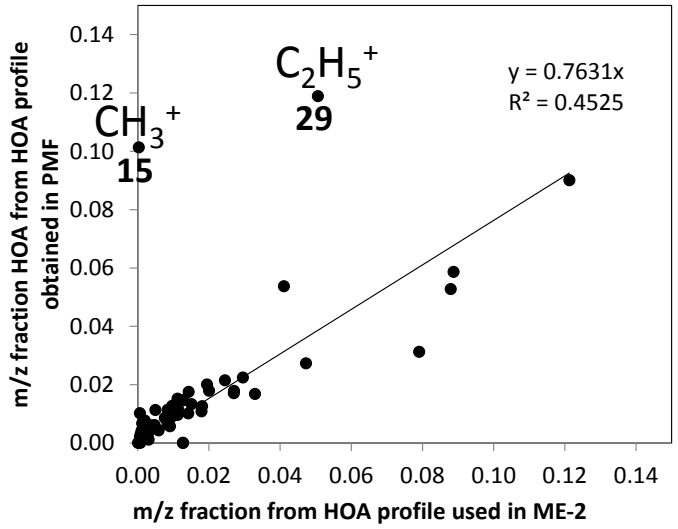
Comparison between PMF and ME-2 results

PMF results
2 factors

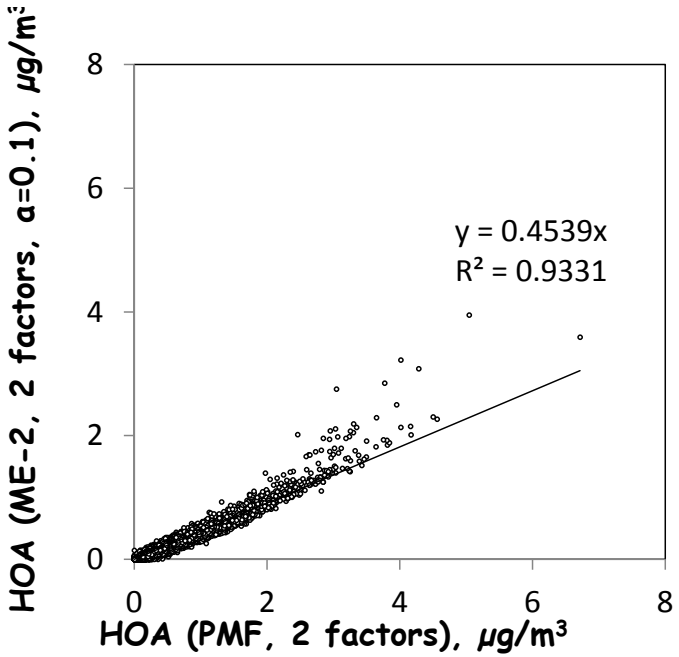
ME-2 results
2 factors



Comparison between PMF and ME-2 results



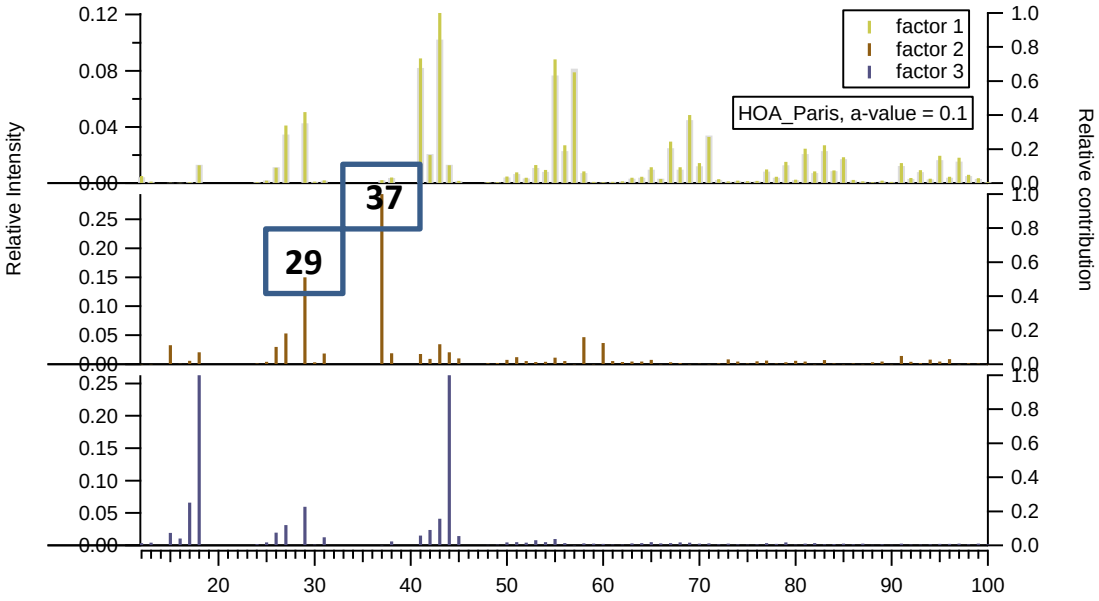
m/z at 15 and 29 are the two major m/z that differs between the 2 mass spectra. Why ?

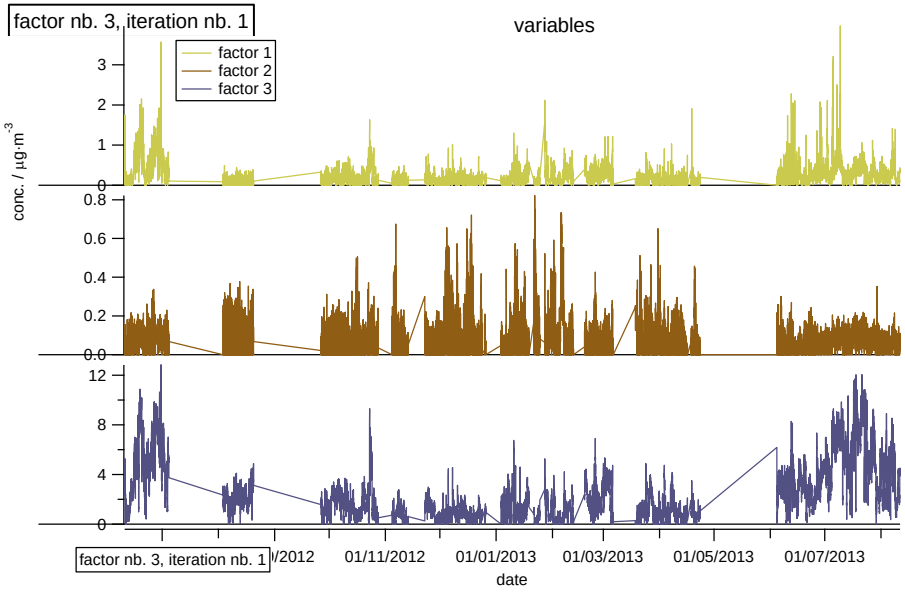


+ ME-2 gives results [HOA] lower compare to PMF. Why ?

+ Why we have different fragments ? Could m/z at 15 and 29 explain this difference ?

ME-2 results
3 factors (1 profile fix = HOA)





+ Factor 2 ???

↓

+ Same results obtained with PMF (3 factors)

+ Could a part of Chloride be in assimilated as OA in m/z 37?

Need for further investigation

Conclusions

+ OA at Cape Corsica are most of the time highly oxidized (even during wintertime) as seen with high *f44*. They even look like more oxidised that what has been observed in E. Mediterranean (Crete Island).

+ Strong variability on OA oxidation state during winter (influence of fast transport with low processes). During summer, OA shows quite high and stable oxidation state (poor dependance of fast transport processes from EU).

+ The highly oxidation state of OA suggest that fragmentation may appear during summertime (heterogeneous processes)

+ PMF and ME-2 leads to different HOA concentration levels but are very consistent (need more investigation)

Thanks for your attention