

Diurnal cycle of fossil and non-fossil total carbon using ^{14}C analyses during CalNex

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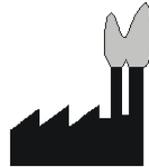
CalNex Data Analysis Workshop – 16th to 19th of May

Introduction

- Why is ^{14}C measured for aerosol samples?
 - Source apportionment for carbonaceous aerosol by $^{14}\text{C}/^{12}\text{C}$

anthropogenic emissions

- ^{14}C decayed completely



biogenic emissions

modern $^{14}\text{C}/^{12}\text{C}$ ratio



$$f_m = \frac{\left(\frac{^{14}\text{C}}{^{12}\text{C}} \right)_{\text{Sample}}}{\left(\frac{^{14}\text{C}}{^{12}\text{C}} \right)_{\text{AD1950}}}$$

f_m ...fraction of modern carbon

- $f_{m_{\text{fossil}}} = 0$, $f_{m_{\text{biogenic}}} = 1$
- After 1950 f_m values have to be corrected for the nuclear bomb excess

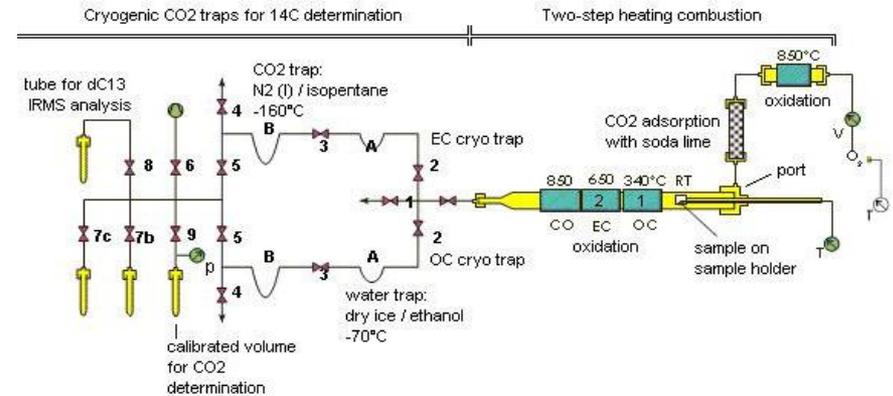
^{14}C Measurement of TC and OC

THEODORE

• Sample preparation with THEODORE

(see Szidat et al. 2004)

- combustion of a filter punch in pure O_2
- TC at 640°C for 12min, OC at 340°C for 10min
- evolving CO_2 :
 - is cryotrapped
 - determined manometrically
 - sealed in glass ampoules

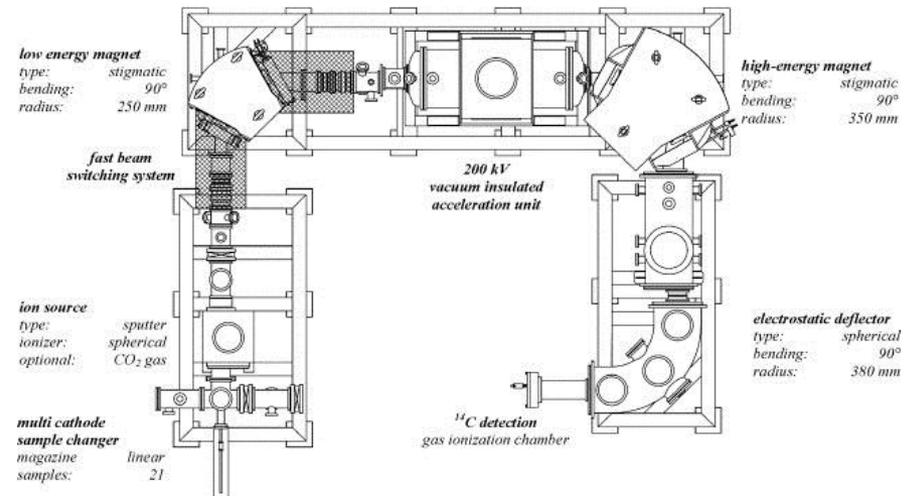


MICIDAS

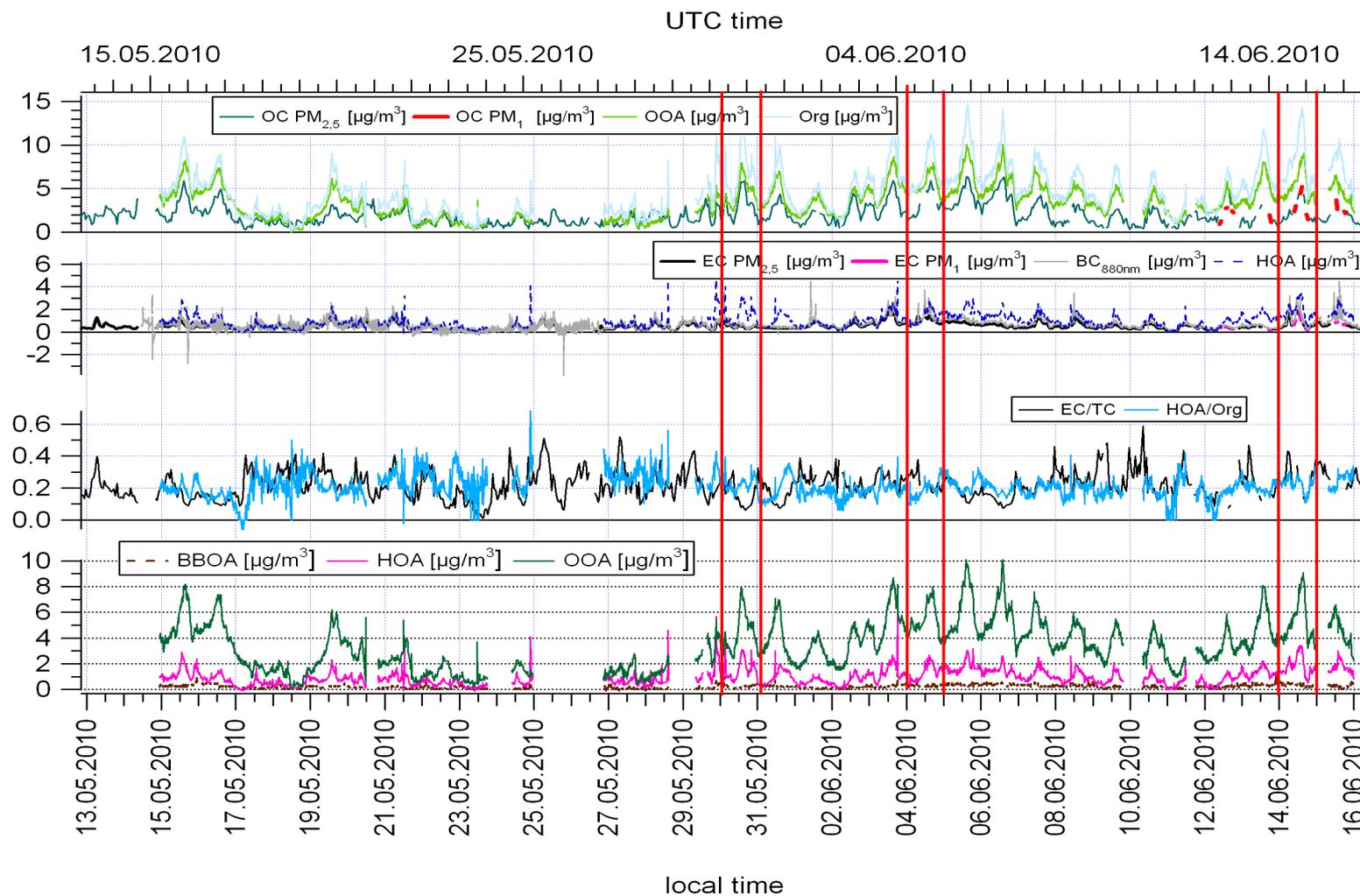
• ^{14}C measurement with MICIDAS

(see Synal et al. 2007)

- Mini Radiocarbon Dating System at the ETH Zürich
- detection limit = $3\mu\text{g}$



Filter Choice



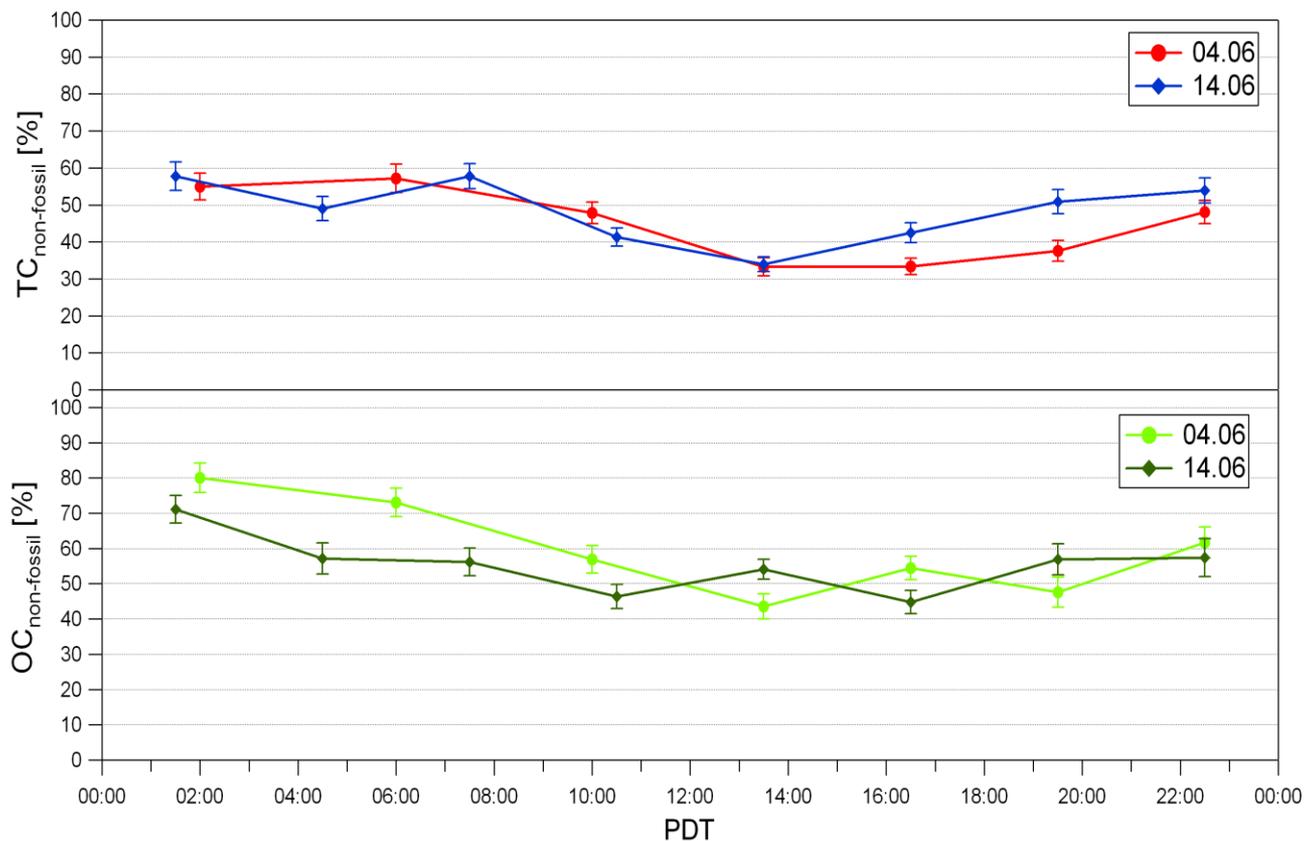
¹⁴C Results

TC_{non-fossil}

04.06	33% - 57%
14.06	34% - 58%

OC_{non-fossil}

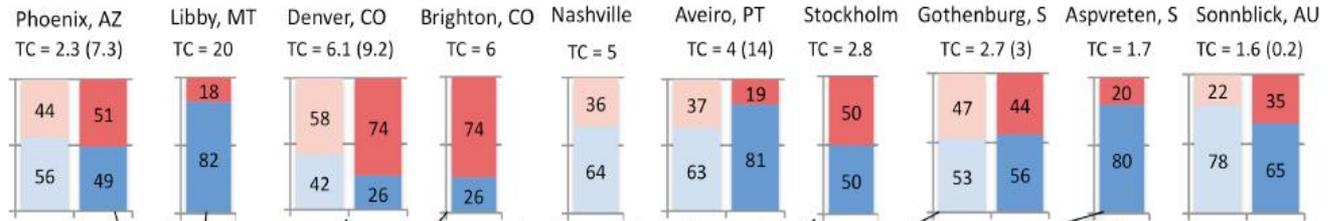
04.06	44% - 80%
14.06	45% - 71%



¹⁴C Results

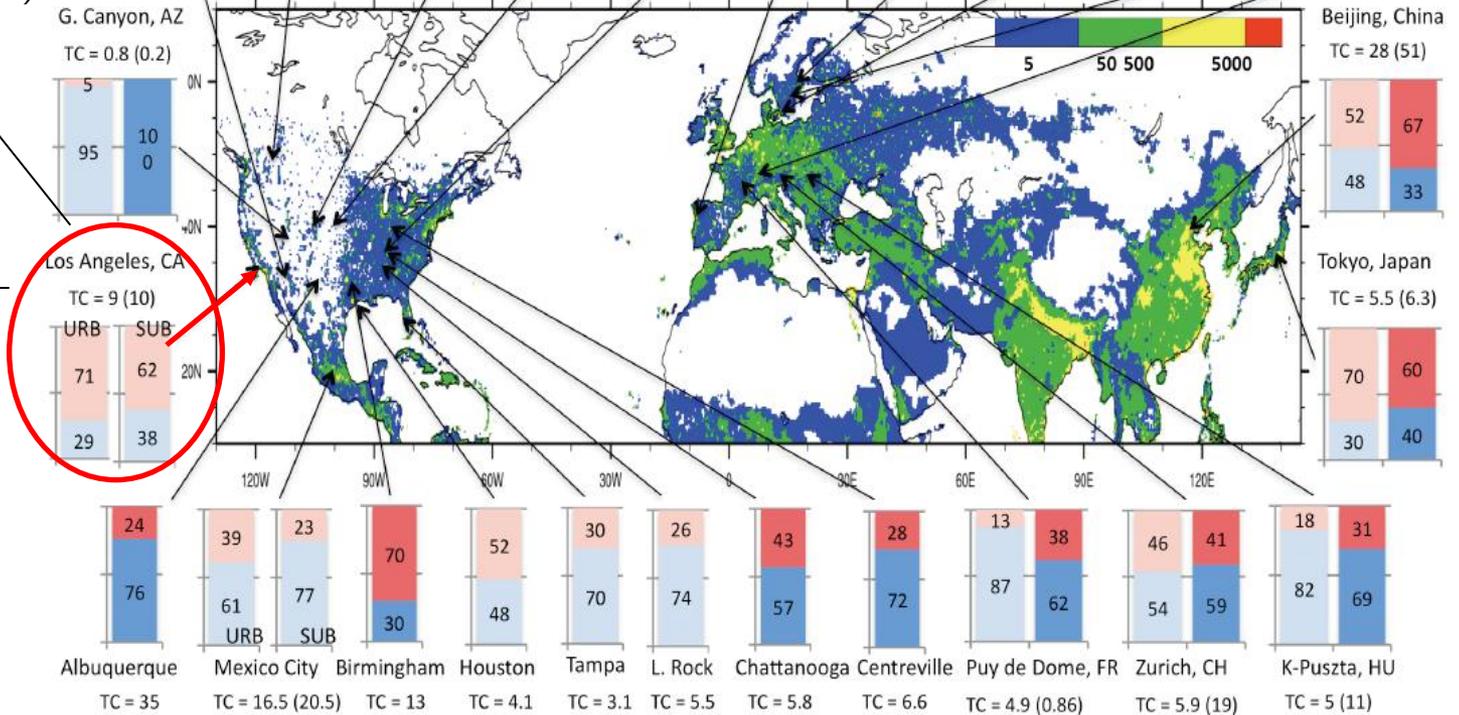
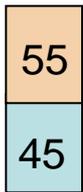
In 1982

(Hildemann et al., 1994)



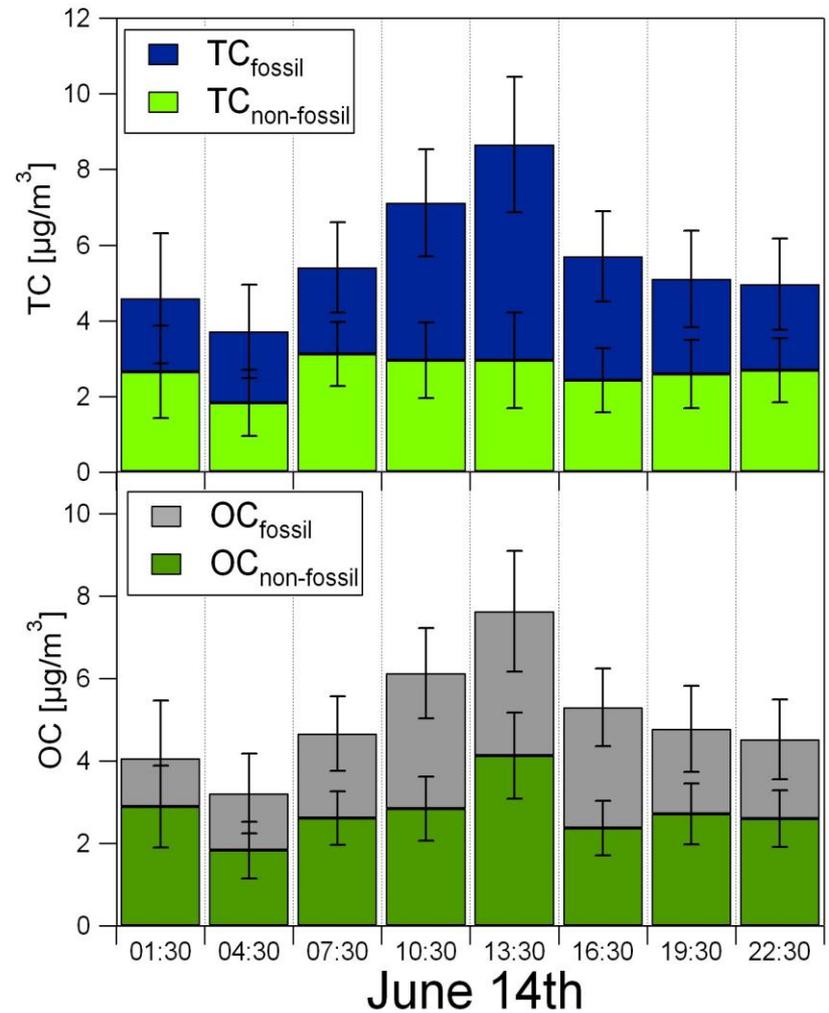
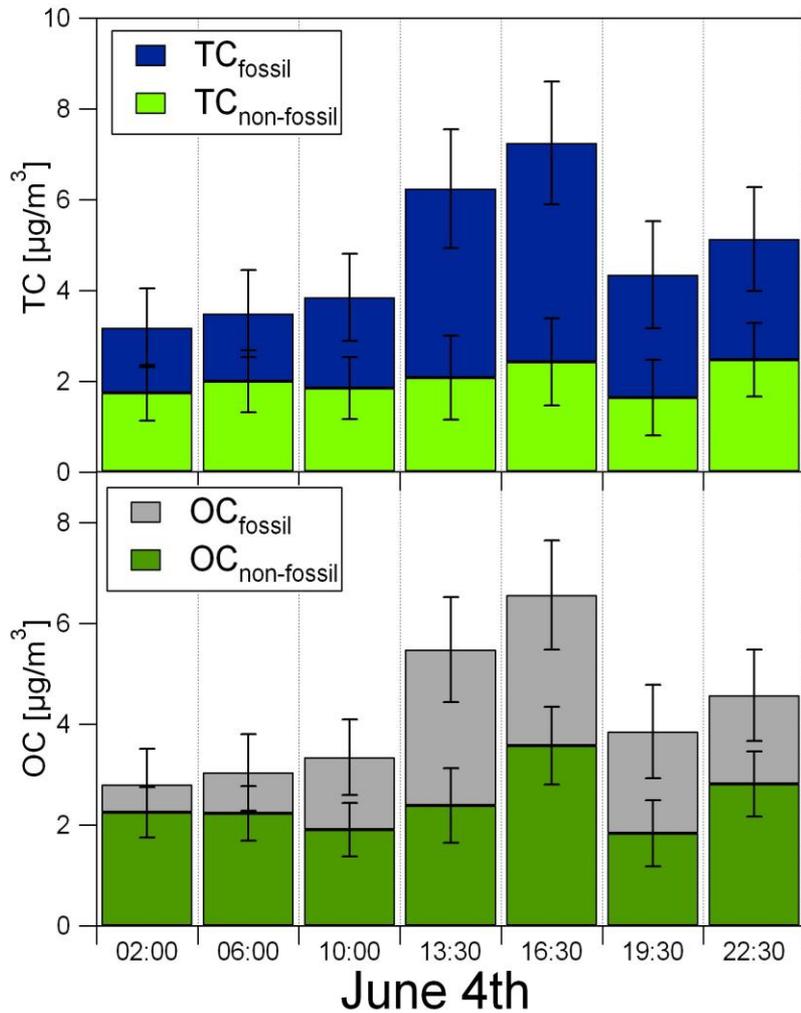
In 2010

04.06 14.06

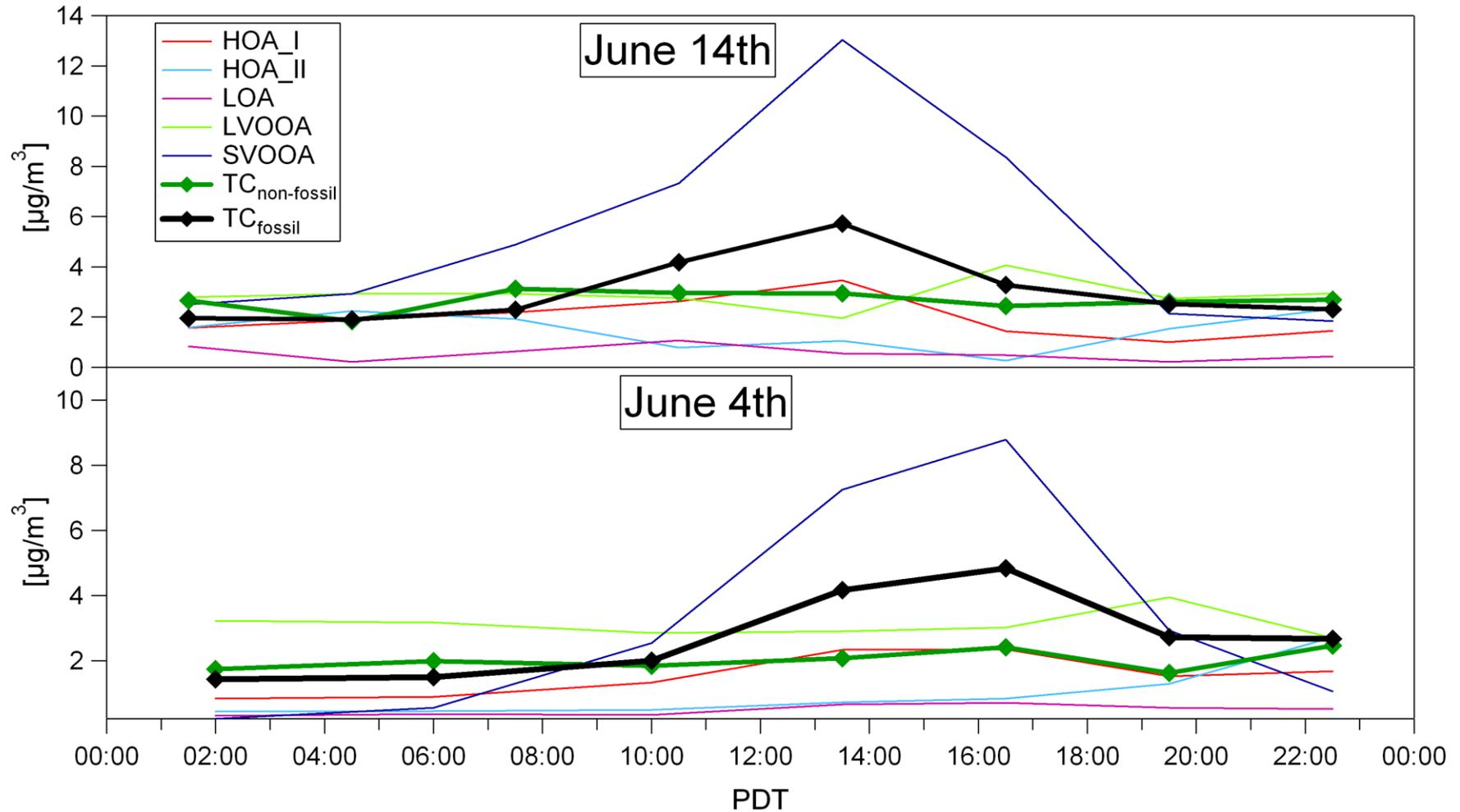


Hodzic et al. 2010

¹⁴C Results



^{14}C Results



¹⁴C Results

- Calculation of $OC_{\text{non-fossil}}$

$$TC_{nf} = EC_{nf} + OC_{nf}$$

$$fm_{TC} \cdot TC = fm_{EC} \cdot EC + fm_{OC} \cdot OC$$

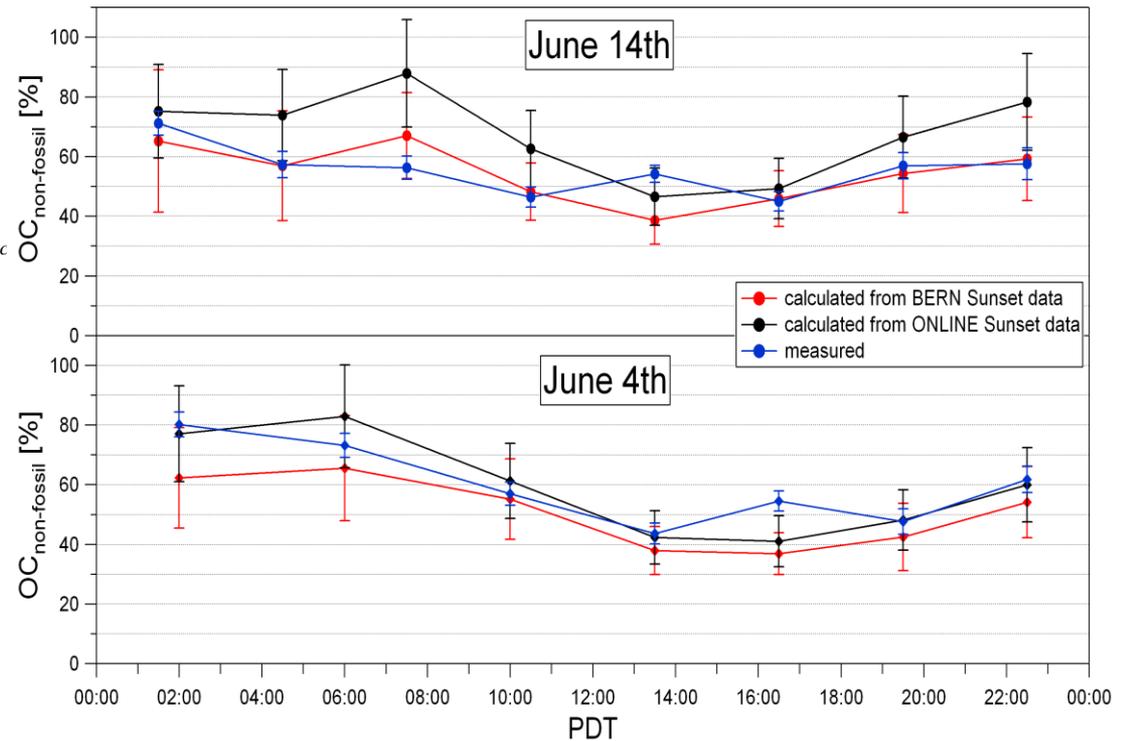
$$fm_{EC} \cdot EC = fm_{EC_{BB}} \cdot EC_{BB} + fm_{EC_{fossil}} \cdot EC_{fossil}$$

$$fm_{OC} \cdot OC = fm_{OC_{BB}} \cdot OC_{BB} + fm_{OC_{biogenic}} \cdot OC_{biogenic}$$

- Assumption

- $EC = 100\% \text{ fossil} \rightarrow fm_{EC} = 0$
- $OC_{BB} = 0$

$$fm_{OC} = \frac{fm_{TC} \cdot TC}{OC}$$

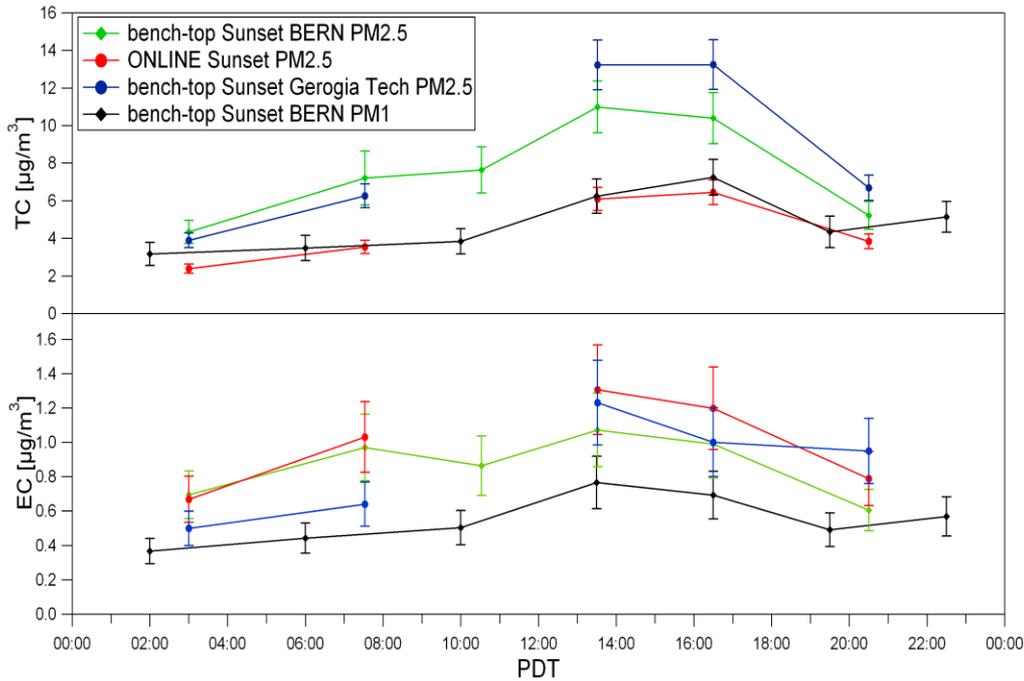


EC OC Comparison

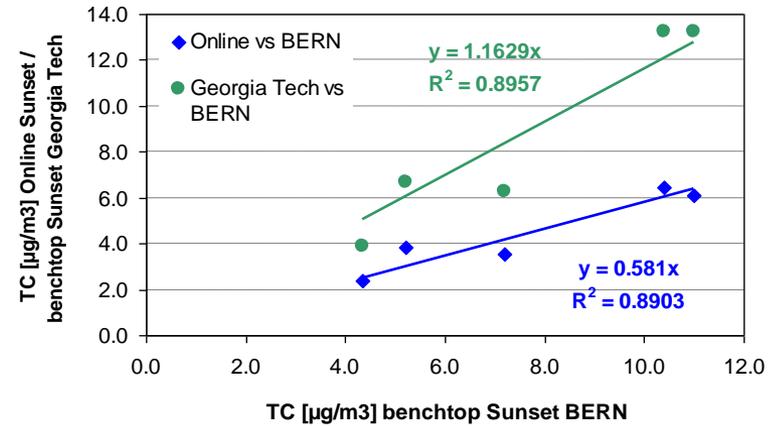
- **3 different Sunset Labs ECOC analyzer**
 - Online Sunset during CalNex-LA
 - NIOSH protocol
 - Bench-top Sunset at University of Bern
 - EUSAAR_2 protocol (*see Cavalli et al. 2010*)
 - Bench-top Sunset at Georgia Tech
 - NIOSH protocol
- Differences in EC and OC due to different protocols expected
- TC should agree within 10% - 15%

EC OC Comparison

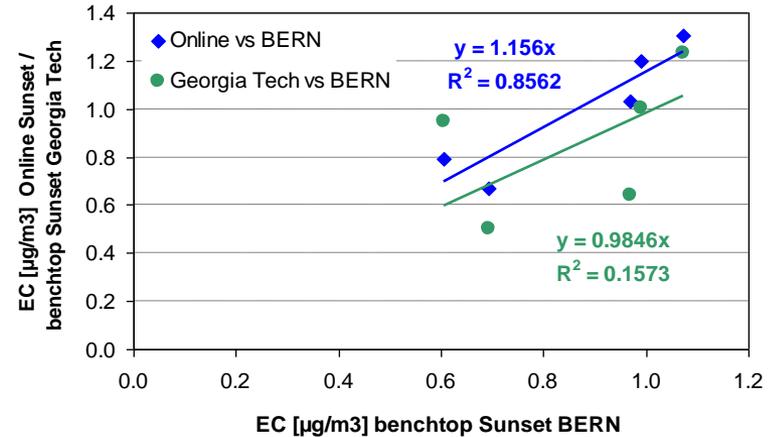
June 4th



TC 04.06 PM2.5 high resolution sampling

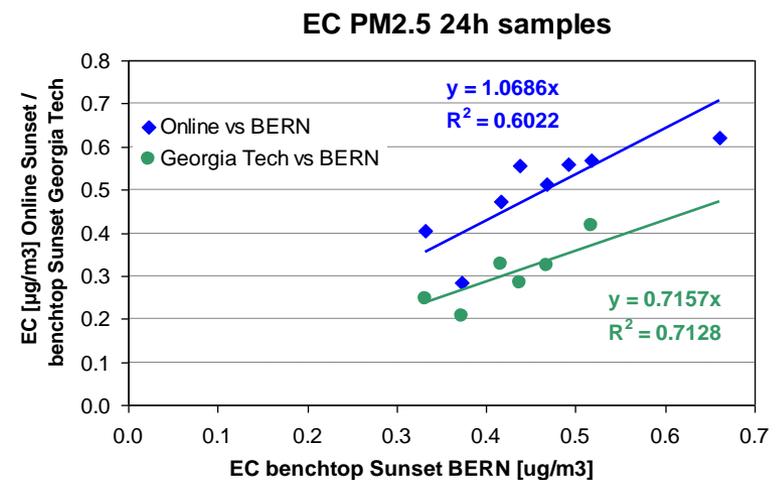
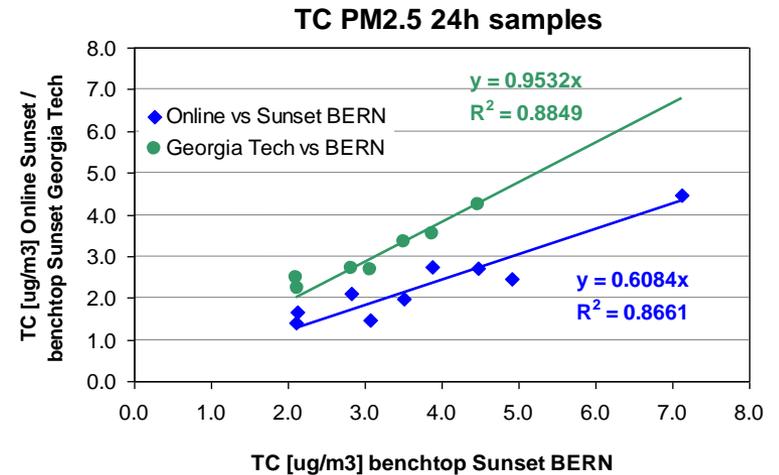
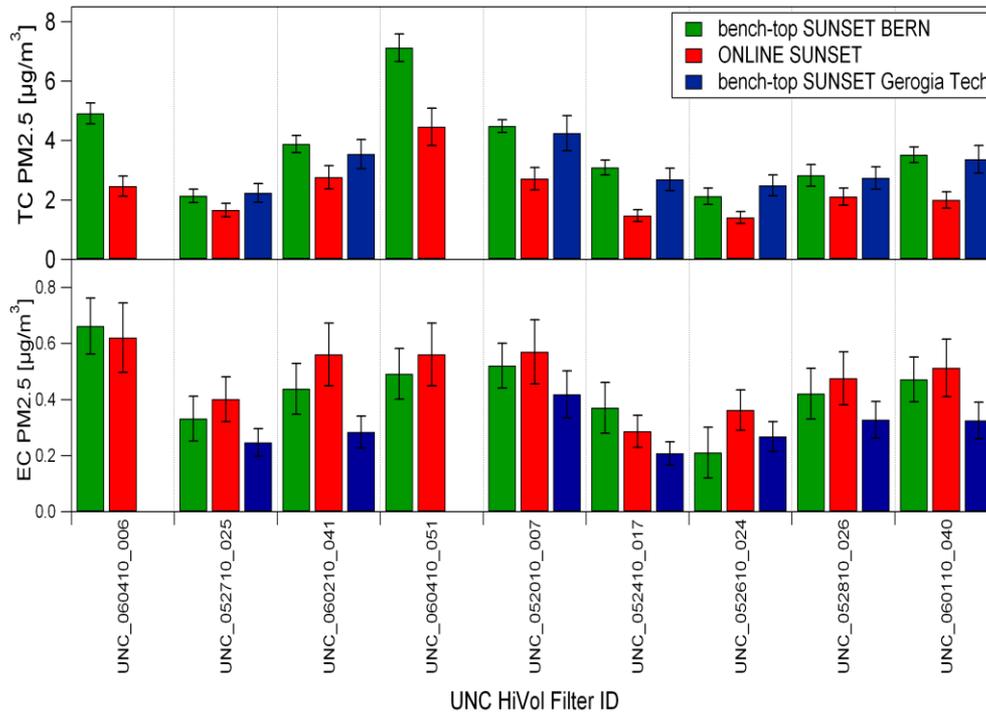


EC 04.06 PM2.5 high resolution sampling

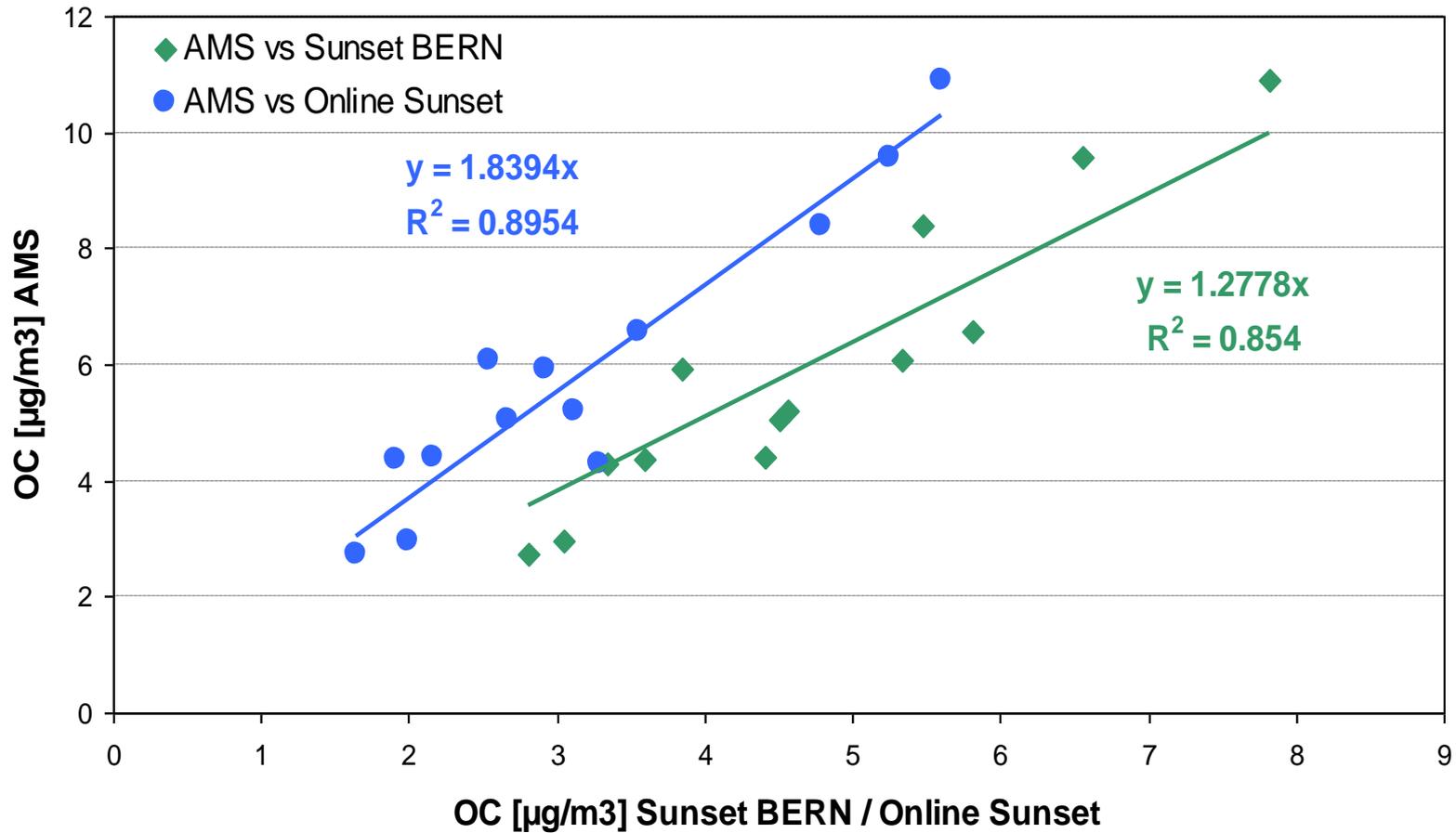


EC OC Comparison

24h samples

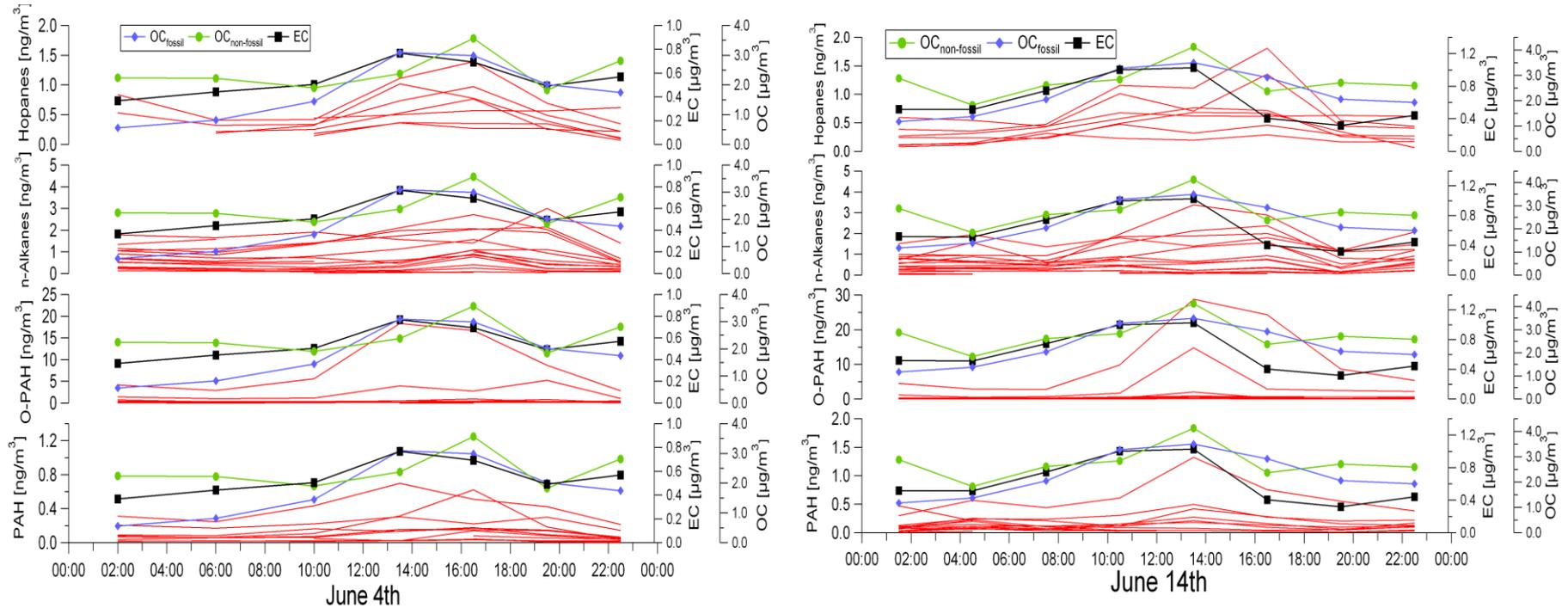


OC Comparison – AMS vs Sunset



Comparison with organic tracers

Measured with a GCMS by the Institute of Epidemiology at the Helmholtz Center Munich



Conclusion

- A clear diurnal cycle of fossil and non fossil TC and OC at the Pasadena ground site was found
- Almost no variation of $TC_{\text{non-fossil}}$ and $OC_{\text{non-fossil}}$ values throughout the day
- The enhancement of TC and OC concentrations due to the L.A plume is mainly fossil
 - this agrees with other findings presented during this meeting

Outlook

- Repeat high time resolution filters from May 30th
- Measure a few 24h samples and compare results with EPA ^{14}C measurements
- Measure ^{14}C in EC for a few 24h samples
- We are happy for any suggestions for more (only a few!) interesting periods to analyze



Thank you for your attention!