PIKA fits of CO^+

for highly-oxidized wood-burning POA

& comparison to standard EA, f_{44}

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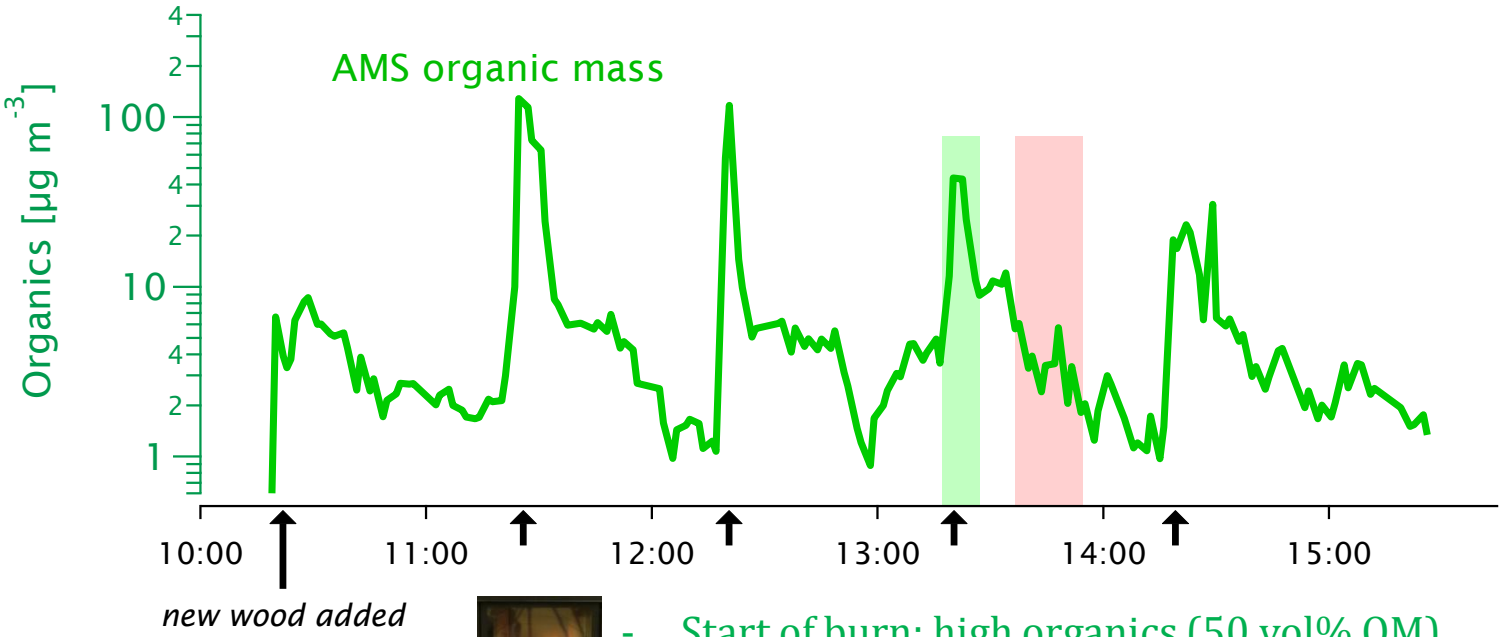
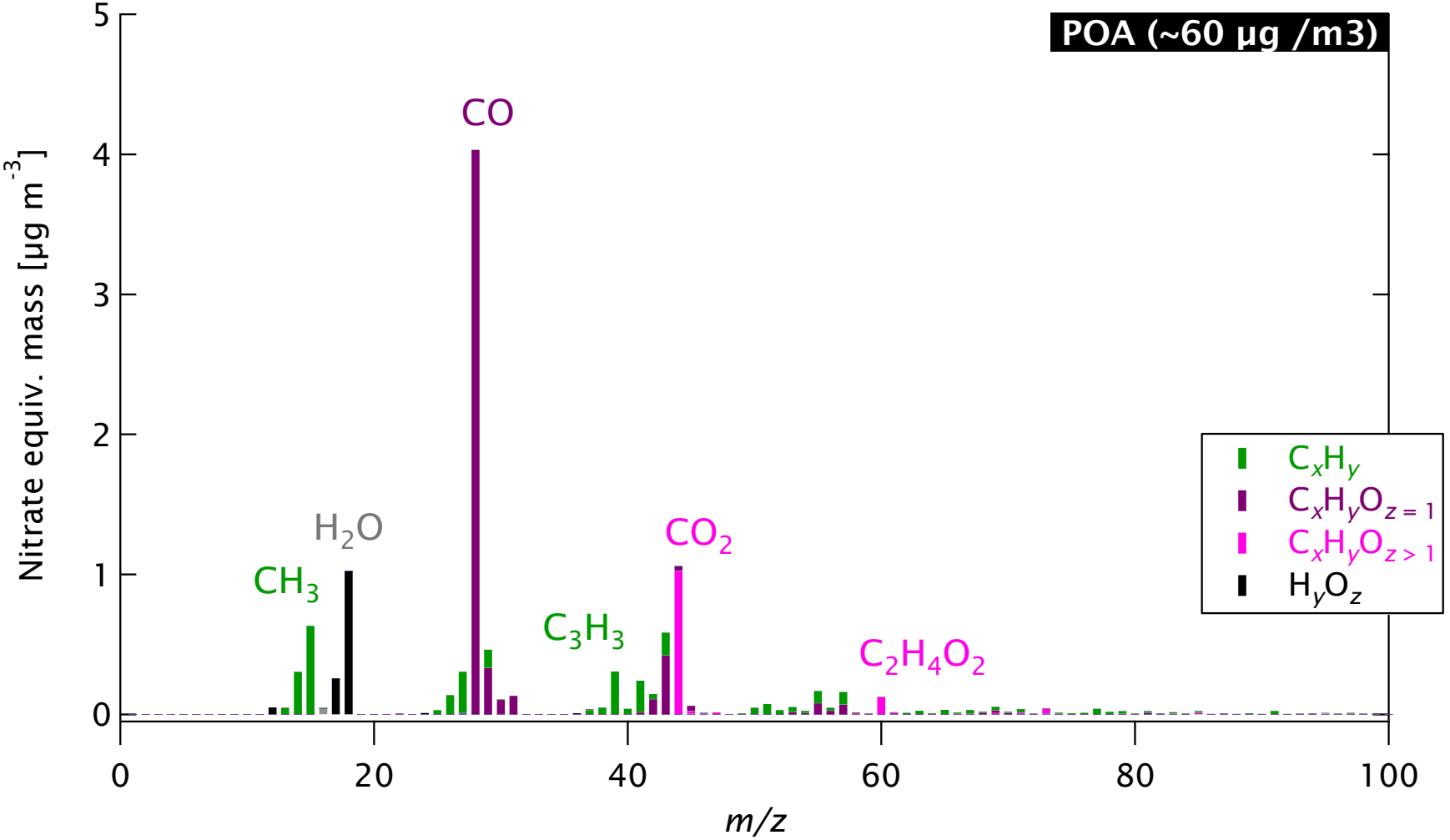
AMS organics during wood-burning



- Start of burn; high organics (50 vol% OM)

- Flaming phase, high rBC (5 vol% OM)

AMS Wood-stove **POA** (primary organic aerosol)



- Consistent with CE=0.7 determined by *Alfarra et al. 2007* without CO^+: f_{CO+}=0.3 (→ CE=1)
- OM/OC (2.3 ± 0.2) consistent with *Turpin and Lim 2006* (2.4±0.2) non-AMS wood-OA data
- Default OM/OC = 1.8 ± 0.1

OM/OC = 2.0 ± 0.2 with default H_2O frag; OM/OC = 1.8 ± 0.1 with all default frags

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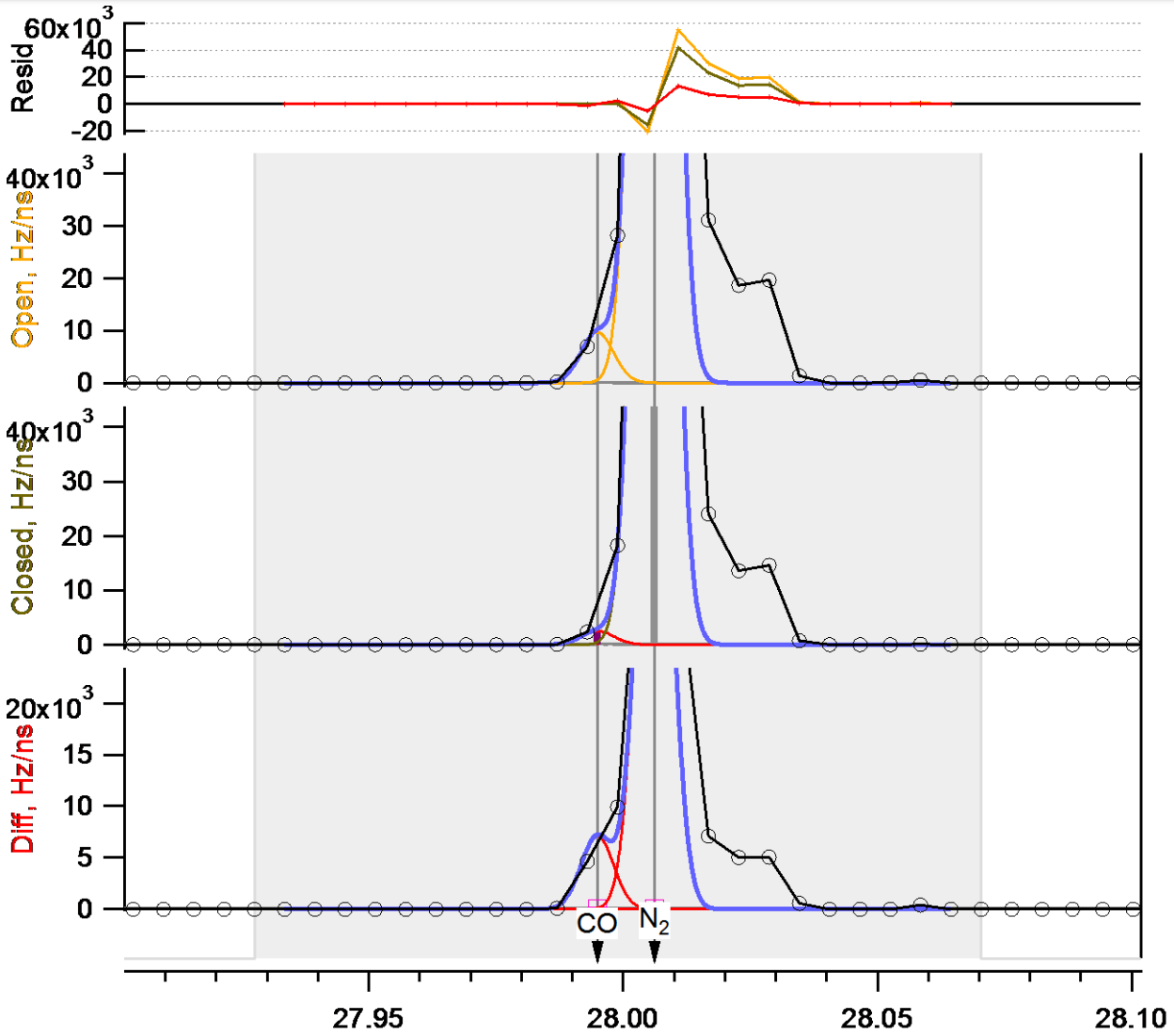
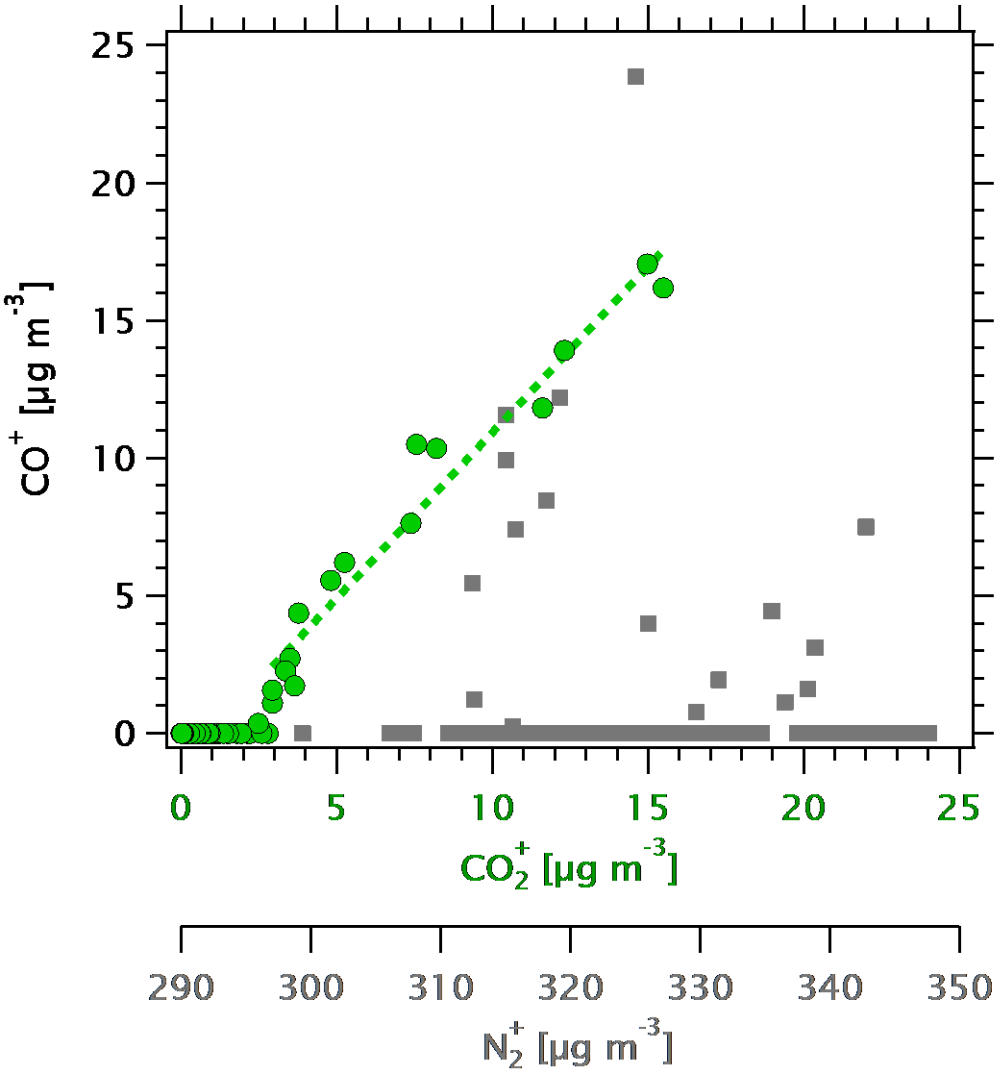
V-mode *m/z* 28: CO^+ before N_2^+



- Mass loading ~50 µg m^{-3} (f_{CO+} ~0.3)
- See also *Ortega et al. (ACPD 2012)*

High loadings needed to fit CO^+

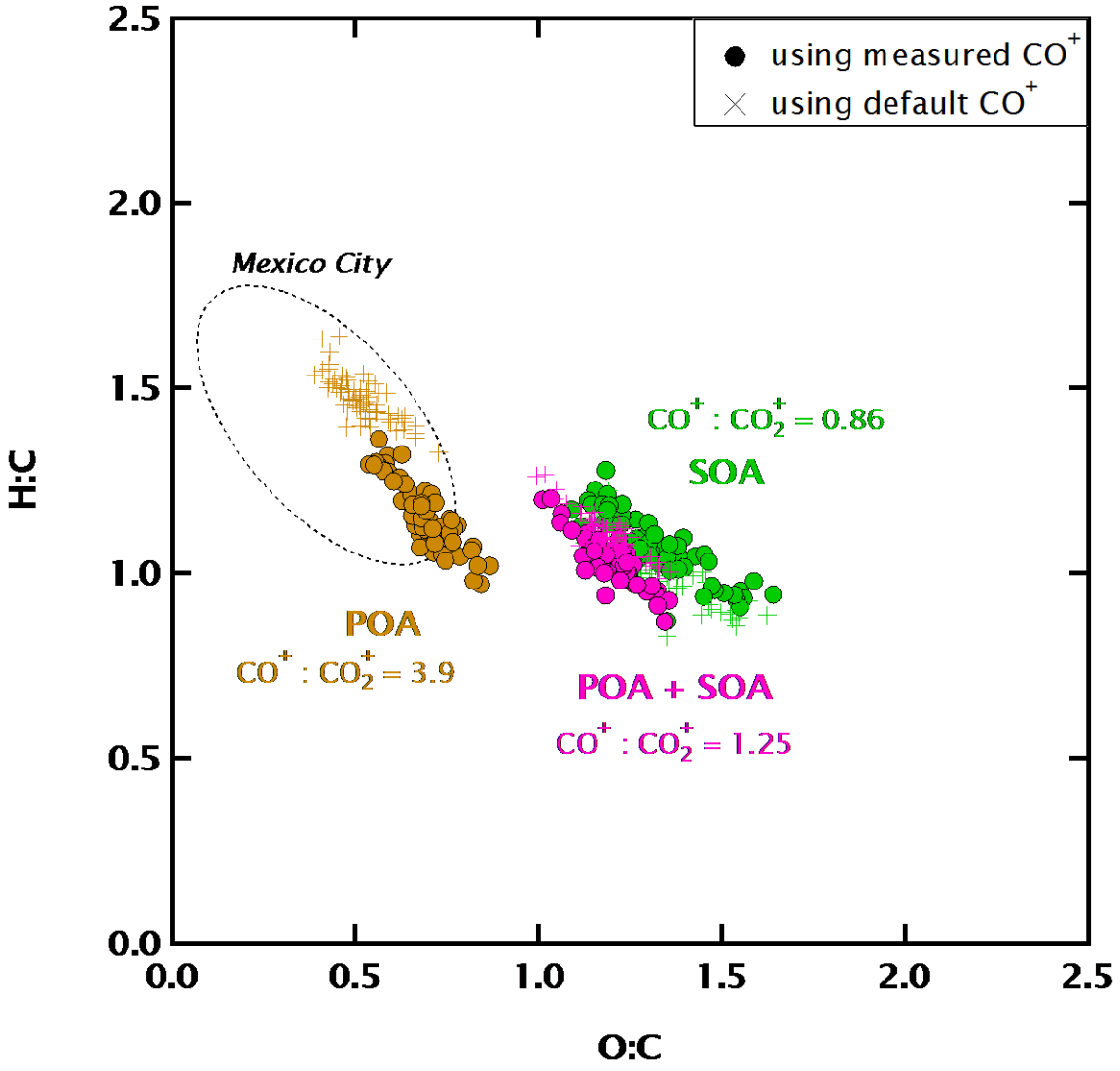


→ Slope for frag table

1. Comparing O:C and f_{44} with and without CO^+

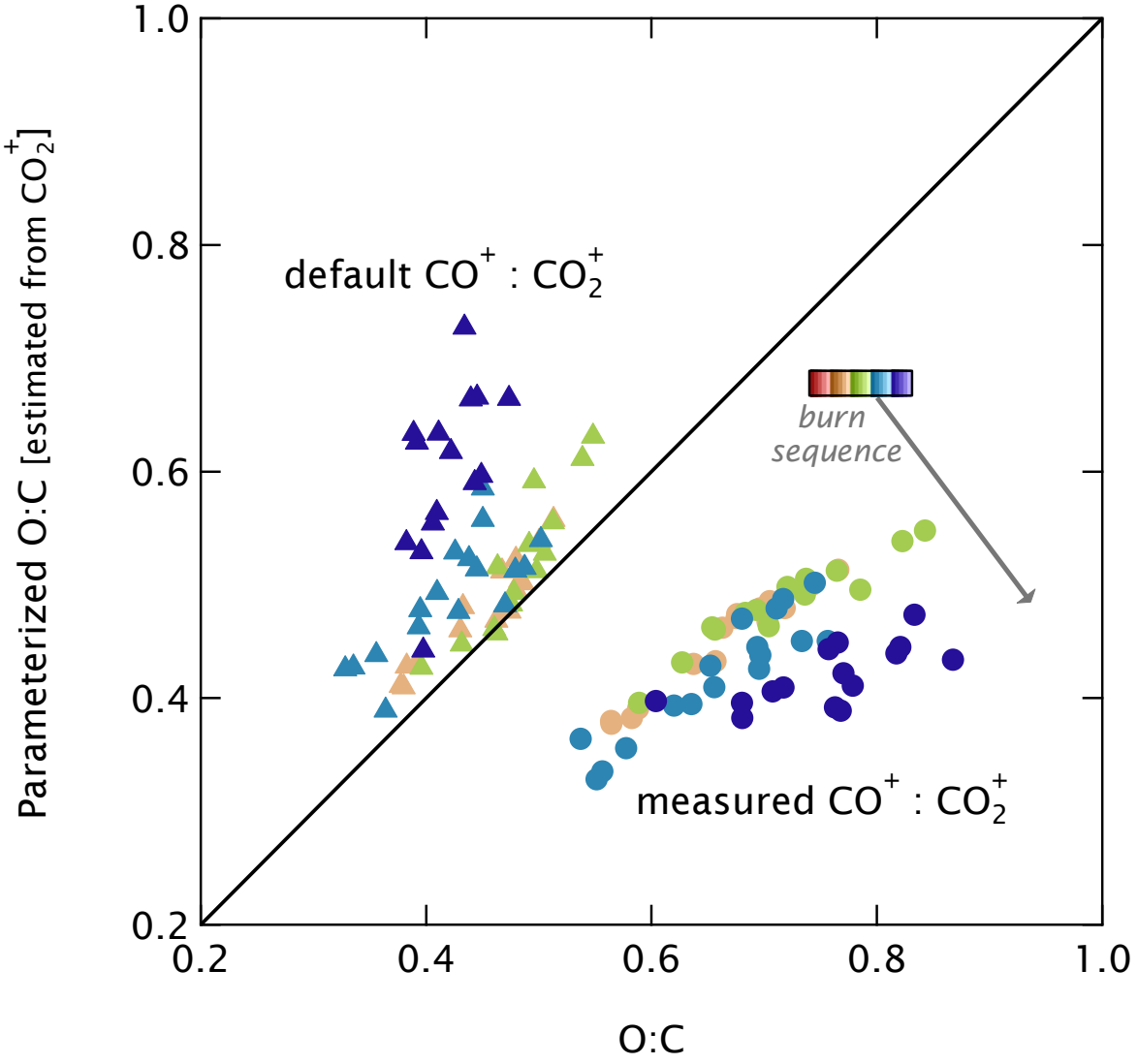
Assuming {orgH2O} = 0.225*{CO_2}

Impact of CO^+ on elemental ratios



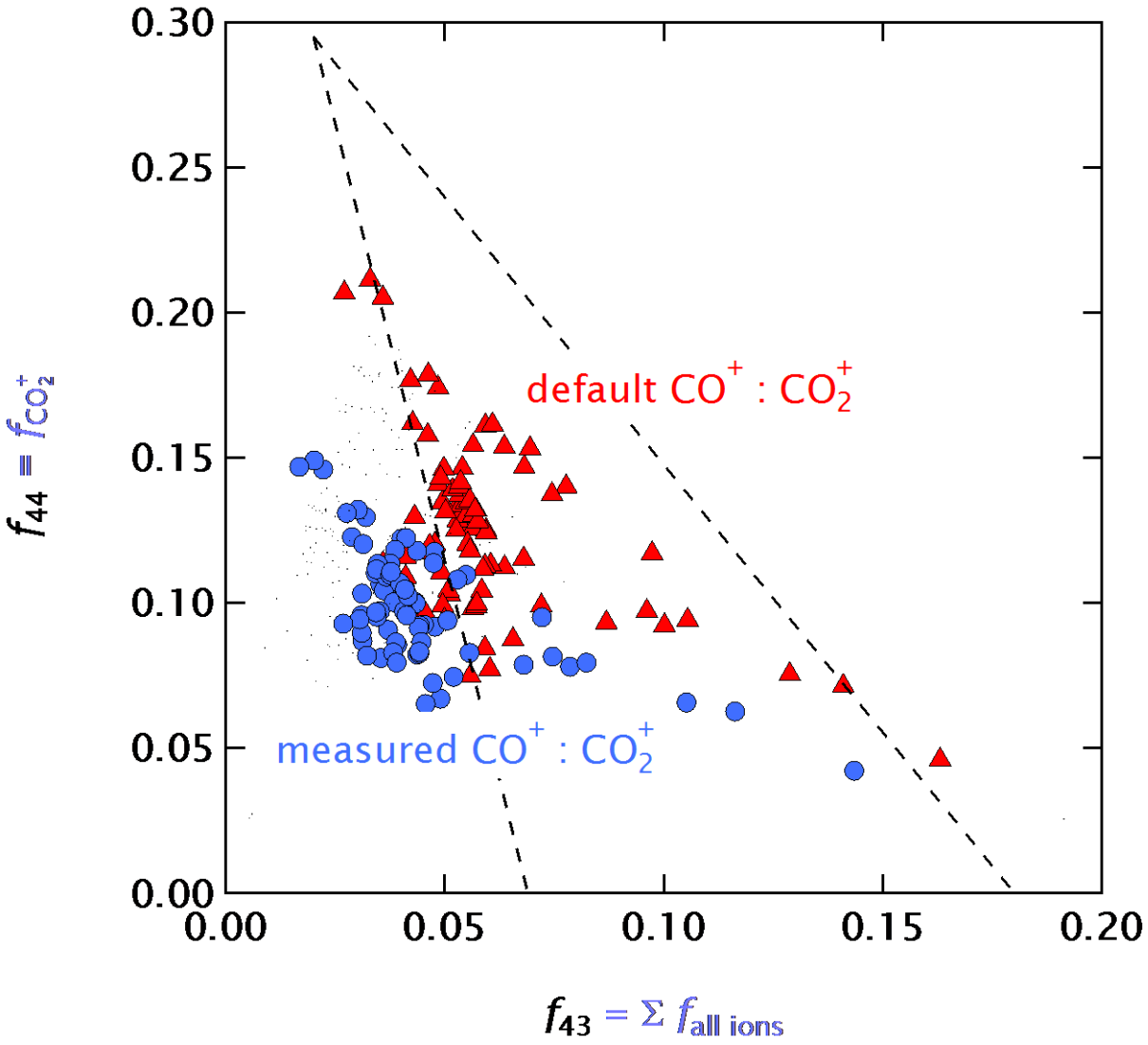
Mexico City: Heald et al., GRL 2010. (2) *"Default CO^+":* Aiken et al., 2008. (3) Chen et al., ES & T 2011

Impact of CO^+ on parameterized "O:C" from f_{44}



y-axis: Aiken et al. (EST 2008) ambient O:C parameterization

Impact of CO^+ on f_{43} / f_{44}



f_x defined as UMR equivalent. Would "agree" with ambient data if uncorrected.

Take-home Messages

1. CO^+ can be fit in PIKA for high loadings, with the right tuning and mass spectrometer.

2. The default frag table represents ambient OA (→ $OH\cdot$ photochemistry), and is likely inappropriate for other fresh organics.

3. Can be important to get mass right.

Finer details:

- When PIKA fits don't work, lab studies can use (i) m/z 28 baseline, (ii) m/z 28 : m/z 32 (iii) PToF (HR or UMR)
- Wood-burning spectra can be considerably less oxidized than shown[1-4], but similar spectra (excluding CO^+) have been observed in lab[5-6] and possibly field[7]
- Sources giving less-oxidized aerosol are likely to have less CO^+ contribution (although $C_2H_4^+$ 28.0313 should not be forgotten[8])

(1) Grieshop et al., ACP 2006; (2) Elsasser et al., Energy Fuel 2013 (3) Axel Eriksson, Pers. Comm. (4) Emily Bruns, EAC 2013 (5,6) Heringa et al., ACP 2011, EST 2012 (7) Alfarra et al., EST 2007 (8) Ortega et al., ACPD 2013

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