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$: f_{CO^+}=0.3 (\rightarrow CE=1)$

- 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$_2$O frag; OM/OC = 1.8 ± 0.1 with all default frags
V-mode $m/z$ 28: CO$^+$ before N$_2^+$

- Mass loading $\sim$50 $\mu$g m$^{-3}$ ($f_{CO^+} \sim 0.3$)
- See also Ortega et al. (ACPD 2012)
High loadings needed to fit CO$^+$
1. Comparing O:C and $f_{44}$ with and without CO$^+$

Assuming $\{\text{orgH2O}\} = 0.225 \times \{\text{CO}_2\}$
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 \(f_{43} / f_{44}\)

\[ f_{44} = f_{\text{CO}_2} \]

\[ f_{43} = \Sigma f_{\text{all ions}} \]

\( f_x \) 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 ($\rightarrow$ OH–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$_2$H$_4^+$ 28.0313 should not be forgotten$^8$)

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