Van Kreven Triangle paper

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Changes in organic aerosol composition with aging inferred from aerosol mass spectra

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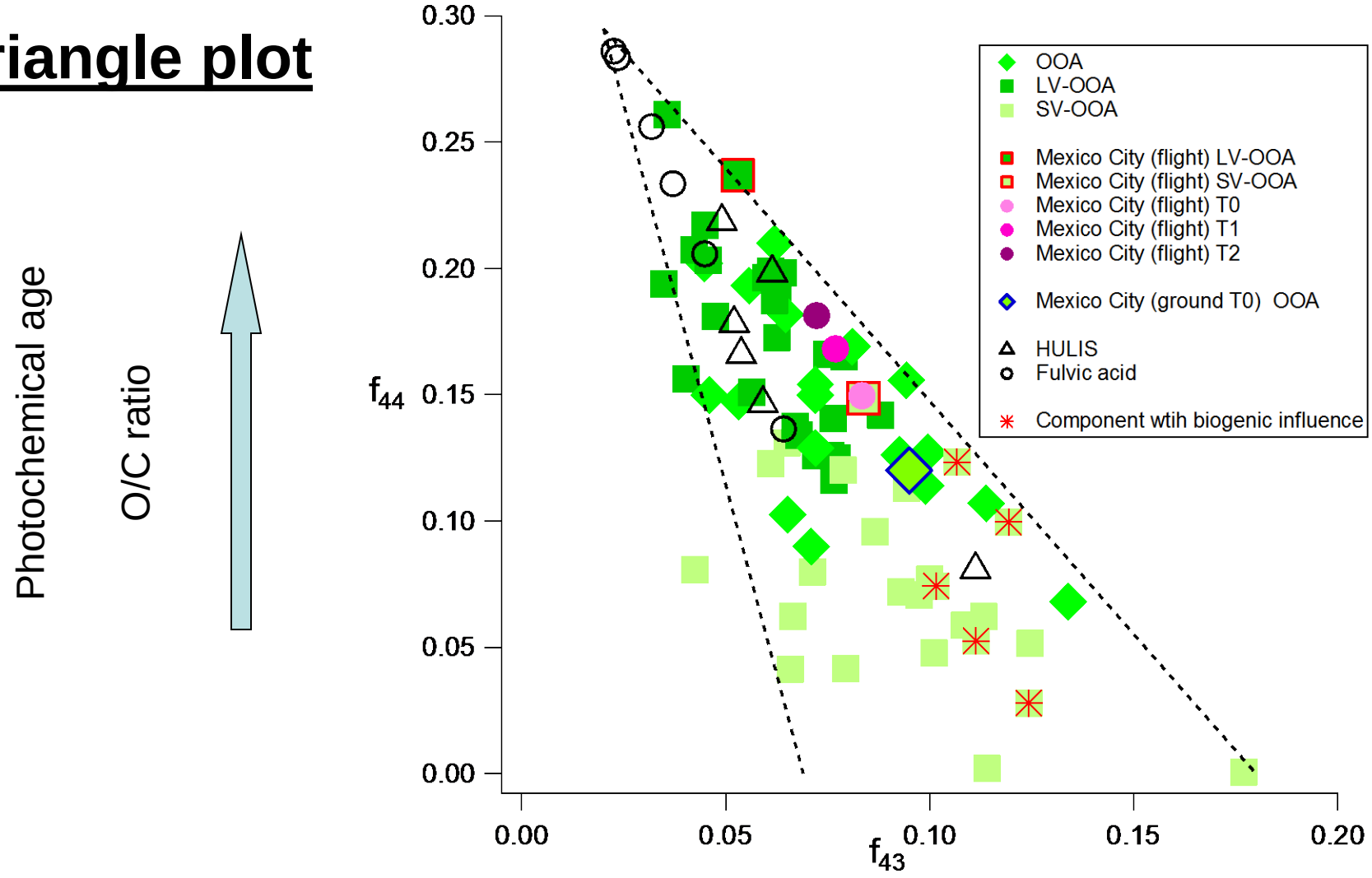
Abstract. Organic aerosols (OA) can be separated with factor analysis of aerosol mass spectrometer (AMS) data into hydrocarbon-like OA (HOA) and oxygenated OA (OOA). We develop a new method to parameterize H:C of OOA in terms of f_{43} (ratio of m/z 43, mostly $C_2H_3O^+$, to total signal in the component mass spectrum). Such parameterization allows for the transformation of large database of ambient OOA components from the f_{44} (mostly CO_2^+, likely space which follows a ΔH:C/ΔO:C slope of ~ -0.5. This slope suggests that ambient OOA aging results in net changes in chemical composition that are equivalent to the addition of both acid *and* alcohol/peroxide functional groups without fragmentation (i.e. C-C bond breakage), and/or the addition of acid groups with fragmentation. These results provide a framework for linking the bulk aerosol chemical composition evolution to molecular-level studies.

Triangle plot

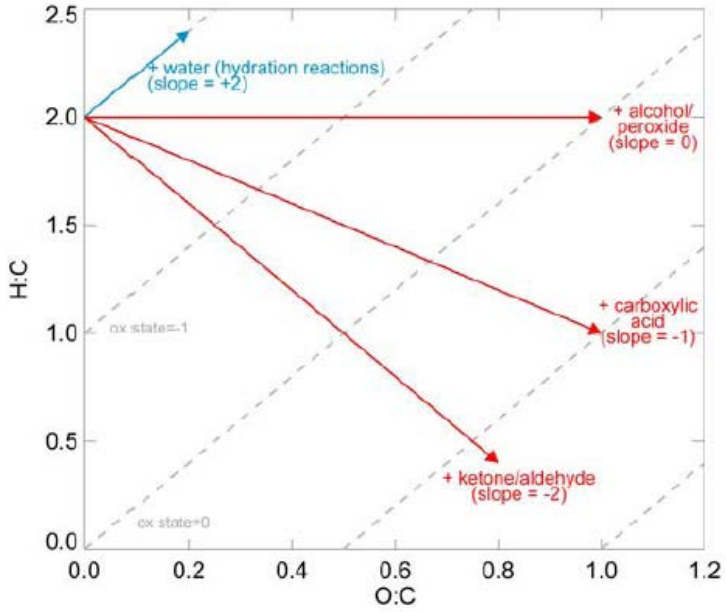


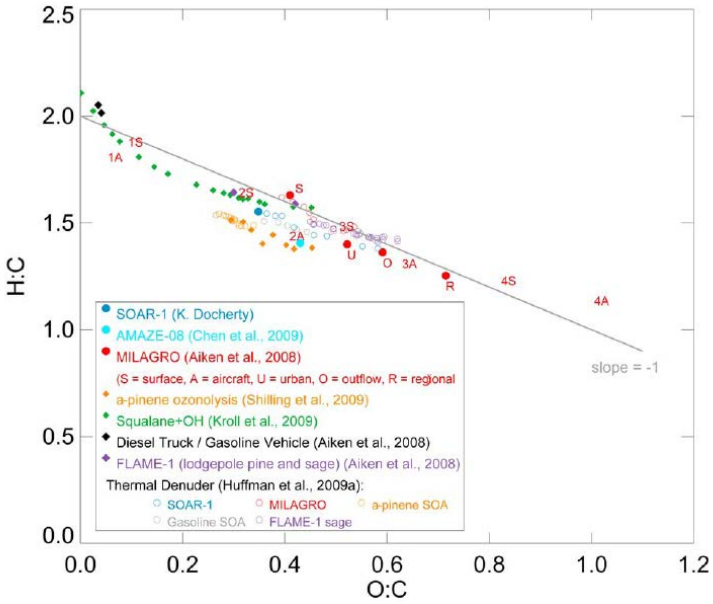
- Characterized OA evolution with f44 and f43

Ng et al., 2010

Van Krevelen Diagram

Heald, Kroll et al., 2010





- The bulk composition of OA from a variety of environments (laboratory and field) occupies a narrow range in the space of a Van Krevelen diagram, characterized by a slope of ~ −1

- Transformation of acid groups NOT unique in the VK diagram
  - Slope -1 → Increase in COOH functionality, OR Equal increase in C=O and OH functionality

Connect Triangle plot and the Van Krevelen diagram

- Triangle plot
  - f_{44} vs. f_{43} (UMR or HR AMS spectra)
  - an empirical way of viewing all new AMS data in the context of available data for characterizing aerosol aging: data obtained from both UMR and HR instruments can be readily plotted in real time in this space

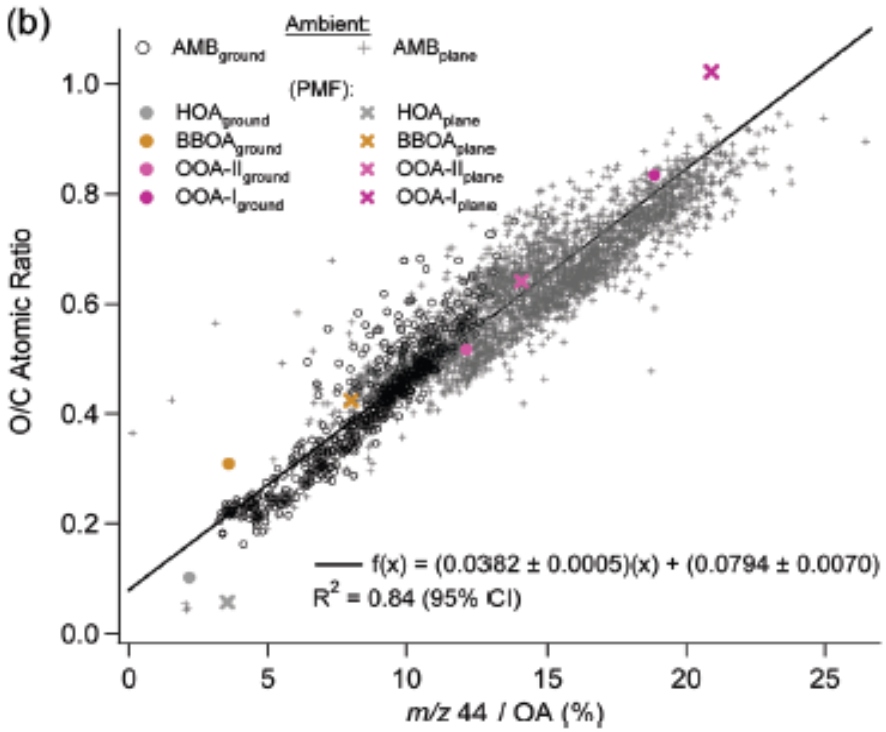
- Van Krevelen diagram
  - H/C vs. O/C (requires HR data)
  - offers more fundamental information on OA composition, but so far could only be generated from HR data after intensive and time-consuming data processing

- This work:
  - link the complementary info of the triangle plot and the Van Krevelen diagram to provide further understanding of organic aerosol evolution
  - Link bulk aerosol composition evolution to molecular-level studies

- Parameterization of H/C, O/C in terms of f_{43} and f_{44}

Parameterization of O/C

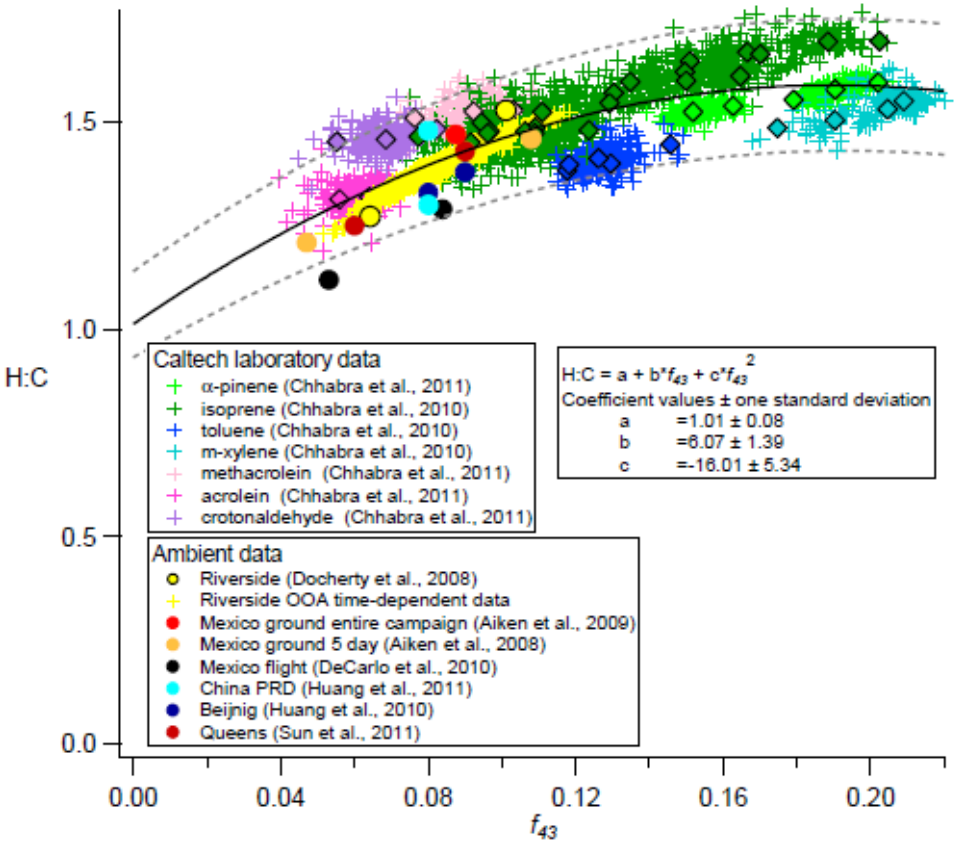
- Mexico city data: O/C can be expressed in term of 44/OA (i.e., f_{44})

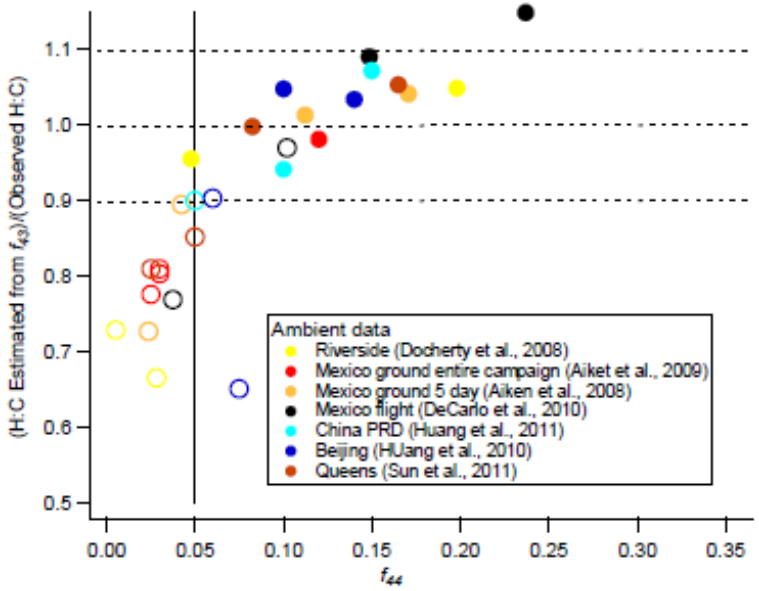


Aiken et al., 2008

Parameterization of H/C

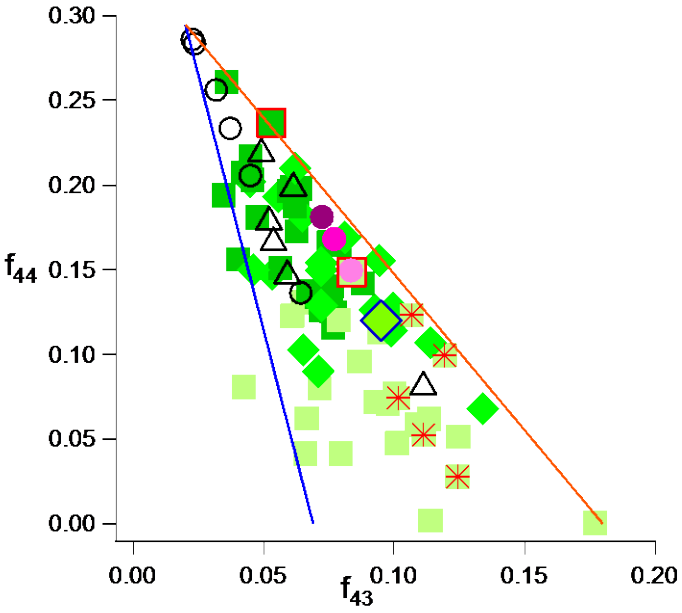
- HR-AMS data: Compilation of field and laboratory
- H/C can be estimated from f_{43}



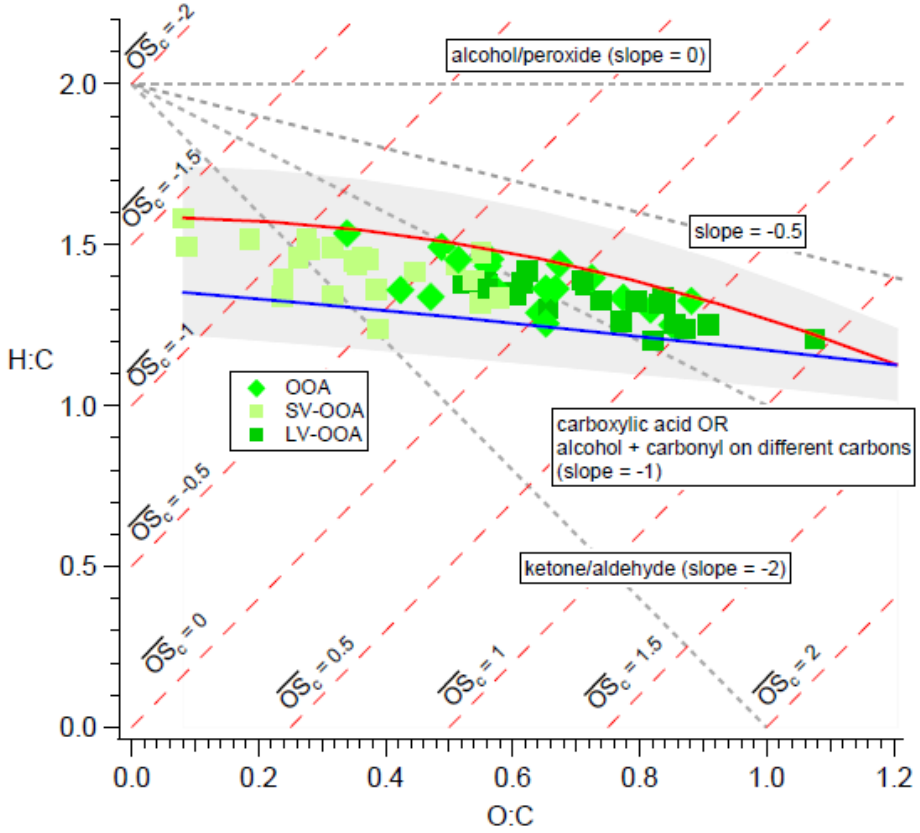


Ng et al., 2011c

VK-triangle: Field UMR data



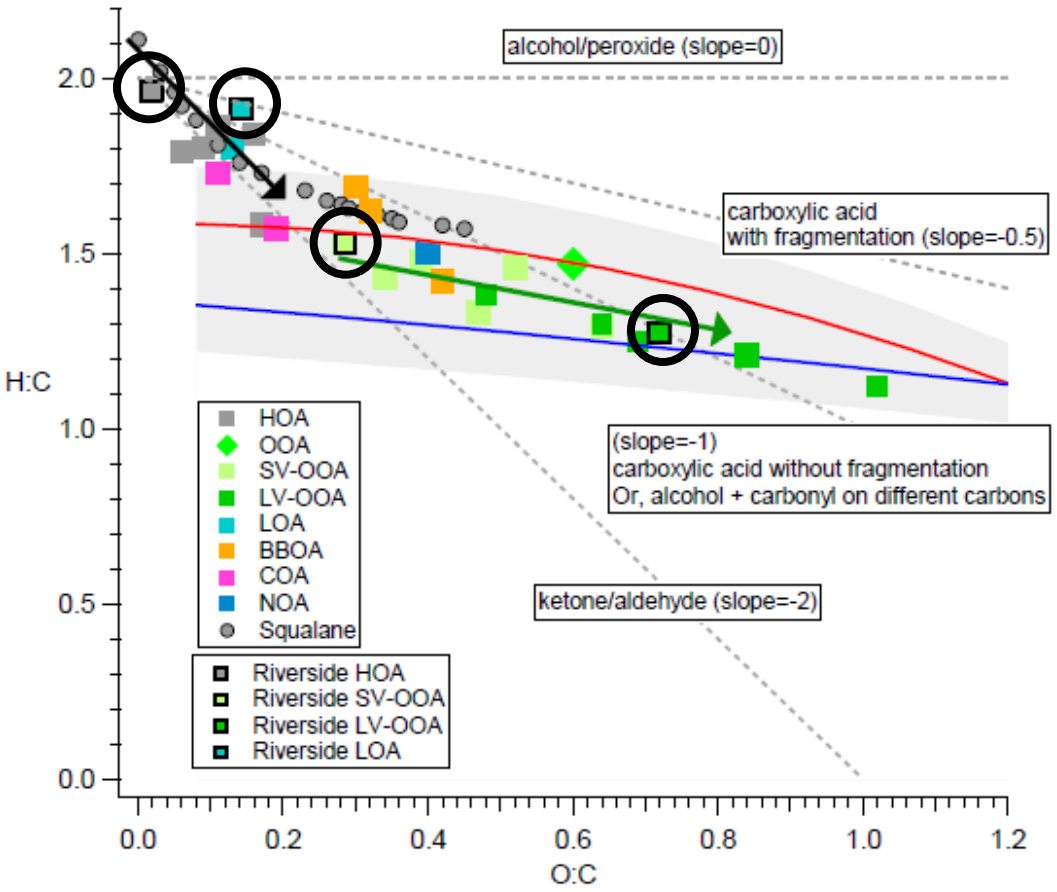
Ng et al., 2010



Ng et al., 2011c

- On average, SV-OOA → LV-OOA transformation follows a shallower line with slope ~ -0.5
  - add COOH *and* OH with no fragmentation; or addition of COOH with fragmentation

VK-triangle: Field HR data



- Mexico City flight (DeCarlo et al., 2010)
- Mexico City ground (Aiken et al, 2009)
- Riverside (Docherty et al., 2008)
- Queens NY (Sun et al., 2010)
- Beijing (Huang et al., 2010a)
- China PRD (Huang et al., 2010b)

- Squalane
  - Steeper slope
  - POA: stronger carbonyl addition

- Evolution of SV-OOA to LV-OOA follows a shallower slope (~ -0.5)

Ng et al., 2011c

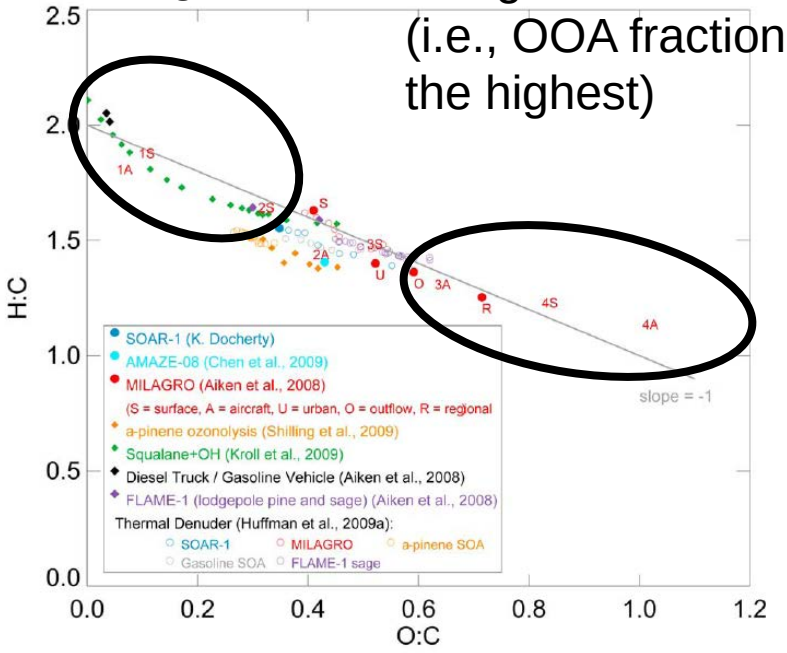
Total OA vs. OOA

Heald et al

Evolution of **TOTAL OA (HOA + OOA + others)**

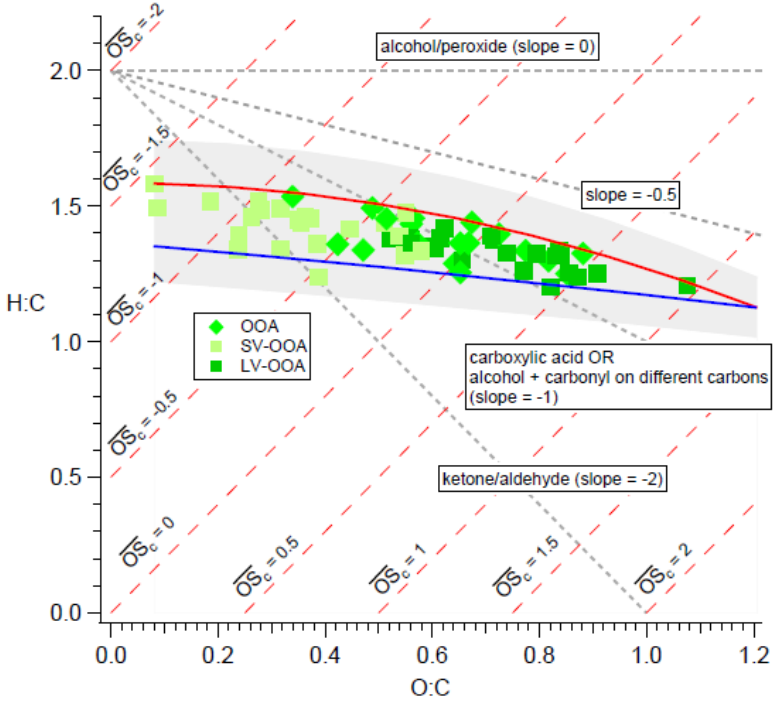
HOA fraction is higher

The slope of the Mexico City aircraft data levels off at higher oxidation (i.e., OOA fraction is the highest)



Ng et al

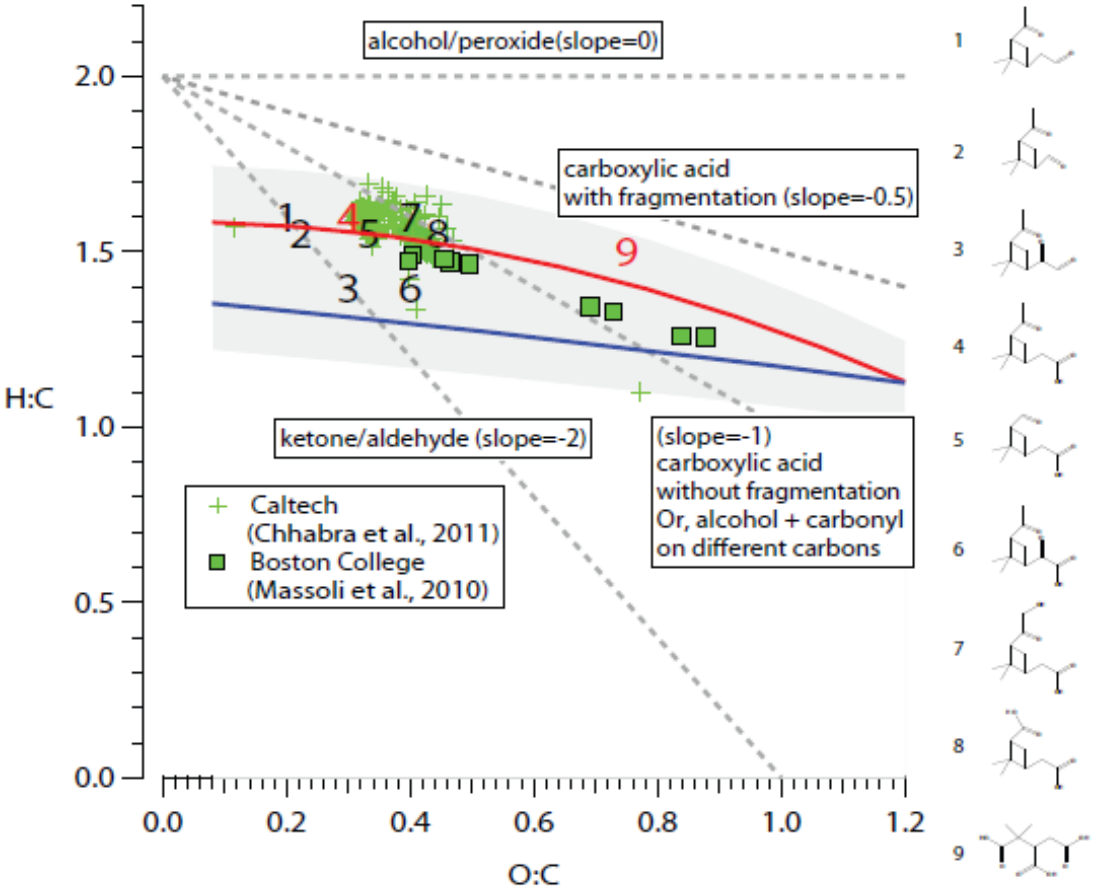
Evolution of **OOA:** provides a means of following ambient secondary OA that is analogous to and can be compared with trends observed in laboratory SOA



Lab data: α-pinene photooxidation

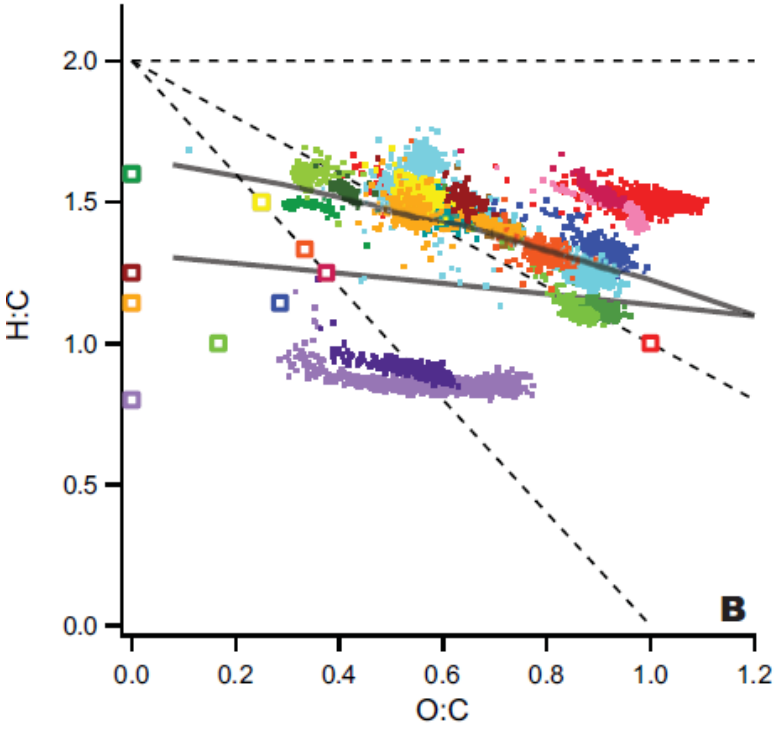
- Chamber and flow tube data span the whole range of O/C observed in ambient data
- Follow a similar slope (~-0.5) as SV-OOA → LV-OOA transformation:

  (add COOH *and* OH with no fragmentation; or addition of COOH with fragmentation)



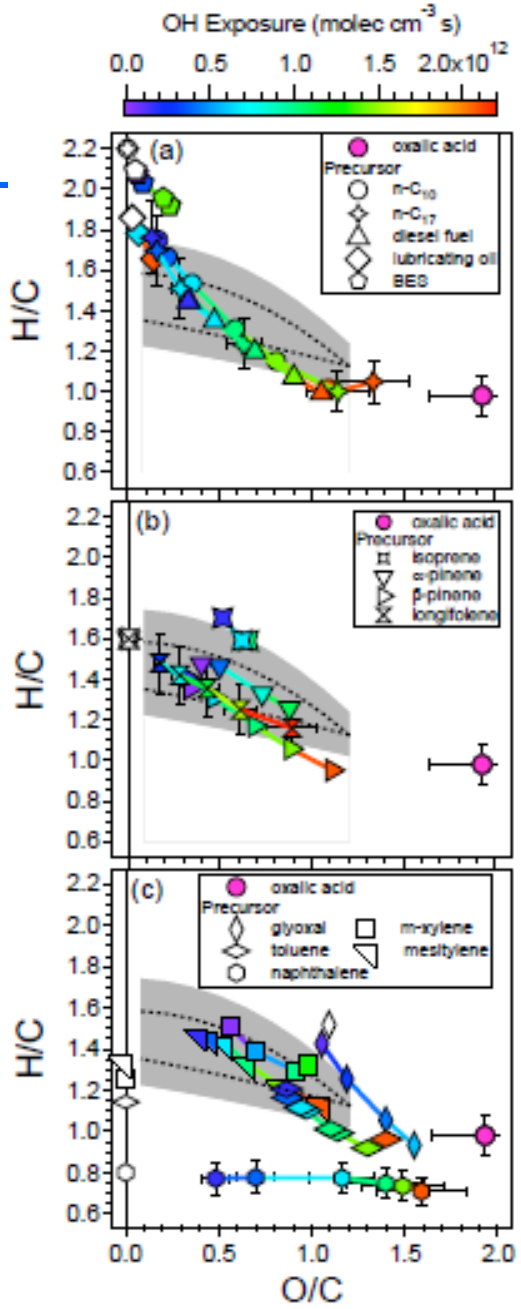
Ng et al., 2011c

More lab data…



Chhabra et al., (2011)

Caltech chamber data



Lambe et al., (2011)

Boston college

PAM flow tube data

Conclusions

- Map the “Triangle” plot and Van Krevelen diagram on the same space
  - Parameterize H/C in terms of f43 based on both ambient and laboratory HR-AMS data

- On average, the change in bulk composition of **OOA** with aging follow a line with slope ~-0.5
  - Consistent with both addition of COOH an/d OH/OOH functional groups with fragmentation
  - And/or addition of COOH without fragmentation

- Provides ambient composition info that is analogous and can be compared with trends observed in lab studies and detailed molecular-level studies