Effects of water-soluble organic carbon on aerosol pH

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Primary Organic Effects on Aerosol pH

- Dilution by the contribution of water associated with organic species (W_o) (Guo *et al.*, ACP 2015)
- Changes in hydrogen ion activity coefficient (γ_{H+}) (Pye *et al.*, ACP 2018)
- Liquid-liquid phase separation (LLPS) (Dallemagne *et al.*, JPhysChemA 2016)
- Dissociation of particle-phase organic acids/meaningful pK_a (Nah *et al.*, ACP 2018)

Key Questions: What are the relative contributions of **organic** species to aerosol pH, and what are their effects on γ_{H+}? Are these effects *significant?*

Methods: Cases for Analysis

Baltimore, MD

- Inorganic aerosol composition fixed
- Gas phase NH_3 fixed
- Temperature fixed (summertime)
- pH (no WSOC) ~ 1
- From *Battaglia et al.* (2017)

Beijing, China

- Inorganic aerosol composition fixed
- Gas phase NH_3 fixed
- Temperature fixed (winter haze)
- pH (no WSOC) ~ 4-5
- From *Wang et al.* (2016)

Variables for ***each*** location:

- Non-acid WSOC compounds added (single compounds and mixtures)
- Organic acids added (single compounds and mixtures)
- RH levels for each composition: 70%, 80% and 90%

WSOC Addition

Organic Acids

- Oxalic Acid (pK_{a1} = 1.23)
- Malonic Acid (pK_{a1} = 2.83)
- Glutaric Acid (pK_{a1} = 4.31)

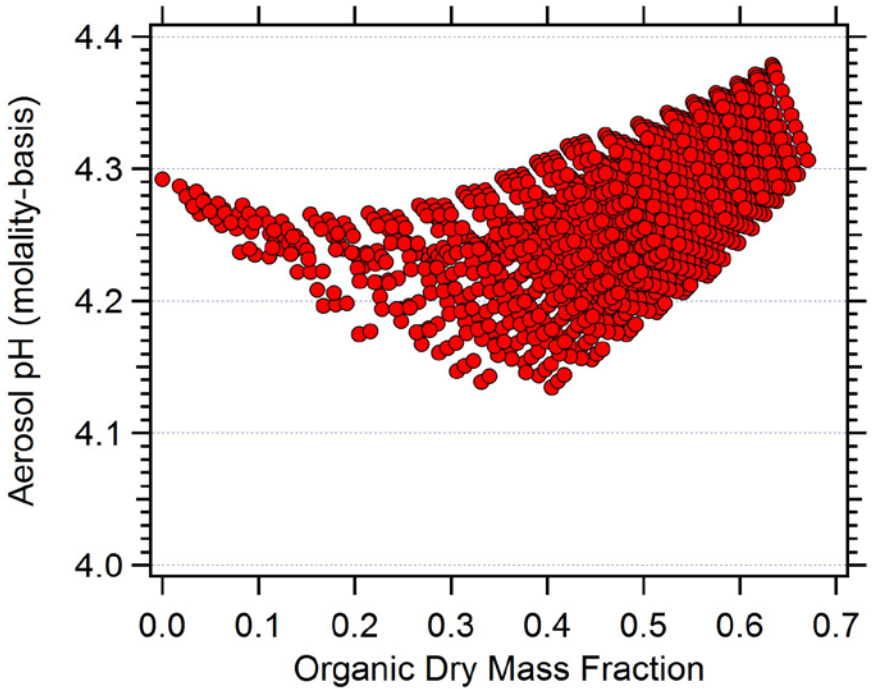
Non-Acid Organics

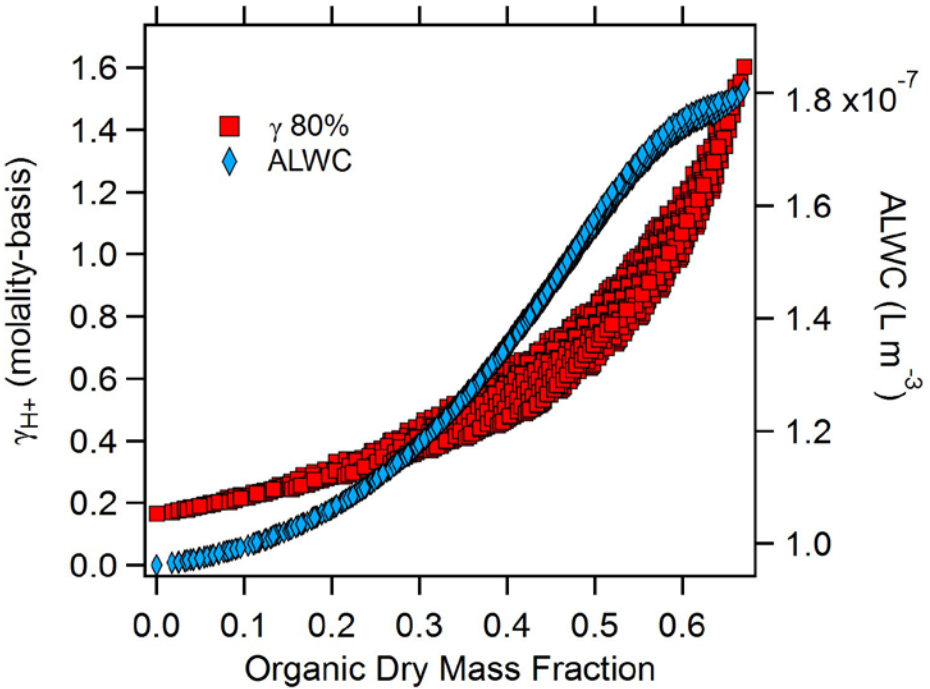
- Levoglucosan ($C_6H_{10}O_5$)
- Tetrahydrofuran ($(CH_2)_4O$)
- 2-methyltetrol ($C_5H_{12}O_4$)

- WSOC compounds modeled from 0 – 0.6 dry aerosol mass fraction
  - 0.0 to 4.0 µg m^{-3} (Eastern USA)
  - 0.0 to 40 µg m^{-3} (Beijing)
- Single component and in combination (*factorial*) with other species in the same category
- 1331 model simulations for each WSOC class, RH level, and location:
  (~1.6 x10^4 total simulations)

Effects of Non-Acid Organics on Molality-Based pH (80% RH)

Beijing



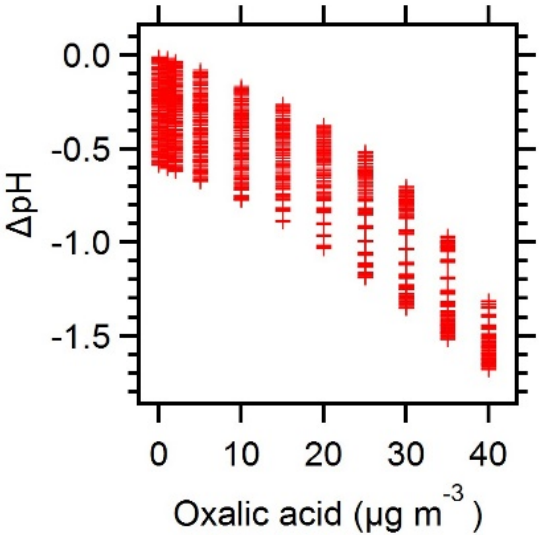


n = 1184, 11% LLPS points

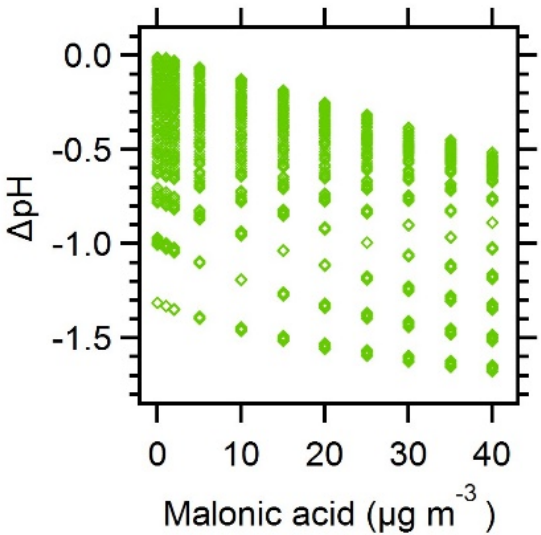
(Battaglia Jr. *et al.*, *ACP* 2019)

Effects of Organic Acids varies by pKa

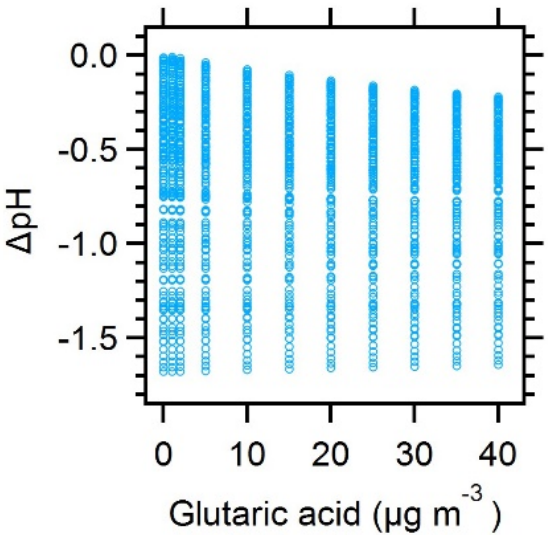
(pK_{a1} = 1.23)



(pK_{a1} = 2.83)



(pK_{a1} = 4.31)



ΔpH_{OA} = -0.018 pH/(μg m^{-3} OA)

ΔpH_{MA} = -0.012 pH/(μg m^{-3} MA)

ΔpH_{GA} = -0.007 pH/(μg m^{-3} GA)

(Battaglia Jr. *et al.*, *ACP* 2019)

Conclusions

- WSOC compounds appear to have limited effect on aerosol pH (< 0.5 pH units, molal-basis), until unrealistically-high organic concentrations are reached
  - These results support the conclusions of previous studies in both the Southeast/Eastern United States (Vasilakos *et al.*, ACPD 2018) and Beijing (Song *et al.*, ACP 2018)

- Organics can increase aerosol water (diluting and decreasing aerosol acidity)

- Organics (acid and non-acid) can also increase γ_{H+}

- When modeling aerosol pH at high RH (single aqueous phase), inclusion of organics may not be critical to the accuracy of the predicted values

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