Characterization of sources and sinks of formic acid and other organic/inorganic acids at the BAO site in summer 2014

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Motivation

- Tropospheric formic acid (FA) sources/sinks not well understood[1]
- Few field measurements of FA in industrialized, peri-urban area
- Tower measurements provide high time/spatial resolution in vertical profiles of FA and other detected species

Site Description

- Boulder Atmospheric Observatory (BAO) in Erie, CO
- Utilized portable Instrument Shelter with Amenities (PISA) tower carriage
- Part of Front Range Air Pollution and Photochemistry Éxperiment (FRAPPÉ), July – August 2014

Experimental Design

- HR-ToF-CIMS deployed in PISA tower carriage (0 – 300 m)
- Acetate/iodide reagent ion switching (only acetate presented here)
- Online calibrations for formic acid

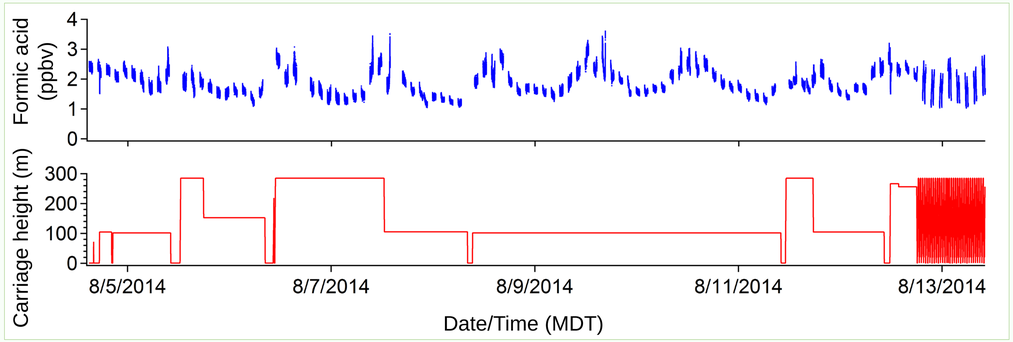
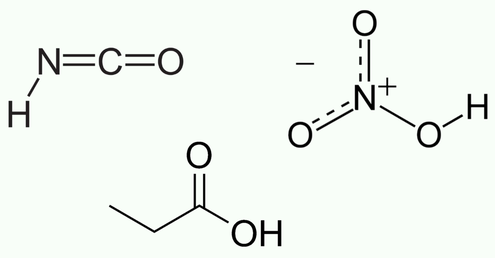


Fig. 1 – Formic acid time series (top) and carriage height (bottom)

How do formic acid sources/sinks compare to other organic/inorganic acids?

Fig. 6 – Isocyanic and nitric acid time series (detected as their conjugate bases) compared to FA time series; r^2 from linear fit to detected acid (ncps) vs. formic acid (ppbv)

- Some detected acids exhibit similar diel cycles to FA (Fig. 6)
- Observed upward fluxes or net deposition near surface (Fig. 7)
  - Isocyanic acid exhibits unique vertical profile



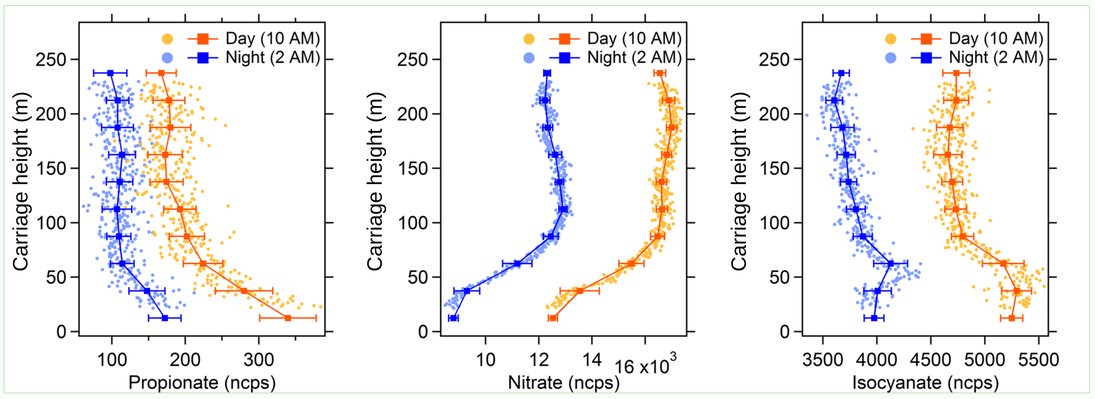


Fig. 7 – Representative "day" and "night" vertical profiles for propionic, nitric, and isocyanic acid (detected as conjugate bases)

*BG subtraction procedure for these acids still in development – reported data are estimates

What are sources/sinks of formic acid?

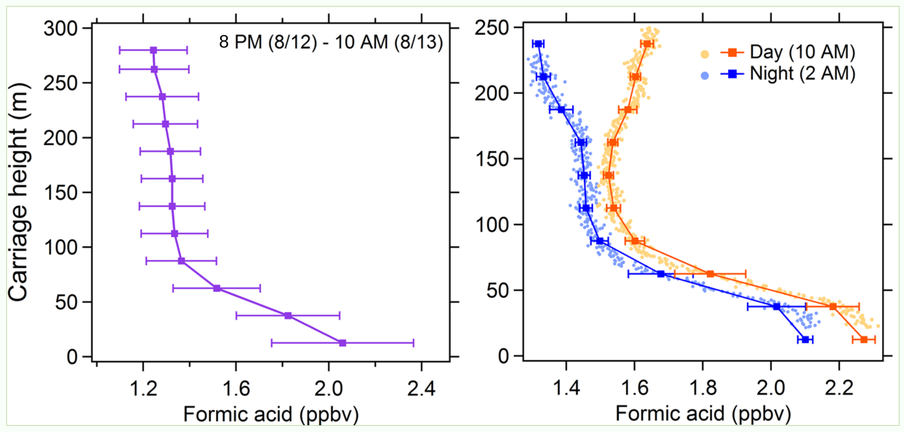
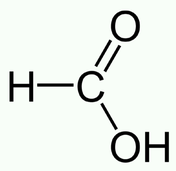


Fig. 2 – Average formic acid vertical profile for 14-hour collection period (left); Representative "day" and "night" vertical profiles (right)



- Upward vertical flux observed during day and night, indicating presence of photochemical and non-photochemical sources near surface (Fig. 2)
- Diel profile indicates strong photochemical source (Fig. 3)

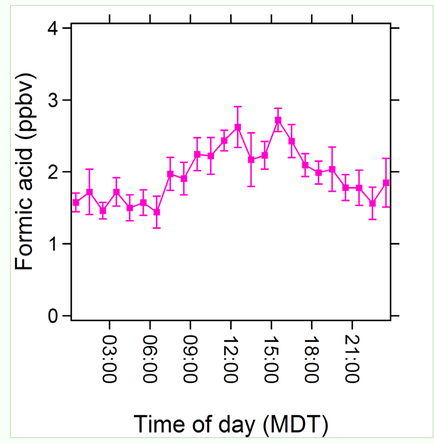


Fig. 3 – Formic acid concentrations vs. time of day

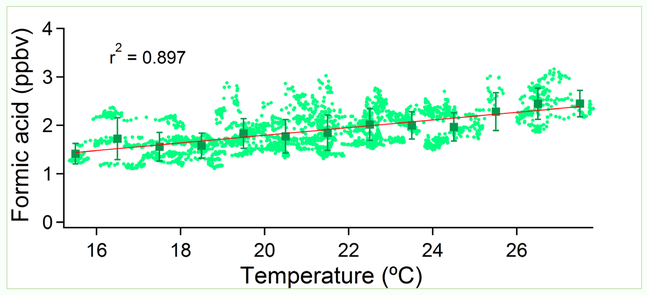


Fig. 4 – FA concentration vs. temperature; r^2 from linear fit to binned values

- Formic acid increases w/ temperature (Fig. 4)
  - 90% variance explained by a linear temperature relationship
- No RH dependence observed
- Some wind directionality dependence during day (Fig. 5)

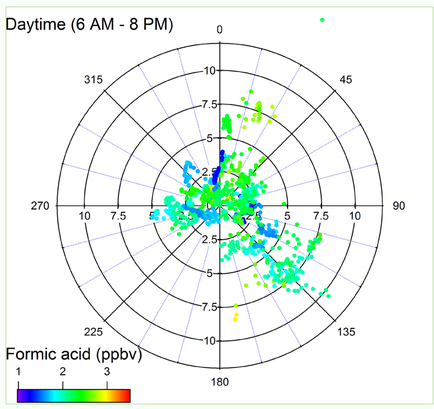


Fig. 5 – Wind speed on radial axes, wind direction on angle axis; colored by FA conc.

Summarized vertical profiles of detected acid species	
Upward flux from surface	Formic, Acrylic, Methacrylic, Propionic, Oxalic, Valeric
Net deposition to surface	Nitric, Pyruvic, Glycolic, Lactic
Other	Isocyanic

Future work

- Flux/deposition velocity calculations using vertical profile data
- Offline calibrations to estimate mixing ratios of detected acids
  - Isocyanic acid concentration estimate using DEFCON and SOAS sensitivity data[2,3] (Fig. 8)

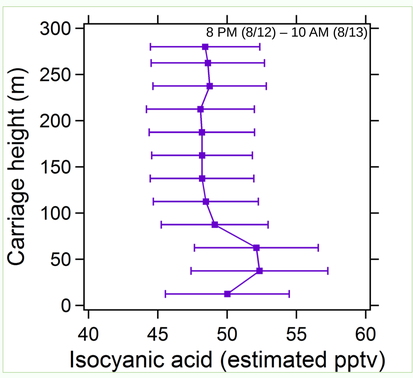


Fig. 8 – Isocyanic acid vertical profile with estimated concentration values

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References

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