Isocyanic acid (HNCO) in MOZART4

Paul Young, Louisa Emmons, Jim Roberts*, Jean-François Lamarque, Christine Wiedinmyer, John Orlando, Patrick Veres*

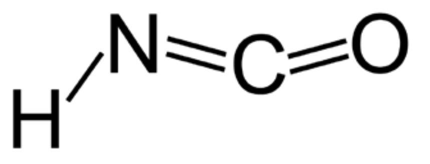
*Showing lots of work from Jim, Patrick and other NOAA types today

Outline

- What is isocyanic acid?
- Where does it come from?
- Why might we be interested?
- How are we modeling it?
- When will I have done more work than this?

What? An organic chemist's dream…

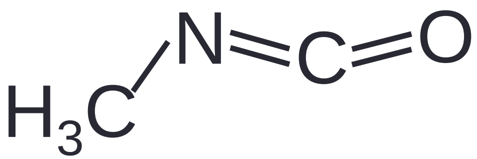
…*every* atom once!



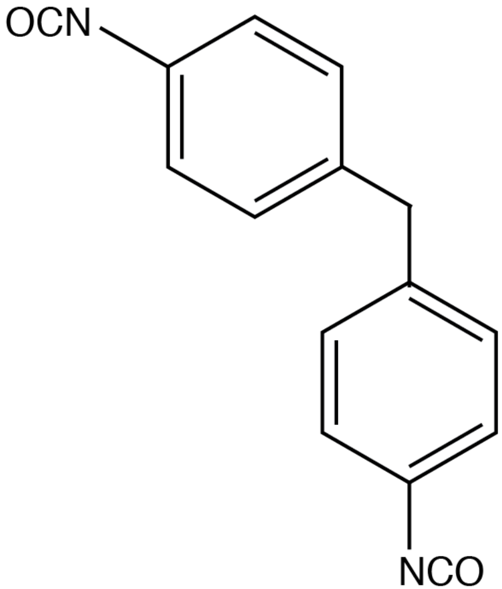
Mildly acidic, $pK_a = 3.7$

Volatile, B.P. = 23.5°C

Other isocyanates…



Methyl isocyanate
(pesticide manufacture)



Methylene diphenyl 4,4-diisocyanate (MDI)
(rigid polyurethane manufacture)

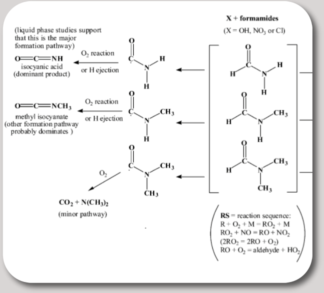
Where?

Biomass burning

Domestic coal combustion

Cigarette smoke

Urea catalysis (SCR)



Chemistry

(Barnes et al., 2010)

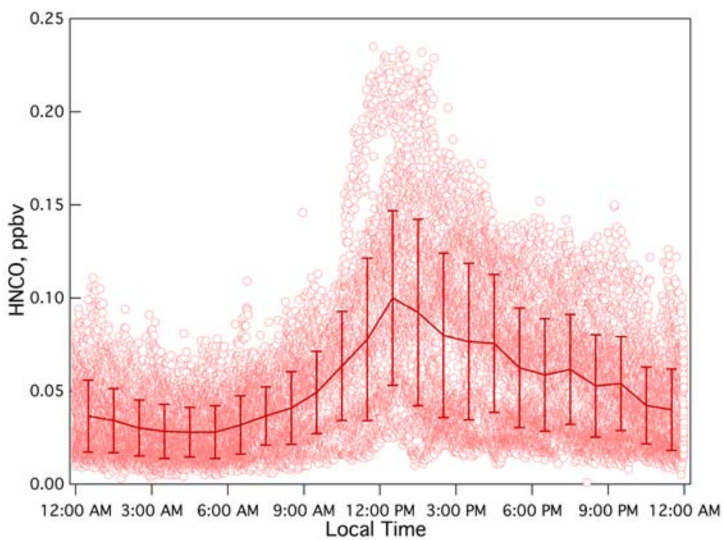
Why? New measurements

NI-PT-CIMS instrument – selective for acids

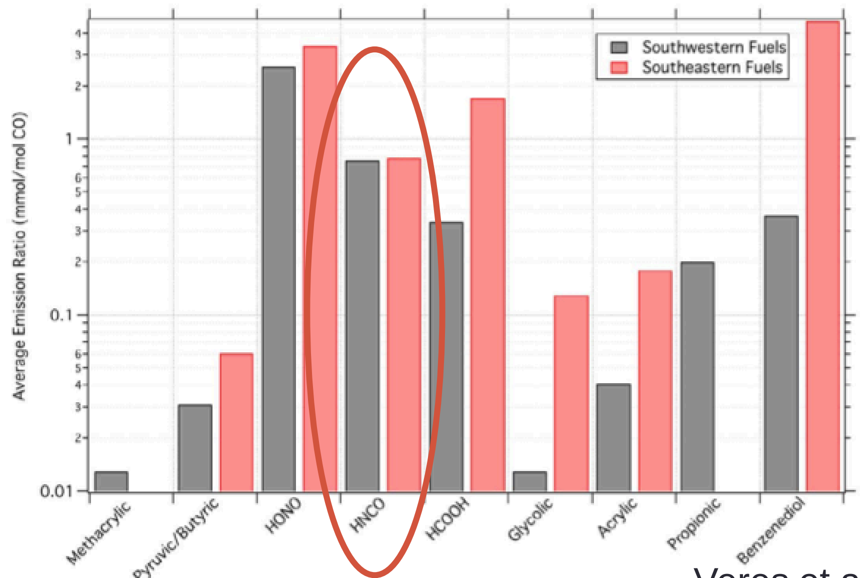
HA + $CH_3C(O)O^-$ → A^- + $CH_3C(O)OH$

Roberts et al. (2008); Veres et al. (2008)

CalNex data (photochem)



Fire lab data

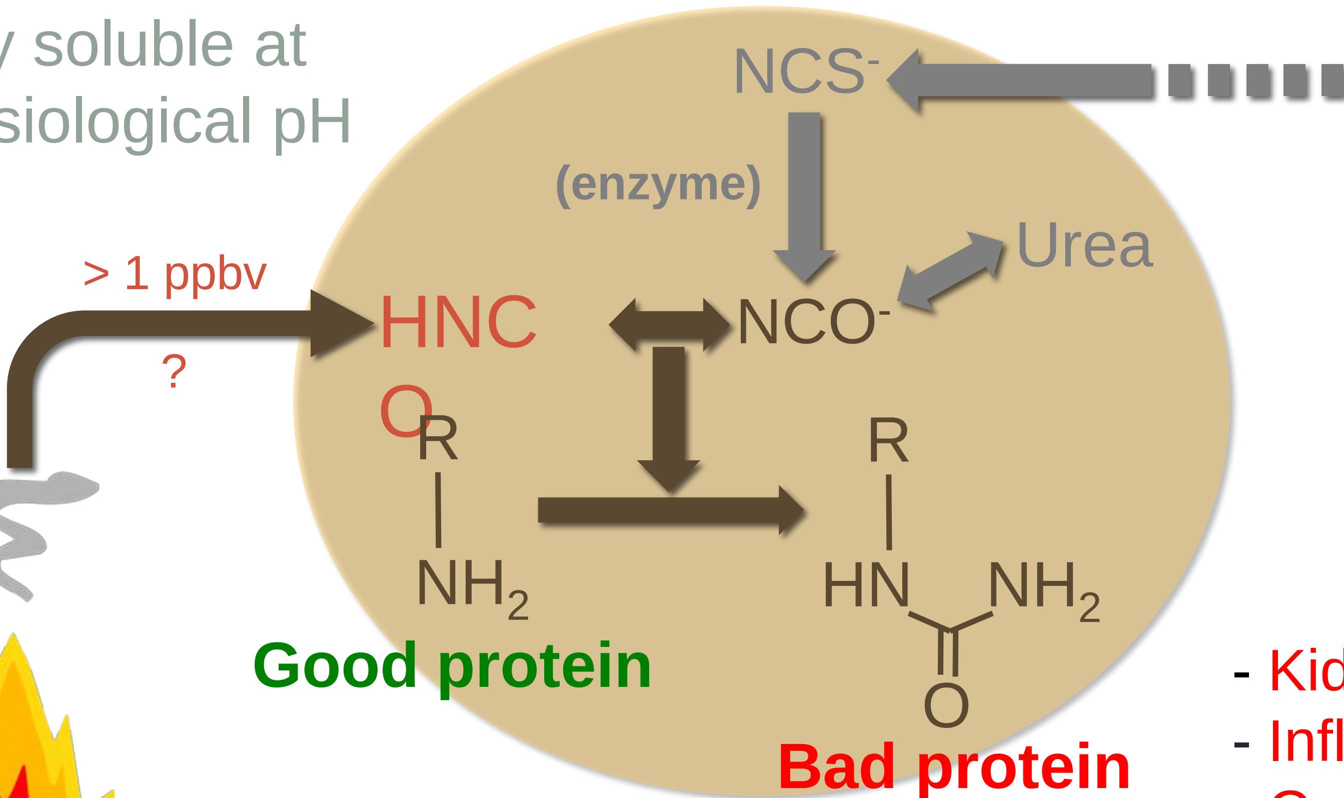


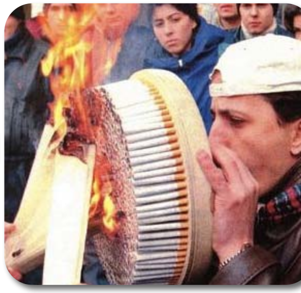
Veres et al. (2010)

Figure 10. Summary of emission ratios for the nine compounds measured in this study. No data were collected for methacrylic and propionic acid in the southeastern fuels sampled.

Why? Bad for health

Very soluble at physiological pH



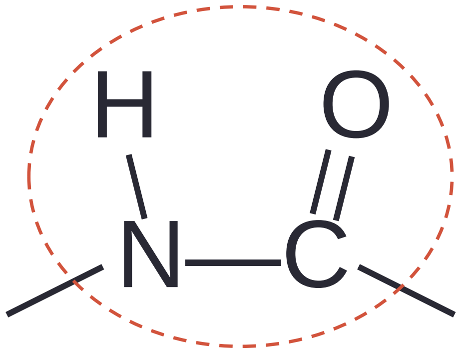


Smoking

Biomass burning

- Kidney disease
- Inflammation
- Coronary artery disease

Why? Probe fires



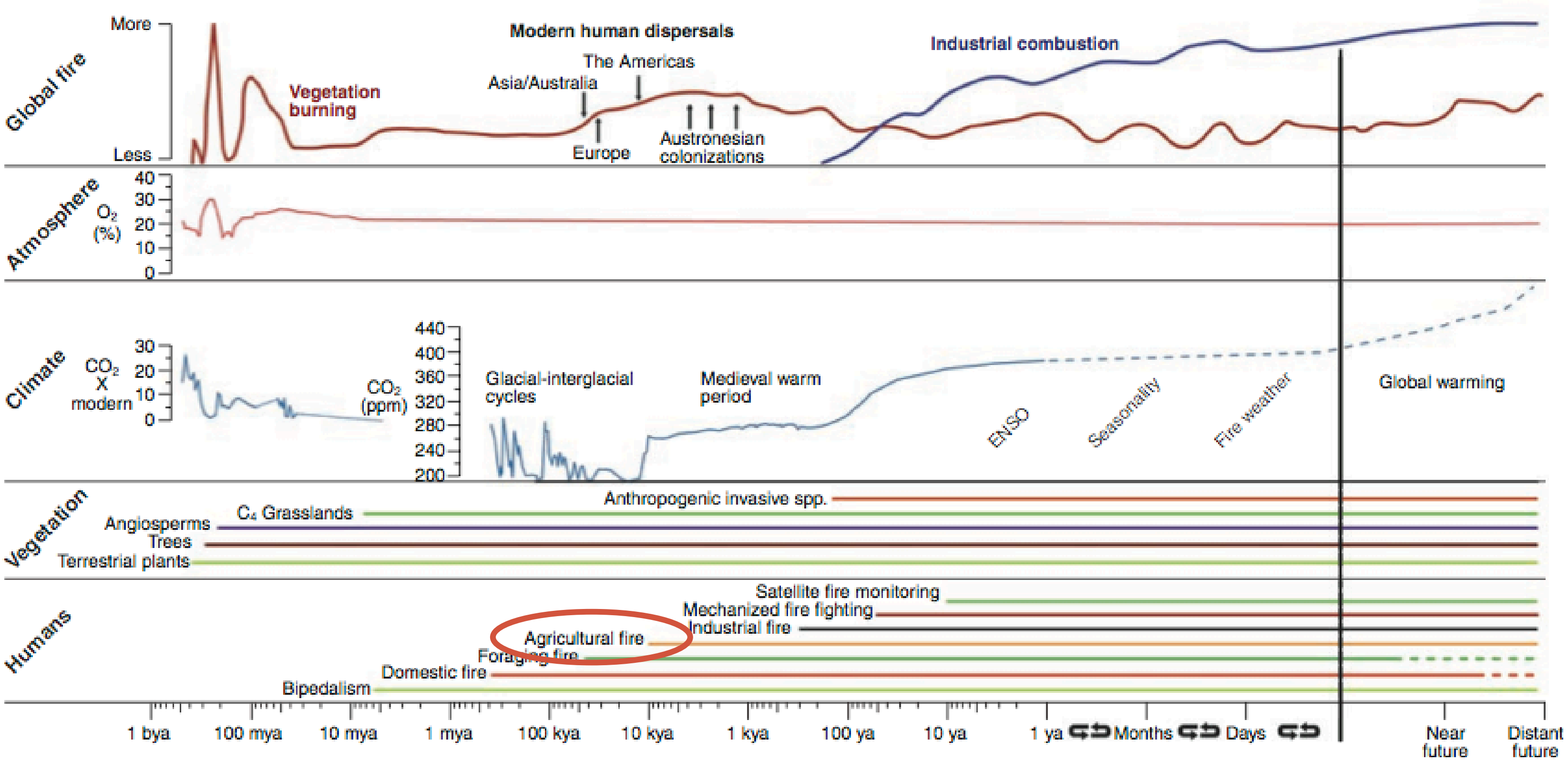
Polyamide pyrolysis
Proteins, Nylon, Urea-formaldehyde foam

200 pptv from Boulder fire

Roberts et al. (submitted)

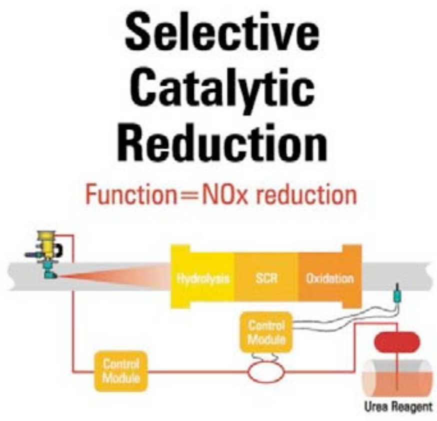
Why? Fires in the Earth system

Past and future occurrences? Increasing biochar production?



Bowman et al., Science (2009)

Why? Expansion of SCR



Diesel engines: urea-SCR de-NO_X system:

$H_2N\text{-}C(O)\text{-}NH_2 \rightarrow HNCO + NH_3$ (pyrolysis)

$HNCO + H_2O \rightarrow NH_3 + CO_2$ (hydrolysis)

$4NH_3 + 4NO + O_2 + \text{Catalyst} \rightarrow 4N_2 + 6H_2O + \text{Catalyst}$

Ideally, no HNCO remains in the exhaust
…But 5-50 ppmv HNCO reported from test engine[1]

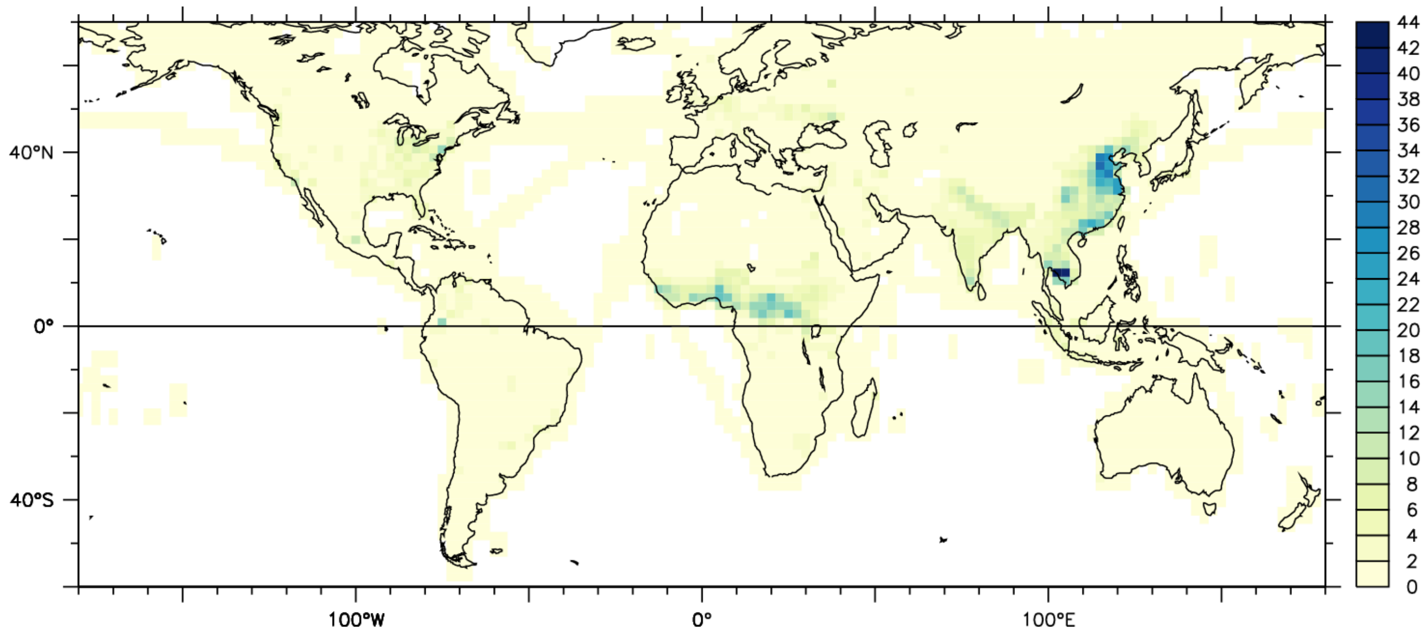
AQ requirements in EU (currently) and CA (by 2013)
…But these can change – i.e. moving target

[1] Krocher et al., *Analyt. Chem. Acta.*, 573, 393, 2005.

How? Emissions (January shown)

Currently scaled to HCN (f = 0.3*)

- biomass burning (FINN)
- biofuel burning (⟶ HCN scaled from anthropogenic CO)



*Observed range: 0.3-0.5 (Roberts et al., submitted)

How? Loss processes

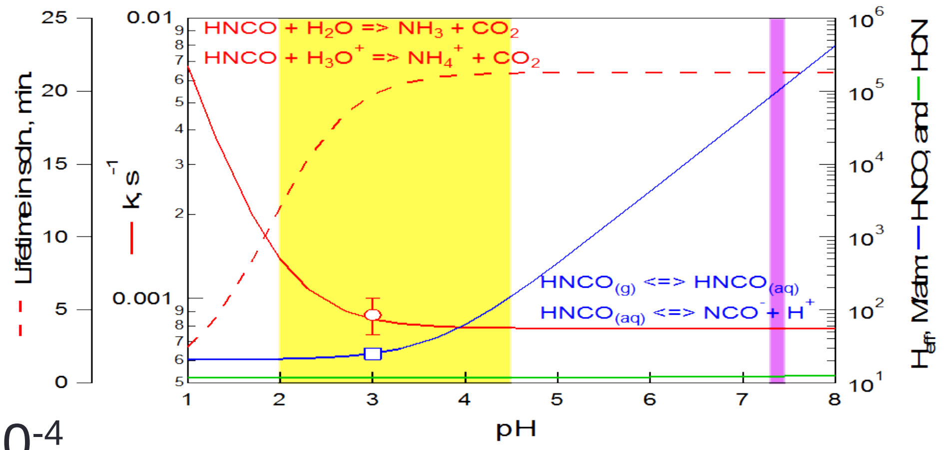
(a) Wet dep in mo_setsox.F90

Allows pH dependence:

$HNCO(g) \rightleftharpoons HNCO(aq)$

$HNCO(aq) \rightleftharpoons NCO^- + H_3O^+$

Figure 3.



$$H_{eff} = H(1 + K_a/[H^+])$$

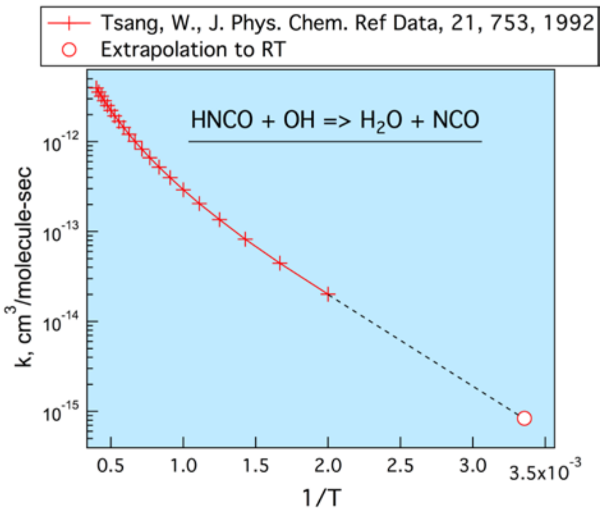
H = 21 M atm^{-1}

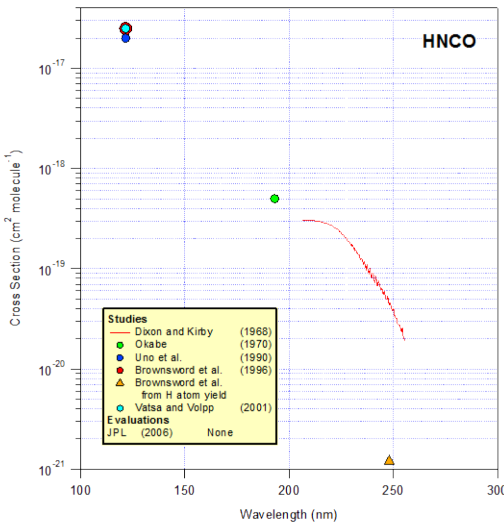
$K_a = [H_3O^+][NCO^-]/[HNCO] = 1.2 \times 10^{-4}$

(b) Dry dep currently like formic acid (HCOOH)

How? What's not included?

Gas-phase chemistry, since it's slow





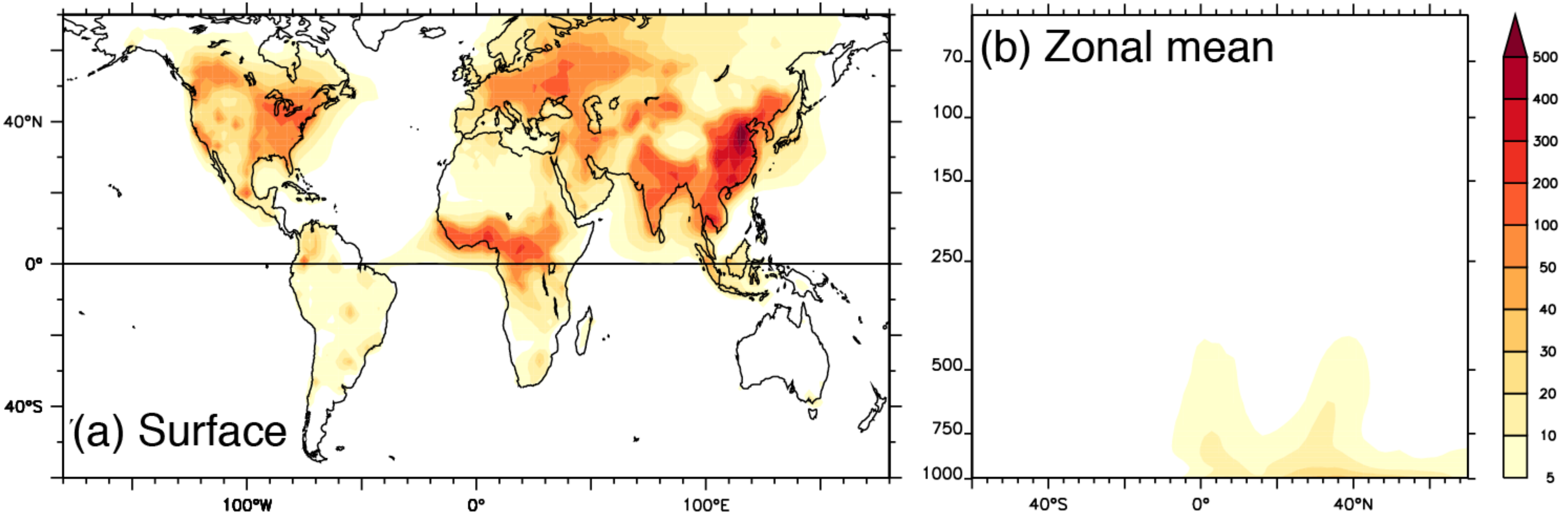
Ignoring gas-phase sources as well, e.g. amides

$$HC(O)NH_2 + X \longrightarrow \bullet C(O)NH_2 \xrightarrow[\text{or H eject.}]{+ O_2 (\rightarrow HO_2)} HNCO$$

$X = OH, NO_3, Cl$

(Another "why?" – pretty easy to model!)

HNCO distribution from January



HNCO / pptv (Jan, test run)

cf. HCN, which has longer lifetime (Randel et al. 2010, Science)

When? After all this…

- Update fire emissions (Christine W)
- Complete test run (what's the pH distribution?)
- Additional emissions?
  - SCR scenarios?
  - Trash burning emissions?

Summary

- Several HNCO sources
- Likely associated with diseases (tobacco, biofuel…)
- What's the global distribution?
  - Policy-relevant (SCR expansion, biochar…)
  - Fire emissions (incl. biofuels)