The WINTER Nitrogen-Halogen Nexus – Summary & Thoughts

- We measured the living s*** out of reactive nitrogen … and did really well (at least in the preliminary data look)
  - All O3, NOy, NOz comparisons agree to 20%, most to 10%, some to 5%
  - Instrument comparison paper(s)
    - NOx, NOy, O3, NOz
    - Speciated wintertime NOz: HNO3, ClNO2, HONO, N2O5
  - Berkeley needs new names for their channels during winter
    - Does the TD-LIF really lose 20% of N2O5 on their inlet?

- Photochemical NOx lifetimes during winter – *much* longer than in summer.
  - NOy partitioning in winter favors NOx (no surprise)
  - NOz partitioning looks remarkably similar to summer (surprise!)
    - Influence of regional transport for longer lived compounds?
  - Need to add day vs night NOx lifetimes to this analysis
  - Comparisons to summer campaigns (FRAPPE, SENEX) will be useful

- ClNO2 yields from N2O5 uptake in offshore pollution plumes
  - Yields universally high (>25%) – no surprise, but need to quantify
  - Vertical variability & evidence for sea salt effluorescence? Maybe … but need to quantify the vertical variability. Lots of (possibly tedious) data to look at in this regard.

The WINTER Nitrogen-Halogen Nexus Continued

- ClNO2 yields from N2O5 uptake in offshore pollution plumes (Continued)
  - Cly partitioning is as important as NOy partitioning for these plumes
  - *Huge* variability in N2O5 uptake and products
    - Stable N2O5 vs rapid conversion to HNO3 vs rapid conversion to ClNO2
  - Box model analysis to derive N2O5 uptake coefficients (and ClNO2 yields, independent method)

- Power plants!
  - We measured a whole bunch of them, in different places
  - Direct emissions of halogens, especially HCl
    - Is it a direct emission? If so, what part of the power plant?
  - Direct emissions and / or secondary production of HONO
    - Time synchronization on the data and correlations with CO2, SO2, NOx, etc.
  - Nighttime plume mixing in the vertical
    - Fanning plumes: 50 m deep, >2 km wide
  - Day (Ohio River Valley) vs Night (Pittsburgh, Atlanta) comparisons
  - Summer (SENEX) vs Winter (WINTER) comparisons

- Isocyanic Acid – directly emitted, long lived, health impacts
  - Emission factors relative to NOx, deposition loss to ocean surface
  - Most of the source looks like vehicular or ship emissions rather than BB
  - Measurements low compared to global model avg, maybe due to lack of summer BB

The WINTER Nitrogen-Halogen Nexus Continued

- HONO – most complete aircraft measurements (potentially) to date
  - 2 instruments, both see lots of HONO and are broadly correlated but specifically disagree
  - Need to resolve instrumental issues before proceeding with an analysis, especially for the background & daytime
  - HONO / NOx ratios = 1% (power plants) - 20% (urban air).
    - 20% at 500 m over land – why?
    - 10% at similar altitude over water – maybe constant as air moves over water?
  - Vertical gradients do show up very clearly in missed approaches

- Radical budgets – HONO, CH_2O, $ClNO_2$ vs O_3 photolysis
  - Vertical variability
  - Compare to CalNex summertime data
  - What is responsible for oxidation in polluted air masses in winter?

- GEOS Chem
  - Reproduces T, RH, Pot T, etc., very well and predicts PBL height
  - NOx emissions. 25% decrease in PP emissions 2011 – 2015
  - Generally good agreement for CO, O_3 CH_2O (last one is the least good)
  - Model is 10% too high for NOy, 10% too low for NOx, 2-3x too high for HNO_3
  - N_2O_5 reacts too quickly, does not produce enough $ClNO_2$ in base model
  - RH has the strongest correlation with lack of agreement in NOz partitioning.
  - Infer γN_2O_5 – generally should be much lower and RH dependent compared to 0.02 base