Effects of Ageing on Aerosol Composition

G-1 Obs. on Mexico City Plateau

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U.S. DEPARTMENT OF ENERGY

- Aerosol concentrations from AMS: organics, SO_4^{2-}, NO_3^-, NH_4^+, Cl^-
  amu 44 (OOA), amu 57 (HOA)
- Restrict data to urban plume on plateau
- Photochemical age = $-Log_{10}(NO_x/NO_y)$
- Normalize results to CO to account for dilution

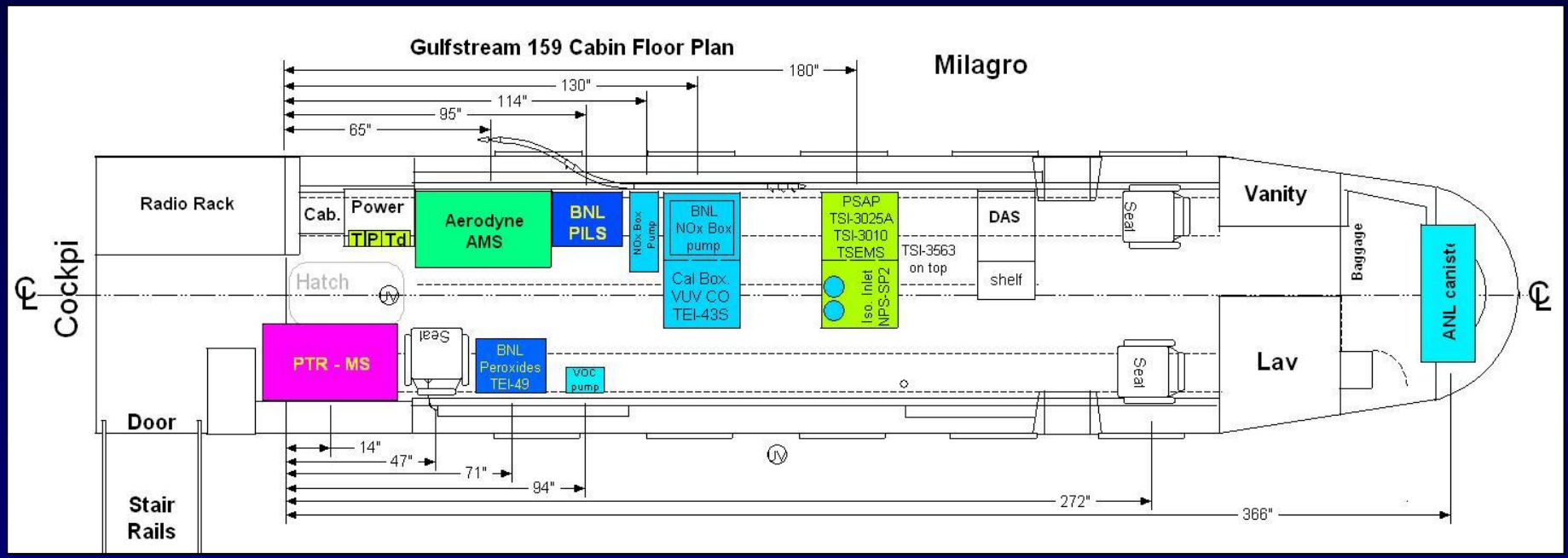
[Aerosol] / (100 ppb urban CO) as a function of photochemical age

Equivalent gas phase VOC

ftp://ftp.asd.bnl.gov/pub/ASP Field Programs/

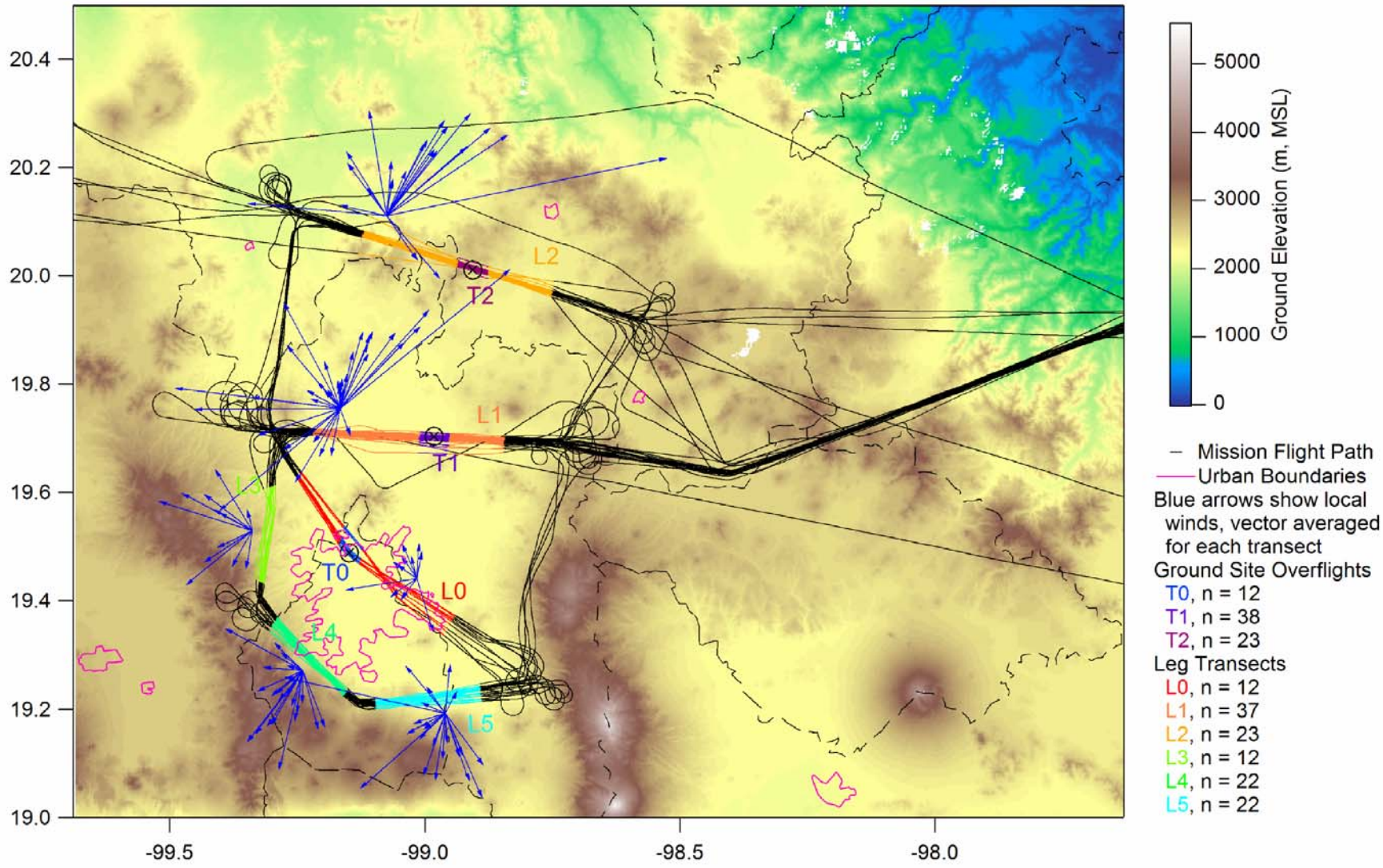
In The Air

G-1 Layout



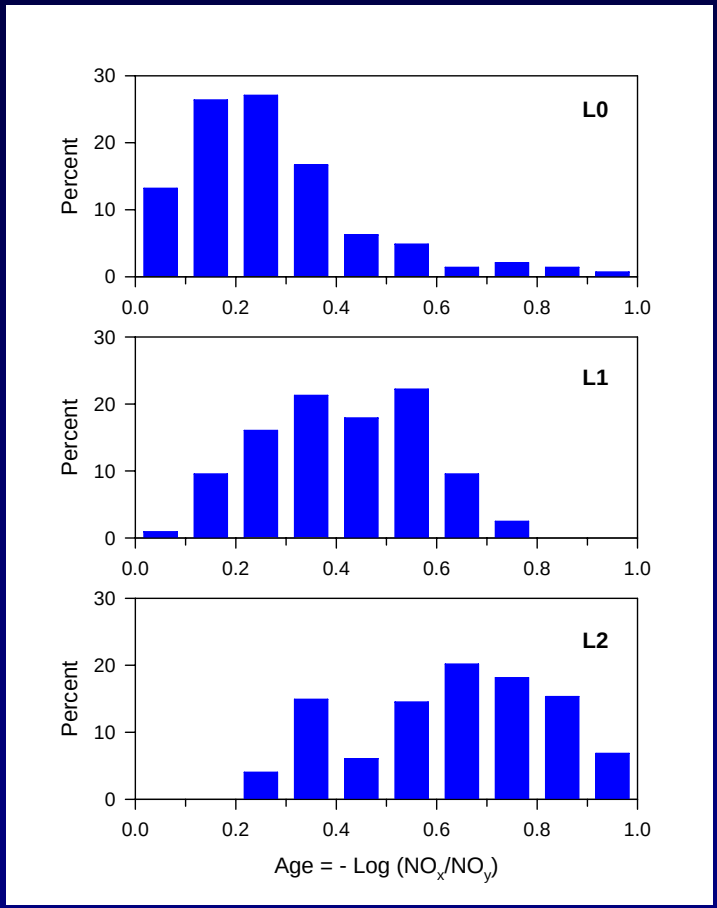
PCASP, CAPS – PNNL, BNL: Senum, Hubbe
State – PNNL: Hubbe
PTRMS - EMSL: Alexander, Ortega
AMS - Aerodyne, EMSL: Alexander, Jayne
Peroxides - SUNY, BNL: Lloyd, Bowerman
VOCs – York: Hubbe, Rudolf
PILS – BNL: Lee

CO, NO, NO_2, NO_y O_3, **SO_2** – BNL: Springston, Senum
PSAP, Neph, CNCs – PNNL: Group
TSEMs – BNL: Wang
MFRs – PNNL: Barnard
SPSP – DMT, CIRPAS: Kok, Jonsson, Senum
Balloons – PNNL: Zaveri, Hubbe
Data – PNNL, BNL: Hubbe, Springston, Senum

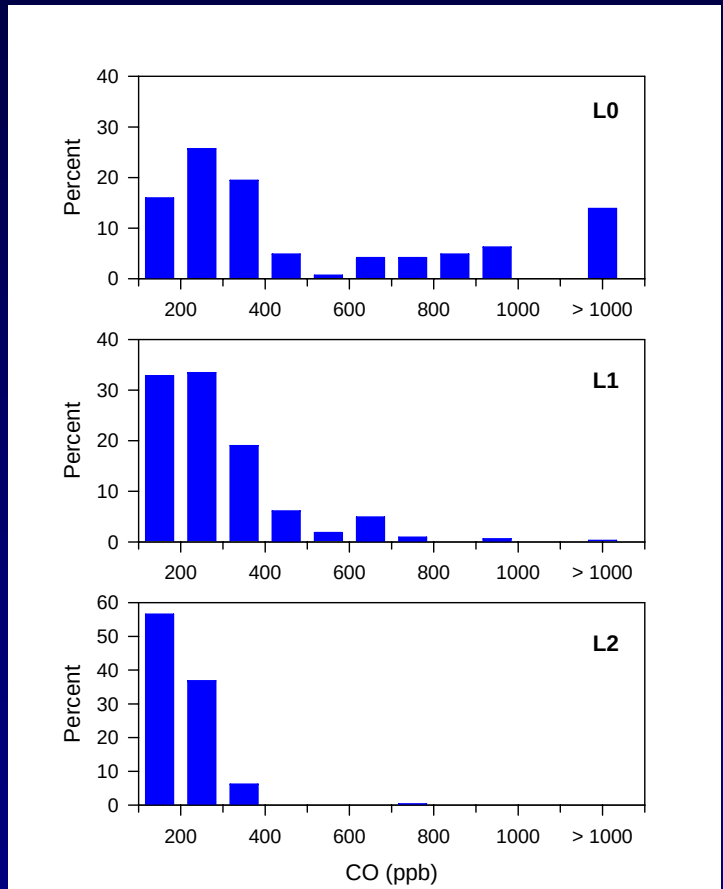

20.4
20.2
20.0
19.8
19.6
19.4
19.2
19.0
-99.5
-99.0
-98.5
-98.0
L2
T2
L1
T1
L3
T0
L0
L4
L5
5000
4000
3000
2000
1000
0
Ground Elevation (m, MSL)
Mission Flight Path
Urban Boundaries
Blue arrows show local winds, vector averaged for each transect
Ground Site Overflights
T0, n = 12
T1, n = 38
T2, n = 23
Leg Transects
L0, n = 12
L1, n = 37
L2, n = 23
L3, n = 12
L4, n = 22
L5, n = 22

Ageing and Dilution

Age



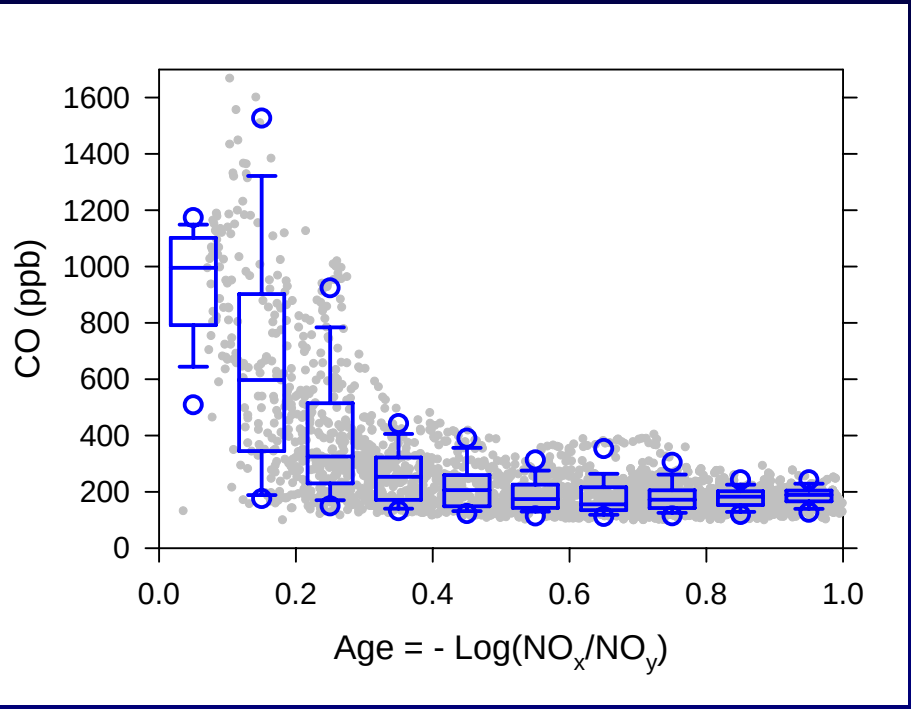
CO



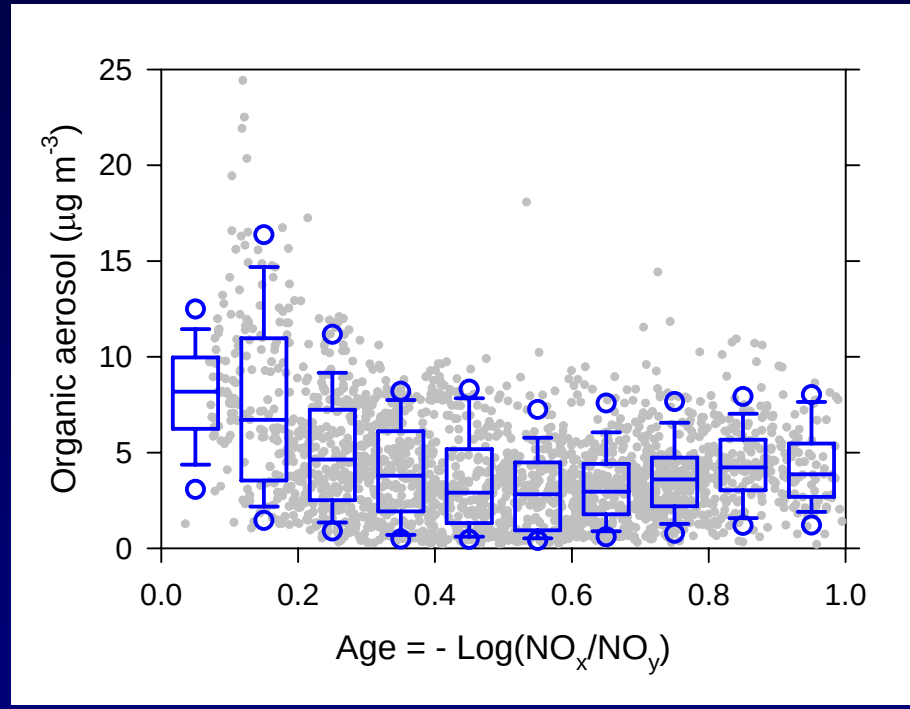
L0 to L1 to L2: Urban emissions spread out and age

Air Mass Ageing

Dilution



Dilution + Production

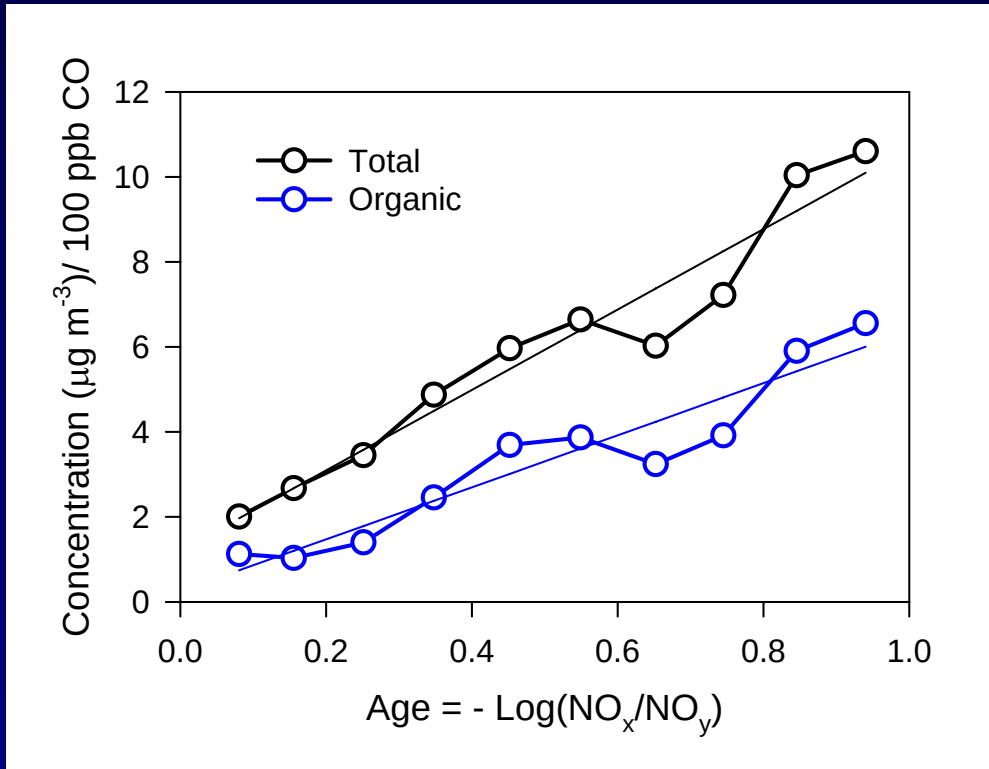


As Age Increases:

- **Dilution decreases primary pollutants**
- **Organic aerosol mass, normalized to CO, increases**

Increase in Aerosol Mass with Age

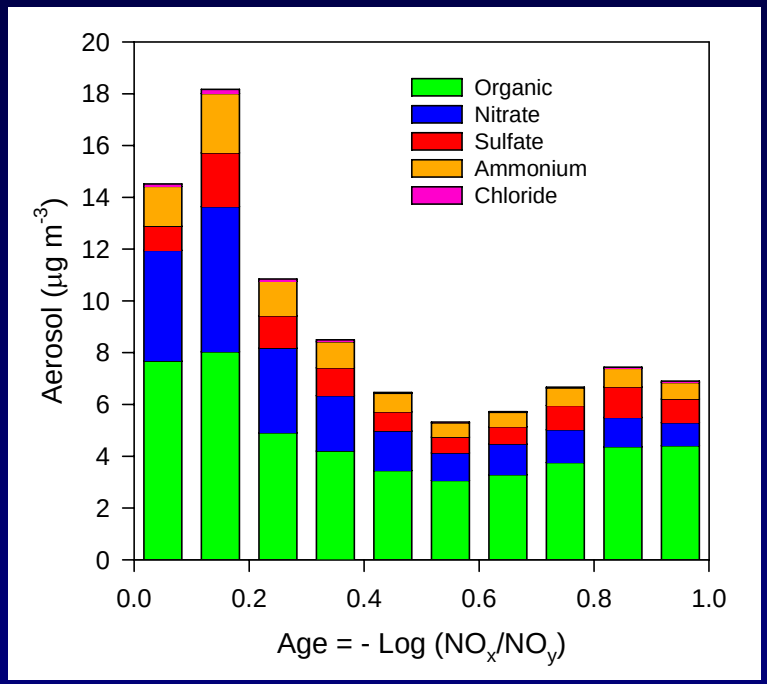
Each point is the slope of a regression of aerosol vs. CO
- don't have to worry about backgrounds -



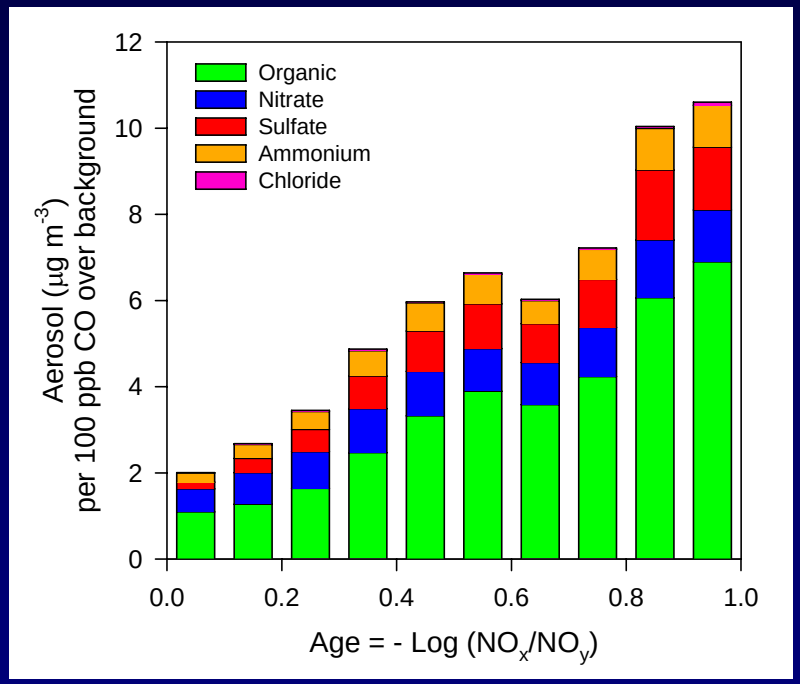
- **6 fold increase in organic aerosol with age**
- **4+ fold increase in total aerosol**

Aerosol Concentration

Ambient



Normalized to CO

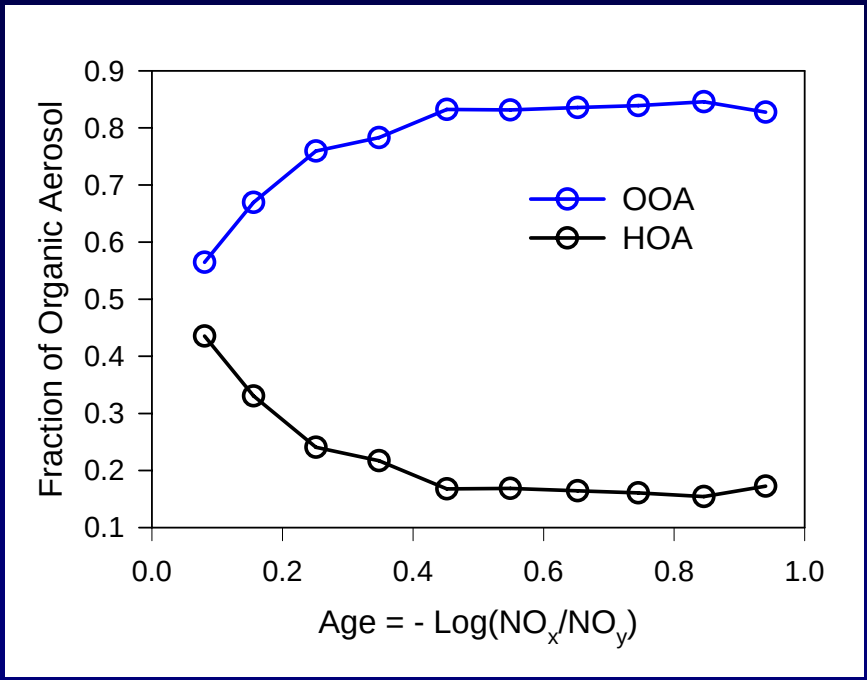


- **After moderate ageing most non-refractory aerosol is secondary**
- **Organics and Sulfate are still increasing in old air masses**
- **Nitrate remains constant after Age ≈ 0.4, growth balances loss**

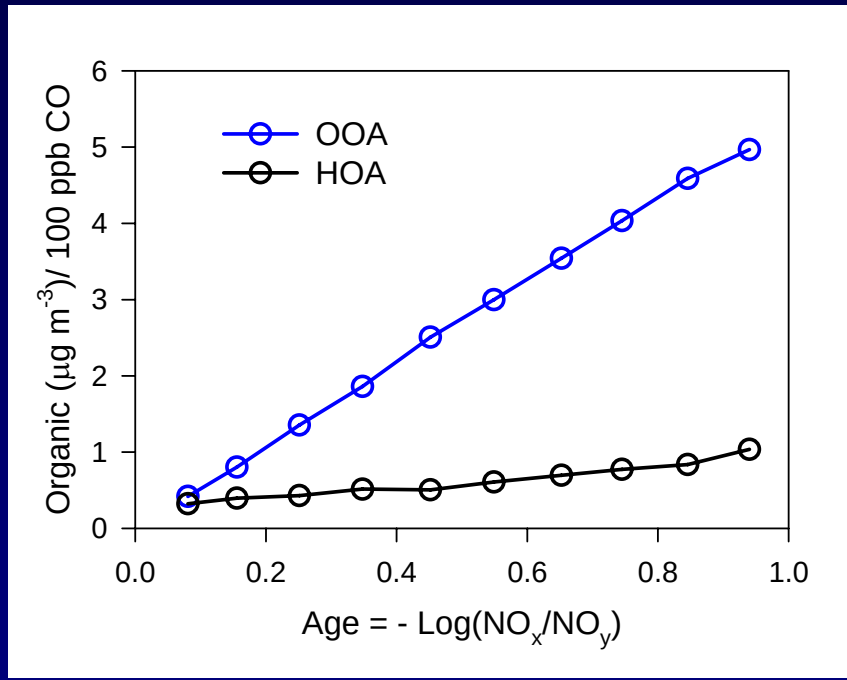
HOA and OOA

Assume HOA ~ amu 57, OOA ~ amu 44

Fraction of HOA, OOA



Growth in HOA, OOA



- **Two components account for 99% of variance in OA**
- **Transition from 50:50 mixture to 85% OOA with age**
- **Growth in "HOA" could be $C_3H_5O^+$**

Conclusions

Moving in General Downwind Direction from T0 to T1 to T2

- Air masses are older and more dilute

With Increasing Age

- Aerosol mass relative to urban tracer, CO, increases more than 4 fold
- Organic and sulfate fraction increase, nitrate decreases
- Both "HOA" and "OOA" increase

Mass Balance

- Toluene/CO ratio = 0.004 ppbv/ ppb CO
- OA increase would require 240% of toluene at 100% aerosol yield
  - *i.e.* at 10% yield, toluene provides 4% of OA

Where does the other 96% come from?