#### NOx Emission Inventories Uncertainties and Approaches to Evaluate Them

#### Presented to Health Effects Institute, The Double Life of NO<sub>2</sub> by Russell R. Dickerson, Univ. Maryland

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UMD/URF Cessna Photo by J. Stehr









When measurements and chemical transport models disagree:

- Dispersion could be wrong.
- Emissions could be wrong.
- Chemistry (formation, sequestering, or removal) could be wrong.
- Some combination of the above.

# Estimating emissions from vehicles is challenging

- Bottom up calculations are challenging.
  - Fleet makeup, vehicle miles traveled (VMT)
  - Driving patterns
  - Stop and go
  - Cold starts
  - High speed, vehicle type, fuel composition, sulfur content of fuel, hoteling ....
- But such models are essential for improving air quality.
- US EPA uses MOtor Vehicle Emission Simulator (MOVES).
- Gross emitters generate a non-Gaussian distribution.
- Measurement methods are understood.
- Trends are consistent.

### Evaluating emissions inventories is essential

- Borrow a classical technique for top down emissions estimates.
- First employed to study biomass burning in the Amazon (Crutzen et al., 1979) later for black carbon (BC) from India (Dickerson et al., 2002).

$$E_{co} = \frac{\Delta CO}{\Delta CO_2} \times E_{co2}$$

$$E_{NOx} = \frac{\Delta NOx}{\Delta CO} \times E_{CO} = \frac{\Delta NOx}{\Delta CO_2} \times E_{CO2}$$

E = emissions;  $\Delta$  = change; CO = carbon monoxide; CO<sub>2</sub> = carbon dioxide; NO<sub>x</sub> = nitrogen oxides

#### Schematic of ratio method



#### DISCOVER-AQ Field Campaign Maryland July 2011



## Let's look at ratios

- Looking at CO/NO<sub>x</sub> or CO/NO<sub>y</sub> eliminates dispersion.
- EPA 2011 inventories estimate CO/NO<sub>x</sub> ~ 7-9 by moles.
- Previous research suggests inventory ratios of CO/NO<sub>v</sub> disagree with observations:
  - Fujita (2012) models overestimate concentrations by 25-40%.
  - Parrish (2006) Inventories are a factor of 2 larger than CO measurements.

### • Research questions:

- What are the emissions ratios of pollutants  $NO_v \& CO$  in Maryland?
- How well do emissions inventories represent these ratios?
- \* NO<sub>y</sub> (reactive, odd nitrogen) = NO<sub>x</sub> (nitrogen oxides) + products HNO<sub>3</sub> (nitric acid ), PAN (peroxyacyl nitrates), RONO<sub>2</sub> (nitrate esters ), NO<sub>3</sub><sup>-</sup> (nitrate)

# Methodology

- Identified 70 spirals from DISCOVER-AQ P3B (P3B is the instrument suite onboard) flights with simultaneous peaks and areas of correlated CO and NO<sub>y</sub> concentration.
- Determined mixed layer from vertical profiles of relative humidity and equivalent potential temperature.
- Calculated, for measured compounds in the mixed layer  $\Delta CO/\Delta NO_v$ .
- Included only those correlations with r<sup>2</sup> > 0.8 and with > 10 data points.
- Average plume age ~ 3 hr.

### From National Emissions Inventory (NEI)



 $Oldsymbol{\otimes}$  CO and NO<sub>x</sub> are important O<sub>3</sub> precursors.

Significant disagreement among studies on NEI's accuracy.

Solution Can we use *in situ* observations to evaluate these numbers?

#### Beltsville CO and NO<sub>y</sub> Vertical Profiles (July 21, 2011, 11:24 EST) Planetary Boundary Layer (PBL) only



# Beltsville, July 21, 2011, 868-953 hPa, 11:27 EST



### Anderson et al. Atmos. Environ., 2014.

CO/NOy ratios in Community Multiscale Air Quality Model (CMAQ) are higher than observed.





**Fig. 7.** a) Regression of measured and modeled CO for all flight days during DISCOVER-AQ. Values after means are  $1\sigma$ . b) Same as a) but for NO<sub>y</sub>. Solid line is the 1:1 line; dashed line, the line of best fit. CMAQ gets CO a little high (bias = +28 out of 136 ppb) but NO<sub>y</sub> much too high (bias +2.7 out of 2.5 ppb).

Obs. = observed Mod. = modeled RMSE = root-mean-square error  $\sigma$  = standard deviation Measurements Of Pollution In The Troposphere (MOPITT) is a NASA satellite instrument measuring tropospheric CO.



**Figure 2.11:** (a) MOPITT monthly averaged CO concentration at the 900 hPa level for July 2011 (b) CMAQ monthly averaged CO concentration at the 900 hPa level with the MOPITT averaging kernel. (c) Regression of measured and modeled CO over the CMAQ modeling domain. The mean of MOPITT CO over the model domain (Obs.), the mean CMAQ CO (Mod.), mean bias (MOPITT – CMAQ), and RMSE are also shown.

CMAQ/CB05/MOVES gets CO about right (15  $\pm$  11% high), but substantially underestimates CO/NO<sub>y</sub> because it overestimates NO<sub>y</sub>.



CB05 = carbon bond reaction mechanism in CMAQ model MOVES = MOtor Vehicle Emission Simulator

### Evaluation of NEI NO<sub>x</sub> Emissions



 National Emissions Inventory overestimates NO<sub>x</sub> emissions by 40-75%.

# Summary of Emissions Ratios

	DISCOVER-AQ Average (mol/mol) ± σ/n <sup>0.5</sup>	Number of aircraft profiles	Fujita <i>et al</i> 2012 (mol/mol)	EPA (mol/mol)	EPA/DISCOVER-AQ
CO/NO <sub>y</sub>	$13.7 \pm 1.4$	60	9.3	7.4+	0.54

\*: Values for 2010 +: Values for 2011; CO & NO<sub>v</sub> data from NEI.

#### The only conclusion that fits the observations: NEI appears to overestimate $NO_x$ emissions by a factor of ~2. Why?

Anderson et al., Atmos. Environ., 2014.

### Has this been seen before?

#### Houston - EPA RTP [Yu et al, 2012]



Compares CMAQ [Weather Research and Forecasting Model (WRF); Carbon Bond Mechanism version 4.2 (CB4.2); EPA's mobile source emission factor model (MOBILE 6) and Biogenic Emission Inventory System (BEIS)] to the Texas Air Quality Field Study [TexAQS] 2006 observations.

They conclude that compared to research aircraft (P3) observations in the lowest 2000 m, the model:

- Does well for CO (124 observed vs. 117 ppb modeled)
- Does well for  $O_3$ .
- Overestimates NO<sub>v</sub> (9.2 vs. 4.6 ppb) and all NO<sub>v</sub> constituents.
- Shows the ozone production efficiency (OPE) substantially less than observed from  $O_3$  vs.  $NO_z$  [=  $NO_y NO_x$ ] (8 vs. 3).

Yu, S. C., et al. (2012), Comparative evaluation of the impact of WRF-NMM and WRF-ARW meteorology on CMAQ simulations for  $O_3$  and related species during the 2006 TexAQS/GoMACCS campaign, *Atmospheric Pollution Research*, 3(2), 149-162.

### Or Since?

"... A major finding from this work is that NEI11v1 for NO<sub>x</sub> (the limiting precursor for ozone formation) is biased high across the US by as much as a factor of 2. Evidence for this comes from (1) SEAC<sup>4</sup>RS observations of NO<sub>x</sub> and its oxidation products, (2) NADP network observations of nitrate wet deposition fluxes, and (3) OMI satellite observations of NO<sub>2</sub>. Presuming no error in emissions from large ...."

Travis et al., Atmospheric Chemistry and Physics, 2016

# Let's look at roadside (NR) monitors.



### From Hall *et al.*, in preparation 2017 Observations from DISCOVER-AQ





Near road measurements of CO,  $NO_{y}$ , and  $CO_{2}$  confirm a temperature dependence and suggest that the oxygen sensor – fuel feedback is involved.

### **Conclusions: What can observations tell us** about emissions?

- CMAQ with CB05 and the NEI overestimate  $[NO_v]$  and  $NO_v/CO$ (factor of ~2) in urban areas, probably due to overestimated NO<sub>v</sub> emissions.
- Comparing emissions to NO<sub>v</sub> deposition indicates that this is true for the US as a whole.
- Strong temperature dependence is partly responsible for the disparity and offers an opportunity to improve MOVES.
- Lower NO<sub>x</sub> puts us on the steeper part of the ozone production curve: NO<sub>x</sub> controls more effective!







