Analysis of long-term observations of NO_x and CO in megacities and application to constraining emissions inventories

G.J. Frost[1] (gregory.j.frost@noaa.gov), B. Hassler[1,2], B.C. McDonald[1,2], A. Borbon[3], D.C. Carslaw[4], K. Civerolo[5], C. Granier[1,2,6], P.S. Monks[7], S. Monks[1,2], D.D. Parrish[1,2], I.B. Pollack[1,2,8], K.H. Rosenlof[2], T.B. Ryerson[2], E. von Schneidemesser[9], and M. Trainer[2]

1 NOAA Earth System Research Laboratory, Chemical Sciences Division, Boulder, USA; 2 CIRES, University of Boulder, Boulder, USA; 3 LaMP, OPGC, CNRS - UMR 6016, University of Blaise Pascal, Clermont-Ferrand, France; 4 Wolfson Atmospheric Chemistry Laboratories, University of York, York, UK; 5 New York State Department of Environmental Conservation, New York, USA; 6 LATMOS/CNRS, Paris and Laboratoire d'Aerologie/CNRS, Toulouse, France; 7 Department of Chemistry, University of Leicester, Leicester, UK; 8 Dept. of Atmospheric Science, Colorado State University, Fort Collins, Colorado, USA; 9 Institute for Advanced Sustainability Studies e.V. (IASS), Potsdam, Germany

Introduction

Accurate knowledge of tropospheric ozone is important for understanding its effects on human health, air quality, and climate. Global chemistry models generally have problems reproducing tropospheric ozone concentrations, seasonal cycles and interannual trends. Successful tropospheric ozone simulations require high quality information on the emissions of ozone precursors, including nitrogen oxides (NO_x), carbon monoxide (CO) and volatile organic compounds (VOCs).

Long-term measurements of NO_x and CO have been made for decades in some world megacities, including the Los Angeles (LA) Basin, London, and Paris. Long-term accurate VOC measurements are sparser than those of NO_x and CO. However, CO and VOC concentrations are highly correlated in megacities where motor vehicle emissions dominate, allowing urban VOC levels to be estimated from their enhancement ratios relative to CO.

Here we use atmospheric NO_x/CO enhancement ratios to evaluate inventory NO_x/CO emissions in US and European cities. Atmospheric enhancement ratios of co-emitted species above a local background can be directly compared to the corresponding emissions ratio in an inventory, because enhancement ratios are conserved at spatial and temporal scales appropriate to urban area sampling and are independent of atmospheric dilution into background air.

Methods

Measurements

- We analyze atmospheric enhancement ratios of NO_x/CO from ambient regulatory monitors, intensive field research campaigns employing ground-based and aircraft sampling, and roadside remote sensing combined with vehicle identification (*Pollack et al., 2013; McDonald et al., 2013; von Schneidemesser et al., 2010; Derwent et al., 2014; Carslaw and Rhys-Tyler, 2013; Parrish et al., 2009*).
- Annual means were calculated from hourly data between 5 am-9 am on weekdays in May-September for each year of data.

MACCity inventory

- 1960-2015 inventory (*Granier et al., 2011*) constructed for chemistry-climate simulations. Based on the ACCMIP inventory (*Lamarque et al., 2010*), a hybrid of the EDGAR-HYDE (*van Aardenne et al., 2001*) and RETRO (*Schultz et al., 2008*) inventories, which were built using conventional bottom-up approaches.
- Annual means were calculated from May-September monthly emissions.

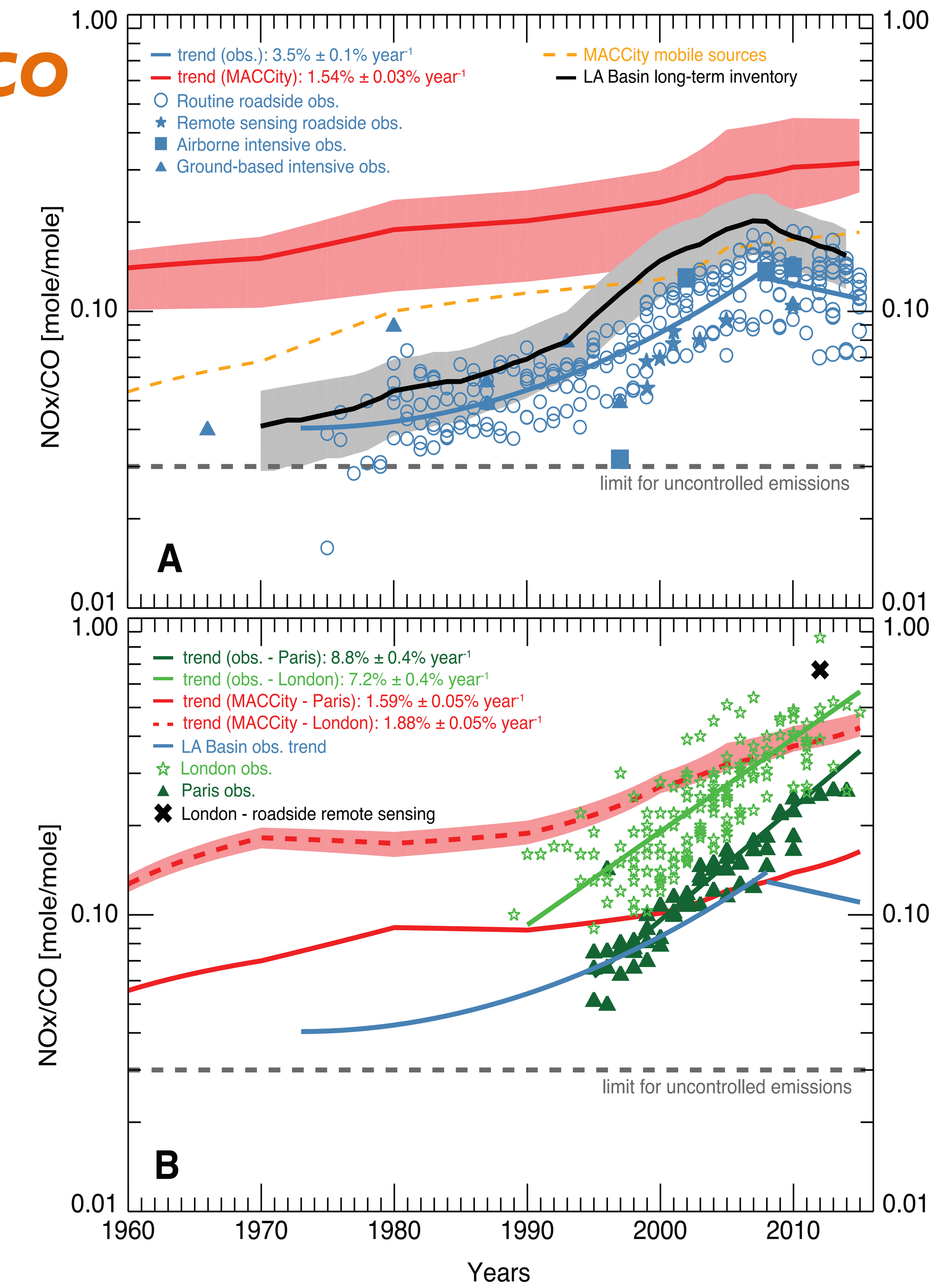
Fuel-based inventory

- 1970–2014 emission estimates were made for mobile sources in the LA Basin. These estimates used fuel sales reports as a measure of engine activity and emission factors from a meta-analysis of real-world roadside observations normalized to fuel use and employing vehicle identification (*McDonald et al., 2012, 2013, 2015; Bishop and Stedman, 2008, 2014; Dallmann et al., 2013*).
- The fuel-based approach can be contrasted to conventional bottom-up methods that express activity with respect to vehicle distance traveled and use emission factors from representative sampling of a few vehicles under idealized conditions.

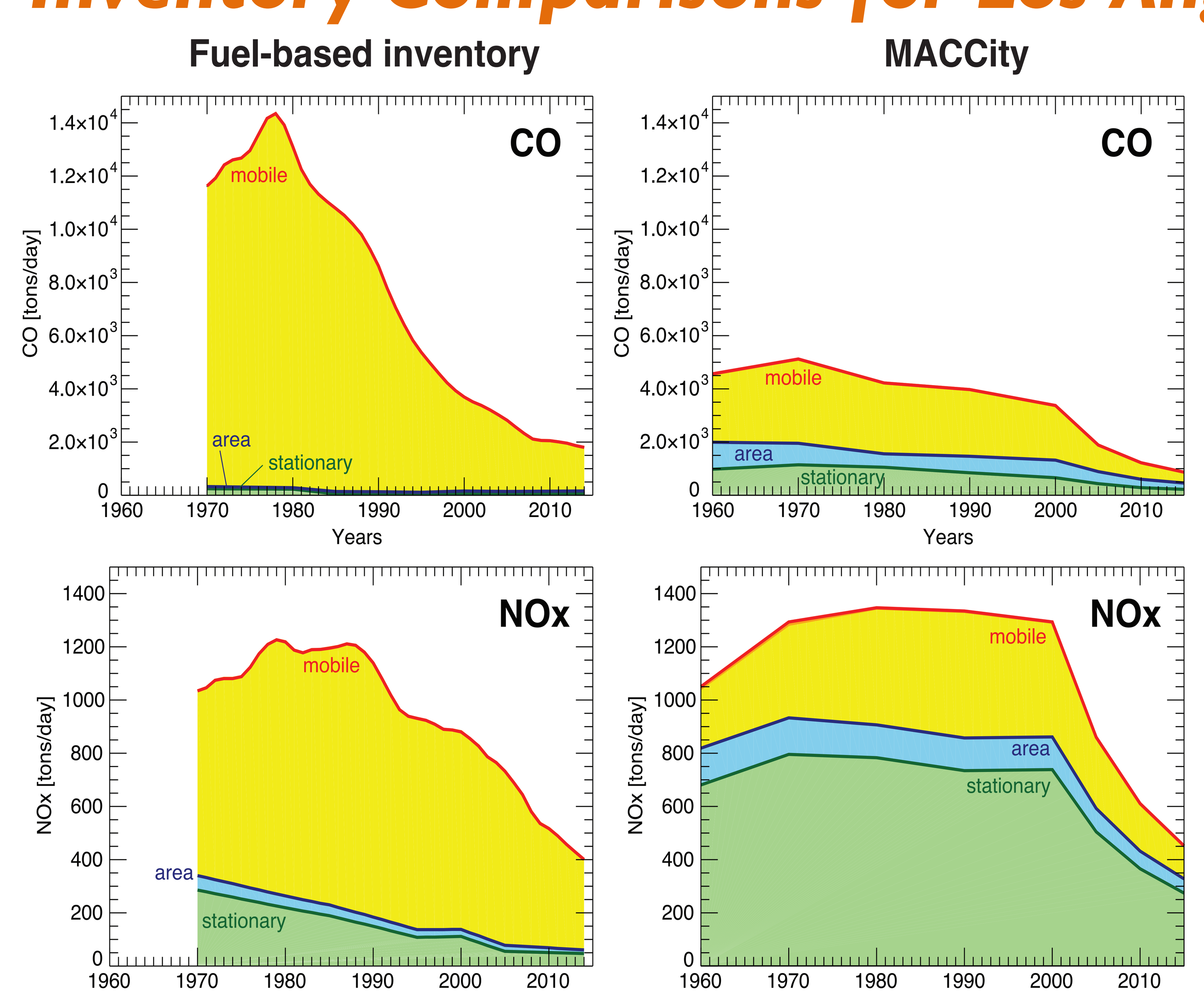
Measured vs. Inventory NO_x/CO

Panel A (top): Measured molar NO_x/CO enhancement ratios for the LA Basin from 10 CARB monitoring stations (blue circles), from remote sensing on LA roadways (blue stars), and from airborne (blue squares) and ground-based (blue triangles) platforms during intensive field campaigns, along with a combination of a quadratic and linear fit to the logarithm of the observed ratios (blue line). Also shown are the LA Basin fuel-based inventory's NO_x/CO total emissions ratios (black line) with their 1-σ uncertainties (gray shading), the MACCity average NO_x/CO total emissions ratios for the entire LA Basin (thick red line) and for each of the 6 grid cells in the LA Basin (red shading), and the average MACCity NO_x/CO mobile source emission ratios for the LA Basin (thick orange dashed line). The NO_x/CO ratio for uncontrolled gasoline vehicle emissions (= 0.03) is also shown (dotted gray line).

Panel B (bottom): NO_x/CO enhancement ratios from roadside monitor measurements at four Paris stations (dark green symbols) and 17 stations in London (light green stars), along with log-linear trends for the Paris (dark green line) and London (light green light) monitoring data. The trend for the LA Basin observations from Figure 1A is shown for comparison (blue line). Also shown are MACCity NO_x/CO emissions ratios for Paris (solid red line) and averaged for all London grid cells (dashed red line) and the range for individual London grid cells (red shading). The fleet-weighted average NO_x/CO ratio from roadway remote sensing at four London sites in 2012 is denoted with a black cross.



Inventory Comparisons for Los Angeles



Upper panels. Total cumulative LA Basin annual CO emissions (given in tons/day) from different sectors in our fuel-based inventory (left) and in MACCity (right), with solid lines and colored areas representing the contributions from mobile (red/yellow), area (dark blue/light blue), and stationary sources (dark green/light green).

Lower panels. Total cumulative LA Basin annual NO_x emissions (given in tons/day) from our fuel-based inventory (left) and from MACCity (right), with sectoral contributions indicated as in the upper panels.

Conclusions

- This study points to the utility of long-term urban atmospheric monitoring for critically evaluating emissions inventories. Maintaining and expanding long-term ozone precursor measurements in the world's megacities could augment such assessments.
- A fuel-based emissions inventory approach that diverges from traditional bottom-up methods explains 1970 – 2015 trends in observed NO_x/CO enhancement ratios in Los Angeles. Fuel-based approaches, which rely on roadway remote sensing of vehicles under real-world operating conditions and use vehicle identification to correlate emissions with engine type, age, and control technology, could be replicated in the world's cities.
- Agreement of Los Angeles measured enhancement ratios with the fuel-based inventory and with measurements in other US cities demonstrates that motor vehicle emissions controls were largely responsible for US urban NO_x/CO trends over the past half-century.
- Differing NO_x/CO enhancement ratio trends in US and European cities over the past 25 years highlight alternative strategies for mitigating transportation emissions, reflecting Europe's increased use of light-duty diesel vehicles and correspondingly slower decreases in NO_x emissions compared to the US.
- The MACCity inventory, widely used by chemistry-climate models, fails to capture long-term trends and regional differences in US and Europe megacity NO_x/CO enhancement ratios. Motor vehicle CO emissions in Los Angeles are clearly underestimated by MACCity when compared to fuel-based estimates. MACCity also incorrectly partitions emissions between sectors, likely reflecting problems with spatial allocation of national-level emissions onto urban scales.
- These systematic differences with observations and the inability to capture regional differences are likely not unique to MACCity, since global inventories rely on similar information about source activity, emission factors, and spatial allocation. Such discrepancies may contribute to the inability of many chemistry-climate models to accurately reproduce observed long-term changes in tropospheric ozone.
- This study demonstrates the need for globally consistent bottom-up inventory methods that incorporate regional knowledge about emissions sources. Constraining bottom-up emissions inventories with historical observations helps to verify that the underlying emissions drivers are understood and gives confidence in using such methods to project future emissions, with attendant improvements in simulating future tropospheric composition, air quality, and climate impacts.

Reference: Hassler, B., et al., **2016**, *GRL*., 43, doi:10.1002/2016GL069894.