Analysis of long-term observations of NO$_x$ and CO in megacities and application to constraining emissions inventories

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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, Paris. Long-term accurate VOC measurements are sparser than those of NO$_x$ and CO. However, CO and VOC concentrations are highly coupled. Based on 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 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 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 Ryhs-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; Bishop and Steinwedel, 2008; Villanueva 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 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 MACCity averaged NO$_x$/CO total emission 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 emissions enhancement ratios for the LA Basin (thick orange dashed line). The NO$_x$/CO ratio for stationary去 infinite vehicle emissions (0.05) is also shown (dotted grey line).

**Panel B (bottom)** NO$_x$/CO enhancement ratios from road-side monitor measurements at four Paris stations (dark green symbols) and 17 stations in London (light green stars), along with linear trends for the Paris (dark green line) and London (light green) monitoring data. The trend for the LA Basin observations is shown in 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 road-side remote sensing at four London sites in 2012 is denoted with a black cross.

Conclusions

- This study points to the utility of long-term urban atmospheric monitoring for critically evaluating emissions inventories. Maintaining and expanding long-term observations of primary ozone precursors in the world’s megacities could augment such assessments.
- A fuel-based emissions inventory approach that diverges from traditional bottom-up methods explains 1990 – 2015 trends in observed NO$_x$/CO enhancement ratios in Los Angeles. Fuel-based approaches, which rely on road-side 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 may be replicated 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. Developing consistent 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.