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1. INTRODUCTION

As part of the Northeast oxidant and particle study (NE-OPS) field campaign in the summer of 1999, NO/NO_y, CO, and O₃ were measured in the surface layer at the Baxter field site in Northeast Philadelphia. The Philadelphia NE-OPS data provide a detailed characterization of precursor pollutants and ozone in a major urban center. For contrast with rural conditions subject to aged pollutants, we examine data from the Harvard Forest site in central Massachusetts that has been operating since 1990.

We address three major questions using this subset of the NE-OPS data: What are the emission ratios for NO_x and CO precursors, how rapidly are nitrogen oxides depleted as polluted air masses age, and what is the level of background ozone?

Accurate emission inventories are essential input parameters to air quality models. Field observations have been used to test the relative emission strengths, or emission ratios of selected primary pollutants (Buhr et al, 1992, Doddridge et al., 1992, Li, 1995, Parrish, et al., 1991) The covariance of NO_y and CO in ambient air yields an estimate of the primary emission ratios for urban pollution sources, and provides a test of emission inventories.

Definition of the emission ratio at the source provides a benchmark for quantifying the simultaneous production and removal of air pollutants. The covariance of O₃ and NO_y or NO_y-NO_x is used to estimate an apparent ozone production efficiency (for example Hirsch, et al, 1996). This ratio is sensitive to differences in the loss rates for O₃ and NO_y. Depletion of NO_y relative to CO can be used to estimate the extent of NO_x oxidation and deposition (Stehr, et al., 2000),

The level of O₃ in background air is critical information to define attainable air quality standards (Lefohn et al, 2001). One approach is to

define a background by the lowest observed concentrations, or based on observations at remote 'background' sites (Altshuller and Lefohn, 1996, Lin et al, 2001). Alternatively, concentrations of pollutant tracers such as NO_y and CO can be used to identify periods with minimal influence by recent addition of pollutants (Bronnimann, et al., 2000, Trainer et al., 1993).

2. METHODS

The 1999 NE-OPS sampling intensive was based at the Baxter Water Treatment Facility northeast of Philadelphia. The site is bordered on the northwest by Interstate 95 and on the southeast by the Delaware River. Additional site details are presented by Philbrick et al (2001). The NO_y, CO and O₃ instruments were located near the western edge of the site, within 300m of the highway. The instruments were housed in a small building with inlets mounted on the roof, approximately 3m above ground level.

The Harvard Forest measurement site is located in north-central Massachusetts. The site is surrounded by forest and is over a km from the nearest highway. Periods with southwest winds provide a representative sampling of air that has passed over major eastern U. S. urban areas. Northwesterly winds at the site are little influenced by urban emissions and provide a sample of continental background air. Details of the site and measurements are presented by Munger et al., (1996, 1998).

NO and NO_y at the Baxter site were measured by chemiluminescence using a TEI 42S. The Molybdenum converter was removed from the instrument and mounted outside with a short Teflon inlet. tube to bring sample air into the converter and a 2 μm filter downstream of the catalyst to prevent particles from reaching the detection cell. The NO inlet was located adjacent to the NO_y and had a particle prefilter. Standard addition calibrations were performed about every 3 hours by adding a small flow of 5 ppm NO at each of the sample inlets.

CO at the NE-OPS Baxter site was measured using non-dispersive infrared gas filter correlation

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analyzer (TEI Model 48S) modified for increased sensitivity including an internal Pd on alumina (Pd/Al₂O₃,) chemical zeroing catalyst heated to 250C and a Nafion sample air drying tube (Dickerson and Delany, 1988; Doddridge et al., 1994). The instrument zero was checked for 5 minutes out of every 30 minutes by diverting ambient air through the catalyst. The calibration factor was checked before and after the field campaign by injection of a NIST-traceable working standard. CO at Harvard Forest is determined using a non-dispersive IR gas-filter correlation analyzer (Dasibi) equipped with a Pt-Pd catalyst for zeroing and glass trap at ~-20C for drying the sample. Calibration gas is substituted for the sample 4 times per day to check the span.

Ozone concentrations were determined by UV absorbance at both the NE-OPS site (TEI-49C) and at Harvard Forest (Dasibi).

3. RESULTS

Figure 1 illustrates the diel pattern for NO_y, CO, and O₃ observed during the NE-OPS study at Baxter in the summer of 1999. A strong rush hour signal is evident in NO_y and CO in the morning hours before the mixed layer deepens. Smaller increases in the primary pollutants are observed during the evening rush hour when deeper mixing and generally stronger winds prevail. Ozone concentrations reach their peak in the mid afternoon. For subsequent analysis, we separately consider conditions during the morning and evening traffic peaks, the afternoon photochemical maximum and the night

From the covariance of NO_y and CO during the morning rush hour time periods we infer an emission ratio of 0.178 moles NO_y:CO, and a baseline CO value of 154 ppb (Figure 2). The mean enhancements of NO_y and CO at 5 am relative to 3 am yields an average emission factor of 0.203 mol/mol. Concentrations of NO_y during the afternoon periods are depleted by 33% on average relative to the morning hours (Figure 3). If we take the Philadelphia data as representative of typical urban emissions in the northeast U. S. the NO_y:CO relationship at Harvard Forest during periods when winds are blowing from the urban corridor, indicates a regional NO_y depletion of 75% (Figure 4).

At Baxter, the observations associated with highest O₃ concentrations are among the most depleted in NO_y. (Solid points in Figure 3) This highlights the potential to misinterpret high O₃:NO_y ratios as enhanced ozone production efficiency

rather than efficient NO_x oxidation followed by deposition.

Finally, we consider the issue of background ozone. Ozone generally increases with NO_y or CO, except for a period of ozone titration on July 20 that has the lowest mid-day O₃ concentrations of the entire study period (Figure 5). This illustrates that simply using the 10%ile concentration of O₃ to define the background could be misleading. Based on the O₃ covariances with NO_y and CO we define a background O₃ as the mean O₃ concentration for the subset of mid-day data with the lowest 10% of either CO or NO_y concentrations. At Baxter the CO and NO_y based background O₃ values are both 47 ppb. The long-term average values for the July 1 to August 15 at Harvard Forest when winds are from the southwest are 40 and 43 ppb. Similarity between the background estimates at both urban and rural sites suggests that regional background O₃ levels can be confidently estimated even from urban sites if precursor concentrations are known as well.

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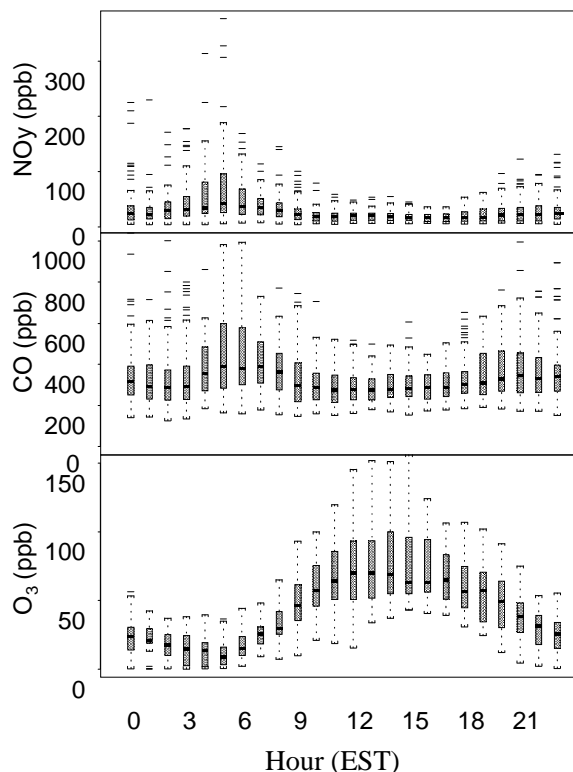


Figure 1 Boxplots show the statistics for NO_y, CO, and O₃ at the Baxter NE-OPS site in the summer of 1999. Median values for each hour of the day are shown by the dark horizontal bars. The shaded bars enclose the central 50% of the data. Extreme values are denoted by the whiskers

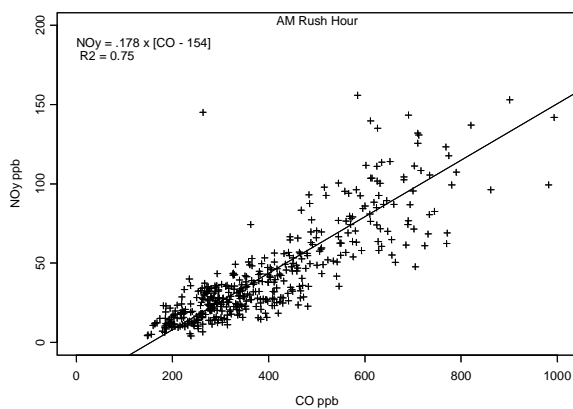


Figure 2 Scatter plot of NO_y and CO concentrations during morning rush hour periods . The molar emission ratio inferred from the NO_y:CO covariance is .178 and the background CO is 154 ppb.

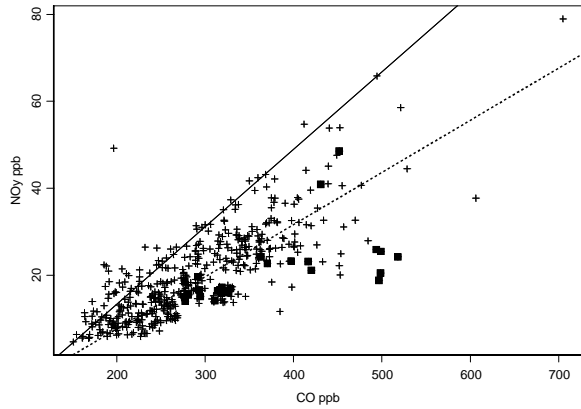


Figure 3 NO_y is plotted against CO for data collected during the period 1200-1600, when photochemical processing and vertical mixing are at their maximum. The solid line follows the slope derived from morning rush hour and is shifted to the left to have a CO background of 125 ppb. The dashed line shows the least squares fit to the data; the slope is 0.12 and the CO background is 133 ppb. Solid symbols are plotted for the observations with $\text{O}_3 > 120$ ppb.

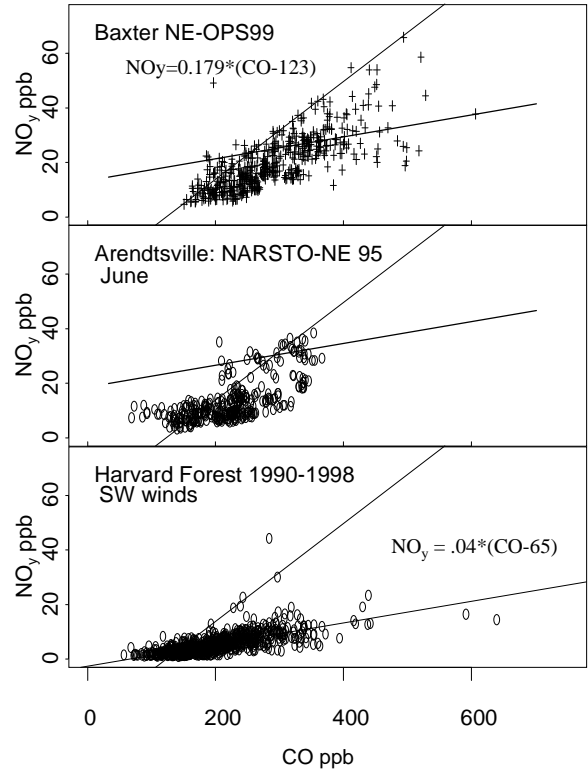


Figure 4 The covariance of NO_y with CO is shown for three sites. Upper panel shows the NE-OPS 1999 data; middle panel is from Arendtsville during the 1995 NARSTO-NE field campaign; lower panel is data from Harvard Forest selected for times when winds are southwesterly. The upper line in the top panel is derived from the upper limit for NO_y :CO in the NE-OPS data, and is shown for comparison on the remaining panels. The lower line is the linear fit through the Harvard Forest data.

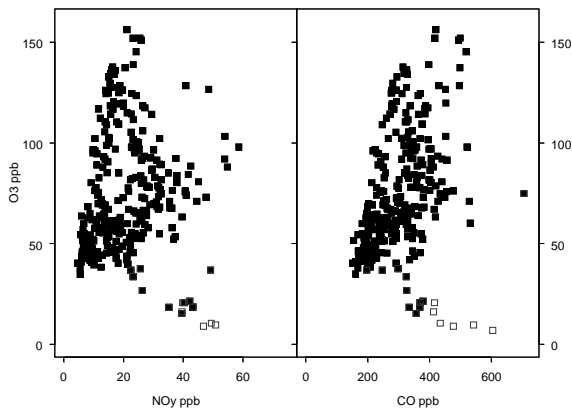


Figure 5 Half-hourly average O_3 is plotted against NO_y (left panel) and CO (right panel). The group of points tending toward lower O_3 with increasing NO_y or CO are from a single episode