Near-road NO_2 concentrations can be theoretically inferred from NO_x concentrations, the NO_2/NO_x fraction in exhaust, UV, and background oxidant levels.

Preliminary Individual Comments on Near-Road Monitoring To Support Measurement of Multiple NAAQS Pollutants. DO NOT CITE OR QUOTE.

Dr. Warren H. White

Initial comments on near-road monitoring

The key to a simple description is that not much chemistry has a chance to occur in the short time air spends near the road. A cross-road wind component of only 1 m/s, for example, carries air from 150 m on one side to 150 m on the other in just 5 minutes. On such a time scale the complex chemistry of smog formation can be considered determined by the surrounding air, independent of the fresh emissions. More precisely, the only reactions needing consideration are the rapid scavenging of O_3 by NO

$$O_3 + NO \rightarrow O_2 + NO_2, \quad [1]$$

and the rapid photolysis of NO2 to yield

$$O_2 + NO_2 \rightarrow O_3 + NO \quad [2]$$

after additional steps. These reactions leave unchanged the concentrations of odd oxygen $[O_x] = [O_3] + [NO_2]$ and nitrogen oxides $[NO_x] = [NO] + [NO_2]$, and their relative rates establish a photostationary state that is generally fairly well approximated in the atmosphere:

$$[O_3][NO]/[NO_2] \approx k_2/k_1. \quad [3]$$

Since O_x and NO_x are chemically conserved near the road, their concentrations respond only to physical dilution and mixing. They can be modeled as the sum of a variable contribution from roadway vehicle exhaust and a uniform background supplied by the surrounding air. For given concentrations $[O_x]_0$ and $[NO_x]_0$ at the monitor, the reactive species can be expressed in terms of NO_2:

$$[NO] = [NO_x]_0 - [NO_2] \text{ and } [O_3] = [O_x]_0 - [NO_2].$$

Substituted into the photostationary equilibrium [3], these identities yield a quadratic equation in $[NO_2]$ that can be solved for $[NO_2]$ in terms of $[O_x]_0$, $[NO_x]_0$, and k_2/k_1. The following plots illustrate some features of the relationship.

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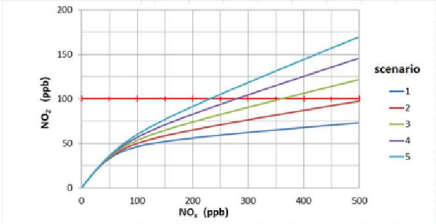
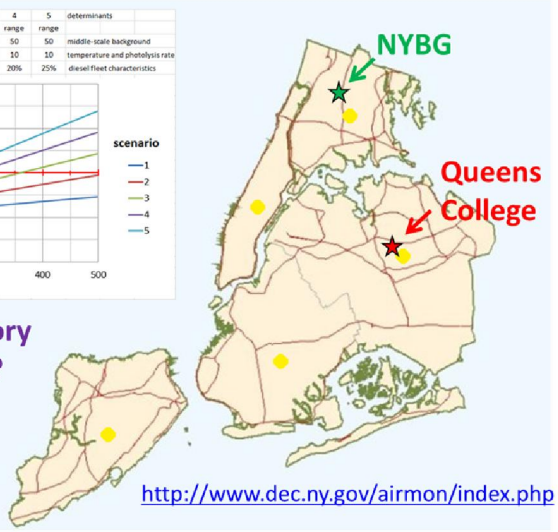
scenario		1	2	3	4	5	determinants
$NO_x = [NO+NO_2]$, ppb	values	range	range	range	range	range	
oxidant = $[NO_2+O_3]$, ppb		50	50	50	50	50	middle-scale background
photostationary ratio = O_3NO/NO_2, ppb		10	10	10	10	10	temperature and photolysis rate
exhaust NO_2/NO_x		5%	10%	15%	20%	25%	diesel fleet characteristics

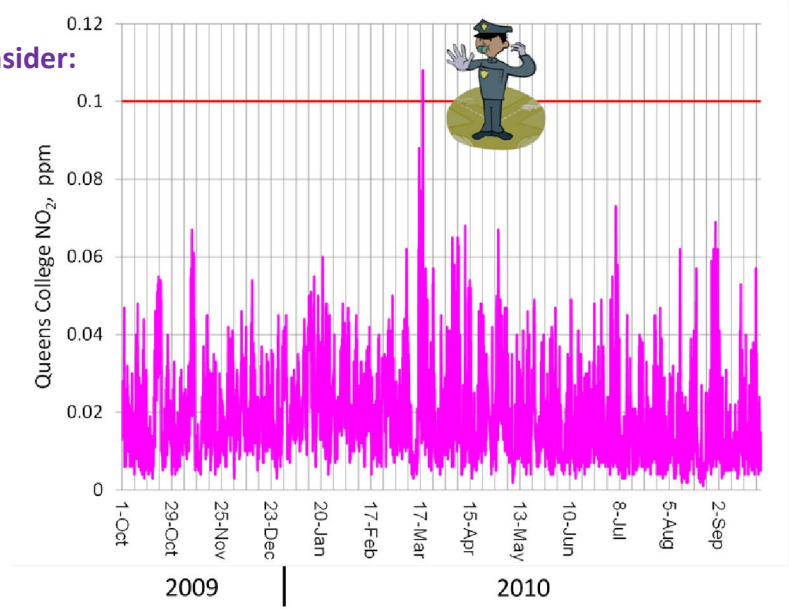




Is this theory realistic?

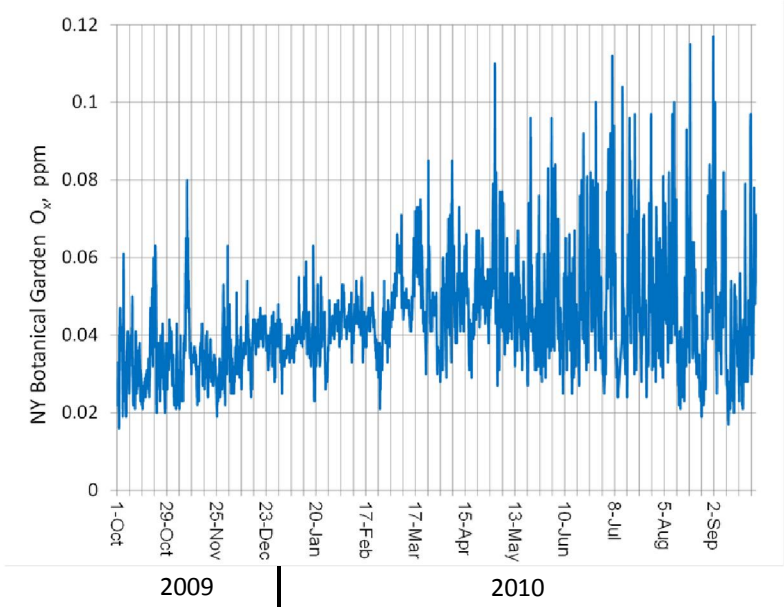
http://www.dec.ny.gov/airmon/index.php

Consider:

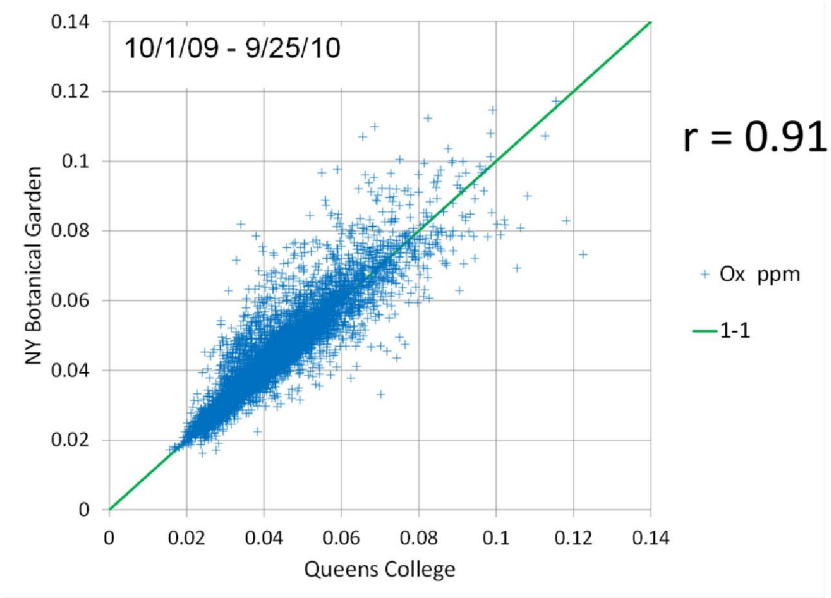


The information used is the first available data from our air quality monitoring network.
The values have not been verified for accuracy or been through the appropriate quality assurance and control validation procedures.

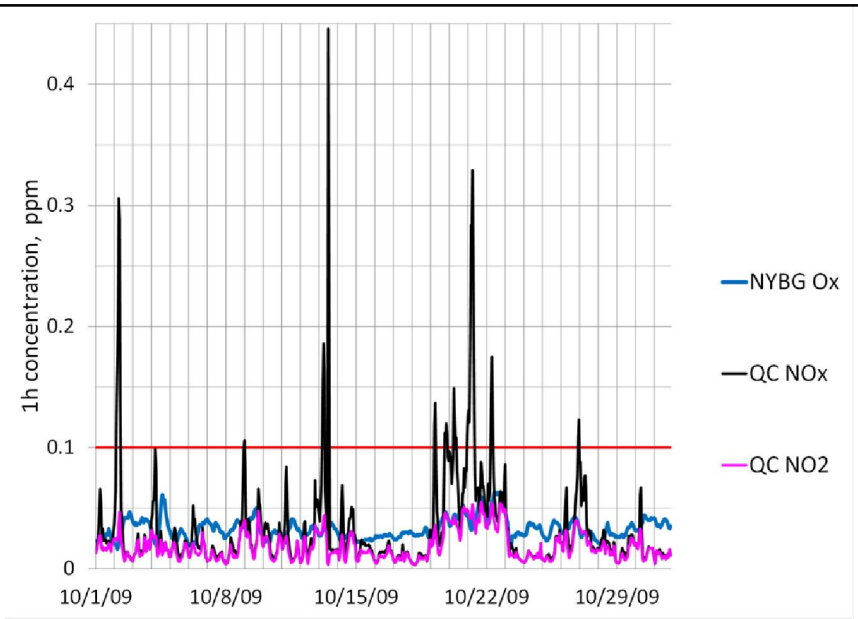
For validated data contact the Bureau of Air Quality Surveillance at (518) 402-8508



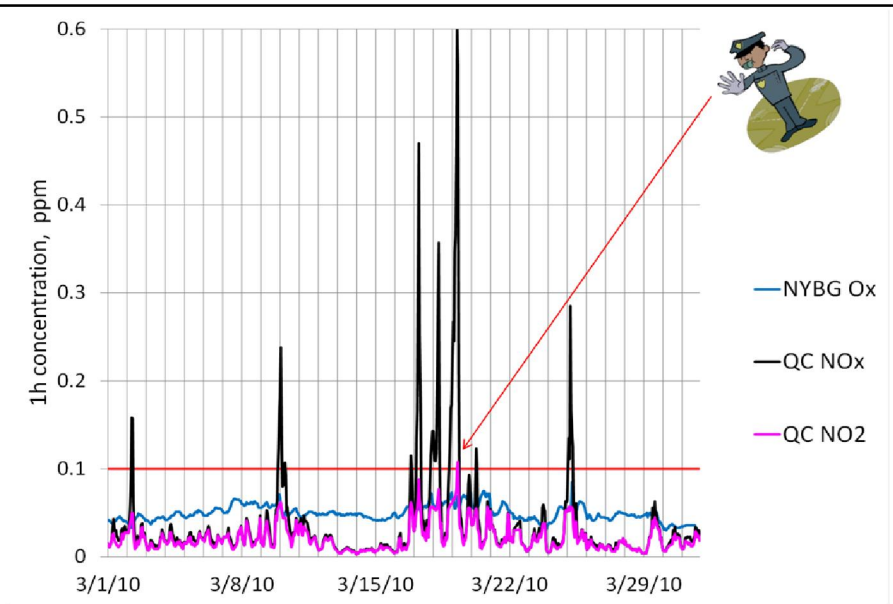
The March 19th NO_2 spike came during an episode of elevated oxidant levels ***throughout the city***.



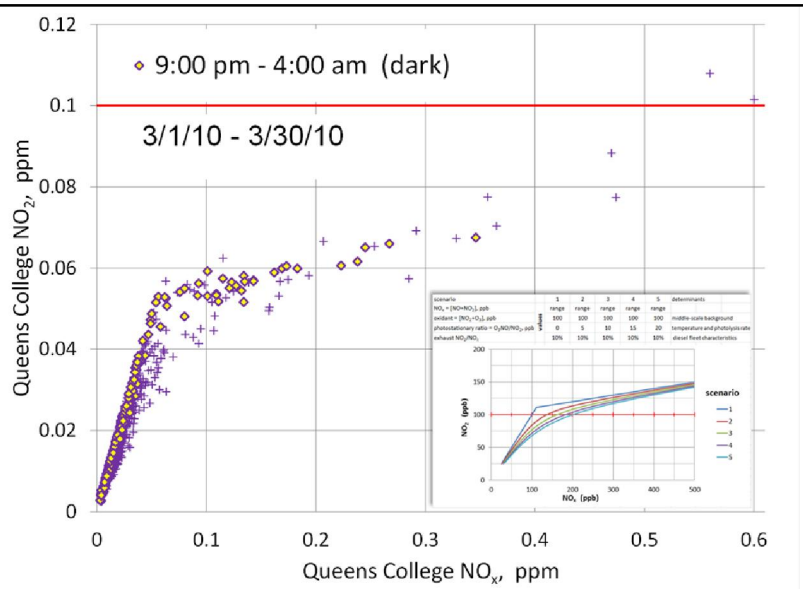
Hourly oxidant ($O_x = O_3 + NO_2$) concentrations show little spatial variation at the urban scale.



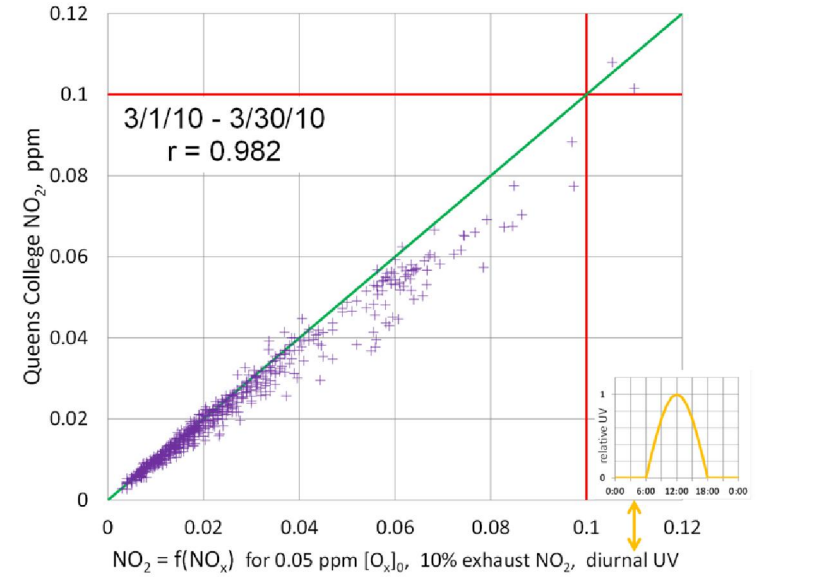
The near-road conversion of NO (most of the exhaust NO_x) to NO_2 is limited by O_x concentrations in the surroundings.



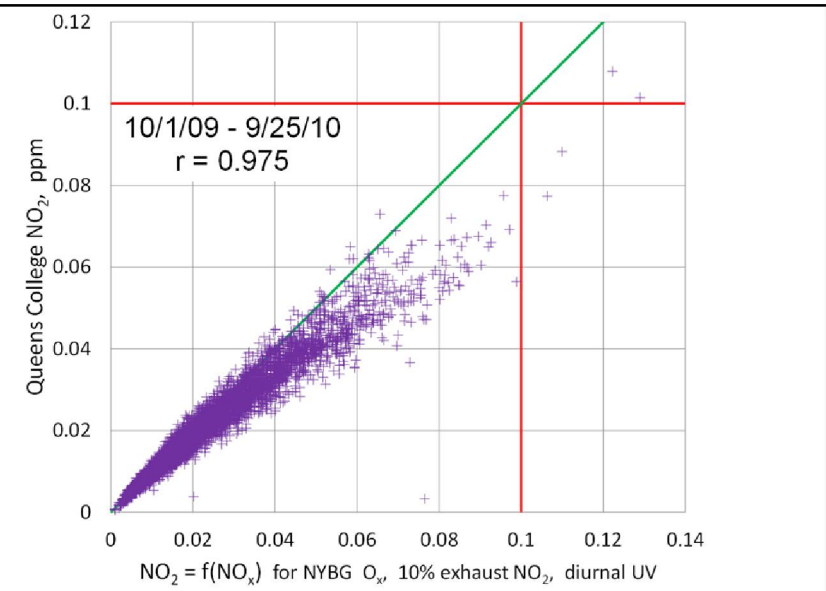
The only other source of near-road NO_2 is its direct emission as a fraction of the exhaust NO_x .



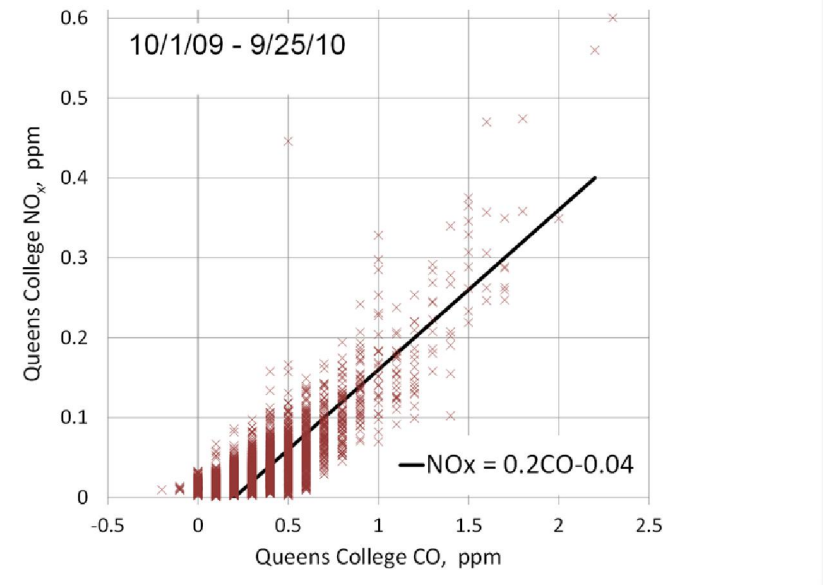
The dependence of near-road NO_2 on NO_x exhibits the expected reduction in sensitivity at NO_x > background O_x, which in this case was around 0.05 ppm.



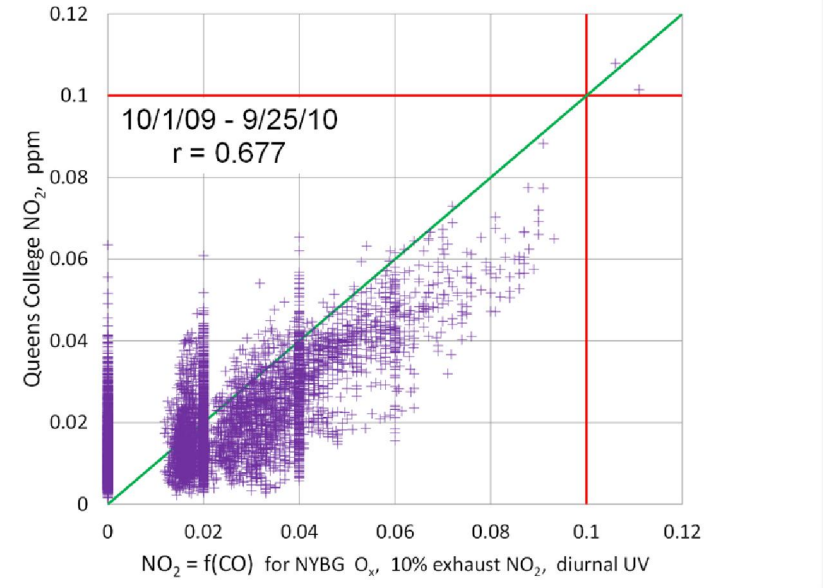
Nominal constant values for background oxidant and exhaust NO_2/NO_x, plus a simplistic diurnal modulation of the photolysis rate, yield adequate predictions of near-road NO_2 from NO_x.



Assuming the background oxidant to vary as observed at the NYBG yields a relationship that holds throughout the year.



We have used NO_x only as a proxy for emission rates and dispersion. Given a value for NO_x/CO in exhaust, we could equally well use CO. Unfortunately, CO data are cruder.



Crude as they are, however, CO data are still good enough to identify the probable NO_2 violations.

SUMMARY:

The near-road ***increment*** in NO_2 is no more mysterious than the increment in NO_x or CO or BC or any other traffic-related species.

It can be understood directly from exhaust emissions and atmospheric dispersion, with no need for complex chemistry.