Near-road measurements for nitrogen dioxide and its association with traffic exposure zones

Luther Smith [1], Shaibal Mukerjee [2*], Kasey Kovalcik [2], Elizabeth Sams [3], Casson Stallings [1], Edward Hudgens [3], James Scott [3], Todd Krantz [3], Lucas Neas [3]

[1] *Alion Science and Technology, Durham, North Carolina, USA*

[2] *U.S. Environmental Protection Agency, Office of Research and Development, National Exposure Research Laboratory, Research Triangle Park, North Carolina, USA*

[3] *U.S. Environmental Protection Agency, Office of Research and Development, National Health and Environmental Effects Research Laboratory, Research Triangle Park, North Carolina, USA*

ABSTRACT

Near-road measurements for nitrogen dioxide (NO_2) using passive air samplers were collected weekly in traffic exposure zones (TEZs) in the Research Triangle area of North Carolina (USA) during Fall 2014. Land use regression (LUR) analysis and pairwise comparisons of TEZs showed NO_2 concentrations were associated with TEZs. Greater NO_2 levels occurred in delay, high volume, and bus route sections versus higher signal light density, urbanized, and "remainder of study" areas. Comparison of near-road passively sampled NO_2 concentrations by TEZ agreed with previous real-time on-road comparisons for NO_2 in these TEZs.

Keywords: Geographic information system (GIS), land use regression (LUR), nitrogen dioxide (NO_2), passive sampler, traffic

1. Introduction

Gaseous and particulate emissions from traffic are major contributors to urban air pollution, especially near busy highways. During 2007, traffic pollutants from on-road vehicles accounted for 33% of nitrogen oxide (NO_x) emissions in the US (HEI, 2010). Nitrogen dioxide

(NO_2) is a component of NO_x and is a criteria air pollutant monitored by the US Environmental Protection Agency (EPA) for compliance and other purposes. The EPA has recently revised its monitoring requirements for NO_2 to include locations near roadways (EPA, 2010).

Nitrogen dioxide is linked to a number of adverse effects on the respiratory and cardiovascular systems as well as birth outcomes (Wilhelm and Ritz, 2003; McConnell et al., 2006; McCreanor et al., 2007; Chang et al., 2009; van den Hooven et al., 2009; Ward-Caviness et al., 2015). Consequently, NO_2 has been studied in numerous spatial-based epidemiology studies relating adverse health effects from exposure to traffic emissions in urban areas. Many of these studies assessing spatial differences of urban air pollutants have employed exposure prediction techniques known as land use regression models (LURs). In LURs, monitoring networks are typically established at a number of sites in an urban area using passive samplers or other field-portable air monitoring devices. Monitored data combined with geographic information system (GIS)-derived variables such as proximity to roadways are used to develop LURs. The LURs can be used to predict ambient levels at residential locations to assess health impacts. Since cost-effective passive samplers such as Ogawa® badges can be easily deployed to measure ambient NO_2, a majority of health and related LUR studies have used this sampling technology to assess spatial difference in NO_2 as a surrogate for traffic pollution (Jerrett et al., 2005; Hoek et al., 2008; Cohen et al., 2009; EPA, 2015). The EPA considers use of passive NO_2 samplers an important monitoring component to augment new NO_2 site location requirements for near road influence (Watkins and Baldauf, 2012).

Prior to the current study, EPA conducted an on-road mobile monitoring study (Brantley et al., 2014) in the Research Triangle area of North Carolina (USA) for NO_2 and other traffic pollutants in real-time at selected roadways and other areas known as traffic exposure zones

(TEZs). The TEZs were developed using detailed information on modeled traffic conditions and census data combined with GIS capabilities. The TEZs are generically described as: traffic delay, high traffic volume, transit routes, signal light density, urban areas, and remainder of the study area. Preliminary analysis of these on-road data suggested areas with large traffic delays showed significantly higher NO_2 concentrations than bus routes or high signal light density areas (Mukerjee et al., 2015).

This paper presents results of a follow-on study in which weeklong concentrations of NO_2 were measured in these TEZs using passive air samplers in near-road settings. Comparison of NO_2 between TEZs was conducted to assess spatial variability. In addition, the influence of TEZs on NO_2 levels was assessed through development of a regression equation (LUR). Evaluation of these TEZs have been used to assess cardiopulmonary association with traffic for the study area (Ward-Caviness et al., 2015). Estimates from the NO_2 LUR here are intended to be used to refine these traffic-health associations based on ambient measurements of near-road air pollution.

2. Methods

Six TEZs were evaluated in this study. Details on the definitions of TEZs are provided in Mukerjee et al. (2015). In brief, TEZs were: traffic delay zone (TEZ 6), high traffic volume > 40 000 vehicles per day (TEZ 5), public transit (bus) routes (TEZ 4), high signal light density (TEZ 3), urban area (TEZ 2), and remainder of study area (TEZ 1). The TEZ numbers indicate the mutually exclusive classification hierarchy; for example, though an area may have qualified as a traffic delay zone (TEZ 6) as well as a high traffic volume area (TEZ 5) or lower numbered TEZ, it was classified for this analysis as TEZ 6.

Ambient NO_2 concentrations were monitored at thirty near-road sites. The thirty sites were located in the North Carolina counties of Durham and Orange and were chosen to cover all TEZs with five sites in each TEZ. Sites (together with alternatives) were initially proposed based on geographic spread across the counties and use of ArcGIS software. Google Street View® was used to conduct an initial visual consideration of each site, and final site locations were based on field visits to ensure logistic feasibility, such as site access and safety. In addition, samples were collected at EPA's Ambient Air Innovative Research Site (AIRS) in Research Triangle Park to be used for precision estimation and evaluation of LUR performance. Figure 1 displays the monitoring site locations.

Samples were collected using Ogawa passive samplers (Ogawa & Co., Pompano Beach, Florida, USA). These sampling methods have been evaluated in laboratory and field studies by EPA (Mukerjee et al., 2004; Mukerjee et al., 2009) and used extensively elsewhere (Cohen et al., 2009; EPA, 2015). Excepting AIRS, the samplers were mounted on utility poles approximately 2.5 m above the ground and near roadways (< 50 m) for easy access. Samplers were sheltered in weathered PVC caps to minimize effects from wind and precipitation. Samples were collected on a weekly basis (Tuesday-Tuesday) by two teams between November 18 and December 16, 2014. Site visits began at approximately 9 am and were completed by approximately 11 am. Each team was responsible for the same set of sites each week, and sites were visited in the same order each week to minimize variability in sampling duration. The AIRS samples were collected separately, but on the same weekly schedule. Duplicate samples at AIRS were collected for three of the four weeks. Upon completion of each week's sample collection, samples were transported directly to the EPA facility for extraction and ion chromatography analysis.

Ion chromatography of the desorbed collection pad extracts was performed with a Dionex® ICS-2000 ion chromatograph using IonPac® AG14 guard (4 x 50 mm) and AS14 (4 x 250 mm) analytical columns (Thermo Scientific, Sunnyvale, California, USA). Samples were injected in duplicate to monitor analytical precision, using an AS40 auto-sampler through a 50 µL sample loop and separated with a 1 mM bicarbonate/3.5 mM carbonate eluent at a flow rate of 1.2 mL/min. External calibrations were performed using a Thermo Scientific 7 Anion Standard and Chromeleon® software.

Averaged NO_2 concentrations by TEZ were statistically analyzed via both pairwise comparisons of TEZs using the Wilcoxon rank sum test and the development of a regression equation (LUR) to predict average NO_2 concentration solely as a function of TEZ (i.e., $NO_2 = TEZ + \varepsilon$). The Wilcoxon test was chosen for the comparisons due to the small number of sites per TEZ. All statistical procedures were performed in SAS® Version 9.3. The SAS GLM procedure was employed in the regression analysis since TEZ is a categorical variable (SAS, 2004a; SAS, 2004b).

3. Results

No sample was below the method detection limit of 0.3 ppb for weeklong sampling. Individual weekly values ranged from 3.6 ppb (TEZ 1) to 33.9 ppb (TEZ 5). Average duplicate values at AIRS ranged from 10.6 to 15.8 ppb. Site averages across the four weeks ranged from 6.1 ppb (TEZ 1) to 25.5 ppb (TEZ 5). Of the eight trip blanks that were collected during the study, only one showed a nitrite chromatographic peak at twice the detection limit. For this reason, no blank correction was performed on the data set. Figure 2 displays the site averages by TEZ. Although results do not permit direct comparison with the NO_2 National Ambient Air

Quality Standard, reported concentrations were below the annual average NO_2 standard of 53 ppb (40 US Code, Part 50.11).

Duplicate sampling at the AIRS site yielded a coefficient of variation of 8.4%. Although restricted to three pairs, precision results were similar to those documented in previous EPA LUR studies using Ogawa samplers for NO_2 (Mukerjee et al., 2009; Smith et al., 2011; Mukerjee et al., 2012) and other exposure studies (Cohen et al., 2009).

Both the LUR and pairwise comparisons indicated a significant dependence of NO_2 on TEZ. The regression was significant ($p < .0001$) and had an R^2 value of 66%. Examination of residuals and diagnostics from leave-one-out cross-validation indicated no important departures from the necessary regression assumptions. Figure 3 displays the predicted values for each TEZ. As suggested by Figure 2, the regression equation indicated a progression of higher pollutant concentrations as the TEZ designation increased through the hierarchy.

Though located in TEZ 1, the AIRS site was not used to develop the regression equation, but to help in its evaluation by comparing predicted to measured NO_2 concentrations. Though the AIRS site average (13.9 ppb) was above the predicted value for TEZ 1 (8.6 ppb), it was within the range of the other TEZ 1 measured values (6.1 ppb – 15.1 ppb). As shown in Figure 2, the difference between the AIRS measured and predicted values was < 6 ppb.

Pairwise comparisons of average NO_2 concentration by TEZ were conducted using two-sided Wilcoxon rank sum tests with the magnitude of the differences given by Hodges-Lehmann estimates (Hollander and Wolfe, 1999). Table 1 reports the outcome of the tests and Hodges-Lehmann estimates of the differences. TEZ 1 showed lower concentrations than each of the other TEZs, at least at the 10% significance level. TEZ 2 was not statistically significantly different from TEZ 3, but was statistically significantly lower (at least at the 5% level) in concentration than either TEZs 4, 5, or 6. TEZ 3 was not significantly different than TEZ 4, but yielded lower concentrations than either TEZs 5 or 6. No statistically significant differences were found among TEZs 4, 5, and 6.

4. Discussion and Conclusion

Traffic pollutant NO_2 was measured at near-road TEZ locations in the Research Triangle study area. Confirming near-road traffic impact, both LUR analysis and TEZ pairwise comparisons found that average ambient NO_2 concentrations from passive air samplers were significantly associated with TEZ (see Table 1 and Figures 2 and 3). Greater average ambient NO_2 concentrations occurred for near-road sections characterized as traffic delay (TEZ 6), high traffic volume (TEZ 5), and bus routes (TEZ 4) than areas of higher signal light density (TEZ 3), urban areas (TEZ 2), or "remainder of the study area" (TEZ 1). For TEZs 3, 4, 5, and 6, the near-road results here parallel the comparisons of Mukerjee et al. (2015) using the on-road measurements of Brantley et al. (2014). That is, the ordering of TEZs with respect to NO_2 concentrations was similar, *i.e.*, generally higher concentration with higher numbered TEZs. Both studies found significant differences between TEZs 3 and 6. Mukerjee et al. (2015) found the on-road measurements yielded significantly higher concentration in TEZ 6 versus TEZ 4, while none was found here. Conversely, this study reports a higher NO_2 level in TEZ 5 compared to TEZ 3, while Mukerjee et al. (2015) did not find one. Neither study found a significant difference between TEZs 5 and 6 for NO_2.

In related health analyses, TEZs 5 and 6 were found to be associated with high-density lipoprotein cholesterol, a factor in the incidence of cardiovascular disease (Ward-Caviness et al, 2015). It is anticipated that the results of this study relating LUR-predicted NO_2 concentration to TEZs will be utilized in a future health analysis.

Though conducted in the same general area, significant methodological differences are noted between this TEZ study and the one in Mukerjee et al. (2015). Brantley et al. (2014) conducted on-road pollutant measurements recorded on a second-by-second basis, as opposed to this study with weeklong passive sampling at fixed sites relatively near roads. Secondly, the earlier study focused on the higher numbered TEZs, and TEZs 1 and 2 were not included in the analyses of Mukerjee et al. (2015). In contrast, the approach taken here explicitly sampled each TEZ with equal emphasis.

Notwithstanding these methodological differences, the results of the earlier study and this one are complementary. Since the overall findings of traffic impact for NO_2 between the two studies were similar, this suggests that passive sampling for NO_2 near roads may be a cost-effective and practical alternative to on-road measurements when comparing the impact of TEZs.

Due to logistical constraints, near-road TEZ associations with NO_2 were limited to the late Fall 2014. Seasonal differences can be influential in LURs (Smith et al., 2011; Mukerjee et al., 2012), and it would have been desirable to monitor across a broader time scale. In addition, monitoring was not conducted in neighboring Wake County, which is part of the Research Triangle area. However, visual examination of the TEZ map in Mukerjee et al. (2015) suggested that the occurrence of TEZs was comparable across the three counties.

Acknowledgements and Disclaimer

We thank Ronald Williams of EPA for providing passive sampler housings and shelters and reviewing this paper. We also thank Rachelle Duvall of EPA for reviewing the paper. Finally, we thank Duke Energy for allowing use of its utility poles for this study. The U.S. Environmental Protection Agency through its Office of Research and Development funded and managed the research described here under contract EP-D-10-070 to Alion Science and

Technology. The paper has been subjected to Agency review and approved for publication. Mention of trade names or commercial products does not constitute an endorsement or recommendation for use.

References

Brantley, H.L., Hagler, G.S.W., Kimbrough, E.S., Williams, R.W., Mukerjee, S., Neas, L.M., 2014. Mobile air monitoring data-processing strategies and effects on spatial air pollution trends. *Atmospheric Measurement Techniques* 7, 2169-2183.

Chang, J., Delfino, R.J., Gillen, D., Tjoa, T., Nickerson, B., Cooper, D., 2009. Repeated respiratory hospital encounters among children with asthma and residential proximity to traffic. *Occupational and Environmental Medicine* 66, 90-8.

Cohen, M.A., Adar, S.D., Allen, R.W., Avol, E., Curl C.L., Gould, T. Hardie, D., Ho, A., Kinney, P., Larson, T.V., Sampson, P., Sheppard, L., Stukovsky, K.D., Swan, S.S., Liu, L.S., Kaufman, J.D., 2009. Approach to estimating participant pollutant exposures in the multi-ethnic study of atherosclerosis and air pollution (MESA AIR). *Environmental Science and Technology* 43, 4687-4693.

EPA (US Environmental Protection Agency), , 2010. Primary National Ambient Air Quality Standards for Nitrogen Dioxide; Final Rule. *Federal Register* 75, 6473-6537.

EPA(US Environmental Protection Agency), 2015. Integrated Science Assessment for Oxides of Nitrogen–Health Criteria. EPA/600/R-14/006. EPA, Research Triangle Park, NC, 1135 pages.

HEI (Health Effects Institute), 2010. Traffic-Related Air Pollution: A Critical Review of the Literature on Emissions, Exposure, and Health Effects, HEI Special Report 17. Health Effects Institute, Boston, MA, 386 pages.

Hoek, G., Beelen, R., de Hoogh, K., Vienneau, D., Gulliver, J., Fischer, P., Briggs, D., 2008. A review of land-use regression models to assess spatial variation of outdoor air pollution. *Atmospheric Environment* 42, 7561-7578.

Hollander, M., Wolfe, D.A. 1999. *Nonparamteric Statistical Methods. 2nd Ed.*, Wiley, New York, p. 125.

Jerrett, M., Arain, A., Kanaroglou, P., Beckerman, B., Potoglou, D., Sahsuvaroglu, T., Morrison J., Giovis, C., 2005. A review and evaluation of intraurban air pollution exposure models. *Journal of Exposure Analysis and Environmental Epidemiology* 15, 185-204.

McConnell, R., Berhane, K., Yao, L., Jerrett, M., Lurmann, F., Gilliland, F., Künzli, N., Gauderman, J., Avol, E., Thomas, D., Peters, J., 2006. Traffic, susceptibility, and childhood asthma. *Environmental Health Perspectives* 114, 766–772.

McCreanor, J., Cullinan, P., Nieuwenhuijsen, M.J., Stewart-Evans, J., Malliarou, E., Jarup, L., Harrington, R., Svartengren, M., Han, I.K., Ohman-Strickland, P., Chung, K.F., Zhang J., 2007. Respiratory effects of exposure to diesel traffic in persons with asthma. *New England Journal of Medicine* 357, 2348–2358.

Mukerjee, S., Smith, L.A., Norris, G.A., Morandi, M.T., Gonzales, M., Noble, C.A., Neas, L.M., Ozakynak, A.H., 2004. Field Method Comparison between Passive Air Samplers and Continuous Monitors for Volatile Organic Compounds and NO_2 in El Paso, Texas. *Journal of the Air and Waste Management Association* 54, 307-319.

Mukerjee, S., Oliver, K.D., Seila, R.D., Jacumin, H.H., Croghan, C., Daughtrey, H., Neas, L.M., Smith, L.A., 2009. Field comparison of passive air samplers with reference monitors for ambient volatile organic compounds and nitrogen dioxide under week-long integrals. *Journal of Environmental Monitoring* 11, 220-227.

Mukerjee, S., Willis, R.D., Walker, J.T., Hammond, D., Norris, G.A., Smith, L.A., Welch, D.P., Peters, T.M., 2012. Seasonal effects in land use regression models for nitrogen dioxide, coarse particulate matter, and gaseous ammonia in Cleveland, Ohio. *Atmospheric Pollution Research* 3, 352-361.

Mukerjee, S., Smith, L., Brantley, H., Stallings, C., Neas, L., Kimbrough, S., Williams, R., 2015. Comparison of modeled traffic exposure zones using on-road air pollution measurements. *Atmospheric Pollution Research* 6, 82-87.

SAS, 2004a. Base SAS® 9.1.3 procedures guide. SAS Institute Inc., Cary, NC, pp. 524-550.

SAS, 2004b. SAS/STAT® 9.1 user's guide. SAS Institute Inc., Cary, NC, pp. 1291-1320, 3143-3162.

Smith, L.A., Mukerjee, S., Chung, K.C., Afghani, J. 2011. Spatial analysis and land use regression of VOCs and NO_2 in Dallas, Texas during two seasons. *Journal of Environmental Monitoring* 13, 999-1007.

van den Hooven, E.H., Jaddoe, V.W.V., de Kluizenaar ,Y., Hofman, A., Mackenbach, J.P., Steegers, E.A., Miedema, H.M.E., Pierik, F.H. 2009, Residential traffic exposure and pregnancy-related outcomes: a prospective birth cohort study. *Environmental Health* 8, doi: 10.1186/1476-069X-8-59.

Ward-Caviness, C., Kraus, W.E., Blach, C., Haynes, C., Dowdy, E., Miranda, M.L., Devlin, R., Diaz-Sanchez, D., Cascio, W.E., Mukerjee, S., Stallings, C., Smith, L.A., Gregory, S.G., Shah, S.H., Hauser, E.R., Neas, L. 2015. Association of traffic-related air pollution with fasting plasma glucose, insulin resistance, and specific metabolic risk factors for cardiovascular disease. *Environmental Health Perspectives* http://dx.doi.org/10.1289/ehp.1306980.

Watkins, N., Baldauf, R. 2012. *Near-road NO_2 Monitoring Technical Assistance Document. EPA-454/B-12-002.* EPA, Research Triangle Park, NC, 135 pages.

Wilhelm, M., Ritz, B. 2003. Residential proximity to traffic and adverse birth outcomes in Los Angeles County, California, 1994-1996. *Environmental Health Perspectives* 111, 207–216.

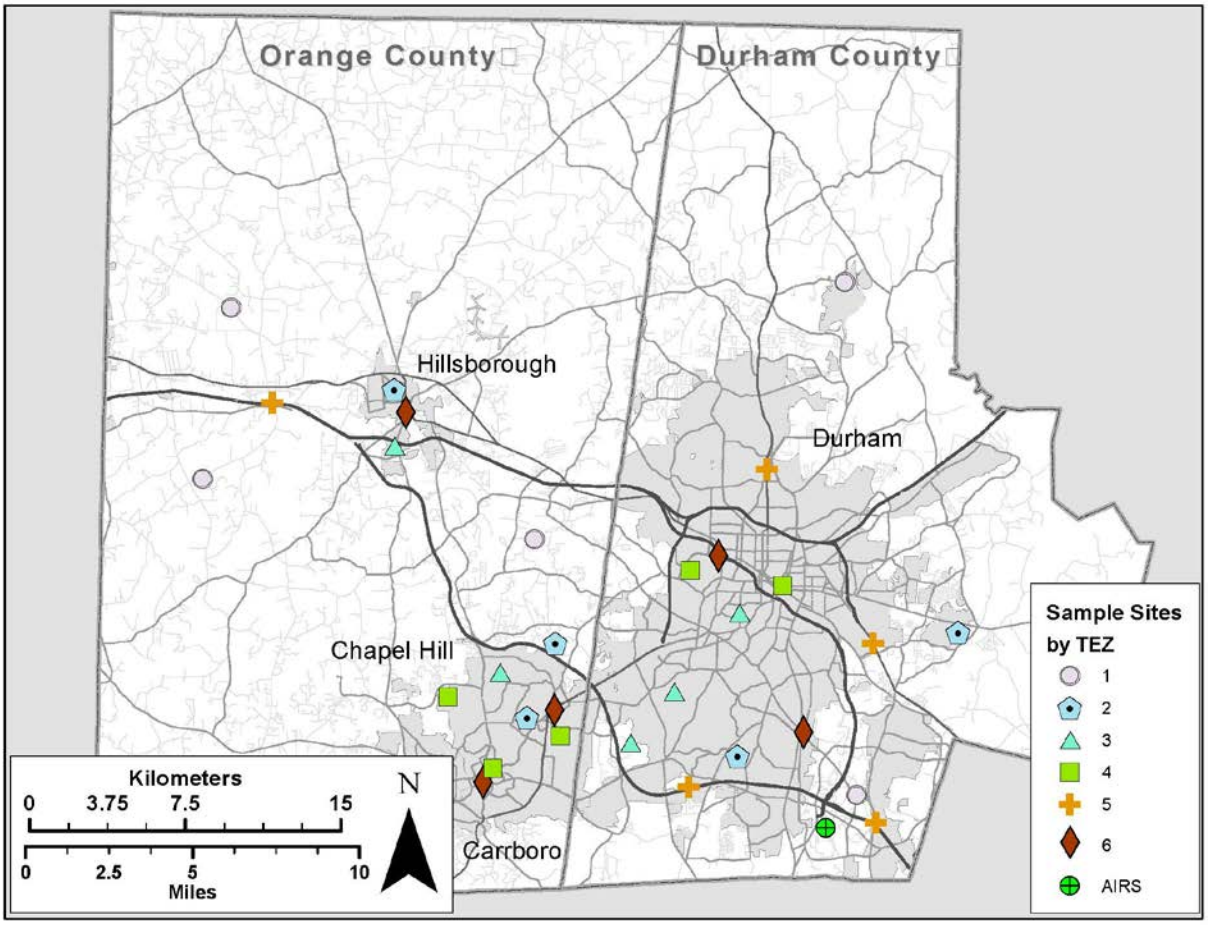

Orange County
Durham County
Hillsborough
Durham
Chapel Hill
Carrboro
Kilometers
0
3.75
7.5
15
0
2.5
5
10
Miles
N
Sample Sites
by TEZ
1
2
3
4
5
6
AIRS

Figure 1.

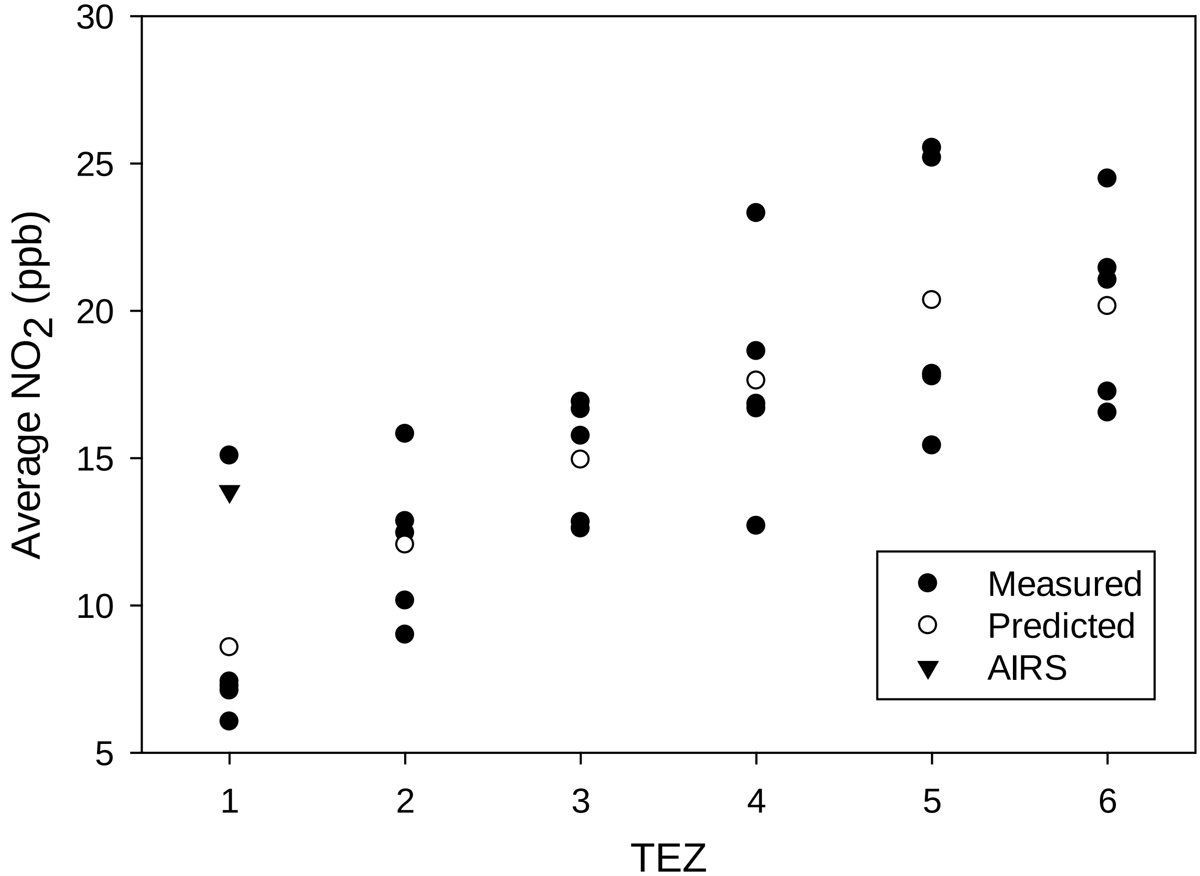
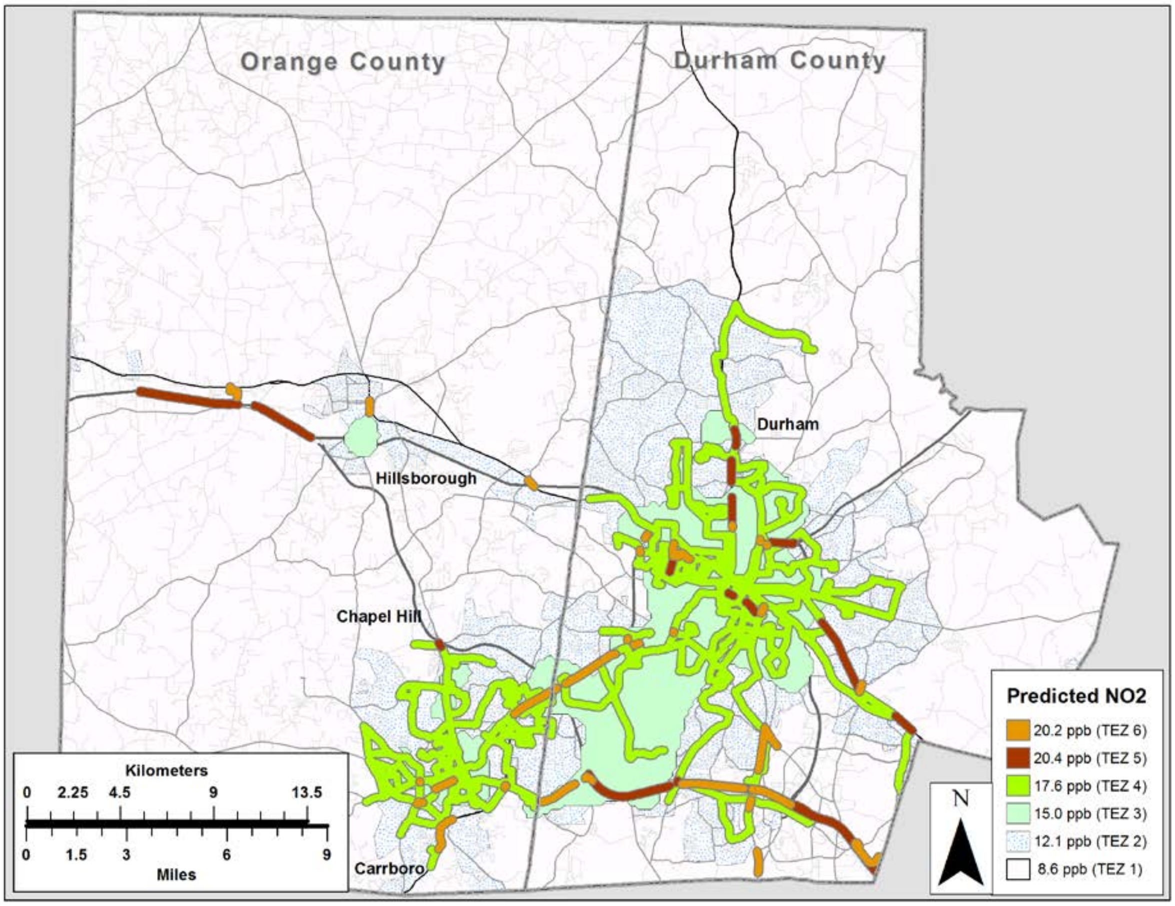

30
25
20
15
10
5
Average NO_2 (ppb)
1
2
3
4
5
6
TEZ
Measured
Predicted
AIRS

Figure 2.



Orange County
Durham County
Durham
Hillsborough
Chapel Hill
Carrboro
Kilometers
0 2.25 4.5 9 13.5
0 1.5 3 6 9
Miles
N
Predicted NO2
20.2 ppb (TEZ 6)
20.4 ppb (TEZ 5)
17.6 ppb (TEZ 4)
15.0 ppb (TEZ 3)
12.1 ppb (TEZ 2)
8.6 ppb (TEZ 1)

Figure 3.

Table 1. *Results of TEZ comparisons for NO_2*

TEZ comparison	p-value (two-sided)	> TEZ	Estimated difference (ppb)
1 vs. 2	.0952*	2	4.1
1 vs. 3	.0317**	3	6.8
1 vs. 4	.0163**	4	9.6
1 vs. 5	.0079***	5	10.6
1 vs. 6	.0090***	6	11.2
2 vs. 3	.1508	3	3.3
2 vs. 4	.0317**	4	5.8
2 vs. 5	.0159**	5	7.7
2 vs. 6	.0079***	6	8.2
3 vs. 4	.2222	4	2.0
3 vs. 5	.0556*	5	5.0
3 vs. 6	.0317**	6	4.6
4 vs. 5	.4206	5	1.9
4 vs. 6	.4206	6	2.8
5 vs. 6	.8413	5	0.6

*: Significant at the 10% level

**: Significant at the 5% level

***: Significant at the 1% level

> TEZ: indicates which of the pair is larger

Figure captions:

Figure 1. *Study area in North Carolina with monitoring sites associated with TEZs, as described in methods section.*

Figure 2. *Measured* NO_2 *concentrations by site and LUR predicted average* NO_2 *concentrations by TEZ.*

Figure 3. *Predicted* NO_2 *concentrations by TEZ in study area; a 200 m buffer around road segments is used to display TEZs 4 to 6.*