Atmospheric Pollution Research 6 (2015) 1082–1086

HOSTED BY

Contents lists available at ScienceDirect

Atmospheric Pollution Research

journal homepage: http://www.journals.elsevier.com/locate/apr

Original article

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

Luther Smith [a], Shaibal Mukerjee [b, *], Kasey Kovalcik [b], Elizabeth Sams [c], Casson Stallings [a], Edward Hudgens [c], James Scott [c], Todd Krantz [c], Lucas Neas [c]

[a] Alion Science and Technology, Durham, NC, USA
[b] U.S. Environmental Protection Agency, Office of Research and Development, National Exposure Research Laboratory, Research Triangle Park, NC, USA
[c] U.S. Environmental Protection Agency, Office of Research and Development, National Health and Environmental Effects Research Laboratory, Research Triangle Park, NC, USA

ARTICLE INFO

Article history:
Received 27 March 2015
Received in revised form
11 June 2015
Accepted 12 June 2015
Available online 12 October 2015

Keywords:
Geographic information system (GIS)
Land use regression (LUR)
Nitrogen dioxide (NO_2)
Passive sampler
Traffic

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.

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

* Corresponding author.
E-mail address: mukerjee.shaibal@epa.gov (S. Mukerjee).
Peer review under responsibility of Turkish National Committee for Air Pollution Research and Control.

http://dx.doi.org/10.1016/j.apr.2015.06.005

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 has 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. Fig. 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, 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 × 50 mm) and AS14 (4 × 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, 2004b).

3. Results

No sample was below the method detection limit of .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. Fig. 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, 2012; Smith et al., 2011) 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. Fig. 3 displays the predicted values for each TEZ. As suggested by Fig. 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 Fig. 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