UC Riverside
2018 Publications

Title
Development and evaluation of the R-LINE model algorithms to account for chemical transformation in the near-road environment

Permalink
https://escholarship.org/uc/item/51n841hj

Journal
Transportation Research Part D: Transport and Environment, 59

ISSN
13619209

Authors
Valencia, Alejandro
Venkatram, Akula
Heist, David
et al.

Publication Date
2018-03-01

DOI
10.1016/j.trd.2018.01.028

Peer reviewed

eScholarship.org Powered by the California Digital Library
University of California

Transportation Research Part D 59 (2018) 464–477

Contents lists available at ScienceDirect

Transportation Research Part D

journal homepage: www.elsevier.com/locate/trd

Development and evaluation of the R-LINE model algorithms to account for chemical transformation in the near-road environment

Alejandro Valencia[a], Akula Venkatram[d], David Heist[b], David Carruthers[c], Saravanan Arunachalam[a,*]

[a] Institute for the Environment, University of North Carolina at Chapel Hill, NC, USA
[b] US EPA, National Exposure Research Laboratory, Research Triangle Park, NC, USA
[c] Cambridge Environmental Research Consultants, Cambridge, UK
[d] University of California at Riverside, Riverside, CA, USA

ARTICLE INFO

Keywords:
Near-road
Dispersion modeling
R-LINE
GRS
Traffic emissions
Nitrogen oxides

ABSTRACT

With increased urbanization, there is increased mobility leading to higher amount of traffic-related activity on a global scale. Most NO_x from combustion sources (about 90–95%) are emitted as NO, which is then readily converted to NO_2 in the ambient air, while the remainder is emitted largely as NO_2. Thus, the bulk of ambient NO_2 is formed due to secondary production in the atmosphere, and which R-LINE cannot predict given that it can only model the dispersion of primary air pollutants. NO_2 concentrations near major roads are appreciably higher than those measured at monitors in existing networks in urban areas, motivating a need to incorporate a mechanism in R-LINE to account for NO_2 formation. To address this, we implemented three different approaches in order of increasing degrees of complexity and barrier to implementation from simplest to more complex. The first is an empirical approach based upon fitting a 4^{th} order polynomial to existing near-road observations across the continental U.S., the second involves a simplified Two-reaction chemical scheme, and the third involves a more detailed set of chemical reactions based upon the Generic Reaction Set (GRS) mechanism. All models were able to estimate more than 75% of concentrations within a factor of two of the near-road monitoring data and produced comparable performance statistics. These results indicate that the performance of the new R-LINE chemistry algorithms for predicting NO_2 is comparable to other models (i.e. ADMS-Roads with GRS), both showing less than ± 15% fractional bias and less than 45% normalized mean square error.

1. Introduction

Living, working, or attending school near major roadways has been associated with a range of health effects (Health Effects Institute, 2010; Vette et al., 2013). Additionally, it is estimated that as much 19% of the U.S. population are in the vicinity of roadways with significant traffic emissions (U.S. Census Bureau, 2007; Health Effects Institute, 2010; Rowangould, 2013). Therefore, understanding near-roadway pollutants and developing models for air quality prediction due to traffic-related emissions has been an area of ongoing research.

In the U.S, motor vehicles account for 60% of the nitrogen oxides ($NO + NO_2 = NO_x$) emissions (USEPA, 2010). In addition, exposure to NO_2 has been linked to adverse respiratory and cardiovascular effects (Samoli et al., 2006; Latza et al., 2009). Thus, the

* Corresponding author.
E-mail address: sarav@email.unc.edu (S. Arunachalam).

https://doi.org/10.1016/j.trd.2018.01.028

Available online 20 February 2018
1361-9209/ © 2018 Elsevier Ltd. All rights reserved.

U.S. Environmental Protection Agency (USEPA) has established NO_2 as one of six principal pollutants with National Ambient Air Quality Standards (NAAQS) to protect public health. The U.S. EPA set a 1-h form of NAAQS for NO_2 in 2010 (set at 100 ppb for a 98th percentile value, averaged over 3 years) to address adverse exposure due to high short-term peaks in the vicinity of the near-road environment. To support NO_2 NAAQS attainment designations, the EPA has also required to set air quality monitoring sites for NO_2 within 50 m from major roads (USEPA, 2010). Considering that robust spatiotemporal monitoring efforts can be cost prohibitive, air quality models (AQMs) can aid to assess NO_2 near roads where measurements from monitors are limited.

Numerous studies have been published which aim to simulate NO_2 and its evolution in the general atmosphere (Gardner and Dorling, 1999; American Petroleum Institute, 2013; Hendrick et al., 2013; Podrez, 2015). The recent USEPA White Papers on Planned Updates to the AERMOD Modeling System discuss improvements to NO_2 modeling in AERMOD (USEPA, 2017). Due to the growing interest in understanding traffic-related air pollutants, several studies have focused on directly modeling NO_2 near roadways (Hirtl and Baumann-Stanzer, 2007; Kenty et al., 2007; Chaney et al., 2011; During et al., 2011; Wang et al., 2011; Kimbrough et al., 2017). Most of these studies predict NO_2 using dispersion models such as CALINE (Benson, 1984), AERMOD (Cimorelli et al., 2005), and ADMS-Urban (McHugh et al., 1997).

The Research LINE source (R-LINE) model was specifically developed for these types of studies (Snyder et al., 2013). To better simulate mobile source pollutant dispersion, it has an emphasis on near-surface releases and near-source dispersion, and models traffic-related sources as line segments. However, R-LINE was designed to simulate primary, chemically inert pollutants. Even though R-LINE has been shown to adequately estimate near-road dispersion (Heist et al., 2013), it does not have the ability to simulate chemically reactive species such as NO_2. Thus, we will develop three methods that will allow R-LINE to simulate the chemical evolution of NO_2 in the atmosphere, and present inter-comparisons of these when compared to observations from a near-road case study.

The first is a linear regression method based on the Dixon-Middleton-Derwent (DMD) method (Dixon et al., 2001) that uses NO_x and NO_2 data from near-road monitors in the U.S. The second approach used to simulate NO_2 consists of a simplified (Two-reaction) chemistry scheme as described in Hess and Cope (1989). The third involves a more robust approach, using the Generic Reaction Set (GRS). All methods are driven with R-LINE, the Research LINE-source dispersion model specifically designed to simulate the dispersion of traffic-related emissions from roadways. NO_2 predictions from all three approaches are compared against near-road measurements along a section of Interstate 96 (I-96) in Detroit, Michigan, USA.

2. Methods

2.1. Study domain and field measurements

Foremost, to evaluate our study, we use data from a field campaign developed to assess the relationship between near-roadway air pollutant exposure and the respiratory outcomes of asthmatic children in the vicinity of major roadways in Detroit, MI (Vette et al., 2013). This study describes the design and methods to support the Near-Road Exposures and Effects of Urban Air Pollutants Study (NEXUS), and additional details about the measurements are available in Kimbrough et al. (2013). From this study, we use a section of I-96 just west of Detroit city limits, to model traffic-related air pollutants and compare against measurements from the field campaign.

Four monitoring sites were commissioned at locations 10 m, 100 m and 300 m north (and downwind) of I-96 around the Eliza Howell Park and another site 100 m south (and upwind) of I-96 (Fig. 1 shows the site locations). Measurements were recorded every 5 min from September 26, 2010 to June 20, 2011 for NO_x and NO_2. Traffic volume (activity) and speed measurements were also collected for each lane of I-96 from September 25, 2010 to April 27, 2011. From these traffic volume measurements, an average annual daily traffic (AADT) of approximately 140,000 vehicles per day was calculated.

Another monitoring station used in this study includes the AQS site at East 7 Mile Road with ID 26-163-0019 (Fig. 1) where hourly NO_2, NO_x, and O_3 concentrations were collected. This site is 22 km away from the I-96 measurement locations. At this distance, it is inside the Detroit metro area, but not influenced by major roads, since it is approximately 4 km away from any primary road and 2 km away from any secondary road. This monitor is used as urban background site to aid in the NO_x to NO_2 conversion schemes. Each conversion scheme uses this background site differently. More details follow in Section 2.3. Several plots describing the background site and how they compare to the I-96 sites have been included in Supplementary Information (Figs. S1, S2, and S5).

2.2. Dispersion models

2.2.1. R-LINE

As previously mentioned, we used the R-LINE dispersion model for this study. R-LINE is a research grade dispersion model developed for near-roadway assessments. The model uses a Gaussian, steady-state plume-dispersion formulation that incorporates newly developed algorithms for predicting concentrations from road sources at receptors near roads. Unlike AERMOD (EPA's recommended dispersion model), R-LINE was specifically designed to model roadways as line segments. A considerable number of models that simulate dispersion of roadways are analytical approximations to the integral associated with modeling a line source as a set of point sources. Nonetheless, these approximations can cause large errors when the winds are light and variable, when the wind direction is close to parallel to the road, and when the source and receptor are at different heights. R-LINE uses a Romberg numerical integration to compute the contribution of the point sources used to represent a line source. This approach incorporates governing processes without including errors associated with approximations of the underlying model framework (Snyder et al., 2013). Finally,

Fig. 1. The zoomed-in domain shows small white squares indicating the four monitoring sites at 10 m, 100 m and 300 m north of I-96 around the Eliza Howell Park and another site 100 m south of I-96. The yellow lines show the representative road links created to model the I-96 roadway segments. The expanded domain shows red lines segments from primary roads as described by the U.S. Census Bureau's Topologically Integrated Geographic Encoding and Referencing (TIGER) road data. The AQS site E 7 Mile Road (26-163-0019) used as representative urban background site is also shown by a small white square. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

when compared to four other models in a model inter-comparison study, R-LINE (while modeling only dispersion with no chemistry) showed comparable model performance statistics and even showed the least amount of fractional bias (Heist et al., 2013).

After a detailed analysis of wind patterns for the year 2010, the NEXUS study (Isakov et al., 2014) determined that, of the available National Weather Service Sites (Detroit City airport, Detroit Metro airport, Windsor airport) the Detroit City Airport site was the most representative of the study area for the local meteorology. This site also had the most data completeness objective. Hourly observations from this site in addition to the nearest upper air station (DTX-72632 Oakland County) were utilized to create the meteorological inputs. After land characteristics around Detroit City were established, we used the AERSURFACE model. Consequently, AERMET was used to process the meteorological data from the Detroit City airport and DTX upper air station to use as inputs for R-LINE. These meteorological inputs were also used to perform air quality modeling in support of the NEXUS study in Detroit. A wind rose plot is included in the Supplementary Information that describes the general wind direction and wind speed for the Detroit-City airport station (Fig. S3).

To represent the selected I-96 segment, two 2-km road links were created that roughly follow the path of the interstate and act as the main emission sources, as depicted in Fig. 1. In this study, a combination of the road network geometry, traffic volumes, temporal allocation factors, fleet mixes and pollutant-specific emission factors were used in combination with meteorological inputs to generate link-based hourly emissions as described by Snyder et al. (2014).

Hourly Emissions, E_i, (grams/mile) were calculated by applying emission factors, EF_i, (grams/vehicle/mile) and activity, A_i, (vehicles) for each road link, i, as shown in Eq. (1).

$$E_i = EF_i \times A_i \tag{1}$$

where

$$\mathrm{EF_i} = \sum_{\mathrm{veh.class}} \mathrm{ef_i(pollutant,speed,month,temperature)} \times \mathrm{fleet\ mix(vehicle\ class)} \tag{1a}$$

The ef_i is the vehicle-class-specific emission factor. When selecting the ef_i, observed speeds were used when available. If observed speed were not available, speeds were estimated according to hour of day. The *fleet mix* represents the fraction of vehicle class activity relative to the total fleet. Additionally, activity was characterized by observed traffic where available. If activity was not available, it was calculated as activity A_i,

$$A_i = AADT_i \times TAF_i(hour,day,month) \tag{2}$$

in which $AADT_i$ is the average annual daily traffic and TAF_i is the temporal allocation factor. More details on this method to calculate hourly emissions can be found in Snyder et al. (2014).

Once all aforementioned inputs were generated, we use the R-LINE dispersion model to estimate concentrations at the four receptor locations where measurements were taken.

2.2.2. ADMS-Roads

Using the meteorological and emission inputs from R-LINE, we ran ADMS-Roads (ADMS-Roads User Guide, 2011) to compare our model results to a previously published dispersion model with NO_2 chemistry. ADMS-Roads is a version of the Atmospheric Dispersion Modelling System (ADMS), a proprietary dispersion model developed by Cambridge Environmental Research Consultants (CERC). Like R-LINE, the ADMS-Roads model is specifically designed to simulate traffic sources as line segments. It also includes modules which account for the chemical conversion of NO_x. This includes the GRS (seven reactions) scheme with an additional slow reaction of NO with O_3 producing NO_2, as well as the simplified NO_x-to-NO_2 polynomial option developed by Derwent and Middleton (1996). The modeling for this study was carried out with ADMS-Roads version 4.1.1, which will be referred to throughout the paper as ADMS.

2.3. NO_x to NO_2 conversion schemes in dispersion models

The methods used to simulate NO_2 transformation in the atmosphere vary widely depending on the dispersion model. They range from empirically determining a NO_x-to-NO_2 ratio to more complex mechanisms with several chemical reactions. For regulatory applications, the U.S. EPA recommends the use of AERMOD to simulate NO_x and then using one of three tiered approaches to predict NO_2 depending on the application. The simplest approach, tier 1, would assume total conversion of NO_x-to-NO_2. Tier 2 assumes either a fixed NO_x-to-NO_2 ratio or determining a NO_x-to-NO_2 ratio using linear regression based on total NO_x levels. The linear regression was developed using nationwide correlated NO_2 and NO_x from the Air Quality System (AQS) data from 2001 to 2010. Finally, a tier 3 approach would consist of one of two methods that are similar in concept: the Ozone Limiting Method (OLM) and the Plume Volume Molar Ratio Method (PVMRM) (Cole and Summerhays, 1979; Hanrahan, 1999). Both of these methods are based on the same chemical assumptions of titration of NO by ozone to form NO_2. Even though both tier 3 methods can be used to simulate NO_2 near roadways, the U.S. EPA specifically recommends using the OLM method (USEPA, 2014), since PVMRM has issues estimating plume volumes near surface releases. Nonetheless, the OLM method is not designed to work with multiple sources, which is typical of modeling road sources. Moreover, both methods only account for the forward chemical production of NO_2 and neglect to consider the age of the plume when calculating O_3 and NO reaction rates. In the paper that develops the PVMRM method, Hanrahan et al. recommend that both these methods not be used to estimate NO_2 from motor vehicles (1999).

Very few, if any, studies have been published evaluating the OLM method or the PVMRM method near major roadways. However, several other methods (Derwent and Middleton, 1996; Romberg et al., 1996) were designed to predict NO_2 from NO_x in near-road environments using linear regression of measurements from sites near roads. These methods were evaluated against measurements near roads and even though point-to-point correlation between the model and observations were generally weak, these methods are successful in capturing average and maximum values (Hirtl and Baumann-Stanzer, 2007). Even though these methods have several assumptions, they offer a relatively simplistic way to estimate NO_2 when necessary inputs are not available.

As mentioned before, the Derwent-Middleton correlation has become a default technique to calculate NO_2 in the ADMS model. However, the recommended method for more detailed NO_2 modeling is the Generic Reaction Set or GRS (Azzi and Johnson, 1993). This chemical mechanism takes into account different background NO_x and O_3 concentrations, and thus requires these concentrations as inputs. Even though this method is more resource intensive, the GRS scheme has been applied to several other AQMs such as HYSPLIT (a Lagrangian model) (Draxler and Rolph, 2003), and DAUMOD (another dispersion model) (Pineda Rojas and Venegas, 2013). Additionally, GRS has been evaluated against measurements in several studies (Tonnesen and Jeffries, 1994; Venkatram et al., 1994; Stein et al., 2000; Chaney et al., 2011; Carruthers et al., 2017) and compared against the Derwent-Middleton method using ADMS (Vardoulakis et al., 2007). Results from the latter study conclude that better results are achieved by using GRS to estimate NO_2 than when using the Derwent-Middleton approach ($\sim$30% less fractional bias and normalized mean-square error when using GRS).

In order to simulate NO_2 using the R-LINE dispersion model, we developed and applied three distinct NO_x-to-NO_2 conversions: the Polynomial method, a simplified Two-reaction method, and the Generic Reaction Set (GRS) method. These approaches have varying barriers to implementation. They also have varying degrees of complexity that range from simple statistical approximations to more complex chemical mechanisms. These assumptions lead us to believe that the more complex approaches would potentially perform better, whereas the simpler approaches would be easier to implement by policy makers, albeit at the cost of accuracy in the estimation. We describe and evaluate each of these schemes below.

2.3.1. The polynomial method

This approach relies on empirical relationships between hourly NO_x and NO_2 first developed by Derwent and Middleton (Derwent and Middleton, 1996). Using a year of NO_x and NO_2 data at one near road site in London, NO_x concentrations were sorted into 10 ppb bins. These NO_x bins were paired to the corresponding NO_2 concentration in time. All values of NO_2 associated with a given NO_x bin were then averaged. A curve was fit through the bin averages for NO_2 versus the upper bin limit of NO_x to create a 4th order polynomial. This polynomial allows straightforward calculations of NO_2 from NO_x.

The above-mentioned approach was later improved by Dixon et al. (2001) by including 7 years of data from 1991 to 1997 at 12 distinct sites in London. Other than the difference in measurement sites, the Dixon, Middleton and Derwent approach also chose to

adjust the underlying form of the function to make it a dimensionless yield of NO_2 for the corresponding NO_x concentration. The yield can be defined as:

$$Y = \frac{[NO_2]}{[NO_x]} \tag{3}$$

where square brackets indicate the hourly mean concentration in ppb.

In this improved approach, the data are once again binned by sorted [NO_x] of 10 ppb and their corresponding [NO_2] concentrations; however, the curve is now fit through the bin averages for NO_2 over the upper bin limit of NO_x versus $f([NO_x])$, as opposed to [NO_2] versus $f([NO_x])$ in the Derwent-Middleton approach. These curves were fitted to [NO_x] and [NO_2] measurements assuming [NO_x] as an independent variable. We realize this is a significant simplification of the chemical processes that determine NO_2 yield and that the assumption of [NO_x] as a sole independent variable is potentially not justifiable. However, we find value in this method as a simple screening tool given its low barrier of implementation which is a need for characterizing local air-quality.

Different combinations of input data (e.g. using sites in the U.S. within 100 m from a primary road, using sites 300 m from a primary road, etc.) and different order polynomials were fit through these datasets. We use the leave-one-out approach to evaluate the polynomial. This iterative evaluation led us to the 4th order polynomial similar to the Dixon, Middleton and Derwent approach to calculate the yield of NO_2 to NO_x. Once the yield was calculated, it is multiplied by the [NO_x] to get the estimated [NO_2].

In the polynomial approach applied in this study, the Dixon, Middleton and Derwent method is used to create a 4^{th} order polynomial using collocated NO_2 and NO_x measurements gathered from the Air Quality System (AQS). Only AQS site measurements recorded at locations considered as "near road" by the U.S. EPA were used (USEPA, 2015). Of the 79 sites deemed as "near road" by the EPA, only 44 had collocated NO_x and NO_2 data. Data for these pollutants were collected and paired from January 2010 to May 2015 to create the polynomial, which has the following form:

$$Y = 0.38156784 - 0.35989596A + 1.06341137A^2 - 0.7146207A^3 + 0.13302576A^4 \tag{4}$$

where Y is the yield or NO_2-to-NO_x ratio, $A = \log_{10}([NO_x])$.

All significant figures were retained when calculating the polynomial. For $0 \leq [NO_x] \leq 15$ ppb, $Y(\log_{10}(15)) \approx 0.52$. The yield is then multiplied by the [NO_x] predicted by R-LINE to predict NO_2. After NO_2 values have been estimated, the corresponding hourly background NO_2 concentrations from the E 7 Mile Road AQS site were aggregated to the simulated concentrations. Note that this background site, which is few kilometers from the I-96 study locations, is still inside the Detroit metro area, but not influenced by emissions from major roads. In other studies, using this regression approach, either NO_x or NO_2 background concentrations are used to aid in the prediction of NO_2. For this study, we have chosen to use background NO_2 concentrations to remain consistent with both the Two-reaction and the GRS approach, which use background NO_2. Results and analysis for the polynomial approach using background NO_x concentrations (as a sensitivity analysis) can be found in the Supplementary Information (Table S2 and Fig. S6).

2.3.2. Simplified Two-reaction method

The second method used for NO_2 estimation uses a simplified chemistry scheme near the source, based on Hess and Cope (Hess and Cope, 1989).

We assume that NO_2 chemistry can be described by the following reactions:

$$NO_2 + h\nu \xrightarrow{r_1} NO + O_3 \tag{R1}$$

$$NO + O_3 \xrightarrow{r_2} NO_2 \tag{R2}$$

These reactions conserve $NO_x = NO + NO_2$ and $O_x = O_3 + NO_2$. If we assume that the background air is entrained into the plume at the source, the conserved quantities become

$$a = NO_x^b + NO_x^m, \tag{5}$$

$$b = O_x^b + O_x^m, \tag{6}$$

where the superscript b represents background values, and the superscript m represents modeled values. The modeled NO_2 corresponds to the modeled NO_x multiplied by the NO_2 *to* NO_x ratio at the source. The modeled O_3 at the source is zero. We assume a constant value of 0.2 for the NO_2 to NO_x ratio at the source. This constant is based on studies that show that NO_2 emissions from road traffic have a ratio in the range from 0.10 to 0.25 (Carslaw and Beevers, 2004; Carslaw, 2005; Mavroidis and Chaloulakou, 2011).

If we assume photo-stationarity,

$$NO_2 = (r_2/r_1)[NO][O_3] \tag{7}$$

Eqs. (5)–(7) yield the following solution for NO_2 (McRae et al., 1982):

$$NO_2 = \frac{1}{2}\left[\left(a + b + \frac{r_1}{r_2}\right) - \sqrt{\left(a + b + \frac{r_1}{r_2}\right)^2 - 4ab}\right] \tag{8}$$

2.3.3. The generic reaction set method

The final scheme used to predict NO_2 is the Generic Reaction Set (GRS) chemical mechanism. This mechanism is a simple yet popular scheme used by several dispersion and trajectory models to transform NO_x to NO_2, as mentioned before. GRS is a simplified semi-empirical photochemical model that consists of seven chemical reactions as shown in equations G1 to G7 and is based on Azzi et al. (1992) and Venkatram et al. (1994) where they separate transport and chemistry. This method includes hydrocarbon reactions, which were ignored in the previous Two-reaction method.

$$ROC + hv \rightarrow RP + ROC \quad \text{(G1)}$$

$$RP + NO \rightarrow NO_2 \quad \text{(G2)}$$

$$NO_2 + hv \rightarrow NO + O_3 \quad \text{(G3)}$$

$$NO + O_3 \rightarrow NO_2 \quad \text{(G4)}$$

$$RP + RP \rightarrow RP \quad \text{(G5)}$$

$$RP + NO_2 \rightarrow SGN \quad \text{(G6)}$$

$$RP + NO_2 \rightarrow SNGN \quad \text{(G7)}$$

where

ROC = Reactive Organic Compounds,
RP = Radical Pool,
SGN = Stable Gaseous Nitrogen products, and
SNGN = Stable Non-Gaseous Nitrogen products.

Reactions (G3) and (G4) represent chemically exact mechanisms, while the rest of the reactions are only approximate representations of their chemical counterparts. ROC in reaction (G1) can be taken to represent a single hydrocarbon and its organic reaction products, or a complex mixture of hydrocarbons and their organic reactions (e.g. Volatile Organic Compounds (VOC)). The rate constant for ROC photolysis was set according to Tonnesen (1994):

$$k_1 = \left(10{,}000e^{-\frac{4710}{T}}\right)k_3 \ (\text{min}^{-1}) \quad (9)$$

where T is temperature in K. The rate constants for Reactions (G2) and (G4) were parameterized according to Venkatram et al. (1994):

$$k_2 = 5482e^{\frac{242}{T}} \ (\text{ppm}^{-1}\,\text{min}^{-1}) \quad (10)$$

$$k_4 = 2643e^{\frac{-1370}{T}} \ (\text{ppm}^{-1}\,\text{min}^{-1}) \quad (11)$$

The NO_2 photolysis rate constant for Reaction (G3) was calculated from the zenith angle (estimated using the time of day and latitude of the Detroit City airport site) and the surface shortwave flux (the solar radiation at the earth's surface assuming clear skies). The remaining rate constants follow those in the original GRS scheme (Azzi et al., 1992).

The implementation of the GRS model within this framework is non-linear and requires adding the precursor contributions from all sources before integration. Thus, as opposed to the previously described Two-reaction method where only NO_x emissions were necessary, this method requires NO, NO_2 and VOC emissions.

Transport and chemistry have been uncoupled in this approach. In other words, the model calculates the dispersion of pollutants from the source first, and then the chemistry is applied to the interval of time associated with the age of the pollutant transported (Venkatram et al., 1994). The age is then calculated as a factor of wind speed, and distance between the source and receptor. The resultant age is taken to be the minimum of the "weighted mean ages" of NO_2 and NO, as shown in Eq. (12).

$$Age = \frac{\sum_{i=1}^{N} C_i d_i / w}{\sum_{i=1}^{N} C_i} \quad (12)$$

where

C_i is the concentration resulting from source i at the receptor,
d_i is the distance between source i and the receptor,
w is the wind speed, and
N is the number of sources.

3. Results and discussion

We first compared the dispersion of NO_x against the observations collected at the four I-96 sites. To accurately estimate total

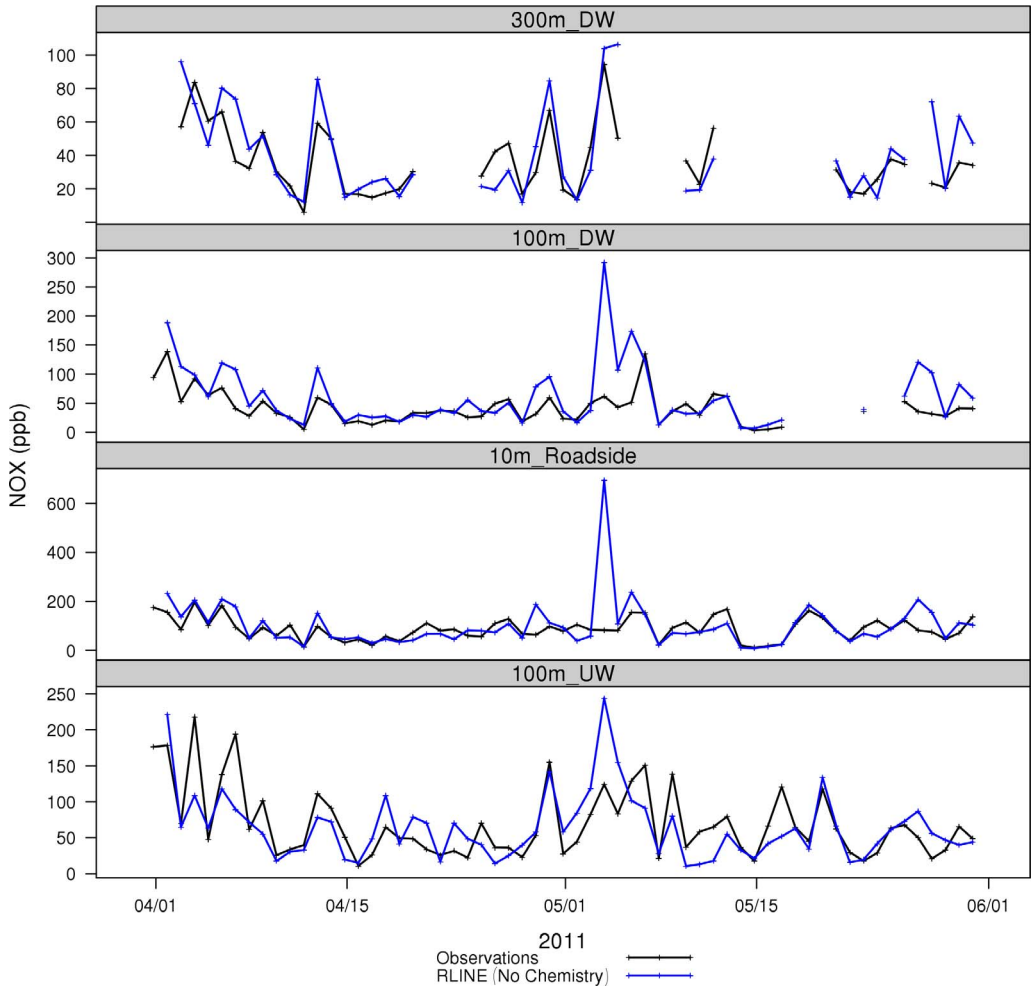

Fig. 2. Time series plot showing daily maximum modeled and observed NO_x concentrations during April and May 2011 at the four I-96 "near road" sites simulated with R-LINE. Modeled estimates represent dispersion without chemical transformation and have been aggregated with background concentrations from the E 7 Mile Road site.

concentrations, we added background NO_x to our modeled dispersion estimates to account for non-traffic-related sources that were not included in our simple two-road segment setup. This NO_x assessment allowed us to evaluate the dispersion model for a pollutant where the performance should be acceptable, i.e., most of the estimates would be within a factor of 2 of the observations. Due to the lack of overlap in availability between background AQS data and the measurement campaign at the I-96 receptors, the hourly simulations were exclusively conducted for the months of April and May of 2011. Thus, all results will be analyzed and presented only for the hours shown in Table S1 in the Supplementary Information. This table shows the total number of simulated hours at the I-96 sites paired to observations for each monitor in April and May.

The complete range of the modeled predictions can be seen from the time series plot in Fig. 2. These plots show the hourly maxima for each day for NO_x at the four I-96 sites. Gaps in the plot are due to missing data in the meteorology, the AQS background sites or the I-96 measurement site. Only daily maxima for days that have 18 hours or more of data are shown in the plot. Thus, even accounting for the missing data, the 10 m roadside and the 100 m downwind sites show the maxima for 61 days. However, the 100 m downwind site shows 59 days and the 300 m downwind site shows only 50 days' worth of maxima. At all sites, 83% of the modeled maxima are within a factor of two of the observations. The 10 m roadside estimate shows the most agreement with observations with 90% of the modeled maxima within a factor of two of the observations. These results imply that R-LINE is adequately capturing the daily maxima. Nonetheless, a distinct peak occurs on May 4th when the model overpredicts observations by a factor of 8. This is attributed to a difficulty in estimating concentration under very stable meteorological conditions: the wind-speed and the Monin–Obukhov length were close to zero. Under these conditions, R-LINE overestimates concentrations, as is typical of other dispersion models (Qian and Venkatram, 2011). More detailed model performance statistics for NO_x dispersion are found in Table 1.

As described in the previous section, three distinct approaches were used to model hourly NO_2 using R-LINE. Fig. 3 shows the time series plot of daily averaged NO_2 at the four I-96 sites. All three approaches have at least 88% of the modeled maxima within a factor of two of the observations at all sites. The GRS approach (93%) predicts daily maxima that are slightly better than the Polynomial

Table 1
NO_2 Model performance statistics for all sites for the 2-month duration of simulation.

		NO_x	NO_2			
		No chemistry	Polynomial	Two-reaction	GRS	ADMS w/GRS
Observed Mean	(ppb)	24.17	15.24			
Model mean	(ppb)	23.52	14.50	16.55	13.03	14.86
Mean bias	(ppb)	−0.648	−0.36	1.69	−1.84	−0.005
Mean error	(ppb)	10.74	5.67	6.82	5.57	5.22
FAC2		0.80	0.80	0.78	0.78	0.83
R		0.63	0.70	0.68	0.71	0.75
NMSE		0.91	0.34	0.44	0.31	0.24
FB		0.02	−0.024	−0.11	0.13	0.0003
Number of hours		5008	5008	5008	5008	5008

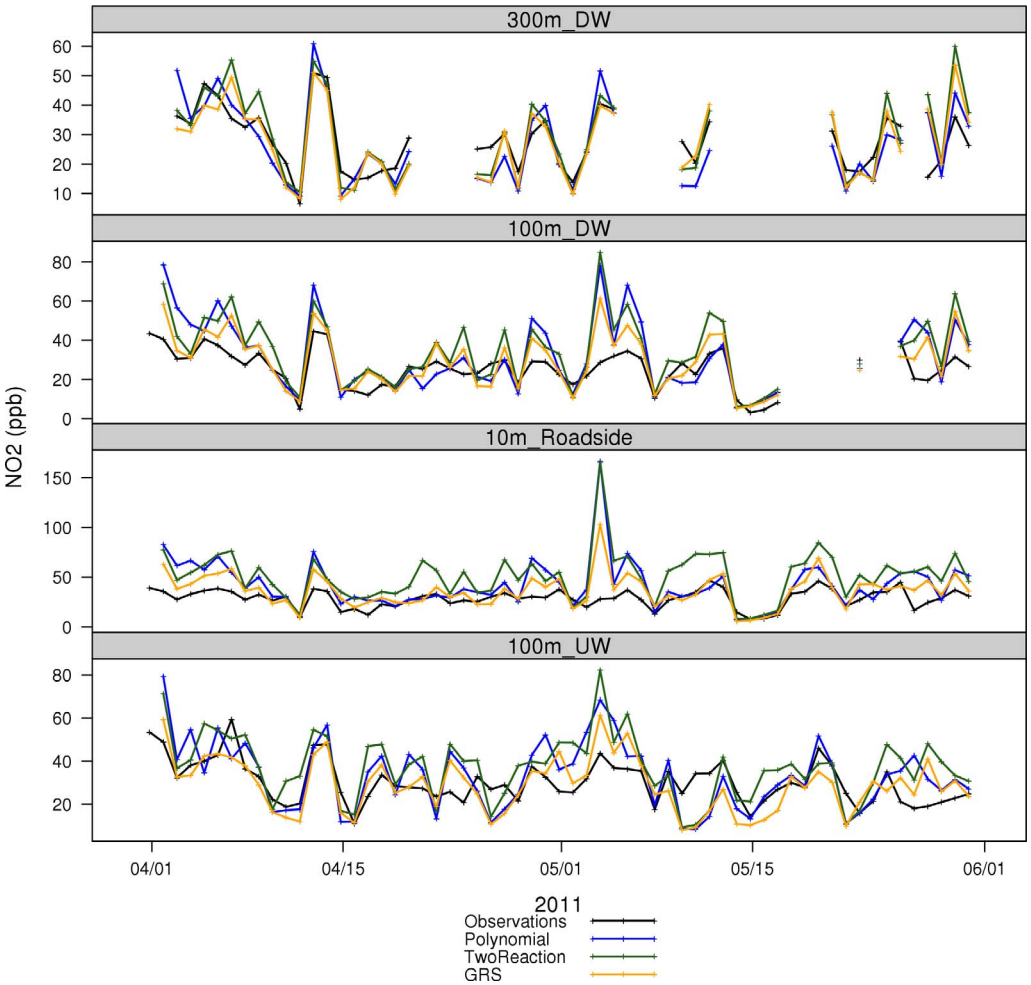

Fig. 3. Time series plot showing daily maximum modeled and observed NO_2 concentrations during April and May 2011 at the four I-96 "near road" sites simulated with the polynomial approach, the simplified Two-reaction approach and the GRS mechanism.

(90%) and the Two-reaction (88%) approach. All three approaches show the best performance predicting the daily maxima at the 300 m downwind site, with around 97% of the maxima within a factor of two of the observations. This is an interesting result given that at this distance, concentrations are likely to be more influenced by background concentrations than the road sources. A time series plot of daily maxima (and means) NO_2, NO_x and O_3 for the background site can be found in the Supplementary Information (Figs. S1 and S2). Finally, the same peak prediction of NO_x without chemistry on May 4th persists in predicting NO_2 for all 3 approaches. This is attributed to the poor performance of the dispersion model on that day, as mentioned previously.

The boxplots in Fig. 4 show the distribution of the log hourly NO_x without chemistry and NO_2 from all three NO_2 conversion

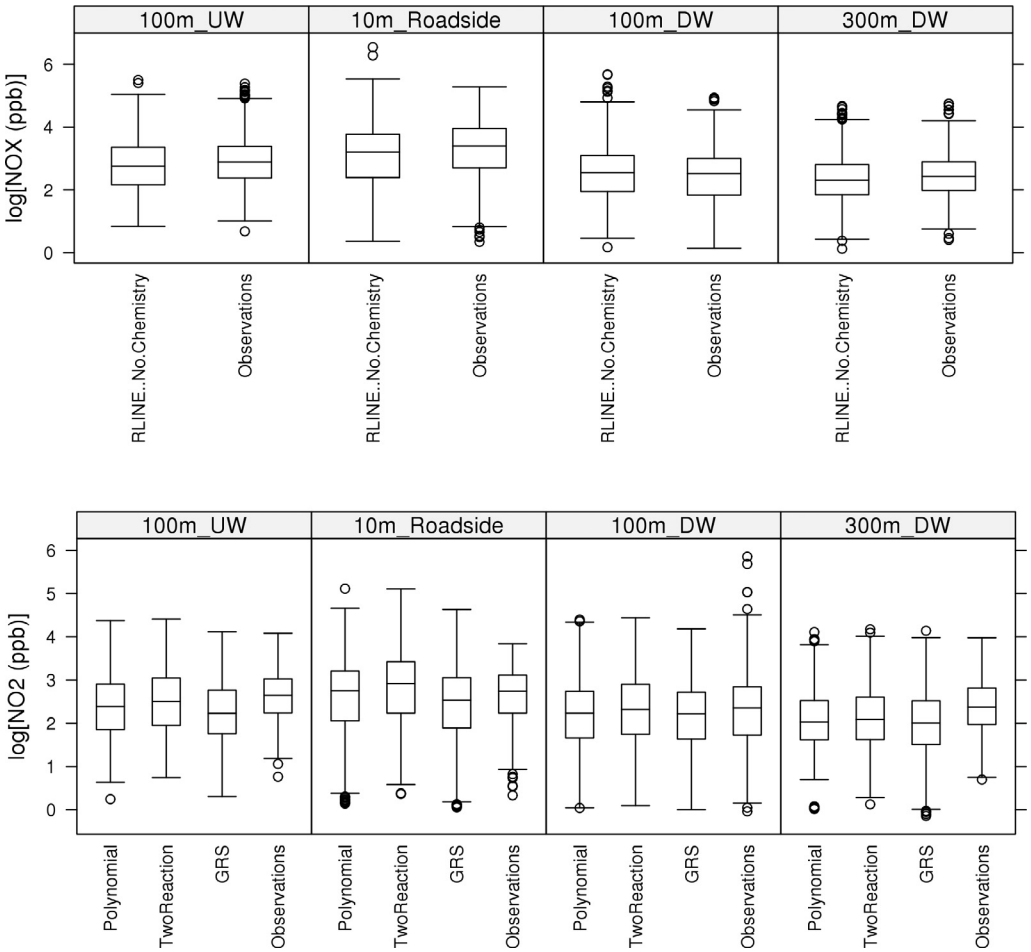

Fig. 4. Box-and-whisker plots showing distribution of the log of hourly observed and modeled NO_x (above) and NO_2 (below) concentrations during April and May 2011 at the four I-96 "near road" sites simulated with the polynomial approach, the simplified Two-reaction approach and the GRS mechanism. The box represents the middle 50% of the data, extending from the 25th to the 75th percentiles; the horizontal line through the center of the box is the median; the whiskers represent 1.5*IQR (the inter-quartile range is the range from the 25th to 75th percentiles); the points are outliers above and below 1.5*IQR.

schemes, compared against observations from the four I-96 monitoring sites. The NO_x boxplot shows differences of less than 2 ppb for 25th, 50th, and 75th quartiles at most sites. The 10 m roadside site shows the most deviations from observations with 5–10 ppb differences from the observed quartiles. These distributions show general underestimation at all sites except for the 100 m downwind site. The NO_2 distribution for all three approaches, on the other hand, are within ~2 ppb from the observed 25th, 50th, and 75th quartiles at most sites. The biggest deviations from observations are seen at higher concentrations in the 75th percentile. Specifically, the Two-reaction approach shows an overestimate of ~8 ppb of the 75th percentile at the 10 m roadside site, the GRS approach shows an underestimation of ~5 ppb at the 100 m upwind site and the polynomial approach underestimates this measure by ~4 ppb at the 300 m downwind site. This shows a general trend where both the GRS and the Polynomial approach show slight underestimation at higher concentrations and the Two-reaction approach shows overestimation at higher concentrations. Of the three approaches, the Two-reaction approach is the most conservative. Overall, it predicts higher concentrations than both the polynomial and the GRS approach. Thus, it consistently shows medians that range from 1 ppb higher at the 300 m downwind site to ~5 ppb higher than both the polynomial and the GRS approach at the 10 m roadside site. When NO_2 predictions are compared alongside NO_x predictions, the 300 m downwind site shows that all approaches underpredict NO_2, similar to NO_x. The biggest deviations are seen in the 10 m roadside site where both the polynomial and the Two-reaction approach overpredict NO_2 while the GRS, conversely, underpredicts NO_2 following the trend of predicted NO_x.

The hourly diurnal trend displayed in Fig. 5 gives some insight into specific hours where the model differs from the observations at the 10 m roadside site. This diurnal plot shows the median at every hour for April and May 2011 as lines and the boxes show the interquartile range (IQR) of the distribution of each of those hours for NO_x without any chemistry and all NO_2 conversion approaches. Given gaps in the dataset, the number of data points used to create the IQR boxes differ each hour. From 59 to 61 non-missing concentrations available per hour, the IQR represents between 29 and 31 non-missing concentrations depending on the time of day. Thus, if we have the maximum number of concentrations available (31 data points) the shaded box represents the 16th to the

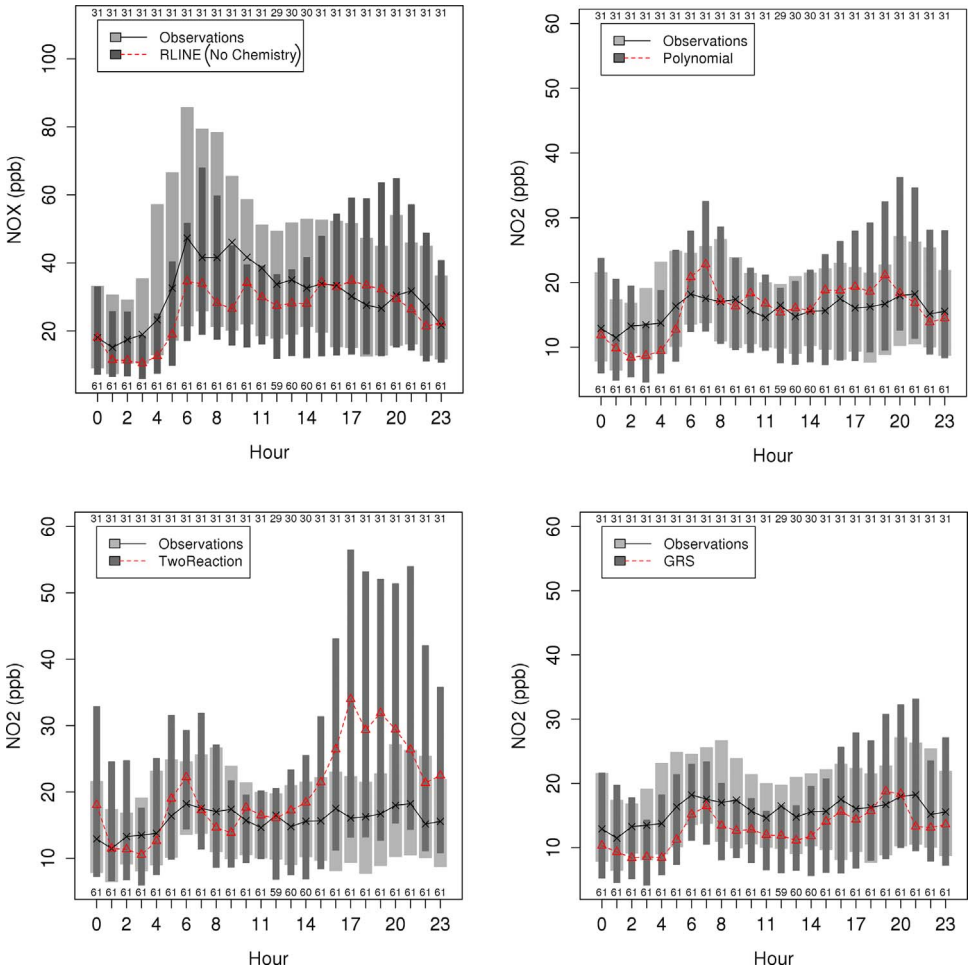

Fig. 5. Hourly diurnal trend observed and modeled NO_x and NO_2 concentrations during April and May 2011 at the 10 m roadside site with no chemistry (top left), the polynomial approach (top right), the simplified Two-reaction approach (bottom left) and the GRS mechanism (bottom right). The shaded boxes represent the inter-quartile range of the observations and model predictions, while the lines represent the median of the observations and model predictions. The numbers below each shaded box represent the number of days that had non-missing concentrations for each hour. The number above each shaded box represents the number of days that had non-missing concentrations in the IQR for each hour.

46th data points. The median is calculated using the number of hours shown in Table S1. The NO_x diurnal plot shows underestimation of the median for the majority of hours. Deviation from the median ranges from an underestimation of 20 ppb at hour 9 to an overestimation of 6 ppb at hour 18. Moreover, the model successfully captures the peak median concentration at hour 6, where both the model without chemistry and the observations have the highest medians, 35 ppb and 47 ppb, respectively. However, observations show a steep decline of 20 ppb from hour 6 to hour 20, while the modeled concentrations remain level. NO_2 predictions with chemical conversion, on the other hand, show distinct peaks in the morning and evening. The polynomial and the GRS approach show peaks at hours 7 and 19, while the Two-reaction approach shows peaks earlier in the day at hours 6 and 17. The observations, on the other hand, show less defined peaks which is contrary to NO_x observations. The polynomial shows that the highest median concentrations occur earlier in the day with 22.8 ppb, while the highest medians in the Two-reaction approach and the GRS approach occur later in the day with 34.0 ppb and 18.4 ppb, respectively. The GRS approach underpredicts the median at all hours except hours 19 and 20, while both the polynomial approach and the simplified Two-reaction approach show almost evenly distributed under-prediction and overprediction depending on the hour of the day. It is of note that the simplified Two-reaction shows most of the overprediction in the evening hours where the modeled distribution shows a range twice that of the observations. The main difference between the GRS and the Two-reaction approach is that the GRS has a time dependent component. Thus, NO, NO_x and O_3 have often not achieved equilibrium with higher proximity to the road and the VOC reactions have but a small contribution to the creation of NO_2. This explains why, generally, GRS has lower NO_2 predictions than the Two-reaction approach, especially at sites closer to the road. Overall, both the polynomial approach and the GRS approach capture the diurnal trend of the measurements better than the Two-reaction approach. It is of note, that the GRS approach is the only chemical conversion scheme that has NO_2 following the modeled NO_x diurnal pattern. This pattern consists of underprediction in the morning and early afternoon with slight over-prediction in the late afternoon.

In Table 1 model performance statistics have been calculated for all monitors using hourly predictions that are paired in time and space over the entire two-month period. In our analysis, we evaluated all three NO_2 chemical transformation approaches developed in R-LINE for this study. In addition, we also included the ADMS with GRS simulation to compare our R-LINE based predictions to an alternate model. Since we combined the metrics for all four sites, we calculated the statistics for a total of 5008 hours during the 2-month period from April – May 2011. The number of observed and modeled pairs is less than the total in Table S1 (by ~5%) since ADMS simulated fewer hours of meteorology from the modeling due to input meteorological parameters being outside the criteria for inclusion. The performance statistics include Mean Bias, Mean Error, the correlation coefficient (R), the fraction of predictions within a factor of two of observations (FAC2), the root mean squared error (RMSE), Fractional Bias (FB), and Normalized Mean Square Error (NMSE) as described in Chang and Hanna (2004):

$$Mean\ Bias = \frac{1}{N}\sum (M_i - O_i) \tag{13}$$

$$Mean\ Error = \frac{1}{N}\sum |M_i - O_i| \tag{14}$$

$$FAC2 = \text{Fraction of data that satisfy} \tag{15}$$

$$0.5 \leqslant \frac{M_i}{O_i} \leqslant 2.0$$

$$R = \frac{\overline{(O_i - \overline{O})(M_i - \overline{M})}}{\sigma_O \sigma_M} \tag{16}$$

$$FB = 2\left(\frac{\overline{O} - \overline{M}}{\overline{O} + \overline{M}}\right) \tag{17}$$

$$NMSE = \frac{\overline{(O_i - M_i)^2}}{\overline{O} \times \overline{M}} \tag{18}$$

where

M is the model prediction,
is the observation,
Overbar ($\overline{M}$) is the average for the dataset, and
σ_M is the standard deviation for the dataset.

Of the three approaches developed for R-LINE, Table 1 demonstrates that the simplified polynomial approach shows the least bias among R-LINE predictions with a FB of −0.024 while the GRS approach shows the most bias with FB of 0.13. While GRS shows the least error with a NMSE of 0.31, the Two-reaction approach shows the most error with a NMSE of 0.44. FB based on a linear scale reflects systematic bias, while NMSE being a measure of scatter reflects both systematic and unsystematic (random) errors, and thus provides additional insight into the models and the metrics. Additionally, more than two-thirds of the predictions from these three approaches are within a factor of 2 of the observations. Altogether, model performance of these chemical conversion schemes is comparable. When comparing all three R-LINE approaches to ADMS with GRS, ADMS shows the best performance. It has the lowest NMSE and FB, 0.24 and 0.0003, respectively and the highest correlation coefficient and FAC2, 0.75 and 0.83, respectively, though not substantially different from the R-LINE based metrics. These results are consistent with the inter-comparison tracer study described by Heist et al.'s (2013), where they compare several dispersion models including R-LINE, and ADMS.

An ideal model will be the one with R = 1, FAC2 = 1, NMSE = 0, and FB = 0. According to Kumar et al. (1993), the performance of a model can be deemed as acceptable if NMSE < = 0.5, −0.5 < = FB < = 0.5, and FAC2 > 0.85. Chang and Hanna (2004) have additional suggestions concerning the magnitudes of the performance measures expected of a "good" model. This includes a FAC2 of about 50% and a Relative Mean Bias, (FB), within ± 30% of the mean (Chang and Hanna, 2004). According to these parameters all of the approaches developed for R-LINE show good/acceptable model performance. In addition, a soccer plot showing Normalized Mean Error vs. Normalized Mean Bias at each of the 4 modeled sites for the polynomial approach, the simplified Two-reaction approach, the GRS mechanism and ADMS with GRS is included in the supplemental material (Fig. S4).

According to Carruthers et al., the evaluation of simulated NO_2 and NO_x should be paired and a "good" performance of a chemistry approach should be judged on its consistency to predicted NO_2 alongside NO_x (e.g. if NO_x is underpredicted so should NO_2) (2017). Throughout our evaluation (overall distribution, diurnal trends, and statistical bias), the GRS approach shows the most consistency underpredicting or overpredicting NO_2 alongside the modeled NO_x. For example, both R-LINE and ADMS models using GRS show positive fractional bias alongside predicted NO_x (0.13, 0.0003, and 0.02, respectively), while the polynomial and the Two-reaction show negative fractional bias (−0.024 and −0.11, respectively).

Even though all methods show good model performance as defined by both Kumar et al. (1993) and Chang and Hanna (2004), each approach has limitations that should be noted. The polynomial approach summarizes data with significant scatter, thus the calculated yield has significant uncertainty. Both the Two-reaction approach and the GRS mechanism to a varying degree summarize complex chemical reactions to estimate NO_2. This is also a source of uncertainty. Moreover, the latter methods assume that all O_3

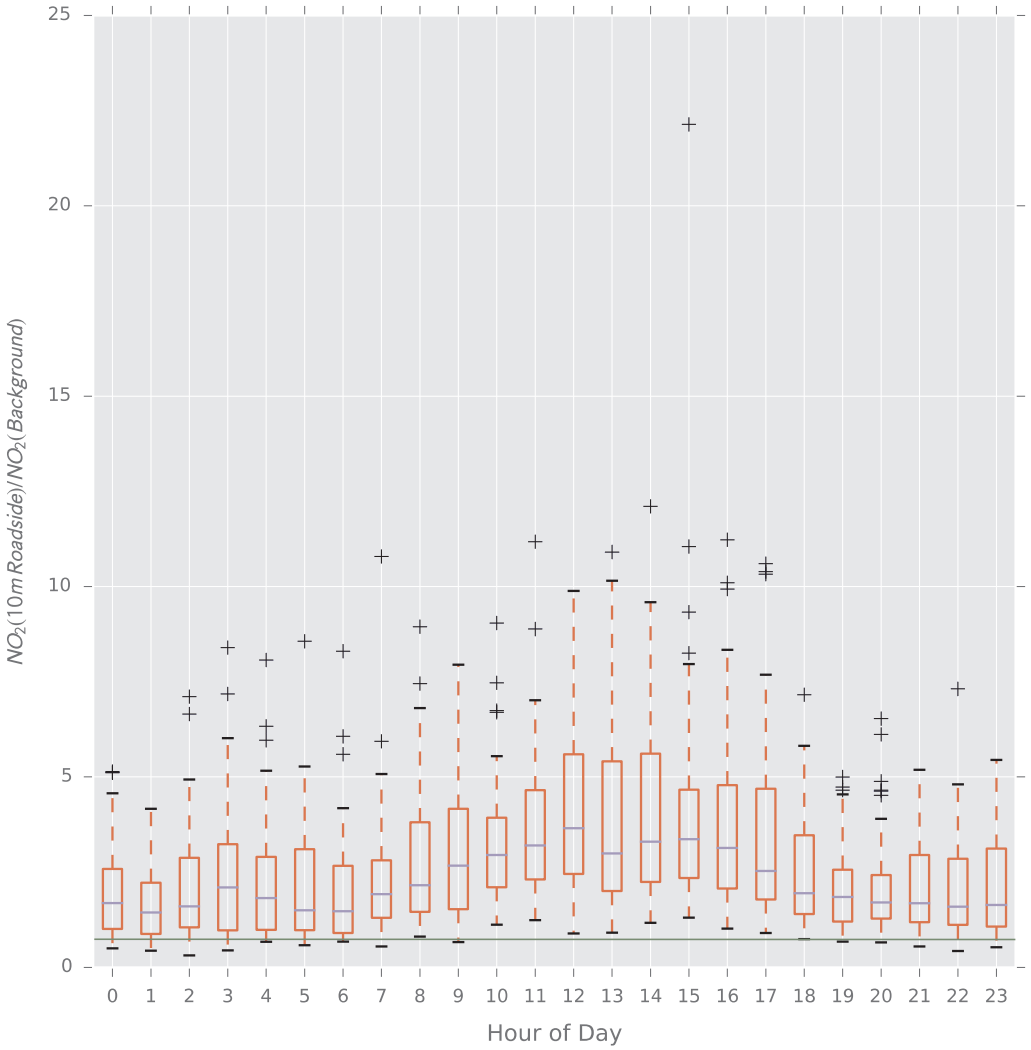

Fig. 6. Hourly proportion of observed NO_2 concentrations over background NO_2 concentrations during April and May 2011 at the 10 m Roadside site. The box represents the middle 50% of the data, extending from the 25th to the 75th percentiles; the horizontal line through the center of the box is the median; the whiskers represent 1.5*IQR (the inter-quartile range is the range from the 25^{th} to 75^{th} percentiles); the points are outliers above and below 1.5*IQR. The green line represents the point when concentrations at the 10 m measurement site is equal to the background site. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

background is available for chemical conversion, even though in reality it might be shared between individual plumes. This assumption can certainly overestimate the O_3 available for NO_x chemistry.

A significant assumption made in this study relies on the observations from the E 7 Mile Road AQS site being a fair estimate of what background concentrations would be in Detroit. Fig. 6 shows the impact of background on each hour by showing the proportion of observed NO_2 concentrations at the 10 m roadside site over concentrations at the background site. Generally, all hours at the 10 m roadside site have at least 75% records above the background observations. During the day (hours 8–17), the distribution of concentrations above background is even higher, up to 99%. At these peak traffic hours, contribution from the road sources are the highest and background concentrations are small compared to the contribution from the road sources. However, at night, more records show that the concentrations at the background site are higher than those at the 10 m roadside site. This is still a significantly smaller proportion of records than during the day. And the magnitudes to which the background is higher than the 10 m site concentrations are not more than a factor of 2. Still, the model would overestimates the observed measurements at these hours given that the background is higher than 10 m site measurement. This analysis highlights the importance of the background concentrations to appropriately predict concentrations that match measurements at near-roadway sites.

All three approaches require knowledge of background concentrations. These concentrations are not easily measured or estimated. Given that a site that measures O_3, NO_2, and NO and is also considered an urban background site is not readily available in all study domains, it can become a significant limitation when trying to apply any of the methods to a region. One option to improve on this limitation would be to attempt to use existing techniques to estimate background concentrations, such as the space-time ordinary

kriging (STOK) approach to develop background concentrations in support of the NEXUS study (Arunachalam et al., 2014). Further research on the latter point would require a sensitivity analysis on how exactly background concentration may affect NO_2 predictions.

Other future work that might improve on this study would entail evaluating all three approaches at different regions types (i.e., varying types of urban environments to more rural settings) and assess how well each approach predicts NO_2 in different environments. Additional stress testing would involve evaluating the algorithms during different meteorological conditions (to explore seasonality) to assess how each method behaves with varying winds, temperatures, etc. Once several tests are identified, a bootstrapping resampling method can be set up to make sure that differences in model performances are statistically significant.

4. Conclusions

In this study, we described the development and evaluation of three new model algorithms for NO_x chemistry in the R-LINE near-road dispersion model for on-road traffic sources. When compared against near-road monitoring data from I-96 in Detroit, Michigan, the results indicate that the implementation of the new R-LINE chemistry algorithms showed model performance defined as acceptable/good for dispersion models. ADMS using GRS used as a reference modeling approach shows slightly better performance, with least error overall.

The polynomial method shows the least bias with a FB of -0.024, and the GRS shows least error with a NMSE of 0.31. Even though, the model performance for all approaches is similar, the GRS method, which relies on chemical processes shows the most consistency in predicting NO_2 when evaluated alongside modeled NO_x.

Acknowledgements

The U.S. Environmental Protection Agency, through its Office of Research and Development, partially funded and collaborated in the research described here under Contract EP-W-09-023 to the University of North Carolina at Chapel Hill. This paper has been subjected to Agency review and approved for publication. Approval does not signify that the contents reflect the views of the Agency nor does mention of trade names or commercial products constitute endorsement or recommendation for use. We also acknowledge the funding from Health Effects Institute under a sub-award from the University of Michigan at Ann Arbor. And finally, we thank Vlad Isakov of the U.S. EPA and Michelle Snyder of the UNC's Institute for the Environment for their inputs and helpful discussions while implementing the NO_2 algorithms in the R-LINE model, and Kate Johnson of Cambridge Environmental Research Consultants for assistance with the ADMS-Roads simulations. We gratefully acknowledge the two anonymous reviewers for their helpful comments.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.trd.2018.01.028.

References

ADMS-Roads, An Air Quality Management System, User Guide, Version 3.1, September 2011.
Cambridge Environmental Research Consultants Ltd., Cambridge, UK.
American Petroleum Institute, 2013. Ambient ratio method version 2 (ARM2) for use with AERMOD for 1-hr NO2 modeling: Development and evaluation report. (Development and Evaluation Report), Washington, DC.
Arunachalam, S., Valencia, A., Akita, Y., Serre, M.L., Omary, M., Garcia, V., Isakov, V., 2014. A method for estimating urban background concentrations in support of hybrid air pollution modeling for environmental health studies. Int. J. Environ. Res. Public Health 11 (10), 10518–10536.
Azzi, M., Johnson, G., Cope, M., 1992. An introduction to the generic reaction set photochemical smog mechanism. Paper presented at the Proceedings of the 11th International Clean Air and Environment Conference, Brisbane. (Clean Air Society of Australia and New Zealand).
Azzi, M., Johnson, G.M., 1993. Airtrak: new developments. Clean Air: J. Clean Air Soc. Aust. New Zealand 27 (4), 191.
Benson, P.E., 1984. CALINE4—a dispersion model for predict- ing air pollutant concentrations near roadways. (Report No. FHWA/CA/TL-84-15.) State of California, Department of Transportation.
Carruthers, D.J., Stocker, J.R., Ellis, A., Seaton, M.D., Smith, S.E., 2017. Evaluation of an explicit NOx chemistry method in AERMOD. J. Air Waste Manage. Assoc. 67 (6), 702–712.
Carslaw, D.C., 2005. Evidence of an increasing NO2/NOX emissions ratio from road traffic emissions. Atmos. Environ. 39 (26), 4793–4802. http://dx.doi.org/10.1016/j.atmosenv.2005.06.023.
Carslaw, D.C., Beevers, S.D., 2004. Investigating the potential importance of primary NO2 emissions in a street canyon. Atmos. Environ. 38 (22), 3585–3594. http://dx.doi.org/10.1016/j.atmosenv.2004.03.041.
Chaney, A.M., Cryer, D.J., Nicholl, E.J., Seakins, P.W., 2011. NO and NO2 interconversion downwind of two different line sources in suburban environments. Atmos. Environ. 45 (32), 5863–5871. http://dx.doi.org/10.1016/j.atmosenv.2011.06.070.
Chang, J., Hanna, S., 2004. Air quality model performance evaluation. Meteorol. Atmos. Phys. 87 (1–3), 167–196.
Cimorelli, A.J., Perry, S.G., Venkatram, A., Weil, J.C., Paine, R.J., Wilson, R.B., Brode, R.W., 2005. AERMOD: a dispersion model for industrial source applications. Part I: General model formulation and boundary layer characterization. J. Appl. Meteorol. 44 (5), 682–693.
Cole, H., Summerhays, J., 1979. A review of techniques available for estimating short-term NO2 concentrations. Retrieved from. J. Air Pollut. Control Assoc. 29 (8), 812–817. http://www.tandfonline.com/doi/pdf/10.1080/00022470.1979.10470866.
Derwent, R.G., Middleton, D.R., 1996. An empirical function for the ratio NO2:NOx. Clean Air 26, 57–60.
Dixon, J., Middleton, D.R., Derwent, R.G., 2001. Sensitivity of nitrogen dioxide concentrations to oxides of nitrogen controls in the United Kingdom. Atmos. Environ. 35 (21), 3715–3728. http://dx.doi.org/10.1016/S1352-2310(00)00476-3.
Draxler, R.R., Rolph, G.D., 2003. HYSPLIT (HYbrid single-particle lagrangian integrated trajectory) model access via NOAA ARL READY website (http://www.arl.noaa.gov/ready/hysplit4.html). NOAA Air Resources Laboratory, Silver Spring, MD. Retrieved from http://www.arl.noaa.gov/ready/hysplit4.html.
During, I., Bachlin, W., Ketzel, M., Baum, A., 2011. A new simplified NO/NO2 conversion model under consideration of direct NO2-emissions. Meteorologische Zeitschrift (Berlin, Germany: 1992) 20(1), 67; 67-73; 73. Retrieved from http://pure.au.dk//portal/files/39728714/s8.pdf.

Gardner, M., Dorling, S., 1999. Neural network modelling and prediction of hourly NOx and NO2 concentrations in urban air in London. Atmos. Environ. 33 (5), 709–719.
Hanrahan, P.L., 1999. The plume volume molar ratio method for determining NO2/NOx ratios in modeling-part II: Evaluation studies. J. Air Waste Manage. Assoc. 49 (11), 1332–1338.
Health Effects Institute, 2010. Traffic-related air pollution: A critical review of the literature on emissions, exposure, and health effects. (HEI Special Report 17).
Heist, D., Isakov, V., Perry, S., Snyder, M., Venkatram, A., Hood, C., Owen, R.C., 2013. Estimating near-road pollutant dispersion: A model inter-comparison. Transport. Res. Part D: Trans. Environ. 25, 93–105. http://dx.doi.org/10.1016/j.trd.2013.09.003.
Hendrick, E.M., Tino, V.R., Hanna, S.R., Egan, B.A., 2013. Evaluation of NO2 predictions by the plume volume molar ratio method (PVMRM) and ozone limiting method (OLM) in AERMOD using new field observations. J. Air Waste Manage. Assoc. 63 (7), 844–854.
Hess, G., Cope, M., 1989. A note on subgrid-scale processes in photochemical modelling. Atmos. Environ. 23 (12), 2857–2860.
Hirtl, M., Baumann-Stanzer, K., 2007. Evaluation of two dispersion models (ADMS-roads and LASAT) applied to street canyons in stockholm, London and Berlin. Atmos. Environ. 41 (28), 5959–5971. http://dx.doi.org/10.1016/j.atmosenv.2007.03.026.
Isakov, V., Arunachalam, S., Batterman, S., Bereznicki, S., Burke, J., Dionisio, K., Snyder, M., 2014. Air quality modeling in support of the near-road exposures and effects of urban air pollutants study (NEXUS). Int. J. Environ. Res. Public Health 11 (9), 8777–8793.
Kenty, K.L., Poor, N.D., Kronmiller, K.G., McClenny, W., King, C., Atkeson, T., Campbell, S.W., 2007. Application of CALINE4 to roadside NO/NO2 transformations. Atmos. Environ. 41 (20), 4270–4280. http://dx.doi.org/10.1016/j.atmosenv.2006.06.066.
Kimbrough, S., Shores, R.C., Whitaker, D.A., Vallero, D.A., 2013. FHWA and EPA National Near- Road Study, Detroit, MI (No. DTFH61-07-X-30015).
Kimbrough, S., Owen, R.C., Snyder, M., Richmond-Bryant, M., 2017. NO to NO2 conversionrate analysis and implications for dispersion model chemistry methods using Las Vegas, Nevada near-road field measurements. Atmos. Environ. 165, 23–34.
Kumar, A., Luo, J., Bennett, G.F., 1993. Statistical evaluation of lower flammability distance (LFD) using four hazardous release models. Process Saf. Prog. 12 (1), 1–11.
Latza, U., Gerdes, S., Baur, X., 2009. Effects of nitrogen dioxide on human health: Systematic review of experimental and epidemiological studies conducted between 2002 and 2006. Int. J. Hyg. Environ. Health 212 (3), 271–287.
Mavroidis, I., Chaloulakou, A., 2011. Long-term trends of primary and secondary NO2 production in the Athens area. Variation of the NO2/NOx ratio. Atmos. Environ. 45 (38), 6872–6879. http://dx.doi.org/10.1016/j.atmosenv.2010.11.006.
McHugh, C., Carruthers, D., Edmunds, H., 1997. ADMS–Urban: An air quality management system for traffic, domestic and industrial pollution. Int. J. Environ. Pollut. 8 (3), 666–674.
McRae, G.J., Goodin, W.R., Seinfeld, J.H., 1982. Mathematical modeling of photochemical air pollution.
Pineda Rojas, A.L., Venegas, L.E., 2013. Upgrade of the DAUMOD atmospheric dispersion model to estimate urban background NO2 concentrations. Atmos. Res. 120–121, 147–154. http://dx.doi.org/10.1016/j.atmosres.2012.08.010.
Podrez, M., 2015. An update to the ambient ratio method for 1-h NO2 air quality standards dispersion modeling. Atmos. Environ. 103, 163–170. http://dx.doi.org/10.1016/j.atmosenv.2014.12.021.
Qian, W., Venkatram, A., 2011. Performance of steady-state dispersion models under low wind-speed conditions. Bound.-Layer Meteorol. 138 (3), 475–491.
Romberg, E., Boesinger, R., Lohmeyer, A., Ruhnke, R., Roeth, E., 1996. NO–$\mathbf{NO_2}$ Umwandlungsmodell fuer die anwendung bei immissionsprognosen fuer kfz-abgase. Gefahrstoffe-Reinhaltung Der Luft 56 (6), 215–218.
Rowangould, G.M., 2013. A census of the US near-roadway population: Public health and environmental justice considerations. Transport. Res. Part D: Trans. Environ. 25, 59–67. http://dx.doi.org/10.1016/j.trd.2013.08.003.
Samoli, E., Aga, E., Touloumi, G., Nisiotis, K., Forsberg, B., Lefranc, A., Katsouyanni, K., 2006. Short-term effects of nitrogen dioxide on mortality: An analysis within the APHEA project. Eur. Respiratory J. 27 (6), 1129–1138 doi:09031936.06.00143905 [pii].
Snyder, M., Arunachalam, S., Isakov, V., Talgo, K., Naess, B., Valencia, A., Hanna, A., 2014. Creating locally-resolved mobile-source emissions inputs for air quality modeling in support of an exposure study in detroit, michigan, USA. Int. J. Environ. Res. Public Health 11 (12), 12739–12766.
Snyder, M.G., Venkatram, A., Heist, D.K., Perry, S.G., Petersen, W.B., Isakov, V., 2013. RLINE: a line source dispersion model for near-surface releases. Atmos. Environ. 77, 748–756. http://dx.doi.org/10.1016/j.atmosenv.2013.05.074.
Stein, A.F., Lamb, D., Draxler, R.R., 2000. Incorporation of detailed chemistry into a three-dimensional Lagrangian-Eulerian hybrid model: application to regional tropospheric ozone. Atmos. Environ. 34 (25), 4361–4372. http://dx.doi.org/10.1016/S1352-2310(00)00204-1.
Tonnesen, S., Jeffries, H.E., 1994. Inhibition of odd oxygen production in the carbon bond four and generic reaction set mechanisms. Atmos. Environ. 28 (7), 1339–1349.
U.S. Census Bureau, 2007. Current housing reports. (American Housing Survey for the United States No. series H150/07). American Housing Survey for the United States, Washington, DC.
USEPA, 2010. Primary national ambient air quality standards for nitrogen dioxide; final rule. (No. Vol 75, No. 26). Federal Register 75.
USEPA, 2014. Memorandum – Clarification on the use of AERMOD dispersion modeling for demonstrating compliance with the NO2 national ambient air quality standard. (Memorandum).Office of Air Quality Planning and Standards. http://www.epa.gov/scram001/guidance/clarification/NO2_Clarification_Memo-20140930.pdf.
USEPA, 2015. Near-road monitoring sites. Retrieved from. http://www3.epa.gov/ttnamti1/files/nearroad/nearroadsites.xlsx.
USEPA, 2017. Memorandum – EPA White Papers on Planned Updates to AERMOD Modeling System. (Memorandum).Office of Air Quality Planning and Standards. https://www3.epa.gov/ttn/scram/models/aermod/20170919_AERMOD_Development_White_Papers.pdf.
Vardoulakis, S., Valiantis, M., Milner, J., ApSimon, H., 2007. Operational air pollution modelling in the UK—Street canyon applications and challenges. Atmos. Environ. 41 (22), 4622–4637. http://dx.doi.org/10.1016/j.atmosenv.2007.03.039.
Venkatram, A., Karamchandani, P., Pai, P., Goldstein, R., 1994. The development and application of a simplified ozone modeling system (SOMS). Atmos. Environ. 28 (22), 3665–3678. http://dx.doi.org/10.1016/1352-2310(94)00190-V.
Vette, A., Burke, J., Norris, G., Landis, M., Batterman, S., Breen, M., Croghan, C., 2013. The near-road exposures and effects of urban air pollutants study (NEXUS): Study design and methods. Sci. Total Environ. 448, 38–47. http://dx.doi.org/10.1016/j.scitotenv.2012.10.072.
Wang, Y.J., DenBleyker, A., McDonald-Buller, E., Allen, D., Zhang, K.M., 2011. Modeling the chemical evolution of nitrogen oxides near roadways. Atmos. Environ. 45 (1), 43–52. http://dx.doi.org/10.1016/j.atmosenv.2010.09.050.