Evaluation of explicit NO_x chemistry methods in AERMOD using a new compressor station dataset

Extended abstract # MO09
Presented at the conference:
Guideline on Air Quality Models: Planning Ahead
March 19-21, 2019
Durham, NC

Jenny Stocker, Cambridge Environmental Research Consultants, Cambridge, UK; David Carruthers, Cambridge Environmental Research Consultants, Cambridge, UK; Cathe Kalisz, American Petroleum Institute, Washington, DC; Robert Paine, AECOM, Chelmsford, MA; Martin Seaton, Cambridge Environmental Research Consultants, Cambridge, UK; Stephen Smith, Cambridge Environmental Research Consultants, Cambridge, UK; Christopher Warren, AECOM, Chelmsford, MA

ABSTRACT

This paper presents preliminary results from the evaluation of AERMOD NO_x chemistry methods for the calculation of NO_2 concentrations using a new dataset. The two currently available Tier 3 methods PVMRM[8,9] (Plume Volume Molar Ratio Method) and OLM[7] (Ozone Limiting Method) are assessed alongside ADMSM[2,3] (Atmospheric Dispersion Modelling System Method), a scheme which explicitly accounts for the rate of titration of NO by ozone as well as photolysis of NO_2. The new dataset is from a 13-month field campaign at a natural gas compressor station in Balko, Oklahoma. There are four main sources of NO_x at this site, although the releases from one Clark TCV-12 engine dominate; the on-site buildings influence the dispersion of emissions from this stack. Hourly concentrations were recorded by four monitors located between 100 and 425 m from the main stacks; two of these monitors were aligned to the north of the site in order to capture the transitional change in the ratio of NO_2 to NO_x concentrations in the predominant downwind direction. Graphical and statistical methods have been used to assess chemistry scheme performance. The analysis highlights the importance of assessing NO_x predictions alongside NO_2 because if NO_x is underpredicted, then NO_2 should also be underpredicted, and vice versa.

After some refinement of the model inputs, for instance including the standard deviation of the horizontal wind direction, sigma-theta, as an hourly input, AERMOD performs moderately well in terms of predicting NO_x concentrations at the monitor locations. As expected, both the ADMSM and PVMRM chemistry schemes demonstrate better performance than OLM in predicting NO_2 concentrations. OLM significantly overpredicts NO_2 due to the assumption of full entrainment of background ozone within the ensemble plume (as opposed to the instantaneous plume). PVMRM predicts some NO_2 concentrations which exceed the OLM values; this demonstrates a possible inconsistency within the PVMRM formulation, as OLM should act as an upper bound. Overall, the statistics and

figures indicate that ADMSM predicts NO_2 concentrations that are more consistent with the NO_x values than PVMRM.

INTRODUCTION

For some industrial installations, demonstrating compliance with the 1-hour NO_2 National Ambient Air Quality Standard (NAAQS) using AERMOD[1] can be difficult. One reason for this is that the currently available AERMOD Tier 3 chemistry methods, OLM (Ozone Limiting Method) and PVMRM (Plume Volume Molar Ratio Method), have a tendency to predict overly conservative concentration values for some model configurations[2]. In an effort to more accurately predict NO_2 concentrations, a new explicit NO_x chemistry method for AERMOD, called the Atmospheric Dispersion Modelling System Method (ADMSM), has been implemented and evaluated[2,3]. ADMSM considers the rate of the chemical reaction between NO and O_3 and the photolysis of NO_2; by accounting for chemical reactions explicitly, the scheme should predict NO_2 concentrations more accurately than current AERMOD methods which approximate the chemical processes using a factor that limits the maximum ratio of NO_2 to NO_x. Another difference between ADMSM and the current Tier 3 schemes is the method used to represent the downwind entrainment of ambient air into the plume: OLM assumes complete entrainment; PVMRM uses a volume based-method; whereas ADMSM uses a plume cross-sectional area method.

An intensive 13-month field data collection program[4] was undertaken by the Pipeline Research Council International, Inc. (PRCI) in order to develop a non-electric generating unit (EGU) dataset associated with a typical natural gas transmission compressor station which would be suitable for performance evaluation of AERMOD, including NO_x chemistry schemes. The specification for this dataset included: hourly onsite meteorological data that is representative of the prevailing conditions for modelling dispersion from the compressor stacks; accurate, hourly-varying emission rates for the major combustion sources and operational tracking of minor sources; and measurements of NO, NO_2 and O_3 at four monitors in the site vicinity situated to record both ‘upwind’ and ‘downwind’ concentrations. An ambient monitoring siting study considering all nearby meteorology was completed and provided to EPA and OKDEQ for review and comment prior to installing the four monitors and meteorological instrumentation.

This paper presents preliminary results from the ongoing performance evaluation of ADMSM alongside OLM and PVMRM using this new dataset. The evaluation approach is to first configure AERMOD to predict NO_x concentrations as accurately as possible prior to using the model to predict NO_2. Results include the comparison of both NO_x and NO_2 modelled and measured concentrations and an assessment of downwind plume chemistry at each monitor location; in addition, the transitional change of the NO_2 to NO_x concentration ratio with distance downwind has been assessed by evaluating data for two monitors that have been located directly north of the site, at different distances downwind of the major sources. The version of the ADMSM scheme used for this work is identical to that used in previous work[2];

i.e., the ADMSM scheme is included in AERMOD version 15181 (but not yet in the current AERMOD version 18081). As there have been changes made to the PVMRM scheme between AERMOD version 15181 and version 18081, PVMRM results from both versions have been assessed.

A brief summary of the AERMOD explicit NO_x chemistry schemes is given below. A description of the new AERMOD evaluation database that has been used for this study then follows. The results of the study are then presented, with some discussion.

SUMMARY OF EXPLICIT NO_X CHEMISTRY SCHEMES IN AERMOD

This section provides a brief summary of the NO_x chemistry schemes included in AERMOD. For further details of the regulatory schemes, refer to the Guideline on Air Quality Models[5] and for a full description of the ADMSM scheme, refer to the original evaluation exercise[2].

In the vicinity of the release of NO_x from an industrial installation, the most important chemical reactions governing the atmospheric concentrations of NO_2 at short time scales (up to several minutes) can be described by the following coupled system:

Equation 1.

$NO + O_3 \rightarrow NO_2 + O_2$

Equation 2.

$NO_2 + \text{sunlight} \rightarrow NO + O_3$

AERMOD includes a number of regulatory chemistry methods for predicting NO_2 concentrations which account for these reactions at varying levels of complexity: Tier 1, which assumes full conversion of all NO_x to NO_2; Tier 2, in which an equilibrium ratio of NO_2 to NO_x is applied to average NO_x concentrations; and Tier 3 where detailed site-specific ratios of NO_2 to NO_x are calculated with knowledge of the hourly ozone background concentration (with ozone oxidation being the dominant process involved for Equation 1). In the most recent U.S. EPA revision of the Guideline on Air Quality Models[5], the Ambient Ratio Method 2 (ARM2[6]) is recommended for Tier 2 calculations and the ozone limiting method (OLM[7]) and the plume volume molar ratio method (PVMRM[8,9]) are recommended for Tier 3.

The AERMOD regulatory Tier 3 methods can be summarised alongside ADMSM as follows:

- OLM assumes an infinite rate constant for Equation 1 and neglects Equation 2. The NO_2 generated as a result of chemical reactions is derived from the NO concentration (determined from the sum of NO from all plumes contributing at the receptor point) and the background O_3 concentration. The total NO_2 concentration is the sum of this NO_2

concentration and the primary NO_2 plume concentration. A constant ambient equilibrium ratio may be applied as an upper limit on the percentage of NO_x that is NO_2. OLM will, in general, overestimate NO_2 concentrations because of the following assumptions: the conversion of NO to NO_2 is instantaneous; photolysis of NO_2 is neglected; and the O_3 concentration in the plume is that of the background. By assuming full conversion, the concentrations calculated by OLM provide an upper bound for NO_2.

- PVMRM also assumes an infinite rate constant for Equation 1 and neglects Equation 2. The NO_2 generated as a result of chemical reactions is derived from the NO concentration as for OLM, but the amount of O_3 available for reaction is more accurately determined from the dilution of the 'relative' (instantaneous) plume using a volume-based entrainment method. Consequently, although there may still be some overestimate of NO_2 concentrations due to the assumption that conversion of NO to NO_2 is instantaneous and photolysis of NO_2 is neglected, the magnitude of any overestimation is likely to be smaller than that of OLM.
- ADMSM explicitly accounts for reactions given by Equations 1 and 2. The NO_2 generated as a result of chemical reactions is derived from the NO concentration as for OLM and PVMRM. ADMSM uses a broadly similar approach to PVMRM for entrainment of ambient O_3 and NO_x, making use of the instantaneous plume spread to determine the O_3 available for chemical reactions occurring within the plume, but it uses a plume cross-sectional area entrainment method which reduces available ozone compared to PVMRM. As ADMSM explicitly accounts for the atmospheric chemical reactions as well as entrainment of ambient O_3 and NO_x, it is likely to result in a more accurate prediction than OLM or PVMRM. However, the scheme still has some limitations, for example in the calculations of the reaction time, which is taken to be a concentration-weighted average of the travel time from each source to the receptor rather than a continuous parameter.

Other aspects to be considered when comparing these Tier 3 methods include the requirement for background concentrations: both OLM and PVMRM require hourly background concentrations of O_3 to be included as input into the chemistry scheme; ADMSM additionally requires background NO_x and NO_2 concentrations. Further, both PVMRM and ADMSM neglect the influence of building-induced turbulence on the growth of the instantaneous plume, which could result in an increase in the rate of O_3 entrainment and lead to an increase in NO_2 concentrations.

NEW EVALUATION DATABASE: BALKO, OKLAHOMA COMPRESSOR STATION

Figure 1 shows the source, building and instrument configuration for the PRCI field campaign; the terrain is flat, scrubby grassland. Four sources of NO_x emissions have been considered as sufficiently significant that they may contribute to the measured NO_2 concentrations: two compressor engines (one larger Cooper-Bessemer engine with a 21 m stack, and a smaller Clark TCV-12 engine with a 10 m stack), a boiler (7 m) and an

emergency generator (8 m). For the two compressor engines, Parametric Emissions Monitoring Systems (PEMS) were used to record hourly engine parameters from which air pollutant emissions have been derived; operation time and emission factors were used to estimate emissions from the smaller sources.

The two compressor engine stacks were located adjacent to buildings with heights similar to the height of the smaller stack (heights 11 m and 13 m for buildings C2 and C3 respectively); the heights of all other on-site buildings were less than 6 m. Meteorological data were recorded at 2 m, 10 m and 30 m on the 'Tower' located in the southwest corner of the site. The meteorological instrumentation on the communications tower was located away from significant buildings and provided a record of upwind conditions.

Figure 1. Balko, OK compressor station PRCI field campaign: four sources shown by red circles with names in italic text and monitoring instrumentation (four locations) indicated by blue circles with names in uppercase letters.



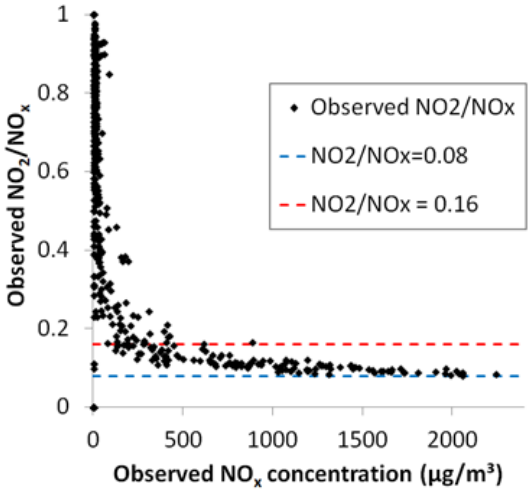
Four air quality monitors recording hourly NO, NO_2 and O_3 concentrations were deployed for a period of 13 months (December 2015 – December 2016). In order to capture downwind

dispersion from the compressor engines, two of the four ambient air monitors were placed in alignment with the stacks and the prevailing wind direction to the north of the site, one at the north fence line ('North Fence') and one outside the site boundary ('Field'), at distances of approximately 140 and 425 m from the main stacks respectively (Table 1). The remaining two monitors were both located within the site boundary, one at the communications tower ('Tower'), and one at the east fence ('East Fence'), the latter being situated primarily to assess building downwash.

The operation of the NO_x sources was not continuous. NO_x emission rates from the Clark TCV-12 engine constituted about 85% of the emissions from all of the units together (making it the dominant source), with the Cooper-Bessemer source constituting most of the rest of the emissions (about 12%). The Cooper-Bessemer engine ran almost exclusively from February to April 2016, supplemented with 27 hours of the Clark TCV-12 during this period. The Clark TCV-12 did not operate between March and July 2016. Both engines operated simultaneously for 1238 hours during the 13-month study period.

The in-stack ratios of NO_2/NO_x for the Cooper-Bessemer and Clark TCV-12 releases were modelled as 0.3 and 0.08 respectively[i]; the former value was derived from stack tests and the latter derived from minimum NO_2/NO_x ratios found in ambient monitoring data. Figure 2 shows the variation of ambient NO_2/NO_x ratios with NO_x concentration for the North Fence monitor, when the Clark TCV-12 engine, the boiler and the emergency generator were operational. Similar minimum ambient ratios of NO_2/NO_x of approximately 0.08 were found corresponding to the highest concentrations at the other two nearby monitors (East Fence and Tower).

Figure 2. Analysis of observed NO_2/NO_x concentration ratios at the North Fence monitor when the Clark TCV-12 engine, the boiler and the emergency generator were operating



[i] In the PRCI study, an in-stack ratio of 0.16 was used for the Clark TCV-12. See Table 11-10 of the PRCI report[4].

Analyses of the monitoring data (not presented here) show that the maximum contribution from the boiler and emergency generator to any of the monitors was less than 100 µg/m³, whereas the minimum ambient NO_2/NO_x ratios values are associated with NO_x concentrations greater than 500 µg/m³. Thus, it is observed from Figure 2 that for the higher NO_x measurements, which are likely to correspond to times when the plume travels directly from the Clark TCV-12 stack to the monitor with minimal ozone titration and minimal influence from other sources, the minimum NO_2/NO_x ratio is approximately 0.08. The in-stack ratios for both the smaller sources were taken as 0.1.

METHODOLOGY, RESULTS AND DISCUSSION

Methodology

AERMOD versions 15181 and 18081 were configured to represent the field study. However, there were negligible differences in the calculated NO_x values between these versions. Consequently, in the following analyses, NO_2 concentrations from ADMSM (version 15181) are shown alongside OLM and PVMRM (version 18081).

All buildings shown in Figure 1 were processed using the Building Profile Input Program (BPIPPRM version 04274) in order to generate direction-specific building heights and projected building widths for input to AERMOD. AERMET version 18081 was used to process the onsite meteorological data, which consisted of measurements of temperature, solar radiation, pressure, precipitation and humidity at 2 m above ground, wind and temperature measurements at 10 m and wind measurements at 30 m, with upper air data from Dodge City, KS and missing surface data filled in by observations from Guymon, OK. Although the area in the vicinity of the site was predominately flat, AERMAP version 11103 was used to process the terrain data for input into AERMOD. Hourly-varying emissions data were included for all four sources; in addition, hourly exit velocities were estimated for the Clark TCV-12 engine using a method dependent on the ratio of permitted to actual hourly emission rate. NO_x, NO_2 and O_3 background concentration data were derived from upwind concentrations, with the Field monitor used as background for wind directions 305°-156° and the Tower monitor used as background for wind directions 156°-305°. Background values were low compared to peak concentrations, with background NO_x concentrations on average approximately 5 µg/m^3 and over 99.5% of hourly values less than 20 µg/m^3.

When evaluating AERMOD's ability to predict NO_2 concentrations, it is important to assess both dispersion and chemistry; it is preferable to optimise the model configuration in terms of dispersion model performance prior to assessing how well the chemistry schemes perform. Dispersion model performance can be assessed by evaluating NO_x concentrations. Full details of the NO_x model configuration optimisation exercise have been omitted from this paper, but some of the aspects considered included: emissions parameters, resulting in the estimation of hourly-varying exit velocities for the dominating source (Clark TCV-12) and the use of the EPA regulatory 'POINTCAP' option to represent the boiler stack rain cap; meteorological input data, leading to the inclusion of the standard deviation of the horizontal wind direction,

sigma-theta, as an hourly input parameter; minimum measured NO_2/NO_x concentrations, leading to an adjustment of the in-stack ratio for the Clark TCV-12 engine relative to the original estimate; and the buildings configuration (combined buildings were considered, but not used for the final configuration). When optimising the model configuration for NO_x, it was noted that the concentrations recorded at the four monitors were primarily a result of the dispersion of emissions from the Clark TCV-12 engine. This was due to the much larger emission rate from that source, as noted above, and because the height of the release from the Cooper-Bessemer engine was significantly above the building roofs.

Stronger indicators of model performance are given when analyses are focussed on cases where emissions are relatively high and the wind advects emissions in the direction of the monitor. Therefore, the concentration data have been pre-processed by emissions such that only cases where at least one of the compressor engines is releasing NO_x are considered within a wind sector which differs for each monitor according to the distance to the source; the wind sector was chosen by inspection of the spread of observed NO_x concentrations with wind direction and the sector specification is summarised in Table 1. This subset of data has been used for all of the analysis, except for when pollutant ratios are considered, where further filtering of the data is required, which will be discussed in relation to Figure 5.

Table 1. Wind direction sectors for analysis of each receptor

Monitor	Distance from Clark TCV-12 engine to monitor (m)	Centreline wind direction	Sector size
Field	425	180.5°	40°
North Fence	140	179.5°	60°
East Fence	101	248°	60°
Tower	185	66°	50°

NO_x evaluation

NO_x quantile-quantile (Q-Q) plots for each of the monitors are presented in the left-hand side of Figure 3. The majority of the NO_x concentrations are significantly overpredicted at East Fence, with the exception of the higher concentrations, where the model appears to perform well. The likely reason for the relatively poor agreement between modelled and observed NO_x concentrations at this monitor is the strong influence of the buildings on dispersion of emissions from the Clark TCV engine. As model performance in terms of chemistry methods is the focus of this work, rather than building downwash, this apparent overestimation was not investigated further. The model underpredicts the higher NO_x concentrations at both North Fence and Tower; model agreement is considered good at the Field monitor, particularly in terms of the modelled mean.

NO_x statistics are presented in Table 2, specifically: period averages (mean); normalised mean square error (NMSE); correlation (R); the number of modelled values within a factor of two of the observed (Fac2); and the ratio of the modelled to observed highest ten concentrations. Dispersion modelling of point sources (as opposed to line / area sources) is particularly challenging due to the greater sensitivity of model predictions to meteorological

parameters, for instance, inaccuracies in wind direction can result in the plume 'missing' the receptor. Taking this into account, AERMOD performs moderately well in terms of predicting NO_x concentrations at these monitors, with correlation coefficient greater than 0.55 for three out of the four monitors, and more than 45% of values lying within a factor of two of the observed at all monitors.

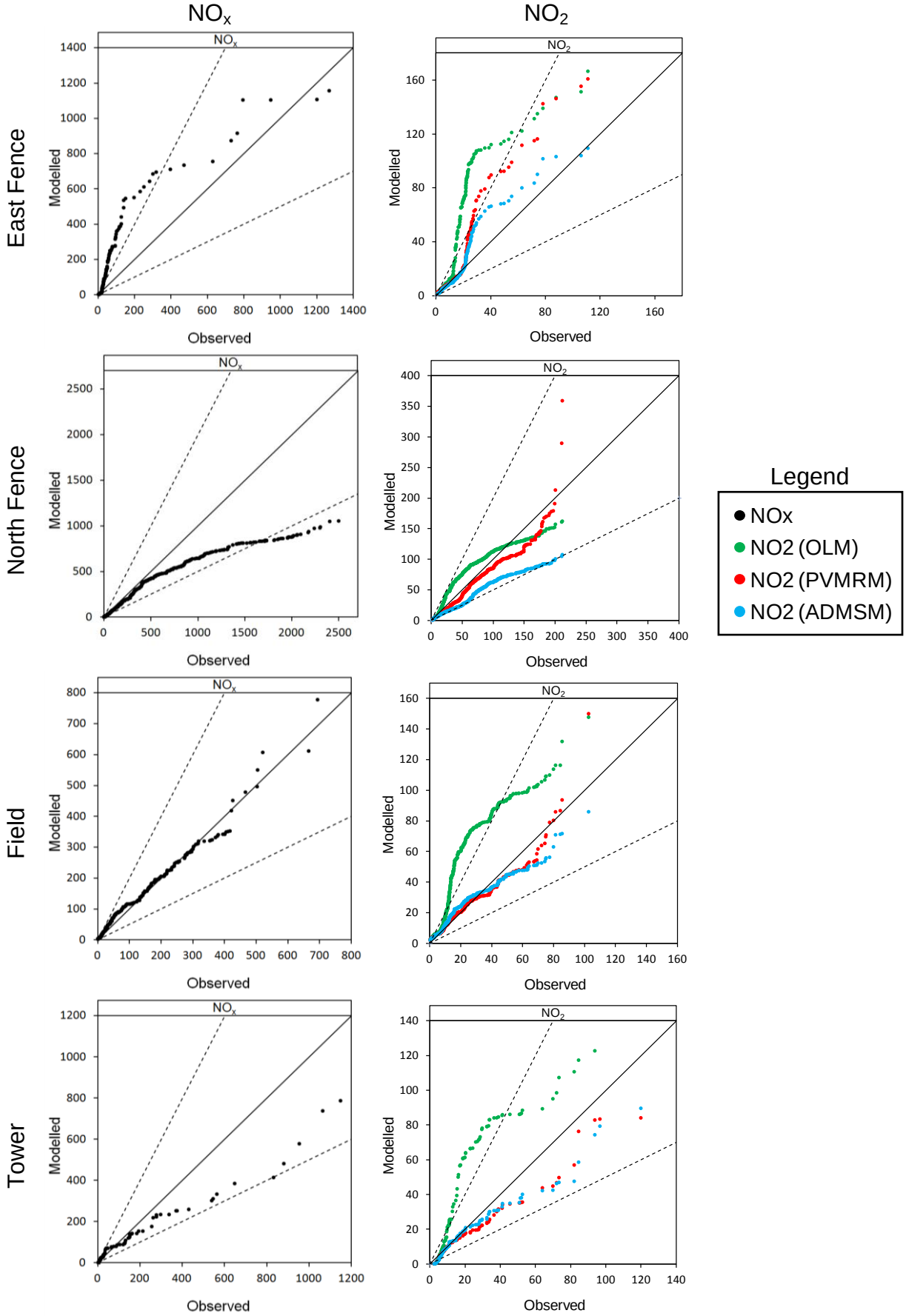
Table 2. Statistics relating to hourly modelled NO_2 and NO_x concentrations (μg/m^3); the NO_x statistics shown in italics; bold represents where the NO_2 statistic is at least as good the NO_x statistic for the NMSE, R and Fac2.

Monitor	No. of values	Pollutant (scheme)	Obs. mean	Mod. mean	NMSE	R	Fac2	Ratio of mod. to obs. mean: high 10 values
East Fence	238	*NO_x*	*64.3*	*120.3*	*4.0*	*0.65*	*0.54*	*1.22*
		NO_2 (ADMSM)	15.5	18.2	**0.8**	**0.71**	**0.68**	1.18
		NO_2 (PVMRM)	15.5	21.8	**1.3**	**0.73**	**0.73**	1.65
		NO_2 (OLM)	15.5	39.4	**2.7**	0.61	0.51	1.79
North Fence	803	*NO_x*	*326.4*	*200.7*	*2.9*	*0.57*	*0.45*	*0.43*
		NO_2 (ADMSM)	48.1	27.1	**1.5**	**0.57**	**0.57**	0.50
		NO_2 (PVMRM)	48.1	39.5	**1.3**	0.39	**0.54**	1.07
		NO_2 (OLM)	48.1	54.8	**0.8**	0.50	**0.53**	0.78
Field	576	*NO_x*	*68.2*	*70.7*	*1.9*	*0.59*	*0.51*	*1.01*
		NO_2 (ADMSM)	17.2	17.5	**0.7**	**0.61**	**0.70**	0.79
		NO_2 (PVMRM)	17.2	16.8	**1.0**	0.45	**0.64**	1.05
		NO_2 (OLM)	17.2	35.3	**1.6**	**0.62**	0.50	1.45
Tower	149	*NO_x*	*95.4*	*69.6*	*5.1*	*0.47*	*0.45*	*0.60*
		NO_2 (ADMSM)	17.2	13.6	**1.4**	**0.56**	**0.58**	0.70
		NO_2 (PVMRM)	17.2	13.4	**1.6**	**0.50**	**0.54**	0.75
		NO_2 (OLM)	17.2	31.4	**1.9**	**0.59**	**0.49**	1.38

NO_2 evaluation

NO_2 Q-Q plots for each of the chemistry schemes are presented in the right-hand side of Figure 3; corresponding statistics are presented in Table 2. When evaluating the chemistry scheme performance as indicated by the Q-Q plots, it is important to understand that the NO_2 concentration predictions should be broadly consistent with the NO_x values; in particular, if NO_x is over/under predicted, then NO_2 should also be over/under predicted. Overall, PVMRM and ADMSM predictions of NO_2 concentrations are broadly consistent with the NO_x concentrations, however PVMRM demonstrates an overprediction for the higher concentrations at all monitors except Tower. At the higher concentrations, PVMRM predictions for NO_2 exceed the upper bound as quantified by the OLM values; this is most obvious at the North Fence monitor, which is located relatively close to the compressor engine and records the highest concentrations. ADMSM performs generally well, although there is some underprediction of the lower concentrations at North Fence.

Figure 3. Quantile-quantile plots of NO_x (left) and NO_2 (right) concentrations (µg/m^3) at all monitors



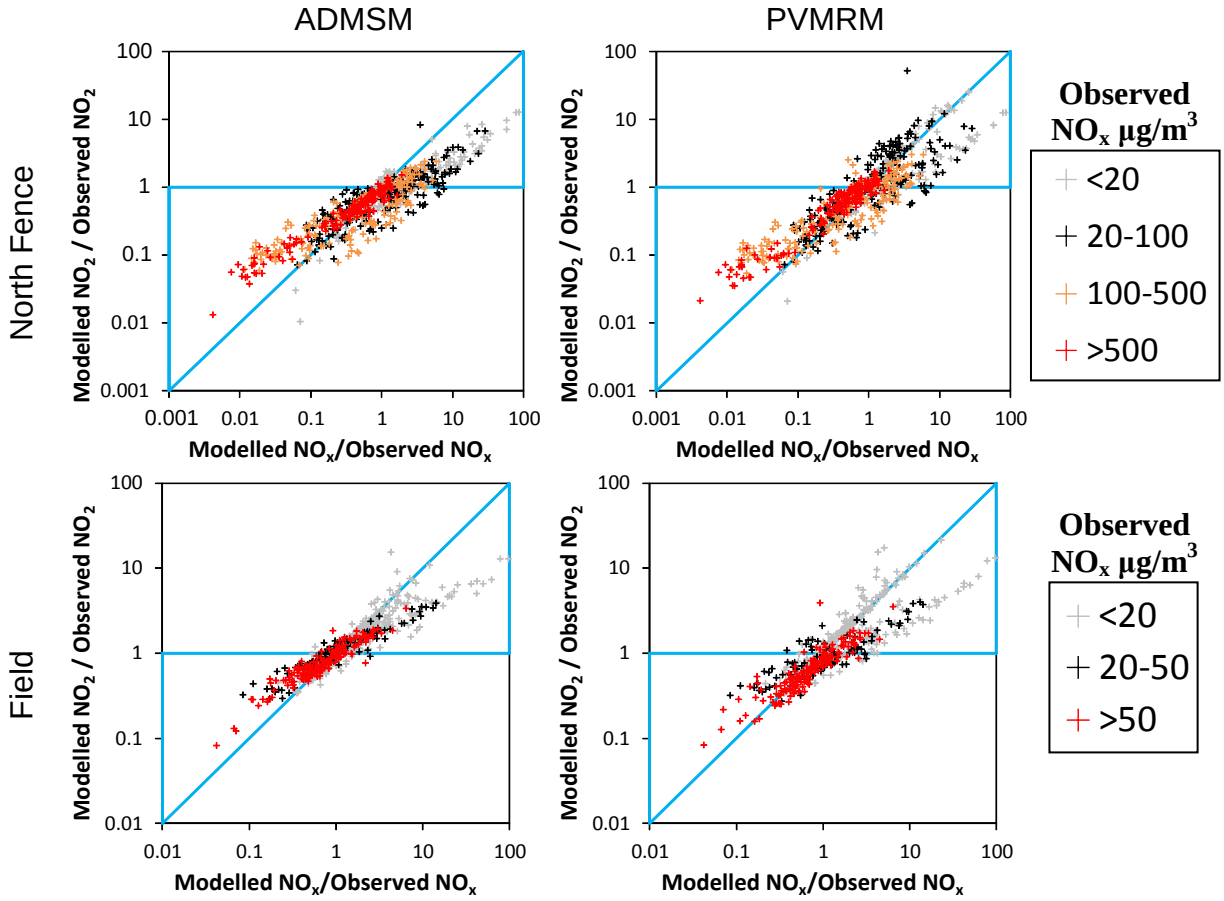
In terms of the statistics presented in Table 2, the NO_2 hourly statistics for ADMSM (NMSE, R, Fac2) are as good as, or better than, the corresponding NO_x values; this is also the case for PVMRM at East Fence and Tower, but that scheme demonstrates relatively poor correlation relative to NO_x at North Fence and Field. Although the correlation coefficient should not be taken as indicative of overall model performance, this reduction in NO_2 correlation relative to NO_x for PVMRM may be indicative of an inconsistency in the underlying chemistry scheme formulation. The statistic shown in the right hand column of Table 2 gives some indication of performance in terms of ability to predict the highest NO_2 concentrations, which are of interest with regard to compliance with the NAAQS metrics; here, the best performance is indicated by the scheme that is able to predict a value for NO_2 close to the corresponding NO_x statistic, but also in the range that lies between the NO_x statistic and unity. ADMSM performs well at East Fence and North Fence in terms of consistency of the modelled-to-observed ratios for NO_2 in relation to NO_x, whereas PVMRM overpredicts NO_2 relative to NO_x at those locations; at Field, ADMSM shows some underprediction compared to OLM and PVMRM; and at Tower, all models overpredict, although ADMSM and PVMRM to a lesser extent compared to OLM.

Further analysis of the performance of the chemistry methods in predicting hourly average concentrations of NO_2 is provided by showing how the ratio of modelled to observed NO_2 varies with modelled to observed NO_x, with data points colour coded according to the observed NO_x concentration (Figure 4). In earlier work[2,10], these 'ratio plots' have helped to assess chemistry scheme performance because they allow for inaccuracies in the NO_x predictions. Good model performance is demonstrated when exact NO_x concentration predictions correspond to exact NO_2 concentrations i.e. points centred on (1,1). Further, as mentioned previously, if NO_x is over/under predicted, then NO_2 should be over/under predicted, *but, relatively, the magnitude of the over/under prediction for NO_2 should be less than for NO_x because the chemical reaction is less than linear;* i.e., the points should lie in the regions shown by the blue triangles. The points are colour coded by NO_x concentration because, for hours with higher NO_x concentrations, there is a strong signature from the source facilitating the detection of near-field chemical processes; the lower NO_x concentrations are more influenced by background levels. Figure 4 shows these 'ratio plots' for ADMSM and PVMRM for the two monitors with the highest number of relevant records; i.e., North Fence and Field. The corresponding plots for OLM and the other monitors show consistent results, but have been omitted for brevity.

At North Fence, the ADMSM 'high NO_x' points shown in red lie in a clear line between the lower left triangle to the upper right triangle demonstrating good chemistry scheme performance. The corresponding values for PVMRM show slightly more spread; in particular, there are more points in the upper left quadrant which indicates NO_2 overprediction. ADMSM has slightly more of the 20 – 500 NO_x µg/m³ points in the lower right quadrant compared to PVMRM, indicating some under-prediction of NO_2 for these cases (this can also be seen in the Q-Q plots in Figure 3). Thus, both ADMSM and PVMRM demonstrate good performance, for instance compared to OLM, with ADMSM giving better predictions for the highest NO_x concentrations.

For the Field monitor, the majority of the ADMSM points lie in a clear line between the lower left triangle to the upper right triangle in Figure 4. For PVMRM, a relatively high proportion of the 'high observed NO_x' points lie in the lower right quadrant, indicating under-prediction of NO_2 for these cases. Overall, the chemistry scheme performance of ADMSM appears better than PVMRM when predicting NO_2 concentrations at this monitor.

Figure 4. Ratio of modelled to observed NO_2 against the ratio of modelled to observed NO_x for ADMSM (left) and PVMRM for North Fence (upper plots) and Field (lower plots). Points are coloured by observed NO_x concentration; good chemistry scheme performance indicated by the points lying in the blue triangles.

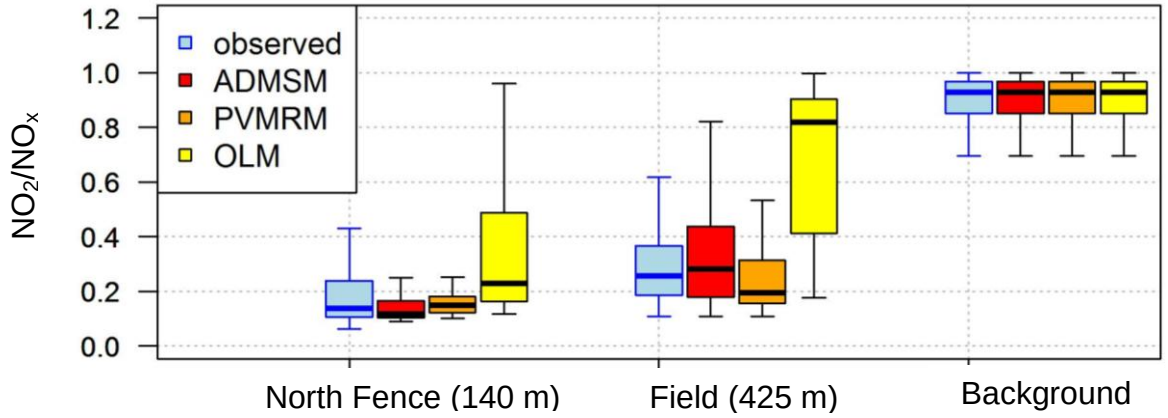


NO_2/NO_x concentration ratios

The in-stack ratio of the most influential release from the Clark TCV engine was estimated at 0.08 (Figure 2); background NO_2/NO_x concentrations are in the range 0.8-1.0. Representing the transitional change in NO_2/NO_x with distance downwind of the source helps to assess chemistry scheme performance. Figure 5 shows a comparison of the ranges of modelled and observed NO_2/NO_x concentration ratios for the North Fence and Field monitors, which are at distances of 140 and 425 m downwind of the main stacks respectively; the background concentrations are also shown for comparison purposes. In this figure, the lower and upper quartiles are the 25th and 75th percentiles, and the lower and upper whiskers are defined as the lowest / higher concentration values still within 1.5 times the inter-quartile range (IQR,

defined as the 75th percentile minus the 25th percentile); data have been filtered according to 'Field' criteria (Table 1) and outliers are not shown. For the closer North Fence monitor, both ADMSM and PVMRM compare well with the observations in terms of the median, with values of 0.12 and 0.15, respectively, compared to a measured value of 0.14, although the IQRs are smaller; OLM overpredicts the ratio, with a much larger spread. Further downwind at the Field monitor, ADMSM again compares reasonably well in terms of the median value as expected as a result of the accurate NO_x prediction (0.28 compared to an observed value of 0.26); PVMRM shows some underprediction (0.19); OLM overpredicts significantly. The far-field ratios shown for comparison are much higher, as expected, demonstrating that the NO_x chemistry continues to be important beyond 0.5 km downwind of the sources. Overall, Figure 5 indicates that both ADMSM and PVMRM are representing the downwind transitional change in NO_2/NO_x concentrations reasonably well.

Figure 5. Comparison of modelled and observed NO_2/NO_x concentration ratios, with distance downwind from the monitor; background values shown for reference. Data points corresponding to observed NO_x < 20 µg/m³ are excluded from the analysis.



SUMMARY

This paper presents the preliminary results of an evaluation of the explicit NO_x chemistry methods in AERMOD using a new compressor station dataset. The chemistry schemes evaluated are the currently available Tier 3 methods, OLM and PVMRM, in addition to a new scheme, ADMSM, which has been implemented in AERMOD version 15181. The PRCI field campaign, which generated this new dataset, was specifically designed with the intention of using the data for NO_x chemistry scheme evaluation. Aspects of the study which have made the dataset superior to those used in earlier work[2] include: the deployment of four (rather than one or two) monitors recording NO, NO_2 and O_3, allowing accurate measurements of both 'upwind' and 'downwind' concentrations; the use of PEMS providing reliable estimates of hourly-varying emissions data for the dominant sources; and a campaign duration of over one year. The short distance to two of the monitors, North Fence and East Fence, also has allowed the evaluation to test the model performance at typical fence line distances. Such closely-spaced monitors have not been available from other NO_2 evaluation databases until now.

AERMOD was first evaluated in terms of NO_x concentrations; the model performs well at some monitors. Performance was found to improve significantly when hourly values of the standard deviation of the horizontal wind direction, sigma-theta, were included in the model configuration. AERMOD overpredicts concentrations for the monitor to the east of the site, which is strongly influenced by building downwash. These preliminary NO_x analyses suggest that this dataset may be suitable for other AERMOD evaluation exercises, for example looking at the differences between measured and default sigma-theta values, and for building downwash assessments.

The chemistry scheme evaluation included: comparing the consistency of NO_x and NO_2 statistics and Q-Q plots; presenting plots showing the ratio of modelled to observed NO_2 against modelled to observed NO_x; and evaluating the transitional change in the NO_2/NO_x concentration ratio with downwind distance from the source. As expected, both ADMSM and PVMRM demonstrate better performance than OLM, with OLM significantly overpredicting NO_2 concentrations at the monitor approximately 0.5 km downwind due to the scheme assuming full entrainment of background ozone within the ensemble (as opposed to instantaneous) plume. PVMRM predicts some NO_2 concentrations which exceed the OLM values; this demonstrates a possible inconsistency within the PVMRM formulation, as OLM should act as an upper bound. In terms of the calculated statistics, the ADMSM NO_2 values are more consistent with the NO_x values than PVMRM. The 'ratio plots' indicate that the ADMSM values are better aligned within the blue triangles compared to PVMRM.

By aligning the North Fence and Field monitors directly north of the site, which experiences a southerly prevailing wind, this dataset generates observations that can be used to evaluate the model's ability to represent downwind chemistry. The evaluation of the spread of NO_2/NO_x ratios is one way of quantifying the chemical transition from in-stack ratio values to background concentrations. Both ADMSM and PVMRM broadly replicate the NO_2/NO_x ratios at the monitors located to the north of the compressor engine releases, and OLM does not. As the median NO_2/NO_x concentration is 0.26 at 425 m compared to the background values of 0.93, in future campaigns it would be of interest to deploy monitors at larger distances.

The ADMSM scheme is currently only implemented in AERMOD version 15181. The authors plan to include the scheme in a more recent (or forthcoming) version of the model.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the American Petroleum Institute for funding this study. Continued consultation, advice, and interest by Dr. Chris Owen and his colleagues at the United States Environmental Protection Agency are also greatly appreciated.

REFERENCES

1. Cimorelli, A.J.; Perry, S.G.; Venkatram, A.; Weil, J.C.; Paine, R.J.; Wilson, R.B.; Lee, R.F.; Peters, W.D.; Brode, R.W.; Paumier, J.O., *AERMOD: Description of Model Formulation*; United States Environmental Protection Agency; EPA-454/R-03-004, 2004.
2. Carruthers, D.J.; Stocker, J.R.; Ellis, A.; Seaton, M.D.; Smith, S.E., *Evaluation of an explicit NOx chemistry method in AERMOD*; Journal of the Air and Waste Management Association. **2017**, 67:6, 702-712, DOI: 10.1080/10962247.2017.1280096.
3. *EPA White Papers on Planned Updates to AERMOD Modeling System*; Air Quality Modeling Group, U.S. Environmental Protection Agency, September 2017.
4. Panek, J.; McCarthy, J.; Huth A.; Krol, A.; Balko, *OK Compressor Station 102 Data Summary and Initial AERMOD Performance Assessment*; Pipeline Research Council International Inc. Report, Catalogue PR-312-15201-R01, 2017.
5. *Revisions to the Guideline on Air Quality Models: Enhancements to the AERMOD Dispersion Modeling System and Incorporation of Approaches to Address Ozone and Fine Particulate Matter*; U.S. Environmental Protection Agency, 40 CFR Part 51, RIN 2060-AS54, 2017.
6. Podrez, M., *An update to the ambient ratio method for 1-h NO2 air quality standards dispersion modelling*; Journal of Atmospheric Environment. **2015**, 103:163-170, DOI: 10.1016/j.atmosenv.2014.12.021.
7. Cole, H.S.; Summerhays, J.E., *A Review of Techniques Available for Estimating Short-Term NO2 concentrations*; Journal of the Air Pollution Control Association. **1979**, 29(8):812-817, DOI: 10.1080/00022470.1979.10470866.
8. Hanrahan, P.L., *The Plume Volume Molar Ratio Method for Determining NO2/NOx Ratios in Modeling - Part II: Evaluation Studies*; Journal of Air and Waste Management Association. **1999**, 49(11):1332-1338, DOI: 10.1080/10473289.1999.10463961.
9. Hanrahan. P.L., *The Plume Volume Molar Ratio Method for Determining NO2/NOx Ratios in Modeling—Part I: Methodology*, Journal of the Air & Waste Management Association, **1999**, 49:11, 1324-1331, DOI: 10.1080/10473289.1999.10463960
10. Smith, S.; Stocker, J.; Seaton, M.; Carruthers, D., *Model inter-comparison and validation of ADMS plume chemistry schemes*; International Journal of Environment and Pollution. **2017**, 62(2-4), 395-406, DOI:10.1504/IJEP.2017.089427.

KEYWORDS

AERMOD, NO_x, NO_2, chemistry, modeling, evaluation, PVMRM, ADMSM, OLM, Balko