



Technical support document (TSD) for NO₂-related AERMOD modifications

EPA- 454/B-15-004

December, 2015

Technical support document (TSD) for NO₂-related AERMOD modifications

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Preface

This document provides a review the scientific merit of the NO₂ options in AERMOD, summarizes existing evaluations of these options, and presents additional testing used to determine appropriate application of these options for these options as part of the regulatory default version of AERMOD.

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1. Introduction

The proposed revisions to Appendix W to CFR 40 Part 51—*Guideline on Air Quality Models* (Appendix W), includes a new version of AERMOD (ADD VERSION #). This version of AERMOD reflects the proposed new regulatory default options for NO₂, including the new Ambient Ratio Method 2 (ARM2, (Podrez, 2015)), the existing Ozone Limiting Method (OLM, (Cole & Summerhays, 1979)), and a revised version of the Plume Volume Molar Ratio Method (PVMRM, (Hanrahan, 1999a)). This TSD reviews the scientific merit of these methods, summarizes existing model evaluations, and presents additional testing used to determine appropriate application of these options for use as part of the regulatory default version of AERMOD.

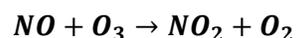
2. Background

The development of the original Ambient Ratio Method (ARM), OLM, and PVMRM precedes both the development of AERMOD in the late 1990's and its promulgation for regulatory use in 2005. Though there are aspects of the implementation of these methods in AERMOD that are specific to AERMOD, the basic approach to NO₂ speciation used by ARM/ARM2, OLM, and PVMRM are not inherent to AERMOD. As a result, there is a notable body of literature focused on the more fundamental science behind these NO₂/NO_x speciation approaches. This section provides a review of the scientific background available for ARM/ARM2, OLM and PVMRM as well as the basics of NO₂ chemistry relevant for these methods.

2.1 NO₂ chemistry

Nitrogen oxides (NO_x) consist of two species, NO₂ and NO. Anthropogenic NO_x is typically formed during high-temperature combustion processes via three main reaction pathways. The most prominent and consistent production route is the thermal oxidation of N₂ via the Zeldovich mechanism (Zel'dovich, Sadonikov, & Frank-Kamenetskii, 1946). The thermal production of NO_x is fairly predictable and the total amount of NO_x and the speciation of NO and NO₂ in the exhaust gas stream from “thermal NO_x” is controlled by the reaction temperature and the amount of available oxygen in the gas stream. NO_x can also be produced when nitrogen-containing fuels, such as oil and coals, are used and the nitrogen contained in the fuel is liberated and subsequently oxidized. “Fuel NO_x” can be minimal or a major contributor to NO_x emissions, depending on the fuel type (e.g., natural gas has virtually no nitrogen, resulting in no fuel NO_x production). The last production route is known as prompt production, which involves the reaction of N₂ with oxygen and hydrocarbon radicals resulting from fuel combustion. “Prompt NO_x” can involve hundreds of reactions of very short-lived species in the combustion chamber and exhaust gas stream and is generally difficult to characterize and predict and instead is estimated as the amount of NO_x that is present that cannot be accounted for as thermal or fuel NO_x. The speciation of NO and NO₂ in the exhaust gas stream from prompt and fuel NO_x is a function of the fuels and the type of combustion process and is very difficult to generalize. NO_x production can continue in the exhaust gas stream until temperatures drop low enough to end combustion.

Once NO_x is in the atmosphere, there a number of potential chemical reactions that can occur, depending on the relative amounts of NO and NO₂, the total NO_x, the ambient meteorological conditions, and other atmospheric trace gasses available for reaction. In most cases, the fastest and most important reactions of NO_x involve ozone (O₃). When there is sufficient ozone present, Reaction 1 dominates all other NO_x chemistry:



Reaction 1

In fairly concentrated plumes, this reaction is initially ozone limited, such that all available ozone will be consumed. As a plume becomes more diluted and more ozone is mixed in, the reaction eventually becomes NO limited. During daytime, NO₂ can be photolyzed back to NO and subsequently reform ozone:



Though Reaction 1 is the fastest of the three, a quasi-equilibrium state, also referred to as the photostationary state (PSS) due to Reaction 2 being driven by sunlight, can be achieved during the daytime between NO, NO₂ and ozone. While the PSS can occur within 1-3 minutes, it must also compete with changes in plume concentrations due to mixing, i.e., entrainment of additional ozone and dilution of NO_x towards ambient levels. Thus, for a fairly concentrated plume, the rate of mixing and the rate of the PSS reactions will compete on relatively equal time scales and Reaction 1 will usually dominate the chemistry. Once a plume becomes relatively diluted, the PSS can be reached, which is dictated by the total amount of NO_x, background ozone and the ambient meteorological conditions. Assuming an equal rate of NO₂ formation and destruction, Reactions 1 and 2 can be used to determine the equilibrium ratio of NO₂/NO_x (Seinfeld & Pandis, 2006):

$$\frac{\text{NO}_2}{\text{NO}_x} = (\text{K}_1)[\text{O}_3]/(\text{K}_2 + \text{K}_1 * [\text{O}_3]) \quad \text{Equation 1}$$

Where K₁ and K₂ are the reaction rates for reaction 1 and 2:

$$\text{K}_1 = \left(\frac{15.33}{T}\right) * \exp\left(-\frac{1450}{T}\right) \quad \text{Equation 2}$$

$$\text{K}_2 = 0.0167 * \exp\left(-\frac{0.575}{\cos(\theta)}\right) \quad \text{Equation 3}$$

The units for K₁ are ppb⁻¹*sec⁻¹ and sec⁻¹ for K₂, where T is the ambient temperature in Kelvin and θ is the solar zenith angle (SZA) in radians from zenith¹. The result from this equation is that the equilibrium NO₂/NO_x ratio is solely a function of ozone, sunlight, and temperature and not a function of the total NO_x. The equilibrium NO₂/NO_x ratios determined from Equation 1 for a variety of conditions are shown in Figure 1. There are clearly a wide range of potential equilibrium ratios. As the available sunlight decreases (95% cloudy) or as there is more ozone available, the preference is for NO_x to remain as NO₂. It is important to note that the solution to Equation 1 holds ozone constant, such that ozone titration is not taken into account within the setting of a plume undergoing dilution and reaction. Thus, for any background ozone concentration, the corresponding equilibrium ratio in Equation 1 is a conservative estimate of conditions present in a plume in the atmosphere.

¹ The rates for K₁ and K₂ given here are taken from (Hanrahan, 1999a). However, it should be noted that there is notable variation in the reported reaction rates for K₁ from various sources. Additionally, K₂ is an estimate of the photolysis rate of NO₂, which was stated as accurate to about 10% for a SZA between 0 and 65 degrees (Dickerson, Stedman, & Delany, 1982). More recent references (e.g., (Atkinson, et al., 2004)) indicate that the rate for K₂ requires an integration of the absorptions rates at the range of wavelengths present for any scenario. Despite these differences in rate constants, the resulting NO₂/NO_x ratio is not anticipated to vary greatly between estimates of the rate for either reaction and that the results indicated in Figure 1 are reasonably representative.

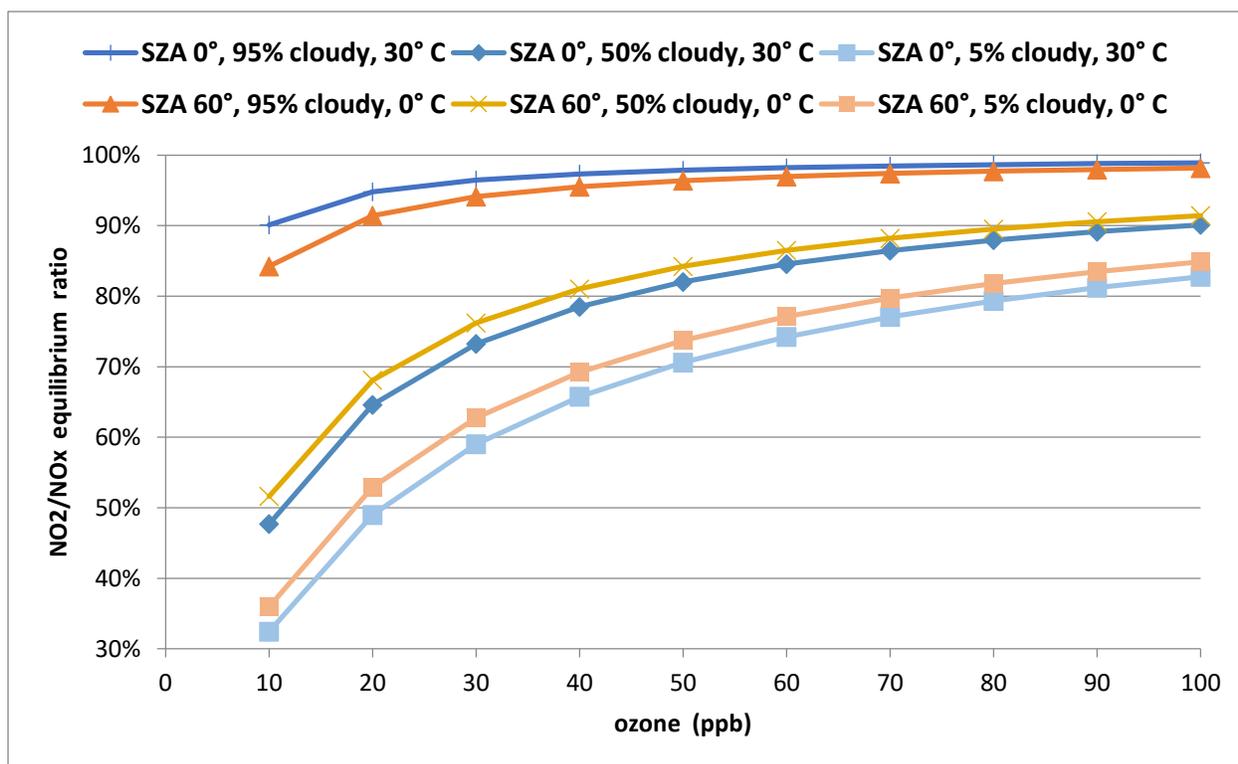


Figure 1 – NO₂/NO_x equilibrium ratios based on the PSS assumption from Equation 1.

Though generally ignored in the realm of NO₂ modeling with Gaussian plume-based models, there are a number of other chemical reactions that can convert NO to NO₂, convert NO and NO₂ reservoir species (e.g., nitrous and nitric acid), and remove NO_x from the atmosphere entirely. At nighttime, there is essentially no ozone production, such that in urban areas (where NO_x emissions continue throughout the day and night), background ozone is generally quite low. As a result, there are fundamentally a different set of daytime and nighttime reactions. In general, nighttime NO_x chemistry favors conversion of NO to NO₂ and conversion of NO₂ to NO₂ reservoir species, which may be removed from the atmosphere or converted back to NO₂ at sunrise.

2.2 Ambient Ratio Method

The original ARM is based on (Chu & Meyer, 1991) and is focused on long-term averages of NO_x concentrations. The basis for the approach assumes that for long-term averages, the partitioning of NO and NO₂ at any location is controlled by the NO/NO₂ partitioning in the ambient background air because: 1) plumes are mixing with ambient air, and 2) as plumes photochemically age, they will ultimately approach the background equilibrium. It can also be assumed that any sources near a monitor will periodically impact a monitor and as a result, the average NO₂/NO_x ratio will reflect plumes in various stages of mixing and photochemical aging. Since most sources are expected to have relatively low in-stack ratios (ISR) of NO₂/NO_x, such periodic impacts of a source on a monitor would be expected to reduce the long-term average NO₂/NO_x ratio. While this would make the NO₂/NO_x ratio from the

monitor more representative of those local source impacts, it would make the NO₂/NO_x ratio less conservative when predicting impacts from new or modified sources. Nevertheless, a NO₂/NO_x ratio controlled by background conditions would still be expected to be conservative for estimating the long-term average impacts from a new or modifying source. Thus, long-term averages of the NO₂/NO_x ratio at any monitor can be used as a surrogate for estimating the long-term NO₂/NO_x ratio at other locations.

The validity of the ARM assumptions were also confirmed with several sets of ambient data. First, (Chu & Meyer, 1991) evaluated 10 years of ambient data from nationwide US networks to determine trends of the long-term averages of the NO₂/NO_x ratios. Their analysis had four major conclusions:

1. The annual NO₂/NO_x ratios ranged from 0.48 to 0.74 over the 10-year period.
2. There was relatively little variation in the median, maximum and minimum ratios over the data period.
3. The year-to-year variability at any single monitor was less than 10%.
4. The 90th percentile value for the most recent 3-years of data (1987-1989) was 0.75.

The fundamental conclusion drawn from the ambient data was that the annual average of the ambient NO₂/NO_x ratio was fairly stable and robust, and 0.75 was recommended as a national default value. Second, in addition to their own analysis of the available ambient data, several older studies, which focused on sampling aging plumes as they were transported downwind, were also cited (Keifer, 1977), (Janssen, Wakeren, Duuren, & Elshout, 1988), (Bultjes, 1981). These studies generally showed that the NO₂/NO_x ratio tends to increase with increasing distance from major sources.

Based on the behavior of the nationwide monitoring data and source-specific studies, the recommended application for ARM included:

1. Use the 3-year average of annual NO₂/NO_x ratios in the vicinity of the new or modifying source (within 15 to 90 km) to apply to annual averaged modeled NO_x to determine the annual NO₂.
2. Monitored values below 20 ppb of NO₂ should be excluded when calculating the annual averages due to uncertainty at these lower concentrations.
3. If the monitor is located in a major urban area, then only daytime measurements should be used in the annual averages.
4. The national default should be used in absence of any nearby monitoring data.

ARM was implemented in the 2005 version of Appendix W with the national default value of 0.75 for annual averages, with a mention of using regional ratios as an alternative. Given that there was no hourly standard available at the time, there was no national default given for short-term standards. However, the EPA issued a guidance memorandum that recommended a national default NO₂/NO_x ratio for usage for the hourly standard (0.8) (U. S. EPA, 2011).

2.3 Ambient Ratio Method 2

The updated ARM2 was developed by (Podrez, 2015) and is focused on short-term (i.e., hourly) averages of NO₂ concentrations. The basis for the approach assumes that due to the nature of NO_x chemistry and typical NO₂/NO_x emission ratios, that the ambient NO₂/NO_x ratios will exhibit a predictable pattern, which will in large part, be a function of the total NO_x present. Given this assumption, a 10-year record (2001-2010) of ambient data from the Air Quality System (AQS, 2014) was analyzed to characterize the

behavior of these data. The analysis showed a decreasing NO₂/NO_x ratio with increasing total NO_x concentrations. In order to develop a NO₂/NO_x ratio response curve, the ambient data was binned based on the NO_x concentrations, the 98th percentile NO₂/NO_x ratio was determined for each NO_x bin, and a 6th order polynomial regression was performed on the selected values from each NO_x bin. The resulting polynomial is used to predict the NO₂/NO_x ratio based on the modeled NO_x concentration, though maximum and minimum limits on the NO₂/NO_x ratio are used at the upper and lower ends of the range of potential NO_x concentrations (0.9 maximum and 0.2 minimum). Figure 2 shows an example of AQS data, comparing the NO₂/NO_x ratio to the total NO_x, demonstrating the relationship found by (Podrez, 2015).

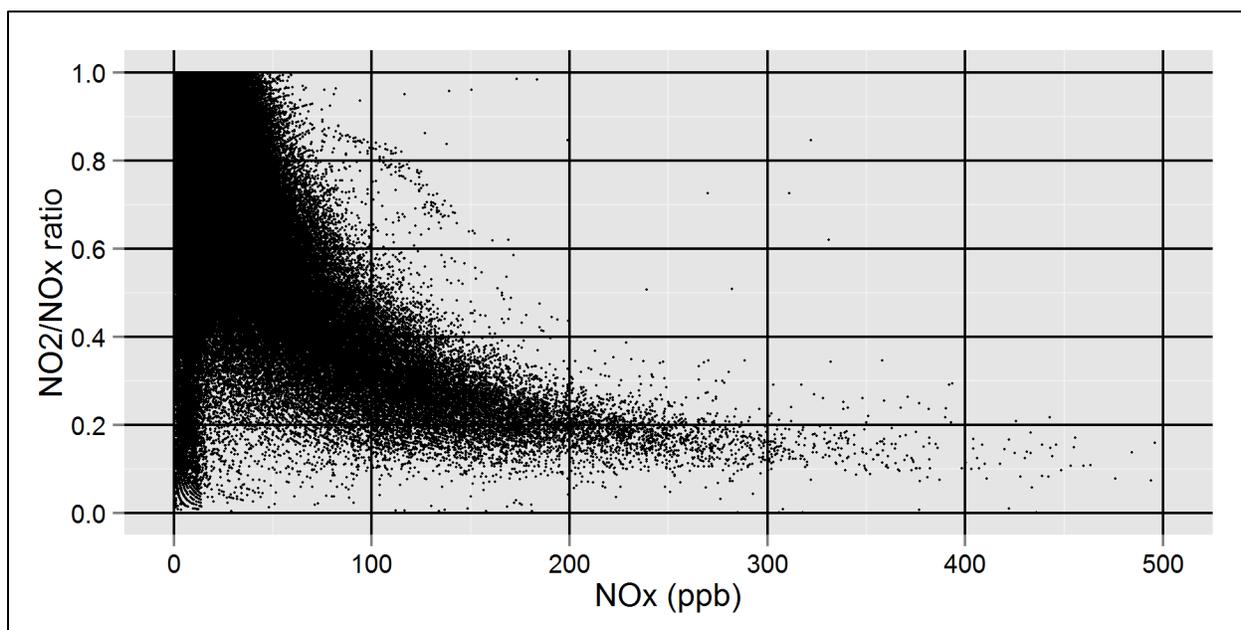


Figure 2 – NO₂/NO_x ratios from AQS for 2012

In addition to developing the ARM2 response curve, (Podrez, 2015) evaluated ARM2 against PVMRM and OLM for three ambient datasets and performed a large number of sensitivity tests with model-based evaluations. The ambient datasets include: 1) a gas processing plant in Empire Abo, NM; 2) a coal-fired power plant in Palaau, HI; and 3) a small diesel-fired power plant in Wainwright, AK. The sensitivity tests included scenarios taken from an earlier report on OLM and PVMRM performance (MACTEC, 2004) and tests to address generalized facilities representative of several other source (diesel generators, an oil refinery, a gas pipeline compressor station, natural gas production fields and processing plants, and a large boiler). These comparisons showed that ARM2 gave generally conservative estimates of the NO₂/NO_x ratio and the total NO₂ as compared to the measurements as well as OLM and PVMRM. The model evaluation report, (RTP Environmental Associates, Inc., 2013), provides more complete details on the evaluation results than the journal article.

2.4 Ozone Limiting Method

(Cole & Summerhays, 1979) is most often cited as the origin of OLM even though this particular paper is a review paper of methods to estimate NO₂ concentrations since there are no earlier citations for OLM. As outlined by (Cole & Summerhays, 1979), OLM assumes NO conversion to NO₂ by reaction with ambient ozone ($NO + O_3 \rightarrow NO_2 + O_2$ Reaction 1), according to the following procedure:

1. Estimate total NO_x using the dispersion model of choice.
2. Divide the total NO_x into two components:
 - a. Component 1 is the “thermal” NO₂ that is emitted directly as NO₂ from the stack (assumed to be 0.10 for most sources)
 - b. The remaining NO_x is assumed to be NO that is available for reaction with ozone.
3. If the ambient [ozone] > 0.9*[NO_x] (the portion of NO_x present as NO), then assume that all NO is converted to NO₂, such that [NO₂] = [NO_x]. If the ambient [ozone] < 0.9*[NO_x], then assume that the amount of NO converted is equal to the available ozone, such that [NO₂] = 0.1*[NO_x] + [ozone].
4. The NO₂ concentration from (3) is added to the background [NO₂] to determine the total [NO₂].

The reaction is assumed to be instantaneous and irreversible and can be applied on an hourly basis (or shorter or longer, depending on the resolution of the model run and background [NO₂] and [ozone] data).

(Cole & Summerhays, 1979) presented no evaluations of OLM, but there have been a number of formal and informal studies that have evaluated OLM based on AERMOD and other dispersion models. The majority of these studies have simultaneously performed evaluations of OLM and PVMRM with results of these studies being summarized below for both OLM and PVMRM.

2.5 Plume Volume Molar Ratio Method

PVMRM was developed by (Hanrahan, 1999a) and is based on the same fundamental chemistry as OLM ($NO + O_3 \rightarrow NO_2 + O_2$ Reaction 1), which is also assumed to be instantaneous and irreversible and can be applied on an hourly basis (or shorter or longer, depending on the resolution of the model run and background [NO₂] and [ozone] data). In contrast to OLM, though, PVMRM attempts to estimate the amount of ozone that has been entrained into the plume(s), rather than assuming all ambient ozone is available for NO conversions. (Hanrahan, 1999a) describes the methodology for PVMRM as follows:

1. Calculated the plume segment volume at the receptor
2. Determine the moles of NO_x present in the plume segment volume
3. Determine the moles of ozone present in the plume segment volume
4. Calculate the ratio of ozone moles to NO_x moles
5. Multiple the ratio found in (4) to the NO_x moles to determine the moles of NO₂
 - a. The original PVMRM assumed that 10% of the NO_x was initially NO₂ upon release, so 0.1 was added to the ratio in (4) to account for the initial NO₂.

Since PVMRM can account for NO conversion in overlapping plumes, PVMRM includes a methodology for determining the volume of overlapping plumes. When considering multiple plumes, the plume volume at each receptor is computed by first identifying the primary source contributing to the NO_x at

the receptor. Then, all additional sources contributing at least half of the amount of NO_x as the primary contributing source are identified as “major contributing sources.” Third, the maximum width between the major contributing sources is found. Finally, the maximum width found in the third step is added to the width of the primary contributing plume to determine the combined plume width. Similarly, for area sources, PVMRM uses the projected width of the area source as part of determining the combined plume width.

2.6 Existing evaluations of OLM and PVMRM

The number of field studies available to evaluate refined NO₂ modeling in the near-field are fairly limited. As a result, the measurement-based model evaluations available for OLM and PVMRM tend to include both models. There are also a number of “sensitivity studies”, that are limited to comparisons modeling scenarios without any measurement data to benchmark model performance. A selection of the model evaluations are summarized here:

1. (Hanrahan, 1999b) presented an evaluation of PVMRM for several field studies, including airplane-based sampling of power plumes in the Netherlands and ground-based measurements from power plants in Hawaii (Palaau) and New Mexico (Empire Abo) as well as a comparison with a large eddy simulation (LES) model. The evaluations were focused on NO₂/NO_x ratios rather than absolute NO₂ and NO_x concentrations and the underlying dispersion model was the Industrial Source Complex (ISC) model. The results of their evaluation showed that the model had some skill in replicating NO₂/NO_x ratios, though there were obvious deficiencies in the model.
2. (MACTEC, 2004) presented sensitivity tests for a variety of single and multi-source scenarios for OLM and PVMRM based on an early version of AERMOD and AERMET. The results of their evaluation showed that both models were reasonably sensitive to source parameters, the NO₂/NO_x ratios tended to be lower for PVMRM than for OLM, and that the NO₂/NO_x ratio tended to be controlled by the volume of the plume for PVMRM versus being controlled by the total NO_x concentration for OLM.
3. (Hendrick, Tino, Hanna, & Egan, 2013) evaluated OLM and PVMRM using a relatively new field dataset from a small diesel-fired power generation facility in Wainwright, AK with a relatively recent version of AERMOD (11103). Additionally, (Hendrick, Tino, Hanna, & Egan, 2013) suggested several improvements to the model code for PVMRM. This study was based on an earlier report (Hendrick, Tino, Hanna, & Egan, 2012), which includes additional details on the Wainwright comparison and a review of other ambient databases used for model evaluations. Three main conclusions were drawn from the study:
 - a. OLM has a tendency to overpredict the NO₂/NO_x ratios, while PVMRM has a tendency to overpredict the ratio at smaller NO_x concentrations and underpredict the ratio at larger NO_x concentrations.
 - b. Neither OLM nor PVMRM have any skill in predicting NO₂ when paired in time and space with measurements. This appears to be driven more by the model’s underlying NO_x prediction rather than with the NO/NO₂ speciation.
 - c. When comparing only the highest unpaired concentrations, both models have a tendency to overpredict the NO₂ concentrations.

4. (Schroeder, 2012) evaluated OLM and PVMRM for a single hypothetical source, but with meteorology and background ozone taken from 4 different locations (Illinois, New Mexico, Utah, and Wisconsin). The source was modeled with 2 emissions rates (1 g/s and 100 g/s) and with 2 ISRs (0.5 and 0.1), resulting in 16 sensitivity tests. The results of the study showed that at lower emission rates, all options showed relatively similar maximum NO₂ concentrations, as there was sufficient ozone relative to NO_x for high conversion rates, while the lower emission rates were sensitive to the ISRs and the ambient ozone.
5. (Podrez, 2015) and the companion report (RTP Environmental Associates, Inc., 2013), though focused on the development of ARM2, also performed extensive testing of OLM and PVMRM with the more recent versions of AERMOD. The analysis completed model-to-monitor comparisons for the field studies from Alaska, New Mexico, and Hawaii, reran the model sensitivity tests initially done by (MACTEC, 2004), and added a number of additional sensitivity tests to include other typical NO₂ sources. The results of the study showed that OLM and PVMRM tended to slightly overestimate the highest NO₂ as compared to the measurement data. All methods tended to show relatively similar maximum NO₂ concentrations when NO_x concentrations were lower, as there was sufficient ozone relative to NO_x for high conversion rates, while the lower emission rates were sensitive to the ISRs and the ambient ozone.

3. Regulatory status of ARM, ARM2, OLM, and PVMRM

EPA is proposing to adopt ARM2, OLM, and PVMRM as non-default options in AERMOD, such that the alternative model approval currently needed for these options is no longer required. However, these methods are still considered screening techniques, and as such, will still require the approval of the appropriate review authority (paragraph 3.0(b) of the proposed Appendix W). This section discusses several aspects of this proposal.

3.1 Regulatory requirements

Under EPA's *Guideline on Air Quality Models* published as Appendix W to 40 CFR Part 51, AERMOD is the preferred model for satisfying New Source Review (NSR) requirements, including Prevention of Significant Deterioration (PSD) for inert pollutants. For inert pollutants, AERMOD is considered to be a refined model, such that within the regulatory framework of a NSR or PSD demonstration, the model is considered not to be biased high or low. NO and NO₂, however, are not inert and conversion from NO to NO₂ must be estimated. At present, under Appendix W, the EPA recommends a 3-Tiered screening approach. The three Tiers should be most conservative at Tier 1 and least conservative at Tier 3, though the selection of any option or setting at any Tier should strive towards the most accurate estimates, rather than the most conservative. While all three Tiers available for NO₂ modeling in AERMOD are considered screening techniques, each Tier has increasing complexity, which includes more refined (and presumably more accurate) estimates of NO and NO₂ speciation, but also increasing data input requirements. Screening models and techniques should not be biased to under predict, i.e., should give conservative modeled estimates. Thus, AERMOD is considered unbiased in its estimates of NO_x concentrations, but estimates of NO₂ concentrations should be either unbiased or conservative. For the Tier 2 and 3, the additional data inputs required may not be available for all facilities, necessitating the

determination of default values to insure that modeled concentrations do not underestimate facility impacts.

3.2 ARM versus ARM2

The original ARM was developed exclusively for long-term average concentrations of NO₂ and the intent was to use national default only when nearby monitoring was not available or at longer transport distances from a source, when a plume would have mixed towards background. The historical implementation of ARM in the NSR and PSD programs, however, has been to use the national default at all distances and all locations, regardless of the availability of nearby monitoring. Fundamentally, this approach for long-term averages is likely appropriately conservative for a Tier 2 method. However, ARM was not intended to estimate short-term average concentrations of NO₂. On the other hand, ARM2 was developed exclusively for short-term average concentrations of NO₂, specifically 1-hour averages. Assuming the implementation of ARM2 is appropriately conservative for estimates of 1-hour NO₂ concentrations, then ARM2 would be preferred to any modifications of ARM for short-term averages. It is also logical that if the 1-hour estimates of NO₂ derived from ARM2 are appropriate, then any long-term averages calculated from ARM2-adjusted 1-hour concentrations should also be appropriate. Given this fact, there is a question as to what method should be used for long term estimates of NO₂ or whether both ARM and ARM2 should be viable options. There are two arguments in favor of ARM2 over ARM. Firstly, ARM has not been implemented according to the recommendation of (Chu & Meyer, 1991), which would a case-by-case analysis of nearby monitoring data to determine the equilibrium ratio rather than using the national default for all cases. Secondly, long-term averages based on ARM and ARM2 would not be identical. Thus, if ARM were used for long-term averages and ARM2 were used for short-term, there would be a discrepancy between the underlying data in hourly values and the long-term averages that could be calculated. This is demonstrated in Table 1 - Comparison of ARM and ARM2 estimated NO₂ concentrations, which has an average NO_x concentration of 235 ppb. Using the ARM national default of 0.75, the estimated NO₂ concentration would be 176 ppb, while the average concentration from ARM2 would be 76.3 ppb. Therefore, if ARM2 is an appropriate tool for estimating 1-hour concentrations, it would be preferred to use the hourly estimates from ARM2 to compute longer-term averages over the application of ARM on average NO_x concentrations.

NO_x	NO₂/NO_x ARM2 curve	ARM2 default applied	NO₂	ARM2 EPA applied	NO₂
50	96%	0.90	45.00	0.90	45.00
100	70%	0.70	69.74	0.70	69.74
150	50%	0.50	75.37	0.50	75.37
200	38%	0.38	76.24	0.50	100.00
250	31%	0.31	78.64	0.50	125.00
400	22%	0.22	89.37	0.50	200.00
500	19%	0.20	100.00	0.50	250.00
<i>Average</i>	<i>Average</i>	<i>Average</i>	<i>Average</i>	<i>Average</i>	<i>Average</i>
235.71	0.47	0.46	76.34	0.59	123.59

Table 1 - Comparison of ARM and ARM2 estimated NO₂ concentrations

3.3 Status of OLM and PVMRM

Currently, OLM and PVMRM are only available for regulatory usage as alternative models, requiring an formal request to the appropriate reviewing authority and technical demonstration for their usage. (U. S. EPA, 2010) and (U. S. EPA, 2011) provided the bulk of the technical demonstration, showing that both models were appropriate as “alternative models”, when applied to the appropriate source configurations. As a result, the usage of OLM and PVMRM has mainly required an administrative request for approval from the appropriate reviewing authority. However, there is a reasonably strong case that both models also meet the requirements of preferred models. Both models are written in a common programming language; the models are well documented; test datasets available for model evaluation; the model is useful to typical users; there are robust model-to-monitor intercomparisons; and the source code is freely available. Given that the EPA has stated that the technical demonstrations supporting the usage of OLM and PVMRM are broadly acceptable for regulatory applications, there is notable scientific merit behind OLM and PVMRM. Additionally, the available databases to test the model indicate that both perform reasonably well and are not biased to underpredict. Therefore, it stands to reason that both methods should be included in AERMOD as regulatory, non-beta preferred options for modeling NO₂.

3.4 The 3-Tiered approach

Despite the fact that OLM and PVMRM are clearly more refined and accurate than full conversion, ARM, and ARM2, both OLM and PVMRM are still considered screening rather than refined models at this point. Thus, a case could be made to eliminate the Tier 1 and 2 methods in preference of OLM and PVMRM. However, the intent in the tiered screening process is to reduce the burden of performing an NO₂ modeling demonstration by providing easier to implement methods. As a result, the EPA intends to maintain the 3-tiered screening for NO₂ modeling but changing ARM2, OLM, and PVMRM to non-beta options.

4. Proposed regulatory options for NO₂ modeling in AERMOD

The Tier 2 and Tier 3 options for NO₂ available within AERMOD have several settings that can affect their results. For some of these settings, facility or area-specific data is not always available, requiring considerations that are appropriate for default regulatory applications. This section reviews these technical details within the context of regulatory requirements.

4.1 ARM2 options

The equation that was derived for ARM2 will indicate NO₂/NO_x ratios above 1 for lower NO_x concentrations and less than 0 for higher NO_x concentrations. As a result, maximum and minimum NO₂/NO_x ratios were selected for each end of the distribution. These maximum and minimum values are discussed further here.

(Podrez, 2015) and (RTP Environmental Associates, Inc., 2013) recommended 0.9 as the maximum ratio, as this ratio has generally been considered an appropriate equilibrium ratio for background air and diluted plumes. The ambient data shown in Figure 2 – NO₂/NO_x ratios from AQS for 2012 indicates that NO₂/NO_x ratios do exceed 0.9 and achieve a maximum of 1.0. Many of these high NO₂/NO_x ratios occur at lower NO_x levels, where instrument uncertainty can be a significant source of measurement error.

Additionally, the PSS analysis shown in Figure 1 – NO₂/NO_x equilibrium ratios based on the PSS assumption from Equation 1. also indicates that when solar radiation levels are relatively low (2 cases with 95% cloud cover) that the equilibrium ratio can approach 1.0. However, the PSS values shown in Figure 1 – NO₂/NO_x equilibrium ratios based on the PSS assumption from Equation 1. assume that ozone concentrations remain constant, i.e., ozone depletion is not accounted for in the calculations. As a result, the NO₂/NO_x ratios shown in Figure 1 – NO₂/NO_x equilibrium ratios based on the PSS assumption from Equation 1. overestimate what would happen in a plume, with ozone titration occurring while converting NO to NO₂.

In addition, the EPA has established that the equilibrium ratio of 0.9 is appropriate for Tier 3 methods based on the recommendations for PVMRM given by (Hanrahan, 1999a). Though there is evidence that equilibrium ratios can be above 0.9, these cases are generally at lower NO_x concentrations and only occur when ozone levels are very high or when ambient light is very low. Since ozone has a daytime maximum and a nighttime minimum, the NO₂/NO_x ratios for higher ozone levels for even moderate light conditions maximize at 0.9. Again, this is an overestimate, as ozone is assumed to be held constant rather than titrated by NO. Likewise, in lower light levels and at nighttime, the ambient ozone will be low and titrated quickly. The resulting NO₂/NO_x ratios for the lower-light scenarios are shown in Figure 1. These ratios would be associated with the lower ozone concentrations only, resulting in a conservative estimate of NO₂/NO_x ratios around 0.9. Thus, based on the information from the PSS analysis, the maximum NO₂/NO_x ratio of 0.9 is reasonable and appropriate as a maximum ratio for ARM2.

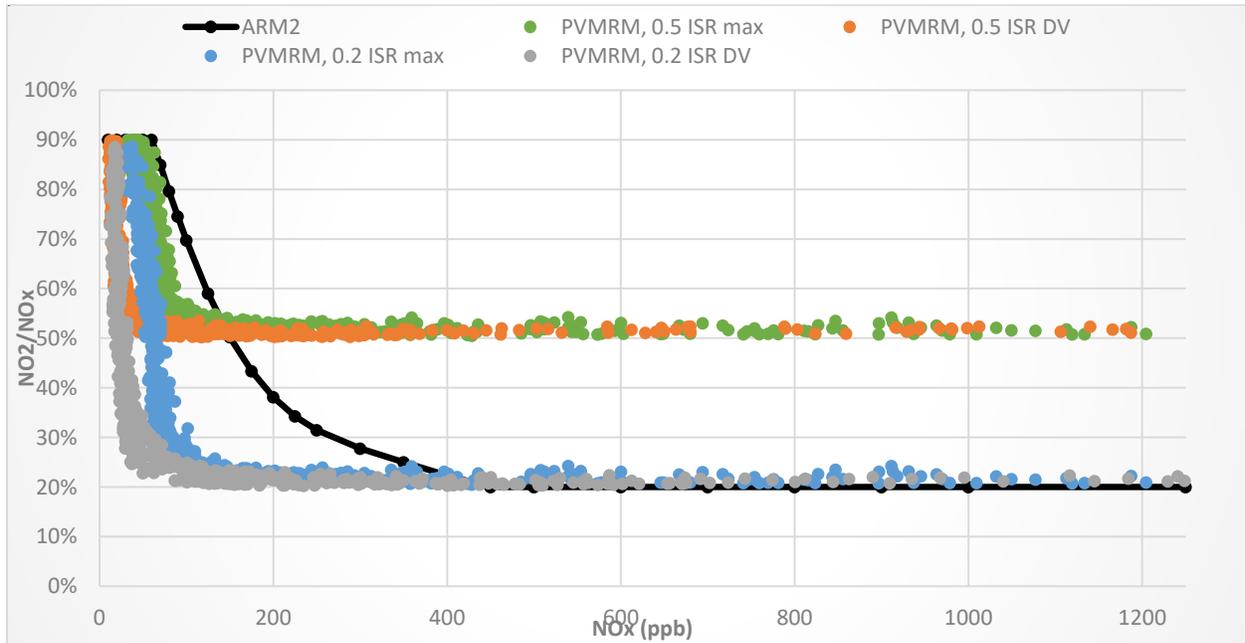


Figure 3 - Comparison of modeled NO₂ concentrations from ARM2 and PVMRM

(Podrez, 2015) and (RTP Environmental Associates, Inc., 2013) recommended a minimum ratio of 0.2, as this value seemed to be the maximum ratio from the ambient data at the higher NO_x concentrations. The minimum ratio of 0.2 appears to be fairly well supported by the ambient data in that there are few

data points above the 0.2 NO₂/NO_x ratio at higher NO_x concentrations. However, the regulatory requirements are important to consider when determining a national default value for the minimum ratio. (Owen & Brode, 2014) discuss at length the regulatory implications of the minimum NO₂/NO_x ratio, concluding that the default 0.2 cannot appropriately account for all sources. While there is general agreement that most sources have relatively low ISRs, there are sources with higher ISRs and it would be inappropriate to allow sources to base their modeling on lower ISRs than they actually have. As discussed in (Owen & Brode, 2014), the minimum ambient NO₂/NO_x ratios in a plume are first and foremost driven by the ISR and that the NO₂/NO_x ratio can only increase from the ISR as mixing and conversions occurs in the atmosphere. (U. S. EPA, 2011) established a national default ISR of 0.5 for sources that did not have site-specific data (which is always preferred over default values) for the Tier 3 methods. This value was considered appropriately conservative, given that most sources are likely to have much lower ISR. (Owen & Brode, 2014) showed that a minimum NO₂/NO_x ratio in ARM2 of 0.5 produced appropriately conservative results for a Tier 2 method relative to sources modeled with PVMRM and an IRS of 0.5, as shown in Figure 3 - Comparison of modeled NO₂ concentrations from ARM2 and PVMRM. Based on the assumption that the 0.5 ISR is appropriate for OLM and PVMRM, then a minimum NO₂/NO_x ratio of 0.5 should also be appropriate as a minimum ratio for ARM2 in evaluating sources with an unknown ISR.

4.2 Default options for OLM and PVMRM

There are two additional inputs required for OLM and PVMRM that are not required for the other NO₂ options. In addition to the equilibrium ratio discussed above, the source's ISR and background ozone concentrations are also required model inputs.

The NO₂/NO_x equilibrium ratio of 0.9 recommended for ARM2 is also recommended for OLM and PVMRM, based on the information from the PSS analysis and ambient data considerations presented in Section 4.1.

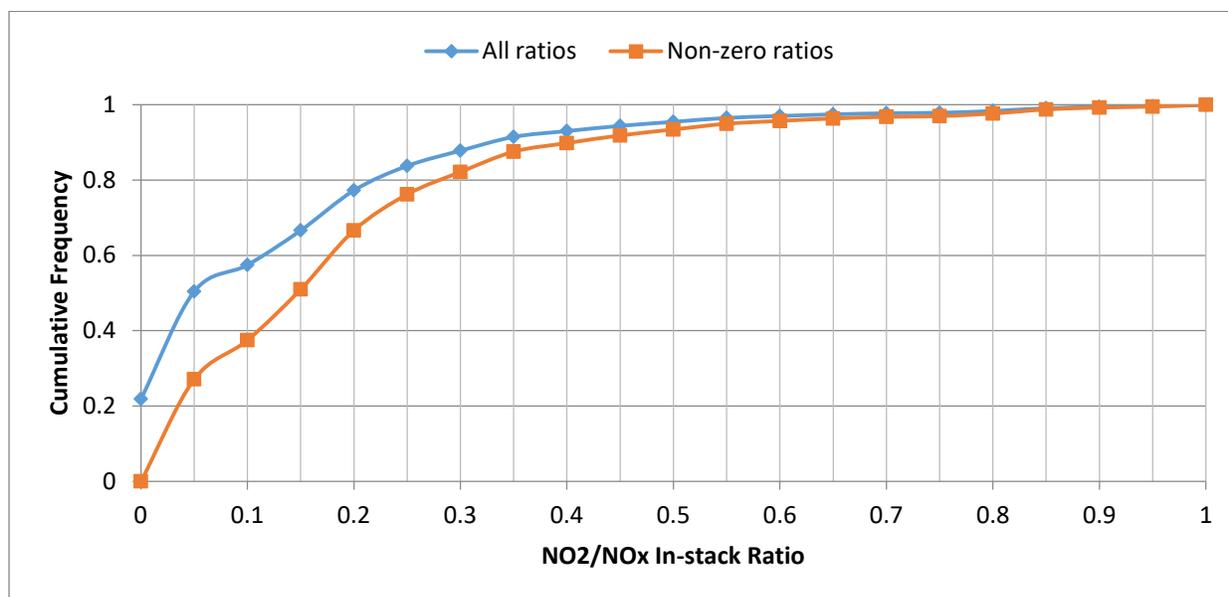


Figure 4 - Distribution of NO₂ ISRs from EPA's database as of June, 2015.

When modeling with OLM and PVMRM, each source requires an ISR be specified. As detailed above, the ISR is the initial driving factor in the ambient NO₂/NO_x ratios and thus can have a major impact on estimated NO₂ concentrations nearest each source. The EPA recently initiated the collection of NO₂/NO_x ISR measurements for compilation in a publically available database for reference in regulatory applications (http://www.epa.gov/scram001/no2_isr_database.htm). The database represents one of the larger collection of samples of NO₂/NO_x ISRs and provides an opportunity to evaluate the relative conservativeness of any particular ISR. The database has over 2300 entries, though only 1580 are non-zero entries. The entries with an ISR of 0 indicate that there is no NO₂ in the exit gas stream, a case that is extremely unlikely. Most NO₂ instruments would still report some low level of NO₂ even when no NO₂ is present (e.g., less than the detection limit, commonly 1 ppb). The fact that zero values (0 ppb of NO₂) are reported for roughly 700 entries suggests that NO₂ was not actually measured (rather than measurement being collected and concentrations of 0 ppb of NO₂ being reported). Therefore, the focus here is on the remaining non-zero entries.

As shown in Figure 4, over 93% of the remaining ISR are less than the traditional default of 0.5, which strongly indicates that this default value will be conservative for most sources and is a reasonable default to insure model results do not underpredict potential source impacts. (Owen & Brode, 2014) recommended that, in the absence of source-specific data, the national default of 0.5 be applied to the new or modifying source and sources in the immediate vicinity of the new or modifying source. However, since the ISR has a diminishing impact on ambient NO₂/NO_x ratios as a plume is transported farther downwind due to mixing and reaction towards background ambient NO₂/NO_x ratios, (Owen & Brode, 2014) recommended that more distant sources could use a default ISR of 0.2 in lieu of source specific data. According to the EPA ISR database, 67% of the tests indicated ISRs less than of 0.2. Given that the greatest impact of the NO₂/NO_x in-stack ratio is typically on the closest/closer receptors to a source and that the highest modeled impact also generally is close to a source, it is reasonable to set 0.2 as a default for the more distant nearby sources. (Owen & Brode, 2014) suggested sources that use a default of 0.2 will generally be greater than 1 to 3 km away from the primary source, with the distance dependent upon the relative strength of the primary and background sources as well as the relative location of the background sources with respect to the prominent wind direction and location of expected maximum impacts from the primary source.

The third required input for OLM and PVMRM are background ozone concentrations. Traditionally, there have not been default inputs for background ozone. Instead, hourly data from a nearby ozone monitor is used (e.g., ozone data taken from AQS (AQS, 2014)). Data gaps from a particular monitor can be filled with: 1) data from another monitor, 2) interpolation between existing data, or 3) substitution with maximum data from the same monitor for similar time periods (e.g., maximum ozone concentrations from nighttime winter might be used to fill a missing hour from 3 am in January). It would be possible to set a conservative national default ozone value (e.g., 90 ppb would likely be conservative in most cases). However, ozone monitors are ubiquitous throughout the nation and ozone is a regional pollutant. Thus, ambient monitoring data from a more distant monitor could easily be appropriate. These facts make it relatively straight-forward to find reasonably representative background ozone data. Given this situation, no default background ozone concentration is suggested for implementation in the model and hourly, site-specific data is recommended.

4.3 Appropriate applications of OLM and PVMRM

The Tier 3 methods of OLM and PVMRM each have strengths and weaknesses that should be considered when applied to a particular modeling scenario. (U. S. EPA, 2010), (U. S. EPA, 2011), and (Owen & Brode, 2014) discussed these aspects of the two models at length. In summary, these memos recommend the following applications for each model:

- PVMRM is recommended for relatively isolated, elevated sources.
- PVMRM is not recommended for area or line sources, near-surface releases, or groups of sources with moderate distances between them due to the potential to overestimate plume volumes in these cases.
- OLM is recommended for all sources where PVMRM is anticipated to overestimate plume volumes, including roadway emissions from mobile sources.
- For most cases, the OLMGROUP ALL option is recommended when using OLM.

4. PVMRM2

In addition to changing the status of PVMRM from an alternative model to an accepted Tier 3 screening technique for NO₂, we are proposing modifications to the current PVMRM formulation. The new PVMRM, called PVMRM2, has 3 major modifications from the current PVMRM formulation:

1. The current formulation of PVMRM uses relative dispersion coefficients, which are most appropriate for convective conditions but are likely to overestimate the plume volume in stable conditions, and therefore the NO₂ concentrations during stable conditions. The PVMRM2 option utilizes the original relative coefficients for convective conditions, but uses a new formulation based on total dispersion coefficients for stable conditions, with appropriate adjustments to the number of sigmas used to define the plume volume.
2. The original PVMRM formulation uses a radial distance from the source to receptor to define the plume volume, which determines the amount of O₃ available for NO-NO₂ conversion. However, due to the meander component, plume impacts can occur upwind of the source resulting from upwind dispersion. These impacts can occur at receptors that are far off the plume centerline. Using the radial distance does not take into account the plume width associated with the concentrations far from the plume centerline. PVMRM2 includes modifications to more accurately account for plume volumes in these situations.
3. In the process of implementing and testing the PVMRM2 option, a number of issues associated with the treatment of penetrated plumes were address that also affected the PVMRM option.

4.1 Comparison of PVMRM vs. PVMRM2 Options in AERMOD

DISTDOM – distance from source to receptor used to calculate the plume volume and the moles of NO_x contained in the plume:

PVMRM:

For POINT & VOLUME sources: DISTDOM = radial distance from dominant source to receptor (using center for VOLUMES);

For AREA/LINE/OPENPIT source: DISTDOM = radial distance from upwind corner of dominant source to receptor.

PVMRM2:

For POINT & VOLUME sources: DISTDOM = downwind distance from dominant source (center for VOLUMEs) to receptor, with minimum of 1m;

For AREA/LINE/OPENPIT source: DISTDOM = downwind distance from center of dominant source to receptor, with minimum of 1m.

Rationale: DISTDOM determines the volume of the plume and therefore the moles of O3 within the plume. DISTDOM is also used to calculate the moles of NOx contained in the plume based on the wind speed. Applying the original approach for receptors located upwind of the source may produce physically unrealistic estimates of NO to NO2 conversion, and using the downwind distance provides a more realistic estimate of NOx conversion consistent with a straight-line, steady-state plume model.

domNOxmoles – moles of NOx in the plume from source to receptor for dominant source based on emission rate, distance and wind speed:

PVMRM:

For all source types: domNOxmoles = Q * DISTDOM/UDOM

PVMRM2:

For all source types: domNOxmoles = Q * (1-NO2Ratio)*DISTDOM/UDOM

Rationale: By using the total NOx emission rate (Q), the original PVMRM formulation effectively double counts a portion of the NO2 emissions by applying the domO3moles/domNOxmoles ratio to determine the conversion of NO to NO2, and adding that to the in-stack NO2/NOx ratio. A similar approach is used for sumNOxmoles (moles of NOx in the “combined” plume) except that AVE_NO2RATIO is used to account for the combined in-stack ratios of NO2 across all contributing plumes.

CWMIN/CWMAX – Minimum and maximum crosswind distances of major contributing sources used to determine the “box” within which emissions from all sources are included:

PVMRM:

For POINT & VOLUME sources: CWMIN/CWMAX = range of crosswind distances for contributing sources (using center for VOLUMEs);

For AREA/LINE/OPENPIT sources: CWMIN/CWMAX = range of crosswind distances for

contributing sources (using center of source), including the projected width for AREA, LINE and OPENPIT sources.

PVMM2:

For POINT & VOLUME sources: CWMIN/CWMAX = range of crosswind distances for contributing sources (using center for VOLUME sources);

For AREA/LINE/OPENPIT sources: CWMIN/CWMAX = range of crosswind distances for contributing sources (using center of source), without including projected width for AREA, LINE, and OPENPIT sources.

Rationale: Including the projected width of AREA/LINE/OPENPIT source to determine the “box” of major contributing sources could significantly increase the moles of O3 within the combined plume, and therefore increase the conversion of NO to NO2.

DWMIN/DWMAX – Minimum and maximum downwind distances of major contributing sources used to determine the “box” within which emissions from all sources are included:

PVMM:

For POINT & VOLUME sources: DWMIN/DWMAX = range of downwind distances for contributing sources (using center for VOLUME);

For AREA/LINE/OPENPIT sources: DWMIN/DWMAX = range of downwind distances for contributing sources (using center of source), including the projected length for AREA, LINE and OPENPIT sources.

PVMM2:

For POINT & VOLUME sources: DWMIN/DWMAX = range of downwind distances for contributing sources (using center for VOLUME sources);

For AREA/LINE/OPENPIT sources: DWMIN/DWMAX = range of crosswind distances for contributing sources (using center of source), without including projected length for AREA, LINE, and OPENPIT

sources.

Rationale: Including the projected length of AREA/LINE/OPENPIT source to determine the “box” of major contributing sources could significantly increase the moles of O3 within the combined plume, and therefore increase the conversion of NO to NO2.

Dispersion coefficients used to calculate the volume of the plume:

PVMRM:

For all source types: Relative dispersion coefficients are used to calculate the plume volume for stable and convective conditions; however, these coefficients are likely to overestimate the plume volume under stable conditions, and therefore overestimate NO2 concentrations.

PVMRM2:

For all source types: Relative dispersion coefficients are used to calculate the plume volume for convective conditions, but the “standard” total dispersion coefficients are used to calculate plume volume for stable conditions. However, since total dispersion coefficients are bimodal (i.e., separate lateral and vertical coefficients) the stable dispersion coefficients are calculated as $\text{SQRT}(\Phi_y * \Phi_z)$.

Rationale: The relative dispersion coefficients used for the original PVMRM option are not appropriate for stable conditions, and will tend to overestimate plume volume and NO2 concentrations under stable conditions.

Defining the extent of the plume used to calculate the plume volume:

PVMRM:

For all source types: The plume volume calculation is based on a radius of four (4) times the relative dispersion coefficient, which accounts for about 99.994% of the plume. A minimum value of 5m is assumed for the radius of the plume to account for near-source effects (e.g., downwash), which is consistent with the initial plume volume assumed by Hanrahan (1999), i.e., $(1.282/4.0) * 15 = 4.8$ (rounded to 5)

PVMRM2:

For all source types:

The radius used to define the plume volume varies based on stability. For stable conditions, the radius of the plume is assumed to be 1.282 times the total dispersion coefficient, consistent with the original PVMRM approach proposed by Hanrahan (1999). This accounts for about 80% of the plume. For unstable conditions, the radius of the plume is defined as 2.58 times the relative dispersion coefficient, which accounts for about 99% of the plume. A minimum value of 9m is assumed for the radius of the plume to account for near-source effects (e.g., downwash).

In addition, since AERMOD incorporates a horizontal meander meander algorithm that increases lateral plume spread beyond that accounted for based on dispersion coefficients, the number of sigmas used to define the plume volume is adjusted to account for meander, i.e.,

$$NSUBZ = \text{MIN}(2.15, 1.282 * (\text{SYEFF}/\text{SY}),$$

where SYEFF is the effective sigma-y value that replicates the plume centerline concentration associated with meander, but based on a standard Gaussian plume calculation. An upper bound of 2.15 is applied, which corresponds with the point at which the concentration is 10 percent of the centerline value, and is used to define the extent of the plume in other contexts (e.g., initial dispersion coefficients for volume sources). The minimum value of the dispersion coefficient is also adjusted based on the ratio 1.282/NSUBZ, where NSUBZ is the adjusted value.

Since the portion of the plume that penetrates above the mixing height during unstable conditions is treated as a stable plume, the minimum relative dispersion coefficient for penetrated plumes (SRMIN3) is a weighted average of the stable and unstable values based on plume penetration factor (PPF), i.e.,

$$SRMIN3 = \text{PPF} * \text{SRMINS} + (1 - \text{PPF}) * \text{SRMINU}$$

In addition, the value of NSUBZ for penetrated plumes is adjusted based on PPF-weighted mean of stable and unstable values of NSUBZ.

Rationale: The approach for the original PVMRM option of using 4 times the dispersion coefficients to define the volume of the plume is excessive. It accounts for about 99.994% of the plume, and corresponds to the point at which the concentration is about 0.00005 times the centerline concentration. That approach effectively assumes full and instant entrainment of ozone within the plume which is physically unrealistic. The PVMRM2 option provides a more reasonable account of the plume volume for purposes of NO_x conversion.

4.2 Comparisons of PVMRM and PVMRM2 for select field studies

Comparisons of PVMRM and PVMRM2 were conducted for the Empire Abo gas plant in New Mexico and the Palaau generating station on the island of Molokai. The Empire Abo data set consists of data from two monitors located near the Empire Abo gas plant, with one monitor located 1.6 km north of the plant, and the other located 2.5 km south of the plant. Data collection included ozone, NO_x, and meteorological data. Ambient data is available for a two year period, from June, 1993, through June, 1995. Emissions from the 20 stacks at the facility were assumed to be constant. The Palaau generating station data set consists of data from one monitor 240 meters from the generating stations. Data collection included ozone, NO_x, and meteorological data. Ambient data is available for a one year period, from January, 1993, through December, 1993.

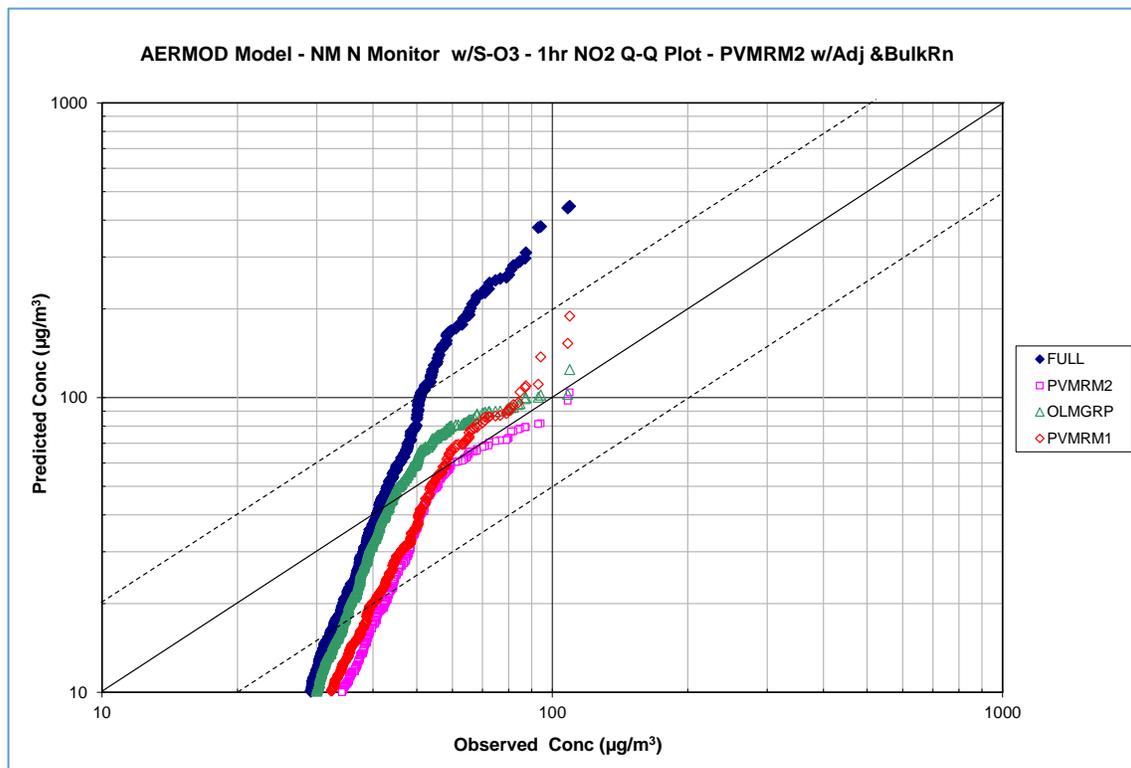


Figure 5 - Comparison of PVMRM and PVMRM2 for the Empire Abo north monitor

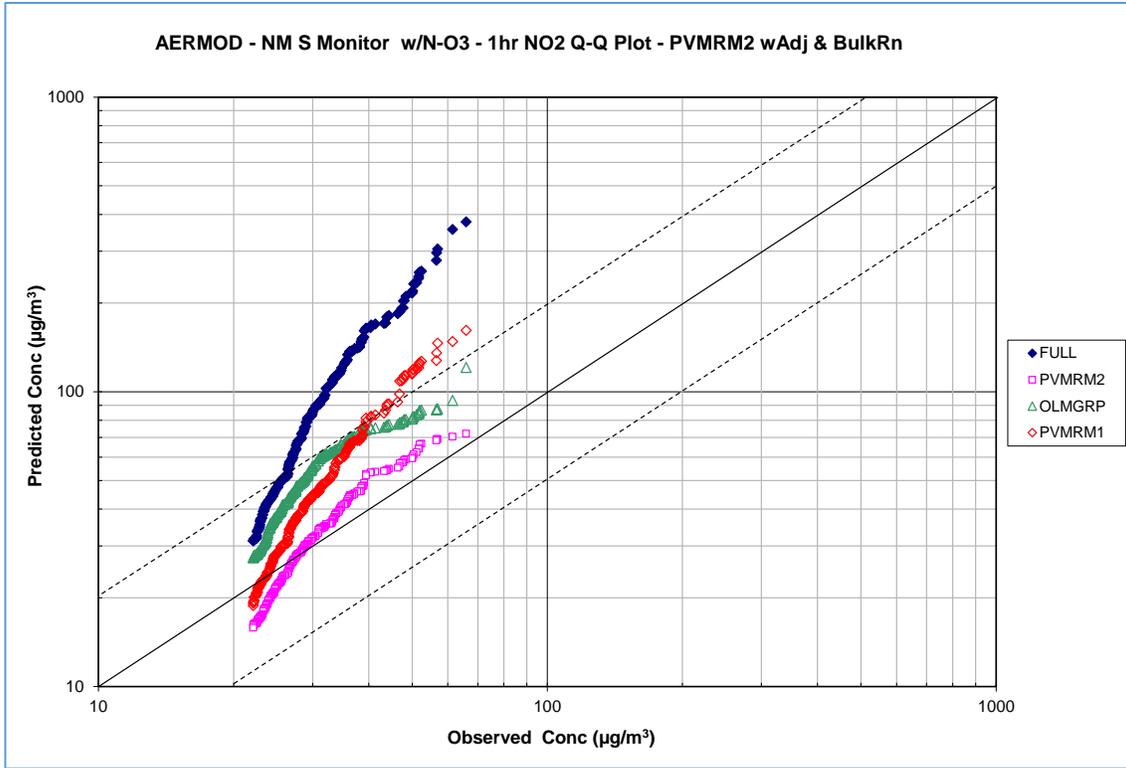


Figure 6 - Comparison of PVMRM and PVMRM2 for the Empire Abo south monitor

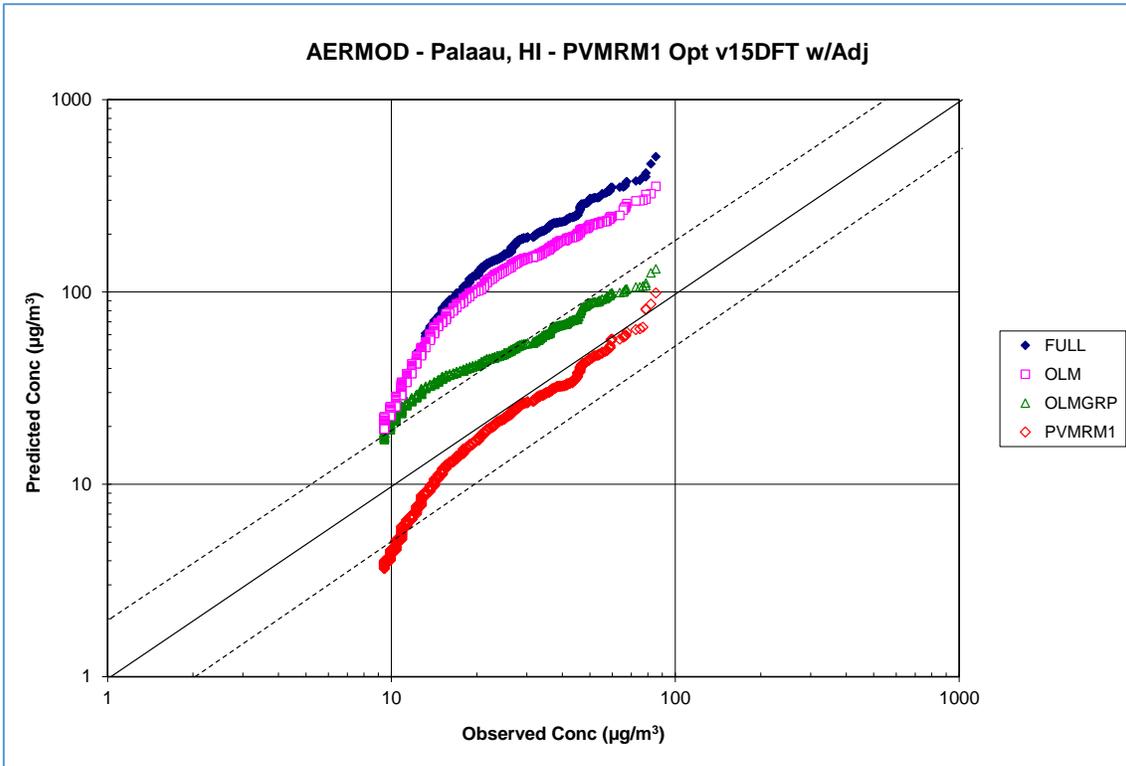


Figure 7 - QQ plot of PVMRM for the Palaau monitor

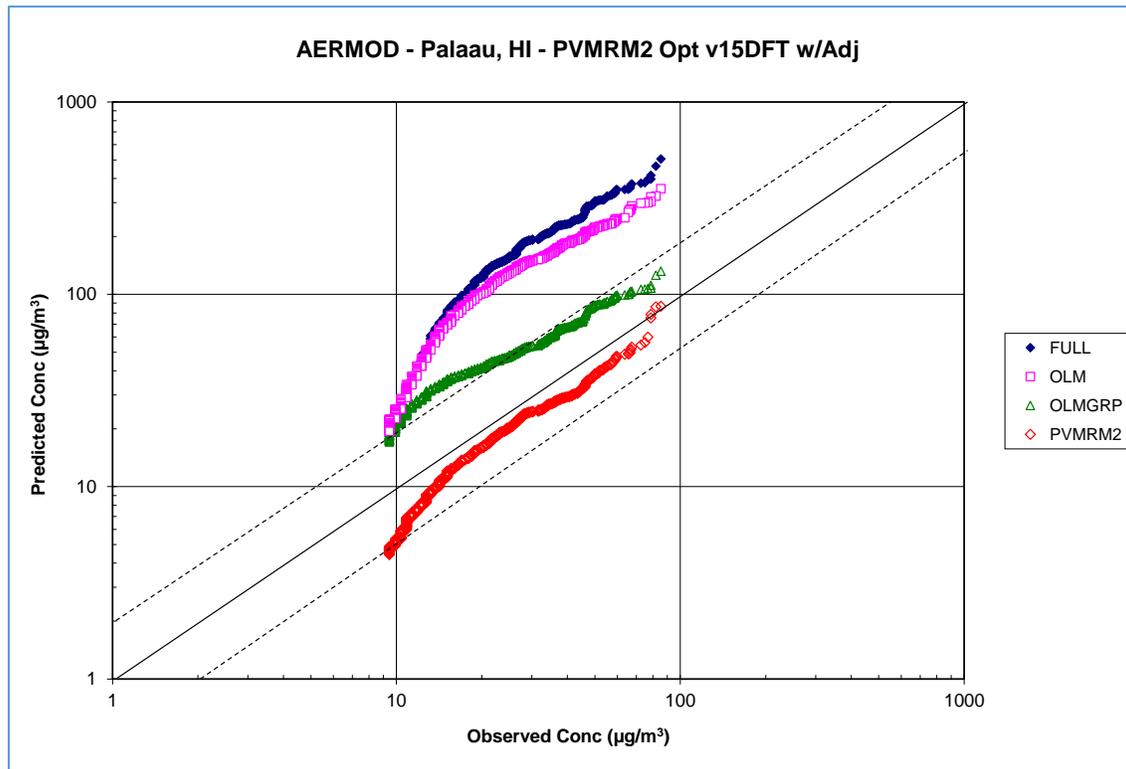


Figure 8 - QQ plot of PVMRM2 for the Palaau monitor

There is clearly a substantial improvement in the results for the Empire Abo field study. Both the north and south monitor show PVMRM2 significantly outperforms PVMRM and is the best performing model from the comparison. For the south monitor, PVMRM is outside the factor of 2 line for highest concentrations, while the PVMRM2 results are within 20% of the measurements. For Palaau, PVMRM2 performs slightly better for the highest few concentrations, but tends to underpredict slightly for much of the upper end of the distribution. Overall, the PVMRM2 performance for Palaau seems to be slightly worse, but the difference is marginal, particularly when compared to the model performance found in the Empire Abo data set. Based on these findings, along with the technical bases for these changes, the EPA believes that it is appropriate to make PVMRM2 the new default, replacing the current implementation of PVMRM.

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United States
Environmental Protection
Agency

Office of Air Quality Planning and Standards
Air Quality Analysis Division
Research Triangle Park, NC

Publication No. EPA-454/B-15-004
[December, 2015]
