

Hourly NO to NO₂ Conversion Methods in AERMOD

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Most emissions of oxides of nitrogen from combustion and other source process emissions are in the form of NO and other oxides; however the related National Ambient Air Quality Standard (NAAQS) is for nitrogen dioxide (NO₂). Consequently, EPA has approved a three-tiered approach for the conversion of NO_x emissions in a plume dispersion model to ambient NO₂ concentrations. While a great number of chemical reactions take place in the atmosphere after initial release of these NO_x-like emissions, they do not all convert to NO₂ and

sources are different in their emissions characteristics as well as physical parameterization, one recommendation does not fit all. This review is intended to raise the awareness of modelers and decision-makers to the vagaries of this modeling adjustment.

Background

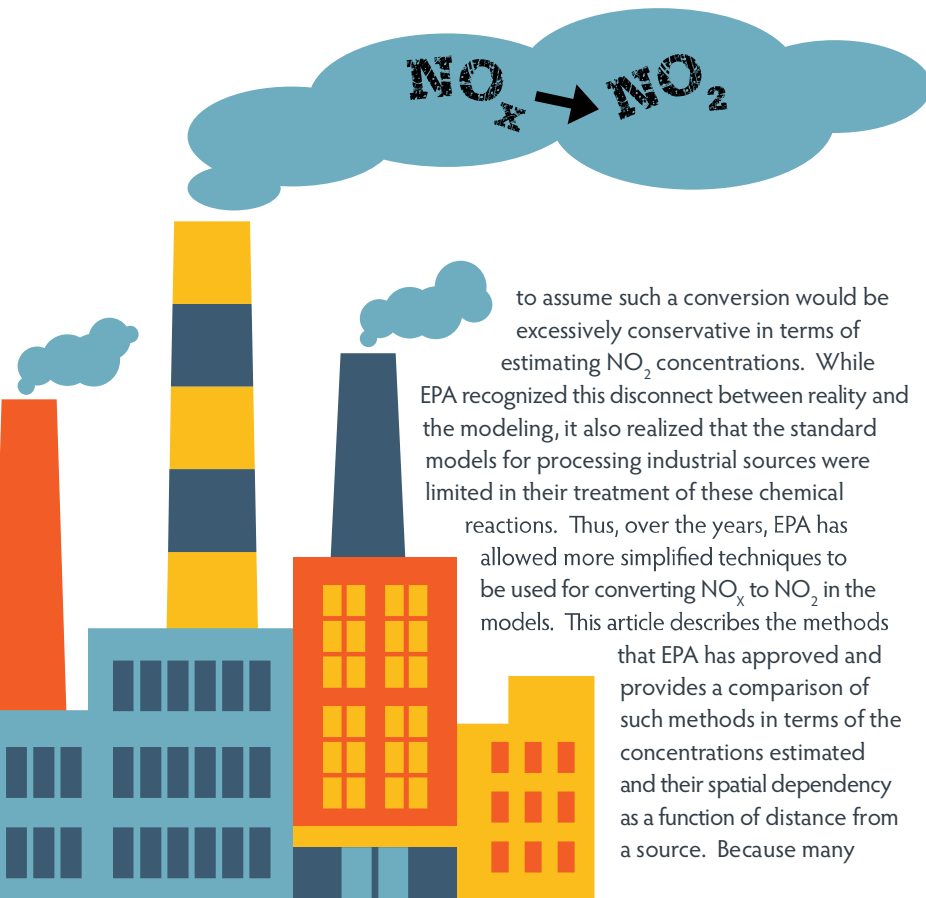
Section 5.2.4 of EPA's *Guideline on Air Quality Models*, Appendix W to 40 CFR Part 51¹ (Appendix W), recommends a three-tiered screening approach to obtain annual average estimates of NO₂ concentrations from point sources for New Source Review analysis, including PSD and SIP planning purposes:

- **Tier 1** – assume a total conversion of NO_x to NO₂
- **Tier 2** – the Ambient Ratio Method (ARM) whereby the model predicted NO_x concentrations are multiplied by empirically-derived NO₂/NO_x ratio, generally based on a ratio derived from ambient monitoring data; an annual national default ratio of 0.75 is recommended in Appendix W
- **Tier 3** – the Plume Volume Molar Ratio Method (PVMRM) or Ozone Limiting Method (OLM) which are more detailed screening methods considered on a case-by-case bases

According to EPA's memorandum on *Applicability of Appendix W Modeling Guidance for the 1-hour NO₂ National Ambient Air Quality Standard*² (June 29, 2010 memo), the Appendix W recommendations regarding the annual NO₂ standard are also applicable to the new 1-hour NO₂ standard. For the original annual



to assume such a conversion would be excessively conservative in terms of estimating NO₂ concentrations. While EPA recognized this disconnect between reality and the modeling, it also realized that the standard models for processing industrial sources were limited in their treatment of these chemical reactions. Thus, over the years, EPA has allowed more simplified techniques to be used for converting NO_x to NO₂ in the models. This article describes the methods that EPA has approved and provides a comparison of such methods in terms of the concentrations estimated and their spatial dependency as a function of distance from a source. Because many



¹ USEPA, 40 CFR Part 51 – Revision to the Guidance on Air Quality Models: Adoption of a Preferred General Purpose (Flat and Complex Terrain) Dispersion Model and Other Revisions; Final Rule. November 9, 2005.

² USEPA, Memorandum – Applicability of Appendix W Modeling Guidance for the 1-hour NO₂ National Ambient Air Quality Standard. June 29, 2010.

average applicability, much of the chemistry and atmospheric variability is averaged out over the longer averaging period and applicability is representative. However, for a 1-hour event, such applicability may be more questionable and additional considerations may apply in the context of the 1-hour standard. The characteristics and ratios of pollutant constituents of the emission sources will dictate the representativeness of the tiered conversion techniques. Again, comparing the techniques but now within the context of the 1-hour NAAQS:

- **Tier 1** – apply to the 1-hour NO₂ standard without any additional justification
- **Tier 2** – apply to the 1-hour NO₂ standard in many cases, but considerations will be needed regarding an appropriate ambient ratio for peak hourly impacts
- **Tier 3** – considered on a case-by-case basis for the 1-hour NO₂ standard, but certain input data requirements that are assumed for Tier 3 applications may be of greater importance for the 1-hour standard than for the annual standard

The AERMOD Model³ is representative of the new generation of dispersion models based on current understanding of micro-meteorology and dispersion, including treatment of both surface and elevated sources, and both simple and complex terrain. While AERMOD does not explicitly consider chemistry in the atmosphere, beginning with AERMOD Version 13350 (released on December 24, 2013), it computes hourly NO₂ concentrations under all three tiers as well as an additional ARM2 method. Tiers 2 and 3 methods are described further below.

Hourly NO_x to NO₂ Conversion Methods in AERMOD —Ambient Ratio Method (ARM and ARM2), Tier 2

Beginning with AERMOD Version 13350, two Ambient Ratio Methods (ARM), namely, the default ARM (as described above), and the non-default/Beta ARM2, are incorporated into AERMOD.

The ARM2 was developed by the American Petroleum Institute (API)⁴ in response to the fact that estimated hourly concentrations using the current three-tier levels were much higher than observed concentrations. The ARM2 method is based on an empirical polynomial equation for the calculation of the ambient ratio and was derived by fitting all 2001-2010 monitoring data. The ARM option is similar to and based on Tier 2 of the

multi-tiered approach for modeling NO₂ impacts discussed in Section 5.4.2 of Appendix W. EPA's memorandum on *Additional Clarification Regarding Application of Appendix W Modeling Guidance for the 1-hour NO₂ National Ambient Air Quality Standard*⁵ (March 01, 2011 memo) recommends "...use of 0.8 as a default ambient ratio for the 1-hour NO₂ standard under Tier 2 without additional justification." ARM2's implementation in AERMOD represents a more refined approach to generating the appropriate ambient ratios.

Ozone Limiting Method (OLM), Tier 3

The Ozone Limiting Method involves an initial comparison of the estimated maximum NO_x concentration and the ambient ozone concentration to determine the limiting factor to NO₂ formation:

- If ozone concentration is greater than the maximum NO_x concentration, then total NO_x to NO₂ conversion is assumed;
- If the maximum NO_x concentration is greater than the ozone concentration, the formation of NO₂ is limited by the ambient ozone concentration.

The limitation of this method is that fresh ozone is assumed to be uniformly and continuously mixed across the cross section of the plume. The OLM does not account for the molar ratio of NO_x to ozone mixed into the plume, nor does it account for the gradual entrainment and mixing of ambient ozone in the plume.

Three publications by EPA, namely, Appendix W, the June 29, 2010 memo, and the March 1, 2011 memo clarified that using the OLM in the AERMOD model should be considered as a Tier 3 application. Because the OLM is currently implemented as a non-regulatory-default option within AERMOD, its use requires justification and approval by the EPA Regional Office on a case-by-case basis.

³ Cimarelli, A. J., Perry, S. G., Venkatram, A., Weil, J. C., Paine, R., Wilson, R. B., Lee, R. F., Peters, W. D. and Brode, R. W.. AERMOD: A Dispersion Model for Industrial Source Applications. Part I: General Model Formulation and Boundary Layer Characterization. *Journal of Applied Meteorology*. 44(5):682-693. 2005.

⁴ API. Ambient Ratio Method Version 2 (ARM2) for Use with AERMOD for 1-hr NO₂ Modeling: Development and Evaluation Report. American Petroleum Institute, Washington, DC. 2013.

⁵ USEPA, Memorandum – Additional Clarification Regarding of Application of Appendix W Modeling Guidance for the 1-hour NO₂ National Ambient Air Quality Standard. March 01, 2011

Plume Volume Molar Ratio Method, Tier 3

The Plume Volume Molar Ratio Method (PVMRM)⁶ calculates the ratio of ozone moles to NO_x moles in an effluent plume segment volume at downwind distance receptor locations. This molar ratio is multiplied by the NO_x concentrations estimated by AERMOD to calculate the NO_2 concentrations in the plume. The PVMRM includes a method to simulate multiple NO_x sources by accounting for how the plumes merge and combine. Similar to the OLM, the PVMRM does not account for the gradual entrainment and mixing of ambient ozone in the plume, and fresh ozone is assumed to be uniformly mixed across the plume cross section.

As with the OLM, the use of PVMRM in AERMOD should be considered as a Tier 3 application, and its use requires justification and approval by the Regional Office on a case-by-case basis.

Both the OLM and PVMRM require two key model inputs in the context of the 1-hour NO_2 standard, namely the in-stack ratios of NO_2/NO_x emissions and background ozone concentrations. The March 1, 2011 memo recommends "general acceptance of 0.5 as a default in-stack ratio of NO_2/NO_x for input to the PVMRM and OLM options within AERMOD, in the absence of more appropriate source-specific information on in-stack ratios." EPA has created a website whereby such NO_2/NO_x may be found, but the number of processes and sources is limited: www.epa.gov/ttn/scram/no2_isr_database.htm.

A Comparison of ARM, OLM and PVMRM

As tools for providing more representative ambient NO_2 concentrations, the tiered methods are reasonable but which tool works the best? For a simple test case, predicted ambient NO_2/NO_x ratios were compared for a stationary elevated point source for a typical summer daytime hour. The point source is 35 meters tall and 2.4 meters in diameter. It emits NO_x at a rate of 50 g/s with a NO_2/NO_x in-stack ratio of 0.1. The exhaust mixture has a temperature of 432 K, and a velocity of 11.7 m/s. The background ozone concentration is 30 ppb.

Tier 1 modeling assumes total conversion of NO to NO_2 , that is, all NO_x in the plume is NO_2 . Therefore, it is convenient for analysis to treat Tier 1 NO_2 concentration as total NO_x concentration. As shown in Figure 1, the NO_x concentration increases

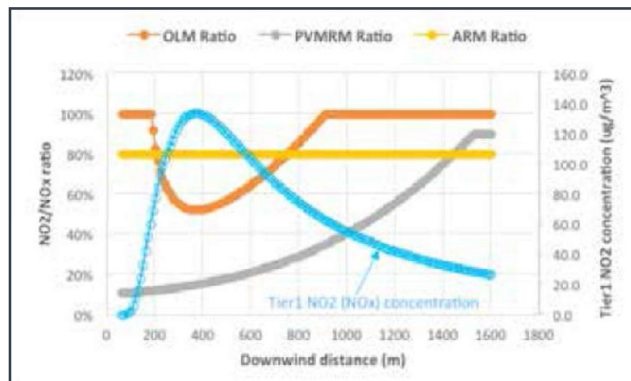


Figure 1. A comparison of ARM, OLM and PVMRM for a simple test case.

as the plume travels downwind (blue line) and, for this source, achieves its maximum at a downwind distance of 370 m, and then decreases with the downwind distance traveled.

For the Tier 3 OLM, Figure 1 clearly shows an ozone-limited region in the OLM analysis, from a downwind distance of 180 m to 910 m for the test case. The OLM assumes all 30 ppb ozone is available for the conversion of NO_x to NO_2 . Outside the ozone-limited region, the ozone level is sufficient to convert all NO_x to NO_2 , and therefore the 100% conversion ratio is achieved. Within the high NO_x impact region, insufficient ozone for complete NO_x conversion results in low conversion ratios. The OLM achieves its lowest conversion ratio when NO_x concentration reaches the peak value. The PVMRM shows a steadily increasing conversion ratio as the plume travels downwind, because the amount of ozone entrained into the plume increases as the plume is diluted by the ambient air (and the volume of the plume increases). Note that the ozone entrained into the plume is assumed to be uniformly mixed across the plume and the portion of ozone not in the plume will not be available for the conversion in the PVMRM. Finally, the Tier 2 ARM technique assumes an 80% ratio at all distances downwind, which is independent of the ozone level and NO_x concentrations.

While these comparisons shed some light on the methods in terms of their varying levels of concentration adjustment, their applicability must still be based on the case-by-case needs of the specific modeling project and the guidance from the regulatory agency. ❖

⁶ Hanrahan, P. L. *The Plume Volume Molar Ratio Method for Determining NO_2/NO_x Ratios in Modeling-Part I: Methodology*. J. Air & Waste Manage. Assoc. 49:1324-1331. 1999.