

Travel time limitation for NO-to-NO₂ conversion

Overview of Issue

The NO₂ modeling techniques currently available in AERMOD estimate the NO-to-NO₂ conversion by ozone in order to estimate total NO₂ impacts (which include both the converted NO and the emitted NO₂). The techniques available to estimate this conversion have three “tiers”, with varying degrees of complexity. Each of the three tiers is considered a screening rather than refined modeling technique. Further development is needed to identify a NO₂ modeling technique that could be selected as a preferred model. One aspect of NO₂ chemistry that is currently not considered in any of the available NO₂ techniques in AERMOD is a consideration of the conversion rate of NO-to-NO₂, i.e., how quickly NO can react with ozone (O₃) to form NO₂. Such a limiting factor could be important for very near-field impacts, with travel times of less than a few minutes.

Current NO₂ Techniques in AERMOD

Per Section 4.2.3.4 of the Guideline, the EPA recommends that NO₂ modeling should be done as a three-tiered screening approach, where each tier increases in complexity and decreases in conservativeness. The first tier (Tier 1) is total conversion, so all emitted NO_x is assumed to be immediately converted to NO₂. There is a single second-tier (Tier 2) method implemented in AERMOD, the Ambient Ratio Method 2 (ARM2). The ARM2 method adjusts the modeled NO_x concentrations based on an empirical relationship between observations of ambient NO_x and ambient NO₂ concentrations. There are two third-tier (Tier 3) methods implemented in AERMOD: 1) the Ozone Limiting Method (OLM) described by Cole and Summerhays (1979), and 2) the Plume Volume Molar Ratio Method (PVMRM) developed by Hanrahan (1999). OLM uses the assumption that either O₃ or available NO_x is the limiting factor in the reaction of NO with O₃ to form NO₂. PVMRM estimates the amount of ozone entrained in the dispersion plume of a source to determine the amount of ozone that is available for oxidation of NO to form NO₂, then applies a limiting factor approach that restricts NO conversion as a function of the amount of O₃ entrained into the modeled plumes.

Summary of Science on NO_x Chemistry

Though the NO_x chemistry regime can involve a larger number of reactions, it is fairly well understood and can be parameterized to include a wide range of the relevant reactions. However, in the near-field (i.e., time scales on the order of minutes), the dominant reactions during the daytime are between NO, NO₂, and ozone:

1. $O_3 + NO \rightarrow NO_2 + O_2$ (k1)
2. $O_2 + NO_2 + hv \rightarrow NO + O_3$ (k2)

where k1 and k2 are the reaction rate constants for each reaction and hv is the incident solar radiation.

These reactions are often summarized to emphasize the main reaction pathways in what's frequently described as the pseudo-steady state (PSS) approximation. The steady-state assumption is based on the fact that both reactions are relatively and equally fast, so equilibrium is reached fairly quickly as well.

The reaction rate is the product of the reaction rate constant (k_1 or k_2) and the concentration of the reactants. So, when we assume steady state, the rates are equal:

3. $k_1[\text{O}_3][\text{NO}] = k_2[\text{NO}_2]$
 - a. $k_1 = (15.33/T)\exp(-1450/T) \text{ ppb}^{-1} \text{ sec}^{-1}$
 - b. $k_2 = 0.0167\exp(-0.575/\cos(\theta)) \text{ sec}^{-1}$
 - c. $\theta =$ zenith angle of sun, function of location latitude and time of day

where T is the ambient temperature in Kelvin.

In the context of AERMOD modeling, where NO is released and NO_x is conserved, we can remove NO_2 from equation 3 with the following:

4. $\text{NO} = \text{NO}_x - \text{NO}_2,$

then substituting 6 into 4, and solving for NO_2/NO_x , we get:

5. $[\text{NO}_2]/[\text{NO}_x] = (k_1[\text{O}_3])/(k_2 + k_1[\text{O}_3])$

Thus, the PSS ratio of NO_2/NO_x is a function of O_3 , temperature, and sunlight. It should be noted that this solution assumes O_3 has reached PSS and thus, the reaction is not O_3 limited. The solution of this equation can provide a theoretical maximum for the NO_2/NO_x ratio derived from other methods.

The time-component (t) of this reaction can be computed based on equation 1 and the value of k_1 :

6. $d[\text{NO}]/dt = k_1[\text{NO}][\text{O}_3]$

Rearrangement gives

7. $d[\text{NO}]/[\text{NO}] = -k_1[\text{O}_3]dt$

Integrating the differential gives

8. $\ln [\text{NO}] = -k_1[\text{O}_3]t + C$

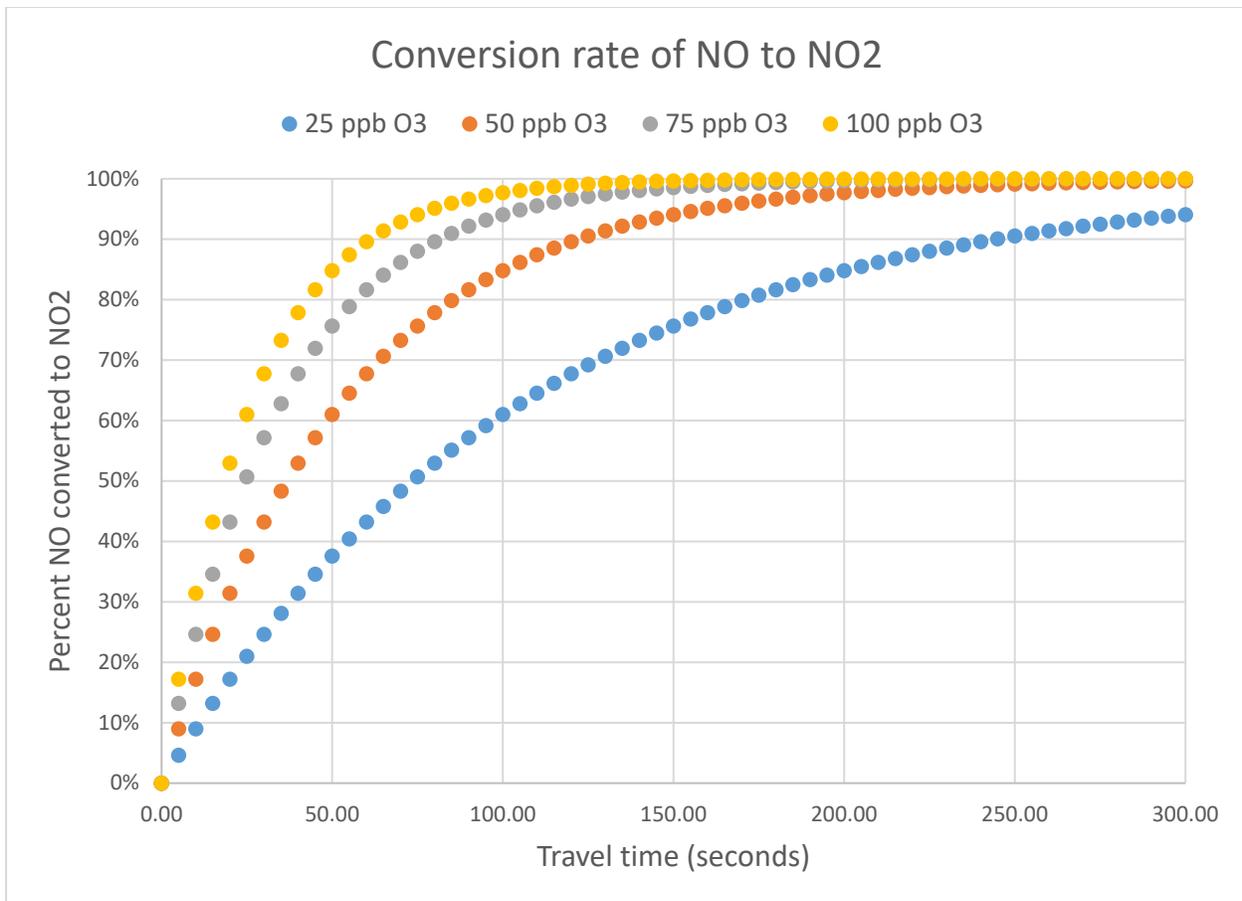
C can be determined with the boundary conditions, when $t = 0$, $[\text{NO}] = [\text{NO}]_o$. $[\text{NO}]_o$ is the original starting concentration of NO , giving $C = \ln [\text{NO}]_o$. The integrated form for $[\text{NO}]$ as a function of time is thus:

9. $\ln [\text{NO}] = -k_1[\text{O}_3]t + \ln [\text{NO}]_o$

This last equation can be rearranged into several formats, such as:

10. $[\text{NO}]/[\text{NO}]_o = \exp (-k_1[\text{O}_3]t)$

11. $[\text{NO}] = [\text{NO}]_o \exp (-k_1[\text{O}_3]t)$



Considerations for Updates in Model System

The information needed for the calculation of the amount of NO converted and to add a travel time limitation parameterization into AERMOD are generally available already in the model (i.e., the inputs to equations 9-11):

- The hourly temperature is provided in the meteorological inputs.
- When Tier 3 NO₂ conversion options are used, there are input pathways for a single “conservative” O₃ value as well as hourly varying O₃.
 - Note that a “conservative” value is conservative regardless of the method being employed, i.e., high O₃ levels lead to rapid conversion (resulting in higher NO₂ concentrations closer to the emission source) and also result in greater NO conversion (higher potential NO₂ concentrations)
- PVMRM includes calculations for the distance from each source to each receptor based on the total distance (i.e., the radial or actual distance from the source to the receptor), the downwind distance (i.e., distance along the wind vector that results in being perpendicular to the receptor), and the crosswind distance (i.e., the distance from the source perpendicular to the wind vector). These three distances make a right-triangle, with the radial distance, which is the maximum straight-line distance from the source to the receptor, as the hypotenuse of the triangle as illustrated in Figure 1, below.

- PVMRM generally uses the downwind distances to calculate plume volumes. However, it's not clear which components would be most appropriate for computing travel time for this method.

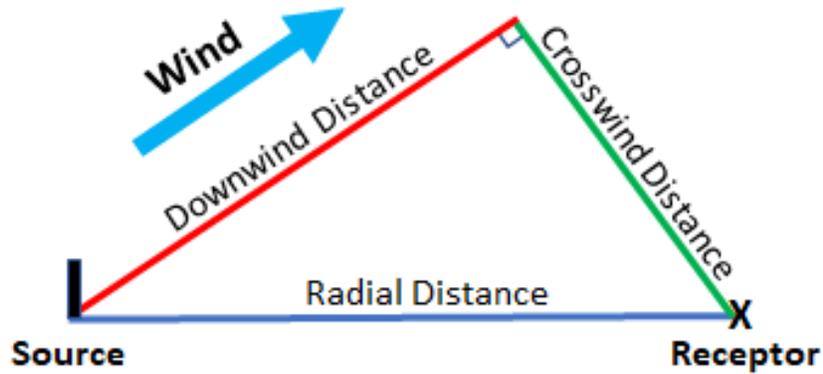


Figure 1. Distance Terms in AERMOD Relative to Source and Receptor Location and Wind Direction

The simple case, involving only one source, results in a fairly straightforward approach for implementation into AERMOD, i.e., there is a single initial NO concentration and travel time for which to calculate conversion. However, scenarios involving multiple sources present a more challenging implementation approach in AERMOD. Potential implementation approaches include:

- Calculating travel time and conversion independently for each source. This approach ignores any competition for O_3 but is relatively straightforward.
- Travel time could be computed as an average for multiple sources. PVMRM computes a composite plume volume for the “major contributing sources.” A similar approach could be adopted for this method.

As mentioned above, equation 5 provides a limiting factor on the maximum value of the NO_2/NO_x ratio that could be achieved given a certain O_3 concentration, temperature, and amount of available sunlight. This can be computed and used as a bounding limit to the amount of converted NO (as opposed to adopting a simple limit like 90% conversion as is used in ARM2, OLM, and PVMRM). A dynamic maximum conversion limit from this calculation could also be applied to the existing Tier 2 and Tier 3 methods.

References

- Cole, H.S. and Summerhays, J.E. (1979). A review of techniques available for estimating short-term NO_2 concentrations. *Journal of the Air Pollution Control Association*, 29(8), pp.812-817.
- Hanrahan, P.L. (1999). The plume volume molar ratio method for determining NO_2/NO_x ratios in modeling—Part I: Methodology. *Journal of the Air & Waste Management Association*, 49(11), pp.1324-1331.