

## Travel time limitation for NO-to-NO<sub>2</sub> conversion

### Overview of Issue

The NO<sub>2</sub> modeling techniques currently available in AERMOD estimate the NO-to-NO<sub>2</sub> conversion by ozone in order to estimate total NO<sub>2</sub> impacts (which include both the converted NO and the emitted NO<sub>2</sub>). 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 NO<sub>2</sub> modeling technique that could be selected as a preferred model. One aspect of NO<sub>2</sub> chemistry that is currently not considered in any of the available NO<sub>2</sub> techniques in AERMOD is a consideration of the conversion rate of NO-to-NO<sub>2</sub>, i.e., how quickly NO can react with ozone (O<sub>3</sub>) to form NO<sub>2</sub>. Such a limiting factor could be important for very near-field impacts, with travel times of less than a few minutes.

### Current NO<sub>2</sub> Techniques in AERMOD

Per Section 4.2.3.4 of the Guideline, the EPA recommends that NO<sub>2</sub> 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<sub>x</sub> is assumed to be immediately converted to NO<sub>2</sub>. 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<sub>x</sub> concentrations based on an empirical relationship between observations of ambient NO<sub>x</sub> and ambient NO<sub>2</sub> 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 O<sub>3</sub> or available NO<sub>x</sub> is the limiting factor in the reaction of NO with O<sub>3</sub> to form NO<sub>2</sub>. 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 NO<sub>2</sub>, then applies a limiting factor approach that restricts NO conversion as a function of the amount of O<sub>3</sub> entrained into the modeled plumes.

### Summary of Science on NO<sub>x</sub> Chemistry

Though the NO<sub>x</sub> 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, NO<sub>2</sub>, 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.  $\theta = \text{zenith angle of sun, function of location latitude and time of day}$

where  $T$  is the ambient temperature in Kelvin.

In the context of AERMOD modeling, where  $\text{NO}$  is released and  $\text{NO}_x$  is conserved, we can remove  $\text{NO}_2$  from equation 3 with the following:

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

then substituting 6 into 4, and solving for  $\text{NO}_2/\text{NO}_x$ , 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  $\text{NO}_2/\text{NO}_x$  is a function of  $\text{O}_3$ , temperature, and sunlight. It should be noted that this solution assumes  $\text{O}_3$  has reached PSS and thus, the reaction is not  $\text{O}_3$  limited. The solution of this equation can provide a theoretical maximum for the  $\text{NO}_2/\text{NO}_x$  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.  $\ln [\text{NO}] = -k_1[\text{O}_3]t + C$

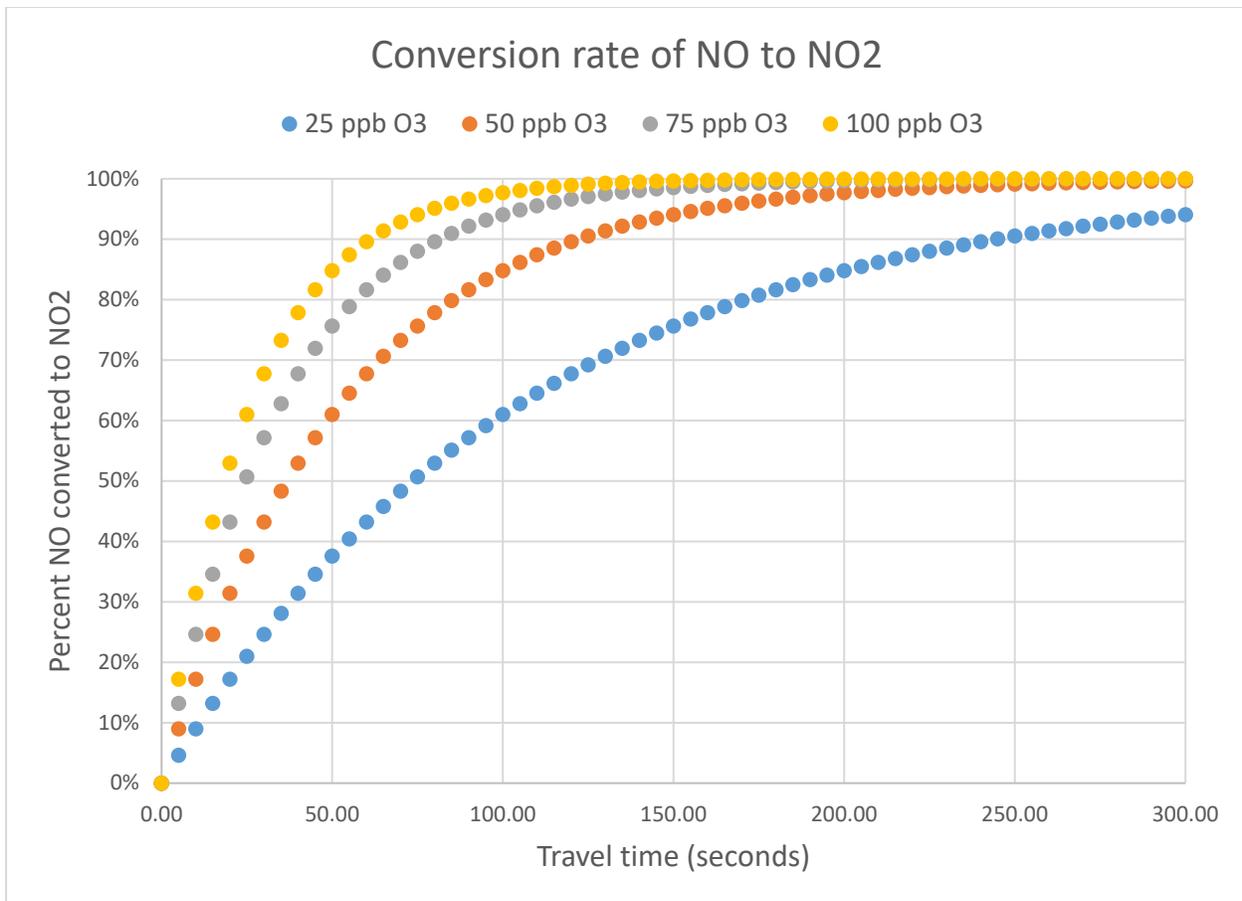
$C$  can be determined with the boundary conditions, when  $t = 0$ ,  $[\text{NO}] = [\text{NO}]_o$ .  $[\text{NO}]_o$  is the original starting concentration of  $\text{NO}$ , giving  $C = \ln [\text{NO}]_o$ . The integrated form for  $[\text{NO}]$  as a function of time is thus:

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 NO<sub>2</sub> conversion options are used, there are input pathways for a single “conservative” O<sub>3</sub> value as well as hourly varying O<sub>3</sub>.
  - Note that a “conservative” value is conservative regardless of the method being employed, i.e., high O<sub>3</sub> levels lead to rapid conversion (resulting in higher NO<sub>2</sub> concentrations closer to the emission source) and also result in greater NO conversion (higher potential NO<sub>2</sub> 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.

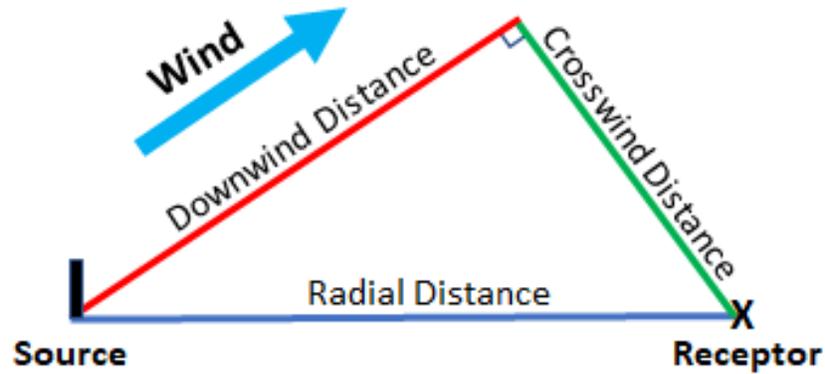


Figure 1. Distance Terms in AERMOD Relative to Source and Receptor Location and Wind Direction

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.