Monitored Ratio Method (MRM):
Location-specific NO_2/NO_X ratios based on NO_X concentration.

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Abstract
Available monitoring data provides historic monitored NO_2/NO_X ratios for scenarios that represent a wide range of situations. This study identified the maximum NO_2/NO_X ratio for each monitored NO_X concentration and fit a curve to the maximum points. Limitations of the curve were analyzed, and minimum and maximum NO_2/NO_X ratios were identified. A method of predicting the maximum possible NO_2 concentration based on the maximum modeled NO_X concentration and in-stack NO_2/NO_X ratios was developed.

Background
The purpose of this document is to investigate the application of monitored NO_2/NO_X ratios for demonstrating compliance with NO_2 standards.

The 1-hour NO_2 modeling results appear to vastly overpredict NO_2 concentrations when compared with monitored values. I modeled all of the New Mexico sources within 100 km of the Bloomfield monitor with AERMOD using the following different options: 75% NO_X to NO_2 ambient ratio method, PVMRM with 0.3 and 0.1 in-stack NO_2/NO_X ratios, and OLM with 0.3 and 0.1 in-stack NO_2/NO_X ratios. Receptors were placed at the three monitors in the area. One year of meteorological data collected near San Juan Generating Station from December, 1993 to November, 1994 was used, with hourly ozone profiles based on maximum month-hour data from Bloomfield in 2009 (for PVMRM and OLM). Monitored concentrations and modeling results are presented in Table 1, below.

Table 1: AERMOD modeling results at Four-Corners area monitors

Location	ID	Monitored 1-hour Background[1] (ppb)	75% NO_X to NO_2 (ppb)[2]	PVMRM, 0.3 in-stack ratio (ppb)[2]	PVMRM, 0.1 in-stack ratio (ppb)[2]	OLM, 0.3 in-stack ratio (ppb)[2]	OLM, 0.1 in-stack ratio (ppb)[2]
Shiprock Substation	1H	47	122	124	100	153	132
Bloomfield	1ZB	47	177	165	138	236	236
Navajo Lake	1NL	50	73	87	86	97	97

[1] Three-year average (2007-2009) of maximum 1-hour concentrations.

[2] Eighth highest concentration modeled at monitor location.

Some adjustments to the modeling analysis must be done in order to yield reasonable results. Doug Blewitt and Dana Wood presented a study[1] (the Study) that compared NO_X concentrations with NO_2/NO_X ratios from monitored data downwind of several industrial sources. They concluded that it should be possible to use the upper bound of these results to estimate maximum conversion of NO_X to NO_2. I will discuss their results with respect to application in New Mexico.

Ambient Ozone Concentrations
The Study analyzed data downwind of the industrial sources. The Study did not link ozone concentrations to the results, so both the ozone concentrations in the study areas and the influence of ozone concentrations on NO_2/NO_X ratios is unknown. The difficulty of knowing ozone concentration acting upon a plume is that it should be monitored before it mixes with the plume or it will be reduced in concentration before reaching the monitor.

It may not be necessary to know the ozone concentration in an area to apply the results, though higher ozone concentrations will certainly produce higher NO_2/NO_X ratios. Data from all of New Mexico's NO_X monitoring stations were graphed, considering all wind directions and all conditions, and compared with the results of the Study. Each of the New Mexico data points had a lower NO_2/NO_X ratio for a given NO_X concentration than the curve connecting the maximum NO_2/NO_X ratios in the Study (provided that NO_2/NO_X ratios above one are excluded). It may therefore be assumed that the ozone represented in the Study is at least as high as the ozone concentrations in New Mexico. Therefore, the maximum NO_2/NO_X ratio curve in the Study would not underpredict concentrations of NO_2 in New Mexico.

The New Mexico NO_X monitors in the northwestern (Bloomfield, Navajo Lake, and Shiprock) and southeastern (Carlsbad, Deming, and Hobbs) parts of the state are in areas rich with combustion sources. The Sunland Park and Santa Teresa monitors are in an area highly influenced by transport of pollutants from Mexico and Texas, with little contribution from local sources.

Maximum and minimum NO_2/NO_X ratios
The highest possible NO_2/NO_X ratio is 1.0, indicating all NO_X is in the form of NO_2. The minimum achievable NO_2/NO_X ratio is not as easy to determine from a conservative modeling perspective, but it would risk underprediction to set a minimum level lower than the in-stack NO_2/NO_X ratio found at the facility being modeled. In-stack ratios can be measured, but are frequently not reported to NMED or EPA. Because NMED has limited data, the applicant should provide some basis for establishing the in-stack ratio (such as actual in-stack testing) and should use either the highest, or the weighted average in-stack ratio at the facility for the lower bound of NO_2/NO_X ratio used in the model.

[1] *1-Hour NO_2 Modeling Issues and Solutions*, Doug Blewitt and Dana Wood, 10/21/2010

EPA approves the use of 0.5 as an in-stack ratio without additional justification[2]. Lean burn engines would be expected to be much closer to the EPA default ratio than would rich burn engines that use much less air in combustion.

Shape of Curve
The Study presented a figure with a straight line between the upper and lower bounds. Each of the data sets clearly follows some type of a curve. Therefore a curve may be a more representative way to model the relationship than a straight line. Selecting data points that make up the maximum NO_2/NO_X ratios for a given NO_X concentration for the cumulative analysis from the Study and from the ambient monitors in New Mexico, I fit an exponential trend line to each set of data using Microsoft Excel. The function appeared to model the relationship fairly well, and application of the result would be no more difficult than using a straight line. The curve fit to the data from the Study was selected instead of the New Mexico monitoring data because the curve based on the Study data would be less likely to underpredict concentrations. The graph of the maximum NO_2/NO_X ratios for a given NO_X concentration is shown below.

Figure 1: Maximum NO_2/NO_X ratio monitored vs. NO_X concentration monitored.

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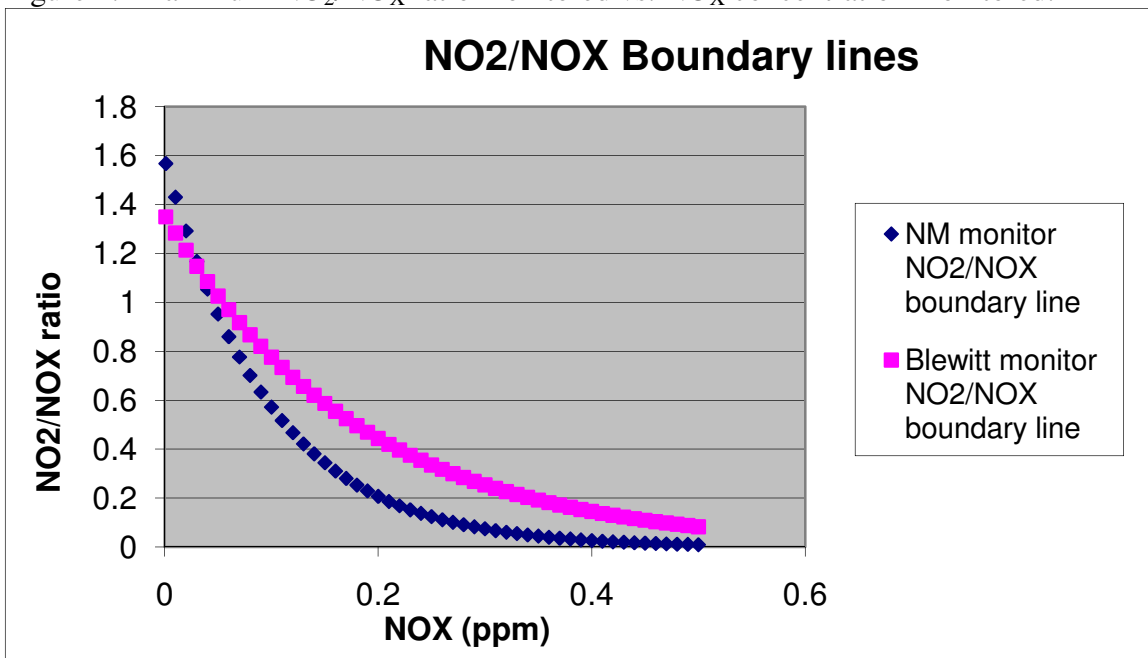
[2] *Additional Clarification Regarding Application of Appendix W Modeling Guidance for the 1-hour NO2 National Ambient Air Quality Standard*, Tyler Fox, March 1, 2011, pg. 5.

Comparison with standards

NO_2 concentration predicted by the curve peaks at about 89.3 ppb, which corresponds to 180 ppb NO_X. This means that any point on the curve will be in compliance with air quality standards, and that the in-stack ratio that determines the lower limit on $[NO_2]/[NO_X]$ will be the determining factor for demonstrating compliance with standards.

Figure 2: Maximum NO_2 concentration monitored vs. NO_X concentration based on the relationship: $[NO_2]/[NO_X] = 1.3571 \ e^{(-5.5897*[NOX])}$
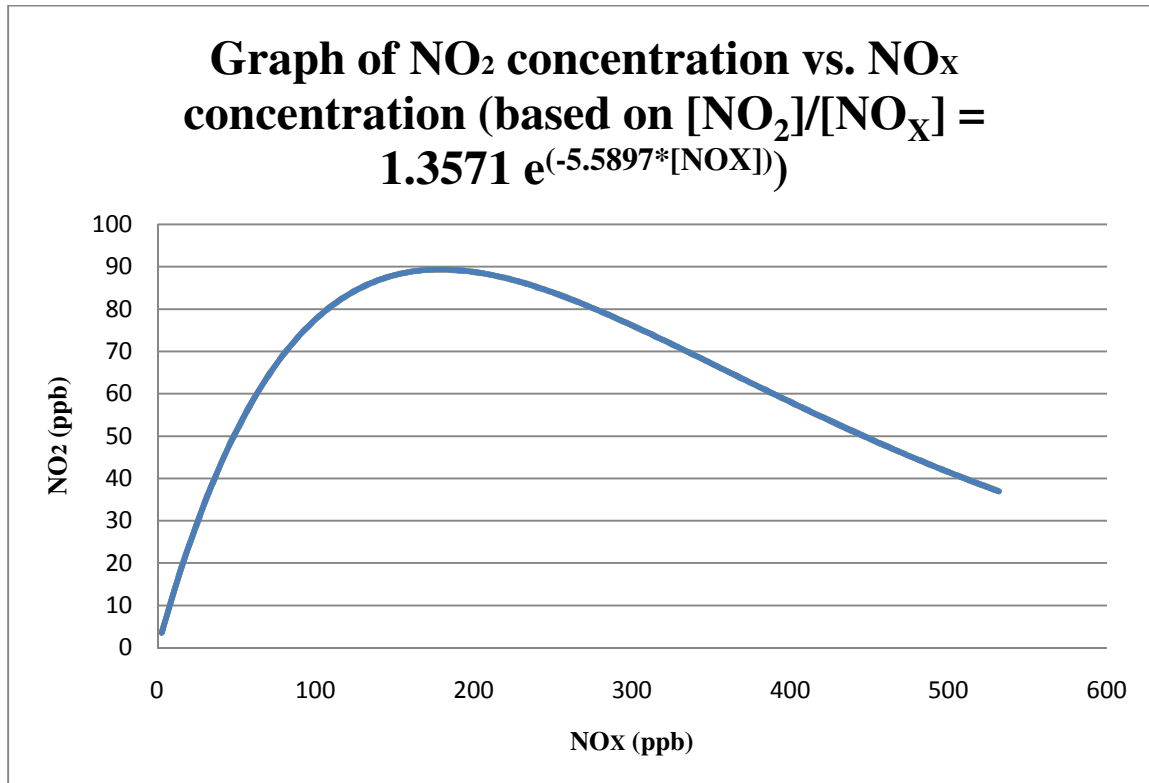

Conundrum?

Parts of the equation predict that adding more NO_X results in less NO_2 in a given volume of air. This does not make sense from the viewpoint of either chemical reactions or conservation of matter. The explanation is that the monitoring data accounts for mixing time and reaction time. The higher the NO_X concentration, the less time the plume has had to mix with ozone and react to form NO_2.

Proposed method

MRM can be applied as a Tier 2 (fixed rate conversion technique) or Tier 3 modeling technique. The Tier 2 approach used the maximum modeled NO_X concentration to determine the fixed rate conversion. The Tier 3 approach requires NO_X concentrations at each receptor at each hour. Both applications result in the same maximum predicted concentration. The Tier 3 approach is presented first because it is easier to understand. The Tier 2 approach simplifies the analysis based on maximum concentrations, and the assumption that all concentrations between zero and the maximum modeled NO_X concentration occur somewhere in the modeling domain.

Figure 3: Example maximum NO_2 concentration monitored vs. NO_X concentration based on the proposed method, with a minimum NO_2/NO_X ratio of 0.3.
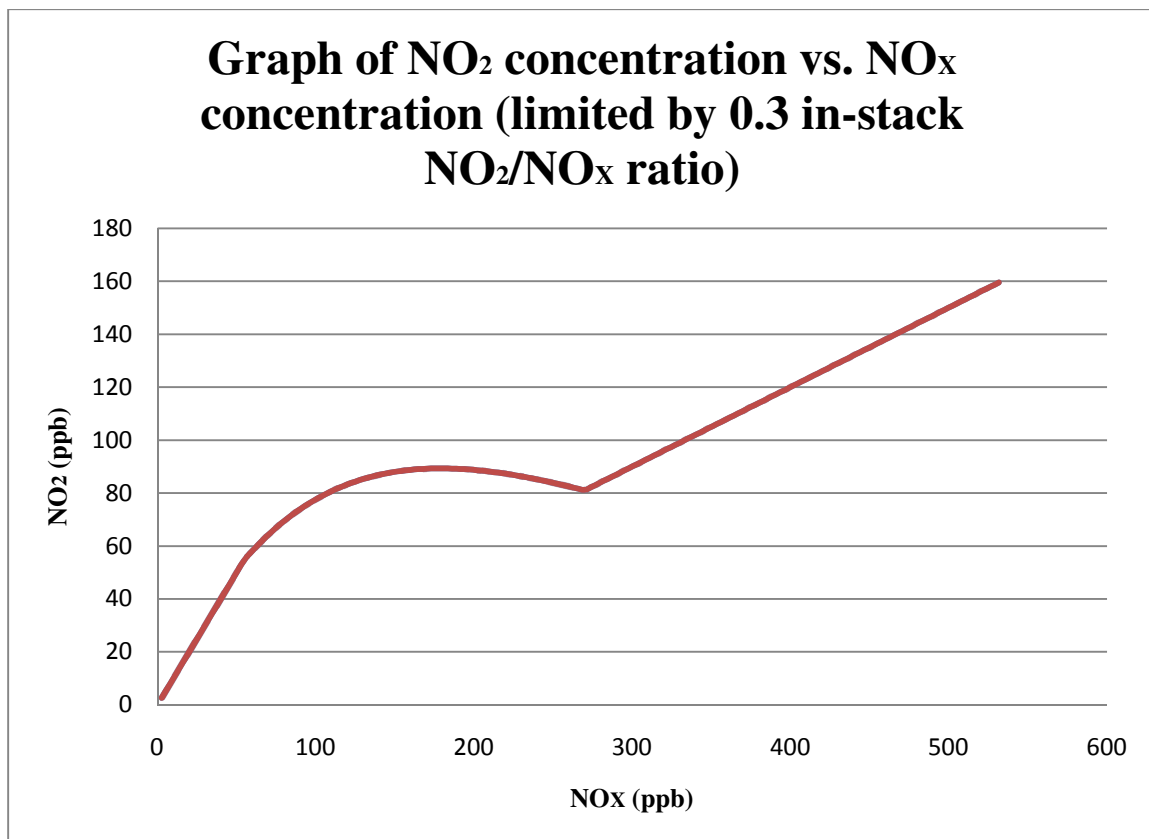
Tier 3/Refined Method (apply to each 1-hour concentration at each receptor):
Note: All concentrations in ppm.

1. Determine $[NO_2]/[NO_X]$ ratio for data point.
   Maximum $[NO_2]/[NO_X] = 1$
   Minimum $[NO_2]/[NO_X]$ = maximum, or weighted average in-stack $[NO_2]/[NO_X]$ at facility
   Otherwise, $[NO_2]/[NO_X] = 1.3571 \ e^{(-5.5897*[NOX])}$

2. Determine [NO_2] at data point.
    [NO_2] = modeled [NO_X] x ([NO_2]/[NO_X])

Tier 2/Simplified Method (apply to maximum 1-hour NO_X concentration in modeling domain):
Note: This method is derived from the refined method, but many of the calculations have been performed ahead of time and simplified, for easy application.

To calculate the in-stack NO_2/NO_X ratio at the facility for MRM, either the maximum ratio for a source at the facility may be used, or a weighted average for the facility may be calculated. The ratio of each emission source must be justified unless the default ratio of 0.5 is used for that source. To determine the weighted average, divide the total hourly NO_2 emissions at the facility by the total hourly NO_X emissions at the facility.

To determine the maximum NO_2 concentration, run AERMOD with all receptors and all sources, including surrounding sources and/or monitored background NO_X concentrations. Determine the maximum modeled NO_X concentration. The following procedure can be used to determine the maximum NO_2 concentration.

Step 1: Determine the maximum concentration from the NO_2/NO_X ratio curve.

> If the maximum concentration of NO_X modeled is less than or equal to 102.7346 $\mu g/m^3$ then use 100% conversion.
> $$ppb\ NO_2 = (NO_{X\ Modeled\ \mu g/m}{}^3 / 1.880553)$$

> If the maximum concentration of NO_X modeled is greater than or equal to 337 $\mu g/m3$ NO_X then use maximum concentration on the curve of 89.316 ppb NO_2.
> $$ppb\ NO_2 = 89.316\ ppb$$

> Otherwise, use the following equation:
> $$ppb\ NO_2 = 0.721649\ x\ (NO_{X\ Modeled\ \mu g/m}{}^3)\ x\ Exp(-5.5897\ x\ (NO_{X\ Modeled\ \mu g/m}{}^3 / 1880.553))$$

Step 2: Determine the maximum concentration based on the in-stack ratio at the facility:

> $$ppb\ NO_2 = (NO_{X\ Modeled\ \mu g/m}{}^3 / 1.880553)\ x\ (in\text{-}stack\ NO_2/NO_X\ ratio)$$

Step 3: Determine the maximum concentration
    The higher of the two concentrations (from Step 1 and Step 2) is the maximum modeled concentration. The location of the maximum NO_X concentration may be used as the location of the maximum NO_2 concentration.

MRM Notes:
The method is not appropriate for determining significance level. Use 75% NO_X to NO_2 conversion or other method to determine impact areas or to analyze for significant contributions.

Monitored NO_X concentrations include all sources in the area. Either include surrounding sources in the modeling run or add the background NO_X concentration monitored in the area. Then apply the MRM method to the combined NO_X concentration. Optionally, background NO_2 may be added after applying the MRM conversion to the facility alone NO_X modeling results.

The method may be used for annual standard demonstrations as well. The annually averaged concentration will necessarily be lower than the 1-hour concentration predicted with this method.

To use this method for Prevention of Significant Deterioration (PSD) increment modeling for minor sources, include all increment consuming sources. The baseline sources and increment expanding sources may be excluded from this model run, which will produce a conservative estimate of increment consumption because conversion will be higher than otherwise predicted.

The method may be refined and applied for each concentration at each receptor, if desired.

Examples:

These are the results that are expected if the maximum modeled NO_X concentration is equal to the value in column 1, below.

Maximum modeled $[NO_X]$ (μg/m3)	in-stack $[NO_2]/[NO_X]$	Predicted $[NO_2]$ (ppb)
50	0.3	26.6
150	0.3	69.3
300	0.3	88.8
400	0.3	89.3
600	0.3	95.7
700	0.3	111.7
50	0.05	26.6
150	0.05	69.3
300	0.05	88.8
400	0.05	89.3
3000	0.05	89.3
4000	0.05	106.4

The following Visual Basic function is designed to calculate concentrations for MRM for either the Tier 2 or the Tier 3 approach.

```
Function dblNOXtoNO2(dblNOXModeled As Double, dblInStackRatio As Double) As
Double
'The purpose of this function is to calculate the maximum modeled concentration
'based on NO2/NOX ratios collected in monitoring data.
'input dblNOXModeled as maximum concentration of NOX modeled in ug/m3.
'input dblInStackRatio as in-stack [NO2]/[NOX] at facility (decimal format).
'Output is the maximum NO2 concentration in ppb.
'Maximum [NO2]/[NOX] physically possible = 1
'Minimum [NO2]/[NOX] = in-stack [NO2]/[NOX] at facility
'Otherwise, [NO2]/[NOX] = 1.3571 e(-5.5897*[NOX])
'[NO2] = modeled [NOX] x ([NO2]/[NOX])

'The maximum concentration on the curve is 89.316 ppb,
'which occurs when the NOX concentration modeled is 337 ug/m3.
Dim dblConcA As Double
Dim dblConcB As Double
Dim dblPPMNOX As Double
Dim dblFactorA As Double

'Convert ug/m3 to ppm
dblPPMNOX = dblNOXModeled / (46.01 * 40.8727)

'Determine concentration from curve.
If dblNOXModeled > 337 Then
   dblConcA = 89.316
Else
   dblFactorA = 1.3571 * Exp(-5.5897 * dblPPMNOX)
   If dblFactorA > 1 Then
      dblFactorA = 1
   End If
   dblConcA = dblPPMNOX * dblFactorA * 1000
End If

'Determine concentration from in-stack conversion.
dblConcB = dblPPMNOX * dblInStackRatio * 1000

If dblConcA > dblConcB Then
   dblNOXtoNO2 = dblConcA
Else
   dblNOXtoNO2 = dblConcB
End If

End Function
```