Use of the Ambient Ratio Method (ARM) for Estimating Ambient Nitrogen Dioxide Concentrations

prepared by the OLM/ARM Workgroup

Draft for Comment
This is not official EPA policy guidance

Introduction

The U.S. Environmental Protection Agency (EPA) recommends a tiered approach for modeling ambient nitrogen dioxide (NO_2) impacts from point sources.[1] The second tier uses the Ambient Ratio Method (ARM), where the ratio of modeled NO_2 to oxides of nitrogen (NOx) is assumed to equal the existing NO_2-to-NOx ratio. EPA has established a national default ARM value (NO_2-to-NOx ratio) of 0.75, but allows site-specific values to be used if representative monitoring data is available.

The OLM/ARM workgroup felt additional guidance is needed regarding site-specific ARM values.[2] This document provides our recommendations, some of which differ from the ARM recommendations originally presented at the 1991 Air & Waste Management Association annual meeting (Chu and Meyer, 1991).

In summary, a site-specific NO_2-to-NOx ratio can usually be developed for areas where the ambient NOx concentrations typically exceed 20 parts per billion (ppb). The resulting ratio can be used to refine modeled estimates of long-term (annual average) NO_2 concentrations. For areas with lower NOx concentrations, a non-guideline method, such as the Ozone Limiting Method, may be required. In all cases, the site-specific NO_2-to-NOx ratio or the non-guideline NO_2 estimating method must be approved by the reviewing authority.

Background

[1] EPA's prescribed method for modeling NO_2 emissions can be found in Section 6.2.3 of the *Guideline on Air Quality Models* (GAQM). The GAQM is codified as Appendix W to 40 CFR Part 51.

[2] The OLM/ARM Workgroup was established during the 1996 annual meeting of EPA/State/Local modelers, to identify technical issues related to NO_2 modeling and to recommend solutions to EPA's Office of Air Quality Planning and Standards. At the time of this writing, the recommendations presented here reflect Workgroup views and do not necessarily reflect EPA policy.

The combustion process typically forms several types of NOx. For modeling purposes, the NOx emissions are typically assumed to be 90 percent (by volume) nitric oxide (NO), and 10 percent NO_2. However, after the flue gas exits the stack, additional NO_2 is created as the exhaust mixes with the surrounding air. The typical atmospheric reactions that create and destroy NO_2 are:

$NO + O_3 \rightarrow NO_2 + O_2$ (*oxidation of NO by ambient ozone*)

$NO + HC \rightarrow NO_2 + HC^c$ (*oxidation of NO by reactive HC*)

NO_2 + sunlight -> NO + O (*photo-dissociation of NO_2*)

Oxidation by ozone is typically the main reaction for NO_2 formation, especially in rural areas. While the reaction rate is essentially instantaneous, the total amount of NO_2 conversion is limited by how quickly the plume entrains surrounding air. Therefore, the amount of NO_2 within the NOx plume increases as the plume travels and disperses downwind of the stack. This increase will continue with time (plume travel), until the reactions that create and destroy NO_2 reach quasi-equilibrium. An illustration of this change in NOx composition with plume travel is provided in Figure 1.

The basic tenant of the ARM theory is that on a long-term (annual average) basis, the *final* plume NO_2-to-NOx ratio will equal the existing ambient NO_2-to-NOx ratio. Therefore, once the ambient NO_2-to-NOx ratio is established, the predicted NO_2 impact can be determined by multiplying the modeled NOx concentration by the ambient ratio, as shown in Equation 1.

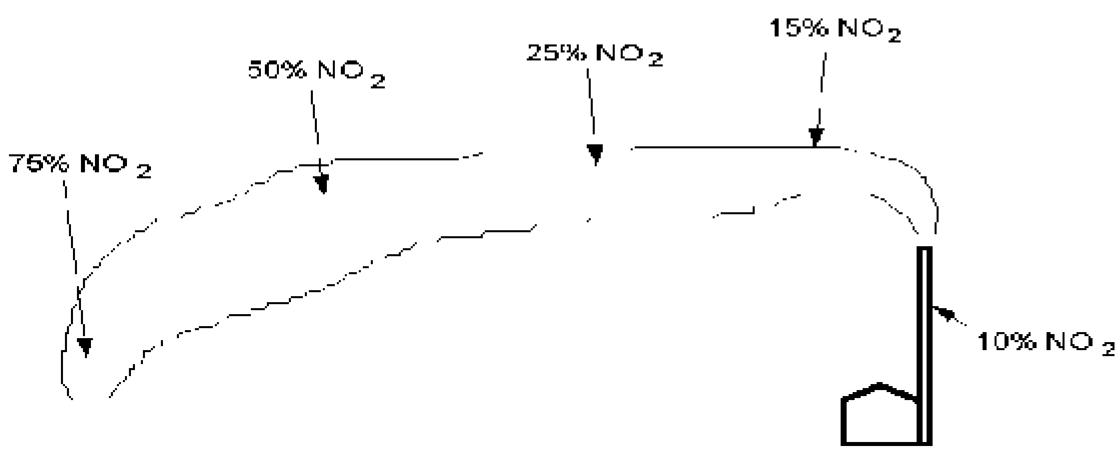
Equation 1: $[NO_2]_{pred} = [NO_2/NOx]_{observed} \times [NOx]_{pred}$

where

$[NO_2]_{pred}$	is the predicted annual average NO_2 concentration,
$[NO_2/NOx]_{observed}$	is the observed (monitored) annual average NO_2 concentration divided by the observed (monitored) annual average NOx concentration, and
$[NOx]_{pred}$	is the predicted (modeled) annual average NOx concentration.

As previously stated, the ARM theory applies at distances where the typical NOx composition within

Figure 1 - The Change in NOx Composition (Percent NO_2) with Plume Travel



the plume has stabilized. The original description of the ARM method indicated this distance could be greater than 10 kilometers (km) from the emission source (Chu and Meyer, 1991). However, the existing ambient ratio (measured at a far-field location) can also be used to conservatively estimate near-field NO_2 impacts.

The ARM theory assumes that the NOx *mass* emission rate of the source(s) is based on the molecular weight of NO_2, rather than an assumed mixture of NO and NO_2. This assumption is used in EPA's Compilation of Air Pollutant Emission Factors (AP-42) and is typically used in vendor NOx data sheets. While this approach is inconsistent with the typical assumptions regarding the initial mixture of NO and NO_2 on a *volume* basis, it eliminates the need for including molecular weight differences in calculating *mass* emission rates. Therefore, observed *volume* ratios can be used in Equation 1 to adjust modeled *mass* concentrations, without adjusting for molecular weight differences.

The GAQM provides 0.75 as a national default of the observed NO_2-to-NOx ratio. This value is based on 106 NOx monitoring data sets from various parts of the country. The GAQM also allows the use of observed NO_2-to-NOx ratios based on local data.

Issues

The Workgroup has identified the following issues regarding site-specific ratios that should be resolved or noted.

1. Monitor Location

The GAQM states that a site-specific ratio may be used "if it can be shown that such a ratio is based on data likely to be representative of the location(s) where [the] *maximum* annual impact from the individual source under review occurs. In the case where several sources contribute to consumption of a PSD increment, a locally derived annual NO_2-to-NOx ratio should also be shown to be representative of the location where the *maximum* collective impact from the new plus existing sources occurs." (emphasis added)

The OLM/ARM Workgroup notes that EPA's recommendation that the NO_2-to-NOx ratio represent the maximum impact site(s) may differ from the original recommendation presented at the Air & Waste Management Association (Chu and Meyer, 1991). Chu and Meyer recommended that the NO_2-to-NOx ratio be based on data collected 15 to 80 km downwind of the predominant emission source, to ensure the data represents a NOx concentration in quasi-equilibrium. From the Workgroup's experience, the maximum NOx impact site(s) typically occur well within 1 km of the predominant NOx emission source. In addition, the maximum impact site(s) appear to be in the region where the composition of the NOx plume is still changing. **Therefore, locating a monitor at the maximum impact site may be contrary to the equilibrium tenant of the ARM, and lead to NO_2-to-NOx ratios that are inappropriate for estimating the NO_2 impact at more distant receptors**.

In contrast, ratios based on more distance monitors may be used for all receptors located between the source and monitor. However, the resulting ratio may be overly conservative at the maximum impact site(s).

2. Averaging Technique

Chu and Meyer recommend a unique approach for determining the annual average NO_2 and annual average NOx concentrations for purposes of determining site--specific NO_2-to-NOx ratios. They recommend calculating the annual average as the average daily average concentration. This approach is different than averaging the hourly concentrations, as used in standard monitoring methods, including those used in NAAQS compliance.

In larger urban areas, Chu and Meyer also recommend limiting the annual concentrations to daylight hours (7 a.m. to 6 p.m.). They stated, "urban ratios of annual averages tend to be biased toward the low side due mainly to the influences of significant nighttime emissions of area sources, particularly, the nighttime traffic." Using only daylight data results in a more conservative NO_2-to-NOx ratio.

3. Data Quality

Chu and Meyer stated that daily average concentrations below 20 parts per billion (ppb) should be eliminated prior to determining the annual average concentration. The purpose is to "avoid potentially large errors introduced by small signal to noise ratios typical of current monitoring instruments at low ambient levels of NO_X." In addition, at least 75% of the days must have daily average concentrations greater than 20 ppb. Annual average concentrations cannot be determined if there are fewer days with acceptable data.

These data restrictions can limit the application of the ARM method in low impact areas. Chu and Meyer summarized this limitation with the following statement:

> The chemiluminescent instruments currently used in NOx monitoring are known to have relatively large errors in detecting NOx less than about 20 ppb. In order to minimize the estimation errors, it is suggested that, until better instruments become routinely available, only data with daily averaged NOx concentrations greater than 20 ppb be used in the calculations. This may eliminate or greatly curtail the use of rural NOx data to derive NO_2/NOx ratios.

Workgroup Recommendations for Developing a Site-Specific Ratio

As previously discussed, the NOx composition within the plume varies with distance. Ideally, the changing ratio could be characterized by an equation that would provide the "observed" NO_2-to-NOx ratio at a given distance between the source and receptor. Site-specific data could then be used to adjust this equation to provide the local NO_2-to-NOx ratios. However, the Workgroup has not been able to develop a generalized equation that would be applicable for a wide variety of modeling scenarios. Therefore, the Workgroup has developed recommendations that provide conservative estimates of the local NO_2-to-NOx ratio for all receptors located within the source-monitor radius.

The following discussion represents the OLM/ARM Workgroup's recommendations on how such a site-specific NO_2-to-NOx ratio should be developed.

Monitoring Equipment, Siting and QA Procedures

The Workgroup recommends siting the NOx monitor at a location sufficiently downwind of the predominate emission source to allow the NOx composition to stabilize. The original recommendation of 15 to 80 km downwind and within the general direction ($\pm 22.5^{o}$) of the maximum impact, is reasonable. A closer site may be used if it can be shown that the distance is adequate for the plume NOx composition to stabilize. A closer site may also be selected if the resulting NO_2-to-NOx ratio will only be used to estimate NO_2 concentrations at receptors within the immediate vicinity of the monitoring site. In this situation, a different NO_2-to-NOx ratio would be required to estimate the NO_2 concentrations at other receptors.

The Workgroup acknowledges that siting a monitor at quasi-equilibrium distances essentially precludes the use of conventional pre-construction monitoring data collected under the Prevention of Significant Deterioration (PSD) program. EPA's *Ambient Monitoring Guidelines for Prevention of Significant Deterioration (PSD)* states "[pre-construction] monitoring data should be representative of three types of areas: 1) the location(s) of *maximum* concentration increase from the proposed source or modification, 2) the location(s) of the *maximum* air pollutant concentration from existing sources, and 3) the location(s) of the *maximum* impact area." (emphasis added). Since NOx plumes typically do not reach quasi-equilibrium at the maximum impact points, PSD applicants subject to NOx review may have to obtain other site-specific NOx data for developing local ARM ratios, or site an additional NOx monitor at a distant downwind location.

NOx monitoring should be conducted using a NOx analyzer and quality assurance (Q/A) procedures approved by the reviewing authority. The EPA designated reference or equivalent method for chemiluminescent NOx analyzers is acceptable in areas with relatively high ambient concentrations (i.e., greater than 20 ppb).

Data Quality and Sufficiency

Hourly NO_2 and NOx data should be collected for an entire year. The data should be validated using the procedures established in the approved Q/A plan.

The current EPA reference method for chemiluminescent NOx analyzers does not include quality assurance procedures for data collected below 30 ppb (the lower limit of EPA's acceptable audit range). In addition, most audit test points occur between 50 and 80 ppb. EPA has certified some NOx analyzers that are capable of measuring concentrations well below 20 ppb, but once again, there are no established Q/A procedures for data collected at this range. Therefore, data below the "lower quantification limit" cannot be assigned a reliable value.[3]

The Workgroup concurs with Chu and Meyer that NO_2 and NOx values below 20 ppb, or the approved lower quantification limit, must be thrown out. Unlike compliance monitoring for the ambient NO_2 air quality standard, data substitution can *not* be used in the ARM method for concentrations below the lower quantification limit. Compliance monitoring essentially deals with one compound, NO_2, and seeks to determine the maximum concentrations. Therefore, accuracy at low concentrations is not required, and the lower quantification threshold value or some other conservative estimate can be substituted for data below this level.

In contrast, ARM monitoring deals with two "compounds," NO_2 and "NOx." In addition, ARM monitoring seeks to determine the *relative* concentrations (NOx composition) across the entire range of recorded values. Therefore, accuracy at all data ranges, low and high, is more critical. Since data below the lower quantification threshold is questionable, there is no reliable method for substituting *both* the NO_2 and NOx concentrations without making an assumption regarding the NOx composition. In effect, one would have to assume a NO_2-to-NOx ratio in order to substitute data, which circumvents the purpose for conducting the ARM analysis in the first place. In rural and low impact urban areas, most or even all of the NOx data may be below the 20 ppb lower quantification limit, which makes the concern with data substitution even more significant.

An ARM database must have acceptable data for at least 75 percent of the year. This equates to 6,570 NO_2 and 6,570 NOx data points greater than the lower quantification threshold (e.g., 20 ppb). The data points do not need to be matched. Databases with fewer values cannot be used to determine annual average concentrations. In these cases, a different approach must be used to estimate annual average NO_2 concentrations.

Averaging Technique

[3] The OLM/ARM Monitoring Subgroup is developing recommended Q/A procedures to allow the use of NO_2 and NOx values measured at concentrations below 20 ppb. In the meantime, the reviewing authority may be able to justify a lower quantification limit below 20 ppb, depending on the sensitivity of the monitor, the selected scale of operation, and the type of quality assurance procedures used in the 0-30 ppb range during data collection.

The next step in the ARM method is to determine the annual average NO_2 and annual average NOx concentrations. The annual average concentrations should be determined using the standard averaging technique where the sum of the values is divided by the number of values.

The Workgroup notes that using the annual average concentrations is different than the average daily average approach recommended by Chu and Meyer. The Workgroup believes the annual average approach is consistent with current monitoring concepts. In addition, the resulting ratio is being used to refine the annual average NOx concentration, not the average daily average NOx concentration. Further, the ARM theory is based on the tenant that the predicted (modeled) NO_2-to-NOx ratio equals the observed (monitored) NO_2-to-NOx ratio. This tenant is only true if the values used to establish each ratio are based on the same averaging technique. Mathematically, the annual average NO_2 to annual average NOx ratio does *not* equal the average daily average NO_2 to average daily average NOx ratio.

The Workgroup concurs with Chu and Meyer that large urban areas can have significant diurnal variations in NOx concentrations. A review of South Coast Air Basin data shows a very noticeable nighttime increase in NO levels, presumably from motor vehicles (Chico, et al., 1998). This diurnal change in NO concentrations leads to relatively low NO_2-to-NOx ratios at night, and high NO_2-to-NOx ratios during the day. The NO_2-to-NOx ratios based on daylight data are presumably more representative of point source emissions. Therefore, the Workgroup concurs that the NO_2-to-NOx ratio for *large urban areas* should be based on the annual average concentrations for daylight hours (7 a.m. to 6 p.m.).

ARM Value

Once the annual average concentrations are determined, the annual average NO_2 concentration is divided by the annual average NOx concentration to determine the site-specific NO_2-to-NOx ratio. The resulting ratio can then be used to estimate the NO_2 concentrations using the methodology shown in Equation 1.

Method Summary

The recommended procedure is summarized below:

1. Site the NOx monitor at a location sufficiently downwind of the predominate emission source to allow the NOx composition within the plume to stabilize.

2. Collect a year's worth of NO_2 and NOx data using a NOx analyzer and quality assurance (Q/A) procedures approved by the reviewing authority.

3. Validate the NO_2 and NOx data using the procedures established in the approved Q/A plan.

4. Eliminate all NO_2 and NOx data below 20 ppb, or the approved lower quantification threshold.

5. Check if at least 75% of the data remains. If not, seek some other NO_2 modeling method.

6. Use the remaining data to calculate the annual average NO_2 and annual average NOx concentrations. For large urban areas, use only daylight data (7 a.m. to 6 p.m.) to determine the annual average concentrations.

7. Divide the annual average NO_2 concentration by the annual average NOx concentration to determine the observed NO_2-to-NOx ratio.

8. Use the resulting ratio and Equation 1 to estimate the ambient annual average NO_2 concentrations.

References

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Chu, Shao-Hang, and Edwin L. Meyer. *Use of Ambient Ratios to Estimate Impact of NOx Sources on Annual NO_2 Concentrations*. Air and Waste Management Association 84th Annual Meeting, June 1991. (AWMA Document Number 91-180.6).

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