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ARM2 METHOD TO ESTIMATE NO2 AIR CONCENTRATIONS BY USING NOX AIR CONCENTRATIONS OBTAINED BY AIR POLLUTION MODELS: VERIFICATION AND ADAPTATION BY USING AIR QUALITY NETWORK OF TUSCANY DATA

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Abstract: We present an adaptation of the US-EPA ”Tier 2” ARM2 method to the local environmental conditions of Tuscany. In particular, we include an NO_2/NOx variable ambient ratio, expressed as a function of 1-hr NOx air concentration, estimated by models obtained considering NOx and NO_2 hourly ambient data from a large number of monitoring stations over a timespan of several years. The data extracted from the Air Quality Monitoring Network archive have been used to obtain three 5th grade polynomial equations - having different degrees of conservativity - which represent the empirically derived relationship between the upper limits of the observed NO_2/NOx ambient ratios versus the NOx air concentration. This study presents a comparison between the Tuscany-data derived polynomials and the ARM2 US-data derived original equation; the differences between these equations and the NO_2 hourly concentrations are discussed. We also discuss the possible application of this method for regulatory purposes in Tuscany.

Key words: *ARM2, industrial emissions, NO_2/NOx ambient ratio.*

INTRODUCTION

The European Air quality Directive 2008/50/EC sets limit values for the ambient concentrations of Nitrogen dioxide (NO_2): 40 µg/m^3 for the annual average concentration, 200 µg/m^3 for the 99.8° annual percentile of the hourly concentrations. The Member states are required to monitor the NO_2 concentrations in their territory and take appropriate measures to reduce them when the limit values are exceeded. Air quality modelling fulfills a key role in air quality management for regulatory purposes.

Nitrogen oxides are emitted as a mixture of NO and NO_2 by the majority of antropic sources (traffic, industrial processes, energy production, etc). Both gases are also highly reactive through the oxidation of NO with ozone and the photo-dissociation of NO_2 to NO. Therefore, it is critical to be able to assess as precisely as possible the actual NO_2 increase in ambient concentrations generated by industrial and traffic sources, whose emission ratios are usually expressed as total Nitrogen oxides (NOx≈NO+NO_2).

US-EPA has approved a three-tiered estimation approach to calculate NO_2 concentrations (US-EPA 2005) based on NOx air concentrations obtained by models, that includes the ”Tier 2” method Ambient Ratio Method (ARM). ARM applies an empirically derived conversion factor, based on observed NO_2/NOx ratios of monitoring data, to the modeled NOx concentrations; this is also mentioned in (Denby 2011).

Until 2013 US-EPA recommended two fixed conversion factor: 0.75 to estimate NO_2 annual average concentrations, and 0.80 to estimate 1-h NO_2 concentrations (US-EPA 2011). However, data indicates that the NO_2/NOx ratio is variable and decreases with the proximity to emission sources characterized by low NO_2/NOx in-stack ratio, which is a common occurrence for traffic and combustion-based industrial processes. This suggests that fixed ratios overestimate NO_2 air concentrations in the near field of the emission, where usually the most relevant impacts are expected.

Therefore, the ARM version 2 (ARM2) has been developed using 1-h air monitoring data to take into account the variability of the conversion factor as a function of NOx concentration (RTP Environmental Associates 2013). Currently US-EPA is proposing, as "Tier 2" approach, to replace the old ARM method with the more refined ARM2 (US-EPA 2014).

The ARM2 empirical relationship (a 6th grade polynomial function) between NOx hourly average concentrations and the corresponding NO_2/NOx ratios has been obtained analyzing a 10-year data set extracted from the US air quality monitoring network. Since the data used come from observations in the US territory, the obtained relationship can maybe provide less accurate results if used to evaluate NO_2 concentrations outside the US.

In the present study we adapt the ARM2 method to the environmental conditions of Tuscany (Italy), by employing a 19 year data-set extracted from the Tuscany Air Quality Monitoring Network database. By using this set of data we derive a similar empirical relationship, to be compared to the US original one.

POLYNOMIAL EQUATIONS FROM THE TUSCANY AMBIENT DATA

In order to adapt the ARM2 equation to the Tuscany environmental conditions, the hourly NO_2/NOx ambient ratios have been calculated by using the Tuscany Air Quality Monitoring Network database and subsequently sorted into NOx (as NO_2) concentration ”bins”, 20 $\mu g/m^3$ wide. The data-set utilized includes all the NOx and NO_2 hourly concentrations from all the stations of the network active from 2007 to 2016, and all the NOx and NO_2 hourly concentrations from the stations active from 1999 to 2006 where the NOx averages are greater than 300 $\mu g/m^3$. This latter addition has been performed because high concentration values of Nitrogen oxides are less frequent in Tuscany in the recent years, given the general decreasing trend in NOx air concentrations. Therefore the inclusion of older data contributes to increase the population in the higher NOx concentrations’ ”bins”. The final data-set contains more than 2.300.000 hourly averages in total.

Figure 1 presents the scatterplot of NO_2/NOx ratio as a function of NOx concentration, as obtained from the Tuscany dataset. It is easily noticeable the expected decreasing trend in the ambient as NOx concentrations increase. At very high concentrations (around 540 $\mu g/m^3$ and above) the large majority of observed ambient ratios clusters to values between 0.1 and 0.3.

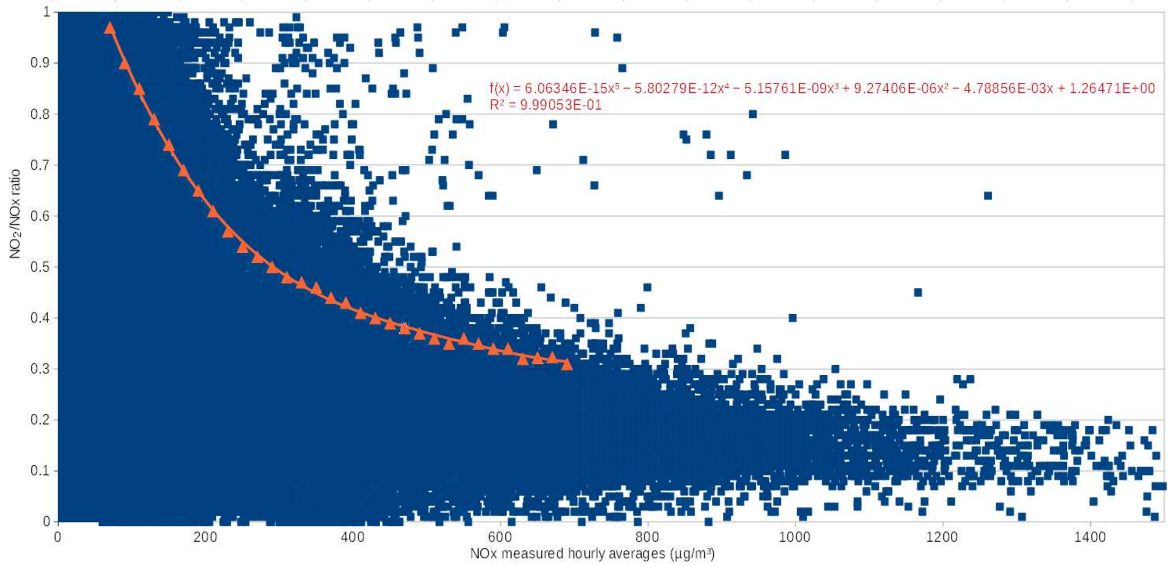

Figure 1. Scatterplot of Tuscanian NO_2/NOx ambient ratios as a function of NOx hourly concentration. In red is represented the plot of the 98th percentile ratios function, associated to the median value of each 20 $\mu g/m^3$ wide NOx ”bin”, and the 5th grade polynomial fit.

To obtain conservative NO_2 hourly concentrations assessments, for each ”bin” the upper bound of the observed NO_2/NOx ratios has been taken into account by selecting the 98th percentile of the ratios, following the same procedure used in the ARM2 original method. See also (US-EPA 2011) for further considerations about the choice of using the 98th percentile.

A ”cut-off” value (60 $\mu g/m^3$) has been applied to the lower NOx concentrations since the 98th percentile of NO_2/NOx ratios turns out about 1 when NOx values lower than 60 $\mu g/m^3$ are taken into account. This is a higher value than the corresponding ”cut-off” one used in data analysis of ARM2 original method (20 ppb, equal to 37.6 $\mu g/m^3$, as NO_2: RTP Environmental Associates, 2013). The decreasing trend of the 98th percentile NO_2/NOx ambient ratios is strictly monotone for values of NOx smaller than 540 $\mu g/m^3$. For higher values the trend behavior becomes less stable, most likely because the data population in each

”bin” decreases as the value of NOx increases. For this reason, also an upper ”cut-off” value (700 μg/m^3) has been applied to NOx concentration database used to extract the percentiles.
In Figure 1 we also plot the 98th percentile of the NO_2/NOx ratios, each one associated to the median of NOx hourly concentrations of the corresponding ”bin” (as x-coordinate). The following 5th grade polynomial is the function that best fits the plot , and it can be used to represent the empirical relationship between the upper limits of the NO_2/NOx ambient ratio (R) and the NOx hourly concentration (x):

$$R_{median} = 6.0635E\text{-}15x^5 - 5.8028E\text{-}12x^4 - 5.1576E\text{-}9x^3 + 9.2741E\text{-}6x^2 - 4.7886E\text{-}3x + 1.2647 \quad (1)$$

In order to assess the magnitude of the variability in the above relationship, the lower and upper boundary values of each ”bin” have also been used as x-coordinates for the corresponding 98th percentile of NO_2/NOx ratios obtaining a ”lower boundary” and an ”upper boundary” plot. Two similar 5th grade polynomials have been obtained, that fit the aforementioned plot:

$$R_{lower} = 6.0635E\text{-}15x^5 - 5.4996E\text{-}12x^4 - 5.3837E\text{-}9x^3 + 9.1159E\text{-}6x^2 - 4.6047E\text{-}3x + 1.2177 \quad (2)$$

$$R_{upper} = 6.0635E\text{-}15x^5 - 6.1060E\text{-}12x^4 - 4.9194E\text{-}9x^3 + 9.4253E\text{-}6x^2 - 4.9756E\text{-}3x + 1.3135 \quad (3)$$

TRENDS

In Figure 2 we plot equations (1), (2), (3) obtained from Nitrogen oxides data measured in Tuscany, and compare them to the ARM2 original equation. It is quite evident that the discrepancies between the three plots of the equations based on Tuscany ambient data are more pronounced for low values of NOx hourly concentration, while they tend to become negligible as NOx hourly concentration increases.
It is also noticeable how ARM2 original equation appears to be more conservative when referring to NOx data of approximately 260 μg/m^3 or less, as its NO_2/NOx ratios estimated values are slightly higher than the Tuscany ambient data adapted ones; the opposite is true for NOx values greater than 260 μg/m^3.

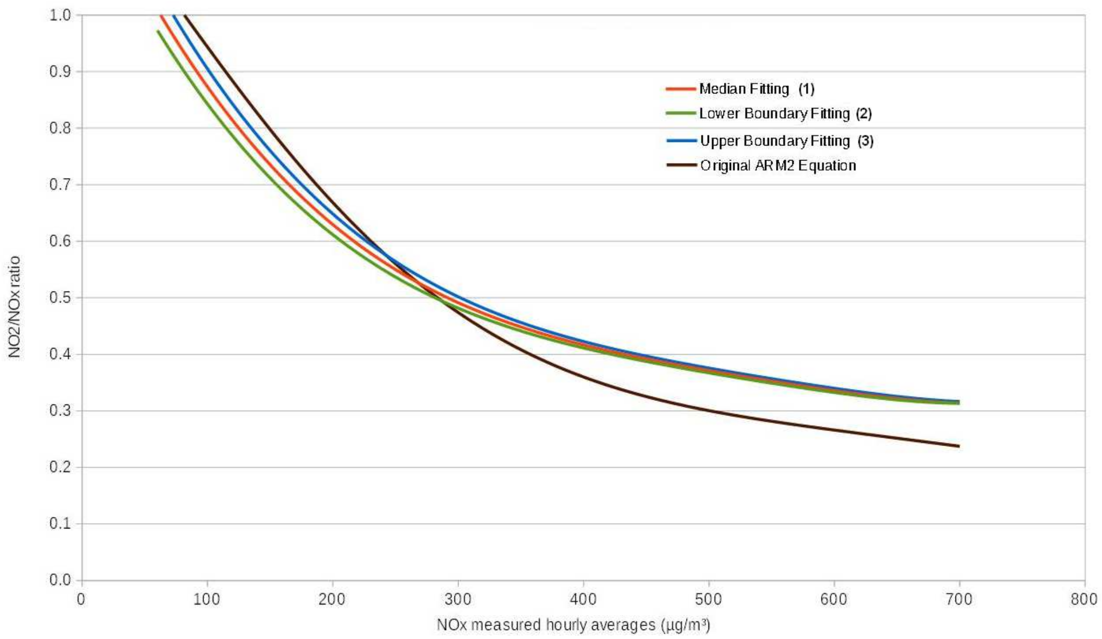

Figure 2. Plots of the polynomial equations relating NO_2/NOx ambient ratio and NOx hourly concentration: Tuscany data derived (green, blu, red lines) and ARM2 original equation (black line; RTP Environmental Associates 2013).

Figure 3 is a plot of the calculated NO_2 concentrations as a function of the NOx concentrations using the ARM2 original equation and the Tuscany ambient data adapted ones.
It is worth reminding that US-EPA assumes 0.9 to be acceptable as the maximum value of NO_2/NOx ambient ratio and - in the absence of locally measured NO_2/NOx in-stack ratios - 0.5 as the minimum

value (Podrez 2015, US-EPA 2015). The plot corresponding to the aforementioned ratios are reported in Figure 3.
It can be noted that the trend of the (1), (2) and (3) equations show a quasi-linear increase in the range of NOx concentrations between 200 $\mu g/m^3$ and 700 $\mu g/m^3$, where NO_2 concentrations increase at approximately 20% with respect to the corresponding NOx growth ratio. Conversely, the NO_2 concentrations obtained with the ARM2 original equation, show an inflection when 300 $\mu g/m^3$ NOx concentration is reached. Actually, it can be noticed that increasing the NOx value from 300 $\mu g/m^3$ to 700 $\mu g/m^3$ generates a corresponding increase of 24 $\mu g/m^3$ NO_2 if ARM2 original equation is used and a more conservative increase of 72 $\mu g/m^3$ NO_2 if the local Tuscany data equation ones.
US-EPA itself has evidenced that the ARM2 method tends to be more conservative when the NO_2/NOx in-stack ratios of the emissions of interest are lower than 0.5 and the ozone ambient concentrations are not very high (lower than 90 ppb, i.e. 180 $\mu g/m^3$).
US-EPA has conducted theoretical calculations using a ”plume volume” method, similar to the Plume Volume Molar Ratio Method (PVMRM), over a range of ozone concentrations and for different NO_2/NOx in-stack ratios: when the in-stack ratio is 0.5 the ARM2 method estimates ambient ratios lower than the pure volume theoretical calculations (US-EPA 2014). This is actually one of the reasons behind US-EPA suggestion of using an NO2/NOx ratio of 0.5 as the minimum ambient ratio, in the absence of locally measured data.

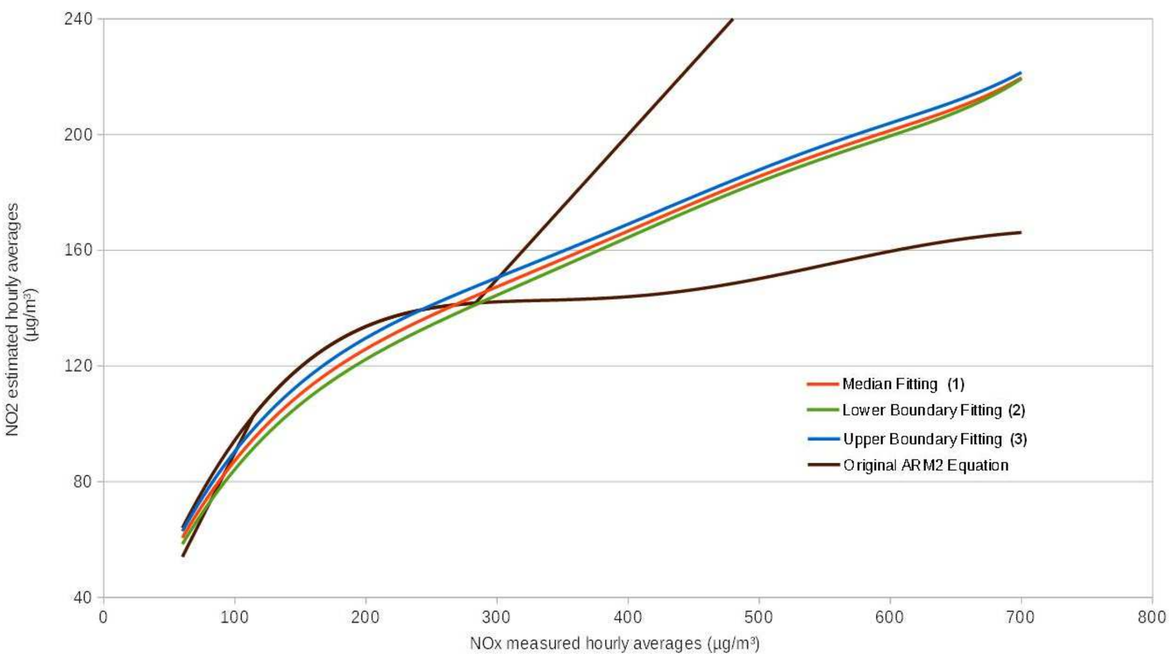

Figure 3. Estimated NO_2 ambient concentrations as a function of the NOx measured ambient concentrations using ARM2 original equation and the Tuscany ambient data adapted ones (equations (1), (2), (3))

The trend due to the above mentioned US-EPA recommendation about the minimum ambient ratio (NO_2/NOx = 0.5) is certainly the most conservative amongst those shown in Figure 3. However, the gap between the estimated NO_2 concentrations and observed ones tends to enlarge a lot as the NOx concentration increases.
For the above reasons, we can conclude that the ARM2 original equation and the polynomial equations derived from the Tuscany ambient data are better suited for representing NO_2/NOx ambient ratios generated by low NO_2/NOx in-stack ratio emissions.

REGULATORY APPLICATION CONSIDERATIONS

The ARM2 equations adapted with the Tuscany ambient data display a very similar trend to the original

US-EPA polynomial for NOx hourly concentrations lower than 300 μg/m^3, although the US-EPA equation is slightly more conservative. As already pointed out, the polynomial equations (1), (2) and (3) become more conservative than the original ARM2 equation for higher than 300 μg/m^3 NOx hourly concentrations. As they are obtained from locally measured data, the adapted equations are probably more coherent with the environmental conditions of Tuscany that of US ones.

Experience in Nitrogen oxides modeling and evaluation for regulatory purposes in Tuscany region suggests that the availability of a good "Tier 2" method is especially crucial to estimate NO_2 concentrations when the modeled NOx hourly concentrations due to antropic sources are expected between 100 μg/m^3 and 300 μg/m^3, without considering the background levels.

This is mainly because concentrations of NO_2 lower than 100 μg/m^3, when added to the typical background levels in Tuscany, usually do not imply the risk of exceeding the European Air quality Directive 2008/50/EC limit values for Nitrogen dioxide ambient concentrations. In such cases, a simple screening evaluation ("Tier 1") is usually enough to proceed.

The opposite is true for the modeled NOx hourly concentrations higher than 300 μg/m^3, usually associated with NO_2 hourly concentrations higher than 150 μg/m^3. Given the fact that such concentrations increase the likelihood of exceeding the air quality limits when added to background levels, it seems advisable whenever possible to further refine the "Tier 2" evaluation, implementing measured NO_2/NOx in-stack ratios of local sources into models that take into account NOx chemistry in the atmosphere.

It is also worth noting that, given the order of magnitude of emissions usually authorized in Tuscany, it is not frequent that NOx hourly ambient concentrations due to a single industrial activity are higher than 300 μg/m^3, without taking into account the background. It is more likely to find very high values of Nitrogen oxides when modeling the impact generated by several sources like other industries and busy roads nearby.

Finally, it has to be taken into account that the ARM2 method is probably less conservative when the sources' NO_2/NOx in-stack ratios are very high (more than 0.5). Such ratios, in Tuscany, are rare enough occurrences to warrant a case-by-case approach.

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