Concentration of Nitrogen Dioxide Estimation from Modeled NO\textsubscript{X} of a Thermal Power Plant

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Abstract: Nitrogen dioxide (NO\textsubscript{2}) is noxious, phototoxic and causes eutrophication. NO\textsubscript{2} is one of the major precursors of ground level ozone pollution. Emission rates and emission concentrations of various pollutants from stationary sources of power plant emissions are calculated using Emission Inventory methodologies. Ground level concentrations of Nitrogen oxide (NO\textsubscript{x}) pollution are predicted by Gaussian dispersion model. About 40% of the Nitrogen oxide pollution is produced from point source of Electric power plant boilers. In this paper it is proposed to estimate ground level concentrations of Nitrogen dioxide at various receptor points of a Thermal Power Project. The estimations are made from modeled Nitrogen oxides of Rayalaseema Thermal Power Project, (Coordinates: 14°42’52”N 78°27’29”E) Kadapa, Andhra Pradesh, India.

Key words: Power Plant Emissions; Stationary Sources; Nitrogen oxides; Estimation; Ground Level Concentrations; Phototoxic; Precursors; ozone pollution.

I. Introduction

1.1 Source
Nitrogen oxides (NO\textsubscript{x}) are produced [15] by high-temperature combustion reactions [20]. Common sources of NO\textsubscript{x} include: Automobiles, gasoline powered equipment, construction equipment, industrial processes, natural gas furnaces, and power generation. About 40% of the NO\textsubscript{x} emissions are produced from point sources of Electric power plant boilers [26]. Here we have taken Rayalaseema Thermal Power Project, as a source.

1.2 Implications
Nitrogen dioxide (NO\textsubscript{2}) is a poisonous gas. Eyes, nose and throat can be irritated with its exposer. it causes difficulty in breath [6]. Sensitive people like Asthmatic [21] and young children [12][13] with, exposure to even low levels of NO\textsubscript{2} may increase bronchial problems and respiratory infections [11]. High levels of NO\textsubscript{2} with Long-term exposure lead to chronic bronchitis. NO\textsubscript{2} is an important critical air pollutant [19]. It reacts in the atmosphere to produce secondary pollutants like ozone (O\textsubscript{3}) and acid rain.

1.3 Equations of Zeldovich
Release of nitrogen oxides (NO\textsubscript{x}) from combustion reactions are mainly in the form of nitric oxide (NO). Zeldovich reactions [17], represents that, nitric oxide (NO) is produced due to the shortage of available oxygen in air i.e., about 200,000 ppm in atmospheric air at temperatures above 1,300°C. At temperatures below 760°C, generation of NO is at very low concentrations or not produced. The production of NO is a function of fuel to air ratio, the Chemicals will enter into the reaction with the same ratio. The Zeldovich reactions are:

\[
\begin{align*}
N_2 + O & \rightarrow NO + N \\
N + O_2 & \rightarrow NO + O \\
N + OH & \rightarrow NO + H
\end{align*}
\]

Major quantity of NO is generated from anthropogenic sources [15]. Biogenic sources contribute less than 10% of total NO emissions [9]. NO is slightly water soluble. Only infants and very sensitive people [12] will be affected with the expose of NO. Presence of NO\textsubscript{2} in atmosphere causes acid rain. It dissolves in water producing nitric acid (HNO\textsubscript{3}). Reaction of NO\textsubscript{2} with a photon leads to transformation of O\textsubscript{2} into O\textsubscript{3}, NO\textsubscript{2} becomes NO. This NO is then oxidized to NO\textsubscript{2} within short period by radicals from the photo reaction of Volatile Organic Compounds (VOC) [26]. Therefore, ground level ozone concentration is the product of both NO\textsubscript{2} and VOC pollution. Both NO\textsubscript{2} and VOC are considered as ozone precursors [20].

1.4 Effect of NO\textsubscript{x} on the Atmosphere
NO\textsubscript{x} are transparent to several wavelengths of electromagnetic radiation [17], NO\textsubscript{x} permit the most of photons to pass through and, therefore, have longer periods. More ozone is produced because NO\textsubscript{2} is reproduced...
from NO by the photo chemical reaction of volatile organic compounds; NO\textsubscript{2} sustains longer periods and it can travel considerable distances before producing ozone.

II. Methodology

2.1 Introduction

Nitrogen oxides are released into the atmosphere mainly in the form of nitric oxide (NO) [15]. In the atmosphere nitric oxide (NO) oxidised to nitrogen dioxide (NO\textsubscript{2}), which is more toxic [6]. The oxidation of nitric oxide into nitrogen dioxide is due to presence of ground level ozone.

\[
\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2
\]

Total NO\textsubscript{x} concentrations do not change because of its one to one transformation reaction [16], the rate of conversion of nitric oxide to nitrogen dioxide is directly related to the ozone concentration in the ambient atmosphere. Here we can ignore the Photochemical dissociation [22] of NO\textsubscript{2} to reproduce NO and decrease of the NO\textsubscript{2} concentrations by ozone up to some extent, in atmospheric air Ozone concentrations show a seasonal variation, during winter it will show with the highest concentrations, Summer concentrations are slightly less. To produce 72\textmu g/m\textsuperscript{3} of NO\textsubscript{2} by oxidation of NO the maximum ozone concentration is sufficient. This is the basic information for the development of simple method to estimates of concentrations of nitrogen dioxide from modelled NO\textsubscript{x} concentrations.

2.2 Comparisons with US EPA Ozone Limiting Method (OLM)

The estimation of nitrogen dioxide levels is having direct relation to the Ozone Limiting Method [4]. The modelling of yearly average levels of nitrogen dioxide is described by the OLM, because of the US National Ambient Air Quality Standards (NAAQS) [9]. It includes yearly average standard of 100\textmu g/m\textsuperscript{3} for NO\textsubscript{2}. However, the Ozone Limiting Method does use hourly average modelling [5], along with one-hour average meteorological data [10], ozone and nitrogen dioxide data, to estimate the yearly averages.

The Ozone Limiting Method model requires one-hour average meteorological data which simultaneously recorded concentrations of NO\textsubscript{2} and O\textsubscript{3} extending over at least one year, with complete valid data [10]. Obtaining data at a single location are associated with significant problems and expensive in locating the monitoring site relative to existing emission sources and the proposed new emission source. More monitoring sites are recommended by US EPA guidance, because of the perceived difficulty of accounting for removal of ozone by nitric oxide.

The proposed methodology described here eliminates the drawbacks present in the Ozone Limiting Method, and the ozone and Nitrogen oxides measurement system.

2.3 Input Data

Total emission rates and concentrations of NO\textsubscript{x} from all stacks in Rayalaseema thermal power plant is produced from emission inventory methodology [1] and represented in the table 1.

Table 1 Total emission rates and concentrations

<table>
<thead>
<tr>
<th>Source</th>
<th>Pollutant</th>
<th>Total Emission rate (kg/h)</th>
<th>Emission Concentration (kg/Nm\textsuperscript{3} at stack reference conditions)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stack-1,2,3,4,&amp;5</td>
<td>NO\textsubscript{x}</td>
<td>249.48</td>
<td>0.212</td>
</tr>
</tbody>
</table>

2.4 Predicted Ground Level Concentration of NO\textsubscript{x}

By giving input variables to the Gaussian based computational program [23] [27], ground level concentrations of NO\textsubscript{x} at various receptor points for Pasquill-Gifford Stability class [7][8] – C and Pasquill-Gifford Stability class – D are presented in table 2.

Back ground concentration of NO\textsubscript{x} is measured as 16 \textmu g/m\textsuperscript{3}.

Table 2 ground level concentration of NO\textsubscript{x} under slightly unstable & neutral conditions

<table>
<thead>
<tr>
<th>Downwind distance (m)</th>
<th>Slightly unstable condition (Pasquill-Gifford Stability class – C)</th>
<th>Neutral condition (Pasquill-Gifford Stability class – D)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\sigma_x(m)$</td>
<td>$\sigma_y(m)$</td>
</tr>
<tr>
<td>5000</td>
<td>438.44</td>
<td>264.29</td>
</tr>
<tr>
<td>10000</td>
<td>814.76</td>
<td>496.96</td>
</tr>
<tr>
<td>15000</td>
<td>1170.73</td>
<td>719.03</td>
</tr>
<tr>
<td>20000</td>
<td>1514.09</td>
<td>934.47</td>
</tr>
<tr>
<td>25000</td>
<td>1848.38</td>
<td>1145.12</td>
</tr>
<tr>
<td>30000</td>
<td>2175.60</td>
<td>1352.03</td>
</tr>
</tbody>
</table>

$\sigma_x$, $\sigma_y$ are standard deviations in y direction and z direction respectively in Gaussian dispersion [2].
2.5 Methodologies for Calculations

If cumulative concentrations\cite{17}\cite{4} of modeled nitric oxides (NOx) are less than 80µg/m$^3$, total nitric oxides are considered to be present as nitrogen dioxide (NO$_2$). The 80 µg/m$^3$ corresponds to 8 µg/m$^3$ of NO$_2$ obtained from a default percentage of 10% of NO$_2$ in emitted NO$_X$ plus 72 µg/m$^3$ of NO$_2$ formed by oxidation of nitric oxide (NO) by ozone. For cumulative NO$_X$ concentrations above 80µg/m$^3$, the nitrogen dioxide concentrations are calculated as follows:

\[ [\text{NO}_2]\text{cum max} = 72 + ([\text{NOx}]\text{bkgrd tot} \times \%\text{NO}_2\text{bkgrd}) + ([\text{NOx}]\text{emiss} \times \%\text{NOx emiss}) \]

Where:

- \([\text{NO}_2]\text{cum max}\) = maximum estimate of total cumulative NO$_2$ from both background NOx and the additional emission under consideration.
- \([\text{NOx}]\text{bkgrd tot}\) = the total background NOx concentration in the receiving air.

- \(%\text{NO}_2\text{bkgrd}\) = the percentage of NO$_2$ in the NOx emitted from the sources contributing to the background levels of NOx.
- \([\text{NOx}]\text{emiss}\) = the concentration of NOx at the receptor originating from the emission.
- \(%\text{NOx emiss}\) = the percentage of NO$_2$ in the NOx emitted from the source under consideration.

If either \(%\text{NO}_2\text{ bkgrd}\) or \(%\text{NOx emiss}\) are not known, the default percentage of 10% used in the OLM is probably the best choice.

If the percentages of NO$_2$ in the emissions are not known, or happen to be 10%, the expression above simplifies to:

\[ [\text{NO}_2]\text{cum max} = 72 + ([\text{NOx}]\text{cum tot} \times 10\%) \]

Where:

- \([\text{NOx}]\text{cum tot}\) = cumulative total NOx conc. including bkgrd NOx and NOx increment at the receptor from the emission under consideration. 72

### III. Results and discussion

Ground level concentrations of Nitrogen dioxide are estimated from modeled NO$_X$ concentrations at various downwind distances for prevailing two stability classes of the project site, which are projected in table 3.

<table>
<thead>
<tr>
<th>Downwind distance (m)</th>
<th>Slightly unstable condition (Pasquill-Gifford Stability class – C)</th>
<th>Neutral condition (Pasquill-Gifford Stability class – D)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NO$_x$(µg/m$^3$)</td>
<td>NO$_x$(µg/m$^3$)</td>
</tr>
<tr>
<td>-----------------------</td>
<td>---------------------------------------------------------------</td>
<td>----------------------------------------------------------</td>
</tr>
<tr>
<td>5000</td>
<td>78.71</td>
<td>15.75</td>
</tr>
<tr>
<td>10000</td>
<td>31.19</td>
<td>39.09</td>
</tr>
<tr>
<td>15000</td>
<td>16.67</td>
<td>39.24</td>
</tr>
<tr>
<td>20000</td>
<td>10.81</td>
<td>34.46</td>
</tr>
<tr>
<td>25000</td>
<td>7.82</td>
<td>29.62</td>
</tr>
<tr>
<td>30000</td>
<td>6.2</td>
<td>25.56</td>
</tr>
</tbody>
</table>

3.1 Conservative Estimation

The calculations give substantial overestimates of NO$_2$ concentrations, under two common situations including:

- The oxidation of nitric oxide by ozone will be enhanced to some extent, during the day.
- Nitrogen dioxide and ozone concentration levels are reduced by reaction with green plants and other absorbents, during stable atmospheric conditions, particularly at night.

3.2 Monitoring Data Validation

Estimation of NO$_2$ concentrations from NOx concentrations predicted at various downwind distances from Ralaseema Thermal Power Project shows that the percentage of NO$_2$ in NOx emissions, contributing to the measured concentrations as 10% is more conservative and that 5% still estimates NO$_2$ concentrations higher than any reliable measured concentrations. This represents the influence of the original percentage of NO$_2$ in...
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NOx emissions being less than 10%, together with removal of NOx and O3 by green plants, and other photochemical reactions.

Ambient Air Quality Standards [25] for Nitrogen dioxide for 24 hours is prescribed as 80μg/m3; all the results are below the Ambient Air Quality Standards, prescribed by the Central Pollution Control Board (Government of India) [18]. Nitrogen dioxide concentrations at various locations from the project site can be used as input values for the modeling of ground level ozone.

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