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Concentration of Nitrogen Dioxide Estimation from Modeled NO_X of a Thermal Power Plant

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Abstract: *Nitrogen dioxide (NO_2) is noxious, phototoxic and causes eutrophication. NO2 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 (NOx) 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 (NOx) are produced [15] by high-temperature combustion reactions [20]. Common sources of NOx include:

Automobiles, gasoline powered equipment, construction equipment, industrial processes, natural gas furnaces, and power generation. About 40% of the NOx 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_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_2 may increase bronchial problems and respiratory infections [11]. High levels of NO_2 with Long-term exposure lead to chronic bronchitis. NO_2 is an important critical air pollutant [19]. It reacts in the atmosphere to produce secondary pollutants like ozone (O_3) and acid rain.

1.3 Equations of Zeldovich

Release of nitrogen oxides (NOx) 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^{0}C. At temperatures below 760^{0}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:

$$\mathbf{N2 + O \rightarrow NO + N}$$
$$\mathbf{N + O2 \rightarrow NO + O}$$
$$\mathbf{N + OH \rightarrow NO + H}$$

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_2 in atmosphere causes acid rain. It dissolves in water producing nitric acid (HNO_3). Reaction of NO2 with a photon leads to transformation of O_2 into O_3, NO_2 becomes NO. This NO is then oxidized to NO_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_2 and VOC pollution. Both NO_2 and VOC are considered as ozone precursors [20].

1.4 Effect of NOx on the Atmosphere

NOx are transparent to several wavelengths of electromagnetic radiation [17], NOx permit the most of photons to pass through and, therefore, have longer periods. More ozone is produced because NO_2 is reproduced from NO by the photo chemical reaction of volatile organic compounds; NO_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_2), which is more toxic [6]. The oxidation of nitric oxide into nitrogen dioxide is due to presence of ground level ozone.

$$\mathbf{NO + O3 \rightarrow NO2 + O2}$$

Total NO_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_2 to reproduce NO and decrease of the NO_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$\mu g/m^3$ of NO_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 [2] NO_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$\mu g/m^3$ for NO_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_2 and O_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_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

Source	Pollutant	Total Emission rate (kg/h)	Emission Concentration (kg/Nm^3 at stack reference conditions)
Stack-1,2,3,4,&5	NO_X	249.48	0.212

2.4 Predicted Ground Level Concentration of NO_X

By giving input variables to the Gaussian based computational program [23] [27], ground level concentrations of NO_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_X is measured as 16 $\mu g/m^3$.

Table 2 ground level concentration of NO_X under slightly unstable & neutral conditions

Downwind distance (m)	Slightly unstable condition (Pasquill-Gifford Stability class – C)			Neutral condition (Pasquill-Gifford Stability class – D)		
	σ_y (m)	σ_z (m)	NO_X ($\mu g/m^3$)	σ_y (m)	σ_z (m)	NO_X ($\mu g/m^3$)
5000	438.44	264.29	70.1	286.67	89.10	12.87
10000	814.76	496.96	26.9	532.73	133.00	34.09
15000	1170.73	719.03	13.7	765.48	166.97	34.22
20000	1514.09	934.47	8.38	989.98	195.78	29.88
25000	1848.38	1145.12	5.66	1208.55	221.25	25.48
30000	2175.60	1352.03	4.10	1422.50	244.36	21.79

σ_y, σ_z are standard deviations in y direction and z direction respectively in Gaussian dispersion [2].

2.5 Methodologies for Calculations

If cumulative concentrations[17][4] of modelled 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/m3 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/m3, the nitrogen dioxide concentrations are calculated as follows:

$[\mathrm{NO2}]\mathrm{cum\ max} = 72 + [\mathrm{NOx}]\mathrm{bkgrd\ tot} \times \%\mathrm{NO2\ bkgrd} + [\mathrm{NOx}]\mathrm{emiss} \times \%\mathrm{NOx\ emiss}$ [17]

Where:

$[\mathrm{NO2}]\mathrm{cum\ max}$
$= \mathrm{maximum\ estimate\ of\ total\ cumulative\ NO2\ from\ both\ background\ NOx\ and\ the\ additional\ emission\ under\ consideration.}$

$[\mathrm{NOx}]\mathrm{bkgrd\ tot} = \mathrm{the\ total\ background\ NOx\ concentration\ in\ the\ receiving\ air.}$

$\%\mathrm{NO2\ bkgrd}$
$= \mathrm{the\ percentage\ of\ NO2\ in\ the\ NOx\ emitted\ from\ the\ sources\ contributing\ to\ the\ background\ levels\ of\ NOx.}$

$[\mathrm{NOx}]\mathrm{emiss} = \mathrm{the\ concentration\ of\ NOx\ at\ the\ receptor\ originating\ from\ the\ emission.}$

$\%\ \mathrm{NOx\ emiss} = \mathrm{the\ percentage\ of\ NO2\ in\ the\ NOx\ emitted\ from\ the\ source\ under\ consideration}.$

If either %NO_2 bkgrd or %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:

$$[\mathrm{NO2}]\mathrm{cum\ max} = 72 + [\mathrm{NOx}]\mathbf{cum}\ \mathrm{tot\ x\ 10\%}$$

Where:

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

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 3 ground level concentration of NO_2under slightly unstable & neutral conditions

Downwind distance (m)	Slightly unstable condition (Pasquill-Gifford Stability class –C)	Neutral condition (Pasquill-Gifford Stability class – D)
	NO_2(µg/m^3)	NO_2(µg/m^3)
5000	78.71	15.75
10000	31.19	39.09
15000	16.67	39.24
20000	10.81	34.46
25000	7.82	29.62
30000	6.2	25.56

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

NOx emissions being less than 10%, together with removal of NO_X and O_3 by green plants, and other photochemical reactions.

Ambient Air Quality Standards [25] for Nitrogen dioxide for 24 hours is prescribed as 80µg/m^3; 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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