

Photochemistry of Air Pollution in Delhi, India

A Monitoring Based Analysis





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This report was conceptualized, drafted, and designed by the members of UEinfo.

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Photochemistry of Air Pollution in Delhi, India: A Monitoring Based Analysis

In National Capital Region (NCR) of Delhi, spreading ~900 Sq. km, the increasing air pollution poses a serious problem due to its direct impact on human health, such as increased incidences of chronic bronchitis, cancer of the respiratory tract, asthma, and induced premature mortality. Increase in motorization (with ~600 vehicles added to the in-use fleet per day), a large diesel based truck fleet operating through the city, series of construction activities (including in the satellite cities of NOIDA and Gurgaon) and industrial emissions (local and global) resulted in deteriorated urban air quality. Increase in the incidence of morbidity and mortality due to air pollution¹, prompted public awareness campaigns for better air quality management. In 2007, the population of NCR was estimated at 16 million. It is expected to reach 22.5 million in 2025². **Table 1** presents the national ambient air quality standards in India.

Table 1: National ambient air quality standards in India³

Pollutant		Units	1 hour	8 hour	24 hour	Annual
PM ₁₀	Residential	µg/m ³			100	60
	Industrial	µg/m ³			150	120
	Sensitive Areas	µg/m ³			75	50
CO	Residential	µg/m ³	4,000	2,000		
	Industrial	µg/m ³	10,000	5,000		
	Sensitive Areas	µg/m ³	2,000	1,000		
NO ₂	Residential	µg/m ³	200		80	40
	Industrial	µg/m ³			120	80
	Sensitive Areas	µg/m ³			30	15
SO ₂	General	µg/m ³	260		80	50
Benzene		µg/m ³			15	5
Ozone	Proposed	µg/m ³	180	90	80	50
PM _{2.5}	Proposed	µg/m ³			60	40
HCHO	Proposed		80	45		

¹ “Delhi is India’s Asthma capital”, March 1st, 2009, In Today News @ http://www.intoday.in/index.php?id=24240&option=com_content&task=view§ionid=5

“The pollution story In Black And Pink”, July 15th, 1999, Down to Earth @ http://www.downtoearth.org.in/full6.asp?foldername=19990715&filename=spr&sec_id=6&sid=4

Jain et al, 2008, “Urban air quality in mega cities: A case study of Delhi City using vulnerability analysis”, Environmental Monitoring Analysis @ <http://www.ncbi.nlm.nih.gov/pubmed/17385052>

² UN HABITAT, 2008, “State of the World Cities” @ <http://www.unhabitat.org/content.asp?cid=5964&catid=7&typeid=46&subMenuId=0>

³ Central Pollution Control Board, New Delhi, India @ http://cpcb.nic.in/National_Ambient_Air_Quality_Standards.php

Among the pollutants, particulates (PM) are the primary concern due to its direct linkages to human health causing chronic and acute respiratory diseases and in some cases premature death⁴. In Delhi, the mix of air pollution sources range from the popular transport and industrial activities to the domestic coal and biomass combustion (mostly in the winter months)⁵. Besides the anthropogenic sources, natural sources also contribute significantly to the air pollution problems in Delhi. The seasonal summer dust, originating in the West is common and the wind erosion and resuspension of dust along the major roads and at the construction sites is a growing contributor.

Other pollutants which are consistently exceeding the standards in Delhi are nitrogen oxides (NO_x), sulfur dioxides (SO₂), and carbon monoxide (CO). SO₂ and CO are primary tracer emissions, mostly linked to coal and diesel combustion, and in some cases biomass burning for CO. NO_x, along with volatile organic compounds (VOCs), form a major part of the transport sector emissions and responsible for the formation of ground level ozone pollution, depending on the mix of sources (including long range transport due to seasonal dust and agricultural clearing), local meteorological and photochemical conditions. Due to increase in the transport sector emissions and the mix of sources⁶, the ground level ozone pollution has seen an increase in the number of days of exceedances⁷. The impact of the ozone pollution is particularly high during the early morning rush hours, when the sunlight catalyzes the interactions between NO_x and VOC to further the production of ground level ozone. **Figure 1** presents typical smog conditions observed in Delhi, India, and long range transport of smog due to agricultural clearing (in November, 2008). Like the PM pollution, Ozone is known to worsen respiratory symptoms such as acute bronchitis and asthma and causes chest pain, coughing, eye irritation, nausea, headaches and chest congestion.

Figure 1: Smog in Delhi - long range transport (left) and local corridors (middle)^{8 9 10}



⁴ Health Effects Institute, USA @ <http://www.healtheffects.org/>

⁵ SIM-22-2009, "AQM in Delhi, India: Then, Now, and Next" @ <http://urbanemissions.info/simair/simseries.html>

⁶ SIM-24-2009, "Motorized Passenger Travel in Urban India: Emissions & Co-Benefits Analysis" @ <http://urbanemissions.info/simair/simseries.html>

⁷ CSE, May 29th, 2009, "Delhi is reeling under high levels of deadly ozone"; presents an analysis of the ozone pollution from three monitoring stations in Delhi for the period of Jan'09 to May'09 @ http://www.cseindia.org/AboutUs/press_releases/press-20090529.htm

⁸ Satellite imagery of haze pollution in Asia @ <http://urbanemissions.blogspot.com/2009/05/dust-storm-haze-pollution-in-asia.html>

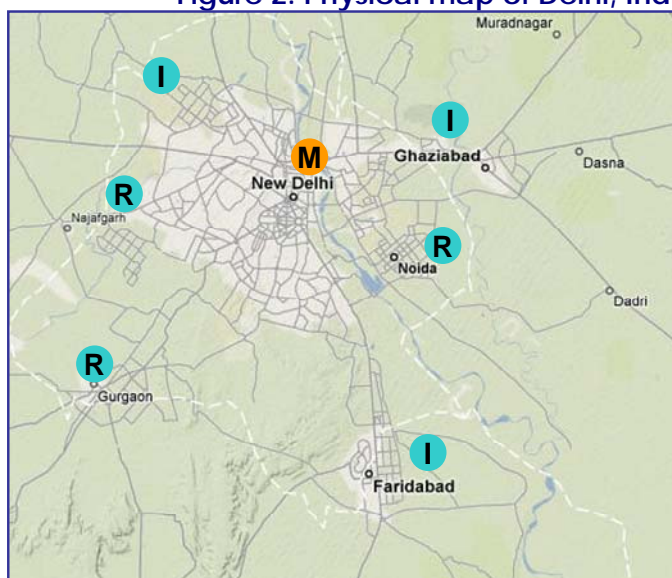
⁹ BBC, November, 2008, "Smog returns to Delhi" @ http://news.bbc.co.uk/1/hi/world/south_asia/7727114.stm

¹⁰ In Today News, March 1st, 2009, "Delhi is India's Asthma capital" @ http://www.intoday.in/index.php?id=24240&option=com_content&task=view§ionid=5

The ozone pollution over the Indian Subcontinent is well documented through observations (ground level monitoring and satellites) and modeling studies; studying the influence of the growing regional emissions, long range transport, influence of urban emissions, and photochemistry through the monsoonal changes¹¹. The urban scale ozone pollution studies are listed in **Annex 1**.

This paper presents an analysis of the air quality monitoring data (from one station) and an understanding of the air pollution chemistry prevalent in the city of Delhi due to the mix of the sources. In **Figure 2**, the location of the station, **Income Tax Office (ITO)** is identified as “M”, the acronym “R” indicates that the area is dominated by residential activities (such as construction and transport) and the acronym “I” indicates that the area is dominated by industrial activities.

Figure 2: Physical map of Delhi, India, and the monitoring station



(illustration of Continuous Air Monitoring System)

¹¹ UNEP, 2009, “Asian Brown Cloud Regional Assessment” @ <http://www.unep.org/pdf/ABCSummaryFinal.pdf>
Magnuz, 2008, “Modelling of near-surface ozone over South Asia” Journal of Atmospheric Chemistry @ <http://www.springerlink.com/content/t2361058p3145174/>

Adhikary, 2008, “Characterization of the seasonal cycle of south Asian aerosols: A regional-scale modeling analysis”, Journal of Geophysical Research @ <http://www.agu.org/pubs/crossref/2007/2006JD008143.shtml>

Fadnavis, et al., 2007, “Seasonal variation of the mesospheric inversion layer, thunderstorms, and mesospheric ozone over India” Journal of Geophysical Research @ <http://www.agu.org/pubs/crossref/2007/2006JD008379.shtml>

Mittal et al., 2007, “Surface Ozone in the Indian Region”, Atmospheric Environment @ <http://dx.doi.org/10.1016/j.atmosenv.2007.04.035>

Kunhikrishnan, et al., 2006, “Regional NO_x emission strength for the Indian subcontinent and the impact of emissions from India and neighboring countries on regional O₃ chemistry” Journal of Geophysical Research @ <http://www.agu.org/pubs/crossref/2006/2005JD006036.shtml>

Guttikunda et al., 2005, “Impacts of Asian megacity emissions on regional air quality during spring 2001” Journal of Geophysical Research @ <http://www.agu.org/pubs/crossref/2005/2004JD004921.shtml>

Khemani et al., 2000, “Study of surface ozone behavior at urban and forested sites in India”, Atmospheric Environment @ [http://dx.doi.org/10.1016/1352-2310\(94\)00293-T](http://dx.doi.org/10.1016/1352-2310(94)00293-T)

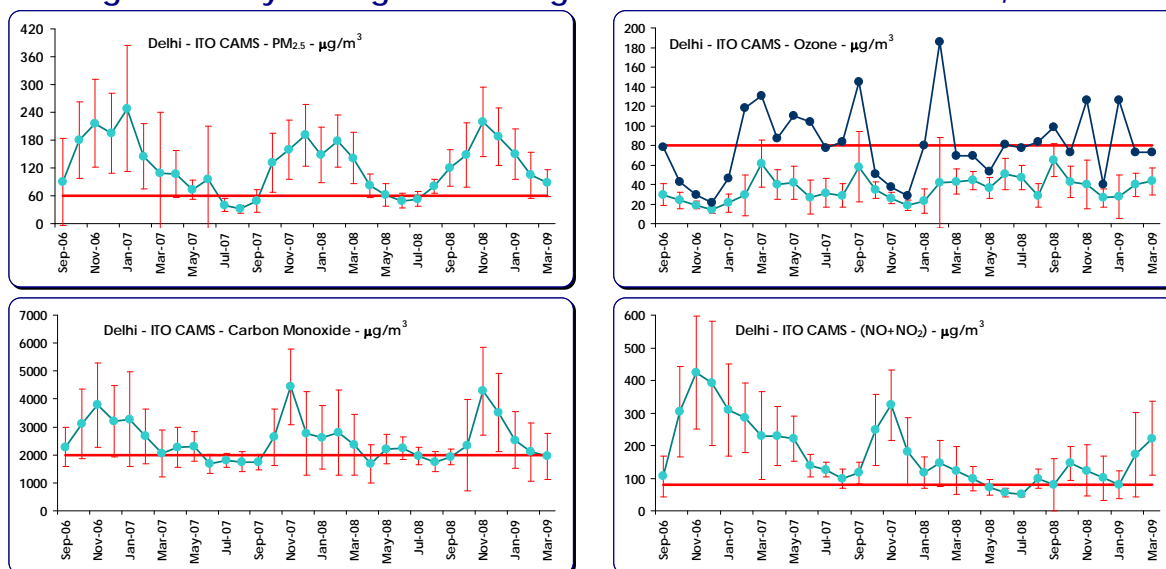
INDOEX, 1999, “Indian Ocean Experiment” @ <http://www.ucar.edu/communications/staffnotes/9904/INDOEX.html>

See **Annex 1** for further references

Air Pollution Monitoring and Trends Analysis

The ITO monitoring station is located along a major transport corridor connecting the east side of the River. This site not only captures the signals from the transport sector, but also the industrial emissions from the East, primarily from the Ghaziabad industrial sectors. **Figure 3** presents the measured 24 hr averages per month for the period of September'06 to March'09, along with standard deviation of the measured daily averages at the site. The continuous monitoring station (illustrated in the **Figure 2**) uses US EPA certified analyzers for monitoring PM₁₀, PM_{2.5}, CO, SO₂, NO_x, Ozone, Benzene – Toluene – Xylene (BTX) and a host of meteorological parameters.

Figure 3: Daily average monitoring data at the ITO station in Delhi, India¹²



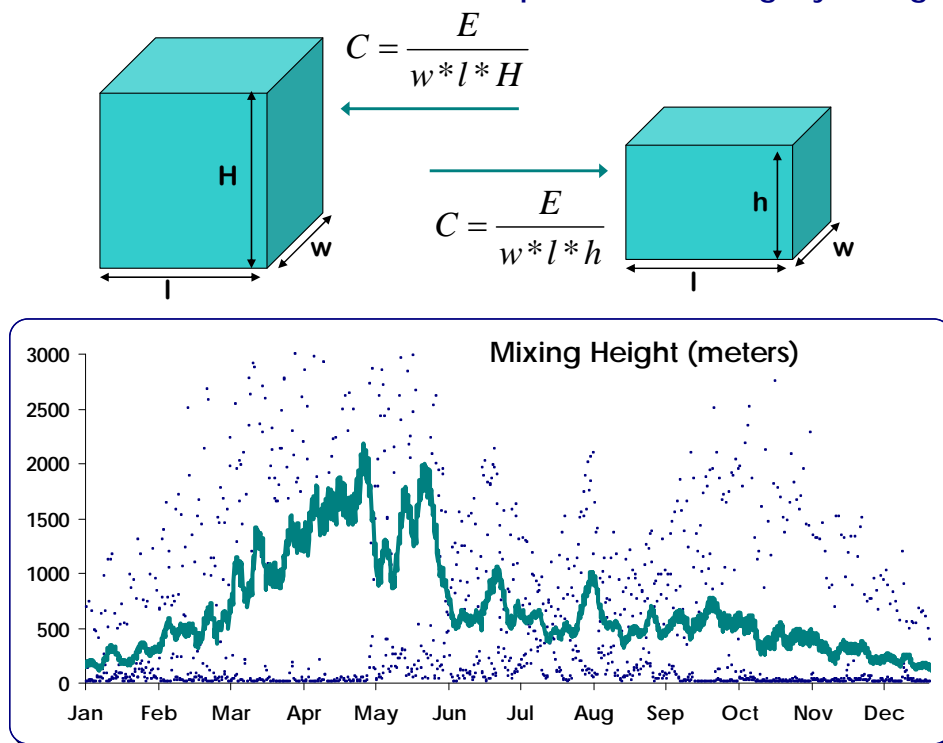
The pollutants of interest are PM_{2.5}, NO_x, BTX (not presented), and CO, all responsible for the production and destruction of ozone. All the criteria pollutants exceed the daily standards presented in **Table 1** and the pollution levels are particularly worse in the winter months for PM and CO.

As expected, the monitoring data confirms the pronounced seasonal peaks coinciding with lower mixing heights of the winter months (**Figure 4**). The measured PM pollution in the winter is at least double the concentrations measured during the rest of the seasons. Similar patterns were observed for the CO and NO_x pollution. Mathematically, represented in **Figure 4**, in the winter months, for the same amount of emissions, the ambient concentrations are higher due to the lower mixing layer heights. However, the emission sources for PM and CO are also diverse in the winter months, due to an increase in the biomass burning for heating purposes.

¹² Data is collected for the period of 2006-09 for the ITO station, from the CPCB, India, which operates a continuous air monitoring station, covering a range of pollutants, including meteorology @ <http://164.100.43.188/cpcbnew/movie.html>

The ozone concentrations (**Figure 3, top right**), on an average, are lower than the proposed limits, but the frequency of exceedances for 1 hour and 8 hour standards is increasing (Report by CSE, India). The graph also presents the observed daily maxima for each month (solid dark line), whose frequency of exceeding the standard is higher in 2008-09. Besides the diurnal and the seasonal cycles of ozone pollution, the variations are influenced by multiple parameters, including the photochemistry which is interlinked decidedly interlinked with the local emission characteristics.

Figure 4: Box model illustration of the impact of the mixing layer height^{13 14}



The diurnal variation of the mixing layer height is also very pronounced in Delhi, which effects the night time concentrations. This is very important for the cities like Delhi, where the diesel operated trucks are allowed to pass through the city only at night, and thus enhancing the night time ambient concentrations. However, since the population exposed to these higher concentrations of PM (mostly diesel soot) and other pollutants is lower during the night time, the impacts of the night time emissions are generally less observed.

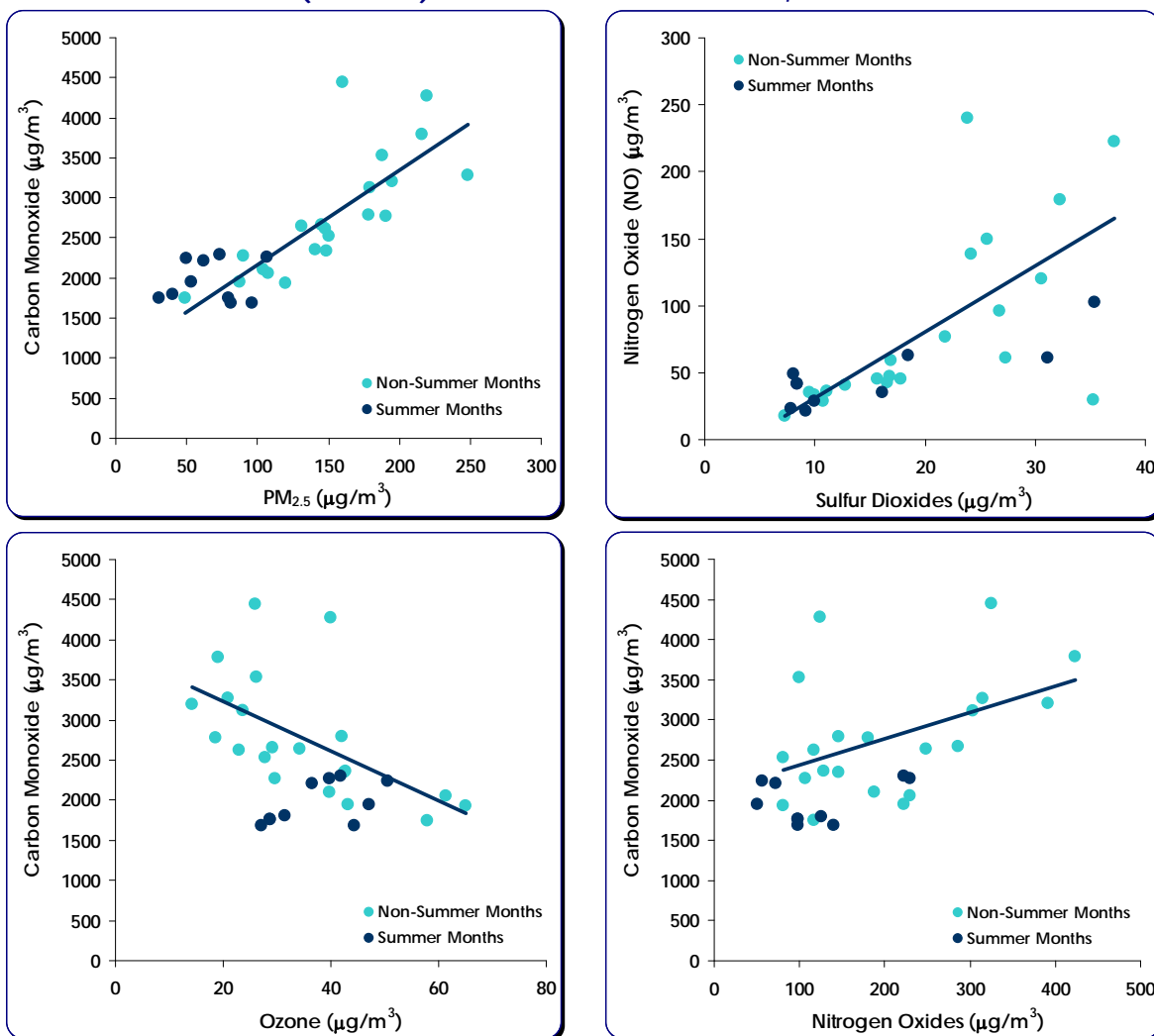
The pollution measured around the ITO station is primary in nature; more linked to the direct emissions and proximity to the sources. This is evident in the correlations between the tracer pollutants like CO, NO, SO₂, and PM_{2.5}. **Figure 5** presents correlations between these key tracer pollutants. Note that the figure indicates measured concentrations and not the

¹³ Key message of this graphical representation is the definition of ambient concentrations, which is mass by volume. For the same emissions, a lower mixing height → higher ambient concentrations. Similar patterns are also evident in the diurnal cycle.

¹⁴ The mixing layer height is compiled from the ECMWF meteorological fields by Mr. Joshua Apte @ University of California, Berkeley. The solid line presents a 15 day moving average.

emissions, and they are only indicative of the sources. The graphs also provide a distinction between the summer (dark dots) and non-summer months, linked to the seasonal differences in the mixing layer heights.

Figure 5: Correlations between criteria pollutants of measured daily averages (2006-09) at the ITO station in Delhi, India



The correlation between the $\text{PM}_{2.5}$ and CO concentrations is an indication of direct emissions, most likely transport and fresh plumes from the industrial areas to the East, given the monitoring station location and the activity levels. The CO concentrations are also sourced to the chemical conversion of VOCs via photochemistry and the fraction of the PM also originates from the chemical conversion of SO_2 and NO_x emissions. The fractional analysis of the secondary contributions is not presented in this paper.

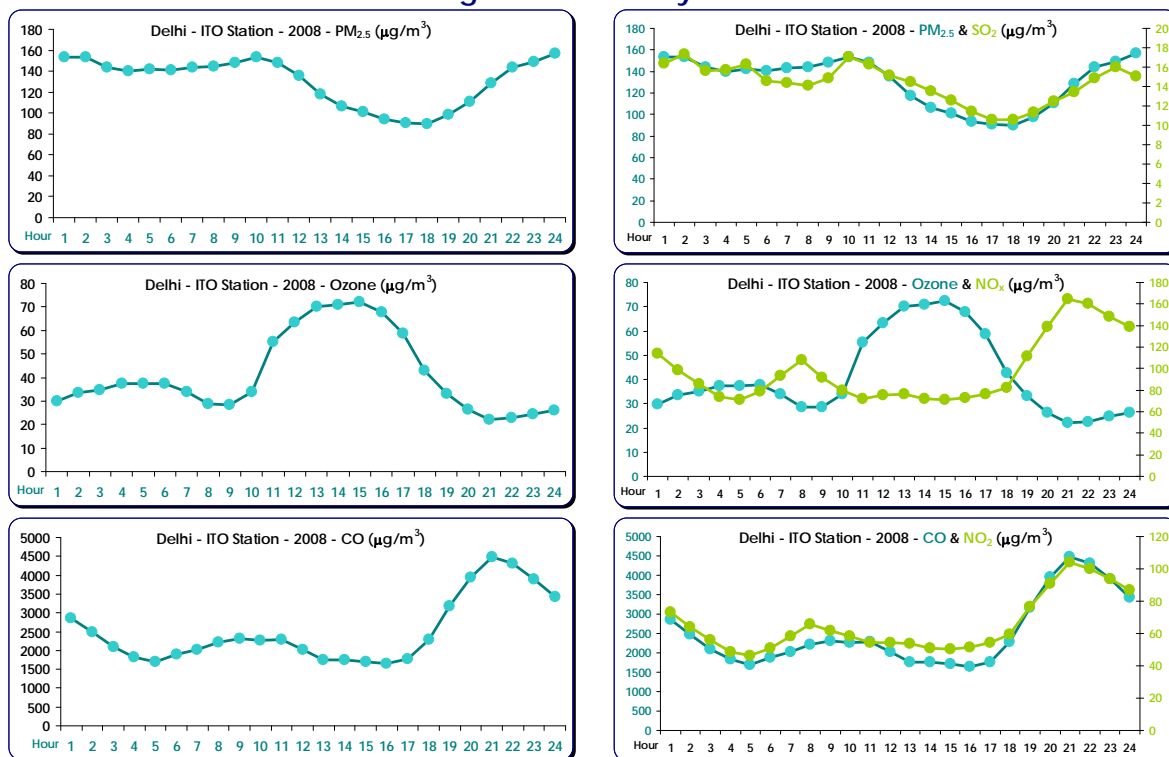
For the NO_x emissions in the transport sector, the nitric oxide (NO) is close to 90 percent of the emissions and readily oxides to nitrogen dioxide (NO_2) in the presence of sunlight. In **Figure 5 (top right)**, again a strong correlation between NO and SO_2 , indicates a direct emission source, which in this case linked to the diesel combustion, from the transportation

sector and possible generator sets in the vicinity. Lower concentrations of NO in the summer months coincide with the faster oxidation to NO₂ in the sunlight. The ozone pollution is higher in the summer months and linked to the presence of VOCs (CO as a proxy in **Figure 5, bottom left**) and the oxidizing capacity of NO_x, details of which are described in the following section.

Diurnal Variations and Urban Photochemistry

In the morning and evening traffic hours, the transport sector is the predominant source of pollution at the ITO monitoring site. **Figure 6** shows typical variation of PM_{2.5}, Ozone, CO, SO₂, NO_x, and NO₂, over a twenty four hour period for the year 2008. The graphs indicate an average of the measured concentrations for each hour over all days in 2008.

Figure 6: Diurnal variation of pollution at the ITO station in Delhi, India, averaged over all days in 2008



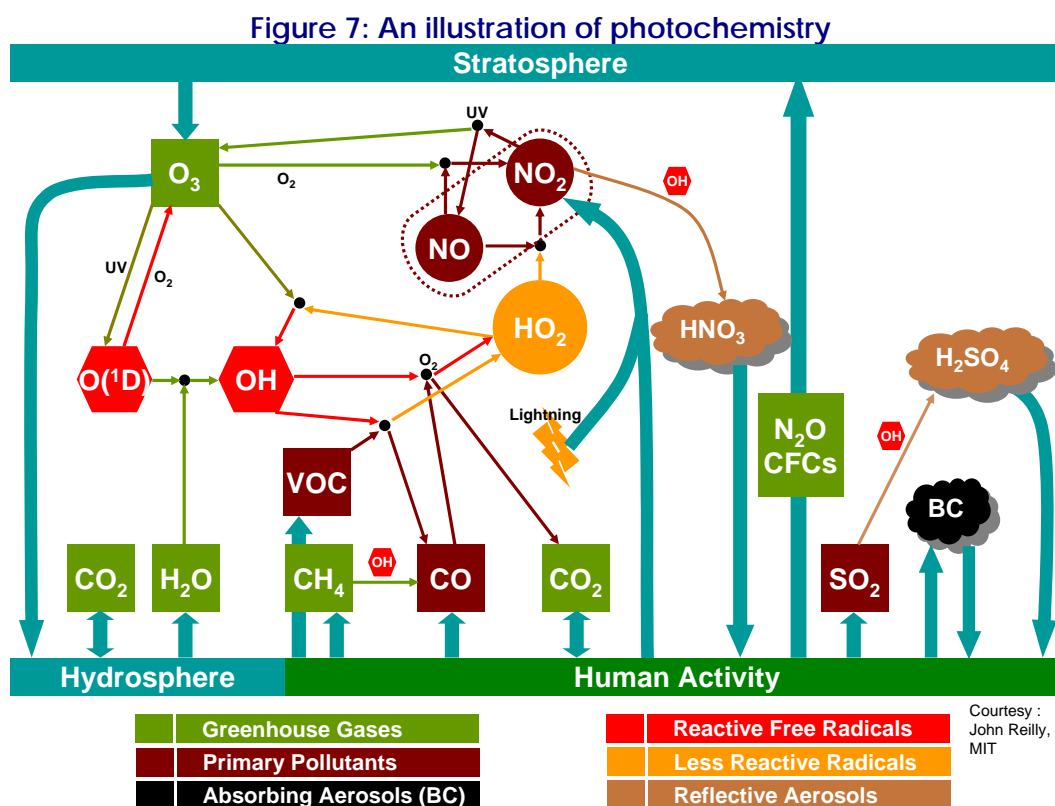
Truck Pollution @ Night

An important observation in **Figure 6, top row**, is the diurnal variation of the PM_{2.5} pollution. Besides the rush hours bumps (8-10 in the morning and 6-9 in the evening) the study increase in the pollution levels is attributed to two reasons – a direct source from trucks, which are allowed to pass through the city after 9 PM and a change in the mixing layer height. The influence of the truck emissions is more evident in the direct correlation of the PM_{2.5} cycle with the SO₂ concentrations, possibly originating from the diesel combustion in trucks.

While the passenger travel in the city has grown over the last decade¹⁵, the importance of the freight transport (via trucks) in the night should not be neglected, since the high concentrations observed during the night tend to linger during the rush hours (mixed with the passenger travel) and beyond (through ~11 AM) and hence increasing the exposure times and related health concerns along the major corridor.

Ozone-CO-NO_x Photochemistry

Ozone is called the "photochemical oxidant." The *photo* part refers to the fact that the energy of sunlight is required for ozone production, and the *chemical* part refers to the fact that chemical reactions are involved. *Oxidant* is included because ozone is an oxidant, chemically. Hence an enhanced formation of ozone observed at the sunrise, sustained production through the day, and destruction following the sunset (**Figure 6, middle left**). Ozone is produced in a cycle of reactions involving two basic pollutants NO_x and VOCs, however the photochemical process is interlinked and complex (**Figure 7**).



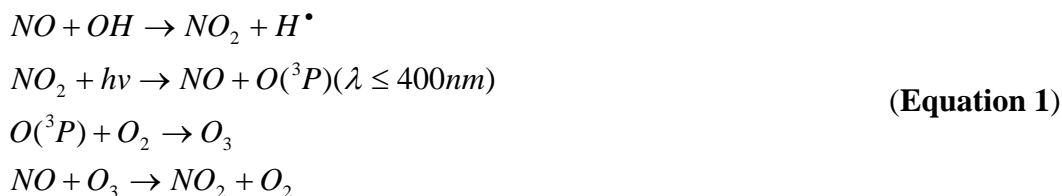
In **Figure 6**, following the increase in the emissions of NO_x and CO during rush hour, Ozone concentrations have built up rapidly after sunrise, and immediately followed by reduction in NO_x and CO concentration owing to oxidation by the Ozone and other hydroxyl radicals. In the evening, a reverse phenomenon is observed where the photochemical activity reduces at sunset, increasing the CO and NO_x concentrations owing to less

¹⁵ SIM-24-2009, "Motorized Passenger Travel in Urban India: Emissions & Co-Benefits Analysis" @ <http://urbanemissions.info/simair/simseries.html>

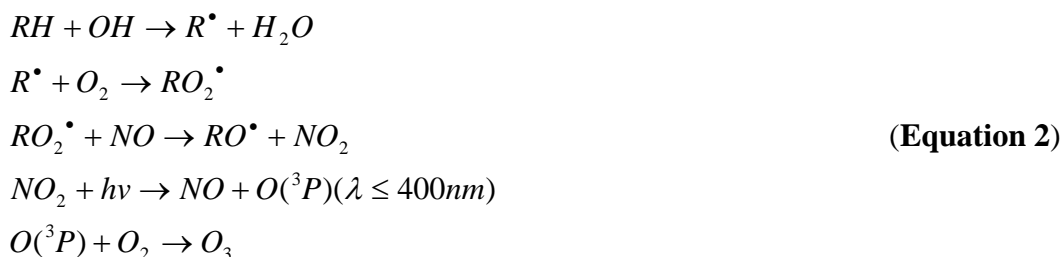
Ozone for initiation of oxidation process and an increase in the emissions from the diesel trucks.

Although the urban photochemistry is well documented¹⁶, some of the aspects of chemistry that relate to ozone sensitivity and indicator species is worth summarizing.

The conversion of NO to NO₂ (via an oxidizing agent) and NO₂ to NO (via *photodissociation*) results in the production or destruction of ozone and formation of the intermediates O(³P) (ground state oxygen atoms) as represented in **Equation 1**. In the following equations, intermediate radicals are indicated with a closed dot next to each species.



However, in the presence of the hydrocarbons, the NO+O₃ reaction in **Equation 1** becomes less important in removing the ozone produced, since much of the NO is oxidized to NO₂ by hydrocarbons rather than by ozone; the hydrocarbons compete with ozone for the NO.



¹⁶ A number of chemical mechanisms were established at varying degrees of complexities and well studied by the “chemical transport modeling community”. These mechanisms cover a wide range of species – direct and indirect, radicals, photolysis schemes, and some even include gas-aerosol interactions in multiple size bins to support the extensive chemical analysis. Commonly utilized chemical schemes include

1. Statewide Air Pollution Research Center (SAPRC) chemical mechanism @

<http://www.engr.ucr.edu/~carter/pubs/#reports>

2. Regional Atmospheric Chemistry Mechanism (RACM) @

<http://www.agu.org/pubs/crossref/1997/97JD00849.shtml>

3. Carbon Bond IV Mechanism (CBM IV) @

<http://www.epa.gov/scram001/photochemicalindex.htm>

<http://www.ccl.rutgers.edu/~ssi/thesis/thesis-node57.html>

Also see

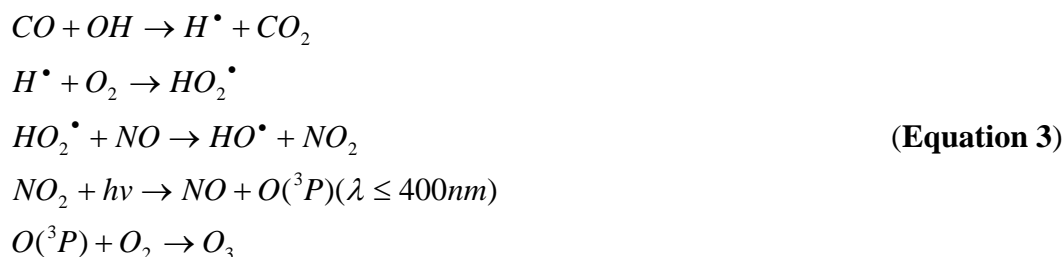
“Fundamentals of Atmospheric Modeling” by Dr. Mark Jacobson, Stanford University @

<http://www.stanford.edu/group/efmh/FAMbook2dEd/index.html>

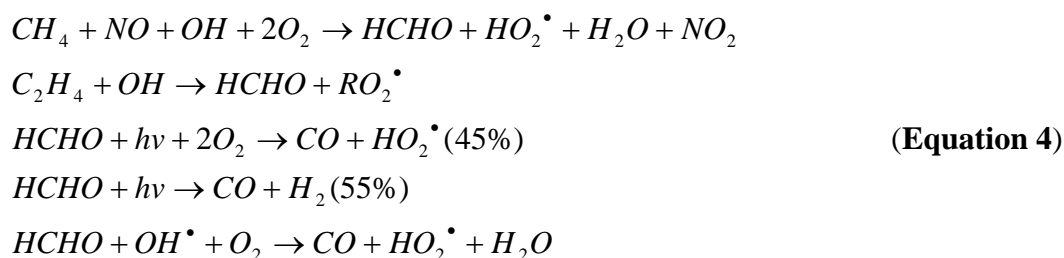
“Atmospheric Chemistry & Physics” by Dr. Sienfeld and Dr. Pandis @

<http://www.amazon.com/Atmospheric-Chemistry-Physics-Pollution-Climate/dp/0471178160>

In polluted environments, as measured in the case of Delhi, CO also contributes to ozone production via reaction with OH radicals and subsequently with NO.

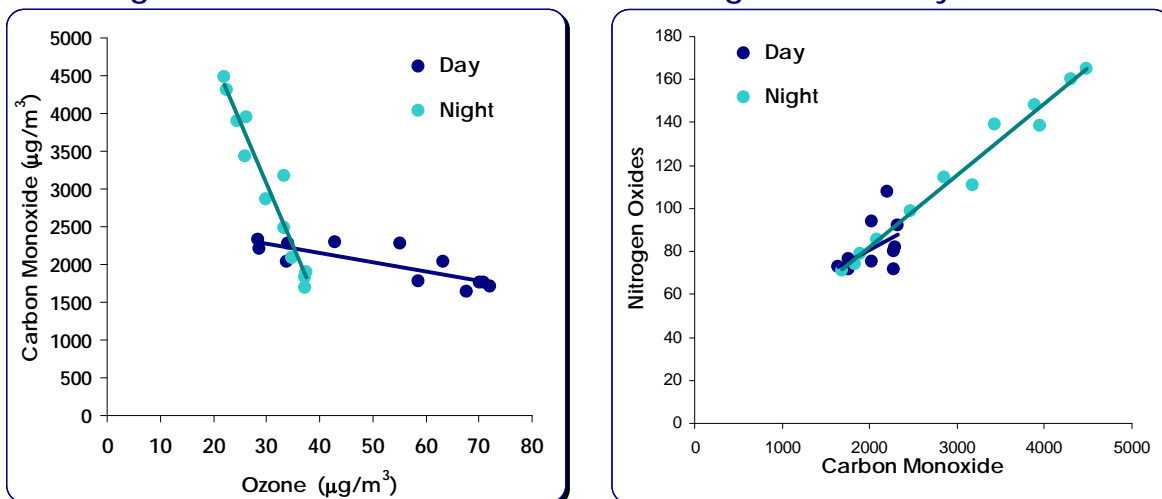


Besides, anthropogenic and biomass CO, CO is also generated during the chemical conversion of hydrocarbons resulting in net production of ozone. Examples of the conversion of methane (CH₄) and ethene (C₂H₄) are illustrated in **Equation 4**.



The formaldehyde (HCHO) is an important intermediate species, which is very short lived undergoing photolysis during the daytime converting to CO, NO₂ and hydrocarbon radicals, which result in net production of ozone. A major source of HCHO in a polluted boundary layer is the chemical conversion of Alkanes (e.g., Methane, Ethane), and Alkenes (e.g., Ethene). Major source of VOCs is the incomplete combustion in the vehicles because of improper maintenance and even adulteration of the fuel, among many reasons. The products of the reaction of hydrocarbons with NO also include other nasty photochemical pollutants such as PAN (peroxyacetyl nitrate), both toxic and irritating.

Figure 8: Correlation between diurnal averages over all days in 2008



However, in an urban environment, in NO_x rich conditions, NO also reacts with ozone producing NO_2 and HNO_3 , determining the steady state called *photostationary state reaction*. At the monitoring site, the constant NO_2 during the day time (**Figure 8, right**) led to a steady state ozone concentration of ~60 ppbv.

At night, with no sunlight, reaction of NO and O_3 is slower, resulting in lesser oxidization of the CO pollution and net destruction of ozone; while the opposite is observed for during the day time (**Figure 8, left**). On the other hand, in an area where VOC (including CO) to NO_x ratio is higher, reaction of RH with OH radicals dominates generating new intermediate radicals and accelerating ozone production. The later scenario is more plausible in an industrial zone with solvent extraction units resulting in higher VOC emissions than NO_x .

Policy Implications

Ozone is a strong oxidant and can lead to respiratory problems in humans, as well as affect plant life. Growing number of vehicles in the city and increasing emissions, the ground level ozone is now entering the health hazard zone along the main activity corridors, which needs further policy interventions. However, in an urban environment, besides the Ozone and CO, the particulates (PM) still remain the primary concern.

In the city, the night time concentration of PM is a growing concern; the night-time concentrations particularly in the winter and spring seasons are approximately twice the day time levels. All the heavy duty trucks are diesel based with an average age of at least 5 years. Also, the lower mixing heights and poor ventilation in the night, prevents proper dispersion of these pollutants, causing this buildup of pollutants. At the sunrise, the buildup of the pollutants is felt among the rush hour commuters. The aerosols from diesel combustion, such as the black carbon and organic carbon also play a critical role in the formation of ozone, providing the necessary surface for photochemical reactions.

While the ozone pollution is critical for health and needs immediate attention, keeping the chemistry and multi-pollutant interlinkages in sight, it is important that the VOC- NO_x mixing ratios in the vicinity and the linked ozone production-destruction regimes are well understood, before a decision is taken to control either or both the emission sources¹⁷.

The monitoring data indicates that the planners and regulatory agencies will have to look beyond 24 hour and annual averages if public exposure to higher concentrations of PM and ozone is to be avoided.

¹⁷ Guttikunda et al., 2005, "Impacts of Asian megacity emissions on regional air quality during spring 2001" Journal of Geophysical Research @ <http://www.agu.org/pubs/crossref/2005/2004JD004921.shtml>; summarizes the influence of changing emission trends on the ozone production and destruction regimes in Asia

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