Increase in NO\textsubscript{x} Emissions from Indian Thermal Power Plants during 1996–2010: Unit-Based Inventories and Multisatellite Observations

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ABSTRACT: Driven by rapid economic development and growing electricity demand, NO\textsubscript{x} emissions (E) from the power sector in India have increased dramatically since the mid-1990s. In this study, we present the NO\textsubscript{x} emissions from Indian public thermal power plants for the period 1996–2010 using a unit-based methodology and compare the emission estimates with the satellite observations of NO\textsubscript{2} tropospheric vertical column densities (TVCDs) from four space-borne instruments: GOME, SCIAMACHY, OMI, and GOME-2. Results show that NO\textsubscript{2} emissions from Indian power plants increased by at least 70% during 1996–2010. Coal-fired power plants, NO\textsubscript{2} emissions from which are not regulated in India, contribute ~96% to the total power sector emissions, followed by gas-fired (~4%) and oil-fired (<1%) ones. A number of isolated NO\textsubscript{2} hot spots are observed over the power plant areas, and good agreement between NO\textsubscript{2} TVCDs and NO\textsubscript{x} emissions is found for areas dominated by power plant emissions. Average NO\textsubscript{2} TVCDs over power plant areas were continuously increasing during the study period. We find that the ratio of ΔE/E to ΔTVCD/TVCD changed from greater than one to less than one around 2005–2008, implying that a transition of the overall NO\textsubscript{x} chemistry occurred over the power plant areas, which may cause significant impact on the atmospheric environment.

INTRODUCTION

Nitrogen dioxide (NO\textsubscript{2}) and nitric oxide (NO), together known as nitrogen oxides (NO\textsubscript{x}), are two of the most important gaseous species in the atmosphere, and they are emitted from both anthropogenic sources (e.g., fossil-fuel combustion and human-induced biomass burning) and natural sources (e.g., wildfires, soil release, lightning, ammonia oxidation). NO\textsubscript{2} plays a crucial role in the formation of ozone and secondary aerosol and is involved in the chemical transformation of other atmospheric species (e.g., CO, CH\textsubscript{x}, VOCs) through feedback on HO\textsubscript{2} (OH + HO\textsubscript{2}). Consequently, NO\textsubscript{x} can have broader effects on human health, atmospheric composition, acid deposition, air/water quality, visibility, radiative forcing, etc. As the second largest NO\textsubscript{x} emitting country in Asia (~16% of total Asian emissions\textsuperscript{3–5}), India is of increasing concern. Thermal power plants are the most important point sources in India, accounting for more than 30% of the national NO\textsubscript{x} emissions (transportation, industry, and other sectors contribute ~35%, ~20%, and ~15%, respectively).\textsuperscript{6} Due to the rapid economic development, the growing electricity demand, and the absence (or weak enforcement) of regulations, NO\textsubscript{x} emissions in the Indian power sector have been reported to increase at a remarkable rate since the mid-1990s.\textsuperscript{1–3,6} Although some previous studies have reported NO\textsubscript{x} emissions from Indian power plants,\textsuperscript{1–7} they have various shortcomings. First, none of them present year-by-year trends with up-to-date activity rates, especially for the period after 2000. Second, NO\textsubscript{x} emission factors are strongly dependent on combustion conditions, fuel quality, boiler size, and NO\textsubscript{x} control technology; however, previous studies simply treated all power plants as one single sector (or subsectors by fuel type) and applied default NO\textsubscript{x} emission factors prescribed by the IPCC.\textsuperscript{7} Third, few of them used activity rates at the plant or unit level but instead at the country or state level, which cannot yield spatially accurate emissions. To overcome these disadvantages, we use a unit-based methodology to develop new NO\textsubscript{x} emission inventories for Indian power plants.

Due to the short lifetime of NO\textsubscript{x} in the atmosphere, satellite NO\textsubscript{2} observations are closely correlated to the land surface NO\textsubscript{x} emissions.\textsuperscript{9–11} In the past few years, tropospheric NO\textsubscript{2} columns retrieved from satellites have been successfully applied to monitor and quantify the spatial distribution (local to global),\textsuperscript{9,10,12,13} temporal variation (diurnal to seasonal),\textsuperscript{14–18} and interannual trends\textsuperscript{11,19,20} of NO\textsubscript{x} emissions from both anthropogenic and natural sources. Especially, because of their high spatial resolution, the new generation of instruments (e.g., SCIAMACHY and OMI) have proved to be able to identify and constrain NO\textsubscript{x} emissions from large point sources (LPS).
such as thermal power plants.\textsuperscript{9,12–14} However, there have been very few applications of satellite retrievals to India using NO\textsubscript{2} retrievals from GOME, SCIAMACHY, and OMI. However, they only gave a qualitative or semiquantitative analysis of the relationship between NO\textsubscript{2} emissions and satellite retrievals over NO\textsubscript{2} hotspots, partially due to the lack of reliable NO\textsubscript{2} emission inventories for LPS. In this study, we examine the India NO\textsubscript{2} emission trend of thermal power plants during the Indian financial years (FY, from 1 April of one year to 31 March of the next year) 1996–2010 from the viewpoints of both unit-based inventories and multisatellite observations. We compare the satellite NO\textsubscript{2} data with bottom-up NO\textsubscript{2} emission estimates over power plant areas in India. The results are intended to provide a better understanding of the large NO\textsubscript{2} releases from the Indian power sector for recent years. In a more general sense, the results contribute to our ongoing attempts to assess the usefulness of satellite retrievals for quantifying LPS emissions.

\section*{METHODS AND DATA SETS}

\textbf{Unit-Based Methodology for NO\textsubscript{2} Emission Estimation.} A bottom-up, unit-based methodology is used to develop the NO\textsubscript{2} emission inventory for Indian public thermal power plants during FY 1996–2010. Captive (privately owned) power plants and public coal-fired units with capacity smaller than 20 MW are not included due to the lack of detailed data at unit or plant level. In total, information on more than 800 units was compiled, including geographical location, boiler size (capacity), fuel type, electricity generation, specific fuel consumption, the exact time when the unit came into operation and/or retired, etc. Most of the information was derived from a series of the Performance Review of Thermal Power Stations\textsuperscript{24} and various reports published by the Central Electricity Authority (CEA), Ministry of Power of India. Where unit-level information was not available, corresponding plant-level information was used. The exact longitude and latitude of each power plant was obtained from the Global Energy Observatory (http://globalenergyobservatory.org/index.php), and verified through Google Earth. As shown in Figure S1 of the Supporting Information (SI), the electricity generation of thermal power plants in India increased dramatically from 321.9 TWh during FY 1996 to 684.5 TWh during FY 1996–2010, with an annual average growth rate (AAGR) of 5.5%. On average, about 87% of thermal electricity was generated from coal-fired power units, followed by gas-fired (\textasciitilde 12%) and oil-fired (\textasciitilde 1%) ones. Coal-fired units with capacity larger than 200 MW are the main boiler type in India, contributing \textasciitilde 72% to the total thermal electricity generation. Figure S1 also shows the official electricity generation statistics from the Government of India,\textsuperscript{24} the United Nations Statistics Division (http://unstats.un.org/unsd/default.htm), and the International Energy Agency (IEA).\textsuperscript{15} They match reasonably well with the data derived from our unit-based database (differences \textasciitilde \pm 3\%), indicating that the current database covers nearly all public generating units in India.

Total NO\textsubscript{2} emissions ($E_i$, Mg yr\textsuperscript{-1}) from thermal power plants for year $i$ are estimated by the following equation:

\begin{equation}
E_i = \sum_j \sum_k \sum_l \sum_m (G_{j,k} \times SFC_{j,k} \times NCV_j \times EF_{j,l,m} \times 10^{-9}) \times 10^7
\end{equation}

where $j$, $k$, $l$, and $m$ stand for fuel type, generation unit, boiler size, and emission control technology, respectively. $G$ represents the electricity generation (kWh yr\textsuperscript{-1}); $SFC$ represents the specific fuel consumption per unit electricity generation (kg kWh\textsuperscript{-1} for coal- and oil-fired units, and m\textsuperscript{3} kWh\textsuperscript{-1} for gas-fired units); and $NCV$ represents the net calorific value (MJ kg\textsuperscript{-1} for coal- and oil-fired units, and MJ m\textsuperscript{3} for gas-fired units). $EF$ is the NO\textsubscript{2} emission factor (g GJ\textsuperscript{-1}).

NO\textsubscript{2} emission factors of power generating units vary with fuel type, fuel quality, boiler size, and NO\textsubscript{x} control technology.\textsuperscript{15} However, due to the absence of India-specific measurement data, nearly all previous studies\textsuperscript{2–4,6} used default EF values prescribed by the IPCC\textsuperscript{8} to estimate NO\textsubscript{2} emissions from the Indian power sector. In India, more than 95% of the coal-fired boilers are pulverized coal (PC) burning type.\textsuperscript{2,26} In this study, boiler-size-specific and emission-control-specific EFs with PC combustion technology were applied to all coal-fired units (see Table 1), and they were derived from not only the IPCC Emission Factor Database (EFDB),\textsuperscript{27} but also 209 field measurements of Chinese bituminous and lignite coal reported by Zhao et al.\textsuperscript{28,29} (Indian coal is of mostly sub-bituminous rank, followed by bituminous and lignite.) We convert the unit EFs from g kg\textsuperscript{-1} to g GJ\textsuperscript{-1} by Zhao et al.’s EFs from g kg\textsuperscript{-1} to g GJ\textsuperscript{-1} on the basis of NCV supplied in the IEA Energy Statistics\textsuperscript{25} to take into account the difference in coal heating values between the two countries. Currently, NO\textsubscript{2} emissions are not regulated in India for coal-fired power plants. Although some new plants were reported to be equipped with low-NO\textsubscript{x} burners (LNB), the actual installation rate, operation, and performance of LNB devices in India are unknown.\textsuperscript{26} To reflect possible alternative NO\textsubscript{2} emission situations in the Indian power sector during FY 1996–2010, we generate five emission scenarios (Table 1). As used in previous studies,\textsuperscript{2–4,6} we first generate the baseline emission scenario (S1), in which the default IPCC EF of 300 g GJ\textsuperscript{-1} is applied to all coal-fired boilers. In scenarios S2–S4, we assume that no boiler (S2), all boilers with capacity $\geq$300 MW (S3)
(S3), and all boilers with capacity ≥100 MW (S4) are equipped with LNB, respectively. In scenario S5, we utilize the assumption made in the GAINS inventory that no boiler built before 1996 was equipped with LNB, but LNB devices were installed in all new boilers built after 1996. These scenarios are also used to analyze the sensitivities and uncertainties introduced by the LNB assumptions. For gas-fired and oil-fired power plants, India has NOx emission standards varying with the age and size of the unit.30 Taking into account both the standards and the EFs prescribed by the IPCC,8 EFs of gas-fired units are set to be 150 g GJ−1 for units built before June 1, 1999, and 100 g GJ−1, 75 g GJ−1, and 50 g GJ−1 for newly installed units with capacity <100 MW, 100–400 MW, and ≥400 MW, respectively. For naphtha-fired units, EFs are 150 g GJ−1 and 100 g GJ−1 for units commissioned before and after June 1, 1999. We assume an EF of 200 g GJ−1 for all other oil-fired power units.

**Satellite Retrievals of Tropospheric NO2.** To compare with our emission estimates, tropospheric vertical column densities (TVCDs) of NO2 from GOME, SCIAMACHY, OMI, and GOME-2 are used. The combined operation time of these instruments covers the entire period of Indian FY 1996–2010. A comparison of the characteristics of each instrument is shown in Table S1 of the SI. In this work, we used the monthly level-3 products of GOME (TM4NO2A v2.0), SCIAMACHY (TM4NO2A v2.0), OMI (DOMINO v2.0), and GOME-2 (TM4NO2A v2.1) developed at the Royal Netherlands Meteorological Institute (KNMI),31,32 which are available from the Tropospheric Emission Monitoring Internet Service (TEMIS) at www.temis.nl. The retrieval processes are similar for all four instruments. First, NO2 slant columns were retrieved using the differential optical absorption spectroscopy (DOAS) technique; second, TVCDs were derived with the KNMI combined retrieval-assimilation-modeling approach.31,32

### RESULTS AND DISCUSSION

**NOx Emissions of Thermal Power Plants during FY 1996–2010.** Annual trends of NOx emissions from Indian thermal power plants during FY 1996–2010 are shown in Figure 1, and detailed results by fuel type, unit size, and major power plants are provided in Tables S2–S3 of the SI. Although the estimates are different under different scenarios, they all show similar increasing trends. In the baseline scenario S1, NOx emissions increase rapidly by 97% from 1213 Gg in FY 1996 to 2391 Gg in FY 2010, with an AAGR of 5.0%. In other scenarios, the AAGRs are in the range of 3.9% to 5.1%, in agreement with values reported in other inventories (2.8%–6.0%).1–3,6 The dramatic change of NOx emissions can be viewed in the context of a 113% increase of electricity generation, an 84% increase of generating capacity, and a 95% increase of fuel consumption in the thermal power sector during FY 1996–2010, reflecting rapid economic and social development driven by growing fossil-fuel use and relatively lax emission control.33 Coal-fired power plants dominate the total NOx emissions from the power sector (93%–98%), followed by gas-fired (2%–6%) and oil-fired (0–1%) plants. In terms of boiler size, coal-fired units with capacity larger than 200 MW are the main contributors, accounting for ~85% of the NOx emission growth.

A Monte Carlo approach is used to determine the uncertainties of the emission estimates in different scenarios. Unless specified otherwise, the term “uncertainty” in this article refers to a 95% confidence interval (CI) around the central estimate. Input parameters and their corresponding probability distributions were incorporated into a Monte Carlo framework with the Crystal Ball software and 10,000 simulations were performed. For fuel consumption data, we applied normal distributions and assigned uncertainties of 5% and 10% to coal and other fuels. Uncertainties of coal EFs were set to be 15% with normal distribution, on the basis of field measurements of bituminous coal and lignite by Zhao et al.29 Normal distributions with 30% uncertainties were assumed for EFs of other fuels based on the authors’ judgment. LNB-related parameters (e.g., application rate, operation rate, and performance) were not included in the Monte Carlo simulation, since it is not possible to obtain the necessary information. Instead, we examined the sensitivity of the LNB assumptions through different scenarios to analyze uncertainties introduced by them. Results show that due to uncertainties in activity rates and EFs alone, the uncertainties of estimated NOx emissions are between ±11% and 15% under all scenarios (uncertainties of scenarios S2 and S4 are shown in Figure 1). The uncertainties are lower than those reported in the TRACE-P inventory (±21%),2 and mainly attributed to the detailed unit-based methodology and reliable unit-level information gathered in this study. Compared to activity rates and EFs, LNB-related parameters seem to be a more crucial factor that influences the accuracy of NOx emission estimates in India. As shown in Figure 1, the difference between emissions estimated in scenario S2 (no boilers with LNB) and S4 (boiler capacity ≥100 MW with LNB) is ~63%, much higher than the uncertainties introduced by fuel consumption data and EFs.

**Figure 1.** Comparison of NOx emission estimates of Indian thermal power plants.
be approximately proportional to changes in NO$_x$ emissions. This makes it possible to identify the NO$_x$ sources from NO$_2$ column maps. Figure 2a and Figures S2a–S4a show the spatial distribution of average NO$_x$ emissions from India, highlighting thermal power plants and all-month averages of NO$_2$ TVCDs over India from four instruments. A number of satellite NO$_2$ hot spots (especially for OMI, SCIAMACHY, and GOME-2, which have finer footprints) are observed over India, and they match the locations and the amounts of NO$_x$ emissions of thermal power plants reasonably well. This is consistent with the findings of Ghude et al. and Prasad et al., because thermal power plants are the major local NO$_x$ emitters and power plants in India were often built in populated areas where other anthropogenic NO$_x$ emissions (e.g., industrial and vehicular) are also high. Influenced by the South Asia monsoon meteorology, India is largely subject to four seasons: winter (December–February), summer/premonsoon (March–June), monsoon (late June–September), and postmonsoon (October–November). The spatial distributions of average NO$_2$ TVCDs by season for each instrument are shown in Figure 2c–f and Figures S2–S4. NO$_2$ columns are high in winter and low in the monsoon season due to the seasonal variation of NO$_x$ lifetime and the effective wet scavenging during the monsoon season.

Three major factors may impact the comparison between satellite NO$_2$ retrievals and emission estimates: uncertainty in the satellite retrievals, seasonal variation of NO$_x$ lifetime, and incomplete conversion of NO to NO$_2$. These factors are the reasons summertime (June–August) NO$_2$ retrievals were always used in previous studies to quantitatively analyze NO$_x$ emissions in the U.S. and China. The short NO$_x$ lifetime, low snow cover, small solar zenith angle, and strong actinic flux in summer make the retrievals more reliable and the link between emissions and the NO$_2$ columns more direct than in the other seasons in these two countries. However, for India, although the NO$_x$ lifetime is short during the monsoon period, late June to September is the worst period to observe NO$_2$ from satellites (Figure 2c–f and Figures S2–S4). In India, more than 70% of the annual precipitation occurs in the monsoon season. The frequent cloud cover and heavy rainfall results in insufficient satellite observation samples and extremely low NO$_2$ surface concentrations, and makes the satellite retrievals highly uncertain. However, the fact that India is closer to the equator (the latitude is ∼20° lower) than the U.S. and China brings tremendous advantages to India for the use of other months’ NO$_2$ retrievals in the quantitative analysis. First, due to the low latitude, temperature and actinic flux are high in India, resulting in a relatively short lifetime of NO$_x$ all year round. Second, low snow cover and favorable satellite measurement geometry at small solar zenith angle make the NO$_2$ retrievals very reliable. Third, compared to the U.S. and China, the seasonality of temperature, actinic flux, NO$_x$ lifetime, and NO$_2$ retrievals in India is weaker, which means that all-year data can be used in the analysis and the NO$_2$ retrievals’ uncertainties are further reduced. Taking into account all the above factors, we select all nonmonsoon months as our study period for India, in contrast to the summer-only NO$_2$ retrievals used in previous studies of the U.S. and China.
favorable condition for quantitative analysis in India is that area NO\textsubscript{x} emissions are smaller and individual NO\textsubscript{x} sources and NO\textsubscript{2} hotspots are more isolated and discernible all over the country (except for the region around Delhi) in contrast to the dense regional NO\textsubscript{2} plumes over the northeastern U.S. and eastern central China.

To compare the NO\textsubscript{x} emissions from thermal power plants with NO\textsubscript{2} TVCDs of different instruments, 81 power plant areas were defined in this study (Figure 2b). Typically, the size of an area with a single plant is 0.625° × 0.625°. We combined the adjacent plants and adjusted the boundaries of the areas based on the shapes of NO\textsubscript{2} plumes with the intent of capturing the major satellite signals over all thermal power plants and excluding signals from nearby sources. The smallest study area is close to or larger than one pixel of SCIAMACHY, GOME-2, and OMI, but smaller than one pixel of GOME in the across-track direction (~320 km). This implies that GOME may be insufficient to detect the power-plant signals, and GOME results may contain larger uncertainties than the other instruments. However, since GOME is the only instrument covering the period 1996−2002, we still include it in the analysis.

For power plant area \textit{n}, we define the NO\textsubscript{x} TVCD attributed to emissions from thermal power plants (TVCD\textsubscript{power}) as

\[
\text{TVCD}_{\text{power},n} = f_{\text{power},n} \times \text{TVCD}_{\text{total},n}
\]

where TVCD\textsubscript{total,}\textit{n} is the TVCD averaged over area \textit{n}, and \textit{f}_{\text{power,n}} is the proportion of power plants’ emissions (\textit{E}_{\text{power,n}}) to total NO\textsubscript{x} emissions (\textit{E}_{\text{total,n}}) in area \textit{n}. In this study, gridded emissions of other anthropogenic sources were taken from EDGAR4.2\textsuperscript{1} for the year 2005 and scaled to 1996−2010 based on the GAINS inventory.\textsuperscript{2} Emissions from natural sources were also derived from EDGAR4.2 for 2005, but kept constant throughout the years 1996−2010. Lightning emissions are not included in total emissions, because they are negligible compared to anthropogenic emissions and they are intensive in the monsoon season, which is excluded from this analysis.

Figure 3 presents the scatter plots of annual \textit{E}_{\text{power}} (based on baseline scenario S1) against annual (corresponding to Indian FY, excluding monsoon period) average TVCD\textsubscript{total} (top) and TVCD\textsubscript{power} (middle) over power plant areas for four NO\textsubscript{2} instruments. \textit{R}\textsuperscript{2} is the square of the linear correlation coefficient between NO\textsubscript{x} emissions and TVCDs. (bottom) Relationship between \textit{R}\textsuperscript{2} and the proportion of power plants’ emissions to total NO\textsubscript{x} emissions (\textit{f}_{\text{power}}). Error bars express the ranges of \textit{R}\textsuperscript{2} in each 0.1 interval of \textit{f}_{\text{power}}. Data points are arbitrarily fitted by quadratic polynomials, and the goodness of fit is shown as \textit{r}\textsuperscript{2}.

\[
\text{TVCD}_{\text{power},n} = f_{\text{power},n} \times \text{TVCD}_{\text{total},n}
\]

\[
\text{TVCD}_{\text{power},n} = \frac{E_{\text{power,n}}}{E_{\text{total,n}}} \times \text{TVCD}_{\text{total},n}
\]

\[
(2)
\]

development
implying that the treatment of TVCD using eq 2 is reasonable. Among the four instruments, GOME has the worst performance because of the large pixel size and the relatively low NO\textsubscript{2} emissions before 2003. Positive intercepts are observed in all scatter plots, and they are probably caused by a combined effect of the exclusion or underestimation of NO\textsubscript{2} emissions from sources other than power plants, the import of NO\textsubscript{2} from nearby areas, and the uncertainties in both satellite retrievals and the emission inventory. The correlations are even better for areas dominated by power plant emissions. As shown in Figure 3e–h, \( R^2 \) values are significantly improved to 0.69–0.91 for areas with \( f_{power} > 0.85 \) (≈12 power plant areas). To further explore the relationship between NO\textsubscript{2} columns and NO\textsubscript{2} emissions over power plant areas, we show the variation of \( R^2 \) with \( f_{power} \) in Figure 3i–l. The higher the proportion of power plant emissions to total NO\textsubscript{2} emissions, the better the agreement between NO\textsubscript{2} columns and NO\textsubscript{2} emissions. This is consistent with previous modeling results of NO\textsubscript{2} columns over power plant areas in the western U.S. and China\textsuperscript{13,37} indicating that area emissions (normally allocated using various spatial proxies such as population density and road networks) are not as well understood as power plant emissions.

**Trends of Tropospheric NO\textsubscript{2} over Thermal Power Plant Areas in India during FY 1996–2010.** We calculate the total NO\textsubscript{2} burden (\( B_{total} \)) and NO\textsubscript{2} burden attributed to power plant emissions (\( B_{power} \)) over all Indian power plant areas as

\[
B_{total(or\ power)} = \sum_n (TVCD_{total(or\ power)} \times A_n)
\]  

where \( A_n \) is the surface area of power plant area \( n \). When divided by \( \sum A_n \), \( B_{total(or\ power)} \) can be further converted to an average NO\textsubscript{2} TVCD over all power plant areas. Figure 4 shows the monthly variations and annual evolution of \( B_{total} \) and \( B_{power} \) (as well as the corresponding average NO\textsubscript{2} TVCD) for the four NO\textsubscript{2} instruments during FY 1996–2010. Theoretically, the temporal overlap of operation periods provides the possibility of cross-validation between different instruments; however, due to the differences in the satellite characteristics, measurement time, and retrieval algorithms, a comprehensive cross-validation is problematic and beyond the scope of this study. Here, we only focus on the trends of NO\textsubscript{2} retrievals. As shown in Figure 4, in line with the dramatic increase of NO\textsubscript{2} emissions in the Indian power sector, tropospheric NO\textsubscript{2} increased during FY 1996–2010 with AAGRs of 1.5–3.2\% for \( B_{total} \) and 3.3–5.4\% for \( B_{power} \) depending on the instrument. Although power plants contributed only ∼50\% to the NO\textsubscript{2} burden, they accounted for more than 90\% of the burden increment over power plant areas and dominated the NO\textsubscript{2} burden trends. Figure 4 also lists the correlation coefficients between NO\textsubscript{2} burden and unit-based NO\textsubscript{2} emission estimates for different instruments. The trends of NO\textsubscript{2} burden are in good agreement with the trends of NO\textsubscript{2} emissions from the power sector, especially for \( B_{power} \) (\( R^2 = 0.74–0.98 \)), further confirming the close relationship between NO\textsubscript{2} columns and NO\textsubscript{2} emissions over power plant areas.

The lifetime of NO\textsubscript{2} depends on its own concentration, because reacting with OH is the main sink of NO\textsubscript{2} while OH concentration in the atmosphere depends strongly on NO\textsubscript{2} concentration. Taking into account the nonlinear feedback of NO\textsubscript{2} emissions on NO\textsubscript{2} chemistry, Lamsal et al.\textsuperscript{38} used a dimensionless factor \( \beta \) to establish the relationship between changes in surface NO\textsubscript{2} emissions and changes in NO\textsubscript{2} TVCD:

\[
\beta = \frac{\Delta E_{total}/E_{total}}{\Delta TVCD_{total}/TVCD_{total}}
\]

\( \beta \) tends to be greater than one in clean (low NO\textsubscript{2}) regions, since an increase in NO\textsubscript{2} emissions increases the OH concentration through chemical feedback and thus decreases the NO\textsubscript{2} lifetime. In polluted (high NO\textsubscript{2}) regions, \( \beta \) tends to be less than one, since increased NO\textsubscript{2} emissions consume OH and increase the NO\textsubscript{2} lifetime. In this study, we calculated the \( \beta \) values in different periods for four instruments, and the results are listed in Table 2. Although there are discrepancies in \( \beta \) between different instruments for a certain period, \( \beta \) values decreased from ∼2 to ∼0.7 during FY 1996–2010. This implies that the overall NO\textsubscript{2} chemistry over Indian power plant areas has changed considerably in the past few years due to the dramatic increase in NO\textsubscript{2} emissions from power plants, as well as an increase from transportation since many of the power plants in India are located in the populated places where vehicular emissions are high.\textsuperscript{21,55} It should be noted that the change of VOCs emissions might also affect the NO\textsubscript{2}–VOCs–O\textsubscript{3} chemistry, and further affect \( \beta \). However, increasing the VOCs emissions by 15\% only increases \( \beta \) by 2.8\%,\textsuperscript{56} implying that \( \beta \) values are not sensitive to VOC emissions. Also, based on the GAINS model,\textsuperscript{2} VOC emissions in India increased by only 6.5\% during 2000–2010. Therefore, the overall NO\textsubscript{2} chemistry change over Indian power plant areas is mainly attributed to the dramatic increase of NO\textsubscript{2} emissions. Table 2 shows that the transition took place approximately between...
2005 and 2008, and this can be confirmed by the dependence curve of OH concentration and NO2 lifetime on NO2 TVCD shown in Figure 4, which is derived from a HOx–NOx steady-state model.39 Increasing NO2 at low NO2 condition (β > 1) results in an increase in OH and a decrease in NO2 lifetime, while the situation is opposite at high NO2 condition (β < 1). The transition occurred at a NO2 TVCD of ≈2.7 × 1015 molecules cm−2, exactly falling in the period 2005–2008. This discussion is focused on the overall atmospheric characteristics over all power plant areas. The NOx chemistry of individual areas with high/low NOx emissions could have changed before/after 2005–2008.

Our results clearly demonstrate a very high growth of surface NOx caused by a continuous increase in NOx emissions from power plants in India during 1996–2010. More importantly, the overall NOx chemistry over Indian power plants changed around 2005–2008. Increasing the same proportion of NOx emissions leads to a greater surface NO2 increase now than in the past, implying that NOx pollution in India becomes more and more serious. Undoubtedly, it has led to a change in the tropospheric chemistry relating ozone and aerosol formation and consequently has affected human health, air quality, atmospheric physics, climate forcing, etc. This should be further investigated with atmospheric chemical transport models at local and regional scales. A further implication of both the growth in emissions and the change in NOx chemistry is that regulations on NOx emissions from coal-fired power plants are urgently needed in India, and high-efficiency NOx control technologies (e.g., selective catalytic reduction) are strongly recommended to policy makers.

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### REFERENCES

(1) Emission Database for Global Atmospheric Research (EDGAR) release version 4.2; Joint Research Centre (JRC)/Netherlands Environmental Assessment Agency (PBL); http://edgar.jrc.ec.europa.eu.


(7) Hemispheric Transport of Air Pollution-Emission Database for Global Atmospheric Research (HTAP-EDGAR); http://edgar.jrc.it/eolo/.


### ASSOCIATED CONTENT

#### Supporting Information

1. Electricity generation of thermal power plants (Figure S1);
2. Spatial distribution of power plants NOx emissions and NO2 TVCDs (Figures S2–S4);
3. Relationship between power plants NOx emissions and NO2 TVCDs (Figures S5–S8);
4. Characteristics of four NO2 instruments (Table S1);
5. Detailed results of NOx emissions (Tables S2–S3).

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**Notes**

The authors declare no competing financial interest.

(30) Central Pollution Control Board (CPCB), Government of India; http://www.cpcb.nic.in/Industry_Specific_Standards.php.


