# Chapter 1
# Introduction to NOx Control

Editor's Note:

Chapters 1, 2 and 3 from the 2000 version of APTI 418 have been consolidated into the current Chapter 1. Original text in these three chapters written by Mike Urban, Bob Hall and Douglas Soloman respectively has been edited and I have written some parts.

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September 2009

# Contents

# 1 Introduction to NOx Control

NOx emissions originate almost exclusively from combustion sources and nearly all combustion sources emit NOx. While the constituents of NOx are toxic, the primary reason for NOx regulation is to control ambient ozone concentration. Emission controls usually begin by reducing the amount of NOx formed during combustion followed, if necessary by a control device such as a selective catalytic reduction (SCR) system.

## REGULATION of NOx

### Historic Overview

The regulation of NOX dates back to the State Implementation Plans (SIPs) that were developed in the early 1970s in response to the requirements contained in the Clean Air Act Amendments (CAAA) of 1970. The regulations contained within SIPs were initially designed to attain the National Ambient Air Quality Standard (NAAQS) for nitrogen dioxide and ozone.

The 1970 CAAA also required EPA to establish New Source Performance Standards (NSPS) that specify control requirements for new sources of any criteria pollutant, including NOx. For example, the NSPS for utility boilers in 40 CFR Part 60, Subpart D, that was established in 1970 includes control requirements for NOx. While the older standards are still in place, the control technology on most new (and some existing) facilities is determined on a case by case basis using "best available control technology" or other governing criteria.

Since a number of areas continued to exceed ambient ozone standards, the regulation and control of NOx emissions continue to be active fields.

### PM$_{2.5}$ NAAQS and Regional Haze

The control of NOX will be one of the less important elements in the development of controls of PM2.5. SO2 and VOCs are the main precursors contributing to the formation of these very small particles in the atmosphere. Nitrates, compounds that form from NOX, are one of the minor constituents of PM2.5 and one of the groups of chemicals that are believed to cause adverse health effects. Figure 1-1 shows the constituents that comprise PM2.5 in the eastern half of the United States. Small particles are the primary cause of regional haze, but NO2, which is visible brown gas, also contributes.
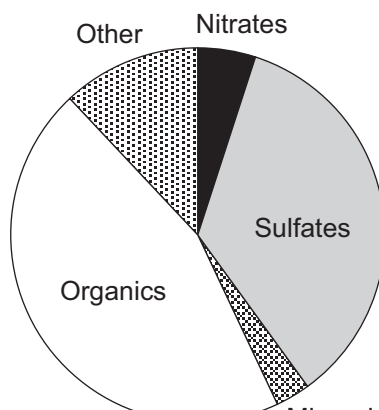
Figure 1-1. Constituents that comprise PM$_{2.5}$ in the eastern half of the U.S.

## Acid Rain

Nitrates that form in the atmosphere from NOx compounds are captured as small particles or as dissolved acid in rain or mist. The nitrates that are deposited in soils can affect the pH of the soils and the uptake of nutrients. NOx contributes to nitrates that reach surface waters such as rivers and lakes increasing the nitrogen content of the water. This nitrification process tends to promote the growth of algae and other organisms that can consume oxygen – effectively suffocating other aquatic life. NOx is a minor contributor to this process compared to fertilizers and agricultural influences

In summary, there are five main issues (NAAQS for NO$_2$, Ozone and PM2.5, Regional Haze, and Acid Rain) that have driving environmental programs toward considerably more stringent NOx control than has been required from past regulatory programs. These regulatory programs related to NOX emissions are discussed in detail in Chapter 2, *NOx Regulatory Programs.*

# OXIDES of NITROGEN

## NOx - Nitric Oxide and Nitrogen Dioxide

NOx by definition is the sum of nitric oxide (NO) and nitrogen dioxide (NO$_2$). Both of these gases are present in the effluent gas streams of most combustion sources. NO is the main form of NOx emitted by traditional combustion sources - 95% or more of the total NOx emissions can be NO as indicated in Figure 1-2. This rule-of-thumb does not apply to many of the newer "low NOx" sources such as turbines and engines with lean pre-mix combustors, where half or more of the NOx may be NO$_2$.
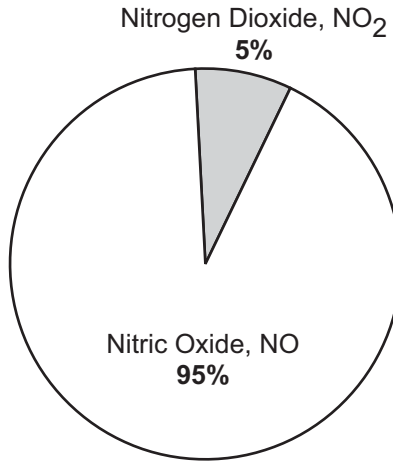
Figure 1-2. Typical NO-NO$_2$ emission ratios from combustion sources

It is important to recognize that NO and NO$_2$ are not independent chemical compounds. Once NOx is emitted to the atmosphere, NO is rapidly oxidized to NO$_2$. Depending on ambient temperature and sunlight, NO reacts in a complex set of photo-chemically initiated reactions to produce NO$_2$ and O$_3$. Figure 1-3 demonstrates the rate and extent of conversion of NO to NO$_2$.
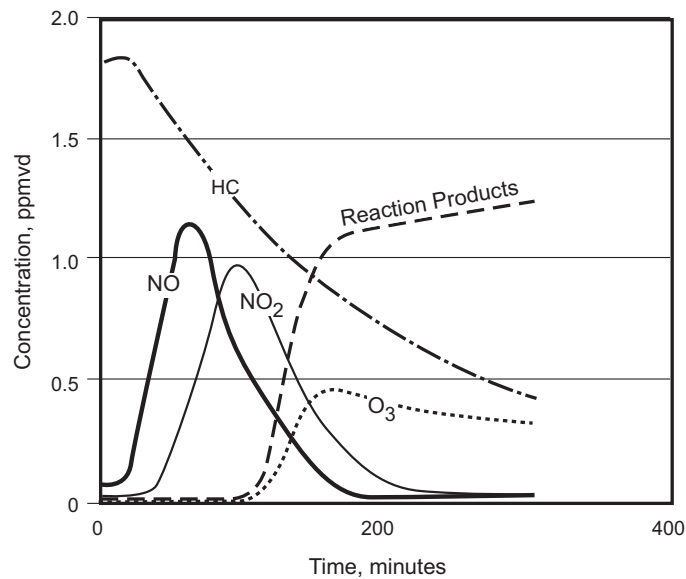


Figure 1-3. Typical photochemical profile

Figure 1-3 shows the conversion of NO emitted mainly from automobiles during morning rush hour. Time expressed in minutes is shown on the x-axis. The concentration of NO, NO$_2$, and ozone are shown on the y-axis. While the presence of

volatile organic compounds (VOC) in sunlight is essential to the photo-chemically initiated conversion of NO to $NO_2$, VOC is nearly always present in ample quantities. Hence regulations to control ozone focus on NOx, rather than on VOC.

The formation of ozone and other photochemical smog constituents increases rapidly as the $NO_2$ concentration peak is reached. Eventually the $NO_2$ reacts further to yield a variety of gas phase and particulate phase smog-related compounds. $NO_X$ emissions from motor vehicles and stationary sources outside metropolitan areas also react in similar photo-chemically initiated reactions. These photo-chemically initiated reactions of $NO_X$ compounds emitted in both urban and rural areas can continue to form ozone over periods of hours to days as air masses travel over multi-state areas.

These reactions contribute to the regional nature of high ozone levels. NO and $NO_2$ emitted from motor vehicles and stationary sources can also react after being absorbed into small water droplets present in the atmosphere as clouds or fog. These reactions further contribute to the regional nature of ozone formation and transport. For these reasons, the total $NO_X$ emissions from a source are calculated on an $NO_2$ basis, as if all the NO converts immediately to $NO_2$. While this is not strictly true from a chemical standpoint, it is a useful regulatory tool to assess total $NO_X$ emissions.

## Dinitrogen Tetroxide

The term $NO_X$ also includes dinitrogen tetroxide ($N_2O_4$). This compound is in constant equilibrium with $NO_2$ as indicated by the chemical reaction shown in Figure 1-4. At high temperatures the $NO_2$ form is favored, while at ambient temperatures most of the $NO_2$ is in the dimer form ($N_2O_4$). Because of this equilibrium condition, $NO_2$ cannot be considered separately from $N_2O_4$. In other words, where $NO_2$ is present, there is also some $N_2O_4$. For this reason, $N_2O_4$ is inherently part of $NO_2$ and isn't regulated separately.

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$$NO_2 \rightleftharpoons N_2O_4$$
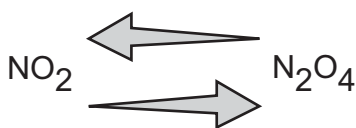
Figure 1-4. Nitrogen dioxide equilibrium with dinitrogen tetroxide

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The properties of $NO_2$ and $N_2O_4$ are very similar. Both compounds readily absorb light in the ultraviolet (UV) range and can, therefore, participate in photochemical reactions that ultimately yield ozone and other compounds. Both $NO_2$ and $N_2O_4$ are moderately soluble in water. They can readily absorb into rain and cloud droplets and ultimately can be absorbed into plants. The primary difference between $NO_2$ and $N_2O_4$ is their color. $NO_2$ is colorless and $N_2O_4$ has a reddish brown color often associated with photochemical smog. This plume is sometimes visible above combustion sources with high NOx emission levels.

NO is the main form of $NO_X$ emitted from fossil fuel-fired boilers and combustion sources without emission controls. Low $NO_x$ sources, with emissions less than 10 ppm may have half or more of their emissions in the form of $NO_2$. Nitric oxide (NO) has entirely different chemical and physical properties than $NO_2$ and $N_2O_4$. NO is colorless, insoluble and does not absorb UV light. Therefore, NO cannot initiate photochemical reactions. However, NO is a very reactive compound in the atmosphere and oxidizes immediately to $NO_2$ if there is any ozone present.

## Nitrous Oxide

NO, $NO_2$, and $N_2O_4$ are not the only oxidized forms of nitrogen in the ambient air. Small quantities of nitrous oxide ($N_2O$) can be emitted from both *anthropogenic* (man-made) and natural sources. $N_2O$ that reaches the stratosphere can cause depletion of the protective ozone layer. It is one of the six principal greenhouse gases.

Sometimes called *laughing gas*, $N_2O$ is not a constituent of $NO_X$. $N_2O$ is slightly soluble in water, does not absorb UV light, and is stable in the atmosphere. Therefore $N_2O$ does not participate in photochemical reactions that produce ozone and other compounds.

$N_2O$ is formed in the early stages of combustion rather than by atmospheric reactions involving NO and $NO_2$ emissions. Because of the unstable nature of $N_2O$ at high temperatures, it is rapidly destroyed in the flame zone of combustion, and only small quantities are emitted into the atmosphere. Coal-fired combustion processes have high combustion zone temperatures and, therefore, generally release only a few parts per million (ppm) of $N_2O$. Low temperature combustion processes, such as fluid bed combustors, can release 70 to 200 ppm $N_2O$. Since it is not regulated (yet), there is limited information on its emission from combustion sources.

Selective catalytic reduction (SCR) systems are another possible source of $N_2O$. SCRs are $NO_X$ post-combustion treatment systems that introduce chemicals such as urea or ammonia; $N_2O$ can form as a by-product of these reagents.

Once in the atmosphere, $N_2O$ is very stable with a half-life of more than 100 years. It does not contribute to ozone formation and is not NOx. Most $N_2O$ remains in the atmosphere until it is dissociated in the stratosphere. Upon dissociation, $N_2O$ breaks the chemical oxygen bonds of $O_3$ and reduces the amount of UV-protecting stratospheric ozone. $N_2O$ is classified as a greenhouse gas because it strongly absorbs infrared radiation.

## Nitrous Acid and Nitric Acid

A variety of other oxidized nitrogen compounds form in the atmosphere because of photochemical reactions. These include nitrous acid ($HNO_2$) and nitric acid ($HNO_3$). Neither of these is considered a $NO_X$ compound and they are not emitted in significant quantities from stationary combustion sources. However, these compounds are environmentally important because both can form in the atmosphere, absorb UV light,

and continue photochemical reaction processes. Furthermore, $HNO_3$ can have a detrimental effect on waterways and plants.

$HNO_3$ is directly emitted into the atmosphere in relatively small quantities from nitric acid plants and other types of industrial processes involving the generation or use of nitric acid. Approximately 70% of $HNO_3$ produced is used in the manufacture of ammonium nitrate ($NH_4NO_3$) used in fertilizers.[1]

# NOx FORMATION MECHANISMS

During combustion, three complex chemical reactions form $NO_X$. The most universal of these is *thermal $NO_X$* formation. In thermal $NO_X$ formation, $NO_X$ is formed by the reaction of $N_2$ in the combustion air with combustion reactants such as O and OH radicals. Thermal $NO_X$ is emitted from virtually all combustion sources.

*Fuel $NO_X$* is formed when the nitrogen bound in the fuel is burned. Obviously, the amount of $NO_X$ formed from this mechanism is a function of the amount of nitrogen in the fuel. Coal and residual oil have significant amounts of nitrogen that can generate half or three quarters of the total NOx emissions. Distillate oils such as #2 or diesel oil typically have very little nitrogen. Natural gas has no fuel nitrogen, and therefore no $NO_X$ is formed by this mechanism – all the NOx from a natural gas fired source is thermal NOx.

*Prompt $NO_X$*, the third formation mechanism, forms $NO_X$ by converting molecular nitrogen to NO via intermediate products. This reaction occurs in the early phase in the flame front with hydrocarbons and is observed in laboratory research studies. While prompt NOx may be responsible for some of the NOx from practical combustors, it isn't normally considered when dealing with NOx emissions control

## Thermal NOx

Thermal $NO_X$ is formed from the reaction of nitrogen and oxygen in the combustion air and is highly dependent on temperature. Although oxygen concentration and residence time influence the formation of thermal $NO_X$, temperature is by far the parameter that most influences its formation. Since the thermal $NO_X$ mechanism is relatively slow, the residence time in some types of combustors such as engines and turbines can be a factor in the amount formed.

Figure 1-5 demonstrates the relation of thermal $NO_X$ formation and temperature. This figure shows that the formation of thermal $NO_X$ peaks between 1900ºC and 2000ºC. Because this is the temperature range in which most stationary combustion sources operate, it is easy to understand that thermal $NO_X$ is a primary mechanism by which $NO_X$ is formed in almost all combustion processes. Few combustion sources operate at the extremely high temperature levels where lower NOx formation rates might prevail.
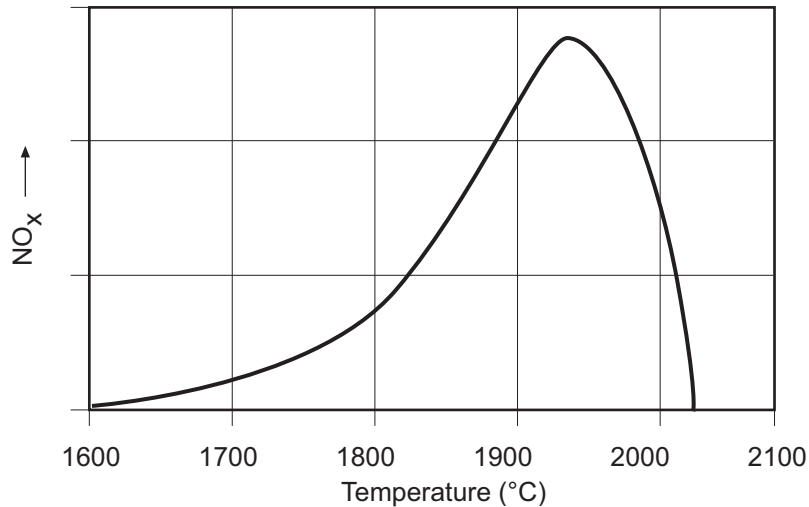
Figure 1-5. Relation of thermal $NO_X$ **formation and temperature**

The overall stiochiometry is shown in global Reaction 1-1.

$$N_2 + O_2 \longleftrightarrow 2NO \qquad\qquad \text{Reaction 1-1}$$

Although Reaction 1-1 provides a simplified summation of thermal $NO_X$ formation, the direct reaction of molecular nitrogen and molecular oxygen is too slow to account for the thermal $NO_X$ mechanism.

In 1946 Zeldovich proposed a reaction mechanism to account for the formation of thermal $NO_X$. Although many reactions are involved, the basic Zeldovich mechanism reactions can be summarized as follows:

$$N_2 + O \longleftrightarrow NO + N \qquad\qquad \text{Reaction 1-2}$$

$$N + O_2 \longleftrightarrow NO + O \qquad\qquad \text{Reaction 1-3}$$

$$N + OH \longleftrightarrow NO + H \qquad\qquad \text{Reaction 1-4}$$

Reactions 1-2, 1-3, and 1-4 are based on the condition that C, H, O, and OH have reached equilibrium for the combustion reactions. Reaction 1-2 is considered the rate-limiting step because of its large activation energy (317 kJ/mol). In near-stoichiometric and fuel-rich combustion zones, Reaction 1-4 becomes the primary source of NO. Thermal $NO_X$ formed by this mechanism is extremely temperature sensitive as shown in Table 1-1.

**Table 1-1**
**Equilibrium Concentrations of NO and $NO_2$ in Air and Flue Gas**

| Temperature (°F) | Air (ppm) | | Flue Gas (ppm) | |
|---|---|---|---|---|
| | NO | $NO_2$ | NO | $NO_2$ |
| 80°F | $3.4 \times 10^{-10}$ | $2.1 \times 10^{-4}$ | $1.1 \times 10^{-10}$ | $3.3 \times 10^{-5}$ |
| 980°F | 2.3 | 0.7 | 0.8 | 0.1 |
| 2060°F | 800 | 5.6 | 250 | 0.9 |
| 2916°F | 6100 | 12 | 2000 | 1.8 |

Note: Calculations are based on the reactions $N_2 + O_2 \leftrightarrow 2NO$ and $NO + 1/2O_2 \leftrightarrow NO_2$ with a gas containing 76% $N_2$ and 3.3% $O_2$.[2]

Table 1-1 is based on theoretical calculations. As stated earlier flue gas $NO_X$ concentrations from traditional combustion sources consist of 90% to 95% NO. The temperature dependence can be attributed to a variety of factors, including the Zeldovich Mechanism. A large amount of energy (941 kJ/mol) is required to break the $N_2$ molecular bond. The rate of formation in Reaction 1-2 only becomes significant at temperatures greater than approximately 2700°F (1500°C).

The vast majority of thermal $NO_X$ is formed in the highest temperature regions of the combustion zone. The global reaction (Reaction 1-1) proceeds rapidly in the forward direction at high temperatures. Once the gas begins to cool, the reaction reverses. The reverse reaction is pre-empted because of the absence of required radicals (C, H, O and OH) and the activation energy. Since Reaction 1-1 is not allowed to proceed in the reverse reaction, the $NO_X$ levels become "frozen,"

The main factors affecting the quantity of $NO_X$ formed by thermal fixation are (1) the flame temperature, (2) the residence time of the combustion gases in the peak temperature zone of the flame and (3) the amount of oxygen present in the peak temperature zone of the flame. (Combustion modifications are discussed in Chapters 4 & 5.) Thermal $NO_X$ reduction is therefore accomplished by various combustion modification techniques that either reduces the peak flame temperature or the oxygen in the primary zone, or both. These methods include: (1) reducing the local oxygen concentration at the peak flame temperature, (2) reducing peak flame temperature, and (3) decreasing the furnace release rate. The theory of this last control method is to increase the radiative heat loss from the flame, which lowers the temperature before equilibrium is reached, so that less NO is formed.

## Fuel $NO_x$

$NO_X$ generated from organically bound nitrogen contained in fuel is termed *fuel $NO_X$*. Organic nitrogen (not $N_2$) in the fuel burns along with the carbon and hydrogen. It either forms $N_2$ or it forms NOx. Although only about 50% or less of the fuel nitrogen converts to NOx, fuel NOx can constitute most of the total NOx emissions from coal or any fuel with a high nitrogen content (excluding $N_2$).

The potential emissions, if all the fuel nitrogen is converted to NOx, can be calculated using conservation of mass. The general formula is:

NOx (lb/mmBtu) = %Fuel N/100 * 46/14 * $10^6$/Fuel HHV

which reduces to: NOx (lb/mmBtu) = %Fuel N / Fuel HHV * 32,900

where: Emissions are expressed in pounds per million Btu (lb/mmBtu)
%Fuel N is the percent nitrogen in the fuel (by weight)
Fuel HHV is the higher heating value of the fuel in Btu/lb
46/14 is the molecular weight of $NO_2$ over the weight of nitrogen

Of course not all the fuel nitrogen is converted to NOx, so this equation gives the maximum possible amount of fuel NOx. In practice coal and residual oil fired boilers are the sources where fuel NOx is the major contributor. U.S. hard coals contain approximately 0.2 wt-% to 3.5 wt-% nitrogen. Anthracite coals constitute the low end, while bituminous coals make up the high end of this range. When crude oil is distilled, nitrogen tends to accumulate in the heavy resins and asphalt fractions that dominate residual oil. In North America, a nitrogen content of above 0.3% is common for heavy residual oils and 0.5% or higher is possible. Natural gas contains no organically bound nitrogen, and therefore does not yield fuel NOx.

How much of the fuel nitrogen coverts to NOx depends on the oxygen levels in the flame. Consequently, the reduction of flame oxygen level is a key element in reducing the emissions that are formed by the fuel NOx mechanism. It is important to note that it is the oxygen level in the flame, not the average oxygen concentration in the combustion chamber that is critical to NOx formation.

The precise mechanism for all fuel NOx formation is not well understood, but the process is divided into two steps - volatile fraction and char combustion mechanisms. are both important in the conversion of coal-bound nitrogen to NOx.

Within the first 300 milliseconds of combustion of pulverized coal, the volatile species containing a portion of the coal-bound nitrogen are vaporized and combusted homogeneously (in the gas phase). During the "devolatilization" of the coal particle, the remaining N in the residual char forms some NOx as the char burns. The possible paths of fuel nitrogen reactions in coal particles are shown in Figure 1-6.
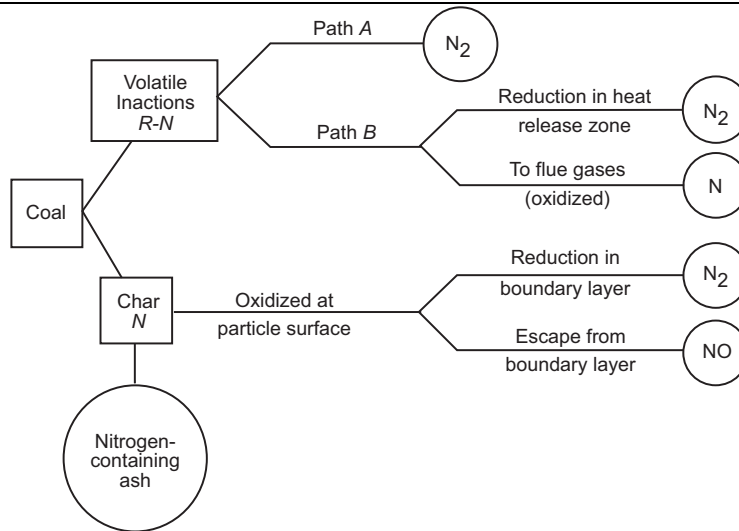
Figure 1-6. Possible paths of fuel nitrogen contained in coal particles during combustion[2]

## Volatile Fraction

The conversion rate of volatile nitrogen to $NO_X$ tends to increase with the combustion zone temperature. In other words, lower temperatures result in a lower amount of fuel nitrogen volatilization. This is one reason why fluidized bed combustors are inherently low $NO_X$ emitters compared to conventional sources. Of course the other reason is that less thermal NOx is formed at low combustion temperatures.

Coal particle devolatilization occurs prior to oxidation in fuel-rich zones when fuel droplets or particles are heated. Gases evolved from burning coal particles form a number of intermediate radicals, such as HCN, N, CN, $NO_X$ and NH. These intermediate radicals are either oxidized to NO or they form $N_2$. The dominant radical for reaction is dependent on the form of the fuel nitrogen in the fuel. Aromatic or cyclic nitrogen is believed to result in the intermediate product hydrogen cyanide (HCN) from the volatile fraction that oxidizes to form NO and $NO_2$. Ammonia has been shown to be the intermediate radical when the fuel nitrogen is in the form of aliphatic amines. The series of reactions involved in fuel $NO_X$ formation is extensive and complex. Presentation of the detailed reactions involved in fuel $NO_X$ mechanisms is beyond the scope of this manual.

## Char Combustion

Char combustion refers to the conversion of nitrogen in the char to either NO or $N_2$ by heterogeneous reactions in the post-combustion zone. The char combustion process is slower than the devolatilization process. Since the char has a little time to cool off, formation of NO is approximately 2.5 times greater for volatile nitrogen combustion compared with char combustion.

Char material formed by devolatilization of fuel particles consists of a mass of pure carbon or incombustible ash. Reactions take place at the surface of the char particle and depends on the rate of oxygen diffusion to the surface.

Figure 1-7 shows the NOx emissions for varying concentrations of nitrogen in the fuel and average oxygen levels in the combustion zone. Data such as this varies from one source to the next depending on the type of coal, burner design and other factors.
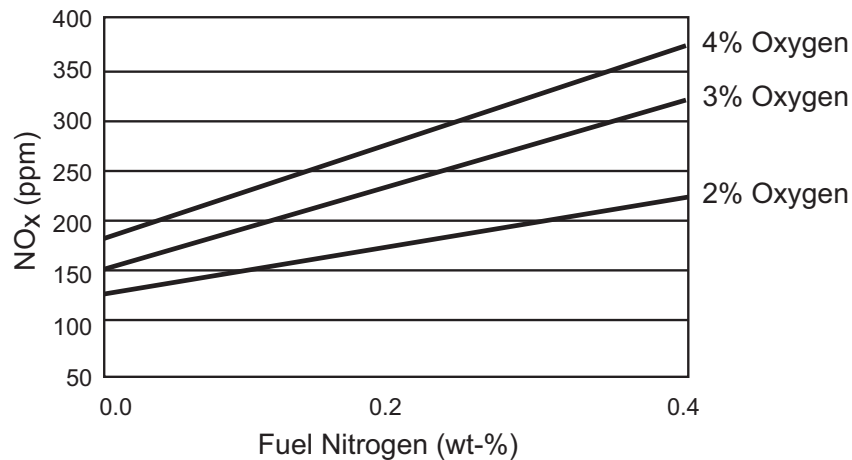


Figure 1-7. Effect of fuel nitrogen on $NO_x$ emissions[2]

The rate of $NO_X$ formation for both fuel and thermal NOx is strongly affected by the local oxygen concentration in the flame and by the mixing rate of the fuel and air. But fuel NOx is not significantly affected by flame temperatures.

One control option for reducing fuel $NO_X$ emissions is to reduce the nitrogen content in the fuel; however, the feasibility of reducing fuel nitrogen depends on the cost and availability of low nitrogen fuel. Therefore, combustion modification techniques (described in detail in Chapters 4 & 5) may be used to reduce $NO_X$ emissions:

- Decrease combustion temperature
- Decrease the $O_2$ in the combustion zone
- Low $NO_X$ burner designs
- Reduce combustion air preheat

# ANTHROPOGENIC SOURCES

Anthropogenic sources include a wide variety of power generation units, industrial manufacturing facilities, motor vehicles, and other transportation sources. The locations of these sources are closely related to population density as indicated in Figure 1-8. The highest concentration of sources in the U.S. is in the northeast, southeast, midwest, and Pacific coastal regions.
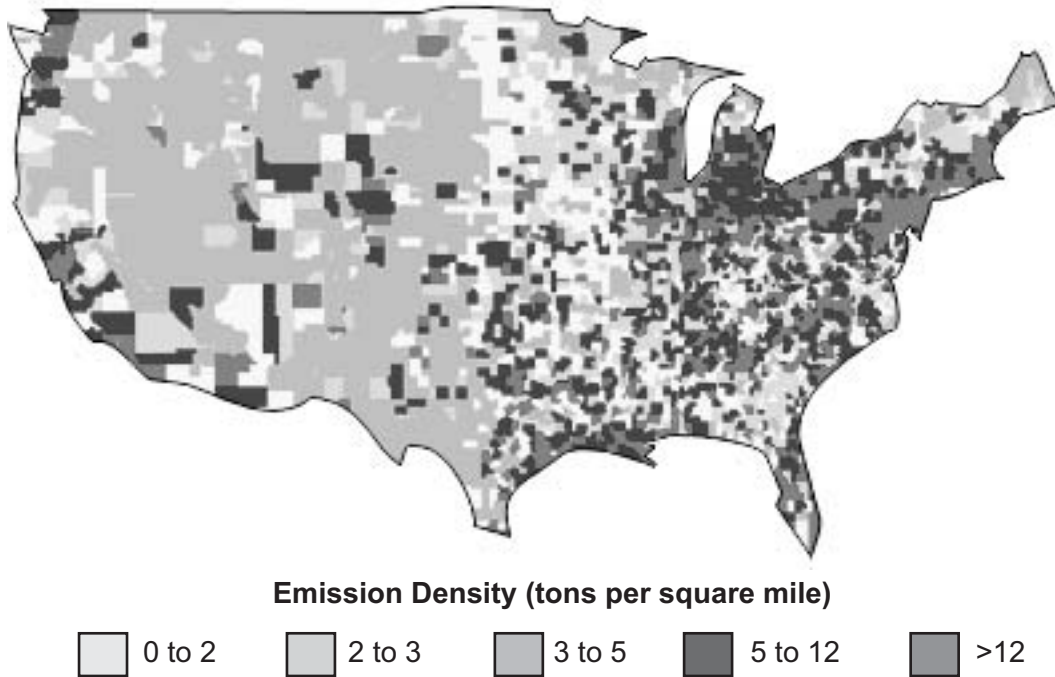


**Emission Density (tons per square mile)**

| 0 to 2 | 2 to 3 | 3 to 5 | 5 to 12 | >12 |

Figure 1-8. Geographic distribution of anthropogenic sources[3]

Anthropogenic $NO_X$ emissions are generated almost exclusively by fuel burning systems. More than 23 million tons of $NO_X$ is emitted into the atmosphere each year as a result of burning fossil fuels.[1] These sources can create local ambient $NO_X$ levels that are ten times greater than those created by natural sources.

Figure 1-9 shows the major sources of anthropogenic $NO_X$ emissions. The leading contributors of anthropogenic $NO_X$ emissions are vehicles and electric generating units (EGUs).
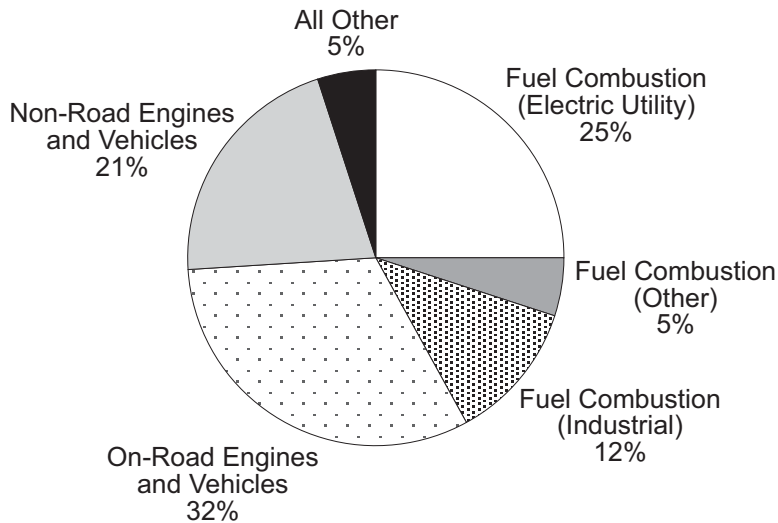
Figure 1-9. Major sources of anthropogenic NO$_x$ emissions[1]

# Electric Generating Units

As indicated in Figure 1-9, the EGU emissions represent approximately 25% of the total U.S. anthropogenic NOx emissions. Electric generating units (EGUs) are defined as combustion sources that produce electricity for sale to a power pool or grid under contract.[4] EGUs are all point sources and are classified as steam generating and non-steam. Steam generating boilers include large stationary coal-, gas-, oil-, and wood-fired electric utility units. Non-steam units include gas turbines and internal combustion engines.

Approximately 6.1 million tons of NO$_X$ (as NO$_2$) was emitted from EGUs in 1998. Approximately 90% of this amount was contributed by coal-fired sources.[2] For the coal-fired EGUs, 65% of NO$_X$ emissions resulted from the burning of bituminous coal, while 30% came from the burning of sub-bituminous coal.[5] The remaining 5% resulted from the burning of anthracite coal and lignite.[2] This source category is the largest emitter of anthropogenic NO$_X$. EGUs are located throughout the U.S.

The data that are contained in the NET comes from a number of data sources. The best source of data is the EPA Acid Rain Division's Emission Tracking System (ETS). As part of the Clean Air Act Amendments of 1990, large combustion sources are required to install continuous emission monitors (CEMs) that continuously record both heat input and emissions data. This CEM data is augmented with data from the Department of Energy. Specifically, utilities are required to report fuel use data using EIA form 767. The fuel use data contained in the EIA 767 report is used to generate emissions data. Data can also come directly from the facilities when the CEM data or the EIA 767 data contain errors. Several emission estimation techniques or algorithms are used to convert the data in the ETS/CEM database to terms of pounds or tons of emissions.

The National Allowance Data Base is another source of $NO_X$ emissions data. Emissions data in this database are mainly generated by using fuel use data and applying standard emission factors to calculate emissions. Emissions data are also generated from stack test data. However, stack test data are available only on an *ad hoc* basis when industrial facilities provide such data. In general, emission estimates from EGUs are generated by a bottom-up technique that uses data at the lowest level of detail and works up to the next level.

# Non-EGU Point Sources

Non-EGU point sources include large sources that can be classified as either non-EGU fuel combustion sources or industrial processes.

## Industrial Fuel Combustion Sources

Industrial fuel combustion sources include numerous small-to-moderate sized boilers used to generate steam and/or electricity for use on site at the facilities. This category also includes cement and lime kilns, industrial furnaces, and other industrial processes using burners for process heat. The dominant fuels used for industrial boilers and industrial furnaces are coal, oil, gas, coke, and wood. Collectively, non-EGU industrial boilers and industrial furnaces are responsible for approximately 12% (3.0 million tons per year) of the U.S. anthropogenic $NO_X$ emissions.[6] Non-EGU industrial boilers and industrial furnaces are located throughout all industrialized areas of the U.S.

## Industrial Processes

Industrial processes are responsible for 5% (0.9 million tons per year) of annual U.S. anthropogenic emissions. [4] This category is comprised of all non-combustion sources of $NO_X$ and related compounds and includes the following:

- Chemical and allied product manufacturing
- Metals processing
- Petroleum refining and related industries
- Solvent utilization
- Storage and transport
- Waste disposal

Facilities that manufacture or use nitric acid are the main contributors of non-combustion $NO_X$ emissions. Nitric acid is produced for the manufacture of fertilizers (ammonium nitrate), synthetic fibers (adipic acid), explosives (nitrobenzene) or use in metal pickling and etching.

In addition to $NO_X$ emissions nitric acid facilities emit small amounts of nitric acid mist  It is an economic benefit for chemical facilities to recover $HNO_3$ so nitric acid emissions from these facilities are typically low.

The available site-specific emissions data for these non-EGU point sources varies according to the location of the facility. For example, data is available for sources emitting as little as 10 tons per year in certain attainment areas. However, in rural and non-attainment areas, data may be available only for sources emitting more than 100 tons per year. Where facility-specific data is not available, the data for these sources will be included in the *stationary area source* category (to be discussed later).

Non-EGU point sources are responsible for 14% of the total anthropogenic $NO_X$ emissions. Forty percent of total $NO_X$ emissions is emitted from major stationary sources (non-EGU and EGU sources), and nearly all of it is generated by combustion processes.

The NET data for non-EGU point sources have a variety of origins. Data is obtained from emission inventories that are developed by state and local agencies using surveys of industrial facilities. This inventory data is then submitted to EPA. In addition, several regional programs and studies have been conducted that involve the collection of emissions inventory data. Some examples include the Ozone Transport Assessment Group (OTAG) study of the eastern two-thirds of the United States and a similar study that was conducted in the western U.S. by the Grand Canyon Visibility Transport Commission (GCVTC).

Another source of emissions data for the NET is the Aerometric Information Retrieval System (AIRS) Facility Subsystem. State air agencies routinely report emissions data to AIRS. Finally, emissions data projected from the National Acid Precipitation Assessment Program (NAPAP) also serve as a source of emissions data for the NET.

Emissions are estimated directly from continuous emissions monitor (CEM) data for some of the large point sources. Stack test data (when available) can also serve as a basis for estimating emissions. Another method for estimating emissions is to conduct a materials balance, although this is not a reliable way to estimate NOx emissions. Most emission estimates for non-EGU point sources are derived using emission factors. Emission factors provide an estimate of emissions based on a specific industrial activity (e.g., amount of $NO_X$ emitted per unit of fuel burned).

## Stationary Area Sources

Stationary area sources are primarily smaller sources that do not meet the size threshold for reporting emissions individually. This group includes smaller industries, commercial/institutional establishments, and residential sources. The category comprises 11% of anthropogenic $NO_X$ emissions. Most of these emissions are associated with "other fuel combustion sources."

"Other fuel combustion sources" includes commercial, institutional, residential and miscellaneous fuel combustion sources. Most of the emissions (90%) are from very small sources. $NO_X$ emissions from this category represent 5% (1.1 million tons per year) of the total U.S. anthropogenic $NO_X$ emissions

It is apparent that residential heating using non-wood fuel (primarily gas and distillate oil) is the dominant $NO_X$ source in this emission category. Commercial/institutional gas heating systems are also major contributors to the $NO_X$ emissions for this source category.

Emissions data in NET for the area source category are obtained through a top-down method. Both demographic and fuel use data are obtained from either the state or national level, and emission factors are applied to generate emission estimates. In addition, EPA has obtained data from some of the regional efforts that were previously discussed (i.e., OTAG, GCVTC, and NAPAP).

Emissions are estimated through a top-down procedure. Emission factors are applied to activity factors at the state level (county level data is used when available) to estimate emissions. In certain urban areas (i.e., urban areas that are non-attainment for ozone) a more detailed emissions inventory may be available and used whenever it is available.

## Non-Road Mobile Sources

Non-road mobile sources include the following:
- Aircraft
- Marine vessels (commercial and recreational)
- Railroads
- Lawn and garden equipment
- Logging and construction equipment
- Industrial engines

This category accounts for 19% of anthropogenic $NO_X$ emission sources.

Based on the 1998 Emissions Trends Report, this category comprises 22% (5.3 million tons annual) of anthropogenic $NO_X$ emission sources. The breakdown of non-road mobile emission sources is shown in Figure 1-10. The pie chart on the left presents the contributions for each of the major types of non-road mobile sources. Most of the non-road mobile source $NO_X$ emissions are from diesel engines. The pie chart on the right presents a further breakdown, showing the types of non-road diesel sources.
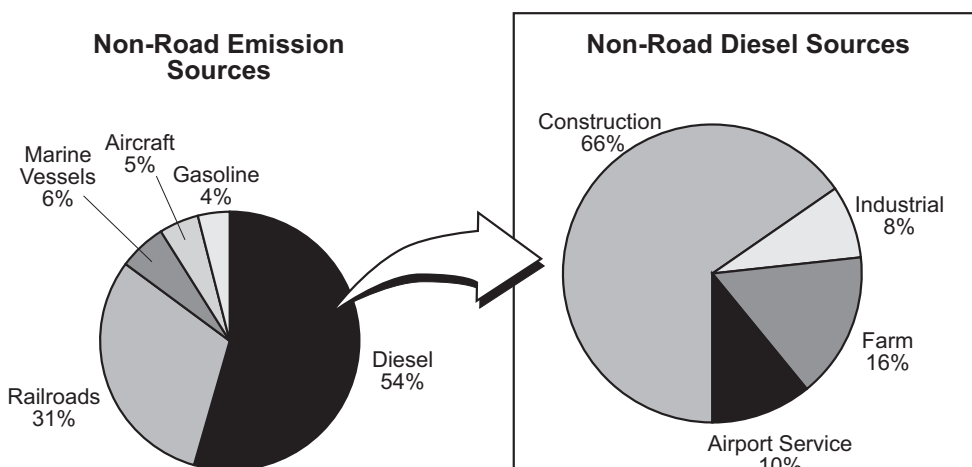
Figure 1-10. Sources of non-road NO$_x$ emissions with detail of diesel source categories[2]

Sources of emissions data for non-road mobile sources in the NET are similar to the sources that are used to obtain emissions data for the stationary source categories. Also similar to stationary sources, the emissions for non-road mobile sources are estimated through a top-down procedure. Bottom-up data is used in those cases where it is available.

EPA's Office of Mobile Sources (OMS) is developing a model that will generate estimates of non-road emissions. This model will allow emissions to be estimated at various geographic levels ranging from a national level to a county level. More information on this model can be obtained from the following website: *www.epa.gov/oms/nonrdmdl.htm*.

As a part of reorganization in January 2000, EPA's Office of Mobile Sources (OMS) was restructured, placed under new leadership, and given a new name: Office of Transportation and Air Quality (OTAQ). OTAQ includes four program divisions and a consolidated laboratory and support services division.

# Highway Mobile Sources

Highway vehicles include passenger cars and trucks, diesel vehicles, pickup trucks and vans, multi-trailer trucks, motorcycles, and sport utility vehicles certified for highway use. Both gasoline- and diesel-fueled vehicles are included in this category which comprises 30% of total U.S. anthropogenic NO$_X$ emissions.

As indicated in Figure 1-9, highway mobile sources are the single largest category of U.S. anthropogenic emissions, representing over 32% (7.8 millions tons annually) of U.S. emissions. [It should be noted that this percentage differs slightly from the other estimates provided in this chapter. This is because the data on the broadcast video is based on 1996 information, and the supplemental information in this manual reflects more recent 1998 data.]
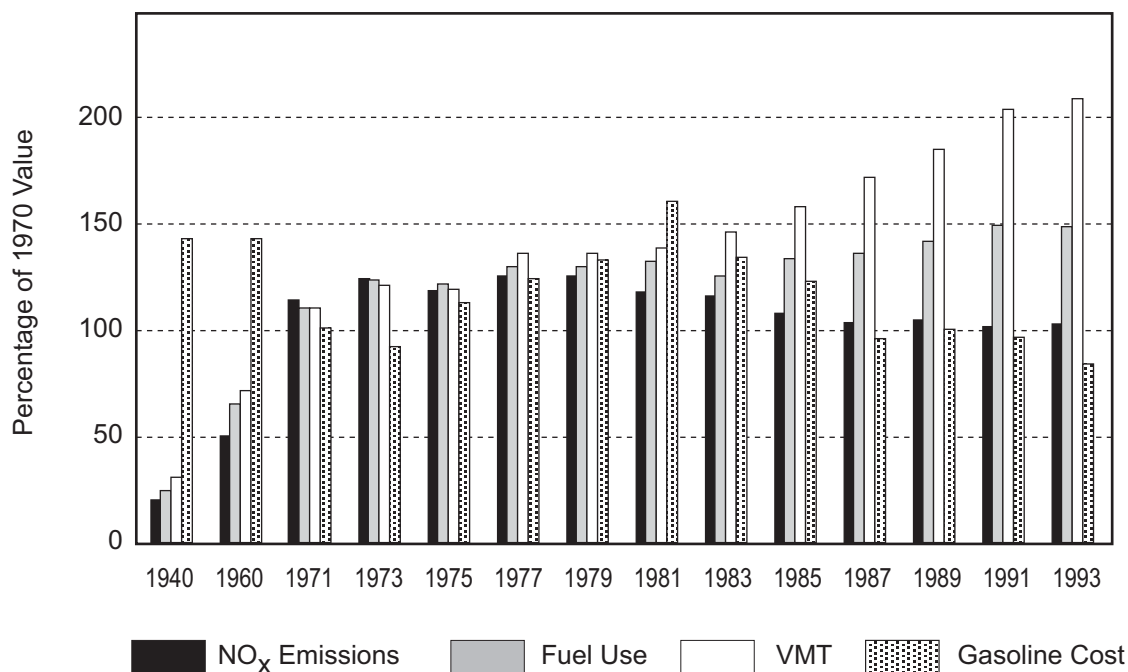
Figure 1-11. Highway mobile NO$_x$ emissions and surrogate indicators[2]

Emissions relative to fuel use, vehicle miles traveled (VMT), and gasoline prices for highway mobile sources are shown in Figure 1-11. It can be seen from the yearly increase of VMT since 1981 that control of mobile source emissions is important in reducing secondary pollutants. The slower increase of fuel use compared to VMT indicates that vehicles built after the 1970s have become increasingly fuel-efficient. After peaking in 1978, NO$_x$ emissions have gradually decreased as a result of lower emissions per quantity of fuel combusted. Reduced emissions are a result of controlling fuel-air mixture, lower nitrogen containing fuels, exhaust gas recirculation, catalysts, and other engine modifications.

An activity enumerator of vehicle miles traveled is used as the basis for estimating emissions for highway mobile sources. VMT is an estimate of the number of miles that individuals are driving. The Federal Highway Administration (FHA) maintains a national database of VMT as part of the Highway Performance Monitoring System (HPMS). EPA uses this database as the source of VMT data for estimating emissions from the highway mobile source category. Emissions are estimated through a top-down procedure using EPA's Office of Mobile Sources MOBILE5b model. OMS is currently developing a MOBILE6 model. Data such as ambient temperature, fuel type, speed information, vehicle type, registration data and control program information (e.g., inspection/maintenance, reformulation) are fed into the model to generate emission factors that can be applied to the VMT data to calculate emissions.

# Miscellaneous Sources

A variety of small combustion sources, small engines, and open burning processes contribute approximately 1% of the total U.S. anthropogenic emissions. Like mobile sources, these sources are classified as *area sources*. Area sources are individual sources that have not been inventoried as specific emission points. Area sources represent a collection of emission points for a specific geographic area, most commonly at the county level.

## Fires

Burning sources include wildfires, prescribed burning, coal refuse fires, agricultural drums, solid waste burning, and structural fires. Emissions from these sources are highly variable and difficult to quantify.

The size, intensity, and frequency of wildfires are dependent on meteorological conditions, types of vegetation, moisture content, and fuel loading. Fuel loading is the amount of combustible material that will be consumed in a fire under specific weather conditions for an area. Wildfires are more prominent in the western U.S., partly due to the higher levels of fuel loading. Estimated fuel loading data and emissions by region are shown in Table 1-2.

**Table 1-2.**
**Estimated Fuel Loading and Emissions for Wildfires by Region[7]**

| Region | Average Fuel Loading (ton/acre) | Total Emissions (ton $NO_X$) |
|---|---|---|
| Rocky Mountain | 37 | 57,300 |
| Pacific | 19 | 44,116 |
| Southern | 9 | 39,162 |
| North Central/Eastern | 11 | 5,119 |
| Eastern | 11 | 2,557 |

Because of numerous variables, estimating emissions is difficult. The topography of the land, along with the availability of fire-fighting personal and equipment, affects the land area burned by wildfires. The wind, ambient temperature, relative humidity, organically bound nitrogen and moisture in the fuel, and compaction of the fuel are all factors that affect $NO_X$ emissions. However, the nitrogen content of the fuel is the most influential factor.[2] Fortunately, burning occurs at relatively low temperatures limiting the $NO_X$ emissions. The formula used by EPA for estimating $NO_X$ emissions resulting from wildfires is given in Equations 1-5 and 1-6.

$$E_{NO_X} = F_{NO_X} A \hspace{4cm} \text{Equation 1-5}$$

$$F_{NO_X} = P_{NO_X} L \qquad\qquad\qquad \text{Equation 1-6}$$

Where:

$E_{NOx}$ = total NO$_X$ emissions (lb NO$_X$)
$F_{NOx}$ = emissions factor (lb NO$_X$ /acre)
A = area of land burned (acres)
$P_{NOx}$= yield for NO$_X$ (4 lb NO$_X$ /ton of forest fuel)
L = fuel loading consumed (ton of forest fuel/acre)

## Problem 1-1

The U.S. Forest Service reports that 7,000 hectares were burned in the southern region during the month of July. Estimate the NO$_X$ emissions (in tons) for this region in July.

From Equation 1-6 and Table 1-2:

$$F_{NO_X} = P_{NO_X} L = \left( \frac{4 \text{ lb NO}_X}{\text{ton of forest fuel}} \right)\left( \frac{9 \text{ tons}}{\text{acre}} \right) = 36 \frac{\text{lb NO}_X}{\text{acre}}$$

From Equation 1-5:

$$E_{NO_X} = F_{NO_X} A$$

$$= \left( \frac{36 \text{ lb NO}_X}{\text{acre}} \right)\left( \frac{\text{ton}}{2000 \text{ lb}} \right)(7,000 \text{ hectares})\left( \frac{2.47 \text{ acres}}{\text{hectare}} \right)$$

$$E_{NO_X} = 310 \text{ tons NO}_X$$

Prescribed burns serve as a means to reduce wildfire occurrences, remove logging debris, limit insect and disease problems, and promote natural new growth cycles. Because prescribed burns limit wildfires, they ultimately help reduce NO$_X$ emissions from open burning.

# NO$_X$ EMISSION TRENDS

The data provided in Table 1-3 provides some perspective in NOx emissions since the beginning of the twentieth century. These trends are due to the dramatically increased motor vehicle use and increased industrial capacity. After 1970, the impact of regulatory programs begins to become apparent. The NO$_X$ emissions have been limited despite a substantial increase in use factors.

**Table 1-3. Percentage Change in National Emissions**

| Year | % |
|---|---|
| 1900 to 1996 | 796 |
| 1940 to 1996 | 217 |
| 1970 to 1996 | 8 |
| 1987 to 1996 | 3 |
| 1990 to 1996 | -2 |
| 1995 to 1996 | -2 |

NO$_X$ emissions in the U.S. from 1940 to 1998 (most recent data available) have been estimated based on emission inventory data and source population data.

Despite some uncertainties regarding the pre-1970 data, it is apparent that the NO$_X$ emissions increased steadily from 1940 to 1970 (Figure 1-14). During this period of rapid industrial growth, the estimated NO$_X$ emissions increased by 300%, from approximately 7 million tons per year in 1940 to more than 21 million tons in 1970.
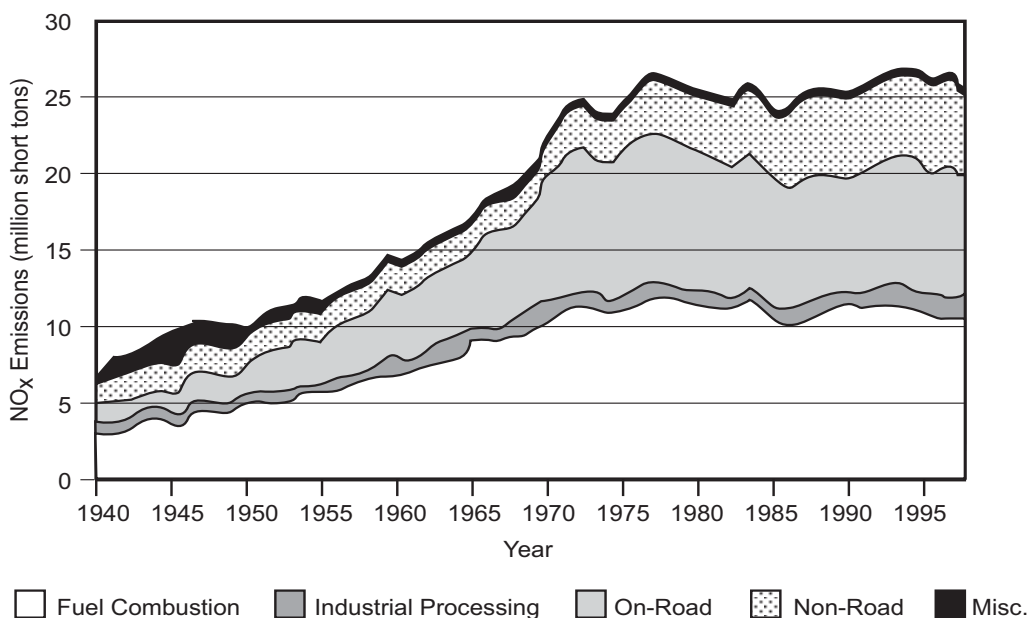


Figure 1-14. NO$_x$ emission trends [1]
(The data in this updated graph is arranged differently than the graph shown on the broadcast video.)

After the enactment of the Clean Air Act Amendments of 1970 (CAAA 1970), $NO_X$ controls imposed on both stationary and mobile sources have kept emissions at levels that are approximately equal to 1970, despite the continued increase in industrial activity and motor vehicle use since then.

Increased industrial activity and motor vehicle use is summarized in Figure 1-15. Considering that $NO_X$ emissions have remained relatively stable, these trends suggest that the $NO_X$ controls applied to motor vehicles and combustion sources have had some beneficial impact.
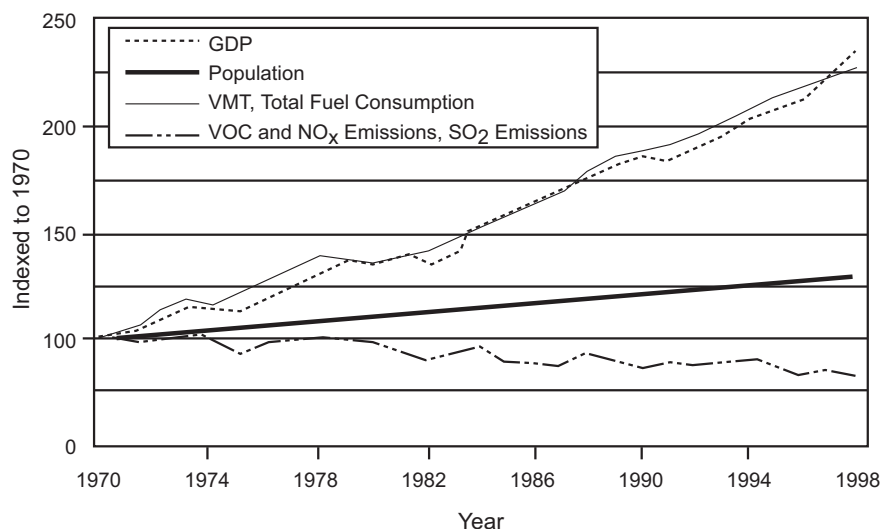


Figure 1-15. Trend of total $NO_x$ emissions and related data, 1970-1998[1]

[Note: This updated graphic is slightly different than the graph used in the broadcast video.]

Despite improvements in motor vehicle emissions and stationary combustion source control, $NO_X$ emissions have remained essentially at 1970 levels. This "unyielding" emissions profile is in contrast to the declining emission rates for other criteria air pollutants such as particulate matter, sulfur dioxide, carbon monoxide, and lead. Increased efforts to control $NO_X$ are being stimulated by (1) the unyielding emission profile and (2) the important role of $NO_X$ in the formation of ozone and other secondary pollutants.

# OZONE SEASON EMISSIONS

Ozone season emissions data are important when discussing $NO_X$ because $NO_X$ is a precursor to the formation of ground-level ozone or smog. Smog occurs in the warmer months and can reach levels that are harmful to the public's health. Ozone formation is more prevalent in the warmer months because the summer meteorology is more conducive to ozone formation and also because summertime activities (e.g., higher electricity use due to air conditioning) produce more ozone precursor emissions such as $NO_X$. As a result of this seasonal variation, much of the $NO_X$ modeling that is performed is done for the ozone season.

INTRODUCTION to NOx CONTROL

Ozone season emissions data are generated using two approaches. One approach is to collect activity data for a specific period of time (e.g., summer) and then use that data to develop the inventory for that period. The other more common approach is to develop an annual emissions inventory and then temporally allocate the annual emissions to the summer months. For example, one could examine the seasonal variation in production levels at an industrial facility and allocate annual emissions based on the seasonal variation in production levels. The main purpose of ozone season emissions data is to allow ozone modeling to be performed and also to allocate emission budgets for the $NO_X$ SIP Call.

# Review Exercises

1. Which of the following is a characteristic of nitric oxide?
   (Select all that apply)
   a. Insoluble
   b. Stable in the atmosphere
   c. Reddish-brown coloration
   d. Absorbs ultraviolet light
   e. Possesses a sharp acrid odor

2. Nitrogen dioxide accounts for approximately what percentage of $NO_X$ emissions from combustion sources?
   a. 100%
   b. 95%
   c. 75%
   d. 50%
   e. 5%
   f. 0%

3. Which of the following regulatory programs are currently driving the control of $NO_X$ emissions?
   (Select all that apply.)
   a. $NO_2$ NAAQS
   b. Ozone NAAQS
   c. Acid Rain
   d. $PM_{2.5}$
   e. Regional Haze
   f. Stratospheric Ozone
   g. All of the above

4. Which of the following pollutants are capable of initiating photochemical reactions?
   (Select all that apply.)
   a. NO
   b. $NO_2$
   c. $HNO_3$
   d. $N_2O$
   e. $N_2O_4$
   f. None of the above

5. What factors favor the formation of thermal $NO_X$?
   (Select all that apply.)
   a. High gas temperature
   b. High oxygen concentrations
   c. High residence time at high gas temperature
   d. Flame impingement
   e. All of the above

6. What mechanism generally describes the formation of thermal $NO_X$?
   a. Homogeneous oxidation mechanism
   b. Zeldovich mechanism
   c. Johnson mechanism
   d. None of the above

7. What fraction of $NO_X$ is generally due to thermal $NO_X$ formation in coal-fired boiler applications?
   a. 95% to 99%
   b. 90% to 95%
   c. 80% to 90%
   d. 50% to 80%
   e. 20% to 50%
   f. 1% to 20%

8. What is the typical wt-% fraction of fuel nitrogen in coal?
   a. 0.2% to 3.5%
   b. 0.1% to 0.2%
   c. 0.01% to 0.1%
   d. None of the above

9. Which fossil fuel has nearly negligible levels of fuel nitrogen?
   a. Residual oil
   b. Distillate oil
   c. Natural gas
   d. Wood
   e. None of the above

10. U.S. anthropogenic emissions of $NO_X$ since 1970 have:
   a. Increased by 40%
   b. Increased by 20%
   c. Remained relatively constant
   d. Decreased 20%
   e. Decreased 40%

11. Which of the following is considered a non-road mobile source?
   (Select all that apply.)
   a. Simple cycle gas turbine
   b. Gasoline-powered lawn mower
   c. Diesel generator
   d. Nitric acid facility
   e. Front-end loader
   f. None of the above

12. $NO_X$ emissions from EGUs are primarily generated by:
   a. Gas-fired boilers
   b. Oil-fired boilers
   c. Coal-fired boilers

d. Wood-fired boilers
e. None of the above

13. During which year were $NO_X$ emissions the highest?
    a. 1940
    b. 1971
    c. 1977
    d. 1988
    e. 2000

14. During which year were highway mobile $NO_X$ emissions the highest?
    a. 1940
    b. 1971
    c. 1978
    d. 1988
    e. 1993

# References

[1] U.S. Environmental Protection Agency, Office of Air and Radiation. August 1997. *Nitrogen Oxides: Impact on Public Health and the Environment.* Research Triangle Park, NC.

[2] U.S. Environmental Protection Agency. November 1977. *Technical Assessment of $NO_X$ Removal Processes for Utility Application.* U.S. EPA 600/7-77-127.

[3] Environmental Protection Agency, Office of Air Quality Planning and Standards. December 1998. *National Air Quality and Emission Trends Report, 1997.* EPA 454/R-98-016. Research Triangle Park, NC.

[5] Radian Corporation. May 1996. *Volume V: Biogenic Sources Preferred Methods-Final Report.* EPA-454/R-97-00. Research Triangle Park, NC.

[6] Environmental Protection Agency, Office of Air Quality Planning and Standards. March 2000. *National Air Pollution Emission Trends, 1900-1998.* EPA 454/R-00-002. Research Triangle Park, NC.

[7] Environmental Protection Agency, Office of Air Quality Planning and Standards. *Compilation of Air Pollutant Emission Factors (AP-42), Section 13.1 Wildfires and Prescribed Burning.* 5th Edition. Research Triangle Park, NC.