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SHORT-TERM NITROGEN DIOXIDE MODELING: CURRENTLY
AVAILABLE MODELS AND THE APPLICATIONS AND
DEVELOPMENT NEEDED FOR ENERGY ASSESSMENT

by

K.C. Chun

Energy and Environmental Systems Division
Integrated Assessments and Policy Evaluations Group

November 1980

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U.S. DEPARTMENT OF ENERGY
Assistant Secretary for Environment
Office of Environmental Assessment
Regional Impacts Division

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FOREWORD

The Energy and Environmental Systems Division at Argonne National Laboratory (ANL) is evaluating, through its Midwest Regional Assessment Program, the impacts and consequences of alternative energy options. As a part of this overall effort, analytical procedures for conducting these analyses are being evaluated, adapted, and developed at ANL and elsewhere.

Assessment of local air quality effects due to energy facilities is an important step in health and ecological impact analyses. Development of models for estimating effects on local air quality of reactive pollutant emissions from energy facilities has lagged behind development of those for mobile emission sources. The conclusions and suggestions made in this review work can serve as guides in the model development effort for nitrogen oxides emitted from energy facilities.

Funding for this project was provided by the U.S. Department of Energy (DOE), Assistant Secretary for Environment, Office of Environmental Assessments, Regional Impacts Division. The DOE project director was Dr. Richard Ball.

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ABSTRACT

The rapid increase in U.S. coal consumption projected for the near future is likely to result in, among other things, increased concentrations of nitrogen dioxide and other nitrogenous pollutants in the ambient atmosphere. The design and siting of new coal utilization facilities could be constrained by the potential promulgation of a short-term ambient air quality standard for nitrogen dioxide and by other regulations. To assess the extent and pattern of such constraints, appropriate air quality models for short-term nitrogen dioxide levels are needed. As an initial step in developing models capable of predicting the short-term impact of nitrogen dioxide due to emissions from coal-burning electric utility and industrial point sources, this report: (1) discusses multiple interdependent factors that affect local short-term concentrations of nitrogen dioxide such as meteorology, air quality, and the characteristics and distribution of emission sources of nitrogen dioxide precursors; (2) evaluates the utility and limitations of existing air quality models for nitrogen dioxide, including empirical, mechanistic and empirico-mechanistic models; and (3) suggests an approach for applying and developing relatively simple models for predicting short-term concentrations of nitrogen dioxide in assessments of regional and national energy development.

1 INTRODUCTION

Coal consumption in the U.S. is expected to increase rapidly in the near future. According to a recent projection, the annual U.S. coal production of 668 million tons in 1978 will almost double in 1990.¹ The bulk of the additional coal produced would be consumed by new stationary combustion facilities such as electric utility and industrial boilers. Since these facilities are important emission sources of man-made nitrogen oxides (NO_x), the increase in coal consumption is likely to increase the emissions of NO_x and, consequently, atmospheric concentrations of nitrogen dioxide (NO_2) and other nitrogenous compounds.

Of NO_x occurring in the atmosphere, NO_2 is the compound of most concern for human health and welfare. To protect the public health and welfare, the Environmental Protection Agency (EPA) has established the National Ambient Air Quality Standard (NAAQS) for NO_2 . The primary and secondary standards are

both 100 micrograms per cubic meter ($\mu\text{g}/\text{m}^3$) or 0.05 parts per million (ppm) as an annual average.² To avoid any violation of this standard, a new NO_x emission source should not increase ambient NO_2 concentrations by more than the differences between the standard and the existing levels of local ambient NO_2 . In areas where the existing NO_2 levels are already high, these differences could be relatively small, imposing certain constraints on the design and siting of new NO_x emission sources. The constraints could be on one or more of the following:

- Size and/or number of units to be constructed at one site,
- Furnace design or efficiency of NO_x control equipment, or
- Distances between a new NO_x emission source and areas with high NO_2 levels or with other new NO_x emission sources.

Under the currently effective NAAQS for NO_2 (100 $\mu\text{g}/\text{m}^3$ or 0.05 ppm as an annual average), siting a large coal-burning stationary source is not constrained to any significant extent for two reasons:

- The maximum increase in annual average NO_2 concentration expected from such a new source that meets the new-source performance standard is only a small fraction of the above standard.
- Annual average ambient concentrations of NO_2 throughout the United States are currently well below the stated standard except for a few locations in large metropolitan areas.³

This situation could change as coal consumption increases and as more coal-burning facilities come into operation. More-severe constraints on the design and siting of new coal-burning facilities could be imposed, if a stringent short-term NAAQS for NO_2 is promulgated. Further constraints could be imposed if a prevention of significant deterioration (PSD) regulation is established for NO_2 in the form of concentration increments not to be exceeded. (See Appendix A for the legal and scientific background for the potential short-term NAAQS and PSD regulations for NO_2 .)

For energy planning and evaluation of an alternative coal utilization policy, both the short-term impact of NO_2 expected from increased coal consumption and the extent and pattern of constraints that may be imposed on the increase in coal use due to the potential short-term NAAQS for NO_2 must be evaluated. These assessments require air quality models capable of predicting the impact of short-term NO_2 concentrations due to additional stationary combustion source emissions on the existing air quality.

Because of the complex atmospheric chemistry involved, air quality models for reactive pollutants such as NO_2 tend to be more complicated than those for relatively inert pollutants. Detailed models for NO_2 that consider multiple sources and multiple interdependent factors associated with precursor emissions (physical processes of transport, dispersion, and removal, and the chemical process of transformation) require large amounts of input information and computer time. Relatively simple techniques for predicting short-term NO_2 concentration are desirable for assessing the impact of point source

emissions and evaluating alternative coal utilization policy on a regional or national basis.

Although relatively simple techniques for predicting NO_2 are available for certain simple situations such as the case for a large, isolated, point-source plume in a rural atmosphere, those for more complicated situations need to be developed and tested. More complicated situations may include those cases for a large, isolated plume in an urban atmosphere, and an area source consisting of many small combustion sources within or at the fringe of an urban area.

The following sections present a discussion of multiple, interdependent factors that affect local short-term concentrations of NO_2 , an assessment of the utility and limitations of existing models for predicting NO_2 levels, and an approach for applying and developing relatively simple techniques for predicting NO_2 levels in regional and national energy assessments.

2 FACTORS AFFECTING LOCAL SHORT-TERM CONCENTRATIONS OF NITROGEN DIOXIDE

Nitrogen oxides (NO_x) emitted into the lower atmosphere are primarily in the form of nitric oxide (NO), with nitrogen dioxide (NO_2) typically accounting for less than 10% for most man-made emissions.³ While being transported and dispersed in the lower atmosphere, NO is oxidized to NO_2 in a number of chemical reactions that occur in the presence of sunlight, reactive hydrocarbons (HC), and/or ozone (O_3). (See Appendix B for the major oxidation mechanisms for NO in the lower atmosphere.) NO_2 is either photolyzed back to NO or further converted into other nitrogenous compounds such as nitric acid (HNO_3) and nitrate (NO_3^-) aerosols. Like many other atmospheric pollutants, all of these nitrogenous species are continuously removed from the atmosphere via dry and wet deposition mechanisms.

Based on the brief account of the atmospheric life cycle for NO_2 presented above, the concentration of NO_2 at any given location and time in an airshed is the net result of the following three broadly defined processes that proceed simultaneously:

- Emissions of NO_2 precursors (NO_x and HC);
- Physical processes of atmospheric transport, dispersion, and removal; and
- Chemical process of transformation.

Precursor emissions in an airshed are primarily influenced by the land use pattern, which determines the extent and spatial distribution of various categories of emission sources. They are also affected by meteorological factors, such as temperature, which determine emission rates of certain categories of sources. In comparison, physical processes (transport, dispersion, and removal) and the chemical process (transformation) are primarily influenced by meteorological and other atmospheric factors. These include:

- Solar radiation,
- Temperature,
- Wind,
- Turbulence,
- Water vapor content and other forms of water, and
- Concentrations of other pollutants.

The above factors are themselves correlated and show random as well as regular variations with time of day, season of year, geographical location (latitude and altitude), topography, and land use pattern. These variations are closely associated with the regular variations in the intensity of solar radiation and its interaction effects with the surface features of the earth. It then follows that the three processes that determine the ambient NO_2 concentration, i.e., the precursor emissions and the atmospheric physical and chemical processes, also vary accordingly as a function of time and space. It is also apparent that such variations would have a certain degree of regularity but a great deal of complexity.

The validity and accuracy of an air quality model for NO_2 would depend on how well these processes are accounted for and how well their spatial and temporal variations are represented, relative to their importance in the application under consideration. These processes, the land use patterns and atmospheric factors affecting them, and their variations and interrelationships are described below to the extent appropriate in illustrating the significance of their roles in determining local short-term concentrations of NO_2 .

2.1 EMISSIONS OF NITROGEN DIOXIDE PRECURSORS

2.1.1 Sources of Precursor Emissions

Although NO_2 precursors are emitted from a variety of natural and man-made sources, the latter sources are far more important in terms of significant NO_2 exposure with respect to public health and welfare. Table 2.1 lists the U.S. emission estimates according to emission source category for several important classes of air pollutants.⁴ The largest of the man-made NO_x emission sources are the stationary combustion sources (installations burning fossil fuels), followed by mobile combustion sources (motor vehicles). They accounted for 56% and 40% of the nationwide NO_x emissions respectively in 1977, while emissions from noncombustion industrial processes were responsible for only 4%.

Emissions of HC, however, are dominated by mobile combustion sources and noncombustion industrial processes; they accounted for 41% and 36% of nationwide HC emissions respectively in 1977. Stationary combustion sources accounted for only 5%, while miscellaneous solvent uses were responsible for 16%. In addition to the difference in the quantities of precursor emissions, each source category possesses a unique combination of characteristics that may influence local short-term concentrations of NO_2 .

2.1.1.1 Mobile Combustion Sources

Mobile combustion sources (motor vehicles) emit NO_x and HC simultaneously with a relatively high HC to NO_x ratio,⁵ an important parameter that determines whether the sunlight-triggered photochemical reactions would dominate the atmospheric chemistry of NO_x (see Sec. 3.2.1). The precursors are inherently well mixed at the source, and the photochemical reactivity of HC emitted is relatively high, both of which are essential for rapid photochemical reactions.

The emissions are released from the ground level and concentrated in urban centers for ready exposure to human and other receptors. The emissions have a distinct diurnal pattern with early morning and evening peaks and a weekday-weekend cycle. Seasonal variations in precursor emissions from mobile sources are not as pronounced, because vehicle-miles-travelled increases during the summer, but precursor (HC) emissions decrease as ambient temperature increases.

Table 2.1 Nationwide Emission Estimates, 1977 (10^6 metric tons/yr)

Source Category	Pollutant Type				
	TSP ^a	SO _x ^b	NO _x ^c	VOC ^d	CO ^e
Transportation	1.1(9) ^f	0.8(3)	9.2(40)	11.5(41)	85.7(83)
Highway vehicles	0.8	0.4	6.7	9.9	77.2
Nonhighway vehicles	0.3	0.4	2.5	1.6	8.5
Stationary fuel combustion	4.8(39)	22.4(82)	13.0(56)	1.5(5)	1.2(1)
Electric utilities	3.4	17.6	7.1	0.1	0.3
Industrial	1.2	3.2	5.0	1.3	0.6
Residential, commercial, institutional	0.2	1.6	0.9	0.1	0.3
Industrial processes	5.4(44)	4.2(15)	0.7(3)	10.1(36)	8.3(8)
Chemicals	0.2	0.2	0.2	2.7	2.8
Petroleum refining	0.1	0.8	0.4	1.1	2.4
Metals	1.3	2.4	0	0.1	2.0
Mineral products	2.7	0.6	0.1	0.1	0
Oil and gas production and marketing	0.8	0.1	0	3.1	0
Industrial organic solvent use	0	0	0	2.7	0
Other processes	1.1	0.1	0	0.3	1.1
Solid Waste	0.4(3)	0	0.1(0.4)	0.7(2)	2.6(3)
Miscellaneous	0.7(6)	0	0.1(0.4)	4.5(16)	4.9(5)
Forest wildfires and managed burning	0.5	0	0.1	0.7	4.3
Agricultural burning	0.1	0	0	0.1	0.5
Coal refuse burning	0	0	0	0	0
Structural fires	0.1	0	0	0	0.1
Miscellaneous organic solvent use	0	0	0	3.7	0
Total	12.4(100)	27.4(100)	23.1(100)	28.3(100)	102.7(100)

^aTotal suspended particulates.^bSulfur oxides.^cNitrogen oxides.^dVolatile organic compounds.^eCarbon monoxide.^fNumbers in parentheses indicate percent of total.

RA zero indicates emissions of less than 50,000 metric tons per year.

2.1.1.2 Stationary Combustion Sources

Emissions from stationary combustion sources have the common characteristic of a low HC to NO_x ratio in comparison with those of mobile combustion sources; the larger the source, the lower the ratio.⁵ Sources burning coal tend to be greater emitters of NO_x than those using oil or gas, because coal has a higher fuel nitrogen content, part of which ends up as NO_x.

Emissions from stationary combustion sources are released through stacks at various elevations. In general, the emission height increases as the size of the source increases. For example, electric utility and large industrial combustion sources have high stacks, 100 meters (m) or more in height, with substantial plume rise, while smaller industrial, commercial, and residential combustion source emissions are released from stacks with heights ranging from near ground level to intermediate heights. Rich in NO but poor in HC, emissions from tall stacks must reach the surface in order to contribute to the ground-level concentrations and to participate in the NO_x-HC-O₃ reaction system.

The large electric utility and industrial sources tend to be isolated point sources. New electric utility combustion sources are more often located in rural areas near the source of fuel and cooling water, while new large

industrial sources are sited in rural as well as in suburban areas and small cities. Small industrial, commercial, and residential combustion sources tend to form area sources in clusters in urban and suburban areas.

Some of the stationary combustion sources display seasonal peaks in emissions that vary from one part of the country to another. These peaks result from increased emissions from space heating during the cold weather and from additional generation of electricity to meet air conditioning demands during the summer months. Diurnal peaks in emissions that may vary according to the season also occur during hours that may differ from the peak emission periods of mobile combustion sources.

2.1.1.3 Noncombustion Industrial and Other Miscellaneous Sources

In general, NO_x and HC from noncombustion industrial and miscellaneous sources are emitted separately and from relatively low elevations. They are either emitted from isolated point sources or area sources. The reactivity of HC from these sources could be higher or lower than the reactivity of the HC present in the emissions from mobile combustion sources.

2.1.2 Spatial Distribution of Emission Source Category

Land use patterns determine the absolute and relative significance and spatial distribution of various categories of emission sources of NO_2 precursors within an airshed. Because the characteristics of the individual categories of emission sources of NO_2 precursors differ widely, the land use pattern exerts profound influence on the spatial and temporal variations in NO_2 concentrations by affecting the characteristics of precursor concentrations and their ratio.

On a national basis, mobile sources account for about 40% of total NO_x emissions (Table 2.1). However, this figure is about 50% in a typical large urban area,⁶ with the remainder from power plants, petroleum refineries, and chemical plants (especially nitric acid plants). This ratio may change as newer motor vehicles with NO_x control equipment replace older ones. The difference between the urban and nationwide percentages reflects the many large point sources of NO_x outside of urban areas.

2.2 METEOROLOGY AND AIR QUALITY

2.2.1 Solar Radiation

Solar radiation provides the energy for triggering a series of chemical reactions in the atmosphere between gaseous organic molecules and NO_x . These reactions produce a wide variety of secondary pollutants such as O_3 , NO_2 , and many other nitrogenous compounds, including nitrites and nitrates. Wavelength distribution and intensity, the important characteristics of sunlight in initiating photochemical reactions in the lower atmosphere, depend on such factors as the concentration of ozone within the stratosphere, the solar zenith angle, cloud cover, turbidity of the atmosphere, and water vapor

concentration. In addition to the diurnal variation, the sunlight intensity also varies with season and geographical latitude. It is highest during the summer, and the maximum intensity is fairly constant throughout the U.S. There is also some variation in intensity with longitude during the summer, with the highest intensity occurring in the western U.S. During the winter, the latitude effect is strong with the maximum intensity at 20° north, decreasing to about one-third at 50° north latitude.⁷

Sunlight warms up surfaces, producing various temperature effects described in the following subsections.

2.2.2 Temperature

Temperature affects the rates of precursor emissions by influencing human and natural biological activities. For example, low temperature causes more emissions as a result of increased space heating, but high temperatures increase emissions of NO_x from power plants supplying electricity for air conditioning demands. High temperatures increase HC emissions from vegetation, although not very significantly. High temperature also increases the rates of most chemical reactions involved in NO_x chemistry.

On a national scale, temperature varies relatively smoothly from north to southeast of the Rocky Mountains with local variations due to topographical features such as mountains or bodies of water. Daily average temperatures in July range from 65°F in Maine to 82°F in Florida and Texas. West of the Rocky Mountains, there are wide variations in daily average temperatures in July: from 80° to 100°F in the desert areas to 60°F on the coast and in the mountain areas.⁷

Variations in the vertical temperature profile of the lower atmosphere are caused by the diurnal variation of solar radiation. The atmospheric stability, an indicator of turbulence, is determined by the vertical temperature profile. Stability and its variations are very important in the dispersion of emissions from ground-level area sources as well as elevated point sources (see Sec. 2.2.4 - Turbulence).

2.2.3 Wind

Wind, the air in motion, carries emissions as they are released from their sources and dilutes their concentrations in proportion to its speed. Wind speed also limits the buoyant rise of plumes warmer than the ambient air, determining whether plumes from tall stacks will remain within the mixing layer (a ground-based layer in which turbulent dispersion occurs) to contribute to the ground-level pollutant concentrations. By dictating the travel course of the plume or the air mass containing the pollutants, wind direction determines the kinds and quantities of additional pollutants to be added to the air mass along its course, thus changing the pollutant concentrations and composition, and determines the locations of receptors to be affected at the ground level.

Surface wind speed and direction, normally available from weather stations and commonly used in air quality prediction analysis, have local

rather than regional characteristics. Although the annual mean wind speed within the contiguous U.S. ranges from 6 to 12 miles per hour (mi/h), wind speed can show wide variations over short distances. Wind direction also shows wide fluctuations, e.g., prevailing winds at places less than 100 miles apart may be in opposite directions. The reason for this is the great influence exerted on the wind by local topography and surface features.

On a regional basis, the rate at which the region's emissions are diluted depends on the average wind speed within mixing layers. During winter mornings, the slowest average speeds are less than 2 meters per second (m/s) and occur in the Far West. However, wind speeds of 4 m/s or less occur over most of California, Oregon, and parts of Nevada, Wyoming, and the four-corners states; in the East the slowest averages (less than 5 m/s) occur over Mississippi, Alabama, and Tennessee. On winter afternoons, the average wind speed pattern is similar to that in the morning, except that the average speeds in the afternoon tend to increase by 1-2 m/s. This diurnal variation is generally true for all seasons. The main difference in the wind speed between winter and summer mornings is that average speeds in the eastern and midwestern states are slower in summer than in winter by about 1-3 m/s.⁸

The speed and direction of wind vary with height from the surface. These variations occur because the frictional effects of surface features and local thermal effects modify winds associated with large-scale circulations. The frictional retardation of wind speed, which is greatest near the surface, decreases with height throughout the planetary boundary layer [approximately on the order of 1 kilometer (km) above the surface]. The difference in the wind direction between the surface and the layer above the planetary boundary layer (geostrophic layer) is also caused by frictional effects that disturb the large-scale circulating pattern of a cyclone or anticyclone and let the surface air be sucked into the low-pressure centers of the cyclones.

Vertical variations in wind caused by differential heating or cooling of various topographical and surface features occur over relatively small areas. Examples include sea-land breezes, mountain-valley winds, and local circulation caused by urban heat-island effects. All of these vertical variations in wind speed and direction result in differences in wind effects such as dilution of emissions from ground-level mobile sources and elevated combustion sources.

2.2.4 Atmospheric Turbulence

Small-scale variations in wind speed and direction constitute turbulence. The stirring of more-polluted air with less-polluted air causes diffusive transfer of pollutants across the wind stream, diluting the pollutant concentration at the same time. This dispersive effect of turbulence brings the emissions from ground-level mobile sources upward and those from elevated combustion sources downward to the ground level.

Atmospheric turbulence is generated in the lower atmosphere by two basic mechanisms. Thermal stirring induced by heated air boiling up from sun-warmed surfaces produces thermal turbulence, and mechanical stirring induced by wind blowing over surfaces or obstacles produces frictional or wake turbulence.

The effect of thermal turbulence on the ground-level concentrations of precursors and NO_2 are far more pronounced under the conditions of weak wind when the mechanically induced turbulence and the diluting effect of wind speed are minimal. Therefore, spatial and temporal variations in thermal turbulence during the periods of weak wind are of particular interest.

Diurnal and vertical variations in atmospheric turbulence are related to the diurnal variation in solar radiation and its interaction with surfaces. During a night with clear sky and weak wind, a surface-based inversion or stable layer commonly develops as a result of surface cooling. Through the inversion layer, temperature increases with height, resisting vertical motions of air mass and limiting diffusive transfer of pollutants. Precursors of NO_2 emitted from motor vehicles into a relatively stable layer during morning rush hours result in very high ground-level concentrations of precursors due to limited vertical dispersion, providing a favorable condition for photochemical reactions later as the intensity of sunlight increases. In flat terrain, NO_x from elevated stationary combustion sources emitted into a stable layer and remaining in the narrow concentrated plume does not reach the ground level. However, high ground-level concentrations result when such plumes impinge upon high-terrain receptors.

When solar radiation warms up the ground surface, the surface-based inversion may be eliminated gradually from the ground level by the upward transfer of turbulence caused by thermal stirring. The bottom of the stable layer moves upward, and the stable layer aloft serves as a lid on vertical dispersion of pollutants beneath it. The layer between the ground and the lid, in which turbulent dispersion occurs, is called a mixing layer. The depth of the layer, called mixing height, determines the vertical extent of space through which pollutants may be dispersed. The lower the mixing height, the higher the ground-level concentrations for emissions both from a ground-level source and from an elevated source remaining within the mixing layer will be.

The mixing height varies diurnally, seasonally, and geographically. As surface heating continues after sunrise, the surface-based inversion is usually eliminated and the mixing height increases to a maximum in the afternoon. Winter mixing heights vary by less than a factor of two for most of the United States. Morning values are highest in coastal areas, with a range of 500 to 700 m. During winter afternoons, the mixing heights for coastal areas increase only slightly to between 800 and 1000 m, but inland mixing heights increase so that in the afternoon they are approximately 50% greater than the coastal mixing heights. The summer pattern is similar, with a larger range of values. Major differences to note are the low afternoon mixing heights on the California coast (600 m) compared with the Pacific Northwest, Atlantic and Gulf coastal areas (1200 m), and those of Great Lakes areas (1600 m) compared with other inland areas (1800-3600 m).⁸

A unique phenomenon called fumigation occurs when pollutants from an elevated source emitted into a stable layer during the night and remaining in a relatively concentrated plume are reached by the thermal eddies of an unstable layer developing from the surface, and mixed vertically downward. Two types of fumigation are known to exist: one associated with nocturnal inversion breakup caused by solar radiation, and lasting about 30-60 minutes (min),⁹ and the other related to stable air from a cold water surface (e.g.,

onshore sea or lake breeze at high latitudes) to warmer ground surface during warm seasons that persists throughout the daylight hours.⁹ These fumigation phenomena are important mechanisms for NO_x from elevated point sources to reach the ground level at relatively high concentrations and perhaps result in high-level short-term concentrations of NO_2 .

2.2.5 Water Vapor Content and Other Forms of Water

Above a certain transition relative humidity, nitrite and nitrate aerosols may form liquid droplets. As the relative humidity increases further, the aerosol size grows due to additional moisture condensation. Mist, fog, and falling rain and snow act as scavengers to remove gaseous or particulate nitrogenous compounds physically from the atmosphere.

Nitric acid produced from NO_2 by photochemical reactions appears to be the main nitrogenous compound being scavenged by rainout and washout processes. Detailed information on the removal of NO_2 by these processes is not available, probably because the half-life of NO_2 by photochemical reactions is rather short, on the order of several hours to a day.⁶ Since NO_2 removal by rainout and washout processes does not occur during the periods of high photochemical activities, it is not relevant in predicting high-level short-term concentrations of NO_2 .

2.2.6 Concentrations of Other Pollutants

Reactive HC and O_3 are the two most important pollutants affecting the ambient NO_2 concentrations. Reactive HC are so important in urban NO_x chemistry that they are considered as one of the NO_2 precursors along with NO. Reactive HC in the urban atmosphere, dominated primarily by the emissions from mobile sources and noncombustion industrial sources, are consumed in the photochemical processes of oxidizing NO before being transported far from the urban areas. In rural areas, turpenes and other hydrocarbons emitted from vegetative surfaces during the day may play some roles in NO_x photochemistry, but their concentrations are generally too low to be significant.

The concentrations of O_3 in urban areas usually reach maximum in the early afternoon as a net result of photochemical production, destruction on surfaces and in reactions with NO at ground level, and downward transport from layers aloft. This O_3 plays a major role in oxidizing NO emitted during evening rush hours. Along with the natural background O_3 [approximately $40\text{--}80 \mu\text{g}/\text{m}^3$ ($0.02\text{--}0.04 \text{ ppm}$)], unreacted O_3 transported from the urban area becomes an important scavenger for NO emitted from combustion sources located in rural areas.

2.3 HIGH-LEVEL SHORT-TERM CONCENTRATIONS OF NITROGEN DIOXIDE AND THE COMBINATION OF FACTORS CONDUCTIVE TO THEIR FORMATION

Air quality data from U.S. monitoring stations in 1975 and 1976 indicate that peak 1-hour concentrations of NO_2 equalling or exceeding $750 \mu\text{g}/\text{m}^3$ (0.4 ppm) were measured in Los Angeles and several other California sites, as well as in Ashland, Kentucky, and Port Huron, Michigan.³ Additional sites

reporting at least one peak hourly concentration equalling or exceeding 500 $\mu\text{g}/\text{m}^3$ (0.27 ppm) include: Phoenix, Arizona; St. Louis, Missouri; New York, New York; 14 additional sites in California; Springfield, Illinois; Cincinnati, Ohio; and Saginaw and Southfield, Michigan. One can conclude from the above observation that very high NO_2 concentrations of a few hours' duration can occur not only in large urban areas like Los Angeles, but also in small cities like Ashland, Kentucky and Port Huron, Michigan.

Hourly concentration data for NO_2 during 1978 and 1979 from a limited network of monitoring stations in the metropolitan Chicago Interstate Air Quality Control Region (AQCR)¹⁰ show that the maximum 1-hour concentration of NO_2 was 600 $\mu\text{g}/\text{m}^3$ (0.32 ppm) in 1978 and 640 $\mu\text{g}/\text{m}^3$ (0.34 ppm) in 1979. The few monitoring sites measuring hourly concentrations of NO_2 in the AQCR (five in 1978 and eight in 1979) suggests that higher concentrations could have been measured elsewhere in the AQCR that were not detected by the monitors at fixed locations. Although not validated by field measurements, recent calculations using a Gaussian dispersion model and the dynamic equilibrium relationship among NO , NO_2 , and O_3 estimated that maximum hourly concentrations of NO_2 due to power plants and other large industrial emissions could be in the range from 1,040 $\mu\text{g}/\text{m}^3$ (0.55 ppm) to 1,670 $\mu\text{g}/\text{m}^3$ (0.89 ppm).¹¹

To analyze the occurrence and potential causes (combinations of causative factors) of high-level short-term concentration of NO_2 in California, Martinez and Nitz reviewed the hourly NO_2 concentrations above 375 $\mu\text{g}/\text{m}^3$ (0.20 ppm) monitored during 1975-1977 at the 51 monitoring stations and evaluated associated emissions and meteorological factors.¹² The findings of the study are summarized below:

- The most frequent causes for high-level hourly concentrations ($>375 \mu\text{g}/\text{m}^3$) of NO_2 are, in decreasing order, NO to NO_2 conversion by peroxy radicals ($\text{RO}_2\cdot$, $\text{HO}_2\cdot$), NO tritration by O_3 to form NO_2 , and effects of point sources.
- High-level hourly concentrations of NO_2 , unlike O_3 , occur most frequently during winter (November through February), possibly due to combined effects of more stagnant meteorological conditions limiting the dilution of precursors and product pollutant, weaker solar radiation and lower temperature slowing the photodissociation of NO_2 formed, and increased NO_x emissions from space heating using natural gas.
- The association between the daily traffic cycle and the hourly fluctuations of high-level NO_2 concentrations, and the simultaneous occurrence of high-level NO_2 concentrations at many monitoring sites suggest that area source emissions due to motor vehicles are the principal proximate cause of the high-level NO_2 concentrations in the area.
- Although not frequently observed, high-level concentrations of NO_2 caused primarily by the effects of point sources are evident, as indicated by the simultaneous peaks in sulfur dioxide (SO_2) and NO_2 concentrations.

The above findings provide substantial insight into the favorable combinations of emissions and meteorological factors conducive to high-level short-term concentrations of NO_2 in large urban areas with NO_x emissions caused primarily by motor vehicles. Similar analyses reported on other areas with different land use patterns and in different regions of the country provide further valuable information.^{3,6}

3 CURRENTLY AVAILABLE MODELS FOR ESTIMATING SHORT-TERM CONCENTRATIONS OF NITROGEN DIOXIDE

The subject of predicting short-term concentrations of NO_2 received little attention until the possibility for a short-term NAAQS for NO_2 was raised. However, relationships among the major constituents of urban smog, i.e., NO_x , HC, and ozone (O_3)/oxidant (O_x), have already been investigated and considered during the course of developing models for predicting ambient O_3/O_x concentrations. Some of the methodology developed for this purpose is available for direct use or has the potential for adaptation to be used in predicting short-term ambient concentrations of NO_2 . Certain models have already been adapted and tested.¹³

Models for predicting (O_x/NO_x)-related air quality can be divided into the following three classes according to the degree of empiricism used in accounting for the three causative processes (i.e., precursor emissions; physical processes of transport, dispersion, and removal; and the chemical process of transformation) and in representing their spatial and temporal variations:

- Empirical models,
- Empirico-mechanistic models, and
- Mechanistic models.

Empirical models attempt to relate precursor emissions in an airshed to (O_x/NO_x)-related air quality by quantifying the following two combined processes using either assumed or statistically defined relationships: (a) combined process of dispersion and sink-removal of precursor emissions, and (b) combined process of photochemical transformation and sink removal of O_x/NO_x . Because the assumed or statistically defined relationships used in empirical models are not cause-effect in nature, these models are intended for use in analyzing the areas for which they were developed and in estimating changes in air quality resulting from changes in emission rates rather than in predicting absolute air quality.

In contrast to empirical models, mechanistic models attempt to use cause-effect relationships to describe the physical processes of transport, dispersion, and removal and the chemical process of transformation that link the precursor emissions to the ambient levels of the secondary pollutant(s). [Because the mechanistic models represent the most fundamental approach to air quality simulation, they are sometimes called air quality simulation models (AQSM).]

Because of their fundamental approach, AQSM are the preferred models from the theoretical point of view. However, simpler models that emphasize either the physical or chemical process, neglecting or providing a simplified treatment of the other, are appropriate in many practical applications. These simpler mechanistic models are referred to as empirico-mechanistic models in this discussion.

All of the available models have certain theoretical or practical limitations for application to situations other than those for which they

were developed. To help identify the need for further development in short-term NO_2 modeling for energy assessment purposes, essential features of available models are discussed in the following subsections.

3.1 EMPIRICAL MODELS

Empirical models used thus far for predicting changes in O_3/O_x levels include linear rollback, modified rollback, and statistical-empirical models. These models are mainly concerned with O_3/O_x control strategy in large urban situations, where precursor emissions are primarily from mobile sources.

3.1.1 Linear Rollback Model

The linear or simple rollback model assumes that the ambient concentrations of a secondary pollutant (O_x or NO_2) above the background level is directly proportional to precursor emissions. In other words, the two combined processes of relating precursor emissions with the ambient air quality are represented by a simple linear proportionality. This relationship cannot be validated experimentally, since such validation would require that emission rates of each and every source be changed identically, or supported by laboratory experiments or theoretical considerations. Therefore, the model based on this assumption is clearly the crudest of those currently available. However, the model has the advantages of computational simplicity and small demand in amount of input information.

3.1.2 Modified Rollback Model

As with the linear rollback models, the modified or graphical rollback model represents the process of dispersion and sink removal of precursor emissions by a simple proportionality. However, it attempts to improve the representation of photochemical formation and the sink-removal process of product pollutant by statistical analysis of ambient monitoring data for the precursor and product pollutants. Because of the real atmospheric data used, this model is also referred to as the observational model.

One example of this model is based on the assumption that early morning precursor concentrations are the indicators of the O_x levels that will occur later in the day. The Environmental Protection Agency's (EPA's) Appendix J Method¹⁴ for calculating oxidant-related control requirement uses an upper-limit curve based on aerometric data from several urban centers. The curve was drawn through the uppermost points obtained by plotting daily maximum 1-hour O_x concentrations against 6 a.m. - 9 a.m. average concentrations of nonmethane hydrocarbons (NMHC). Each data point was constructed from the oxidant and NMHC data taken at the same monitoring site located in the central business district of the respective urban center. Thus, the upper limit curve is considered to depict the relationship between the NMHC precursor and the oxidant formed within the source-intensive areas under meteorological conditions most conducive to O_3 formation.

Overall, the Appendix J Method is judged to be no more valid than the simple rollback model, because the upper limit curve:

- Probably depicts the dependence of O_x on the dispersion factor rather than the dependence on the NMHC precursor factor,
- Disregards the NO_x factor, and
- Is based on limited ambient data.

However, the method has some validity when derived and used in one and the same locality, with the possibility of further improvement with use of a longer period of data collection.

3.1.3 Statistical-Empirical Model

The statistical-empirical model uses statistically defined relationships for better representation of the dispersion and photochemical processes that link the precursor emissions with the ambient air quality. Most of these models use the regression analysis technique, a statistical method for determining the parameters that make an assumed relationship best fit a given set of data.

Some modelers used regression analysis to relate the precursor concentrations (e.g., 6 a.m. - 9 a.m. concentrations of NO_x and NMHC) to the daily maximum 1-hour O_x concentration at various monitoring sites.¹⁵ Others used the technique either to incorporate the effects of meteorological factors by weighting O_x concentrations measured at various locations according to the direction and speed of the morning-to-noon wind¹⁵ or to introduce some spatial resolution of precursor emissions by using the emission levels of reactive HC integrated over the prevailing wind stream corridor (with a defined width) to the O_x monitoring site.¹⁵

Except for the use of the regression analysis technique, the statistical-empirical models still treat the conversion of precursor emissions into ambient secondary pollutant concentrations as one process, i.e., dispersion of emissions, transport, and chemical reactions are not delineated and treated separately. Therefore, these models also lose much of their validity when applied to areas with characteristics widely different from those of the area for which they were developed. To improve this aspect, Tiao et al.¹⁶ developed a statistical model that treats the dispersion, advection, and reaction processes separately but lacks any spatial resolution. Thus, the model could be applied to conditions with different meteorology but not to situations where emission characteristics differ widely.

The statistical-empirical models have the advantages of being constructed statistically from real atmospheric data, yet they retain computational simplicity and require a relatively small amount of input information. However, these models have limited predictive validity, especially when used to predict beyond the range of data used to derive the models. Like rollback models, they suffer from the lack of a cause-effect relationship, and, in general, the lack of spatial and temporal resolution.

3.2 EMPIRICO-MECHANISTIC MODELS

3.2.1 Chemical Kinetics Model

A chemical kinetics model attempts to describe the relationship among precursors and secondary product pollutants by a chemical reaction mechanism, neglecting, or at most providing a simplified treatment of, emission discrimination and physical processes of transport and dispersion. The EPA's Empirical Kinetic Modeling Approach (EKMA) is based on a chemical kinetics model utilizing a reaction mechanism derived from a smog chamber study of automotive exhaust mixtures.¹⁷ The EKMA is used to predict impacts of mobile source emission changes on ambient air quality and to calculate O₃-related control requirements. For this, EKMA utilizes a set of O₃ isopleths which depict maximum afternoon concentrations of O₃ downwind from a city as a function of initial (i.e., morning) concentrations of NMHC and NO_x under a given irradiation condition. In deriving the isopleths, area- or city-specific conditions on NMHC and NO_x emissions occurring later in the day, dilution rate, reactivity of the precursor mix, and concentrations of O₃ and precursors transported from upwind areas could be taken into consideration.

The EKMA concept was recently applied to the analysis of ambient NO₂ concentrations.¹³ Isopleths for NO₂ in Los Angeles under certain summer and winter conditions show a clear three-zone structure indicating that the peak NO₂ concentration is rather insensitive to precursor HC concentration in zones 1 and 3, while the dependence is quite strong in zone 2 (Figs. 3.1 and 3.2).

The EKMA has certain advantages over most of the empirical models, including the cause-effect nature of precursor-to-NO₂/O₃ relationship and the quantitative consideration of both HC and NO_x precursors. However, the model also suffers from a number of possible imperfections such as:

- Bias in relationship of precursor to NO₂/O₃ due to simplifications and perturbations inherent to smog chamber experiments,
- Applicability limited to urban areas,
- Inability to discriminate effects of emissions other than area sources, and
- Lack of detailed spatial and temporal resolution.

3.2.2 Gaussian Model

This class of model is based on the atmospheric diffusion equation that describes the physical processes of downwind transport and crosswind (horizontal and vertical) dispersion, neglecting or providing a simplified treatment of chemical processes of atmospheric transformation.

There are several approaches in describing the atmospheric dispersion process, a process more complex than the horizontal transport process by wind:

Fig. 3.1 Summer NO_2 Isopleths for Los Angeles Obtained by Using the EKMA Model (Source: Ref. 13)

Fig. 3.2 Winter NO_2 Isopleths for Los Angeles Obtained by Using the EKMA Model (Source: Ref. 13)

- The Gaussian concept, in which the pollutant distribution at any cross section of a plume downwind of its source is assumed to be statistically normal, or Gaussian;
- The K-theory, in which the rate of pollutant diffusion is assumed to be proportional to the spatial gradient of its concentration; and
- Statistical theories, in which pollutant diffusion rates are empirically related to the results of experiments with known fluid particle motions.

Among these, the Gaussian concept is most widely used, primarily because of the mathematical simplicity of the Gaussian probability function. In actual application, the atmospheric diffusion equation is reduced to a simple form that can be solved algebraically, assuming steady-state conditions for the emissions and meteorological variables.

Gaussian models were initially designed for application to point source emissions and for short-term averaging periods (3-10 minutes). The model concept has been extended to treat line source (highway) and area source emissions, and for longer averaging periods (up to 1 hour or longer), utilizing certain empirical relationships. Many computational algorithms (computer codes) using the basic Gaussian model concept have been developed and can now be applied to a wide variety of air quality problems.

There are, however, several limitations that originate from simplifying the atmospheric diffusion equation. The most important include:

- Assumptions on steady-state emissions and meteorology (lack of temporal resolution),
- Assumptions on uniform wind and turbulence throughout the atmospheric boundary layer,
- Derivation of dispersion parameters from experimental data of limited scope, and
- Limited capability to treat reactive pollutants with complex chemistry.

Because Gaussian models cannot handle reactive pollutants with complex chemistry, they have been applied traditionally to pollutants that can be considered essentially inert or approximated to be linearly reactive. However, the models' utility was recently evaluated¹⁸ as part of a two-step procedure for estimating maximum ground-level concentrations of reactive NO_2 due to emissions from large point sources.

In the first part of the two-step procedure, the physical processes of downwind transport and dispersion are considered by using a Gaussian model to estimate the maximum NO_x concentration at ground level. The second step deals with the chemical processes of atmospheric transformation by applying a certain simple technique to estimate the portion of the NO_x that exists as NO_2 .

The simple technique available for performing the second step is based on one of the following assumed, empirical, or simple mechanistic relationships between NO emitted and ground-level NO₂ concentrations:

- Total or partial conversion that assumes all or a part of the NO emitted is converted to NO₂ before it reaches the ground level,
- Exponential decay that assumes a certain half-life for conversion of NO to NO₂,
- Empirically derived conversion curves based on plume measurements,
- Ozone-limited conversion based on the principle that the conversion of NO to NO₂ is limited by ambient O₃ concentration with a correction factor to account for in-stack and near-stack thermal conversion of NO to NO₂, or
- Dynamic equilibrium among NO, NO₂, and O₃.

The total and partial conversion and exponential decay methods are all simple, but the conversion percentage or conversion rate must be arbitrarily assigned. These assumed arbitrary relationships that do not consider atmospheric chemistry are the major drawback of these techniques.

The empirically derived conversion curve is a fine concept, but plume measurement data with simultaneous NO, NO₂, and O₃ concentrations, as well as prevailing meteorological conditions are very rare and limited to elevated power plant plumes. The conversion curves derived from available measurements may not represent the conditions of maximum conversion, and the applicability of such curves to other situations or to low-level emissions is doubtful.

In the ozone-limiting method, the oxidizing potential of atmospheric ozone is properly considered, but the factor for conversion of NO to NO₂ must be assigned arbitrarily. The dynamic equilibrium technique has an added feature over the ozone-limiting method in that the photodissociation of NO₂ is accounted for (see Appendix B). Both of these methods, however, suffer from the assumption that molecular-level mixing of the plume and ambient air is complete by the time the plume reaches ground-level receptors exposed to the maximum NO_x concentration. Los Alamos Scientific Laboratory has recently attempted to correct the difficulty arising from the assumption of complete molecular-level mixing.¹⁹

3.3 MECHANISTIC MODELS

Mechanistic or air quality simulation models (AQSM) include Eulerian or grid and Lagrangian or trajectory models. The theoretical basis for both types of models is the same atmospheric diffusion equation; the main difference is in the system of coordinates used. The third type of AQSM, the modified particle-in-cell model, can be considered as a hybrid form of the other two types of models.

3.3.1 Eulerian or Grid Model

Eulerian or grid models are based on a stationary two- or three-dimensional array of grid cells, within which pollutants are emitted, transported from cell to cell, diffused by turbulence, transformed by chemical reactions, and removed from the grid region by dry and wet deposition. In other words, mechanisms of the three causative processes for the ambient NO₂ levels are all considered in detail. Examples of grid models include the one developed by Systems Applications, Inc.²⁰ and the Livermore Regional Air Quality Model (LIRAQ).²¹ These models use the most detailed meteorological input data available, sophisticated chemical reaction mechanisms, and advanced diffusion theory (the K-theory). Temporal and spatial resolutions are limited only by the details of input emissions and meteorological data.

As a natural consequence of the complexity and sophistication, grid models require a large computing and data base. Therefore, grid models can be applied only to situations where sufficient data are available. Even when data are available, errors and lack of details in the data hamper detailed modeling. Other limitations of grid models include errors due to the uncertainty in the chemical reaction mechanism used, numerical diffusion resulting from approximate solution of the atmospheric diffusion equation, high cost, and the lower limit in grid size that may obscure local maximum pollutant concentrations.

Because of the practical limit in grid size, the grid models are suited for assessing area-wide problems of reactive air pollutants in areas where emissions are relatively homogeneous in terms of their heights and spatial variations.

When the number of grids is reduced to one, a limiting case for a grid model, i.e., a box model, results.²² However, a box model can be used only to obtain order of magnitude estimates of the pollutant burden in an urban area, and to estimate trends in air quality over a long term.

3.3.2 Lagrangian or Trajectory Model

Lagrangian or trajectory models are another type of AQSM that uses a hypothetical air parcel or cell moving under the influence of local meteorological conditions to describe pollutant transport. Emissions are injected into the parcel and undergo vertical mixing. Concurrently, pollutants undergo chemical reactions in the parcel. An example of this model is DIFKIN (diffusion kinetics model).²³ The model disregards horizontal diffusion, vertical wind, and wind shear and assumes constant volume of the air parcel; these assumptions could introduce substantial errors in the prediction.

An advantage of the trajectory model is its capability for analyzing episodes of pollution very efficiently. A major drawback of the model is that it cannot be applied in areas of rough or complex terrain, where winds usually have a significant vertical component and considerable variation in the horizontal components with height.

A special type of trajectory model, a "reactive plume model" (RPM), has been specifically designed for predicting concentrations of reactive

pollutants (including NO_2) within a plume downwind of an individual point source.²⁴ A major feature differentiates the RPM from the typical trajectory model: in the RPM, reactants from other sources encountered are represented by their concentration in the ambient atmosphere.

The RPM has the advantage of being capable of dealing with the effect of the elevated point source plume when the plume is brought down to the surface in an urban area under fumigation conditions. For an elevated point source, the assumption of homogeneous distribution of pollutant at any cross section perpendicular to the plume axis is a crude approximation, but its validity improves after full mixing under conditions of fumigation or trapping. Due to the presence of reactive HC in urban air, NO from the plume could be rapidly oxidized to result in high-level NO_2 concentrations at ground level. The need to assume ambient concentrations of reactants may be considered as a limitation of the RPM.

3.3.3 Particle-in-Cell Model

To eliminate some of the errors resulting from the approximate solution of the Eulerian and Lagrangian formulations, Sklarew et al. developed a new method for solving the atmospheric diffusion equation, utilizing the concept of Lagrangian mass points or particles moving through an Eulerian grid.²⁵ In this modified particle-in-cell method, the mass of pollutants is discretized or separated into individual elements, and the centroids of these discrete masses or particles are tracked. In other words, the particles are individually considered as Lagrangian cells transported by the sum of the mean and turbulent flux velocities, or the total equivalent transport velocity. Using Eulerian cells, the concentrations are defined by mass averages based on the number of particles in each cell at a given time.

The particle-in-cell models are most effective in evaluating various candidate sites for a new facility in terms of their potential impact. In comparison, Eulerian or grid models are best suited for regional air quality simulation, while Lagrangian or trajectory models serve well for episode analysis.

3.4 POTENTIAL APPLICABILITY OF EXISTING MODELS FOR ENERGY ASSESSMENTS

Of the three classes of air quality models described above, the empirico-mechanistic models appear to be most appropriate for application in evaluating the impact of NO_2 due to new stationary combustion sources on air quality and in assessing constraints on increases in coal use by a potential short-term NAAQS for NO_2 . Use of empirical models is rejected mainly because these models lack both a cause-effect relationship in linking precursor emissions with the product pollutant concentrations and spatial resolution to deal with emissions released from various elevations. High cost and common unavailability of the detailed input information required do not justify the routine use of mechanistic models or AQSM in a regional or national assessment study.

When a coal-burning stationary source, either an isolated elevated point source or a low-level industrial area source (see Table 3.1 for a

Table 3.1 Summary of Characteristics of New Coal-Burning Stationary Sources

Characteristics	Coal-Burning Stationary Source Category		
	Electric Utility	Large Industrial	Small Industrial
Site location	Rural, small city. Sea or lake shore. Large contiguous urban area (e.g., northeastern U.S.).	Suburban, small city a a	Urban, suburban, small city a a
Point or area source	Point	a	Area
Stack height	High	a	Low to intermediate
Precursor emissions HC/NO _x ratio	Low	a	Low, but higher than electric utility
Peaks			
Seasonal	Summer and winter	b	b
Diurnal	Daytime	b	b
Meteorological conditions conducive to high NO ₂ concentrations	Winter or summer under fumigation or slightly unstable conditions for the plume to reach ground level at relatively high NO _x concentration. Stable atmospheric conditions (near high terrain receptors).	a a	Winter with low winds, which also limits the dilution of automotive emissions
Background air quality			
Ozone	Important	a	Not important in urban area
Hydrocarbon			
Natural origin	Not significant	a	a
Urban origin	Not significant	a	Significant

^aSame as electric utility.

^bPatterns common to various industries do not exist.

summary of their characteristics), is located in a rural or small city environment with low ambient concentrations of reactive HC, the plume NO_x chemistry is primarily affected by the background O₃ concentration. In these circumstances, prediction of the short-term impact of NO₂ in the downwind area could be performed with relative ease using the two-step procedures based on the Gaussian model described in Sec. 3.2.2. However, NO_x chemistry in the plume may become more complicated if the stationary combustion source is located in the vicinity of a large urban area with high concentrations of reactive HC. Prediction of short-term NO₂ concentrations in the area where the stationary combustion source plume and the urban plume overlap or interact may require use of other modeling techniques, e.g., EKMA, for the situation with a low-level industrial area source within or at the fringe of a large urban area.

The key parameter that determines the degree of such plume interaction and the choice of an appropriate modeling technique is the distance between the stationary combustion source and the urban area. Other significant parameters include wind direction, atmospheric dispersion characteristics, and the sizes of the stationary sources and urban area involved. Table 3.2 summarizes the possible effects of the plume interaction, i.e., how the upwind plume affects the downwind source area, and the potential applicability of existing empirico-mechanistic models for simple situations involving a low-level industrial area source or an elevated point source. When the

Table 3.2 Potential Applicability of Existing Empirico-Mechanistic Models for Predicting Short-Term Impact of Nitrogen Dioxide Due to Emissions from Stationary Combustion Sources

Stationary Combustion Source (SS)	Distance to Urban Area (UA)	Meteorological Conditions		Effect of Upwind Source on Downwind Source Area in Terms of Precursor or Scavenger	Applicable Model
		Wind Direction	Dispersion Characteristics for Maximum Interaction		
Small industrial area source	Large	SS to UA	Inversion, low mixing height	Relatively small increase in background NO_x conc.	EKMA with slightly lower initial HC/ NO_x ratio
	Large	UA to SS	Inversion, low mixing height	Some increase in background O_3 conc.	Gaussian (area source) -- O_3 -limited method
	Small	SS to UA	Inversion, low mixing height	Substantial increase in background NO_x conc.	EKMA with somewhat lower initial HC/ NO_x ratio
	Small	UA to SS	Inversion, low mixing height	Substantial increases in NO_x and HC conc.	EKMA with later NO injection considered
Electric utility or large industrial point source	Large	SS to UA	Fumigation or unstable	Small increase in background NO_x conc.	EKMA with slightly lower initial HC/ NO_x ratio
	Large	UA to SS	Fumigation or unstable	Some increase in background O_3 conc.	Gaussian (point source) -- LASL method
	Small	SS to UA	Fumigation or unstable	Substantial increase in NO_x conc. over a relatively small area from midmorning	EKMA with later NO injection considered
	Small	UA to SS	Fumigation or unstable	Substantial increase in NO_x and HC conc.	EKMA with later NO injection considered

separation distance is large, the effect of the upwind source plume on the downwind source area is to add relatively small concentrations of NO_x or O_3 to the background concentrations of the air moving toward the downwind source area, thus enabling the use of existing empirico-mechanistic models with minimum amounts of adjustment.

For cases involving small separation distances and multiple stationary combustion sources with various stack heights, the effects of upwind sources on downwind source area would no longer be as simple as in the cases with large separation distances. Prediction of short-term NO_2 concentrations for these cases may require additional adjustments in the use of existing empirico-mechanistic models, use of different models in sequence, or even development of certain hybrid models, depending on the particular combination of parameters that affect the degree of plume interaction.

4 APPROACHES FOR APPLYING AND DEVELOPING SIMPLE MODELING TECHNIQUES FOR SHORT-TERM CONCENTRATIONS OF NITROGEN DIOXIDE

To conduct a regional or national energy assessment study with respect to short-term concentrations of NO_2 , relatively simple modeling techniques are required. These techniques should be able to deal with all representative simple and complex interactions between stationary combustion sources and urban area plumes under various combinations of meteorological and topographical conditions conducive to high-level short-term concentrations of NO_2 .

The following five tasks are suggested as the necessary steps for proper application and adaptation of available empirico-mechanistic models and for systematic development of hybrid or any other new modeling techniques.

Screen Data from Air Quality Monitoring Stations for High-Level Short-Term Concentrations of NO_2 and Analyze Associated Causative Factors. Screen recent data on hourly ambient NO_2 concentrations from various sources such as SAROAD,²⁶ RAMS,²⁷ and electric utility monitoring networks for high-level NO_2 concentrations (above a certain level or percent exceedance). Analyze the following parameters associated with the identified high-level NO_2 concentration data for systematic identification and categorization of combinations of land use, topographical, and meteorological factors conducive to high-level short-term concentrations of NO_2 :

- Monitoring station location -- e.g., distance to urban centers and urban areas;
- Significance of emissions from area sources versus point sources;
- Topography -- e.g., basin, sea or lake shore, high terrain;
- Time of occurrence -- season, day of the week, hour of the day;
- Diurnal variations of air quality data during the days of high-level NO_2 concentrations -- NO_2 , NO_x , O_3 , SO_2 , CO , and HC , if available; and
- Diurnal variations of meteorological factors during the days of high-level NO_2 concentrations -- sunlight, temperature, wind, stability, inversion, mixing height, and fumigation potential.

Identify and Categorize Combinations of Causative Factors Conducive to High-Level Short-Term Concentrations of NO_2 . Based on the analysis of causative factors made in the first task, identify distinct sets of combinations of these factors (distance to urban centers and topographical and meteorological factors) for each category of emission sources (e.g., urban mobile source, electric utility point source, industrial park or residential heating source) implicated as being primarily responsible for the high-level short-term concentration of NO_2 . Categorize the sets according to various regions of the nation.

Analyze the Trend in Siting Pattern of New Stationary Combustion Sources. To provide guides for assuming the siting pattern of future new sources, identify recent trends in the size of new sources (e.g., sizes of power plant and industrial park) and their location (e.g., proximity to urban centers) for each of the electric utility, industry and residential heating emission source categories for various regions of the nation.

Classify Geopolitical Units According to the Combination of Causative Factors Conducive to High-Level Short-Term Concentrations of NO₂. Identify each AQCR with the combinations of land use (e.g., presence, size and major industry of urban areas); topography and other prominent surface features, meteorology and background air quality, etc., that are most favorable for causing each category of stationary combustion source to produce high-level short-term concentrations of NO₂.

Apply, Adapt, Develop, and Validate the Model. To accomplish the fifth task:

- Conduct an analysis of the short-term effect of NO₂ concentrations for each of the prototype (in terms of unit size, number, NO_x emission factor) stationary combustion sources (elevated electric utility point source, intermediate and low-level industrial and residential sources) under the frequently identified combinations of causative factors by applying available empirico-mechanistic model(s), either directly, with adaptations, or in combinations.
- Check the results of the above analysis using the predictions obtained by running a certain AQSM and/or monitored set of NO₂ concentrations and meteorological data.
- For future energy assessments, establish the most appropriate modeling approaches (available empirico-mechanistic models, with or without adaptation, or in hybrid form) for each category of stationary combustion sources under each combination of causative factors conducive to high-level short-term concentrations of NO₂.

5 SUMMARY AND CONCLUSIONS

The following paragraphs summarize information presented in the preceding sections and provide conclusions drawn therefrom:

1. Future U.S. coal production, the bulk of which will be consumed by stationary combustion sources such as electric utility and industrial boilers, is expected to increase rapidly. The increase in coal consumption is likely to result in increased atmospheric concentrations of NO_2 .

2. Assessments of the impact of short-term concentrations of NO_2 due to increased coal use and of the extent and pattern of potential constraints that may be imposed on coal use increases by a short-term air quality standard for NO_2 are needed for energy planning and for evaluation of alternative coal utilization policy. To perform the assessment tasks, appropriate air quality modeling techniques for NO_2 are required.

3. Ambient concentration of NO_2 at any given location and time in an airshed is the net result of three simultaneously occurring processes: emissions of precursors (NO_x and HC), physical processes of transport, dispersion and removal, and the chemical process of transformation. These causative processes are influenced by interrelated factors of land use, meteorology (solar radiation, temperature, wind, turbulence, etc.), and composition of the background air that vary in space and time with certain regularity associated with time of day, season, geographical location, and topography.

4. Analysis of monitored data for NO_2 and other air pollutants along with data on associated meteorology and land use (emission inventory) indicates that, for most high-level short-term concentrations of NO_2 recorded, a certain combination of prominent meteorological and emissions-related factors were identifiable. This observation suggests that certain factors less dominant or relevant under a given situation could be neglected or given a simplified treatment in modeling short-term concentrations of NO_2 .

5. The most detailed air quality models capable of accounting for the various characteristics of stationary combustion source categories and their interaction with existing urban air pollution problems are mechanistic or air quality simulation models (AQSM). However, practical consideration of the relatively high cost and common unavailability of necessary detailed input data precludes routine use of these models in a regional or national assessment study.

6. Simpler air quality models that may be applicable to NO_2 modeling analysis include empirical and empirico-mechanistic models. Empirical models based on assumed or statistically defined relationships between the precursor emissions and secondary pollutant concentrations may be used to assess the precursor control requirement for a given situation dominated by area sources. However, because of the lack of both spatial and temporal resolution, as well as any cause-effect relationships, this class of models cannot be utilized in situations with multiple sources including elevated point sources.

7. Empirico-mechanistic models attempt to relate the precursor emissions with the secondary pollutant concentrations by representing either one of the physical or the chemical processes with a cause-effect relationship and neglecting or providing a simplified treatment of the other and emission discrimination. Models based on the Gaussian concept providing detailed spatial resolution are appropriate for predicting short-term NO_2 concentrations due to emissions from various stationary combustion sources located in a rural or small city environment. In large urban areas where NO_2 precursors are primarily from widespread emissions from motor vehicles with chemical processes of transformation dominating, neglect of detailed spatial and temporal resolution may be tolerated to a certain extent. The empirical kinetic modeling approach (EKMA) is an empirico-mechanistic model developed for such situations.

8. When new stationary combustion sources are sited in a rural or small city environment separated by large distances from urban areas, currently available empirico-mechanistic modeling techniques appear to be adequate for predicting the short-term impact of NO_2 concentrations. However, if these sources are located within or near large urban areas, plume NO_x chemistry becomes more complex. Under these circumstances, existing empirico-mechanistic models may no longer be appropriate in many situations.

9. For proper application and adaptation of available empirico-mechanistic models and systematic development of hybrid or any other new modeling techniques for a regional or national energy assessment with respect to the short-term impact of NO_2 , the following tasks are suggested:

- Screen data on high-level short-term concentrations of NO_2 from air quality monitoring stations and analyze the associated causative factors.
- Categorize combinations of causative factors conducive to high-level short-term concentrations of NO_2 .
- Analyze recent trends in siting of new stationary combustion sources.
- Classify geopolitical units according to the combinations of causative factors conducive to high-level short-term concentrations of NO_2 .
- Establish appropriate modeling techniques by model application, adaptation, development, and validation for each category of stationary combustion sources under each combination of causative factors conducive to high-level short-term concentrations of NO_2 .

APPENDIX A

BACKGROUND INFORMATION ON THE SHORT-TERM STANDARDS
AND REGULATIONS FOR NITROGEN DIOXIDE

The Clean Air Act Amendments of 1977 (CAAA) require the administrator of the U.S. Environmental Protection Agency (EPA) to consider promulgation of a short-term average (over a period of not more than 3 hr) primary national ambient air quality standard (NAAQS) for NO_2 .²⁸ The EPA is currently revising the existing document on air quality criteria for nitrogen oxides (NO_x) that will provide the basis for determining the need for such a short-term primary standard for ambient NO_2 .³

The level that might be considered for a short-term primary NAAQS for NO_2 could be as low as $190\text{--}320\ \mu\text{g}/\text{m}^3$ ($0.10\text{--}0.17\ \text{ppm}$) for a maximum 1-hour exposure (not to be exceeded more than once per month), as recommended by a World Health Organization (WHO) Task Group on Environmental Health Criteria for NO_x .²⁹ When compared with the above range of concentrations recommended as an ambient standard, data on ambient air quality in the U.S. for 1975 and 1976 indicate that recurrent 1-hour NO_2 concentrations in excess of $250\ \mu\text{g}/\text{m}^3$ ($0.14\ \mu\text{g}/\text{m}^3$) were quite common throughout the country and that peak 1-hour concentrations equalling or even exceeding $750\ \mu\text{g}/\text{m}^3$ ($0.40\ \text{ppm}$) were measured in Los Angeles and several other California locations; Ashland, Kentucky; and Port Huron, Michigan.²⁹ Therefore, promulgation of a short-term NAAQS for NO_2 at a level comparable to the range recommended by the WHO group could severely limit the siting of new large stationary coal-burning facilities in or near areas where short-term concentrations of NO_2 are already high.

The CAAA also requires the administrator of EPA to promulgate regulations on the prevention of significant deterioration (PSD) of air quality for several air pollutants including NO_2 . In the case of pollutants for which NAAQS are promulgated after the date of the enactment of CAAA, the PSD regulations must be promulgated not more than two years after the date of promulgation of such standards. If a short-term NAAQS for NO_2 is promulgated in the near future, PSD regulations for short-term concentrations of NO_2 could be promulgated two years thereafter, which would increase existing constraints in the nation's capability to site new stationary coal-burning facilities.

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APPENDIX B

CHEMISTRY OF NITROGEN DIOXIDE IN THE LOWER ATMOSPHERE

The important chemical reactions that convert NO to NO₂ in the atmosphere include:

Oxidation of NO by ozone (O₃)

Oxidation of NO by peroxy radicals (RO₂• and HO₂•)

The reaction in Eq. 2-1 between NO and O₃ is a part of the NO/NO₂/O₃ cycle in air contaminated with NO_x only:

in which the dissociation of NO₂ by sunlight forms equal numbers of NO molecules and oxygen atoms (O). The latter are rapidly converted to O₃ molecules, which then react with NO again on a one-to-one basis to reform NO₂. Only a small steady-state concentration of O₃ results from this cycle.

The reactions in Eqs. 2-2 and 2-3 are part of the NO/NO₂/O₃ cycle in air contaminated with NO_x and reactive hydrocarbons (HC):

(2-5)

When HC or other reactive contaminants are present, they can form RO₂• and HO₂• that oxidize NO directly to NO₂, leaving very little NO to react with O₃, thus building up high O₃ concentrations.

Another chemical reaction that converts NO to NO₂ is the thermal reaction between NO and O₂ molecules:

(2-6)

The reaction in Eq. 2-6 is too slow to be significant at typical ambient NO concentrations. However, it can be important within stacks or immediately downwind where NO concentrations are greater than about 1 ppm.

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