

1. Nitrogen oxides in ambient air — properties, sources and concentrations

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Physical and chemical properties of nitrogen oxides

Chemically, nitrogen (N) can have seven different oxidation states: -3 (NH_3), -1, +1, +2, +3, +4 and +5. This possibility leads to the occurrence of several different nitrogen oxides in the ambient air: nitrous oxide (N_2O), nitric oxide (NO), dinitrogen trioxide (N_2O_3), nitrogen dioxide (NO_2), dinitrogen tetroxide (N_2O_4), nitrogen oxide (NO_3), and dinitrogen pentoxide (N_2O_5). NO, NO_2 and NO_3 are free radicals. Of these, NO and NO_2 are considered to be the most important in ambient air because they can be present in significant concentrations. The mixture of NO + NO_2 is usually called NO_x .

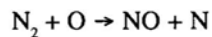
N_2O is a product of natural biological processes, but it is also formed in different combustion processes. N_2O is not generally considered to be an air pollutant of health concern. However, N_2O is a greenhouse gas and also takes part in chemical reactions involving the ozone layer in the stratosphere.

The other nitrogen oxides play a role in atmospheric chemical reactions, but they are present in very low concentrations.

Table 1.1 shows some important physical properties of nitrogen oxides under standard temperature and pressure (25°C and 1 atmosphere), and the figures for converting parts per billion (ppb) to micrograms per cubic meter ($\mu\text{g}\cdot\text{m}^{-3}$).

Nitric oxide

In combustion processes at elevated temperatures, NO is primarily formed as follows:



and

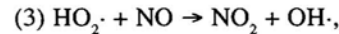
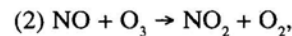
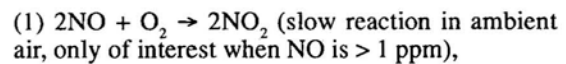


In general, NO accounts for about 85-95% of NO_x in ordinary combustion processes. At 500°C and above, NO_2 decomposes to NO.

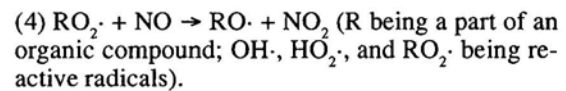
NO is primarily formed from the nitrogen in combustion air, but some fuels, such as coal and residual fuel oil, contain nitrogen compounds which are somewhat converted to nitrogen oxides. The formation of nitrogen oxides is favored by elevated temperature.

Nitrogen dioxide

In the atmosphere, NO can be oxidized by the following reactions and form NO_2 :

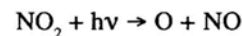


and



The last three reactions are fast, and reaction numbers 2 and 3 are the most important for the formation of NO_2 in ambient air.

NO_2 plays an important role in the formation of photochemical smog. By photolysis, NO_2 is converted to NO and atomic oxygen:



and

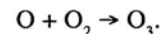


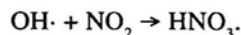
Table 1.1. Some physical properties of selected nitrogen oxides and conversion factors for these oxides.

Oxide	Molecular weight ($\text{g}\cdot\text{mol}^{-1}$)	Boiling point (°C)	Solubility in water (20°C) ($\text{cm}^3\cdot 100\text{ g}^{-1}$)	Conversion factor
NO	30.01	-152	7.34	1 ppb = 1.23 $\mu\text{g}\cdot\text{m}^{-3}$
NO_2	46.01	21.2	Reacts with water forming nitric and nitrous acid	1 ppb = 1.88 $\mu\text{g}\cdot\text{m}^{-3}$

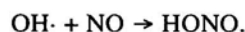
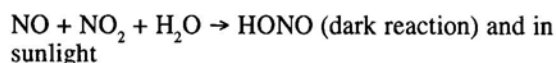
Reaction 4 contributes with the formation of new NO_2 and in this way to more ozone. In this manner volatile organic compounds (VOC) contribute to the formation of photochemical smog after they have been converted to peroxy radicals ($\text{RO}_2\cdot$).

Other nitrogen components of interest

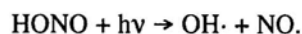
Nitric acid, HNO_3 , is formed by the following reaction:



Nitrous acid, HNO_2 , is formed by the following reaction:



During the day, atmospheric concentrations are limited by the reverse reaction:



Thus nitrous acid is an essential source of the important OH radical.

Sources, concentrations and trends in air quality

The most important sources of nitrogen oxides are transportation, combustion, and industrial processes. The emissions from different sectors and the total amount are shown in table 1.2 (1, 2). Road traffic contributes with 50% of the total emission of nitrogen oxides. A great part of the emissions, 30%, takes place in the three greater city areas in Sweden.

In Swedish cities, road traffic contributes with 70-80% of the local emission of nitrogen oxides. It has not been possible to reduce the emission of nitrogen oxides in the 1980s. Catalytic cleaning for passenger cars was introduced in 1989 and emission standards for heavy vehicles will be set in 1993. These measures will produce a greater effect in the 1990s.

Concentrations of NO_2 in Stockholm, Göteborg, and Malmö are shown in table 1.3, and concentrations in background air are presented in table 1.4 (3). The time trend for NO_2 concentrations is uncertain. The latest winters have been warm and windy. The measurements presented in table 1.3 are "above roof" concentrations (>20 m). In heavily trafficked streets the concentration can be 30-50% higher for NO_2 at street level than at roof level.

For Swedish cities in general, the winter means of NO_2 are around $10\text{--}40\text{ }\mu\text{g}\cdot\text{m}^{-3}$, the highest daily means are around $100\text{ }\mu\text{g}\cdot\text{m}^{-3}$, and the highest hourly

Table 1.2. Past, present and predicted future emissions of nitrogen oxides (t) in Sweden (with the current emission regulations).

Type of emission	Year			
	1970	1980	1988	2000
Combustion	90 000	96 000	64 800	63 000
Industrial processes		34 000	17 000	15 000
Transportation				
Road traffic	120 000	167 000	192 000	127 000
Shipping		23 000	33 000	45 000
Aircraft		10 000	11 000	17 000
Work vehicles		67 000	72 000	73 000
Railway		1 000	1 000	1 000
Total		398 000	390 000	341 000

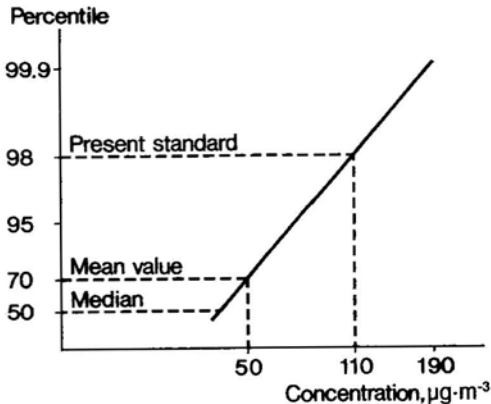
Table 1.3. Concentrations ($\mu\text{g}\cdot\text{m}^{-3}$) and trends for nitrogen dioxide (NO_2) in urban air at some selected places according to year of determination - winter mean (October-March *); central city; "above roof".

Stockholm			Göteborg			Malmö		
81/82	86/87	90/91	81/82	86/87	90/91	81/82	86/87	90/91
34	35	29	69	41	37	-	38	23

* The air quality standard for nitrogen dioxide is $50\text{ }\mu\text{g}\cdot\text{m}^{-3}$.

Table 1.4. Concentrations ($\mu\text{g}\cdot\text{m}^{-3}$) of nitrogen dioxide (NO_2) in background air (outside cities) - winter mean 1990-1991.

Western Sweden Rörvik (Göteborg)	Middle Sweden Aspvreten (Stockholm)	Southern Sweden Vävihill (Malmö)
11	5.7	10

**Figure 1.1.** Log-normal distribution for hourly values of nitrogen dioxide (NO_2).

values are around $250 \mu\text{g}\cdot\text{m}^{-3}$. These are "above roof" values. In streets with heavy traffic the values can be higher.

Concentrations of NO are not regularly reported, as there is no air quality standard for NO in Sweden. Measurements performed in Göteborg (4), shown in table 1.5, indicate that high concentrations can be recorded "above roof" ($>20 \text{ m}$).

Some methods used for determining nitrogen oxides

In principle, NO_x in ambient air can be determined in the following two ways:

- (1) use of continuous instruments which give short-time values, commonly mean hourly values;
- (2) sampling with simpler equipment (wet or dry methods) which give mean daily values, active or passive sampling.

Chemiluminescence (CLS) and differential optical absorption spectroscopy (DOAS) (5, 6) are the most common continuous techniques. Both can measure NO and NO_2 . The principal difference is that CLS is a point measurement method and that DOAS meas-

Table 1.5. Total concentration ($\mu\text{g}\cdot\text{m}^{-3}$) of nitrogen dioxide + nitric oxide (NO_x), concentration ($\mu\text{g}\cdot\text{m}^{-3}$) of nitrogen dioxide (NO_2), and nitric oxide (NO) in Göteborg - yearly mean "above roof".

	1990			1991		
	NO_x	NO_2	NO^a	NO_x	NO_2	NO^a
Mean value	52.9	26.1	17.5	53.0	29.4	23.6
Highest 24-h mean value	501	107	196	349	83	327
Highest 1-h mean value	1659	269	910	1177	213	1186

^a $\text{NO} = \text{NO}_x - \text{NO}_2$ in ppb, 1 ppb NO = $1.23 \mu\text{g}\cdot\text{m}^{-3}$, 1 ppb NO_2 = $1.88 \mu\text{g}\cdot\text{m}^{-3}$.

ures over a distance (500-1000 m) and records the mean concentration in the air in this path. For measurements "above roof" the methods give comparable results.

For 24-h measurements in ambient air, both wet and dry methods can be used. In the latter case, impregnated filters are used (5).

NO_x can be actively or passively sampled. Active sampling requires a pump to obtain a flow of air through the collection media. Active samplers are suitable for continuous and long-term studies, and they are also more sensitive than passive samplers due to the larger volume of air sampled. Passive sampling is based on molecular diffusion and the trapping of NO_2 on collection media (no power supply needed). Passive samplers must have high sensitivity and low blank values, since smaller amounts of air are sampled than with active methods. The sampling rate of the passive sampler is affected by wind velocity, temperature, and relative humidity. (See also chapter 2.)

Relations between 1-h, 24-h and long-term mean values

Concentrations of air pollutants generally fit a log-normal distribution; for example, the logarithm for the cumulative frequency of concentration against the logarithm of concentration will generally give a straight line (figure 1.1) (7).

Accordingly the relations presented in table 1.6 can be calculated for NO_2 (8). For example, if the winter mean is $40 \mu\text{g}\cdot\text{m}^{-3}$, the 98th percentile for 1-h mean values will be $88 \mu\text{g}\cdot\text{m}^{-3}$.

Percentiles are a statistical concept to indicate that the levels should lie below a given value for a given portion of the time. The 98th percentile for 1-h means that the standard value should not be exceeded by more than 88 h per half year, while for the 24-h mean

Table 1.6. Relations between the 1-h mean, the 24 h mean and the corresponding percentile values (in $\mu\text{g}\cdot\text{m}^{-3}$).

Mean value period	Percentile			
	70	95	98	99.9
1 h	50	90	110	190
24 h	50	70	75	100

Table 1.7. Air quality standards and guidelines for nitrogen dioxide (NO_2 in $\mu\text{g}\cdot\text{m}^{-3}$) in Sweden, the European Economic Community (EEC), the United States (US) (those of the Environmental Protection Agency), and the World Health Organization (WHO) for Europe.

	Sweden (standard value)	EEC (limit/guide values)	US EPA (limit value)	WHO Europe (guideline value)
1-h mean	110 ^a	200 ^b 135 ^c		400
24-h mean	75 ^a			150
Winter, six months	50 ^d			
1-year mean		50 ^e	100	

^a 98th percentile for the winter half of the year.^b 98th percentile for one year, limit value.^c 98th percentile for one year, guide value.^d Arithmetic mean value.^e 50th percentile (geometric mean) for 1-h mean values during one year.

value they should not be exceeded by more than 4 d per half year.

Atmospheric chemistry and dispersion models

The use of atmospheric models has become more and more important. Today, there are models for use at the street (9), city (10, 11), and regional (12) level. The models are more or less sophisticated. Many use the Gaussian theory concerning dispersion, and they are useful for the components that do not undergo transformation in the atmosphere.

Models have been developed that include chemical transformation and the formation of photochemical oxidants (13). Research is in progress to improve these photochemical models.

Once developed, an atmospheric model has to be verified against measured data.

After air pollutants have been emitted, different things happen. Part is removed from the atmosphere by wet or dry processes (14). The wet deposition depends on the solubility of the component in rain, and the dry deposition on the ability of the component to adhere to vegetation, ground, and sea.

While in transport, air pollution components can undergo transformation to other substances. The degree of transformation depends on the air temperature, the intensity of sunlight, the humidity, the transport range, and the like. Many components have long half-lives, whereas others have very short half-lives, depending on the chemical stability.

The emission of nitrogen oxides can exemplify the complexity of these processes (15). Mainly wet and dry deposition takes place only after NO_x has been converted to nitric acid (HNO_3). The deposition rates for NO and NO_2 are very low.

Together with hydrocarbons, nitrogen oxides can form photochemical oxidants (eg, ozone), and there is chemical equilibrium between NO, NO_2 , and ozone. The photochemical processes involved in the formation of photochemical oxidants are extremely important to air chemistry. They degrade organic compounds. New organic compounds are formed, perhaps with more serious effects than those caused by the original compounds.

Fixed stations versus personal samplers

In principle, exposure doses can be calculated from measured or calculated air concentrations in a grid over a city. For components with long-term effects, the mean value for a year can be sufficient. For substances like nitrogen oxides, ozone, and sulfur dioxide with acute effects, there must be better resolution (eg, 1-h or 24-h mean values).

Data from fixed stations or data calculated with models seem to give yearly means similar to those obtained with the use of personal samplers, but they over- or underestimate the doses for certain groups of people (upper and lower quartile) for short-term values (16). See also chapter 2.

The use of personal samplers is a promising method (17) for NO_2 . Research is in progress to develop passive samplers for NO.

Air quality guidelines and standards for nitrogen dioxide

The air quality standards and guidelines for Sweden (8), the European Economic Community (18), the United States (19), and the World Health Organization for Europe (20) are shown in table 1.7.

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