NITROGEN OXIDES (NO-NO_2)

What is NOx? Where, when and how is it formed? What are its dangers? Are NO_2 emissions regulated? How can we get rid of it? What is the warning threshold for NO pollution? Here are some answers.

What is NOx?

NOx sometimes refers to nitric oxide (NO), a colorless gas, sometimes refers to nitrogen dioxide (NO_2), a red gas. Nitric oxide (NO) is a short-lived gas, it instantly changes to nitrogen dioxide (NO_2) by contact with oxygen (O_2) in the air.

NO_2 is the chemical symbol of the nitrogen dioxide molecule. This molecule consists of a nitrogen atom (chemical symbol N) and two oxygen atoms (chemical symbol O).

What are the dangers of NO_2 ?

Four strong reasons to consider NO2 as a powerful pollutant:

- NO_2 is an irritating toxic and stiffing gas, so it is a real danger for living beings.

- NO_2 is a greenhouse gas with a warming power per unit mass much higher than that of carbon dioxide (CO_2).

- NO_2 is a precursor of ozone (O_3), a powerful irritating gas which is formed spontaneously in the air in the presence of NO-NO_2 by mutation of atmospheric oxygen (O_2).

- NO2 is not biodegradable; once in the atmosphere and by mixing with water vapor, it can turn into nitric acid (HNO_3) at the origin of acid rain that dissolves vegetation, stone and concrete.

What is the NO2 pollution threshold?

Air quality in large cities has become a constant concern. In Ile-de-France (the 1st region of France with 11 million inhabitants) this quality is constantly monitored by about fifty sensors, including ten in Paris intramural.

These sensors measure the concentration in air of major pollutants such as nitrogen dioxide (NO_2), ozone (O_3), sulfur dioxide (SO_2) and particles (PM).

There are two levels of nitrogen dioxide pollution: the alert threshold which is a concentration of 200 micrograms (2×10^{-7} kg) of NO_2 per cubic meter of air, the danger threshold being set at 400 micrograms (4×10^{-7} kg) of NO_2 per cubic meter of air.

The alert threshold is like the presence of a single gram of NO_2 in a volume equivalent to that of a five-storey building!

The danger threshold leads to a systematic 5 mph reduction in speed limits applicable outside built-up areas.

The nitrogen dioxide alert leads to a 10 mph reduction in speed limits applicable outside built-up areas, but traffic restrictions or outright bans can be imposed in case of persistent pollution.

What is the pollution threshold for ozone?

There are two levels of ozone pollution: the alert threshold which is a concentration of 180 micrograms (1.8×10^{-7} kg) of O_3 per cubic meter of air, the danger threshold being set at 360 micrograms (3.6×10^{-7} kg) of O_3 per cubic meter of air.

Given the correlation between nitric oxide (NO) emissions and the ozone pollution, the ozone warning threshold is usually reached first.

Ozone pollution leads to the same measures as for nitrogen dioxide.

How is NO-NO_2 formed by automobile engines?

The transport sector is responsible for more than half of total NO-NO_2 emissions to the atmosphere. Indeed, it is formed during the combustion of any fuel under conditions of high pressure and high temperature, by reaction of the components of the air that are oxygen (O_2) and nitrogen (N_2).

The quantities emitted are very variable, they depend on many factors: the driving style of course, but especially the type of vehicle, its engine type, its fuel, the traffic conditions and atmospheric conditions.

It is assumed that diesel engines emit on average 4 times more nitric oxide or nitrogen dioxide than gasoline engines of the same category, because of the large volume of air introduced into the cylinders at the intake (supercharging) and the strong compression rate inherent in this type of engine.

It has also been found that, whatever the engines, these discharges increase significantly in urban traffic, especially in traffic jams, and more particularly in periods of high heat or strong sunshine.

About NO_2 regulations

The first anti-pollution regulations enacted in France date from 1972 and only concerned the carbon monoxide (CO) emissions measured at stop. Since then, the anti-pollution standards evolve regularly according to the requirements of the environment and the technological progress of the engines, they now apply to all the European countries (norms EURO).

Contrary to the American legislation which does not take into account the engine type, the EURO standard for cars makes a distinction between gasoline and diesel fuel, particularly with regard to emissions of NO_2:

passenger cars	EURO IV (2005)	EURO V (2009)	EURO VI (2014)
gasoline	0.06 g/km	0.06 g/km	0.06 g/km
diesel	0.25 g/km	0.18 g/km	0.08 g/km

The EURO standard for industrial vehicles takes into account the energy produced, so as not to penalize large trucks:

industrial vehicles	EURO IV (2005)	EURO V (2009)	EURO VI (2014)
(trucks, bus…)	3.5 g/kWh	2 g/kWh	0.4 g/kWh

How to interpret this standard? A modern truck (*) traveling at a constant speed of 55 mph (25 $m.s^{-1}$) on a horizontal road must develop a power of about 115 kW and therefore produce an energy of about 115 kWh (**) to travel 55 miles.

Under these conditions, the maximum emission of 2.55 grams of NO_2 per kilometer was reduced to 0.51 grams of NO_2 per kilometer in 2014, it is still enough to pollute a volume equivalent to that of a five-storey building in less than 2 kilometers and in less than 2 minutes. But this is a limitation, we hope that the best will do better...

How can we get rid of NO_2?

Since NO_2 is not biodegradable, the source must be removed or, where this is not possible, work to reduce it, in the chemical sense of the term.

Only two technologies are able to reduce the quantities of nitrogen oxides emitted by the engines:

- EGR valve (*Exhaust Gas Recirculation*), a primitive technique that consists in reintroducing the exhaust gases to the intake in order to reduce the nitrogen dioxide by the combustion of an excess of fuel. This process is based on the affinities between the oxygen of the pollutant (O_2 of the molecule NO_2) and the hydrogen of the fuel (H of the molecule HC). The reaction produces carbon dioxide (CO_2), water vapor (H_2O), nitrogen gas which is a non-toxic gas (N_2) and carbon (C) as particles.

- SCR technology (*Selective Catalyst Reduction*), currently the most successful technique of reducing the nitrogen dioxide in the exhaust gas, through a chemical reaction by a catalyst. This process is based on the affinities between the oxygen of the pollutant (O_2 of the molecule NO_2) and the hydrogen of the additive (H_3 of the molecule NH_3). A catalyst has the function of lowering the energy required for a reaction.

In addition to its significantly higher manufacturing cost, this technology has the disadvantage of having to operate with an ammonia-based additive (NH_3) stored in an independent tank. For the sake of convenience and safety, this additive is not pure ammonia but a dilute preparation based on urea [(NH_2) 2CO] marketed under the trademark AdBlue® in Europe, under the acronym DEF (*Diesel Exhaust Fluid*) in the United States.

The additive is injected directly into the exhaust line, upstream of the catalyst. The reaction reduces nitrogen dioxide (NO_2) to carbon dioxide (CO_2), gaseous nitrogen (N_2) and water vapor (H_2O) which are harmless (***). To treat 1 gram of nitrogen dioxide requires 1.3 grams of pure additive. The reaction produces about 1 gram of carbon dioxide (CO_2), 0.9 gram of nitrogen gas (N_2) and 0.8 gram of water vapor (H_2O).

To produce carbon dioxide to get rid of nitrogen dioxide, is that not contradictory? The dangerousness of nitrogen dioxide being proven, it means that between two evils, it is better to choose the least. Diesel enthusiasts will have to do it: with the lowering of the imposed thresholds, SCR technology, a time reserved for trucks, has become compulsory since 2014 for all new cars destined for the European market.

(*) *Characteristics of the truck: frontal surface 10 m²; drag coefficient 0.9; chassis mounted on 12 wheels and tires each supporting an average load of 3.3 tons and generating a rolling resistance of 25 N / t.*

(**) *The kilowattheure (symbol kWh) is an energy unit: 1 kWh = 3.6 MJ.*

(***) *Carbon dioxide is not toxic, but it is a greenhouse gas (see ADILCA file "Carbon Dioxide"). Nitrogen gas, also known as nitrogen (to distinguish it from the nitrogen element), is the major component of ambient air (76% by mass).*

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CHEMICAL REACTIONS

Atoms molar mass (g.mol^{-1}):

hydrogen (**H**): 1
carbon (**C**): 12
nitrogen (**N**): 14
oxygen (**O**): 16

Nitric oxide formation:

$$N_2 + O_2 \rightarrow 2\ NO$$

N_2: nitrogen
O_2: oxygen
NO : nitric oxide

Nitric dioxide formation:

$$2\ NO + O_2 \rightarrow 2\ NO_2$$

NO: nitric oxide
O_2: oxygen
NO_2: nitrogen dioxide

Ozone formation:

$$3\ O_2 \rightarrow 2\ O_3$$

O_2: oxygen
O_3: ozone

Reduction of nitrogen dioxide by excess fuel:

$$26\ NO_2 + 4\ C_{7.25}H_{13} \rightarrow 13\ CO_2 + 26\ H_2O + 13\ N_2 + 16\ C$$

NO_2: nitrogen dioxide
$C_{7.25}H_{13}$: diesel fuel
CO_2: carbon dioxide
H_2O: water
N_2: nitrogen
C: carbon

By referring to the molar mass of each element of this reaction, one obtains the following proportions:

1,196 g of nitrogen dioxide + 400 g of diesel fuel
$\rightarrow$
572 g of carbon dioxide + 468 g of water + 364 g of nitrogen + 192 g of carbon

Reduction of nitrogen dioxide by ammonia:

$$6\ NO_2 + 8\ NH_3 \rightarrow 12\ H_2O + 7\ N_2$$

NO_2: nitrogen dioxide
NH_3: ammonia
H_2O: water
N_2: nitrogen

By referring to the molar mass of each element of this reaction, one obtains the following proportions:

276 g of nitrogen dioxide + 136 g of ammonia $\rightarrow$ 216 g of water + 196 g of nitrogen

Reduction of nitrogen dioxide by AdBlue® (Diesel Exhaust Fluid):

$$2\ NO_2 + 2\ [(NH_2)_2CO] + O_2 \rightarrow 2\ CO_2 + 3\ N_2 + 4\ H_2O$$

NO_2: nitrogen dioxide
$(NH_2)_2CO$: AdBlue® (Diesel Exhaust Fluid)
O_2: oxygen
CO_2: carbon dioxide
N_2: nitrogen
H_2O: water

By referring to the molar mass of each element of this reaction, one obtains the following proportions:

92 g of nitrogen dioxide + 120 g of pure AdBlue® (DEF) + 32 g of oxygen
$\rightarrow$
88 g of carbon dioxide + 84 g of nitrogen + 72 g of water

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