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## How to select efficient diesel exhaust emissions control strategies for meeting air quality targets in 2010?

### Background

During the past decade, a proliferation of medical studies have pointed out key roles of particulates (PM) and nitrogen oxides (NO<sub>x</sub>) emissions from vehicles powered by diesel engines. PM exposition health effects were associated with PM direct actions while NO<sub>x</sub> were not estimated dangerous for their direct impact, but through their potential chemical reactivity in atmosphere to form ozone with support of intense energy from sun light. Atmospheric chemistry at various distances above the ground and in various climatic conditions is extraordinary complex and involves a lot of variable parameters; but public and legislators needs information expressed as “digest” messages for an efficient communication. This ended to an extreme simplification of the messages about exposure risks in the two following equations

$$\begin{aligned} \text{PM (solid)} &= \text{inflammation of lung tissues} \Rightarrow \text{lung cancer} \\ &\quad \& \\ \text{NO}_x + \text{VOC (*)} + \text{sun} + \text{O}_2 &\Rightarrow \text{O}_3 = \text{lung functions deterioration} \end{aligned}$$

(\*) *VOC = volatile organic compounds*

As lung cancer appeared rapidly being not sufficient to explain all consequences associated with PM exposure, especially mortality and mortality occurring immediately after peaks of PM emissions, the equation for PM was modified to an extremely confusing equation

$$\text{PM (coarse)} + \text{PM (fine and ultra fine)} = \text{lung cancer} + \text{other acute effects}$$

Both sides of the equation are in fact complex matrixes with plenty of parameters and nobody has been able so far to weigh up contributions of each of these parameters. Therefore communication with the public ended to be a very simple and efficient formula:

**“PM are bad for your health”.**

This message is indeed not sufficient to elaborate strategies for diesel exhaust emissions for improving air quality as it addresses all sources of PM and as diesel powered transport traffic represents only about one quart of the total PM<sub>10</sub> present in cities atmospheres.

When looking at nitrogen oxides, careful observers will be surprised by the fact that air quality recommended by WHO (World Health Organization) [1] or enforced by EU Directive 1999/CE/30 are targeting mainly NO<sub>2</sub> and ozone, without mention of NO, while vehicle emissions (in USA, Europe and Japan) are expressed only in NO<sub>x</sub> (implying precursor of O<sub>3</sub>). NO<sub>x</sub> are a complex mixture of diverse oxides of nitrogen, mainly NO and NO<sub>2</sub> in proportions varying with engine types and their operating conditions, nature of the exhaust control devices and measuring protocols. NO<sub>x</sub> as a whole family is said to be easy to measure, as well as NO alone, which leads to express NO<sub>2</sub> by calculation according to equation  $\text{NO}_x - \text{NO} = \text{NO}_2$ .

This leads obviously only to an approximation. It is well known today that nitrogen protoxide - N<sub>2</sub>O - (laughing gas) is a very critical molecule for greenhouse effects, it is part of the NO<sub>x</sub> but is also measured for itself to keep its formation under control through some emission control devices (TWC for gasoline engines).

Direct measurement of NO<sub>2</sub> is more complex than it seems as CVS (dilution tunnel) and chemo-luminescence introduce a lot of artefacts leading sometimes to quite important underestimations, which, by the way, impact a lot the measured values of NO<sub>x</sub> at tailpipe [2]

| Part of procedure   | Option   | Remarks  | Suitable?   |
|---------------------|--|--|---|
| Sampling method     | Bag  | long delay before analysis-<br>>conversion NO->NO <sub>2</sub> | No  |
|                     | Diluted online   | effect of dilution air   | No  |
|                     | Raw online   |  | Yes   |
|                     | Mini-dilution  | no experience  | ??  |
| Sample conditioning | heated lines   |  | Yes   |
|                     | dehumidifier (wet/dry)                                 | wet; washing NO <sub>2</sub> /NH <sub>3</sub>                  | dry Yes<br>wet No   |
| Analysis            | Chemiluminescence with NO <sub>x</sub> to NO converter | SCR reaction with NH <sub>3</sub> ?                            | Yes. But possible underestimation in case of NH <sub>3</sub> emission   |
|                     | Chemical mass ionisation Spectrometry (CMIS)           | kalibration, speed   | Yes   |
|                     | FTIR   | Widely used in UK emission measurement programmes              | Yes. This technique offers a direct measurement of NO <sub>2</sub> . Interferences with other compounds needs to be investigated. |
|                     | NDUV<br>Non-dispersive Ultra Violet                    | EPA approved   | Yes   |

Table 1: the proper way to measure NO<sub>2</sub> emitted at tail pipe(TNO)

Looking back in the 80s, there are some facts helping to understand why NO<sub>2</sub> was not measured in tailpipe emissions:

- 1- When emissions limits were first established, NO<sub>2</sub>/NO<sub>x</sub> ratio was quite stable for diesel engines and averaged at a maximum of 5% over most of legal test driving cycles.
- 2- NO ↔ NO<sub>2</sub> equilibrium is subject to quick changes in the storage bags or in lines of the measuring devices => bad repeatability between measures of individual species
- 3- NO is not at a stable state of oxidation and will transform itself in NO<sub>2</sub> and other nitrogen species in atmosphere, the end of the transformation being ozone [3] Fig1; as it was estimated that ozone was the only critical gaseous specie, it was believed that NO was indirectly as dangerous as NO<sub>2</sub> was directly; NO and NO<sub>2</sub> were considered only progressive steps in ozone production

## **Is there a need, nowadays, to reconsider the message about NO<sub>x</sub> impacts?**

Answer to this question is that this need exists since the introduction of DOCs in diesel exhaust lines, but industries and regulators were so much focused on PM and NO<sub>x</sub> reductions that they forgot to keep an eye on NO<sub>2</sub>. In addition they did not get any help from the chemists of atmosphere and persons in charge of air quality strategy who continued to use in their models the 5% ratio, even when it was no more valid. This lack of continued validity was known from certain institutes, but there was officially no urgent care for checking the variations. It is true to say that it would have represented a complete readjustment of models used to communicate with decision makers.

It is useless to try now to identify who should take responsibility for this lack of vigilance during past decades, but better to list the facts which justify an urgent action to avoid further deterioration:

- 1- the today priority is to look more at limits of populations exposure to NO<sub>2</sub> than at limits of vehicles emissions, in other words emissions control is only a mean for keeping under control exposures of population to poisonous pollutants; human beings, as well as animals and vegetation, are not directly exposed to vehicles emissions but inhale an air which is modified by emissions and their combinations with other air components. This concept was well established for years to explain health impacts of ozone but today air regulators are focussing on local air quality instead of the famous “background” air quality that so few people actually inhale. Local air contains indeed the background air but with addition of the primary emissions from the vicinity, which are not yet dispersed in atmosphere. In case of NO<sub>2</sub>, dispersion is more difficult as NO<sub>2</sub> is denser than oxygen and tends to be stagnant in non ventilated areas such as city canyon streets.
- 2- Before the introduction of rules to regulate NO<sub>x</sub> emitted by vehicle, NO<sub>2</sub> direct exposure was already regulated; it was produced in large quantities by industries and power generators implemented in the vicinity of agglomeration. Most of these industries were moved away or their chimneys were fitted with equipments to eliminate NO<sub>2</sub>; this gaseous pollutant is nowadays mainly produced by diesels engines - traffic or stationary – (outdoor air) or by heating/cooking devices which burn natural gas (indoor air).
- 3- In cities and on highways, NO<sub>x</sub> exposures were progressively and nicely reduced and are today at about half the level they were 20 years ago; this is considered as a success of the policy of reducing nitrogen oxides, but NO<sub>2</sub> never decreased and remained stable until 1999-2000; from 2000, it started to increase over highways and large traffic roads in city centres [4, 5].
- 4- Some scientists in epidemiology have revisited previous studies designed to evaluate PM impacts and they have found that NO<sub>2</sub> is not only a marker of diesel traffic but has its own impact on mortality and morbidity. It remains difficult to determine which pollutant (PM or NO<sub>2</sub>) is a confounding factor of the other one. But recent series of calculation within European APHEA2 study (30 cities representing altogether about 60 million inhabitants) have established that for a same level of PM, mortality and morbidity increase significantly with higher exposures to NO<sub>2</sub>. Most recent published results tell that peaks of NO<sub>2</sub> have an impact which is similar to peaks of PM [6, 7].
- 5- Some of the very efficient technologies for removing soot and most of less efficient ones are transforming a large portion (>50%) of NO in NO<sub>2</sub> in the tailpipe, emitting the toxic gas at ground level as a primary emission [2].



## DISCUSSION

### 1- It is essential to curtail NO<sub>2</sub> for achieving Air Quality as regulated by Directive 1999/30/CE

This directive was adopted roughly at the same time as Euro4 for cars and Euro4/5 for HD. Following guidelines of WHO [1], EU Council and Parliament ruled out that PM and NO<sub>2</sub> have to be controlled in air, in order to limit exposures of populations. This directive has been ratified by most of EU members and the values of exposure are the national values.

The same directive introduced the concept that nowhere exposures should exceed the limits defined for 1-day average exposure (PM<sub>10</sub>), 1-hour average exposure (NO<sub>2</sub>) and 1-year average exposure (PM & NO<sub>2</sub>). This measure was evidently targeting mainly PM exposure from traffic, which is at its maximum around roads with high traffic density, but has generated a collateral effect due to some PM abatement strategies which cause a significant increase of NO<sub>2</sub> in the same microenvironment. Without street level (or curb side) monitoring stations giving alarming messages, this article would certainly not exist.

The specificity of street level and nearby exposure lies in the fact that equilibrium of the complex atmospheric chemistry is not yet attained and the famous “background” air quality is far from being what huge populations inhale. High traffic density means that at least a large quantity of drivers, passengers of any type of road-level transportations (including cyclists and users of bus or trams) and pedestrians, close to street inhabitants, commerce dealers and office clerks are exposed to a mixture of the background air with primary emissions. A CARB-sponsored study achieved in 2003 [11] demonstrated that a standard employee, living inside Los Angeles area, has to drive at least one hour per day; during this time she (or he) is getting 50% of its daily exposure to PM and nitrogen oxides. (Fig. 2)

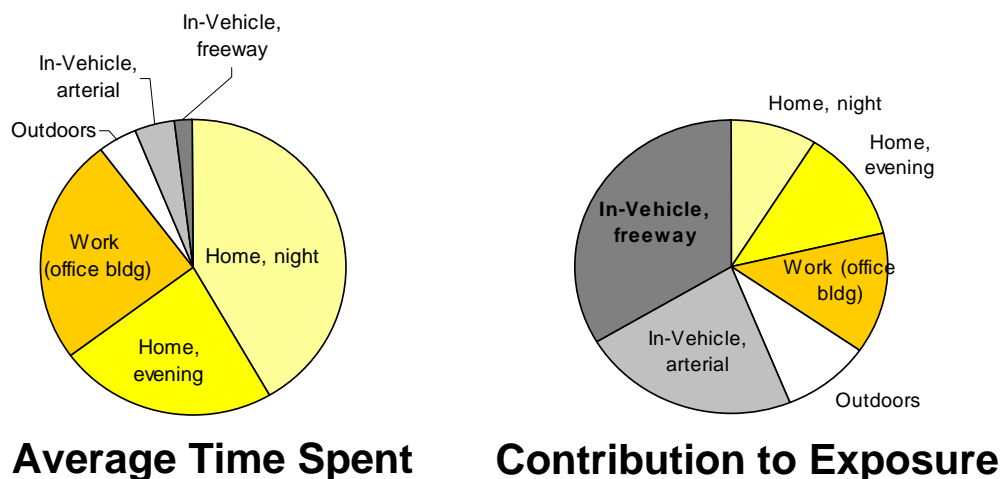


Figure 2: More than 55% of a daily exposure to NO<sub>x</sub> corresponds to driving time of an average Los Angeles commuter (CARB)

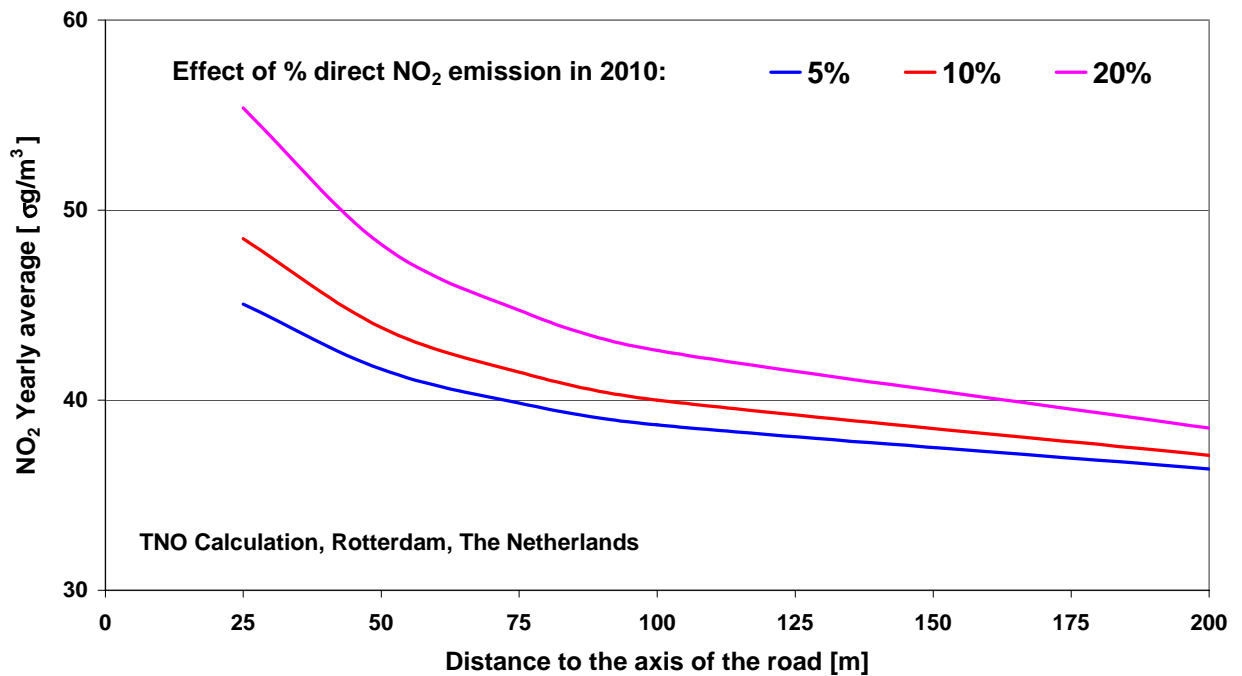


Figure 3: How NO<sub>2</sub>/NO<sub>x</sub> ratio impacts on possibility to reach legal annual value of 40 $\mu\text{g}/\text{m}^3$

Looking now specifically at NO<sub>2</sub>, a very interesting model calculation was introduced by TNO-Automotive at Transport and Pollution Symposium 2004 in Boulder (Colorado) [12]. This calculation shows (Fig.3) that a high traffic road leads population within 75 meters distance to be overexposed (above the annual mean value level of exposure) when the “historical” ratio of NO<sub>2</sub>/NO<sub>x</sub> of 5% was applied. When mass ratio of 20% is applied this contaminated zone will increase to around 170 meters. It is important to keep in mind that the absolute value of this mass ratio is higher than the commonly used volume ratio as NO<sub>2</sub> has a density 1.5 times higher than NO. Volume ratios higher than 20% are commonly measured in high traffic streets in European cities. London and Stuttgart are “references” because they are under observation in programs operated by recognized institutes such as ITS-Leeds and IFEU-Heidelberg, but similar values are reported from many other cities. (Fig. 4 & 5)

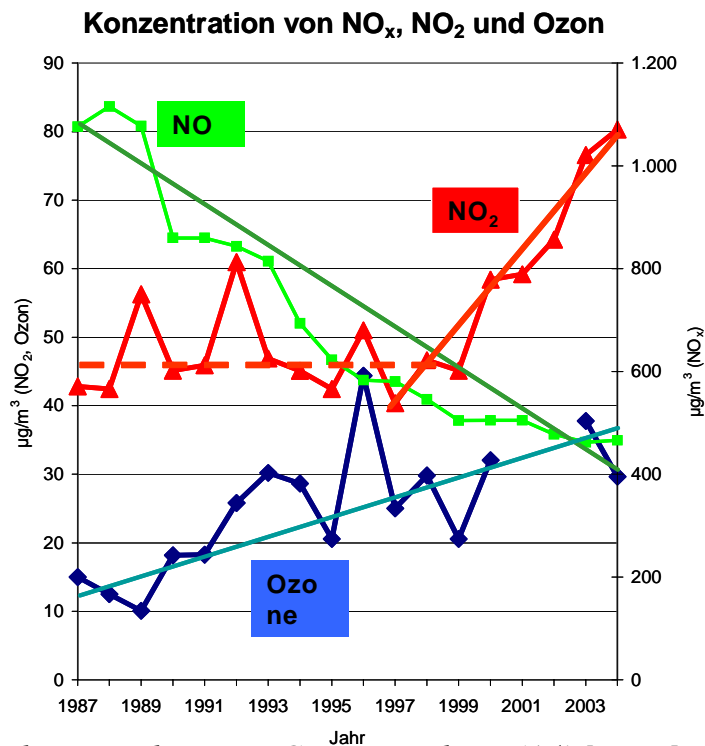


Figure 4: Evolution of oxidants in the atmosphere on a German Highway (A4) [IFEU]

Fig. 4 represents the measurement of diverse gaseous pollutants with a monitoring station installed on the central reservation of a German highway [4]. It is clear that NO has been decreasing from 1990 in a regular manner, but this reduction was without any effect on NO<sub>2</sub> until 1999 and was accompanied by a severe deterioration of NO<sub>2</sub> after 2000. Fig 5 is about the number of exceedances of the legal limit for 1-hr maximum exposure (200 µg/m<sup>3</sup>) in a central London location. In 2010 this number will be less than 18 times per year. Main contributor to these too high frequency events is primary NO<sub>2</sub>.

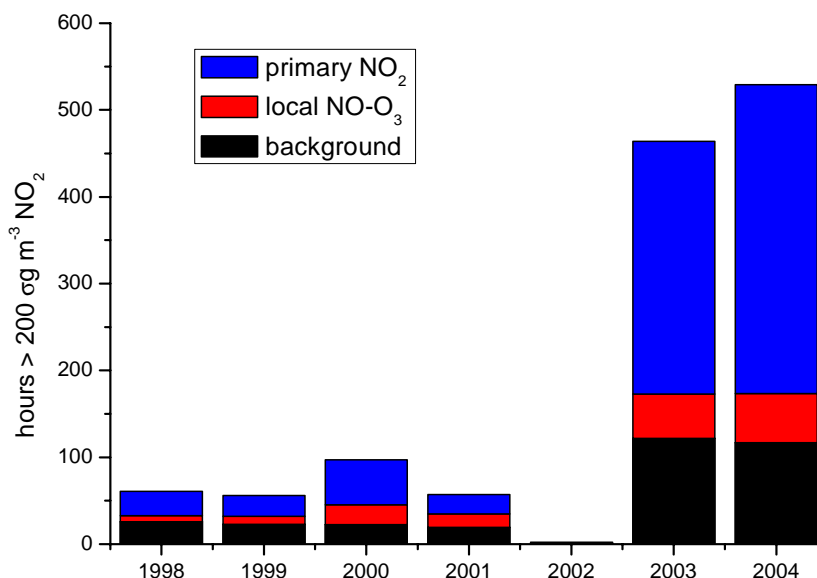


Figure 5: number of exceedances of 1-hour maximum exposure (should be 18 in 2010) [ITS]

## 2- Main changes in exposure risks are due to primary emissions from vehicles exhausts

Current monitoring networks in many cities are not able to detect variations at curb side, just because the first monitoring stations (and still a large majority of existing ones) were (and still are) installed at roofs level to measure the pollution falling down from industrial chimneys (those being older than 40 have certainly seen the brown plume pouring down from coal- or oil-burning power plants chimneys while the white cloud of water steam was climbing in the sky to join its brother clouds). NO<sub>2</sub> is notably denser than oxygen and NO.

| GAS                                | Weight per unit of volume at 15°C<br>g/l at 1013 hPa |
|------------------------------------|--|
| Nitrogen – N <sub>2</sub>          | 1.185  |
| Oxygen – O <sub>2</sub>            | 1.354  |
| Ozone – O <sub>3</sub>             | 2.141  |
| Nitric oxide - NO                  | 1.270  |
| Nitrogen dioxide – NO <sub>2</sub> | 1.947  |

Table 2 Weight per unit of volume (data from Elsevier Handbook)

These stations were remarkably efficient in detecting industrial abuses but are nowadays helpless for detecting excesses in vehicles primary emissions, especially when these emissions are so dense that only winds and rain can disperse or dilute them. They remain still very valid for detecting ozone, which is even denser than NO<sub>2</sub>; mainly produced in higher atmospheric levels, ozone fall down to ground levels. But it would also be important to know actual ozone concentrations at ground levels, where ozone falling down from higher levels is mixed with freshly emitted NO and NO<sub>2</sub>; this situation is likely to provoke changes in the chemical equilibrium within the pollutants soup.

**3- Decreasing NOx levels in urban environment are absolutely not accompanied by a reduction of NO<sub>2</sub>, it's even the contrary which currently occurs**

Reports on Air Quality (AQ) published European Commission (EC), auto-industry and some member states governments before 2005 were quite triumphalist when speaking of the noticeable reduction of NOx in urban cities during the past five years. This is quite symptomatic of the prevalence taken by emissions criteria over exposure (AQ) criteria. AQ is not focused on NOx as a whole family but specifically on NO<sub>2</sub>. This is quite similar to a parent checking the temperature of the bath water in order to check if his baby has fever. There is no doubt that automobile and catalyst industry were impressively successful for reducing NO, the major component of NOx, but what about NO<sub>2</sub>, which is the true concern when AQ is considered?

**Directive 1999/30/CE on Air Quality  
NO<sub>2</sub> or its part in NOx**

| Averaging period                              | Limit value                                      | Attainment target |
|---|--|-------------------|
| Nitrogen dioxide - 1h                         | 200 µg/m <sup>3</sup><br>18 exceedances per year | 1 January 2010    |
| Nitrogen dioxide – 1 year                     | 40 µg/m <sup>3</sup>                             | 1 January 2010    |
| NOx (expressed as their NO <sub>2</sub> part) | 30 µg/m <sup>3</sup> (protection of vegetation)  | 1 January 2010    |

Thanks to implementation of AQ Directive 1999/30/CE in 2004, reports had to be sent, each year, to Commission about poisonous pollutants listed in the Directive. End of 2005, after collecting enough of these reports, it became obvious that there was a growing and huge problem of NO<sub>2</sub>; some analysts immediately understood that a further reduction of NOx will not be sufficient to curtail NO<sub>2</sub> emissions and service contracts and workshops are organized in urgency.

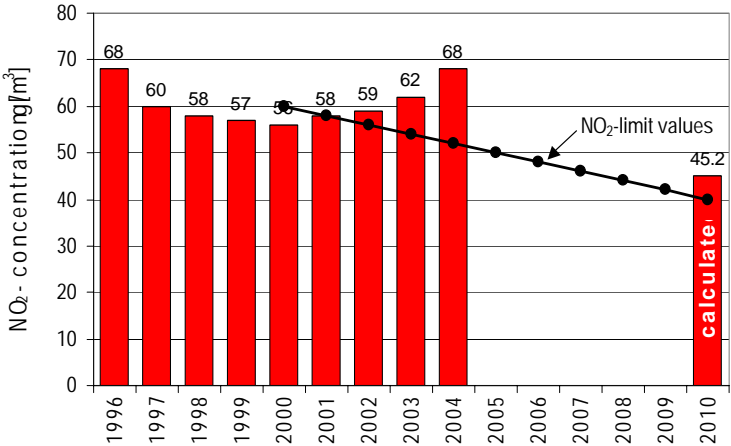


Figure 6: Situation in Düsseldorf Cornelius Strasse; divergence between model and reality [13]

A limited selection of figures (Fig. 6, 7, 8) published in different presentation of IFEU (Institute for Environment and Energy Research in Heidelberg Germany) and of some other German Institutes gives a quite robust documentation of the problem [14, 15 & 16].

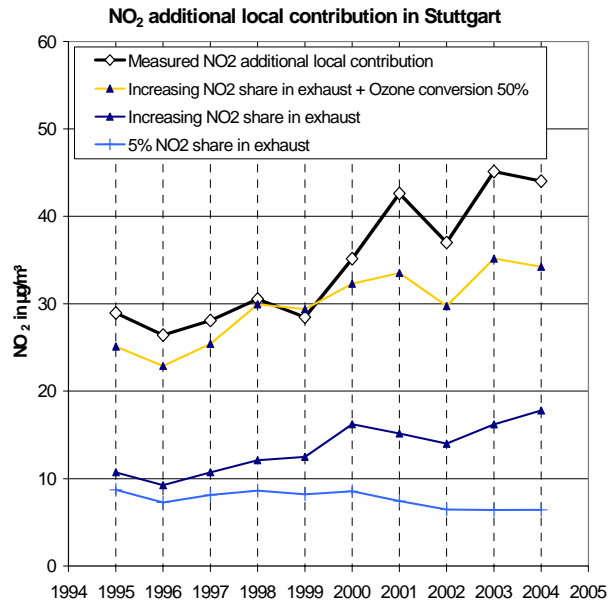


Figure 7: Additional NO<sub>2</sub> emissions coming from different origins (IFEU)

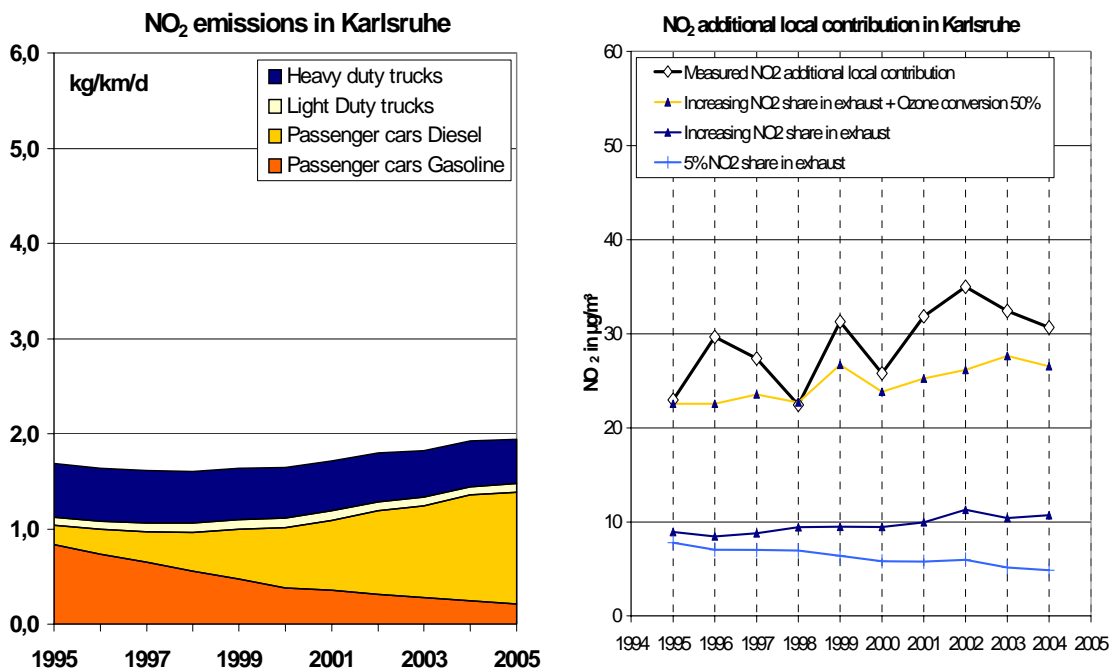


Figure 8: NO<sub>2</sub> emissions and different sources contribution in Karlsruhe (IFEU)

Fig.9 provided by AVISO GmbH shows that the phenomenon is identical in other cities of Bade-Württemberg [16].

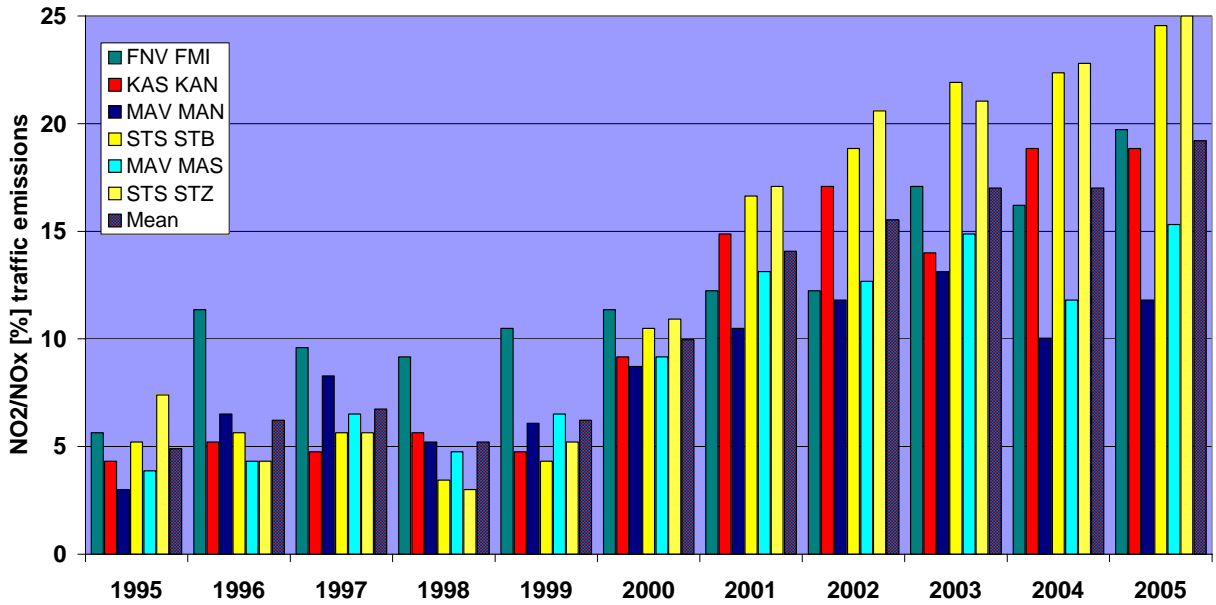


Figure 9: NO<sub>2</sub>/NO<sub>x</sub> ratio in Freiburg, Karlsruhe, Mannheim and Stuttgart (AVISO GmbH)

This recording is particularly instructive as the monitoring station is located on the central reservation, between the traffic lanes, which means that whatever direction of wind is, probe is to leeward of traffic. But it is on highway and is not representative of urban air, the main concern.

Same institute has gathered NO<sub>x</sub> and NO<sub>2</sub> values in Stuttgart and Karlsruhe since 1995 (Fig. 7 & 8) and has modelled the contribution of different vehicles (Fig. 10).

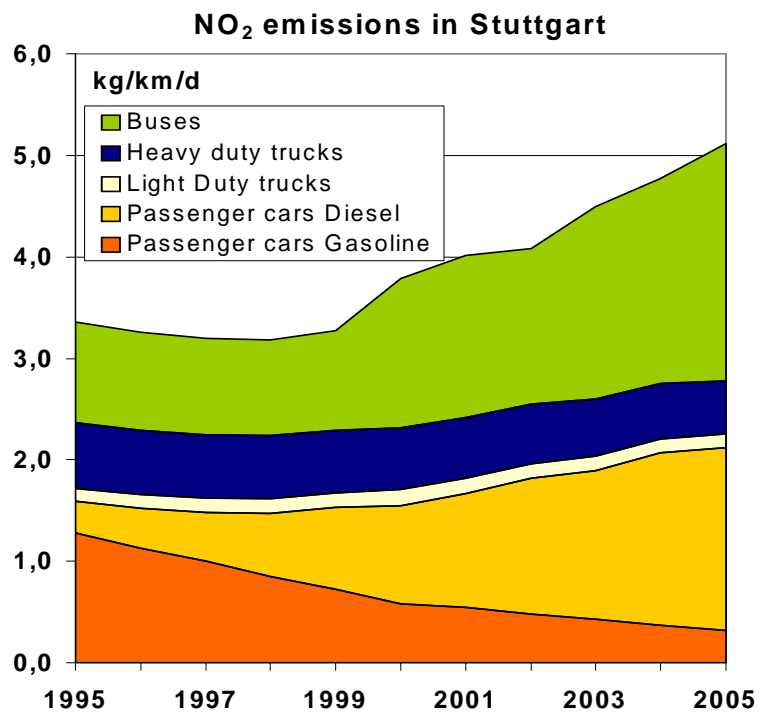


Figure 10: IFEU modelling for determining contribution of different categories of vehicles (IFEU)

Looking at measurements in air (Fig. 7 & 8), it is clear that NO<sub>x</sub> has continued to decrease at street levels even after 2000, while NO<sub>2</sub> remains stable in Karlsruhe and is increasing in Stuttgart. Both background values for NO<sub>x</sub> and NO<sub>2</sub> in Karlsruhe and Stuttgart are decreasing in a similar manner, proving that the divergence between NO<sub>x</sub> and NO<sub>2</sub> is “created” in streets.

In a following paragraph figure 12 will confirm that some vehicles are causing a huge deterioration of NO<sub>2</sub> emissions [2]. The specific contribution will be discussed later but it is already important to keep in mind some strong messages from this figure. Gasoline cars have dramatically reduced emissions of NO<sub>2</sub> since 1995; this reduction is largely compensated by a significant increase of NO<sub>2</sub> emissions from diesel cars with an accelerated deterioration in 2000. This explains the relative stability in Karlsruhe. Worse situation in Stuttgart is due to traps fitted on buses to eliminate diesel soot; Karlsruhe has no similar devices on its buses

#### **4- NO<sub>2</sub> is really dangerous for itself, this is a new conclusion of APHEA2**

It is not the intention in such an article to discuss results of an epidemiological study, but it is certainly the interest of engineers to know why they have now to concentrate their efforts on the proper means to eliminate both PM and NO<sub>2</sub>, while they were asked before to eliminate PM and NO<sub>x</sub>.

Most of the work dedicated to curtailing PM was justified by many US epidemiological studies on long term exposure to PM<sub>10</sub>, the main danger of such exposure being identified as lung cancer. But lung cancer was not the only consequence of peaks of pollution caused by traffic and further studies were launched in order to check acute effects of peaks (short term exposure). There were indeed revisits of the US data banks and a large European study was set up by European Commission under the title APHEA (Air pollution on Health: a European Approach). First stage of the study covered 15 cities having enough data collected on PM and gaseous pollutants. Results of this first stage highlighted the concept of premature deaths and morbidity. Huge numbers were printed on first pages of newspapers and convinced population that it was urgent to clean diesel exhausts.

Initial results being considered as a not precise enough, an additional stage was added to better investigate the consequences of air pollution on population at risks (children and elderly) and the number of cities was increased to 30. This additional study was called APHEA2; the panel of authors is composed by Europeans and by Joel Schwartz from Harvard School of Public Health in order to achieve a link with major US studies in which Harvard School of Public Health is a central point of expertise. This team has recently published a report “Short-term effects of nitrogen dioxide on mortality: an analysis within APHEA project” European Respiratory Journal – June 2006.

This is quite a revolution in regulatory circles, where it was not appropriate to speak about NO<sub>2</sub> for its own toxic effects but only as a surrogate (marker) of PM<sub>10</sub> from the traffic. NO<sub>2</sub> is quite exclusively produced by traffic of diesel vehicles (and gas cooking), it is then easy to use it for correlating changes in air pollution with changes in traffic and therefore to attribute a portion of PM<sub>10</sub> to diesel traffic.

Already in 2003 APHEA2 results on mortality in the elderly [6] mentioned in the summary this sentence “*The effect size [of PM exposure] was modified by the long-term average levels of nitrogen dioxide – higher levels were associated with larger effects -*”. This sentence was

completed in the detailed results by this one “Thus, it can be seen that, for the most important modifier identified, long-term NO<sub>2</sub> concentration, the effect of PM10 on daily number of deaths among elderly, ranges from 0.30% in cities with low long-term average NO<sub>2</sub> (about 40 µg/m<sup>3</sup>) to 0.97% in cities with high long-term average NO<sub>2</sub> (about 70 µg/m<sup>3</sup>)”.

Report published in June 2006 [7] are concentrating on the short-term effects of NO<sub>2</sub> mentions: “a significant association of NO<sub>2</sub> with total, cardiovascular and respiratory mortality was found with stronger effects on cause-specific mortality” In the results section it is written “For 10 µg/m<sup>3</sup> increase in the daily NO<sub>2</sub> concentrations, the increase in total deaths was 0.30%, for cardiovascular mortality the associated increase was 0.40% and for respiratory mortality 0.38%”.

Putting together both studies may suggest that NO<sub>2</sub> is as dangerous as PM. It seems difficult at the current stage of knowledge to decide which pollutant is the surrogate of the other one, and therefore necessary to apply completely the principle of precaution.

### 5-1- Are treatments of gaseous pollutants and devices for removing diesel soot responsible of this worrying increase of NO<sub>2</sub>?

This pessimistic question could be drawn from the previous chapters of the discussion, but hopefully its answer is not the same for all existing emission control devices; some favourite commercial are high contributors, while some other commercial systems produce less than half NO<sub>2</sub> and some prototypes can even reduce NO<sub>2</sub> produced by engines during combustion cycles.

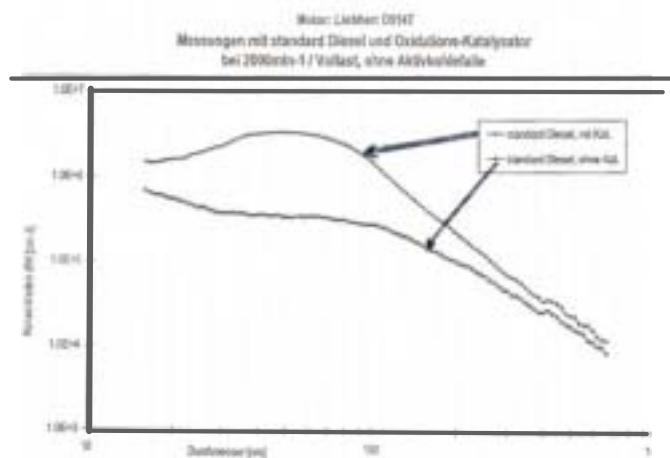


Figure 11: Diesel oxidation catalyst was never a solution to reduce numbers of PM (VERT)

Gaseous pollutant control was the major reason for installing Diesel Oxidation Catalysts on passenger cars from 2000. These devices are nearly totally inactive for carbonaceous soot [17] elimination but they oxidize CO and volatile HCs which are measured in the mass of PM, and therefore they reduce PM mass. When solid PMs are counted, efficiency of DOC is nil or even negative (Fig. 11). Heavy platinum (Pt) loadings are necessary to get a good efficiency in destruction of CO and HC. But such loading have also the negative impact of transforming about 50 – 80 % of NO to NO<sub>2</sub> as it is shown in Fig. 12. This figure was presented jointly by TNO-Automotive, EMPA and TRL during Environment & Transport 2006 Conference [2] and is part of the report published by UK Defra [18].

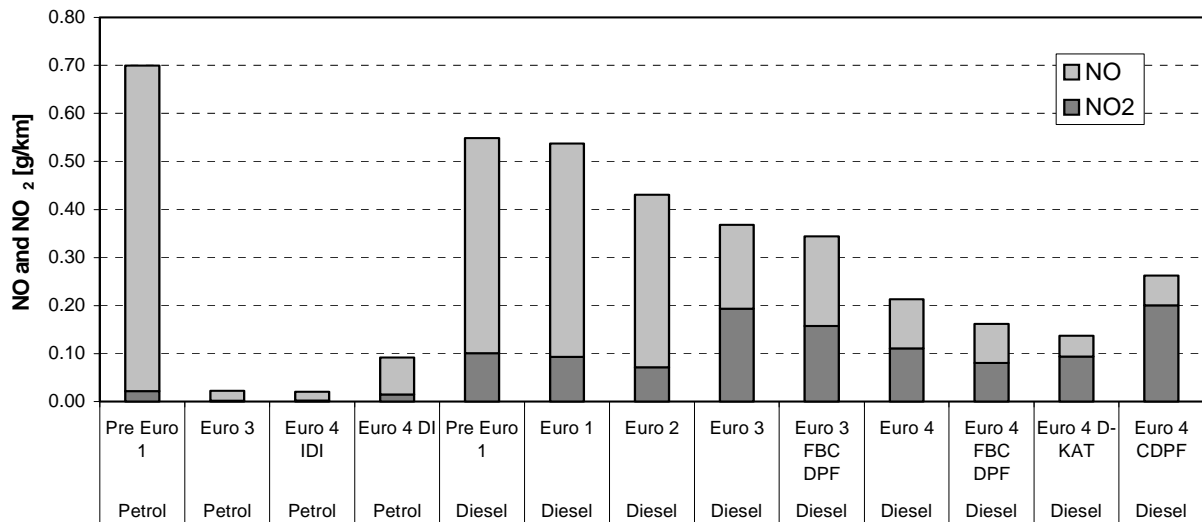


Figure 12: typical NO<sub>2</sub> production corresponding to vehicles certified at different Euro levels (TNO, EMPA)

Soot filtering does not introduce any increase in NO<sub>2</sub>; on the contrary collected soot consumes a part of the NO<sub>2</sub> formed during combustion in engine cylinders. NO<sub>2</sub> formation is only the consequence of the strategy used for regenerating filters.

Thermal regenerations (electrical heater or fuel burners) do not produce NO<sub>2</sub> but they are difficult to implement on cars and even trucks.

Using FBC (Fuel Borne Catalyst), such as cerium or iron and mixtures based on these metal oxides is a clever way to lower burning temperatures of soot at levels of the highest exhaust temperatures; filter regeneration can be achieved spontaneously when exhaust temperature is high enough and oxygen content in exhaust gases is sufficient. When both conditions are not reached, regeneration has to be assisted by engine measures such as delayed injection. This technology is currently implemented on about 2 millions passengers powered by PSA group engines (Peugeot, Citroën, Ford, Mazda, and Volvo). This technology has the lowest impact on NO<sub>2</sub> as shown on the Fig 12.

Biggest potential contributors to NO<sub>2</sub> are catalysed filters using Pt as main oxidizing phase as also shown in this figure and confirmed in Fig.13. It would help knowing the type catalytic coating for a better understanding of this figure. Impressive is the very small dispersion with the 3 cars equipped with a CDPF, it seems obvious that Pt loadings are very similar. When regarding now diesel oxidation catalysts (Euro 3 and 4), impact of coatings can come from the composition (Pt, Pd, Pt + Pd, other metals) and/or the quantity of PGM coated. This figure proves that load can be customized to lower NO<sub>2</sub> production.

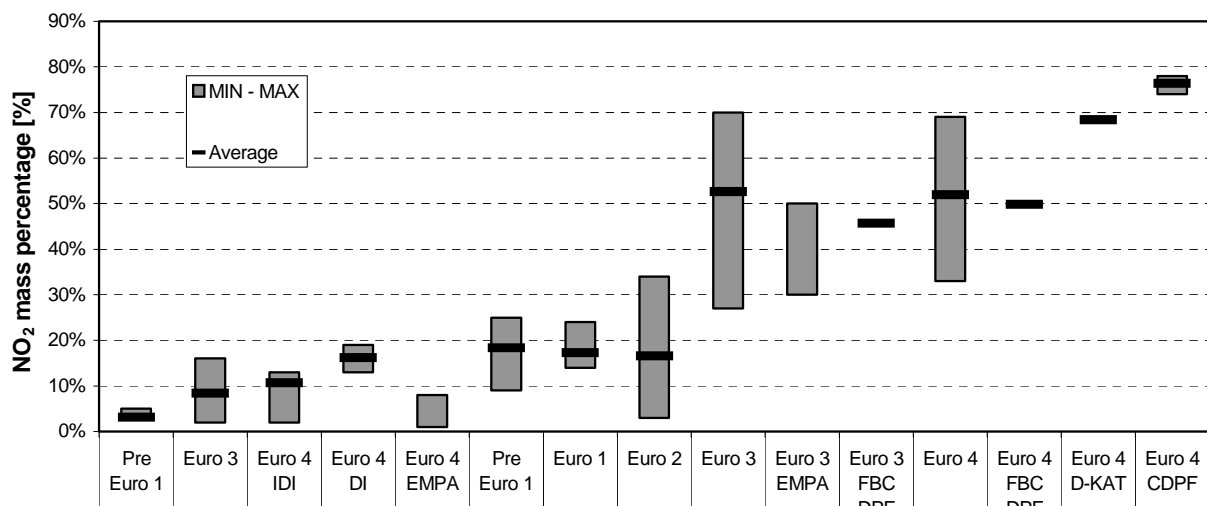


Figure 13: Dispersion of emissions of NO<sub>2</sub> within similar Euro levels (TNO, EMPA)

Is it acceptable to establish a balance between reduction of PM and urban NO<sub>2</sub>? Is it possible to see European or local authorities accepting compromises for preserving the future of Diesel (meaning local auto industry interests) at the expenses of public health? This possibility is not so unlikely when German government is considering the opportunity of offering partial filters retrofit some tax incentives, as it did in the past with DOC. Getting results from independent sources about filtering efficiency of such devices (in mass as well as in number) is one of the essential steps leading to consider such device as a filter. The other essential step is to check its production of NO<sub>2</sub>; knowing the huge NO<sub>2</sub> contribution of DOCs and the fact that soot bed is the only way to consume part of this excessive NO<sub>2</sub>, it is reasonable to expect that ultra fine PMs would not be significantly reduced and that NO<sub>2</sub> emissions would be at least equivalent or even higher than those of a full filter.

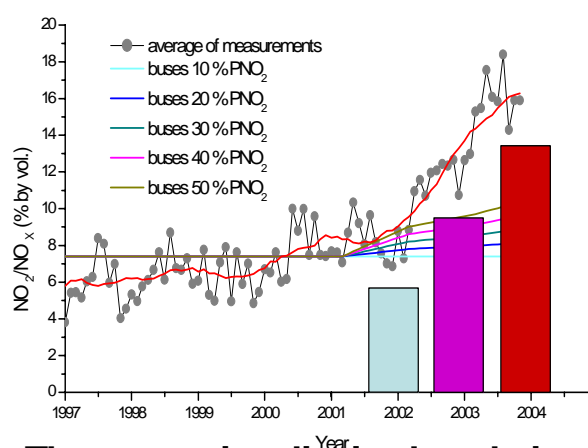
**5-2- Some of the most efficient strategies to regenerate filters utilize NO<sub>2</sub> as major oxidant of carbon soot**

**CRT (Continuous Regeneration Trap)**

Principle of using NO<sub>2</sub> as oxidant medium to burn the carbonaceous part of diesel soot has been patented and the acronym CRT<sup>®</sup> registered as a trade name (followed by CCRT<sup>®</sup> and PCRT<sup>®</sup>). It is a fact that NO<sub>2</sub> is a stronger oxidant of carbon than oxygen, and therefore allows a light on of soot burning at temperatures existing in exhaust line. But this works only with a large excess of NO<sub>2</sub>, which has the consequence of large NO<sub>2</sub> emissions, especially when soot emissions are low, as it is the case during city driving. As long as the number of these systems remains low enough, people were impressed by the efficiency of the filters and easiness of controlling regeneration. London was the first city to notice the negative impact thanks to a monitoring station located in the middle of a bus routes concentration. (Fig.14) shows clearly that ratio of NO<sub>2</sub>/NO<sub>x</sub> is well correlated with the number of buses equipped with these systems, but is not limited to Central London as shown on figure 15 [5].

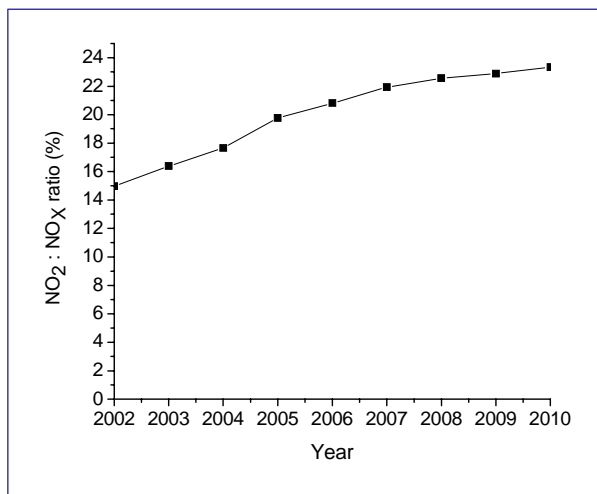
The link between date of introduction of DPF on buses and beginning of increasing NO<sub>2</sub>/NO<sub>x</sub> ratio is impressive

|                | 2001 | 2002 | 2003 | 2004 |
|----------------|------|------|------|------|
| All buses      | 6593 | 6703 | 7596 | 7966 |
| Buses with DPF | 0    | 2632 | 4230 | 6330 |
| % with DPF     | 0    | 39   | 56   | 79   |

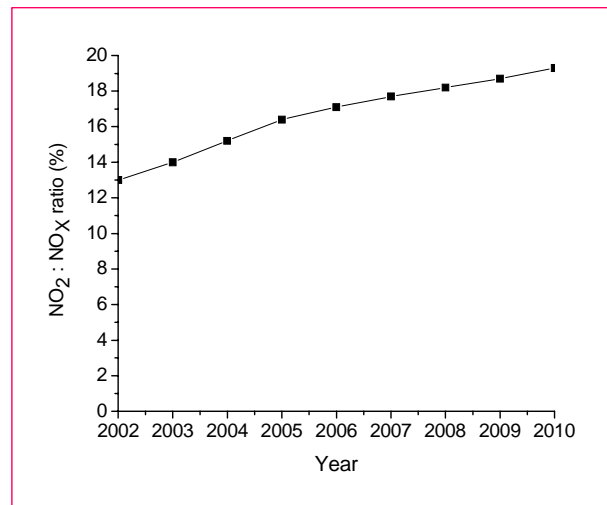


The proportionality is also obvious, but other sources have also to be considered: DOCs on taxi cabs and number of diesel cars

Figure 14: correlation between number of bus equipped with CRT and increase in NO<sub>2</sub>/NO<sub>x</sub> ratio (ITS Leeds)



**NO<sub>2</sub>/NO<sub>x</sub> ratio in Central London**



**NO<sub>2</sub>/NO<sub>x</sub> ratio in all-London**  
source ITS Leeds

Figure 15: increase in NO<sub>2</sub>/NO<sub>x</sub> ratio is not limited to Central London (ITS Leeds)

### CDPF (Catalysed Diesel Particulate Filter)

This acronym designates filters which are coated with a catalytic phase able to facilitate the burning of the soot during filter regeneration. NO<sub>2</sub> formation is highly dependent on the catalyst formulation. Lighting on burning soot bed through burning of condensed HC is not sufficient and contribution of NO<sub>2</sub> produced by in-situ oxidation of NO is definitively a must actively targeted by coaters, who use in this case heavy Pt loadings. Systems designers are also often combining CDPF with a DOC upstream; it is then very difficult to differentiate the system from a CCRT<sup>®</sup>.

CDPF approaches offer a large variety of variants of coating, using palladium instead or in combination with Pt. Even base metals could be used. Formulations which are not rich in Pt need regeneration assistance by FBC and/or active regeneration means. But the ones used in automotive post-treatments are designed to work on their own and are therefore using a lot NO<sub>2</sub> as oxidative reagent, causing huge proportion of NO<sub>2</sub> in exhaust gases.

Before implementing such systems in mass production of vehicles to be used in urban micro-environments (buses, delivery and urban trucks and passenger cars), it is essential to check each vehicle NO<sub>2</sub> production in an appropriate way in order to maintain NO<sub>2</sub> at an acceptable level in all the streets of the cities.

### 7- Measurements of NO<sub>2</sub> at tailpipe is biased by dilution tunnel and current analysis devices; more specific driving test cycles must be selected to be representative of real life conditions of operating buses, urban trucks and passenger cars within city limits

When a current dilution tunnel with cooling is applied to an exhaust generated by a vehicle following a legal cycle such as NEDC, conditions of underestimating NO<sub>2</sub> are cumulative and can lead to divide the actual emission values by a factor of 3 to 4.

It could be a repetition, but it is essential to remind readers that NO<sub>2</sub> is not a severe problem when vehicles are driving on highways, far from cities limits, but is a real concern these days when traffic is inner city (Fig. 16). When emitted outside of the city, NO<sub>2</sub> will be rapidly mixed with other components of the atmosphere by turbulences of vehicles driving at higher speeds and by winds. When emitted in a canyon street or in a congested traffic, primary NO<sub>2</sub> emissions take more time to be dispersed and populations are directly exposed to them. High density of NO<sub>2</sub> is indeed an aggravating factor.

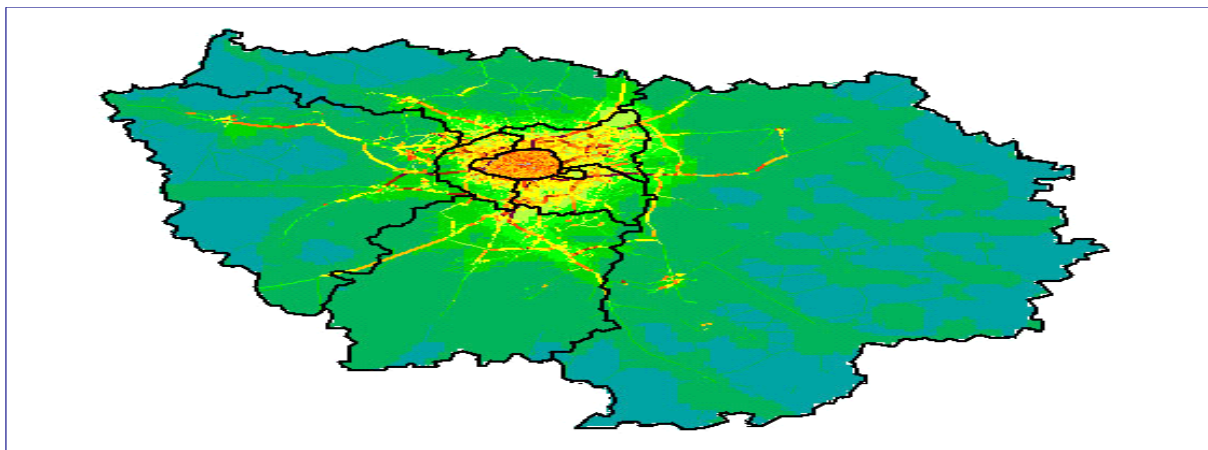


Figure 16: modelling of exposure to NO<sub>2</sub> in Paris and the great region Ile-de-France (Airparif)

When measuring NO<sub>2</sub> at tailpipe it is important to measure what tailpipe really emits, i.e. hot exhaust, and examine its transformation in real life conditions. Going through usual CVS (Constant Volume Sampling) will not only cool artificially the emitted gases but will also induce some chemical reaction and transformation of NO<sub>2</sub> into nitric acid which is liquid and therefore no more analyzed as a gas.

The work made in Biel University and shown in Fig.17 points out effects of cooling leading to a true disappearance of NO<sub>2</sub> in cool gas, which has also some real impact on NO<sub>x</sub> values when a large proportion of NO<sub>x</sub> is under the form of NO<sub>2</sub> [19].

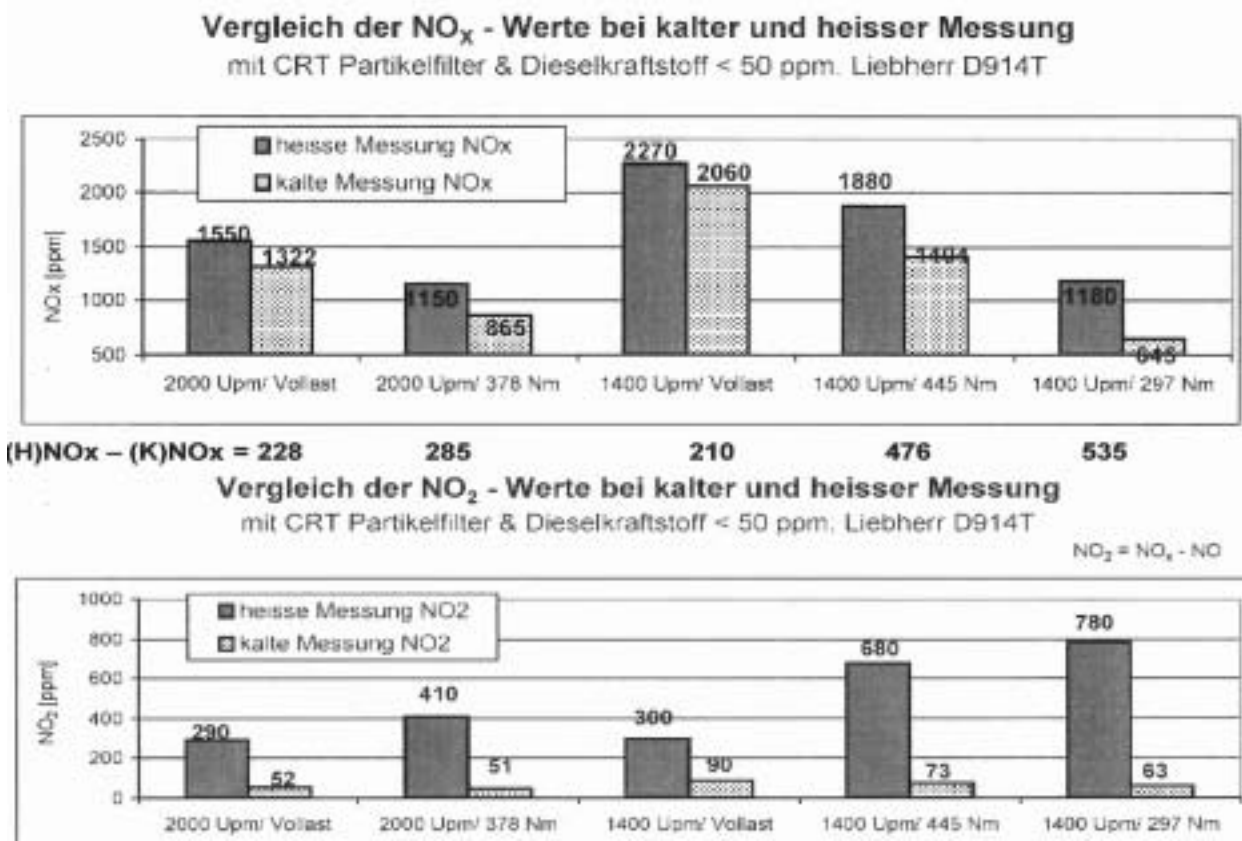


Figure 17: influence of measuring  $\text{NO}_2$  in hot gases or after cooling the exhaust; cooling is eliminating most of  $\text{NO}_2$  and can lead to underestimation not only of  $\text{NO}_2$  but also of  $\text{NO}_x$  (Biel University)

In their joint presentation at Environment & Transport 2006, TNO-Automotive, EMPA and TRL listed all drawbacks of CVS and chemo-luminescence [2]. It seems that everything is added up to get the most inaccurate values for emissions of  $\text{NO}_2$ ; it was certainly not under purpose, but this means that it is urgent to change ways of measuring this gas at tailpipe.

US main cities have developed specific driving cycles for urban buses already shown on figure 2. California indeed was in first row to show that such cycles induce a high conversion of  $\text{NO}$  in  $\text{NO}_2$  [20]; this trend was also confirmed by EMPA measuring  $\text{NO}_2/\text{NO}_x$  ratio on different steady states operating points [21] and finding that higher output are observed at medium/low speed and load, exactly the operating points representative of city driving conditions (Fig. 18 & 19).

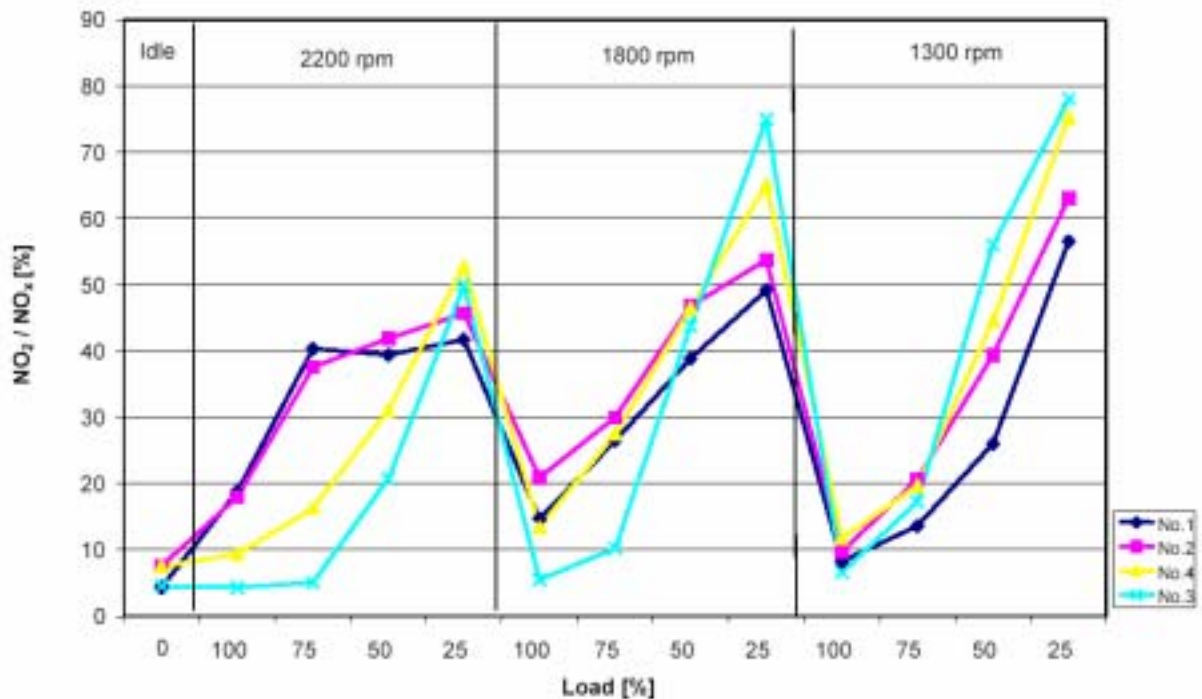


Figure 18: variation of  $\text{NO}_2/\text{NO}_x$  with speed/load conditions of some bus engines (EMPA)

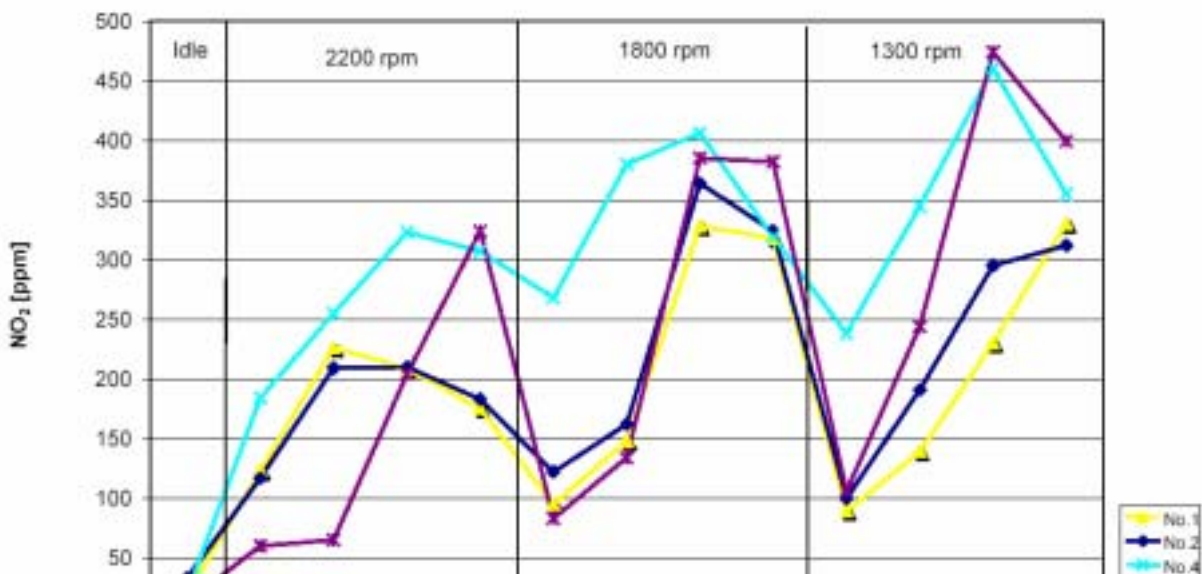
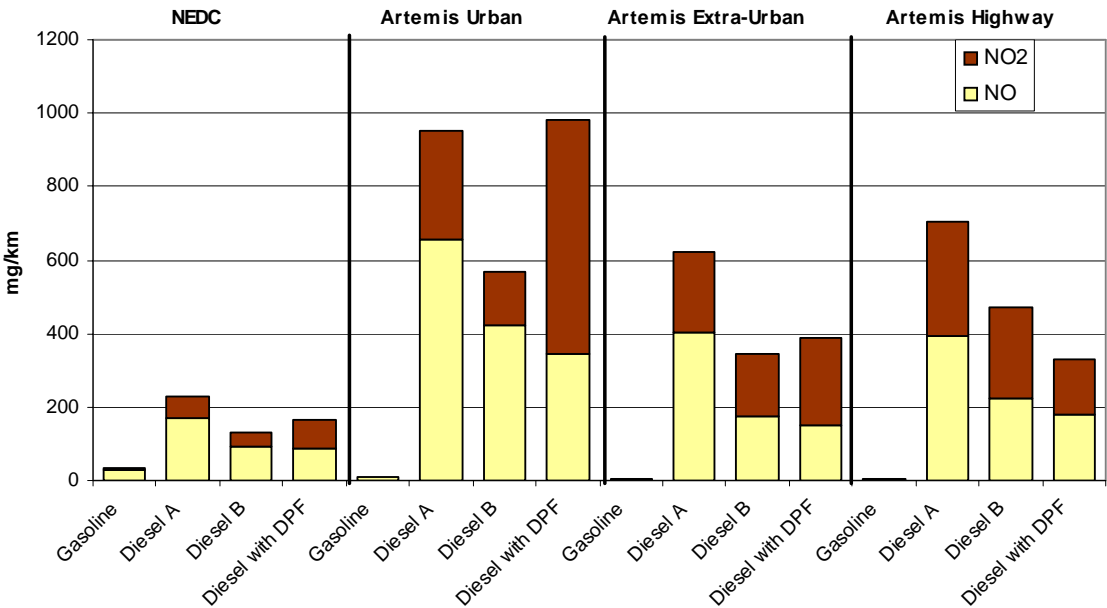


Figure 19: Variation of NO<sub>2</sub> direct and total emissions at exhaust of buses in different driving conditions. (EMPA)

More recently a similar behaviour was identified on cars and published by AECC, The driving cycle, on which emissions are measured, has a tremendous impact as it is shown on fig. 20 [22]. ARTEMIS cycles are the results of an EU attempt to represent real life driving cycles. It is obvious that NEDC, the official and only one cycle used for vehicles certifications, does not represent real life emissions of NO<sub>x</sub> and NO<sub>2</sub> in urban conditions, which appear to be 3 to 5 times higher (ARTEMIS Urban) than those measured on NEDC. As NEDC emission factors are used for modelling impacts of traffic emissions in atmosphere, including in urban area, it is easy to understand that actual values diverge more and more from estimated values based on modelling. In order to better understand the figure it is important to introduce works made under acronym ARTEMIS [22]. European Commission, being convinced that NEDC does not represent real life driving conditions, is financing a joint work of different institutes for defining a set of tests more adapted. A certain number of cycles, especially for city driving, are considered to replace NEDC in future regulations. Even if these cycles are not yet official, results obtained through them give a quite fair appreciation of what are real life emissions and show that electronic management of engine does not control yet bad emissions when vehicle is tested outside of NEDC conditions. This way of developing emission controls mainly (or even only) to satisfy emission limits when measured on a given cycle is generally known as cycle gaming (or beating) and is practiced for certifications everywhere in the world. US Department of justice considered this practice as an offence and the major heavy duty engine producers where obliged to sign a Consent Decree to avoid penal charges and agreed to stop using what was called a “defeat device”, the target was to save fuel while driving on highway, the consequence was to multiply NO<sub>x</sub> emission by 3 to 5 times. When looking at the factors between NEDC and Urban ARTEMIS, which are exactly the same, it is legitimate to raise the question of a possible cycle gaming of European auto makers, especially regarding urban driving conditions and to wish that European Commission will rapidly adopt the NTE (not to exceed) protocol adopted by EPA, which include, in the certification, some steady state points randomly determined.



*Figure 20: Influence of driving cycle on NO<sub>x</sub> and NO<sub>2</sub>; it is impressive how both emissions are widely underestimated by the “official” cycle on modern diesel engines (???)*

## Conclusion

Keeping simultaneously PM and NO<sub>2</sub> under control at levels which are targeted for 2010 in European cities is still an ambitious and complex task. Complexity is not only at technology levels but also lies on economical factors and necessity of preserving population easy access to city centres and to individuals' working place. In other words, measures to achieve these targets must also be cost-effective in the wider acceptance of this notion, i.e. including public health related cost. It is also essential not to neglect potential impacts of such measures on global warming: GHG (Green House Gases) could be formed by some technologies.

The second component of the equation is not within the domain of engineering skills, the first one is, but is itself a matrix in which all parameters are subject to optimisation:

PM10 control, ultra fine PM number control, NO<sub>2</sub> control, NO control,  
Adapted test cycles to achieve good Air Quality in agglomerations  
Adapted measurement methods at tailpipe  
Optimized implementation of monitoring stations and adapted measurement methodology

Without forgetting N<sub>2</sub>O and GHG control!

Answering the question in title is indeed the solution of the whole equation and engineers in pollution control devices are only responsible of a part of it, but this part is essential. As long as engineers will continue to consider that cost-effectiveness (in the narrowest acceptance of the concept, i.e. lowest cost for producers) is the favourite way, cycle beating would remain the consequence of this choice.

Engineering skills are able to design control devices achieving good emission levels even in the worst conditions, but the concept of Best Available Technology (BAT) is strongly rejected by industry managements. It seems that they forget that a BAT can become a cost-effective device when industry will it, as TWCs have demonstrated, leading to added improvements such electronic injection and ECU (Electronic Control Unit).

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