Joint Research Centre

Ammonia emissions from light duty vehicles

European Commission
Joint Research Centre, Ispra
Institute for Energy and Transport
Sustainable Transport Unit

Ammonia as precursor of ammonium nitrate and ammonium sulfate

- Ammonium sulfate, ammonium bisulfate and ammonium nitrate are formed by reaction of sulfuric and nitric acid with ammonia (NH_3)

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$$

$$NH_3 + H_2SO_4 \rightarrow NH_4HSO_4$$

$$NH_3 + HNO_3 \rightarrow NH_4NO_3$$

Finlayson-Pitts and Pitts, 1986

- Several studies have indicated that NH_3 is an important precursor in the formation of fine particles:
  - United States (Heald et al., 2012; Benedict et al., 2013; Gong et al., 2013; Li et al., 2014), Europe (Minguillón et al., 2012; Reche et al., 2012), India (Behera and Sharma, 2010), Japan (Sakurai and Fujita, 2002; Aikawa et al., 2013), Korea (Phan et al., 2013), and China (Hu et al., 2008; Shen et al., 2011).

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$$NH_3 + H_2SO_4 \rightarrow NH_4HSO_4$$

$$NH_3 + HNO_3 \rightarrow NH_4NO_3$$

Finlayson-Pitts and Pitts, 1986

- **40%** of the total $PM_{2.5}$ in some **European cities** (Sillanpää et al., 2006)
- up to **17%** of $PM_{2.5}$ in **South Coast Air Basin** (Kim et al., 2000)
- **34% to 48% of $PM_{2.5}$** in Taiwan (Tsai et al. 2014)

Kim, B.M., et al. Journal of the Air & Waste Management Association, 2000. 50(12): p. 2034-2044.
Sillanpää, M., et al. Atmospheric Environment, 2006. 40, Supplement 2(0): p. 212-223.
Tsai, J.-H., et al.. Science of The Total Environment, 2014. 494–495(0): p. 74-83.

Emissions regulations

Initiatives that aim at reducing the emissions of NH_3 (among other gases):

Europe

- The National Emission Ceilings Directive 2001/81/EC (NECD)
- The Gothenburg Protocol under the United Nations Convention on Long-Range Transboundary Air Pollution (LRTAP Convention) (UNECE 1999) and
- The IPPC Directive (2008/1/EC)

In two decades **agriculture and waste management** have **reduced** NH_3 emissions by **29 and 24%**

Road **transport** emissions have **increased** by **378%** (EEA Technical report No 6/2013)

USA

- National Ambient Air Quality Standard (NAAQS) for $PM_{2.5}$

NH_3 emission from **gasoline LDVs** have **decreased** by **4%** since 2005 (National Emission Inventory, 2011)

Vehicular contribution to NH_3 emissions

Vehicular NH_3 emissions account for ~2% of the total in Europe & USA

They are the 3rd largest source after agriculture and waste management

Vehicles are an important source of NH_3 in the urban environment

- **18%** in the California South Coast Air Basin, and
- **70%** in Charlotte and Fresno during winter

(Chitjian et al., 2000; Battye et al., 2003)

Battye, W., et al. Atmospheric Environment, 2003. 37(27): p. 3873-3883.
Chitjian, M., et al. Final report to the south coast air quality management district, 2000.

Vehicular ammonia emissions

In the **Three-Way-Catalyst** of the gasoline vehicles NH_3 is formed via:

- Reaction of NO with molecular hydrogen H_2
  - Steam reforming from hydrocarbons (Whittington et al., 1995)
  - H_2 produced from a water/gas shift reaction between CO and water (Bradow and Stump, 1977; Barbier and Duprez, 1994)

NH_3 is emitted after catalyst light-off and during acceleration events

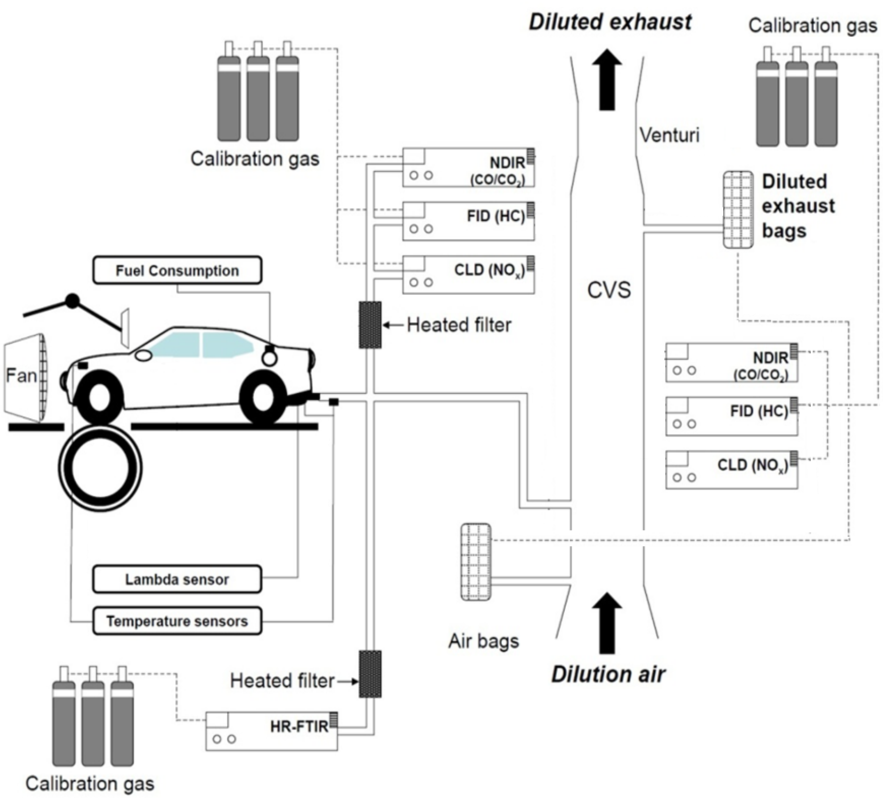
$$CO + H_2O \rightarrow CO_2 + H_2 \quad (1)$$

$$2NO + 2CO + 3H_2 \rightarrow 2NH_3 + 2CO_2 \quad (2)$$

$$2NO + 5H_2 \rightarrow 2NH_3 + 2H_2O \quad (3)$$

Barbier Jr, J. and D. Duprez. Applied Catalysis B: Environmental, 1994. 4(2–3): p. 105-140.
Bradow, R.L., Stump, F.D. SAE Technical Paper No. 770369, 1977

Experimental setup



Vehicle Emission Laboratory(VELA)

- Two 1.22 m roller benches
- Temperatures: -7 & 22 ^{o}C
- Relative Humidity: 50%
- Constant Volume Sampler (CVS)

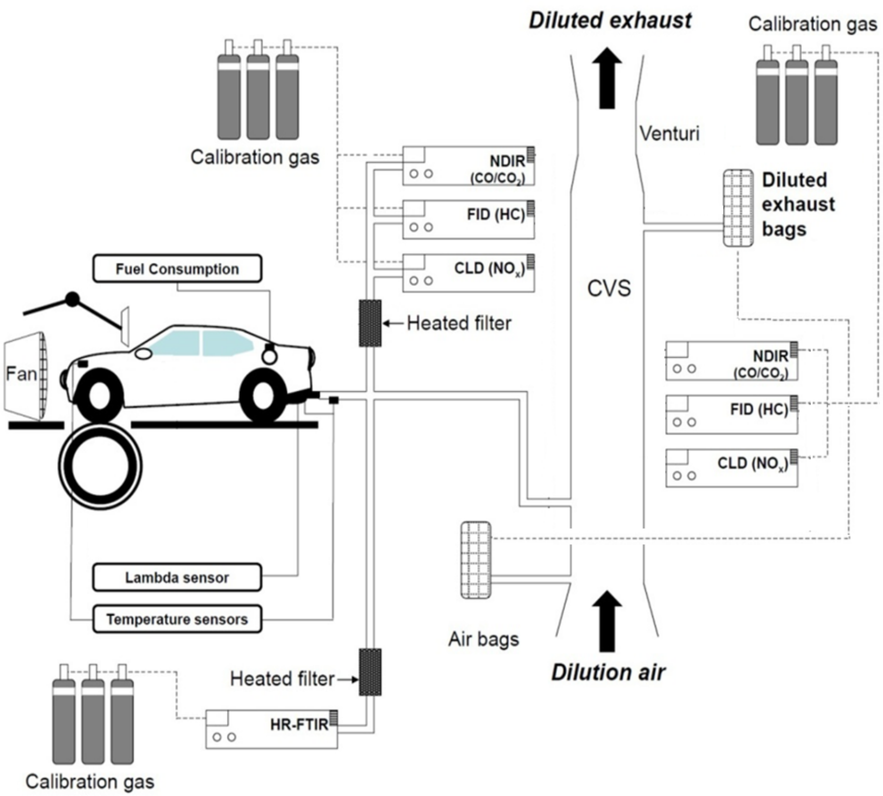
Directive 70/220/EEC

- Non-dispersive infrared (CO/CO_2),
- Chemiluminescence (NOx)
- Flame ionization detector (THC)

High Resolution Fourier Transform Infrared spectrometer

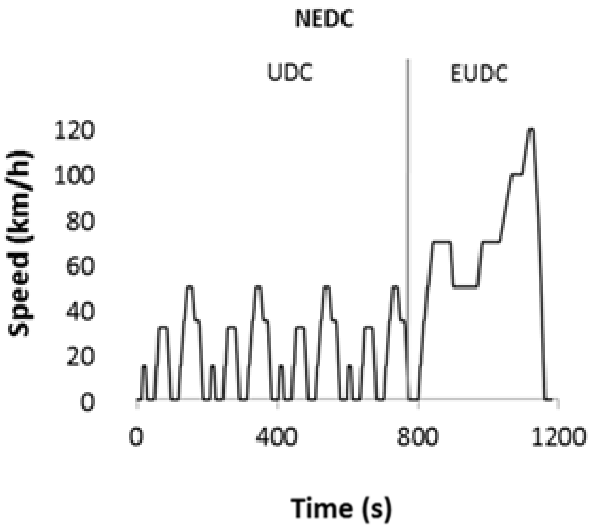
- Sampling at the tailpipe
- Sampled volume: 10 l min^{-1}
- Sampling line (PTFE) is heated at 190 ^{o}C

New European Driving Cycle (NEDC)



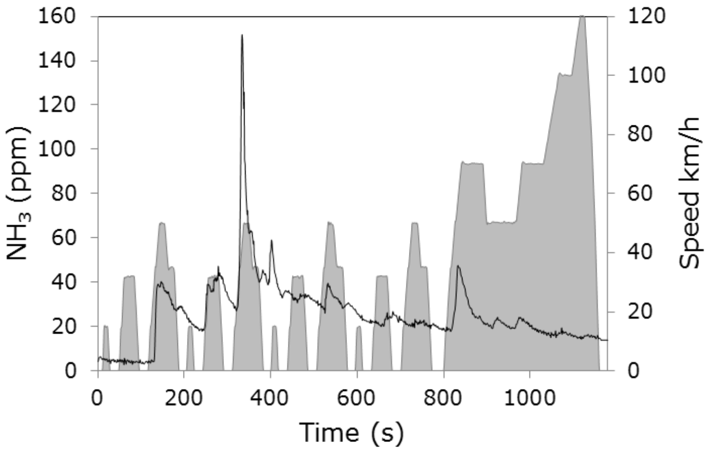
Vehicle Emission Laboratory(VELA)

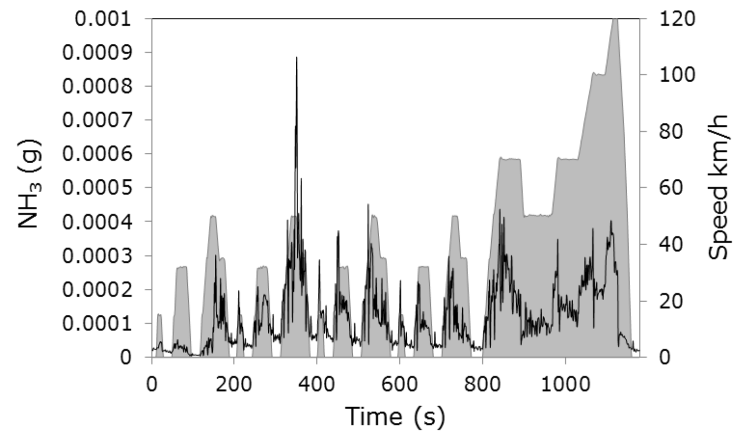
- Cold-start driving cycle
- Soaking time 12 h.
- Urban phase of 780 s (**UDC**)
- Extra-urban phase of 400 s (**EUDC**).



European Commission

Ammonia Emissions





Vehicles	Car 1 E85/E75		Car 1 E5		Car 2	Car 3	Car 4	Car 5		Car 6		Car 7	
Temperature °C	22	-7	22	-7	22	22	22	22	-7	22	-7	22	-7
NH_3 (mg km^{-1})	**5**	**6**	**4**	**5**	**4**	**7**	**9**	**11**	**30**	**27**	**21**	**35**	**53**
Av [NH_3] (ppmV)	11	11	7	10	6	14	24	26	62	23	21	66	100
Max [NH_3] (ppmV)	**47**	**27**	**14**	**34**	**16**	**35**	**203**	**96**	**216**	**192**	**149**	**433**	**748**

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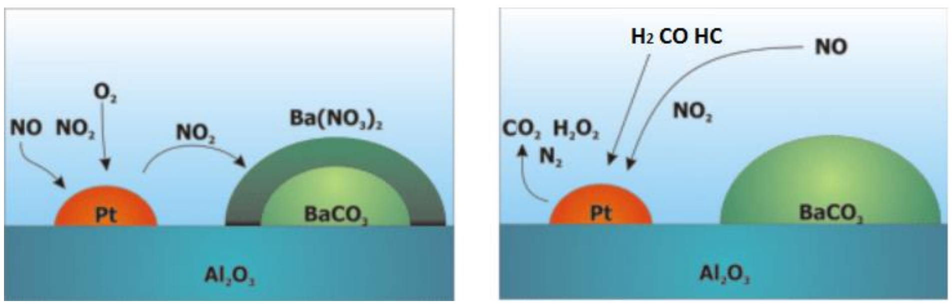
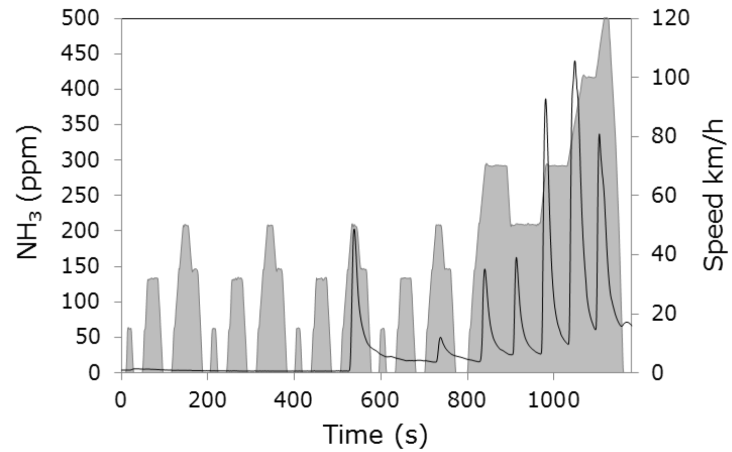
Ammonia Emission Euro 6 Gasoline

NOx Storage Catalyst (NSC)





Vehicles	Car 1 E85/E75		Car 1 E5		Car 2	Car 3	Car 4	Car 5		Car 6		Car 7		Car 8		Car 9
Temperature °C	22	-7	22	-7	22	22	22	22	-7	22	-7	22	-7	22	-7	22
NH_3 (mg km^{-1})	**5**	**6**	**4**	**5**	**4**	**7**	**9**	**11**	**30**	**27**	**21**	**35**	**53**	**62**	**70**	**12**
Av [NH_3] (ppmV)	11	11	7	10	6	14	24	26	62	23	21	66	100	108	107	6
Max [NH_3] (ppmV)	**47**	**27**	**14**	**34**	**16**	**35**	**203**	**96**	**216**	**192**	**149**	**433**	**748**	**547**	**528**	**20**

Ammonia Emission Euro 6 Gasoline

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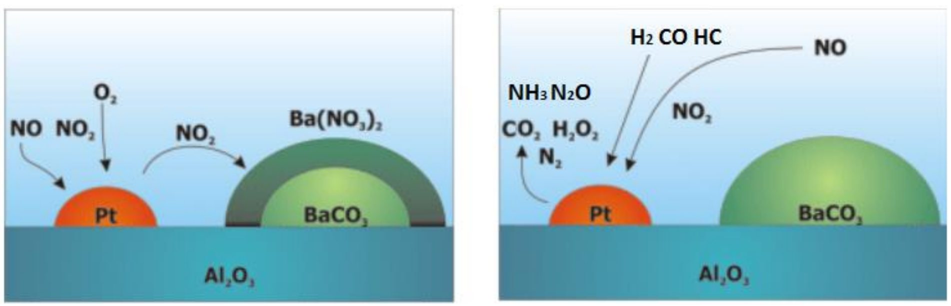

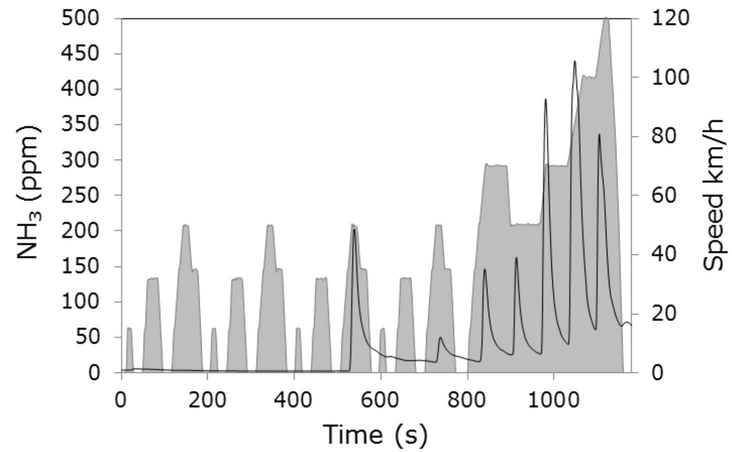

Vehicles	Car 1 E85/E75		Car 1 E5		Car 2	Car 3	Car 4	Car 5		Car 6		Car 7		Car 8		Car 9
Temperature °C	22	-7	22	-7	22	22	22	22	-7	22	-7	22	-7	22	-7	22
NH_3 (mg km^{-1})	**5**	**6**	**4**	**5**	**4**	**7**	**9**	**11**	**30**	**27**	**21**	**35**	**53**	**62**	**70**	**12**
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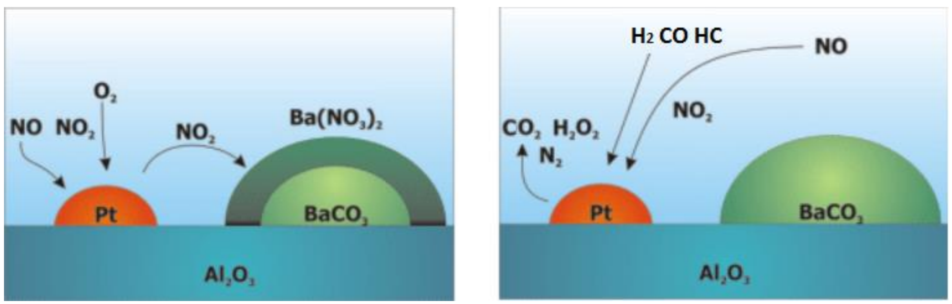
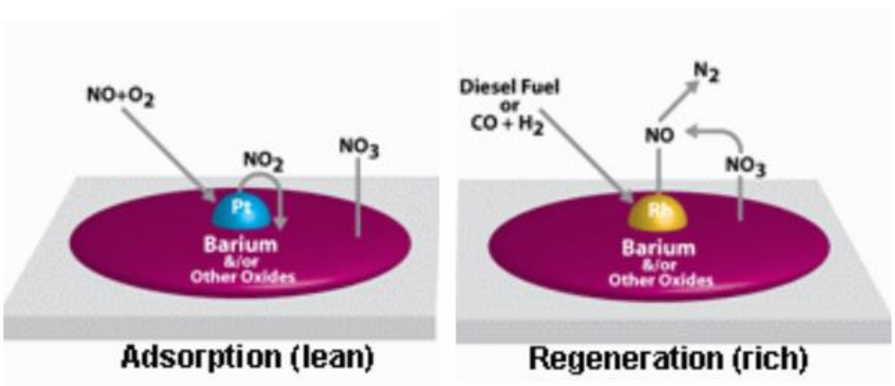
Euro 6 vehicles after-treatments



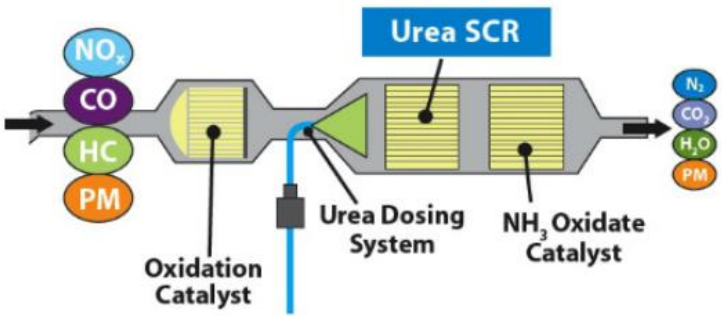
NOx Storage Catalyst (NSC)



Lean NOx Trap (LNT)

Euro 6 Diesel after-treatment

Selective Catalytic Reduction (SCR)



$$4NO + 2(NH_2)_2CO + O_2 \rightarrow 4N_2 + 4H_2O + 2CO_2$$

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$$

$$2NH_3 + NO_2 + NO \rightarrow 2N_2 + 3H_2O$$

$$4NH_3 + 2NO_2 + O_2 \rightarrow 3N_2 + 6H_2O$$

Vehicles	Car 1 E85/E75		Car 1 E5		Car 2	Car 3	Car 4	Car 5		Car 6		Car 7		Car 8		Car 9
Temperature ° C	22	-7	22	-7	22	22	22	22	-7	22	-7	22	-7	22	-7	22
NH_3 (mg km^{-1})	5	6	4	5	4	7	9	11	30	27	21	35	53	62	70	12
Av [NH_3] (ppmV)	11	11	7	10	6	14	24	26	62	23	21	66	100	108	107	6
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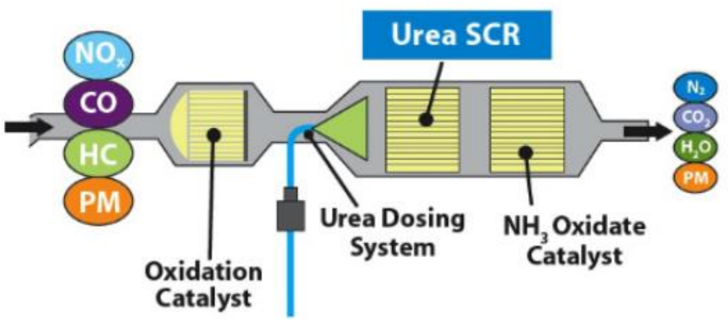
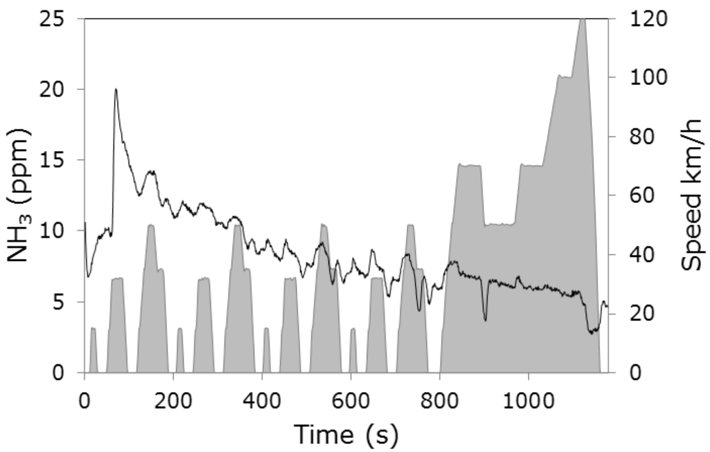
Ammonia Emission Euro 6 Diesel

Selective Catalytic Reduction (SCR)





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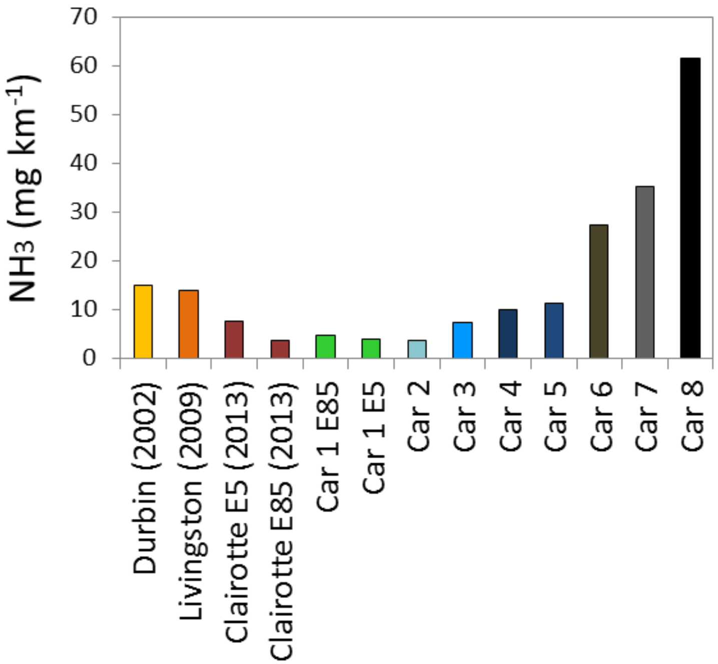
Ammonia Emission Rates



Spark ignition emission limits (mg km^{-1})

	Year	THC	NOx	CO
Euro 3	2000	200	150	2300
Euro 4	2005	100	80	1000
Euro 5	2008/9	100	60	1000

- Emissions of regulated gases (NOx, CO, THC) have decreased over the years
- For Euro 5 compliant vehicles, NH_3 emissions are, on average, similar to vehicles >10 years older (14 mg km^{-1})
- New technologies as NSC, LNT or SCR are deteriorating the situation
  Car 8 with NSC -> Euro 6
  NH_3 emission factor 62 mg km^{-1}

Emissions in urban areas

- Modena and Florence
    - **6.5 trips** per **day**
    - About **8 km** per **trip**

- Average NH_3 emission rate:
    - **22 mg km^{-1}** (4-62 mg km^{-1}) at 22 ^{o}C
    - **36 mg km^{-1}** (5-70 mg km^{-1}) at -7 ^{o}C

- **London**
    - 1.8 millions gasoline light duty vehicles (70% of the total fleet)[1]
    - **2.1 to 3.4 Tons** per **day** NH_3

[1]UK Department for transport

Conclusions

- Enforcement of emission regulations have led to vehicles that emit less CO, NOx and THC but NH_3 emissions remained similar or higher

- Very large amounts of NH_3 are emitted every day in the urban areas

- An NH_3 emission limit for light duty vehicles is needed

European Commission

Acknowledgements

The VELA staff is acknowledged for the skilful technical assistance

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