Supplement of Atmos. Chem. Phys. Discuss., 15, 15355–15396, 2015
http://www.atmos-chem-phys-discuss.net/15/15355/2015/
doi:10.5194/acpd-15-15355-2015-supplement

Atmospheric Chemistry and Physics
Discussions
Open Access

Supplement of

Black carbon, particle number concentration and nitrogen oxide emission factors of random in-use vehicles measured with the on-road chasing method

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Supplementary material

Supplementary material S1 – BC, NOx and PN formation in combustion engines

NO_x and BC do not have the same formation process in the engine: while NO_x is formed in fuel lean conditions and at high temperatures, BC is formed in fuel rich conditions. Most of the NO_x in the engine is formed by the Zeldovich mechanism, where NO is formed from atmospheric nitrogen (and its destruction) (Heywood, 1988). Soot (or BC) formation does not have as clear a formation path. According to Xi and Zhong, 2006, the soot formation steps can be summarized as the: "(1) formation of molecular precursors of soot, (2) nucleation or inception of particles from heavy polycyclic aromatic hydrocarbon molecules, (3) mass growth of particles through the addition of gas phase molecules, (4) coagulation via reactive particle-particle collisions, (5) carbonization of particulate material, and, finally, (6) oxidation of polycyclic aromatic hydrocarbons and soot particles".

In gasoline engines, the fuel and air are mixed before they are injected in the combustion chamber: the mix is homogenous and the engine can smoothly operate close to stoichiometric or slightly fuel-rich mixture. In fuel rich conditions, hydrocarbon (HC) and carbon monoxide (CO) formation is high, and soot emissions can also occur; in lean to stoichiometric conditions, NO formation increases. Because engines operate in different modes, several (and different) emission control techniques are necessary to reduce all pollutants. The reason diesel engines emit more soot and NO than gasoline engines is because in diesel engines the fuel is injected in the chamber just before the combustion starts. The fuel-to-air ratio in the mixture and the combustion temperature are not homogenous, leading to higher NO formation in the close to-stoichiometric regions and to soot formation in the rich unburned-fuel containing core of the fuel spray. The majority of soot particles thus formed, can then oxidize in the presence of unburned oxygen (Heywood, 1988).

In diesel vehicles, high soot emissions occur when the relative air-fuel ratio drops to very low values during the early cycles of a transient event, when the air supply by the compressor cannot meet the higher fuel flow during load increase; since the fuel pump responds much faster than the air supply, the combustion efficiency deteriorates and leads to a slow engine (torque and speed) response and an overshoot in particulate, gaseous, and noise emissions. There are various delays that affect the transient engine response; in wide spread turbocharged diesel engines, the poor load acceptance is even worse than in naturally aspired engines because of the flow and the dynamic inertia of the turbocharger (Tavčar et al., 2011, and references therein).

Particles emitted from the vehicle exhaust consist mainly of highly agglomerated solid carbonaceous material, ash and volatile organic and Sulphur compounds (Kittelson, 1998). Carbonaceous soot particles are formed in the combustion process and are mostly found in the accumulation mode; at the tailpipe where the exhaust dilutes and cools the volatile precursors may nucleate or adsorb on pre-existing particles (Kittelson et al., 2006). The composition of the exhaust particles changes under different vehicle load conditions (Ježek et al., 2015; Kittelson, 1998; Sharma et al., 2005). Unlike particle mass (PM), particle number (PN) concentration is not conserved in the atmosphere (Kittelson, 1998). The particle number and size distribution strongly depend on dilution and sampling conditions; the gas to particle conversion processes, nucleation, condensation and adsorption are non-linear and extremely sensitive to conditions, thus the on-road emissions are not easy to reproduce in laboratory (Kittelson et al., 2006). In the atmosphere the residence time for particles in diameter range 0.1-10 μm is about a week and for 10 nm particles about 15 minutes (Harrison, 1996). In this time smaller particles coagulate with larger ones, thus losing their identity as individual particles but ultimately remaining in the atmosphere for the same amount of time (Harrison, 1996, Kittelson, 1998). Smaller particles – in ultrafine and nanoparticle diameter range, may be more health hazardous as they can penetrate deeper in to lungs and eventually in the blood system (Dockery et al., 1993; Kennedy, 2007). With the newest vehicle emission standard Euro 6 (European Parliment, 2007) also PN emission standards for both gasoline and diesel cars came in to force.

Figure S1. Stills from the on-road measurement campaign. The image on the top left is the background measurement, the top right is the beginning of a chase of a truck with a trailer; and the lower image depicts a car chase.

Supplementary material S2 – additional Eurostat data information

European countries that reported passenger cars fleet composition for year 2011 were: Belgium, Czech Republic, Germany, Estonia, Ireland, Spain, Croatia, Italy, Cyprus, Latvia, Lithuania, Hungary, Malta, Netherlands, Poland, Portugal, Romania, Slovenia, Finland, Sweden, United Kingdom, Norway, Switzerland, Former Yugoslav Republic of Macedonia, and Turkey

Unfortunately this type of Eurostat data was not available for France, which has the third largest segment (13.3%) of Europe's car fleet (according to Eurostat data for 2010). However, the ACEA (European Car Manufacturers' Association) reported a similar percentage of diesel and gasoline cars in the European fleet in their 2012 pocket guide (ACEA, 2012); they included the following countries: Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Italy, Latvia, Lithuania, Netherlands, Poland, Romania, Spain, Sweden and the UK; they report 61.5% of vehicles using gasoline, 35.3% using diesel and 3.2% using other fuel types. The portion of diesel passenger cars in Europe is therefore around 35%.

Countries that reported lorries fleet composition: Malta, Latvia, Estonia, Cyprus, Slovenia, Croatia, Lithuania, Romania, Finland, Czech Republic, Ireland, Switzerland, Norway, Portugal, Netherlands, Sweden, Italy, Spain and Germany. Some countries reported different total numbers of their lorries regarding the age and size segregation. We kept most but excluded Poland because the difference between the two was over two million.