Volatile Organic Emissions from a Spark Ignition Engine during NEDC and High Speed

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Keywords: VOC, photoionisation, ethanol blend, petrol, gasoline
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In the last 15 years, the number of motor vehicles has increased from 475 to 550 per 1000 inhabitants in Germany. Despite the emissions of diesel vehicles dominated the recent reports in media, petrol-driven cars produce a variety of toxic compounds as well. Most studies cover only total hydrocarbon concentration (THC), inorganic permanent gases (e.g. CO or NO_x) or particles, but unregulated volatile organic compounds (VOC) carry great weight with toxicity and the potential of secondary aerosol formation (Claxton 2015, Bahreini 2012). In particular, the dependence of the emission on speed is a matter of public interest in Germany because it is one of three countries (incl. New Zealand and the U.S. state of Oregon) with motorways without speed restrictions.

The speed-emission dependence of a flexible-fuel spark ignition engine (EURO5) fuelled with E10 and E85 (10 and 85 vol-% of bioethanol) was investigated on a test bench. Time-of-flight mass spectrometry (TOFMS) equipped with a Nd:YAG-laser for single-photon ionisation (SPI) at 118 nm and resonance-enhanced multi-photon ionisation (REMPI) at 266 nm was applied to detect the fast shift of the VOCs during the "New European Driving Cycle" (NEDC) and a self-designed "High-Speed Driving Cycle" (HSDC) with speeds from 80 km/h up to 180 km/h. REMPI is known as a soft and selective technique for the ionisation of aromatic compounds, whereas SPI is a more universal ionisation technique, which generates molecular ions from compounds with ionisation energies below the photon energy.

Both NEDC and HSDC, including engine cold start, were performed 11 times with additional idling to cover a full time period of 4 hours. Alkylated benzenes and small polyaromatic hydrocarbons (PAH) were qualitatively equally detected by REMPI-TOFMS for both types of fuels and driving cycles. Apart from the first NEDC (including the engine cold start) which produces about 50 % of the total 4 h emission (calculated by peak areas of SPI spectra), highest concentrations were observed during acceleration in NEDC (Figure 1) and constant driving at 180 km/h in HSDC. In SPI mass spectra, ethanol as the major component in both fuels revealed highest abundance during cold start, but it decreased rapidly after a few seconds with a simultaneous increase of acetaldehyde, which indicates a direct conversion. However, the combustion of E85 compared to E10 generally reduced detected VOCs by 60 % for HSDC and 75 % for NEDC on average, except for ethanol and acetaldehyde. Additionally, all quantified aromatic hydrocarbons were even diminished by 86 % for HSDC and 91 % for NEDC on average.

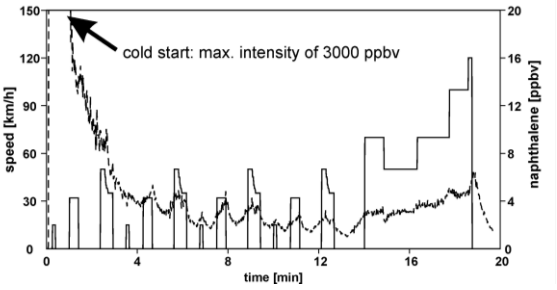

Figure 1. Naphthalene concentration from (dashed line) and speeds (solid line) in first NEDC with E10.

Interestingly, calculated emission factors of pollutants related to the covered distances were higher for NEDC than for HSDC (Table 1). It seems that many start-stop and acceleration scenarios, e.g. in city traffic, lead to higher VOC emissions than a constant fast driving on motorways. Furthermore, it was made use from the simultaneous analysis with SPI and REMPI. Knowing photoionisation cross sections at both wavelengths, emission factors for isobaric aromatic compounds, such as phenanthrene and anthracene, were calculated by solving a system of linear equations.

Table 1. Emission factors of BTX aromatics over 4 h.

[mg/km]	$NEDC_{E10}$	$HSDC_{E10}$	$NEDC_{E85}$	$HSDC_{E85}$
benzene	1.2505	0.1372	0.0062	0.0051
toluene	1.5822	0.1502	0.0151	0.0055
xylenes	1.1197	0.1058	0.0088	0.0035

This work was supported by Helmholtz Virtual Institute of Complex Molecular Systems in Environmental Health (HICE).

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