EMPA

Desulfurization events of oxidation catalysts from time-resolved SO2 measurements with CI-MS

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** Corresponding author (norbert.heeb@empa.ch)*

INTRODUCTION

Oxidation catalysts not only decompose carbonous material but also convert sulfur containing compounds. Sulfur oxidation products can accumulate in surface-rich systems like oxidation catalysts or particulate traps but may be released again at higher temperatures. CI-MS was applied to detect sulfur dioxide (SO2) which may be indicative for stochastic desulfurization events.

METHODS

Vehicle testing

Three diesel-fueled EURO-2 light-duty vehicles (LDV) model years 1999-2000, equipped with 2.2, 2.4 and 2.9 l engines and oxidation catalysts were operated with low- (<10 ppm) and high-sulfur (190 ppm) diesel in the Common Artemis Driving Cycle (CADC) at the EMPA dynamometer.

Mass spectrometric analysis

Chemical-ionization mass spectrometry (CI-MS 500, V&F GmbH, Absam, Austria), was used to monitor the [M]+-ion of SO2 at m/z 64 applying xenon as ionizing gas (Xe+, 12.2 eV). Quantitative analysis was performed from undiluted exhaust gas.

RESULTS

Figure 1 displays CO2 and SO2 mass flow of a LDV during transient driving in the CADC. As expected, SO2 levels decrease by about one order of magnitude when using low- instead of high-sulfur diesel. Stable ratios of cumulated SO2/CO2 mass emissions of 0.003 x 10-3 and 0.060 x 10-3 where found when applying 10 and 190 ppm sulfur diesel, respectively, indicating that fuel consumption and SO2 emissions where well correlated for this vehicle during the entire CADC.

Figure 2 shows CO2 and SO2 mass flow of another LDV. Several events of increased SO2 emissions were detected. The sulfur level of the diesel seems to have only a moderate effect on peak height during such emission events. Repetition of the test after a desulfurization event revealed, that sulfur compounds have been released successfully from the catalyst and the SO2 emissions remained lower during the consecutive cycle.

CONCLUSIONS

In general, SO2 and CO2 emissions are well correlated. Therefore a reduction of fuel sulfur level will reduce SO2 emissions as well.

Nevertheless, episodes of high SO2 emissions occurred, preferentially at high engine loads, e.g. at highway driving. For extended periods of time (up to 10 minutes) the amount of released sulfur exceeded the sulfur intake of the vehicle based on actual fuel consumption (see e.g. increased SO2/CO2-ratios in Fig. 2). It is assumed that decomposition and release of sulfur containing compounds, which have been accumulating in the oxidation catalysts during preceding vehicle operation, resulted in these stochastic SO2 emission peaks.

Associated with such desulfurization events is the release of ultra-fine particulates which may be of health concern.

Figure 1: CO2 and SO2 mass flow [g/h] of a low- (<10 ppm) and high-sulfur (190 ppm) diesel-fueled LDV (Mercedes-Benz Vito 110 CDI, 2.2 l) during the CADC. The velocity profile [km/h] of the CADC and the ratio of cumulated SO2/CO2-mass emissions [‰] are also given as gray curves.

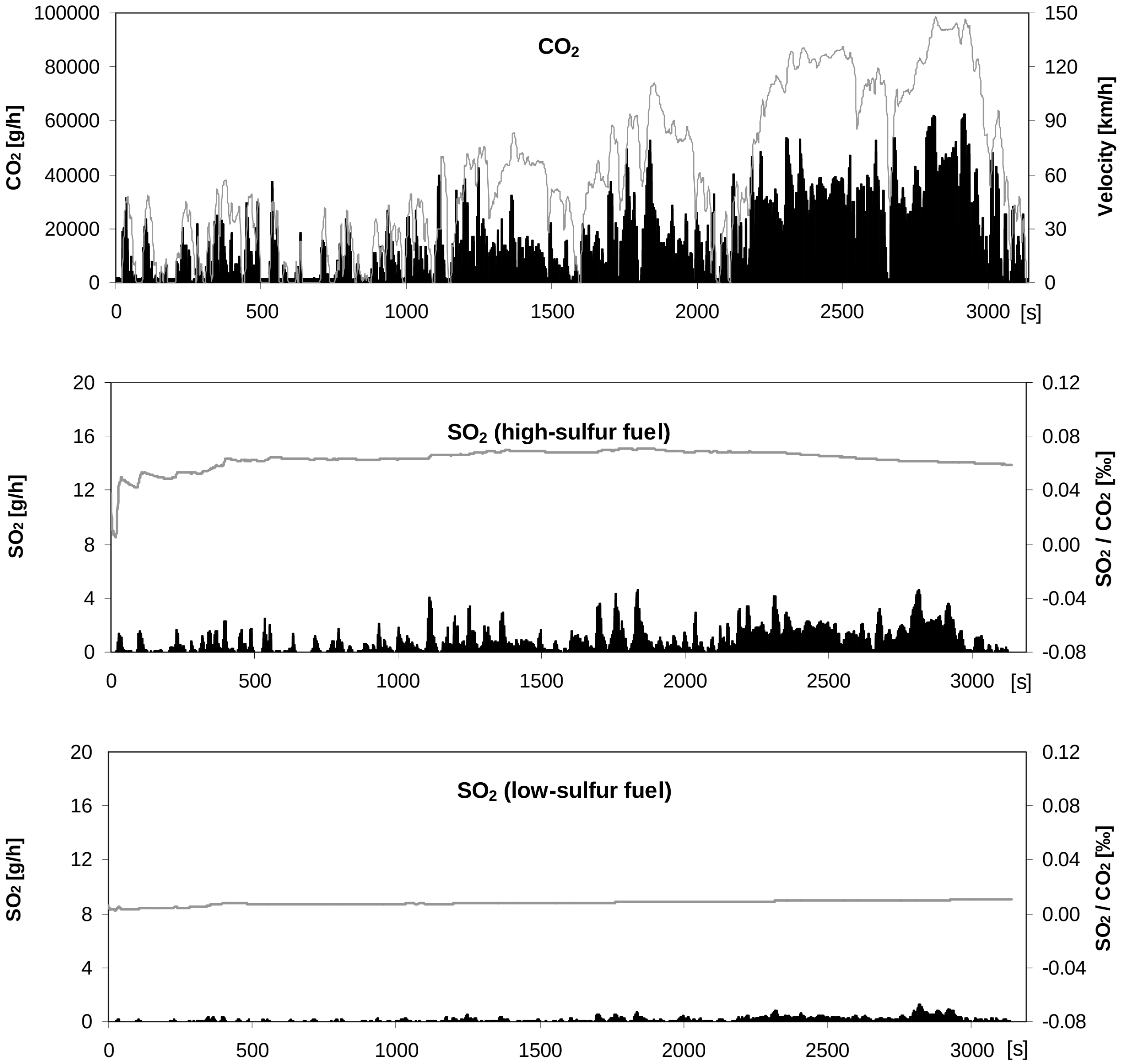

Figure 2: CO2 and SO2 mass flow [g/h] of a low- (<10 ppm) and high-sulfur (190 ppm) diesel-fueled LDV (Toyota Hiace TD, 2.4 l) during CADC. The velocity profile [km/h] of the CADC and the ratio of cumulated SO2/CO2-mass emissions [‰] are also given as gray curves.

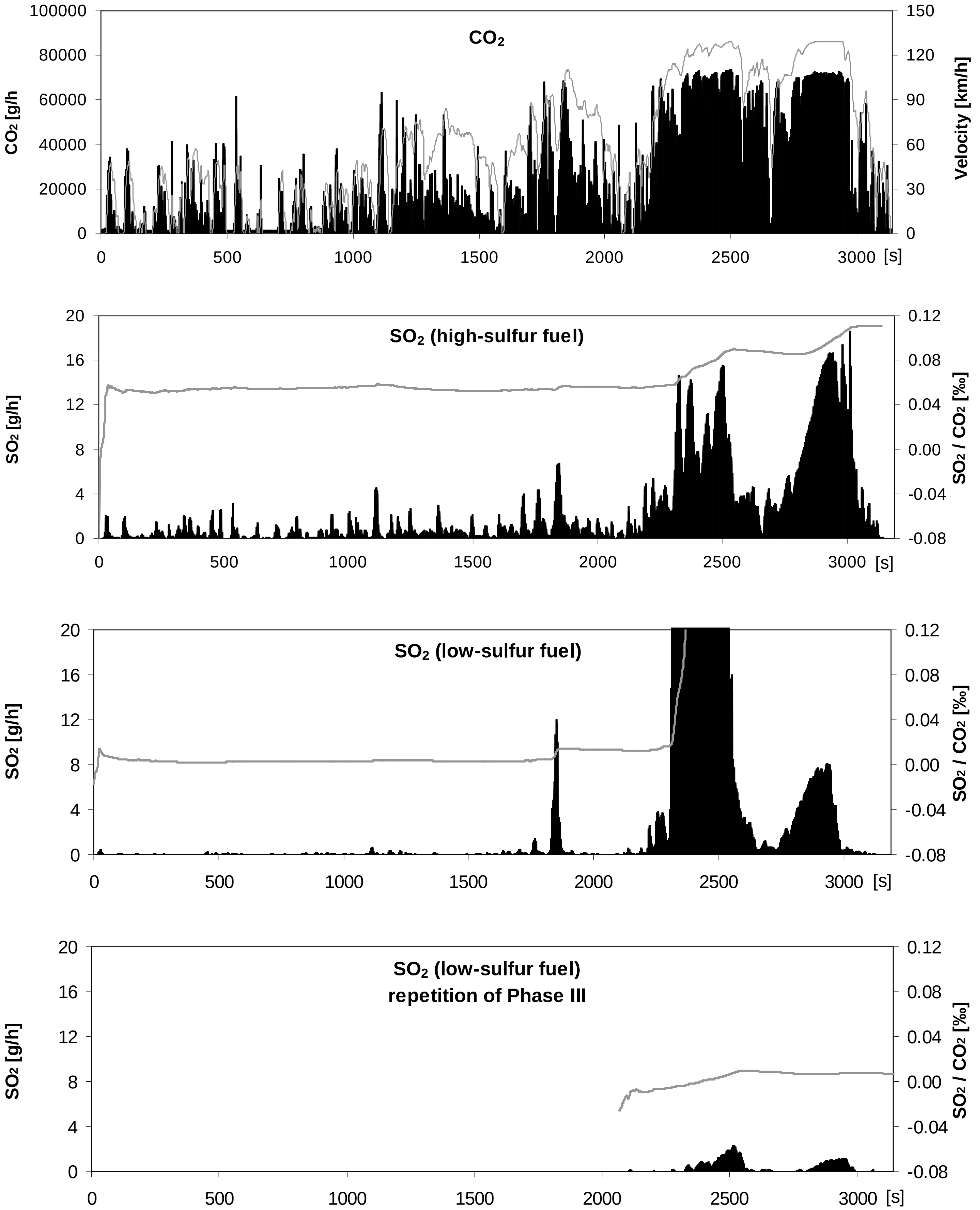

Table 1: Fuel-consumption related SO2 emission factors [mg/l] of a EURO-2 LDV fleet

LDV (model)	CADC cycle phase	SO_2 (low-sulfur fuel) [mg/l]	SO_2 (high-sulfur fuel) [mg/l]
Mercedes (Vito 110 CDI)	I II III	20 28 32	165 195 149
Toyota (Hiace TD)	I II III III (rep.)	7 49 1180 25	150 156 394
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LDV (average)	I II III	12 ± 5 18 ± 16 320 ± 520 (mean of 7 vehicles)	155 ± 9 172 ± 20 268 ± 123 (mean of 3 vehicles)

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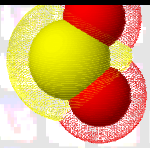

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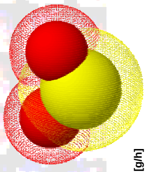

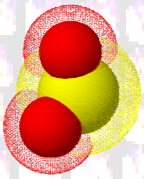

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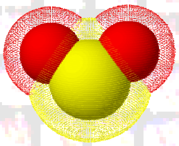

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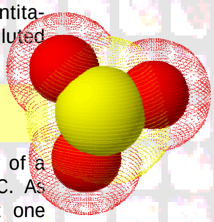

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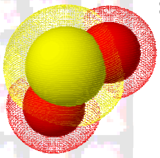

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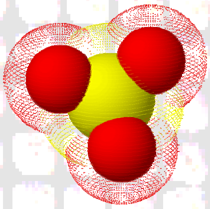

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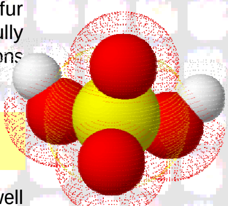

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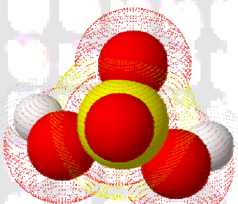

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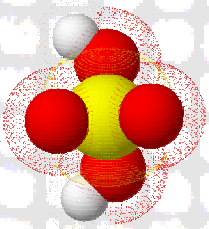

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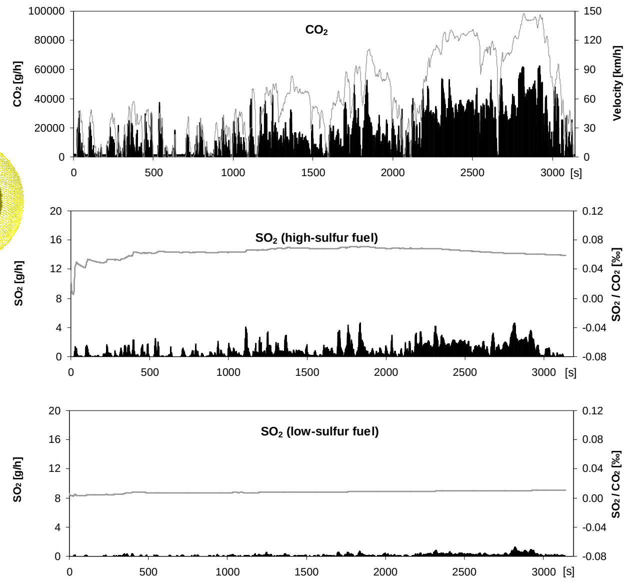

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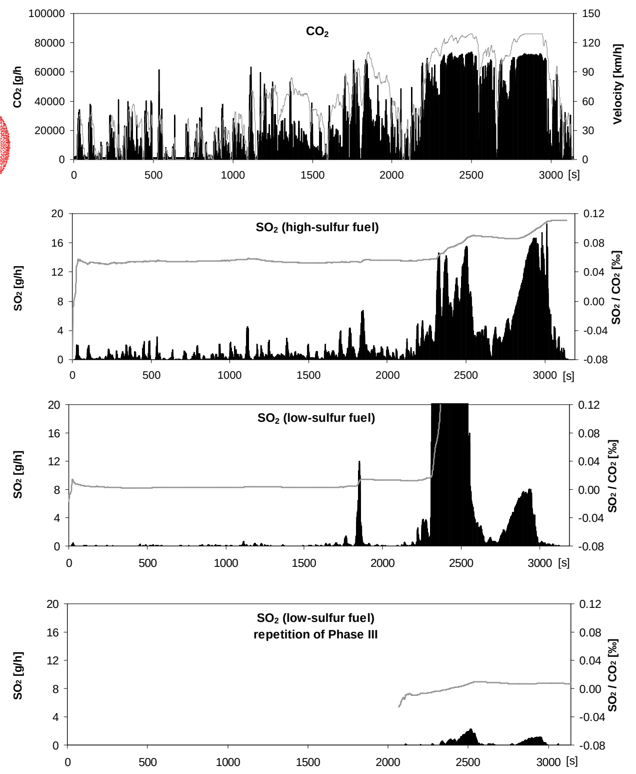

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