PCDD/F formation in active DPFs: The inconvenient truth about biofuels

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INTRODUCTION

Iron-catalyzed diesel particle filters (DPFs) are widely used in Europe and millions of vehicles are operated on our roads today. Iron-catalyzed DPFs are considered as safe with respect to their potential to form polychlorinated dibenzodioxins/ furans (PCDD/Fs, **Fig. 1**). So far, only one Cu- and two bimetallic Cu/Fe- and Fe/K-fuel borne catalysts were found to support a de novo PCDD/F formation in filters **[1,2]**. We realized that biofuels may contain up to 5 µg/g potassium and we hypothesized that the use of biofuel instead of diesel might convert an inactive iron-catalyzed DPF in an active one supporting a PCDD/F formation. In this paper, we compare PCDD/F emissions of three different iron-catalyzed DPFs and discuss their impact on PCDD/F formation and congener patterns.

METHODS

A heavy duty diesel engine (6.4 L, 116 kW, Liebherr 934 D) was operated in the 8-mode ISO 8178/4 C1 cycle either with diesel fuel (no catalyst, reference) or with iron-doped (Satacen-3) diesel and biofuel (rapeseed FAME) or with iron/potassium-doped diesel. Fe- and K-fuel levels were 85, 77 and 69 µg/g and <1, 7 and 46 µg/g, respectively. Three identical SiC DPFs (100 cpsi, 22.8 L, DINEX) were used with the different fuels. For each configuration 5-7 m^3 undiluted exhaust was collected in 200 min (2 cycles). The clean-up and analysis of PCDD/Fs with GC-HR-MS (DB-DIOXIN, MAT 95) has been described in detail **[1,2]**. On average, 58±19% of spiked ^{13}C-HxCDD could be recovered and all relevant PCDD/F congeners could be detected.

RESULTS

Fig. 2 compares emissions of 2,3,7,8-TCDF and 2,3,7,8-TCDD for different fuel-, catalyst- and filter configurations with the reference (engine-out, no catalyst, n=5). Emissions were not affected with Fe-doped diesel fuel, also in combination with a DPF, but on average increased 170- and 90-fold when Fe-doped biofuel was used with a DPF. **Fig. 3** displays the fold increase of tetra- to octa-chloro-dibenzodioxin/furan congeners for different fuel-, catalyst- and filter-configurations. Mainly tetra- and penta-chloro-DD/Fs are formed in both active filters whereas hexa, hepta- and octa-DD/F emissions are not affected. These trends are also highlighted in the congener patterns (**Fig. 4**). Whereas Cl_4- (red) and Cl_5-DFs (pink) account for ~15 and ~12 mol% in engine out exhaust, they represent ~85 and ~10 mol% in active systems.

CONCLUSIONS

The iron-catalyzed DPF does not support a de novo PCDD/F formation when operated with diesel but converts in an active system with biofuel which typically contains trace amounts of potassium. PCDD/F emissions immediately increased up to ~100-fold when iron and potassium are available. As large effects were obtained for the Fe/K-catalyzed filter operated with diesel. The inconvenient truth is that Fe-DPFs are used in millions of cars in Europe. These vehicles are now fueled with blends containing up to 10% biofuels.

ACKNOWLEDGEMENTS

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[1] Heeb et al., Environ. Sci. Technol. **2007**, *41*, 5789-5794.
[2] Heeb et al., Environ. Sci. Technol. **2013**, *47*, 6510-6517.

Figure 1: Structures, numbering and general formulas of PCDFs and PCDDs.

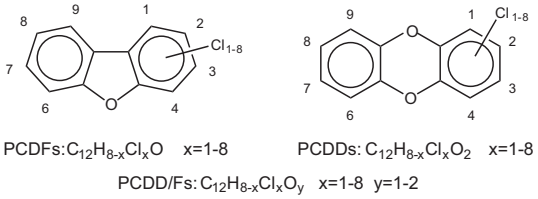

Figure 2: Fuel-, catalyst- and filter effects on emissions (pg/L fuel, logarithmic scale) of 2,3,7,8-TCDF and 2,3,7,8-TCDD. Iron-doped diesel (upper), iron-doped biofuel (middle) and iron/potassium-doped diesel (lower) with Fe contents of 85, 77 and 69 and K contents of <1, 7 and 46 µg/g were used without and with DPFs. All fuels contained Cl (10 µg/g).

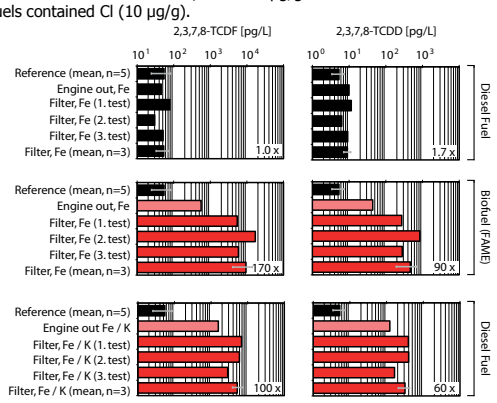

Figure 3: Fold increase (logarithmic scale) of Cl_4-Cl_8-DD (open symbol) and Cl_4-Cl_8-DF emissions (filled) after the DPF relative to the reference configuration (engine-out, no catalyst). Iron-doped diesel (upper), iron-doped biofuel (middle) and iron/potassium-doped diesel (lower diagrams) were used.

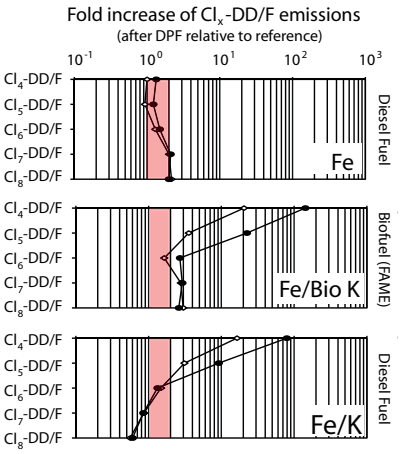

Figure 4: Fuel-, catalyst- and filter-effects on PCDD/F congener patterns. Molar proportions of Cl_4-Cl_8-DDs are colored from white to black, those of Cl_4-Cl_8-DFs vary from red to blue. Iron-doped diesel (upper), iron-doped biofuel (middle) and iron/potassium-doped diesel (lower diagrams) were used.