

INFLUENCE OF THE POP CONCENTRATION IN INPUT WASTE ON PCDD/F FORMATION MECHANISMS IN DEDICATED WASTE INCINERATORS

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Introduction

In state-of-the-art dedicated waste incinerators, POPs in the input waste are almost completely destroyed in the furnace where temperatures of at least 850 °C and residence times of at least 2 seconds are applied.¹ In the post combustion zone, including boiler and flue gas cleaning equipment, however, POPs, mainly PCDD/Fs and PCBs are newly formed. Over the last three decades, a lot of research has been performed to better understand PCDD/F formation in waste incinerators. Based on the results of numerous lab scale incineration experiments, three main formation mechanisms were put forward: homogeneous (gas phase) condensation of precursor molecules such as chlorinated phenols and benzenes, heterogeneous (gas phase/solid phase) condensation of precursor molecules and de novo synthesis involving direct formation from carbon in ash particles.²⁻⁴ Each of these mechanisms is characterized by a typical PCDD/F congener distribution or "PCDD/F fingerprint". Formation through homogeneous precursor condensation typically yields more PCDFs than PCDDs and the degree of chlorination is low. Formation through heterogeneous precursor condensation typically yields more PCDDs than PCDFs, and the degree of chlorination is high. Finally, de novo synthesis yields more PCDFs than PCDDs, but in contrast to homogeneous precursor condensation the degree of chlorination is high. In lab scale experiments, precursor condensation appeared about 100 times faster than de novo synthesis, from which it can be expected that precursor condensation is dominant in real scale waste incinerators. PCDD/F fingerprints of boiler and fly ash of real scale municipal solid waste (MSW) incinerators are however dominated by high (hepta en octa) chlorinated furans⁵⁻⁶, indicating that de novo synthesis is the main formation mechanism. This however only holds for MSW incineration, where indeed the precursor concentrations in the flue gas are generally too low for precursor condensation to be of importance. In some types of industrial waste e.g. automotive shredder residue (ASR) and in hazardous waste, the concentration of POPs such as PCBs that are easily thermally decomposed into precursors, is much higher than in MSW. So, in real scale industrial and hazardous waste incinerators, the PCDD/F precursor condensation in the flue gas is likely much higher than in MSW incinerators, which may result in a change of the dominant PCDD/F formation mechanism from de novo synthesis to precursor condensation. So far, this has not been reported in the literature. Therefore, this study investigates the influence of the POP concentration in the input waste on the dominant PCDD/F formation mechanism by comparing the PCDF/fingerprint of the boiler and fly ash of an MSW incinerator, of an MSW incinerator co-incinerating ASR and of a hazardous waste incinerator.

Materials and methods

The first case considered in this study is a fluidized bed combustor (FBC), located in Doel (North of Belgium) incinerating about 470 000 t/year of a mixture of wastewater treatment sludge (30%), MSW and comparable industrial waste (together 70%) at temperatures of at least 850 °C. The incineration gases are led through a boiler for heat recovery after which they are de-dusted in an electrostatic precipitator (ESP). Subsequently they flow through a flue gas cleaning installation before release to the atmosphere. The average PCB concentration in the incinerated waste mix is 350 µg/kg_{dw}.⁶ The other POPs measured in the input waste mix are PCDD/Fs, but their average concentration (about 1.3 µg/kg_{dw}) is negligible compared to the PCB concentration. As the installation only incinerates non hazardous waste, also the concentration of other POPs such as chlorinated pesticides is assumed negligible.

The second case considered is the same FBC, co-incinerating ASR (25%) with wastewater treatment sludge (50%) and MSW and comparable industrial waste (together 25%). The average PCB concentration of the incinerated waste mix is 3760 µg/kg.⁶ As for the first case, the concentration of other POPs is considered negligible.

The third case considered in this study is a rotary kiln incinerator (RKI), located in Antwerp (North of Belgium) incinerating about 90 000 t/year of hazardous waste at temperatures above 1100 °C. The incineration gases flow

through a boiler, are subsequently de-dusted in an ESP and then cleaned in a four-step wet gas washing unit. The hazardous waste incinerated is very heterogeneous: it consists of e.g. hospital waste, used solvents, hazardous household waste, contaminated soil etc. About 1.5% (15000000 µg/kg) of the incinerated waste consists of PCB oils and obsolete chlorinated POP pesticides. Again, the concentration of other POPs in the input waste is considered negligible.⁷

The ash samples considered in this study are a mixture of ash collected at the bottom of the boiler and ash retained in the ESP and will further be referred to as “boiler and fly ash”. These ashes are collected in and directly after the boiler in which the PCDD/Fs are formed, before any flue gas cleaning e.g. injection of PCDD/F adsorbent that may influence the PCDD/F concentration distribution. The concentration of the 17 PCDD/F congeners with WHO TEF-values in the boiler and fly ash was determined with GC-MS after soxhlet extraction according to the German AbfKlärV, Annex1. A detailed description of the analytical procedures followed is given in previous work.^{1,7} All PCDD/F analyses were performed by an accredited laboratory that had to participate regularly in government-organised inter-comparisons in order to demonstrate quality.

Results and discussion

Figure 1 gives the PCDD/F fingerprints of the boiler and fly ash of the FBC incinerating the usual sludge/MSW waste mix, the FBC co-incinerating ASR, and the RKI. The boiler and fly ash of the FBC incinerating the usual sludge/MSW waste mix clearly contains the lowest PCDD/F congener concentrations, ranging from < 1 to 1400 ng/kg_{dw}, with a total PCDD/F concentration of about 3000 ng/kg_{dw}.

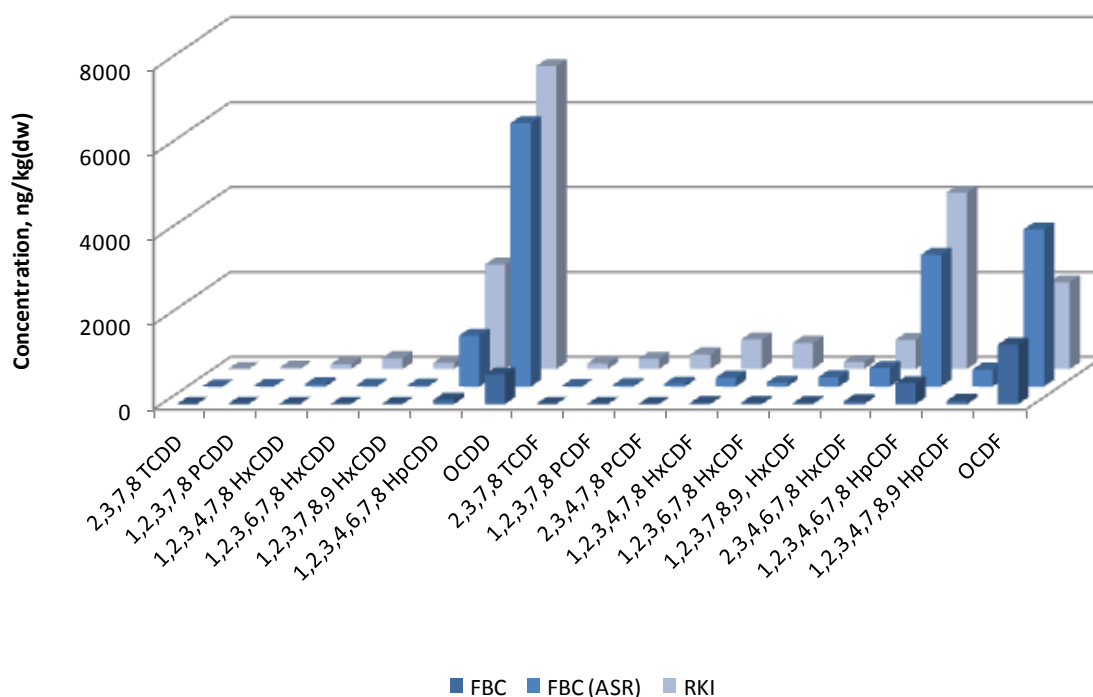


Figure 1: PCDD/F congener concentrations in the boiler and fly ash of the FBC, the FBC co-incinerating ASR, and the RKI

The PCDD/F congener concentrations in the boiler and fly ash of the FBC co-incinerating ASR are about 3 to 10 times higher than in the boiler and fly ash of the FBC incinerating the usual sludge/MSW waste mix, and the total PCDD/F concentration is about 15 800 ng/kg_{dw}. The highest congener concentrations are found in the boiler

and fly ash of the RKI, that contains in total about 19 500 ng PCDD/Fs/kg_{dw}. So the higher is the POP concentration in the waste input, the higher the PCDD/F concentration in the boiler and fly ash. As explained in the introduction, the PCDF/PCDD ratio and the degree of chlorination reveal important information on the dominant PCDD/F formation mechanism. To examine these aspects, Figure 2 depicts the congener concentrations as percentage of the total PCDD/F concentration in the boiler and fly ash of the three incineration cases considered in this study.

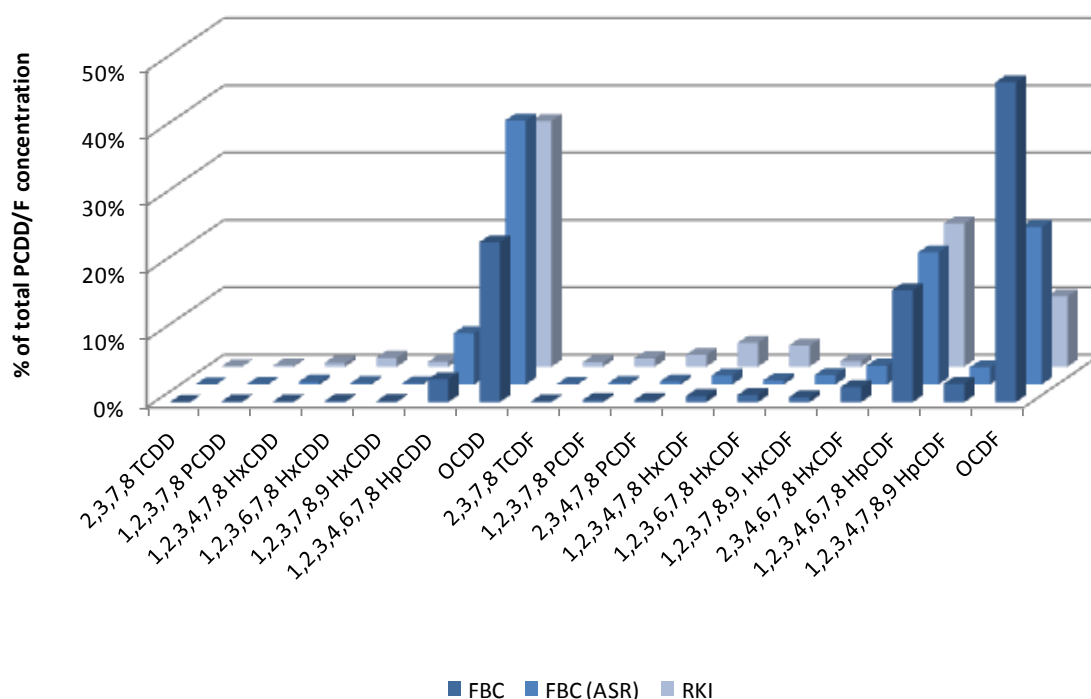


Figure 2: PCDD/F congener concentrations as percentage of the total PCDD/F concentration in the boiler and fly ash of the FBC, the FBC co-incinerating ASR and the RKI

The fingerprint of the boiler and fly ash of the FBC are dominated by PCDFs, reflected in a PCDF/PCDD ratio of 2.6. Furthermore, the high (hexa to octa) chlorinated congeners account for more than 99% of the total PCDD/F concentration. These two characteristics are typical for de novo synthesis, confirming that in the FBC incinerating sludge and MSW-like wastes, de novo synthesis is the dominant formation mechanism. The fingerprint of the boiler and fly ash of the FBC co-incinerating ASR is characterized by a PCDF/PCDD ratio of 1.1 and similar to the boiler and fly ash of the FBC incinerating sludge and MSW-like wastes, the high chlorinated congeners account for more than 99% of the total PCDD/F concentration. So also in this case, de novo synthesis appears the dominant formation mechanism. The increase of the relative contribution of higher chlorinated PCDDs, mainly OCDD, however suggests that heterogeneous precursor condensation mechanism has gained in importance. As OCDD is the most abundant congener in the ASR, another explanation for the relatively high increase of the OCDD concentration is that fine ASR particles were entrained from the fluidized bed directly into the boiler.⁷ The PCDD/F fingerprint of the boiler and fly ash of the RKI is dominated by PCDDs (the PCDF/PCDD ratio is 0.9), indicating that heterogeneous precursor condensation is the dominant formation mechanism in this hazardous waste incinerator. Furthermore, relatively more low (tetra and penta) chlorinated furans are present; they account for about 4% of the total PCDD/F concentration. These lower chlorinated furans are typical products of homogeneous precursor condensation. It can be concluded that, if the

POP concentration in the waste to be incinerated slightly increases (about 10 times higher than in MSW), as is the case when ASR is co-incinerated in the considered FBC, de novo synthesis remains the dominant PCDD/F formation mechanism. If however the waste to be incinerated contains much (about 40 000 times) more POPs, as is the case in the considered hazardous waste incinerator, the PCDD/F precursor condensation in the flue gas becomes high enough for homogeneous and heterogeneous precursor condensation to become the dominant formation mechanism. These findings surprisingly confirm the suggestions of Huang and Buekens² that in MSW incinerators de novo synthesis is dominant because the precursor concentrations in the flue gas are generally 10^5 to 10^6 times too low for precursor condensation to be of importance.

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