

Appendix 2: Small-Scale and Other Combustion Systems/Processes: Studies Relevant to the Relationship of Chlorine Input and Dioxin Formation^a

Combustion System or Process	Source	Key Excerpts and Notes
Internal combustion engine	Broz et al. (2000) ¹	<p><i>“The effect of synthetic and mineral oils on the formation of polyaromatic hydrocarbons (PAHs), polychlorinated dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs), and biphenyls (PCBs) in emissions from a spark ignition engine was studied on a Skoda Favorit engine fueled with leaded gasoline. ... The restriction of PCB and PCDD/F in emissions can be achieved by exclusion of the presence of halogens, especially of chlorine in the reaction system, regardless of whether it is organic- or inorganic-bond.”</i></p>
Open barrel	Gullett et al. (2000) ²	<p><i>“... the test container consisted of a 208 L (55 gal.), steel, precleaned barrel with 24 2 cm diameter ventilation holes around the base. ... The last two baseline tests had values of 429 and 609 ng TEQ/kg. ... One open burn (waste pile) test ... with the baseline waste composition resulted in emission of 59 ng TEQ/kg. This suggests that open burning produces less PCDDs/Fs than containerized barrel burning, but this remains to be verified by replicate tests. ... PCDD/F emissions increase with higher amounts of Cl, whether organic or inorganic, and higher amounts of Cu catalyst.”</i></p>
Domestic furnace	Launhardt and Thoma (2000) ³	<p><i>“Various herbaceous biofuels (straw, whole plant cereals and set aside hay) and spruce wood were tested The trials were conducted in an automatically charged multi-fuel furnace for domestic applications (50 KW_{th}). Both flue gas and the different ash fractions were analysed. However, for the PCDD/F, PCPh and PCBz increased emissions were detected when herbaceous fuels were applied. This may be attributed to their higher chlorine concentration and the high ash content, which is responsible for increased dust emissions during combustion. Similar observations were also found for the</i></p>

^a This compilation of studies is not a fully comprehensive collection of all such studies on this topic.

		<i>PCDD/F-concentrations in the ashes. ... Investigations on modern biomass combustion plants in Bavaria (Huber and Friess 1998) showed, that PCDD/F emissions are slightly higher for straw and whole crops, compared to wood. A dependence of PCDD/F-emissions on the chlorine content in the fuel can also be found for the biomass tested here ..."</i>
Open barrel	Lemieux et al. (2000) ⁴	<i>"This study measured the emissions of several pollutants, including polychlorinated dibenzo- p-dioxins and polychlorinated dibenzofurans (PCDDs/PCDFs), from burning mixtures designed to simulate waste generated by a "recycling" and a "nonrecycling" family in a 208-L (55-gal) burn barrel at the EPA's Open Burning Test Facility. Emissions of PCDDs/PCDFs appear to correlate with both copper and hydrochloric acid emissions. ... the percentage of PVC for the avid recycler rose from 0.7% to 4.5%. ... In general, PCDDs/PCDFs emissions were higher for the avid recycler than for the nonrecycler. ... These data suggest that increases in emissions of either copper or HCl may be associated with increases in PCDD/PCDF emissions."</i>
Semi-open household waste burner	Ikeguchi et al. (2000) ⁵	<i>"Levels of dioxins in the flue gas ranged widely, from 0.3 ng-TEQ/Nm³ to 4500 ng-TEQ/Nm³, reflecting a kind of waste and a combustion condition ... Especially corrugated paper mixed with polyvinyl chloride (PVC) recorded higher value, more than 100 ng-TEQ/Nm³ while corrugated paper mixed with polyethylene (PE) and polystyrene (PS) accounted dioxins level below 50 ng-TEQ/Nm³, as similar as in the cases of wood chip, newspaper, and garden waste. ... As shown dioxins [sic] level increases as chlorine concentration in waste increases irrespective with the type of chlorine, i.e., organic or inorganic chlorine."</i>
Small waste incinerator	Nakao et al. (2000) ⁶	<i>In "a small incineration with a combustion capacity of 50 kg/hr On the other hand, a mixture of combustions of chloric plastic (No. 7) and electric wire (No. 8) gave a remarkably high concentration [of dioxins]. From these results, it is clear that generation of dioxin analogues increased by a mixture of combustion with chloric plastic. "</i>

Simulated house fire	Ruokojarvi et al. (2000) ⁷	<p><i>“Simulated apartment fires were arranged in the two floor block of flats normally used for fire fighting practice. Pieces of chipboards and old furniture were used as fire loads. ... Adding PVC plastic material to the fire (samples G5 and G7) did not increase the PCDD/F concentrations in combustion gas samples, even though the concentrations of CPhs, which have been regarded as PCDD/F precursors, did seem to increase. The highest PCDD/F concentrations were in samples 5, 6 and 7, however, and no PVC had been added to the fire in the case of sample 6. ... The highest PCDD/F concentrations in the wipe samples were in sample W4, collected during the fires with additional PVC, but the concentrations in sample W1 were nearly as high, so that it cannot be concluded that the extra PVC was responsible for the increase.”</i></p> <p>[Note: No attempt was made to determine either the chlorine content or the PVC content in the materials burned in these experiments. The materials contained in each of the seven `fireloads' were highly variable. However, additional PVC was included in two of the seven `fireloads'. Among the three `fireloads' that resulted in the highest air concentrations of dioxins, in TEQs, two had added PVC. Also, as the authors noted, the wipe samples having the highest dioxin concentrations were those from the two PVC-augmented `fireloads'.]</p>
House heating systems	Launhardt et al. (1998) ⁸	<p><i>“The PCDD/F-concentrations in fluegases using untreated wood were in the range of 2-25 pg I-TE/m³. The combustion of paper, cartons, painted wood and wood with 2-5% PVC gave PCDD/F-concentrations from 38 to 952 pg I-TE/m³ and 380 to 2,240 ng I-TE/kg (chimney soot). ... Analogous to the emission the concentration in the chimney soot increases with the content of chlorine (up to 2 240 ng I-TE/kg). The PCDD/F-concentrations in chimney soot using natural wood were on a low level of 32 ng I-TE/kg.”</i></p>
House-heating stove – tile with air circulation	Thuss et al. (1997) ⁹	<p><i>“Lignite briquettes with different salt contents (“normal”-coal, 300 ppm w/w, “salt”-coal, 2000 ppm w/w) were burned in a common type of a house heating facility. The content of polychlorodibenzodioxins and furans (PCDD/F) in</i></p>

		<p><i>the flue gas and in the bottom ash were determined. The values calculated from the homologue sums were significantly higher for the "salt"-coal briquettes regarding their flue gas concentrations and slightly increased in respect to the bottom ashes. Taking into account a wide variety of additional analytical parameters and considering mechanistic aspects, our assumption was proved that the higher chlorine content of the "salt"-coal briquettes is responsible for the increased values. ... From the discussion of the single parameters it can be deduced that the higher PCDD/F-emission of the "salt"-coal combustion is caused by the higher chlorine content of the "salt"-briquettes. All other alternative approaches to explain this difference were found to be non-relevant ... The only plausible explanation for the higher PCDD/F content of the "salt"-coal bottom ash is the higher chlorine content as well."</i></p>
Open barrel	Lemieux (1997) ¹⁰	<p><i>"It is probable that the fraction of PVC in the refuse contributes significantly to the total amount of PCDDs/PCDFs produced. ... [E]missions of PCDDs/PCDFs are significantly higher for the avid recycler. This phenomenon is likely due to several factors, including the higher mass fraction of PVC in the avid recycler's waste, a different temperature profile, and possibly a different mix of metallic catalysts"</i></p>
House-heating stove – tile with air circulation	Thuss and Popp (1995) ¹¹	<p><i>"Investigations of emissions of PCDD/F from lignite domestic heating were performed. ... Two sorts of lignite briquettes were investigated: "salt" coal briquettes from the former open cast mine Merseburg-Ost (chlorine content: 2000 ppm w/w) which belonged to the preferred fuels in the GDR and "normal" coal briquettes from the open cast mine Profen (chlorine content: 300 ppm w/w) which have been widely used in the eastern part of Germany. It is shown that the PCDD/F concentrations of the flue gases of the "salt" coal combustion are about 7- fold higher than the corresponding values of the "normal" coal. The patterns of the congeners and the homologue profiles are nearly the same. ... From this investigation, we deduced that the higher PCDD/F emission of the salt coal combustion can be</i></p>

		<i>correlated with the higher chlorine content of the "salt" briquettes. All other alternative approaches to explain this difference were found to not be relevant because the corresponding parameters do not differ significantly ... Various investigations with synthetic coals under defined conditions produced the result that PCDD/F-formation during coal combustion processes is strongly dependent on the chlorine supply originating from the used feed stock."</i>
Open fire	Merk et al. (1995) ¹²	<i>In the fire experiment 500 kg wood and 40 kg PVC were completely incinerated. The fumes dispersed throughout the closed hall ... The concentrations of PCDD/F in the fumes of PVC fire (about 5 ng TE/m³) are in the same range as the concentrations of PCDD/F in stack gas of municipal waste incinerators. ... These results show that incineration of PVC in open fires result on considerable amounts of PCDD/F, which demonstrate the toxic potential of these industrial material in accidental fires.</i>

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