

CONCENTRATION OF PCDDs, PCDFs AND PCDTs IN BOTTOM ASH FROM DOMESTIC HEATING SYSTEMS AS AN EFFECT OF FUEL COMPOSITION

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Introduction

Levels and patterns of PCDD/Fs in emissions and ashes from industrial combustion systems have been well recognized and described for almost all possible installations. As industrial installations, especially waste incinerators, are under regulation and subject to monitoring, emissions from these sources have been reduced over the last few years. That reduction results in other sources becoming more significant, and attempts to reduce uncontrolled sources of pollution have been made since the end of the 20th century.

The domestic combustion of the fossil fuels used in heating and/or cooking is neither regulated nor controlled, despite the fact that this has frequently been discussed in terms of its being possible source of dioxin and furan emissions. Domestic heating systems are usually considered the main explanatory factor underpinning uncertainties in dioxin balances between emission and deposition. The last decade has seen a number of investigations carried out to focus on different aspects of this topic. From the various studies, it can be concluded that combustion of liquid or gaseous fuels in common heating appliances does not lead to significant PCDD/F formation^{1,2}. By contrast, the burning of solid fuels, like coal, lignite or wood may cause increased dioxin emissions³. Of these fuels, only wood, in some European countries the predominant household energy source, has been suspected of constituting a considerable source of dioxin emission when burnt⁵. This is particularly due to the high emission factors found if contaminated wood (i.e. that treated with wood preservatives like PCP or wood containing other chlorinated compounds) is combusted. As the amount and composition of the contaminated wood burned in households is not well known, the dioxin emission can only be estimated with a high degree of uncertainty. Investigations of wood combustion are focused mainly on treated wood, as PCP or copper-based fungicides may result in dioxin formation.

By contrast, whenever investigated, dioxin emissions from coal combustion have been found to be comparatively low; a default emission factor of 2 µg TEQ per tonne fuel being applied for emission estimations in the report on Stage I of the DG XI European Dioxin Project⁴. Using this factor, the overall annual PCDD/F release from domestic coal combustion in 17 European countries is found to be at the level of only around 40 g I-TEQ (equivalent to less than 1% of the total PCDD/F emission). However, in 1998, the Austrian *Umweltbundesamt* presented an unexpectedly high emission factor for the combustion of hard coal from Poland in a simply-constructed single heating stove⁵. Application of this emission factor (range: 108 to 663 µg I-TEQ/tonne fuel at 0% O₂) would at least double the emission estimate for domestic combustion in Austria, and would increase the Stage-I European estimate by two orders of magnitude. This would after all leave the domestic combustion of coal as the most relevant emission source in Europe, especially since coal is still used in many EU countries.

Observations made in Poland emphasise that various materials are subject to combustion in domestic ovens and heating systems. Material varies from pure wood and high-quality coal, through to paper and other printed matter, including color magazines (journals) whose different inks are based on heavy metals. The effects of the combustion of such materials have not been studied so far.

The presence of sulfur analogues of dioxins, e.g. polychlorinated dibenzothiophenes (PCDTs), as reported by Czerwinski *et al.*⁶ in the emissions from the Hospital Waste Incinerator, has not been so widely studied either. Levels of PCDTs in domestic installations have not been measured, as the toxicity of dibenzothiophenes is still under discussion. But incineration of coal (with a high sulfur content) and paper (produced by the "sulfite method") are suspected potential sources of PCDT generation.

Thermal processes

Leaving aside emissions, the levels of PCDDs, PCDFs, and PCDTs in ashes from domestic combustion (i.e. the bottom ash from heating systems) may of themselves cause problems and act as additional dioxin sources. All countries' regulations treat the bottom ash from Waste Incinerators as hazardous waste, yet ash from private heating installations is not made subject to proper disposal or utilisation.

Materials and Methods

PCDD, PCDF and PCDT concentrations were measured in the bottom-ash from four similar systems in different households in which the dominant fuel comprised such different materials as beech wood, willow (*Salix viminalis*), hard coal (from the Bogdanka coal mine and with a sulfur content of ca 1.2%) and waste paper. To meet the needs of the experiments, special incinerations based on 100% glossy paper were performed. Beech wood was in turn selected as a reflection of the confusing nature of information contained in the literature. Some authors⁷ claim that emissions of furans from beech incineration were lower than those from other types of wood, while others⁸ found that dioxin levels from beech were higher than those from pine. All experiments were repeated 3 times, with measurements performed in 3 repetitions.

Samples were collected into pre-washed glass containers. Before extraction, ash samples of 20 g dry weight were spiked with a mixture of ¹³C-labeled solution of PCDD/Fs (from CIL), and extracted in Soxhlet apparatus for 18 hours with toluene. The extracts were concentrated to incipient dryness and transferred to hexane, before being purified via a 3-stage (multilayer silica, alumina and carbon/silica) open-column chromatography procedure. Finally, the samples were concentrated to incipient dryness prior to the addition of the recovery standard. After that, samples were analyzed using a GCQ Finnigan GC/MS/MS system equipped with a DB-5ms column. The precise determination method for PCDTs is as described by Czerwiński *et al.*⁶. Recoveries for PCDD/Fs were determined by analysis of DX-1 reference material and for PCDTs by addition of standards for previously-extracted bottom ash.

For the determination of trace-metal contents, 0.5g of ash samples were digested in a microwave oven (MDS-2100 CEM) with a mixture of concentrated nitric and hydrochloric acids at 3:1 (v:v). Analysis was carried out on a Hitachi Z-8200 atomic absorption spectrometer. Zinc, copper, iron and lead were analysed, on account of their suspected catalytic effects on dioxin formation as well as their expected occurrence in incinerated materials.

Results and Discussion

Results for the PCDD, PCDF and PCDT determination in bottom ashes from different incineration runs are as presented in Table 1, while selected metal concentrations are brought together in Table 2.

The coal used in the experiments was of "high" quality, with a sulfur content at 1.2%. The paper was the "glossy" paper used in magazines and journals. Beech wood was typical for the region. There is no information in the literature specifically about the accumulation of dioxins or metals by beech wood.

Willow has become a very popular fossil fuel. It is cultivated in degraded polluted areas and incinerated at a number of installations. Attempts to use willow as a fuel in cement plants have also been made in different countries. In this case, willow was cultivated in the area near the city of Lublin south-eastern Poland, this mainly being an agricultural region. The willow field is nevertheless situated close to a road that is used intensively in the summer season, taking the main traffic from Lublin, a city of almost 400,000 inhabitants, to a lake recreation area nearby. Orchards were grown in the area years before willow. Copper and zinc may originate from pesticides used in the orchards. Today only unleaded petrol is used in Poland, but the soil may still hold lead from earlier contamination when leaded petrol was still in use just a few years ago.

Thermal processes

Table 1. Mean concentrations of PCDDs, PCDFs and PCDTs (ng/kg) in ashes from the different combustion experiments.

Congeners	Coal from "Bogdanka Mine"	Beech wood	Waste paper	Willow	LOD
<i>Dioxins</i>					
1,2,3,4-TCDD	21	nd	56	12	2
2,3,7,8-TCDD	23	nd	61	7.2	2
1,2,3,7,8-PeCDD	9	nd	17	6	1
1,2,3,4,7,8-HxCDD	6	2	11	19	1
1,2,3,6,7,8-HxCDD	nd	nd	6.5	nd	1
1,2,3,4,6,7,8-HpCDD	nd	nd	nd	4	1
OCDD	nd	nd	nd	nd	2.5
Σ PCDDs	59	2	151.5	48.2	
WHO TEQ	32.6	0.2	79.75	15.14	
<i>Dibenzofurans</i>					
2,3,7,8-TCDF	119	44	139	115	2
1,2,3,7,8-PeCDF	34	nd	49	54	1
2,3,4,7,8-PeCDF	42	21	43	21	1
1,2,3,4,7,8-HxCDF	32	21	nd	nd	1
1,2,3,6,7,8-HxCDF	nd	nd	6.2	13	1
2,3,4,6,7,8-HxCDF	4	2	11	48	1
1,2,3,7, 8,9-HxCDF	6	nd	4	nd	1
1,2,3,4,6,7,8-HpCDF	14	nd	23	3.6	2
1,2,3,4,7,8,9-HpCDF	2	nd	2	8.2	1
OCDF	nd	nd	nd	nd	2.5
Σ PCDFs	222	88	277.2	262.8	
WHO TEQ	38.96	17.2	40.22	30.92	
<i>Dibenzothiophenes</i>					
2,3,7,8-TCDT	27	13	45	89	2
1,2,3,7,8-PeCDT	9	nd	53	42	1
2,3,4,7,8-PeCDT	27	6	26	33	1
1,2,3,4,7,8-HxCDT	21	12		7.3	1
1,2,3,6,7,8-HxCDT			6.25	16.2	1
2,3,4,6,7,8-HxCDT	2	nd	7	11	1
1,2,3,7, 8,9-HxCDT	2	nd	nd	nd	1
1,2,3,4,6,7,8-HpCDT	6	nd	23	31	2
1,2,3,4,7,8,9-HpCDT	nd	nd	nd	3.6	2
OCDT	nd	nd	nd	nd	2.5
Σ PCDTs	94	31	160.25	233.1	

Table 2
Mean concentration of selected metals (mg/kg) in ashes from the different combustion experiments.

Metal concentration	coal from "Bogdanka"	beech wood	waste paper	willow	LOD
Zn (mg/kg _{pr})	112	120	3000	1254	0.5
Cu (mg/kg _{pr})	264	39	369	132	0.5
Fe (mg/kg _{pr})	17400	75	42050	5340	0.5
Pb (mg/kg _{pr})	28	9	1039	973	0.2

As Table 1 shows, all the ash samples had levels of dioxins lower than those of furans and dibenzothiophenes. This confirms previous findings to the effect that emissions of furans from wood combustion are greater than those of dioxins¹².

Dioxins, furans and dibenzothiophenes concentrations were lowest in the ash from beech wood incineration and highest in ash from waste-paper incineration. For most of the samples, concentrations of lower-chlorinated congeners were higher than higher-chlorinated, the exception being beech wood, in which tetra- and penta-chlorinated dioxins were present below detection limits (only hexachlorinated congeners were detected for dioxins). The total concentrations of PCDDs for coal ash were lower than PCDF concentrations, but the sum of the toxicity factors (WHO-TEQ) were similar for dioxins and furans.

TEQ toxicity for the ash of beech wood and willow (fossil fuels) derives mainly from furans, while in the case of coal, dioxins and furans are of equal relevance. The highest toxicity was measured for ash from waste paper. In the examined samples, the toxicity due to dioxins was twice as severe as in the case of furans.

The total concentrations of furans for coal, waste paper and willow were at a similar level (above 200 ng/kg), but concentrations of dioxins varied, the lowest being for willow and the highest for waste paper. Concentrations of dibenzothiophenes were lowest in the case of beech wood, highest for willow (above 200 ng/kg). The figure for waste paper was of only 160 ng/kg.

Willow, recognized as an environmentally-friendly biomass fuel, did not give rise to high levels of dioxins, but concentrations of dibenzofurans and dibenzothiophenes were distinctly high. This may be an effect of the high concentrations of iron and zinc in willow and paper, as these metals are known for their catalytic effects where the chlorination of hydrocarbons is concerned⁹. Nevertheless, unexpectedly, the highest concentration of dibenzothiophenes was found in the ash from willow combustion. This ash was also characterized by the highest concentration of metals, as willow is known for its cumulative properties. Coal containing sulfur, and waste paper, when processed using the sodium sulfite method, gave ash with a lower concentration of sulfur analogues of furans. Copper has been recognized as catalyzing dioxin formation, such that higher levels of it in the ash samples were reflected in higher generated concentrations of PCDDs. This effect could not be observed for PCDFs and PCDTs, however.

Results show that ash from the domestic combustion of solid fuels may be an important source of dioxins and dioxin-like compounds to the environment. This is especially true where a variety of waste materials, e.g. paper, are used for burning.

Equally, properly-run ovens working on 100% coal or untreated wood give rise to lower levels of dioxins in ash, and probably also in the emissions they produce.

Acknowledgements

This research was carried out under Project No. 1269/T09/2004/27, as financed by the Ministry for Scientific Research and Information.

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