

EMISSIONS OF PCDD/Fs AND WHO-12 PCBs FROM STACK FLUE GASES OF SINTER PLANTS IN THE UK

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Introduction

Steel made in the UK and most European countries is mainly produced at integrated works using a series of closely-linked processes : coke ovens, sintering, blast furnace, basic oxygen steel making (BOS), casting and rolling. Amongst steel-making processes, previous studies showed that the sintering of iron ore is a significant source of dioxins (PCDD/Fs)¹. Investigations carried out in the period 1994-1999 at the five sinter plants operated by Corus in the UK showed that the overall PCDD/F stack emission concentration was 1.21 ng I-TEQ / Nm³, yielding an estimated mass release between 37 and 40 g TEQ / year². Since 1998, a group of 12 PCBs, exhibiting a 'dioxin-like' behaviour, has been identified by the World Health Organisation (WHO) and the individual members of the group have been assigned toxic equivalent factors (TEFs) relative to that of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin³. These so-called WHO-12 PCBs are included as part of the overall dioxin concentration and should now be systematically investigated in industrial emissions. Therefore, Corus group has recently modified its PCDD/F analytical procedure in order to allow quantitative determination of WHO-12 PCBs by isotope dilution using a method derived from US EPA method 1668A⁴.

As a very limited amount of data is available with regard to PCBs in emissions of the iron ore sintering process, sampling trials were carried out in 2002 and 2003 at the three sinter plants operated by Corus in the UK. This study summarises the PCDD/F and PCB results obtained during those investigations. The congener profiles of PCDD/Fs and WHO-12 PCBs in the stack flue gases of these three sinter plants are presented and compared. The annual emission quantities of PCDD/Fs and WHO-12 PCBs estimated from the emission factors of each sinter plant were also determined.

Iron Ore Sintering in the Integrated Iron and Steelmaking Process

In the integrated iron and steelmaking process, the production of steel involves a series of processes whereby iron is extracted from iron ores in the blast furnace and converted to steel in the basic oxygen steelmaking (BOS) process. Iron ore is prepared as a feed suitable for the blast furnace by sintering, an agglomeration process, depicted in Figure 1. Full description of the sintering process is available in the literature^{5,6}. The objective is to convert coarsely powdered iron ore into lumps, which provide the necessary open structure for blast furnace operation. The feed of

the process consists of a moist agglomerate of fine-grained iron ores, recycled materials, coke breeze and limestone. The feed is laid on a moving grate and coke particles in the top layer of the materials are ignited by gas burners thus creating a combustion front. Air is drawn downwards through the sinter bed into a series of wind boxes beneath the strand. The temperature of the bed reaches 1300 - 1480°C. At the end of the bed, the sinter product falls off into a cooling system, typically a carousel. The gases withdrawn through the wind legs are combined in the wind main, de-dusted by means of an electrostatic precipitator (ESP), and are emitted to the atmosphere via the main stack.

The process is carried out by wet mixing the ore with 3 - 4 % weight of coke breeze and the other additives and spreading the mixture on a base moving at 2 - 3 m min⁻¹, typically 2 - 4 m wide to a depth of 0.4 - 0.5m.

The combustion process is initiated at the top of the bed and drawn through it by induced draught fan via a series of ducts below the bed. A gas fired igniter coke particles at the surface of the bed, thereafter combustion is self-sustained. As the coke fines burn in the bed, the generated heat sinters the fine particles. The temperature of the bed reaches 1300 - 1480°C. At the end of the bed, the sinter product falls off into a cooling system, typically a carousel. The gases withdrawn through the wind legs are combined in the wind main, de-dusted by means of an electrostatic precipitator (ESP), and are emitted to the atmosphere via the main stack.

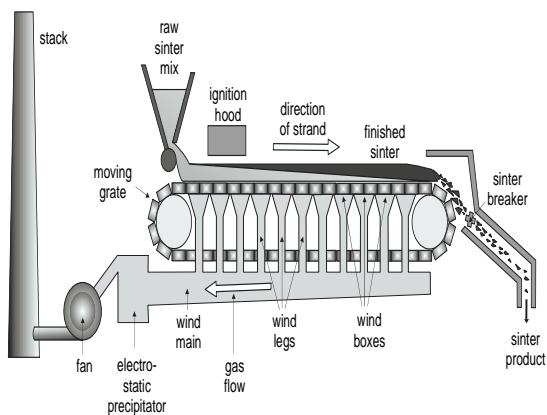


Figure 1 : Schematic of a typical sinter plant

Experimental

Sampling details

Stack emission samples were collected at three sinter plants operated by Corus in the UK during 2002-2003 [Sinter plants A (09/2002 ; 10/2002), B (09/2002 ; 04/2003), and C (06/2003)]. For each trial, triplicate emission samples (duplicate only for sinter plant B) and a sampling method blank were collected from the main sinter plant stacks. Sampling was achieved using an UKAS-accredited method (ISO17025) derived from US EPA Method 23. The sampling train, a Graseby Andersen Manual Stack sampling train (Graseby Andersen, Bedfordshire, UK), was composed of a heated glass-lined sampling probe and filter equipped with a glass fibre filter element and a water-cooled XAD-2 sorbent trap. Samples were collected isokinetically through a heated glass-lined sampling probe, particulate were collected on a glass fibre filter contained in a heated filter box whilst vapour phase PCDD/Fs and PCBs were trapped on XAD-2 resin contained in a water-cooled trap. XAD-2 sampling kits were previously spiked with PCDD/F and PCB sampling standards (EDF-4054 / EC-4978, Cambridge Isotope Laboratories, LGC Promochem, UK). The analytical samples consisted of the filter, XAD-2 resin, and solvent washings from the glassware of the sampling train.

Analytical procedure

The operation of the laboratory for PCDD/Fs and PCBs analysis has been described in more detail elsewhere⁴. Samples were analysed using UKAS-accredited (ISO17025) methods for PCDD/Fs and WHO-12 PCBs. Briefly, samples were spiked prior to extraction with the ¹³C₁₂ internal standard solutions of the methods US EPA 23 and 1668A (EDF-4053 / EC-4977, Cambridge Isotope Laboratories, LGC Promochem, UK). Samples were extracted with toluene by accelerated solvent extraction (150°C, 2000 psi) using a Dionex ASE 200. Multi-layered silica chromatography columns were used for the initial clean-up of total extracts, Florisil chromatography was used to separate PCDD/Fs from PCBs, then basic alumina chromatography was performed to remove large amounts of saturated hydrocarbons from the PCB fractions. Prior to analysis, recovery standards were added to the final PCDD/F and PCB fractions (EDF-4055 and EC-4979, Cambridge Isotope Laboratories, LGC Promochem, UK). Analyses for PCDD/Fs and PCBs were conducted by high resolution gas chromatography - high resolution mass spectrometry (HRGC-HRMS) using a Hewlett-Packard 6890 gas chromatograph fitted with a 60 m x 0.25 mm x 0.25 µm DB5-MS capillary column and coupled to a Micromass Autospec Ultima high resolution mass spectrometer. The MS was operated at 10,000 resolution in the positive ion mode at 34 eV energy with perfluorokerosene as the mass range calibrant.

Results and Discussion

Typical PCDD/F and WHO-12 PCB congener profiles in stack emissions from UK sinter plants

Information on the congener profile or 'fingerprint' of an emission may usefully be presented in two ways, either as concentration profiles of the 12 PCB and 17 PCDD/F targeted compounds, or alternatively, in terms of the relative contribution of each congener to the total TEQ [WHO-TEQ + I-TEQ]. Figure 2 shows the WHO-12 PCB and 2,3,7,8-PCDD/F congener profiles in the emissions of the three sinter plant operated by Corus in the UK.

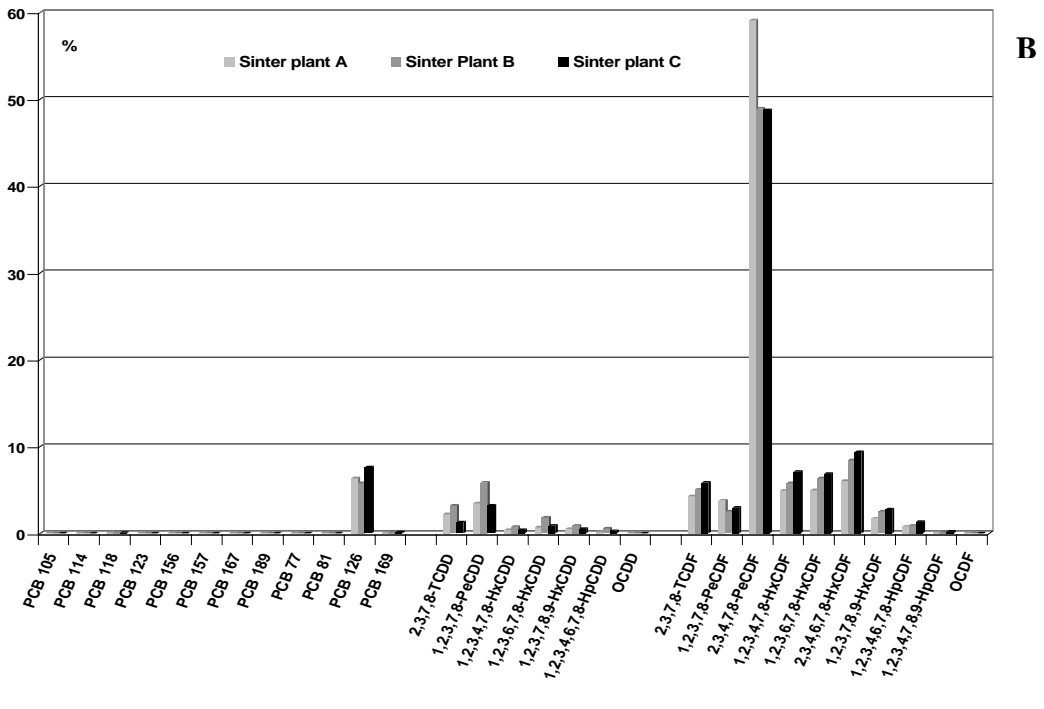
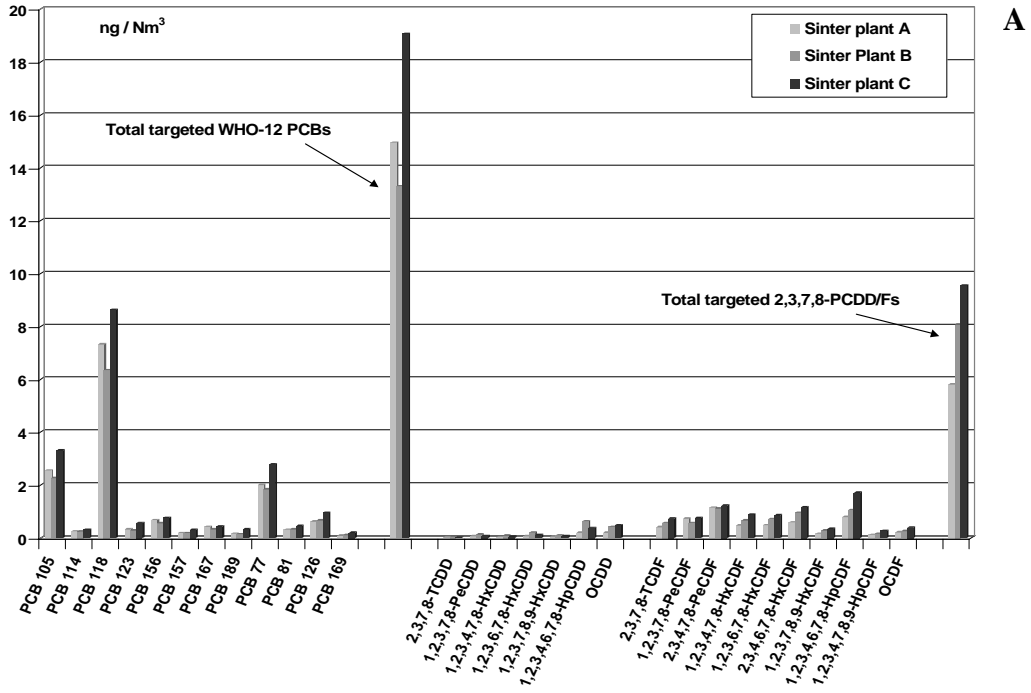
As shown in Figure 2A, UK sinter plants exhibited a very similar congener pattern for both WHO-12 PCBs and 2,3,7,8-PCDD/Fs. With regard to WHO-12 PCBs, the most abundant congeners were PCBs 118 (6 to 9 ng Nm⁻³), 105 (2 to 4 ng Nm⁻³) followed by 77 (2 to 3 ng Nm⁻³). All other WHO-12 PCBs were detected in sintering emissions but at concentrations typically lower than 1 ng Nm⁻³ (Fig. 2A). PCDD/F congeners were detected at concentrations below 2 ng Nm⁻³. The most toxic PCDD/F (2,3,7,8-TeCDD) was generally not detected in sintering emissions. PCDF congeners were found at higher concentrations than PCDDs. Globally, PCDFs constituted approximately 87% of the total 2,3,7,8 PCDD/F concentrations. When comparing total WHO-12 PCB and 2,3,7,8-PCDD/F concentrations, sintering emissions appeared to be clearly dominated by WHO-12 PCBs. In emissions of sinter plant C, the total concentration of WHO-12 PCBs was 19.06 ± 5.96 ng Nm⁻³ whereas the total 2,3,7,8 PCDD/F concentration was 9.55 ± 5.25 ng Nm⁻³. As shown in Figure 2A, this finding was also observed at sinter plant A and B, and typically the total WHO-12 PCB concentrations were systematically higher (two to three times higher) than the total targeted PCDD/F concentrations. Interestingly, relative proportions of WHO-12 PCBs and 2,3,7,8-PCDD/Fs in emissions appeared to be very different from the ones that were found in waste dusts from ESP of UK sinter plants in a previous study⁴. For instance, a waste ESP dust from sinter plant C was characterised by a total 2,3,7,8-PCDD/Fs concentration of 1708 ng kg⁻¹ and a total WHO-12 PCBs concentration of 333 ng kg⁻¹. Those differences between emission and waste dust samples may be explained by the fact that PCBs are more volatile than PCDD/Fs and hence are adsorbed to

a lesser extent onto particulates. However, despite the fact that PCBs were predominant in sintering emissions, their relative contribution to the overall TEQ remained low. As is evident from Figure 2B, the main contributors to the total TEQ were the PCDFs, particularly the 2,3,4,7,8-PeCDF (ca. 60-75% contribution). Globally, for all sinter plants, PCDFs accounted for more than 85% of the overall TEQ. For PCBs, the only noteworthy contributor to total TEQ was PCB 126 (5% to 11%), mainly due to its relatively high TEF in comparison with the other WHO-12 congeners. Finally, the contribution of PCDD congeners to the total TEQ was almost identical to the contribution of PCB 126.

I-TEQ and WHO-TEQ concentrations in stack emissions from UK sinter plants

Concentrations of 2,3,7,8 PCDD/Fs and WHO-12 PCBs, expressed as I-TEQ and WHO-TEQ respectively, have been determined for the three sinter plants investigated. Results are summarized in Table 1. I-TEQs were calculated using the TEFs defined by NATO/CCMS for PCDD/F congeners⁷, whereas WHO-TEQs were determined using the WHO-12 PCBs TEFs proposed by the WHO³. As may be seen from Table 1, I-TEQ and WHO-TEQ data were very consistent within a trial, very little differences were observed between trials as well as between sinter plants.

NONTHERMAL SOURCES AND SOURCE INVENTORIES



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Figure 2 : WHO-12 PCB and 2,3,7,8-PCDD/F congener profiles in stack emissions of the three sinter plants operated by Corus in the UK. (A) WHO-12 PCB and PCDD/F concentrations and (B) % contribution of individual congeners to overall TEQ (I-TEQ + WHO-TEQ).

Table 1. TEQs emission data for the sinter plants operated by Corus in the UK

Plant	WHO-TEQ	I-TEQ	Total TEQ	Contribution
Sampling period	WHO-12 PCBs (ng WHO-TEQ Nm ⁻³)	2,3,7,8-PCDD/Fs (ng I-TEQ Nm ⁻³)	I-TEQ + WHO-TEQ (ng TEQ Nm ⁻³)	PCBs to Total TEQ (%)
<i>Sinter plant B</i>				
09 / 2002 (N = 2)	0.062	0.57	0.632	9.8
	0.046	0.38	0.426	10.8
04 / 2003 (N = 2)	0.070	1.16	1.230	6.0
	0.082	1.51	1.592	5.4
Mean	0.065	0.81	0.875	7.4
Emission estimate (Mean g TEQ yr ⁻¹)	0.7	8.1	8.7	
<u>Sinter plant C</u>				
06 / 2003 (N = 3)	0.042	0.78	0.822	5.1
	0.064	1.24	1.304	4.9
	0.056	1.19	1.246	8.0
Mean	0.054	1.07	1.124	6.0
Emission estimate (Mean g TEQ yr ⁻¹)	0.4	8.7	9.2	
<u>Sinter plant A</u>				
09 / 2002 (N = 3)	0.098	0.98	1.078	9.1
	0.077	0.75	0.827	9.3
	0.097	0.87	0.967	10.0
10 / 2002 (N = 3)	0.108	1.57	1.678	6.4
	0.102	1.43	1.532	6.6
	0.111	1.30	1.411	7.9
Mean	0.098	1.15	1.245	8.2
Emission estimate (Mean g TEQ yr ⁻¹)	0.9	10.0	10.9	
<u>Sinter plants A + B + C</u>				
Total emission estimate (Mean g TEQ yr ⁻¹)	2.0	26.8	28.8	

With regard to PCDD/F emissions, sinter plants A, B and C exhibited mean I-TEQ concentrations of 1.15, 0.81 and 1.07 ng I-TEQ Nm⁻³, respectively. All measurements were in the

range 0.38-1.57 ng I-TEQ Nm⁻³. With regard to WHO-12 PCBs, this study shows that WHO-TEQ concentrations were very low in comparison with I-TEQs for all the sinter plants investigated. As may be seen from Table 1, sinter plants A, B and C exhibited mean WHO-TEQ concentrations of 0.098, 0.065 and 0.054 ng WHO-TEQ Nm⁻³, respectively. Based on those measurements, it can be concluded that WHO-TEQ concentrations for PCBs in UK sinter plants are typically within the range 0.042-0.111 ng WHO-TEQ Nm⁻³. As a consequence, the relative contribution of WHO-12 PCBs to the total TEQ (I-TEQ + WHO-TEQ) was relatively low, typically comprising between 5% and 11 % (Table 1). In other words, the inclusion of WHO-12 PCBs in the overall dioxin concentration only resulted in an increasing of about 5 to 11% of the I-TEQ value.

Annual mass release for WHO-12 PCBs and PCDD/Fs have also been estimated by taking into account emission flow rates of each sinter plant investigated. With regard to PCDD/Fs, annual emissions were 10.0, 8.1 and 8.7 g I-TEQ yr⁻¹ for sinter plants A, B and C, respectively. WHO-12 PCBs annual mass release were significantly lower, typically below 1.0 g WHO-TEQ yr⁻¹ per sinter plant. In a previous study, measurements carried out at the five sinter plants operated by Corus over the period 1994-1999 resulted in an estimated annual mass release of PCDD/Fs of 38 g I-TEQ per annum (Anderson and Fisher, 2002). Nevertheless, updated annual mass releases were needed to include the contribution of WHO-12 PCBs to the overall TEQ and to take into account the fact that Corus only operated three sinter plants in 2003. Based on the results of this study, it has been estimated that the total annual mass release of WHO-12 PCBs and 2,3,7,8-PCDD/Fs for UK sinter plants is now approximately 29 g TEQ per annum.

Conclusions

Investigations have been carried out at the three sinter plants operated by Corus in the UK to characterise PCB emissions. The results of this study indicate that the WHO-12 PCBs congener profile is substantially the same on all UK sinter plants suggesting that it is characteristic of the process. Quantitative data showed that the contribution of WHO-12 PCBs to the overall TEQ (I-TEQ + WHO-TEQ) was relatively low, typically in the range 5% to 11%. The main WHO-12 congener contributing to the total TEQ was PCB 126, which exhibit the highest toxic equivalent factor amongst the 12 targeted PCBs. Data have been combined to provide an estimated annual mass release of WHO-12 PCBs and 2,3,7,8-PCDD/Fs from UK sinter plants. The results indicate that emissions from the three UK sinter plants represent an annual mass release of approximately 29 g total TEQ per annum. The contribution of WHO-12 PCBs appeared to be very low : 2,3,7,8-PCDD/Fs and WHO-12 PCBs accounted for 27 g I-TEQ yr⁻¹ and 2 g WHO-TEQ yr⁻¹, respectively.

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