Dioxin-like PCB emissions in the Flemish Region (Belgium)

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Introduction

Since a couple of years, monitoring campaigns have revealed elevated levels of the dioxin-like PCB-126 in both deposition samples and cow's milk at a few 'hot spots' in the Flemish Region (Belgium). The contamination with dioxin-like PCB (dl-PCB) is related to the activities of scrap metal recycling plants, especially shredder plants for end-of-life vehicles (ELV) [1]. A health risk assessment study indicated that consumption of free-range eggs from the vicinity of a shredder plant could lead to an increased health risk, especially for children [2]. In recent years, dl-PCB are getting increasing attention as contaminants of the food chain. However, there is a general lack of environmental data on these compounds. Therefore, in 2004, the EIS conducted a measurement campaign and investigation on the emissions of dl-PCB. This consisted of stack measurements at 12 plants, including a number of shredders. Additionally, at the shredder plants, on site deposition measurements were performed and sweep samples of on site dust were analyzed.

Methods and Materials

In the Flemish Region, the general and sector-related environmental conditions for industrial activities are all integrated in Vlarem II (first published in 1995), which is an implementing order of the 1985 Environmental Licence Decree. The Flemish environmental legislation is based upon the principle of prevention of pollution, nuisance and damage. The EIS is the authority responsible for the enforcement of the Flemish environmental health legislation. The EIS aims to reach a high-level, planned and co-ordinated enforcement, by combining a preventive and a repressive approach [3].

All stack emission measurements of PCDD/F have been performed according to EN 1948 (parts 1,2,3), using the filter/condensation method for sampling. Dioxin-like PCB were sampled in the same way, and analyzed using an accredited in-house method of the lab, based on EN 1948, part 3. For the deposition measurements, sampling was done on a monthly basis, using Bergerhoff type gauges, with subsequent analysis of the deposited material [4]. The sweep samples of dust were analyzed for PCDD/F and dl-PCB in the same way as the flue gas samples. Their total PCB content (sum of 7 congeners: PCB-28, PCB-52, PCB-101, PCB-118, PCB-138, PCB-153 and PCB-180) was analyzed using the Flemish reference method for oils, based on EN 12766. All measurement results for PCDD/F are expressed in I-TEQ (sum of 17 congeners) and those for dl-PCB in WHO-TEQ (sum of 12 congeners). Congener concentrations below the detection limit were not considered.

Results and Discussion

The scrap metal shredders, considered in this paper, are mainly treating end-of-life vehicles (ELV) and waste from electronic and electrical equipment (WEEE). The shredding output consists of various reusable fractions, such as ferrous and non-ferrous metals. The process also generates new waste materials. The largest waste fraction is the shredder light fraction (SLF) or "fluff", consisting mainly of plastics, dirt and dust. The flue gas cleaning system generates filter dust (dry system, e.g. from cyclones) or a sludge-type residue (wet system). ELV shredder plants are mentioned in Annex C, Part III of the Stockholm Convention on POP as one of the potential source categories for the unintentional formation and release of PCDD/F and PCB. There is not sufficient evidence that in the process new formation occurs of PCDD/F or PCB, but the releases are related to oils, dielectric fluids and other materials introduced via the scrap input [5]. The shredding process, including the handling of scrap and residues, generates high amounts of dust, which is very susceptible to dispersion towards the environment. Thus, both stack and diffuse emissions should be considered when investigating the environmental impact of these plants.

Very little data of stack emission measurements at shredder plants are available in the public domain. The European dioxin inventory [7] mentions PCDD/F emission data from German shredder plants, reported in 1996 and 1997, with concentrations ranging from 0.002 to 0.43 ng TEQ/Nm^3. Between 2002 and 2004, the EIS has performed stack emission measurements at 7 shredders in the Flemish region. The results of these measurements are compiled in Table 1. This shows that most of the PCDD/F concentrations in the flue gases were very low, with an average of 0.05 ng TEQ/Nm^3 and a maximum of 0.37 ng TEQ/Nm^3. This is very similar to the German data. Concentrations of dl-PCB were generally higher than those of PCDD/F. They varied much more between different shredders and even between consecutive measurement days. The average dl-PCB concentration was 0.63 ng TEQ/Nm^3. At 2 plants, more than 1 ng TEQ/Nm^3 was measured. In one case, this could be linked to a high dust emission, showing that there was a problem with the flue gas cleaning system. However, in general, no correlation was seen between dust emissions and PCB or PCDD/F emissions. Neither is there a correlation between PCDD/F and dl-PCB emissions. This probably indicates that different factors are playing a role in the emission of these compounds. For dl-PCB, the day-to-day variations most likely reflect the fluctuating PCB-content of the input material. For PCDD/F, thermal processes can be expected to play a role. Extrapolating these data leads to an emission of about 60 mg TEQ/year of PCDD/F and 715 mg TEQ/year of dl-PCB for the whole of these 7 shredder plants. The average share of dl-PCB to the total WHO-TEQ (PCDD/F + dl-PCB) was 90%.

Table 1. Stack emission measurements at 7 scrap metal shredder plants

shredder	flow rate	dust	PCDD/F		dioxin-like PCB	
	Nm^3/h	mg/Nm^3	ng TEQ/Nm^3	mg TEQ/y	ng TEQ/Nm^3	mg TEQ/y
1 (non-ferrous)	33000	6.2	0.0027	0.2	0.012	0.8
2 (stack 1)	25600	7.6	0.116	6.0	2.2	114
2 (stack 2)	42700	1.32	0.0052	0.5	0.067	5.8
3	20000	250	0.129	2.7	3.0	49.9
3		178	0.009		0.19	
3		17.6	0.120		1.58	
4	83500	10.2	0.010	1.3	0.23	23.5
4		7.9	0.011		0.18	
5	62500	12.2	0.009	17.3	0.17	53.4
5		22	0.37		0.34	
5		14.6	0.025		0.73	
6	72000	23	0.077	29.5	0.74	444
6		3	0.043		1.06	
6		3.6	0.022		0.3	
7	80000	4.4	0.0098	1.5	0.048	24
7		1.8	0.012		0.41	
7		3	0.0048		0.073	
7		3.2	0.0004		0.025	

In addition to the stack emission measurements, the EIS also measured the on site deposition of PCDD/F and dl-PCB at 4 shredder sites. Although the results of these measurements varied strongly, depending on the location of the gauges and the meteorological conditions, they showed that the on site deposition of dl-PCB was clearly higher than in the surroundings. At several sites, values over 100 pg TEQ/m^2.day were measured [1]. Only at one site, this coincided with very high PCDD/F depositions. This confirms that the emissions of PCDD/F and dl-PCB are not correlated. The high dl-PCB deposition in the close vicinity of the shredders can not be explained by the stack emissions only. Therefore, it is a strong indication of the importance of local diffuse emissions. The congener profile of the deposition samples was investigated. It proved to be very similar to that of the on site sweep dust samples.

In order to get an idea of the on site accumulation of PCDD/F and PCB due to both stack and diffuse emissions, the EIS took 5 sweep dust samples at 4 shredder sites. These samples were mainly collected next to the shredders or near scrap piles. Besides PCDD/F and dl-PCB, also the total PCB content (sum of 7 congeners) was determined. The results, given in Table 2, show much higher concentrations of dl-PCB compared to PCDD/F (on the average about 15 times). This is in agreement with the findings from the stack measurements and, to a lesser extent, the deposition samples [1]. All total PCB concentrations (sum of 7 congeners) were below 50 mg/kg dm, which is the limit value to consider a waste material as 'PCB-containing'. When calculating the total PCB content according to EN 12766 (i.e. 5 times the sum of 6 non-dioxin-like congeners, excluding PCB-118), 50% of these samples contained more than 50 mg/kg dm. Furthermore, 3 cyclone dust samples were collected at shredder plants. Therein, concentrations of PCDD/F (95 - 157 ng TEQ/kg dm), dl-PCB (473 - 2396 ng TEQ/kg dm) and total (sum of 7 congeners) PCB (7 - 28 mg/kg dm) were very similar to those of the sweep dust samples. These results are slightly higher than average concentrations in SLF and filter residues, as recently reported in Germany [6]. The average share of dl-PCB to the total WHO-TEQ (PCDD/F + dl-PCB) was 88%, with little sample-to-sample variation.

Table 2. Sweep dust samples collected at shredder plants (5 samples per plant)

shredder	PCDD/F	dioxin-like PCB	PCB (sum of 7)
	ng TEQ/kg dm	ng TEQ/kg dm	mg/kg dm
1-2	75 - 189	1007 - 2125	9 - 35
3	25 - 151	818 - 1355	3 - 18
4	12 - 79	41 - 1463	7 -20
5	47 - 159	435 - 2986	6 - 31
average (n = 20)	**74**	**1167**	**15**

At the end of the EIS study, all data on stack emissions, depositions, and sweep dust composition were evaluated, taking into account the congener profiles. It was concluded that diffuse emission sources are having a major impact on the environmental contamination, especially for dl-PCB. These diffuse emissions are mainly caused by the dispersion of PCB-contaminated dust. Major sources of these emissions include handling of scrap and manipulation and outside storage of dry flue gas cleaning residues (filter dust). To improve emission control of the dust, scrap and residues should be manipulated as little as possible and fine dry residues should be stored in such a way that dispersion is minimised. Furthermore, mixing of PCB-contaminated dust with other materials should be avoided.

In order to limit the emissions and to prevent damage or nuisance, the plant operators are obliged to apply the Best Available Techniques (BAT). By the end of 2004, the EIS had ordered the shredder plant operators to initiate an action plan to reduce the environmental contamination by PCDD/F and (dioxin-like) PCB. The EIS stressed that both primary and secondary measures had to be investigated, including an improved selection of incoming scrap, advanced treatment of the flue gases (high efficiency dust removal), closed storage of the cyclone dust and measures to avoid dust generation during scrap handling. Several shredder plants are currently implementing these measures in order to reduce their PCB-emissions. It is expected that the effect of these measures soon will become visible in the environmental and food chain levels in the surroundings.

Besides the shredders, the EIS also measured the stack emission of dl-PCB at 8 other plants: one hazardous waste incinerator (HWI), 3 municipal solid waste incinerators (MSWI), 2 metal smelters, an iron ore sintering plant and a coal-fired power plant. This campaign thus covered the main potential PCDD/F source types. At 7 plants, emission reduction measures with a proven effect on PCDD/F had been taken. At the power plant, no significant PCDD/F emission had been measured in the past. The waste incinerators were selected in order to cover different PCDD/F emission reduction techniques.

The results are compiled in Table 3. They show very low emission concentrations of dl-PCB, generally even lower than the PCDD/F emissions. At all of the waste incinerators, the emissions of both PCDD/F, dl-PCB, as well as their sum, were clearly below the EU emission limit value for PCDD/F (0.1 ng TEQ/Nm^3). The share of dl-PCB to the total WHO-TEQ (sum of PCDD/F and dl-PCB) varied strongly. At the iron ore sintering plant, it was the lowest, with the emission of dl-PCB only about 10% of that of PCDD/F. This confirmed the results of earlier measurements by the plant operators. As is the case for PCDD/F, this plant is the main source of stack emissions of dl-PCB in the

Flemish Region. Its dl-PCB emission is of the same size as the total stack emission from the 7 scrap metal shredder plants.

Table 3. Results of the stack emission measurements at various plants

	ref. O_2	dust	PCDD/F		dioxin-like PCB		ratio *
	%	mg/Nm³	ng I-TEQ/Nm³	mg I-TEQ/y	ng TEQ/Nm³	mg TEQ/y	%
HWI	11	< 1	0.0019	0.6	0.0051	1.5	71.7
MSWI 1	11	1.2	0.0014	0.9	0.0008	0.4396	33.9
MSWI 2	11	< 2	0.0014	0.6	0.045	6.96	97.0
MSWI 3	11	1.0	0.012	4.1	0.0034	1.2	21.6
Al smelter	19.4	31	0.074	10.2	0.0169	2.34	18.3
Cu smelter	19.8	18.9	0.096	39.1	0.046	18.8	31.5
iron ore sintering plant	16	55	0.65	6370	0.058	474	6.7
power plant	6	17.8	0.0003	0.4	0.0009	1.17	77.1

* % share of dl-PCB to the total WHO-TEQ (PCDD/F + dl-PCB)

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