DIFFUSE EMISSIONS OF PCDD/F AND DIOXIN-LIKE PCB FROM INDUSTRIAL SOURCES IN THE FLEMISH REGION (BELGIUM)

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Introduction

In Belgium, and especially in the Flemish region, the contamination of the environment and food chain with PCDD/F and PCB has been a major public concern during the past decade. The largest point sources of PCDD/F emissions have been monitored and tackled by the Environment Inspection Section (EIS) since 1993. This has caused a very significant emission reduction, which in its turn had a considerable impact on lowering the environmental and food PCDD/F levels, both in the immediate surroundings of the sources and on a regional scale. However, at a few measurement locations, levels of PCDD/F in deposition samples and in cow's milk remained increased despite the stack emission reduction of nearby sources. Recently, also increased dioxin-like PCB levels were found at some locations. This has led to an investigation of the contribution of diffuse emission sources, revealing the importance of such sources at particular plants, mainly in the non-ferrous metal and scrap metal sectors.

Methods and Materials

Environmental legislation and enforcement: In the Flemish region, the general and sector-related environmental conditions for industrial activities are integrated in Vlarem II (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. Vlarem II contains a legally binding PCDD/F emission limit value for waste incinerators, brickworks, oil refineries, crematories, ferrous and non-ferrous metals plants and iron sintering plants [1].
The Environment Inspection Section (EIS) of the Ministry of the Flemish Community is responsible for the enforcement of the environmental health legislation. The EIS aims to reach a high-level, planned and co-ordinated enforcement, by combining a preventive and a repressive approach [2,3].

Environmental and food chain monitoring of PCDD/F and dioxin-like PCB: In the Flemish region, intensive monitoring of environmental levels of PCDD/F and in the food chain is carried out since many years. The Flemish Environmental Agency (VMM) has a deposition measurement

programme at some 70 locations [4]. Sampling is done on a monthly basis in Bergerhoff type gauges, with subsequent analysis of the deposited material [5]. Since 2002, VMM also analyses the dioxin-like PCB-126 in these deposition samples.
The Belgian Federal Agency for the Safety of the Food Chain (FAVV) is responsible for the monitoring of the food chain. The sampling strategy and methods to determine the PCDD/F and dioxin-like PCB content of cow's milk and dairy products have been presented before [6].
Through mutual co-operation, there is a synergy between the authorities responsible for environmental enforcement (EIS), environmental monitoring (VMM) and food chain monitoring (FAVV). On the one hand, sampling locations for food chain and environmental monitoring are often chosen based on emission data, provided by the EIS. On the other hand, unknown emission sources have been detected near sites of high deposition and/or food chain contamination and thus could subsequently be cleaned up.

Results and Discussion

Regulated stack emissions of PCDD/F and dioxin-like PCBs and remaining 'hot spots': Since the early 1990's, large efforts have been made in the Flemish region to reduce the presence of PCDD/F in the environment and food chain. Stack emissions from major sources, such as waste incinerators, iron sintering plants, non-ferrous metals plants and crematories were all reduced by over 95% after taking process-integrated and end-of-pipe measures. These emission reduction measures were ordered and followed-up by the EIS in order to obtain compliance with the legal emission limit values and to prevent any nuisance, damage and danger for men and the environment [2,3,7]. Between 1995 and 2002, the total yearly PCDD/F point source emission from industry in Flanders decreased from 194 g TEQ to 6.2 g TEQ.
Generally, clean-up of the stack emissions quickly led to a sharp decrease in deposition levels and cow's milk concentrations in the surroundings of the sources. Also, the average PCDD/F level of Belgian cow's milk has steadily been decreasing since the mid 1990's [6]. However, the ongoing monitoring programmes kept revealing a few remarkable spot contaminations, which could not be explained by stack emissions. Two of the most striking cases will be highlighted: PCDD/F contamination on and around a non-ferrous metals plant (copper smelter) and PCDD/F and dioxin-like PCB contamination around scrap metal shredders.

Recycling of PCDD/F containing fly ashes: The thermal treatment of metals in smelters or foundries is a well-known source of PCDD/F emission. Especially copper smelters may cause important emissions, as this metal functions as a catalyst during the PCDD/F formation process. For such plants, injecting an adsorbent into the flue gas stream and using a fabric filter for dust removal has proven to be effective in reducing stack emissions of PCDD/F [3].
A disadvantage of this technique of dioxin removal is that it doesn't lead to destruction of the molecules, which will eventually end up in the filter dust residue. Thus, such fly ash can be highly enriched in PCDD/F and be itself a potential source of environmental contamination. As the filter residue may contain precious metals, it is often re-used as an input material for metal smelters. This recycling activity causes an international trade in potentially PCDD/F contaminated fly ashes, originating from smelting processes of various metals.

PCDD/F source investigation at a non-ferrous metal plant: Since several years, elevated PCDD/F deposition values (> 50 pg TEQ/m².day) have been measured now and then near the border of a large non-ferrous metal plant. The EIS ordered the plant operators to initiate an action plan in order to find and clean up the emission source(s). Initially, PCDD/F emissions were measured at all 22 relevant stacks. The yearly stack emission from the whole site was estimated at about 60 mg TEQ/year. Such limited emission could not fully explain the deposition peak values nearby. Therefore, diffuse sources had to be playing an important role. The EIS exhorted the plant operators to investigate all potential diffuse PCDD/F sources more thoroughly.
Samples of different types of granular materials stored on site were collected and analysed. This included ores, fly ashes, scraps, and various kinds of secondary input materials. Also, on site soil dust was analysed. The results are summarised in the following table. It clearly shows the increased PCDD/F content in the external fly ashes stored on site to be recycled in the process. Most of these fine granular materials are being stored inside in closed vessels. However, the fly ash residue from a copper smelter, containing the highest PCDD/F concentration, arrives on site by bulk transport in a humidified condition and is being stored outside under a roof. By the end of 2001, there was almost 250 ton of this material stored on site.

type of material	PCDD/F concentration range ng TEQ/kg dry matter
soil dust on site	10 – 300
waste water treatment sludge	100 – 1000
sweeps mixtures (fine residue materials)	100 – 10000
flue gas dust (fly ashes)	1000 – 100000
activated carbon/lime (fly ash) from copper smelter	100000 – 600000

In order to detect on site ‘hot spots’, 8 PCDD/F deposition gauges were set up all over the plant during several months. Despite large month-to-month variations, the region near the storage of the input materials showed up having recurring high depositions (often > 100 pg TEQ/m².day).

Sources of diffuse PCDD/F emissions at a non-ferrous metal plant: Based on the measurement data collected in 2001 and 2002, the contribution of the various emission sources to deposition levels in the surroundings has been evaluated. It was concluded that diffuse emissions due to transport, loading and storage of PCDD/F-containing raw materials and intermediate products were generally contributing about 90% to the near-site deposition. Emissions from stacks and production halls were responsible for only about 10%. It was seen that the deposition samples showed a PCDD/F congener profile very similar to that of the fly ash of the copper smelter, stored on site for recycling. This confirmed what could be expected, given the large amounts of this extremely highly PCDD/F loaded material being stored outside. During its long storage time, this filter dust was not permanently kept humid, thus becoming more susceptible to dispersion during further manipulation.

Prevention of diffuse PCDD/F emission: As a consequence of these findings, the plant operators took a number of measures to reduce and control the diffuse PCDD/F emissions. Input materials, which are suspected to contain PCDD/F, will be screened before handling using an in house analytical method. Better care will be taken of the storage and handling of granular PCDD/F containing streams. As before, the finest flue dust type materials will only be accepted and stored in

fully closed vessels. The fly ash from the copper smelter, being the main potential source of diffuse PCDD/F emissions, will keep arriving on site in a humidified condition. The amount stored is limited to less than 50 tons. Much more attention will be given though to keep it humid on site and to prevent dispersing it during manipulation. General measures of good housekeeping will help to minimise dust emissions. The on site roads are permanently swept and the personnel is being trained in order to obtain emission-free manipulations. Slowly but steadily, the effect of these measures is starting to show up in a decrease of the PCDD/F deposition near the site.

PCDD/F and dioxin-like PCB contamination in the city of Menen: Since more than a decade, increased levels of PCDD/F have been measured in deposition samples and cow's milk in the city of Menen, located at the Belgian-French border. Initially, this contamination was related to the emissions from 2 nearby waste incinerators. Since 1998, the Flemish incinerator has an extended flue gas cleaning system in operation, reducing PCDD/F emissions permanently below 0.1 ng TEQ/Nm³. The French waste incinerator has been closed down and replaced by a new state-of-the-art plant since 2000. Recently, the open fires, which occurred frequently along the border, were halted. Since these events, a steady decrease in the deposition and cow's milk levels of PCDD/F has been noticed in the Menen area. Still, elevated PCDD/F deposition peak levels were seen now and then in one part of the city, which could not be accounted for by known stack emissions.
Early 2002, the first results of the PCB-126 deposition measurements by VMM became available. The highest deposition was measured at one Menen sampling station: 41 pg TEQ/m².day. At nearly all other stations, many of which are located in the vicinity of known or potential PCDD/F sources, such as waste incinerators, iron sintering plants and metal smelters, the PCB-126 deposition was less than 5 pg TEQ/m².day. This already indicated that the Menen 'hot spot' had to be related to a specific source type. Soon afterwards, analyses of cow's milk, sampled at farms in Menen, confirmed the PCB contamination and this caused a great deal of concern from the local population.

PCDD/F and dioxin-like PCB contamination around scrap metal shredder plants: Looking for potential specific sources of dioxin-like PCB in Menen, the EIS soon started to investigate the activities of a local scrap metal shredder plant. This plant is turning end-of-life vehicles (ELV) and waste from electronic and electrical equipment (WEEE) into various reusable fractions. In order to investigate the potential relationship between dioxin-like PCB and shredders, the EIS asked VMM for additional deposition measurements around other shredder plants. The first results of these measurements were available by the end of 2003. They confirmed the connection between scrap metal recycling activities and increased levels of (dioxin-like) PCB in the surroundings. This relation was further proven by new measurements, although large month-to-month variations in deposition levels occur.
An overview of the average, minimum and maximum monthly deposition values, measured between April 2003 and April 2004 in the surroundings of 4 shredder sites is given in the following table (data obtained from VMM).

deposition measurements near:	PCDD/F (pg TEQ/m².day) average (min – max)	PCB-126 (pg TEQ/m².day) average (min – max)
shredder 1 (gauge 1)	16 (7 – 25)	43 (8 – 102)
shredder 1 (gauge 2)	27 (12 – 41)	66 (23 – 123)
shredder 2	29 (11 - 54)	52 (17 – 83)
shredder 3	29 (10 – 45)	137 (21 – 223)
shredder 4	27 (17 – 34)	86 (14 – 142)

These results show that the deposition levels of PCB-126 are generally higher than the PCDD/F ones and that there is no clear correlation between both compounds. This could indicate that PCDD/F and PCB-126 have different sources and/or pathways to the environment. No conclusions should be derived from comparison of deposition data between the different shredders, as the figures will be influenced by the size of the plants, the distance of the gauges to the sites and the meteorological conditions during the measurements.

Stack emission of PCDD/F and dioxin-like PCB from scrap metal shredders: Currently, the Flemish legislation contains no emission limit value for PCDD/F or dioxin-like PCB for shredder plants. Until now, only a limited number of stack emission measurements of PCDD/F and dioxin-like PCB has been performed or ordered by the EIS at these plants. An overview of the available results is given in the following table. These shredders have at least a cyclone filter system for dedusting the flue gases. Flue gas flow rates are typically about 75000 Nm³/h. All PCDD/F concentrations, except one, were below 0.1 ng TEQ/Nm³. Concentrations of dioxin-like PCB varied significantly between different shredders and measurement days. This is related to differences in flue gas cleaning and to the type and PCB-content of the material being shredded during the measurements. The results indicate that stack emissions may contribute to the overall environmental contamination, though it is unlikely that this will be the main source. During these measurements, no particular correlation could be found between dust emissions and PCDD/F or PCB emissions. In the next months, the EIS will perform emission measurements at 3 more shredders.

emission measurements	PCDD/F ng TEQ/Nm³	dioxin-like PCB (sum of 12) ng TEQ/Nm³
shredder 1	0.0098	0.048
	0.012	0.41
	0.0048	0.073
	0.0004	0.025
shredder 2	0.077	0.74
	0.043	1.06
	0.022	0.30
shredder 3	0.0088	0.171
	0.37	0.34
	0.025	0.73

On site deposition measurements at scrap metal shredder plants: As the first results from stack measurements indicated that there had to be other emission sources influencing the environmental levels, the EIS decided to start an on site investigation. As a first step, deposition gauges were installed on site at a shredder plant in order to detect local 'hot spots'. As the initial deposition levels of both PCDD/F and PCB-126 on site were even much higher than in the surroundings, this programme was later extended. An overview of the available on site deposition measurement results from shredder plants is given in the next table. At all sites, 3 gauges at 3 different locations were used. It is obvious from these figures that frequently high depositions of PCB-126 are found. The image is less clear for the PCDD/F depositions, as the high values found at shredder 1 were not confirmed at other plants. No significant correlation could be seen between PCDD/F and PCB-126. The big variations between the various levels measured will be caused by varying meteorological conditions, the location of the gauges within the plant and the intensity and nature of site activities.

deposition measurements at:	PCDD/F pg TEQ/m².day	PCB-126 pg TEQ/m².day
shredder 1 (3 periods)	18 - 38 – 156 12.5 - 46 – 131 40 - 73 – 191	23 – 69 – 174 21 – 101 - 258 32 – 100 - 194
shredder 2	18 – 32 – 8.1	38 - 6.5 - 211
shredder 3	13 – 6.6 – 26	49 – 14 - 131
shredder 4	25 – 58 – 50	18 – 267 - 121
shredder 5	11.1 – 10.7 – 10	41 – 21 – 31

Sources of PCDD/F and dioxin-like PCB at scrap metal shredders: Evaluation of the available data on emissions and depositions led to the conclusion that diffuse emission sources must be playing an important role, especially for dioxin-like PCB. However, little is known about the PCB-content of the various incoming and outgoing materials at these plants and therefore an effective control strategy is difficult to implement. The large scale of the plants, the often-unknown origin and heterogeneity of the incoming materials and the fact that chemical analyses will be needed for PCB-screening, makes this task even more difficult. The plant operators are steadily becoming aware of the PCB problem and will have to take up their responsibility. Therefore, the EIS has ordered a number of shredder plant operators to initiate an action plan, leading to the reduction of the environmental contamination by PCDD/F and (dioxin-like) PCB. On the one hand, efforts will be needed to prevent PCB-containing materials to enter the shredder. This will necessitate an improved screening of the incoming scrap material. On the other hand, emission prevention will have to be focussed on diffuse sources by limiting the formation and emission of dust through good housekeeping and improved manipulation.

Further research activities on dioxin-like PCB: As still too little is known about the exact sources of dioxin-like PCB at these plants and their pathways to the environment, further research is needed. This should help the plant operators to choose effective and efficient emission reduction measures. On a regional level, the EIS is currently performing an extensive study on the emissions of dioxin-like PCB from various sectors. Stack emissions from waste incinerators, smelters, sintering plants, foundries and shredders are being measured. At the shredder plants, additional on site deposition measurements of dust, PCDD/F and dioxin-like PCB are performed. Soil dust and shredder residue samples will be analysed. It is expected that these investigations will lead to a

more thorough knowledge of the sources and environmental pathways of dioxin-like PCB, helping to solve the contamination problem found around scrap metal recycling sites.

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