DL-PCBs, i-PCBs AND PCDD/Fs EMISSION FACTORS FROM 19 WASTE TREATMENT PLANTS

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Introduction

In 2007, 68 kg of PCBs were emitted into the atmosphere each year because of human activities in France. 80% of these emissions originated from two source categories: energy production and industrial production. Both categories include waste processing plants. However, knowledge on PCB source categories is still scarce and is associated with high uncertainties. In Europe, a measurement standard [1] on PCB emission was published only in 2010 and first measurement campaigns using this standard have been carried out only for the last few years. In France, the need to enhance the knowledge on PCB emission factors has recently increased because of two main reasons. Firstly, France is a Party to the Stockholm Convention which has targeted PCBs since 2001 and to the Aarhus Protocol on POPs (under the Geneva Convention on long range transboundary air pollution). In December 2010, the Executive Body of the Geneva Convention decided to incorporate PCBs into annex III of the Aarhus Protocol. Therefore, robust emission factors are needed in order to optimize the French national inventory, as a support to reduction objectives set in these two international legally binding instruments. Secondly, at the national level, negotiations conducted in 2007 between a large number of stakeholders led to commitments on a better assessment of impacts arising from different waste treatment options and on an increase in mandatory information and in transparency regarding thermal treatment of wastes. On top of these commitments, a national plan on PCBs was released in February 2008, as a consequence of unexpected and unexplained high concentrations of PCBs in sediments and fishes from several French rivers. One measure of this plan consists in exploring all possible sources of such local contamination, including the emission compartment. In addition, for more than ten years, the European Waste Incineration Directive (now included in the Industrial Emission Directive - IED) [2] has set a PCDD/F European-wide emission limit value (ELV) of 0.1 ng I-TEQ/m_0^3 for waste incineration and co-incineration plants. Although, from a theoretical point of view, this PCDD/F ELV is supposed to help lowering PCB emissions as well, it is still unclear whether it has a reel strong impact on PCB emissions.

Therefore, the French Agency for Environment and Energy Management commissioned a measurement campaign in order to derive emission factors from a number of waste treatment industrial installations. The main objective of this measurement campaign consists in deriving robust emission factors. Hence, to enhance repetability, a single accredited laboratory was chosen for the whole study, namely Apave SAS.

Materials and methods

Such measurement campaign focused on incineration and co-incineration plants as well as one combustion plant (CP) which uses an alternative fuel produced from a waste oil refinery. 19 plants were investigated with a view to derive emission factors which would be more robust, from a statistical point of view. Among these plants, 8 of which are municipal solid waste incineration plants (MSWI) burning municipal wastes, medical wastes or sewage sludge alone or mixed, 5 of which are hazardous waste incineration plants (HWI) and 5 of which are co-incineration plants producing cement (CEM). Table 1 provides technical details for these installations, in terms of waste type, furnace type and air pollution control devices.

For each installation, two measurement campaigns were carried out, under conditions which were as close as possible, especially regarding process operating conditions and waste types in the feed. With the exception of one installation, the second campaign was carried out more than three months after the first one. With respect to installation #11, measurement campaigns were achieved on two different incineration lines (but which are assumed to be identical). During the second campaign on installation #16, no oil waste was fed into the kiln, as opposed to the first campaign.

Measurements were achieved for dioxin-like PCBs (DL-PCBs), indicator PCBs (i-PCBs) and PCDD/Fs congeners as defined in EN-1948-4 and EN-1948-1 measurement standards. Sampling was carried out according to the filter/condenser method as described in EN 1948-1. Sampling, extraction, clean-up, identification and quantification requirements of EN 1948-1 to EN 1948-4 standards were strictly applied. In particular, sampling trains were validated in terms of trapping efficiency for PCDD/Fs and PCBs. Sampling volumes ranged from 4 and 7 m^3 , for a sampling period of 6 hours, and detection limits were around 0.5 pg/m_0^3 for each congener. Other parameters were also measured: flow rate, temperature, oxygen content, moisture content and other pollutants at the stack (VOCs, CO, dust).

Field blank values were assessed : 15 pg/m_0^3, 900 pg/m_0^3 et 7800 pg/m_0^3 for PCDD/Fs, DL-PCBs and i-PCB respectively. PCDD/F field blank values were higher than PCDD/F measured concentrations in 5 instances (out of 38), both as concentrations and TEQ concentrations. PCB field blank values were higher than PCB measured concentrations in 7 instances (out of 38), both for DL-PCBs and i-PCBs. Generally speaking, this is observed for remarkably low concentrations only.

Installation #	Category	Waste type	Furnace	Air pollution control device
1	MSWI	Municipal waste	Grate + boiler	DeNOx SNCR + ESP + cooling and co-current tower + FF
2	MSWI	Municipal waste	Grate + boiler	Lime injection (semi-wet process) + activated carbon + FF + DeNOx SCR
3	MSWI	Municipal waste	Grate + boiler	Lignite coke injection + ESP + wet scrubbers + DeNOx SCR
4	MSWI	Municipal waste + medical wastes	Grate + boiler	DeNOx SNCR + sodium bicarbonate injection + activated carbon + FF
5	MSWI	Municipal waste + medical wastes	Grate + boiler	ESP + lime injection (dry process) + activated carbon + FF + DeNOx SCR
6	MSWI	Municipal waste + sewage sludge	Grate + boiler	DeNOx SNCR + Lime injection (semi-wet process) + activated carbon + FF
7	HWI	Liquid and gaseous hazardous wastes	Static + boiler	Wet scrubber (2 stages) + Wet ESP
8	HWI	Solid and liquid hazardous wastes	Rotating + boiler	DeNOx SNCR + activated carbon injection + ESP + wet scrubber (2 stages) + activated carbon adsorption in the scrubbers
9	HWI	Solid, liquid and gaseous hazardous wastes	Rotating + boiler	DeNOx SNCR + lime injection (dry process) + FF + activated carbon + second FF
10	HWI	Solid, liquid and gaseous hazardous wastes	Rotating+ boiler	Sodium bicarbonate and activated carbon injection + FF
11	MSWI	Sewage sludge	Fluidized bed + heat exchanger	DeNOx SNCR + ESP + wet scrubber (2 stages) + activated carbon fixed-bed
12	MSWI	Sewage sludge	Grate	Sodium bicarbonate injection + FF
13	HWI	Contaminated soil	Rotating	Cyclone + post-combustion zone + FF + wet scrubber (1 stage)
14	CP	Oil waste and other alternative fuels	Boiler	None
15	CEM	Oil waste and other alternative fuels	Shaft kiln	Lime injection + ESP + FF
16	CEM	Oil waste and other alternative fuels	Dry process	DeNOx SNCR + FF
17	CEM	Animal meal, oil waste, shredded vehicle waste, other solid alternative fuels	Dry process	DeNOx SNCR + FF
18	CEM	Oil waste and other alternative fuels	Dry process	DeNOx SNCR + FF
19	CEM	Oil waste and other alternative fuels	Wet process	DeNOx SNCR + ESP

Table 1 : Waste treatment installations which were investigated. Air pollution control device acronyms: selective non catalytic reduction (SNCR), selective catalytic reduction (SCR), electrostatic precipitator (ESP) and fabric filter (FF)

Results and discussion

Variability between the two measurement campaigns was quite low, as the ratios between concentrations measured at the two different campaigns are ranging from 0.5 to 2 for 66% of the measurements. Highest ratios can reach 5 (installations # 4, 11, 14 and 16) and 40 for installation#18. On the whole, emission factor robustness can be considered satisfactory. Table 2 provides mean concentrations of PCDD/Fs, DL-PCBs and i-PCBs for each installation. To be consistent with current EU legislation, I-TEQ PCDD/F concentrations are based on NATO toxicity equivalent factors, whereas I-TEQ DL-PCBs are based on 2006 WHO assessement. Table 3 gives, for each installation, emission factors of PCDD/Fs (as TEQ), DL-PCBs (as TEQ) and i-PCBs, based on measured concentrations and measured flows and expressed as per ton of waste except for installations #14 to 19. For installation #14, emission factors are expressed as per ton of oil waste (thermal content: 37 TJ/kt). For installations #15 to #19 (CEM installations), emission factors are expressed as per ton of clinker. Table 3 also provides two ratios: DL-PCBs/(DL-PCBs+PCDD/Fs) and i-PCBs/(DL-PCBs+i-PCBs).

For all installations, PCDD/F concentrations, expressed as TEQ, range from 0.0005 to 0.063 ng/ m_0^3 and are therefore significantly lower than the ELV set in the IED. The upper range consists of MSWI (apart from sewage sludge incinerators) and some HWI.

PCDD/F congener distribution patterns are different depending on source categories. For MSWI and HWI, OCDD, 1,2,3,4,6,7,8-HepCDD and furans have been identified as the predominant congeners. Regarding sewage sludge incinerators and CEM, the following congener are the most typical: 2,3,7,8 TCDF, 1,2,3,7,8-PeCDF and 2,3,4,7,8-PeCDF.

For 18 installations, DL-PCB concentrations, expressed as TEQ, range from 0.0002 to 0.0086 ng/ m_0^3 and are therefore significantly lower than the PCDD/F ELV set in the IED. In addition, for these installations, sums of DL-PCB and PCDD/F concentrations (expressed as TEQ) are also lower than the IED ELV. For instance, the sum of DL-PCB and PCDD/F concentrations is 50.6 pg I-TEQ / m_0^3 for installation #10. Only installation#8 shows a major difference, since measured DL-PCB concentrations are as high as 0.57 ng I-TEQ/ m_0^3 which is higher than the IED ELV for dioxins. Non-TEQ DL-PCB concentrations are the highest for CEM, CP and some HWI.

The DL-PCB contribution to DL-PCB+PCDD/F TEQ is highly variable among all the investigated installations, since the DL-PCB/(DL-PCB+PCDD/F) ratio ranging from 1% to 93%. If non-TEQ concentrations are considered, this ratio will range from 21% to higher than 99% which is still highly variable. If source categories are considered, categories where variability is the lowest are: MSWI (1 to 13% as TEQ) and CEM (90 to 99% as non-TEQ)

Regarding i-PCBs, measured concentrations range from 0.7 to 90 ng/m_0^3. As mentioned above for DL-PCBs, non-TEQ DL-PCB concentrations are the highest for CEM, CP and some HWI. Again, as observed for DL-PCBs, i-PCB concentrations (non TEQ) are significantly higher than those of PCDD/Fs.

For 18 installations, i-PCB concentrations are far higher than those of DL-PCBs, as the i-PCB/(i-PCB+DL-PCB) concentration ratio is higher than 83% for those installations. Only installation#8 shows a major difference as this ratio falls down to 37%.

Installation #	Ref. O2	PCDD/Fs		DL-PCBs		i-PCBs
	%	pg/m_0^3	pg I-TEQ/ m_0^3	pg/m_0^3	pg I-TEQ/ m_0^3	pg/m_0^3
1	11	40	3.6	168	0.4	2033
2	11	453	20.4	1601	3.0	11619
3	11	443	63.8	114	0.8	706
4	11	1544	34.5	505	2.8	3615
5	11	388	29.3	228	1.0	1092
6	11	317	10.3	174	0.9	886
7	11	156	16.1	443	2.1	5321
8	11	601	40.2	60383	570.5	36303
9	11	11	0.5	259	0.2	1996
10	11	749	47.3	360	3.3	2405
11	11	80	3.1	1681	2.4	14489
12	11	23	1.6	551	0.6	4852
13	-	85	12.0	7650	5.8	69365
14	3	46	1.9	9513	2.2	89833
15	10	220	31.6	6837	8.6	46125
16	10	68	7.5	590	0.8	5058
17	10	44	1.4	4538	1.4	66248
18	10	78	9.3	4094	2.3	21893
19	10	18	2.3	2401	1.0	14391

Table 2. PCDD/F, DL-PCB and i-PCB measured concentrations (referring to dry flue gas at specified reference oxygen level and at standard state).

Installation #	Ref. O2	DL-PCBs/(DL-PCBs+PCDD/Fs) (%)		i-PCBs/(DL-PCBs+i-PCBs) (%)	PCDD/Fs emission factors	DL-PCBs emission factors	i-PCBs emission factors
	%	Non-TEQ	TEQ	Non-TEQ	ng I-TEQ/t	ng I-TEQ/t	µg/t
1	11	81	9.2	90	19.8	6.0	12
2	11	75	13.8	84	115.4	17.4	64
3	11	21	1.3	86	349.5	4.5	2
4	11	23	6.9	86	212.6	17.6	22
5	11	35	2.9	83	146.3	5.0	6
6	11	34	7.8	84	51.7	4.5	5
7	11	74	11.1	92	102.3	13.7	34
8	11	99	93.2	37	163.7	2369.6	154
9	11	96	35.0	88	1.4	0.4	6
10	11	34	7.0	85	267.5	19.5	15
11	11	95	42.7	89	5.6	4.4	28
12	11	94	26.2	89	3.3	1.3	12
13	-	99	33.3	91	21.1	10.4	127
14	3	100	60.3	91	22.7	28.2	1141
15	10	97	25.4	86	68.3	10.6	176
16	10	90	19.2	88	24.0	2.7	16
17	10	99	41.4	95	2.8	2.9	138
18	10	98	19.8	84	30.7	7.7	72
19	10	99	29.3	86	12.1	5.2	79

Table 3. Emission factors for PCDD/Fs, DL-PCBs and i-PCBs. PCB/PCDD/F and DL-PCB/i-PCB ratios.

For all installations, differences in PCB and PCDD/F concentrations and congener distributions do not seem to be associated with air pollution control devices. These differences might be due to the kind of process used: in MSWI, PCDD/Fs usually predominate whereas, in CEM, DL-PCBs and i-PCBs predominate whatever the air pollution control device is. HWI show more widespread results, suggesting that PCB and PCDD/F emissions are more strongly linked to the waste parameters as well as the air pollution control device parameters.

Acknowledgements:
This project was commissioned by ADEME and full report in French is available on line. Co-authors of this paper would like to thank operators of the investigated sites for their involvement as well as members of the steering committee : local authorities from Rhône-Alpes, Nord-Pas de Calais, Île-de-France and Haute-Normandie administrative regions and the French Ministry in charge of the environment.

References:

1. CEN standard EN 1948-4: Stationary source emissions. Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs. Sampling and analysis of dioxin-like PCBs (2010)
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