

PAH, PCB and PCDD/F EMISSIONS FROM SIMULATED FOREST AND LANDFILL FIRES

COLLET S¹, FIANI E²

¹INERIS, BP 2, 60550 Verneuil-en-Halatte; France ²French Agency for Environment and Energy Management (ADEME), BP 90406, 2 square Lafayette, 49100 ANGERS, France

Introduction

During the 1980 – 2000 period, an average of 5,218 forest fires per year was counted in France, representing a surface of 30,738 hectares (source: French Ministry of the Interior). Although these figures have tended to decrease during the last decade (an average of 23,024 hectares per year), pollutants emissions from these seasonal phenomena could be important. These non-characterised emissions are currently not integrated into the French national inventory. Under poor conditions of combustion, many pollutants are formed : PAHs, PCDD/Fs, etc. The uncertainty of the estimation of these emissions is still high, because of the lack of studies on this area. For PCDD/Fs, some studies have shown high concentrations (20 pg/m^3)¹ in the air in the vicinity of forests fires and high emission factors^{2, 3} through simulated forests fires (20 ng/kg of biomass burned)^{2,4}. Moreover, for PCDD/Fs, the presence of inorganic chlorinated molecules such as NaCl could play a role on the emissions but is not essential for the formation of these pollutants which mainly depends on combustion conditions. These accidental fires also represent a seasonal phenomenon which mainly occurs in southern France and from which emitted pollutants are still badly known. Due to the heterogeneity of wastes in landfills, these fires are also likely to produce PCDD/Fs emissions.

Materials and methods

To simulate forest fires, samples were collected during the month of August 2003, during a dry period, in the southeast (Bouches-du-Rhône county) and in the southwest (Landes forest) of France, the main French forest fires being located in these two geographical zones. Samples were collected at places located at 10 and 50 kilometers from the coast in order to take into account the influence of the sea spray on the emissions of PCDD/Fs. The samples consisted of litters, mosses, heathers, brackens, conifer needles, pine cones, shrubs, barks, pine and oak branches of small diameter (less than 3 - 4 cm). The collected samples approximately correspond to a cleared surface of 4 m^2 . To simulate landfill fires, samples were directly collected from two landfills located in Aquitaine (south-west of France). Municipal wastes and non-hazardous industrial wastes were containing various plastic matters, wood, rubber, rags, etc. Only the superficial part of the ground was collected, namely the first 15 cm. Collected samples correspond to a surface of 2 m^2 . Each sample was kept in airtight bags in order to avoid water evaporation.

Test campaigns were carried out in a combustion chamber of 80 m^3 which allows the burning of samples of several kilograms. This device is equipped with a fan located above the combustion zone. An extraction flow of $1,800 \text{ normal m}^3/\text{h}$ was set, corresponding to 22.5 volume changes per hour, to simulate open burn conditions. The combustion air is introduced through the door of the chamber. The combustion progress is visually verified by windows located on each side of the chamber.

The samples were layed on a circular metallic bowl. The bottom of the bowl was covered with earth or sand collected on site. The bowl had a diameter of 80 cm and was equipped on his circumference with a raised edge (15 cm high) in order to keep the sample in its position during the test. It was also set on a precision scale, so that the weight of the bowl and the sample was continuously measured. The combustion gases coming from the chamber passed through a scrubber before their emission to the atmosphere. Pollutant samplings were carried out before the scrubber on a straight and horizontal portion of the stack in accordance with the French standard NF X 44-052 (similar to European EN 13284-1). A blank procedure was also carried out prior to the tests in order to ensure that results are not biased by the experimental device. For PCDD/Fs, the first measured field blank value was $6.19 \text{ pg I-TEQ/normal m}^3 \text{ dry}$ (blank test n°1).

The following tests were carried out :

- 2 tests with the samples collected in the southwest of France, the first test was achieved with the samples collected at 50 km from the coast (test n°1), the second with the samples collected at 10 km from the coast (test n°2),

Formation, sources and source inventories

- 2 tests with the samples collected in the southeast of France, the test was achieved with the samples collected close to the coast (test n°3), the second with the samples collected at 50 km from the coast (test n°4),
- 2 tests were carried out with the samples from two waste landfills : the first one with a mixture containing 70.5% of non-hazardous industrial wastes and 29.5% of municipal solid wastes (test n°5), the second one with a mixture containing 33.5% of non-hazardous industrial wastes and 66.5% of municipal solid wastes (test n°6),
- 1 test was carried out with samples collected in the southeast of France at 50 km from the coast, sprayed with sea water and dried at 40°C (test n°7). The latter test was carried out in order to simulate the use of sea water spraying to extinguish forest fires.

Test blanks were conducted between every type of fire tests in order to check the lack of contamination of the combustion chamber and the stack. Emission factors were set in terms of emitted pollutant mass / biomass or waste mass burned.

Each measurement was carried out according to existing standards : French NF X 43 329 for PAHs and European EN 1948-1-2-3 for PCDD/Fs and PCBs.

Results and discussion

Method validation : field blank tests. Results are presented in the following tables (table 1).

Tests number (sample type)	1 (forest fire)	2 (forest fire)	Blank n°2	3 (forest fire)	4 (forest fire)
8 PAHs ^a (µg/nm ³)	23.2	40.4	0.69	26.0	21.5
16 PAHs ^b (µg/nm ³)	168	448	2.7	350	322
12 PCBs ^c (pg I-TEQ/nm ³)	1.29	0.95	0.33	6.18	1.89
PCDD/Fs (pg I-TEQ/nm ³)	28.1	2.76	4.79	68.2	30.9
8 PAHs (mg/kg)	8.6	14.9		9.9	8.4
16 PAHs (mg/kg)	62.4	166		133	126
12 PCBs (ng I-TEQ/kg)	0.48	0.35		2.34	0.74
PCDD/Fs (ng I-TEQ/kg)	10.4	1.02		25.9	12.1
8 PAHs (mg/m ²)	40.5	92.8		61.5	109
16 PAHs (mg/m ²)	294	1030		828	1628
12 PCBs (ng I-TEQ/m ²)	2.25	2.18		14.6	9.5
PCDD/Fs (ng I-TEQ/m ²)	49.1	6.3		161	156

Tests number (sample type)	Blank n°3	5 (landfill fire)	6 (landfill fire)	Blank n°4	7 (forest fire)
8 PAHs (µg/nm ³)	0.11	7.83	7.10	0.26	15.7
16 PAHs (µg/nm ³)	2.13	103	92.7	3.78	209
12 PCBs (pg I-TEQ/nm ³)	1.14	19.7	23.8	2.32	1.17
PCDD/Fs (pg I-TEQ/nm ³)	24.07	483	334	147.9	16.8
8 PAHs (mg/kg)		3.9	4.9		3.1
16 PAHs (mg/kg)		51.8	64.6		41.5
12 PCBs (ng I-TEQ/kg)		9.9	16.6		0.23
PCDD/Fs (ng I-TEQ/kg)		242	233		3.3
8 PAHs (mg/m ²)		22.4	28.1		27.4
16 PAHs (mg/m ²)		295	366		365
12 PCBs (ng I-TEQ/m ²)		56.3	94.2		2.04
PCDD/Fs (ng I-TEQ/m ²)		1380	1321		29.3

Table n°1: test results

^a Fluoranthene, Benzo[a]anthracene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[a]pyrene, Dibenzo[ah]anthracene, Benzo[ghi]perylene and Indeno[1,2,3-cd]pyrene

^b Naphtalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benzo[a]anthracene, Chrysene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[a]pyrene, Dibenzo[ah]anthracene, Benzo[ghi]perylene and Indeno[1,2,3-cd]pyrene

^c Dioxin-like WHO-TEQ

Formation, sources and source inventories

For PAHs, blank values are far lower than the measured values (<3%). In addition, results show that, after high emissions of PCBs and dioxins, it is difficult to obtain low blank values (cf. blank test n°4). However, blank values are far lower than the directly following measured value, with the exception of the last test which appears to be an outlier due to the high gap time (one month) between blank test n°4 and test n°7. Nevertheless the result of this last test does not seem to be biased by the high blank value. Blank values which were observed show that this parameter is to be carefully taken into consideration, especially when the measured values are low.

Forest fire simulations

Emission factors expressed as kg of burned biomass are particularly homogeneous. Differences arise however depending on the origin of the vegetation (Landes or Bouches-du-Rhône) but also and especially on its moisture content. Visually speaking, the vegetation coming from the southwest zone (tests n°1 and 2) were damper than those coming from the southeast (tests n°3 and 4) and were far more humid than those used for test n°7. This parameter could play a major role on the emissions of organic micropollutants and this assumption may also explain the lower emissions of persistent organic pollutants on test n°7. However, this assumption would require a higher number of tests to be checked and confirmed. PAHs emissions are very consistent, as only test n°7 shows an emission factor clearly lower than the others. For PCDD/Fs, results are rather consistent, except for test n°2 which shows a concentration close to n°1 and 2 blank test values: concentrations were ranging from 28.1 to 68.2 pg I-TEQ/nm³ and from 10.4 to 25.9 ng I-TEQ/kg and were much higher than blank values, giving a mean value of 13.1 ng I-TEQ/kg (average of tests n°1, 3 and 4). For the reasons mentioned above, the results of tests n°2 and 7 were considered separately. The profile of test n°2 is rather different than the other ones with lower quantities of 1,2,3,4,7,8,9 heptaCDF. The sea spray influence, taken into account by sampling the biomass at positions located at less than 10 km from the coast (tests n°2 and 3), on HCl, PCDD/Fs and PCBs emissions was not evident. The addition of sea water (test n°7) does not seem to have an important influence either. The influence of this parameter was probably balanced by the drying of the biomass sample which considerably improved the combustion.

Waste landfill fire simulations

In the case of landfill fires, waste moisture could also have a significant influence on the emissions of organic micropollutants. The moisture content of municipal wastes being more important than the one of non-hazardous industrial wastes, the emissions of PAHs are higher when the proportion of domestic waste burned increases. The same arguments may be used for PCDD/Fs emissions. Concerning test n°5, this phenomenon is probably balanced by the high chlorine concentrations in the non-hazardous industrial wastes : HCl emissions of this test were about 30 times higher than the emissions of test n°6. If PAHs emissions from landfill burning are lower than those from forest fires, PCDD/DFs and PCBs emissions are far higher in the case of landfill burning (roughly 10 times higher).

Congeners distributions : PCDD vs PCDF

In terms of toxic equivalent, furans are prevailing. Concerning forest biomass burnings, furans represent a mean percentage of 77.5% of the emissions. Concerning waste burnings, furans represent 85.5 and 84.6% of the emissions (tests n°5 and 6 respectively).

Congeners distributions : PCBs vs PCDD/Fs

PCBs represent about 6% of the toxic equivalent (PCB + PCDD/F). This value ranges from 4% (test n°5) to 8% (test n°3) with the exception of test n°2 where PCBs represent 26% of the toxic equivalent. The distribution PCB-PCDD/F between the forest biomass burnings and the waste burnings is similar.

Forest fires: first estimation of the French emissions

Based on emission factors estimated by these experiments and our knowledge of burned surfaces in France (30,000 hectares per year in average on the two last decades), the French annual emissions have been estimated and are shown in table 2.

Pollutants	Units	test 1	test 2	test 3	test 4	mean value
16 PAHs	kg/year	88,2	309,0	248,6	244,3	222,5
8 PAHs	kg/year	12,2	27,9	18,4	16,3	18,7
PCDD/DFs	g I-TEQ/year	14.7	1.9	48.4	23.4	28.8*
PCBs	g I-TEQ/year	0.68	0.65	4.4	1.4	1.8

* the result of test n°2 is considered apart from the others for the reasons mentioned above

Table n°2: estimation of the French annual emissions from forest fires

Formation, sources and source inventories

It should be stressed that this calculation is very approximate because of the possible low representativeness of the sampled surface. First, the mass of biomass per hectare (5,900 kg) seems to be low indeed. Secondly, it poorly takes into account the high vegetation mass, which could lead to an under-estimation of the emissions. However, the emission factors expressed as kg of burned biomass seems to be more reliable. Hence, they can be used in order to quantify the French annual emissions, provided that the mass of biomass by hectare in different French geographic zones is known precisely enough. Only PCDD/Fs emissions represent a significant part of the French emissions (roughly 7.5% in 2003). For emissions from landfill fires, the annual burned surfaces being statistically not known, it is difficult to estimate the annual emissions.

Acknowledgements

This study was supported by the French Ministry of Environment and the French Agency for Environment and Energy Management.

References

- ¹ CLEMENT, TASHIRO *11th International Symposium on Chlorinated dioxins and related compounds* 1991
- ² GULLETT, TOUATI *Atmospheric Environment* 2003;37:803
- ³ MEYER, BEER, MULLER *Australian Government - National Dioxins Program Technical report n°1*
www.deh.gov.au/industry/chemicals/dioxins/pubs/report1a.pdf
- ⁴ GULETT, 22nd *International Symposium on Halogenated Environmental Organic Pollutants and POPs* 2002