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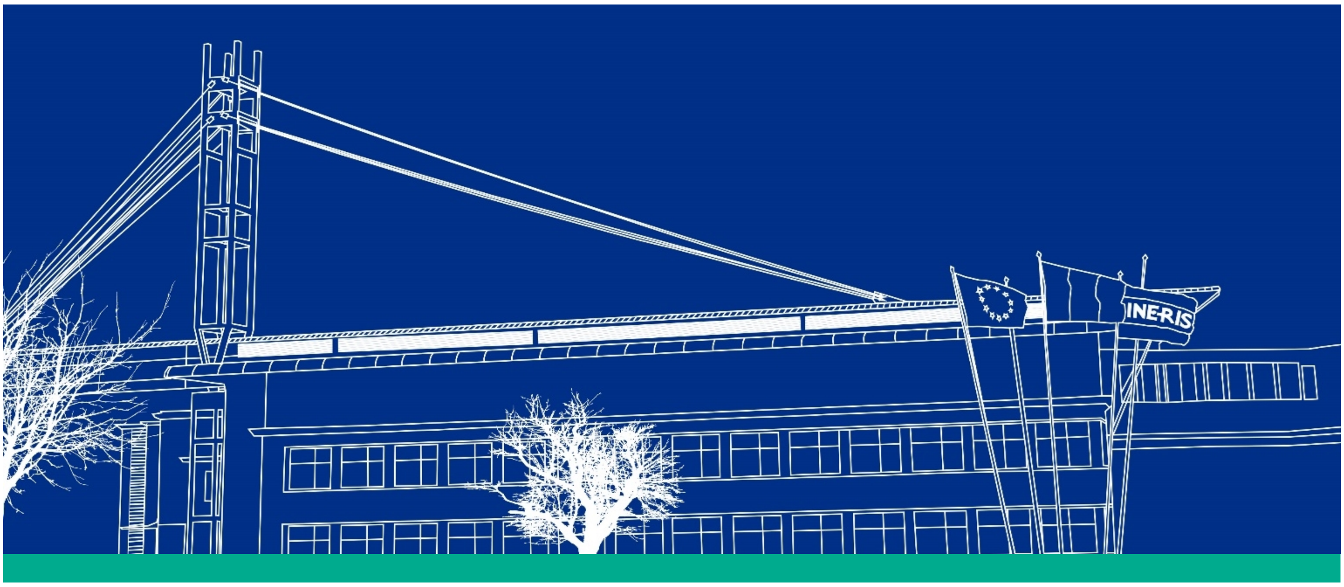

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Analysis of dioxins and furans in ashes and soot from private households and in biomass power plant fly ashes

FOREWORD

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Executive summary

The POPs (Persistent Organic Pollutants) Regulation has been revised in 2022. In Annex IV, the limit value in waste for polychlorinated dibenzo-p-dioxins (PCDDs, dioxins) and polychlorinated dibenzofurans (PCDFs, furans) now includes dioxin-like polychlorinated biphenyls (dl-PCBs). Moreover, their threshold content in waste has been lowered from 15 to 5 µg/kg. Domestic burning soot and ashes, as well biomass power production fly ashes, are waste streams that could be impacted by the lowering of this threshold value. Members States must collect information on the presence of PCDD/PCDF and dl-PCBs in ashes and soot from private households and fly ashes from biomass units for heat and power production.

For domestic burning (of wood and coal) soot and ashes, due to lack of data, samples were collected all over France. A total of 55 ash samples, 96 soot samples and 3 samples from chimney sweep vacuum tanks were collected. All types of home burners were considered. Regarding the PCDD/F concentration values measured in the 55 ash samples collected, none of the samples were classified as POPs waste (values below 5 µg/kg), and 2% of the samples had dioxin/furan levels > 0,5 µg/kg. Concerning the 96 soot samples collected, only one was classified as POPs waste (value above 5 µg/kg). Nevertheless, 15% of the soot samples (i.e. 14 samples) contained high levels of dioxins (> 0,5 µg/kg). PCB-dl levels measured in all samples were very low. Based on the samples collected and the analyses carried out, ash and soot from domestic wood burning are therefore not classified as POPs waste.

For biomass plants, a number of recent data on dioxin levels in fly ashes are available in the literature. These data were considered as sufficient, and no fly ash samples were collected. By considering the values presented in the literature, fly ash from biomass power plant are not considered as POPs waste.

Use the link provided below for quotations:

French national institute for industrial environment and risks (Ineris), Analysis of dioxins and furans in ashes and soot from private households and in biomass power plant fly ashes, Verneuil-en-Halatte : Ineris - 227377 - v1.0, 21 janvier 2025.

Keywords:

Ash, soot, dioxins, PCDD/F, PCB-dl, POPs

1 Introduction

The EU POPs[1] (Persistent Organic Pollutants) Regulation has been revised in 2002 (regulation 2022/2400 of 23 November 2022[2]). In Annex IV, the limit value for polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F) now includes dioxin-like polychlorinated biphenyls (dl-PCBs). The dl-PCBs are: PCB 77, PCB 81, PCB 105, PCB 114, PCB 118, PCB 123, PCB 126, PCB 156, PCB 157, PCB 167, PCB 169 and PCB 189. In addition, their threshold content in waste is reduced from 15 to 5 µg/kg (Σj(PCDDj x TEFj) + Σj(PCDFj x TEFj) + Σj(PCBj x TEFj), with the TEFs (Toxic Equivalency Factors) of the World Health Organization scheme (WHO-TEQ).

Ashes and soot from domestic burning and fly ashes from biomass units for heat and power production are waste that could be impacted by the lowering of this amended concentration limit. In application of Article 1 of the revised regulation 2022/2400, this concentration limit of 5 µg/kg will apply from 1 January 2024 for fly ashes from biomass units and from 1 January 2025 for ashes and soot from domestic fireplaces.

According to the recital (5) of the regulation 2022/2400: « *In order to enable Member States to collect data on the actual amount of PCDD/PCDF and of dioxin-like polychlorinated biphenyls (dl-PCBs) in ashes and soot from private households, as well as in fly ashes from biomass units for heat and power production, and to afford Member States sufficient time to take measures necessary to give effect to Regulation (EU) 2019/1021, the amended concentration limit for the sum of PCDD/PCDF and dl-PCBs should, with regard to ashes and soot from private households and for fly ashes from biomass units, apply at a later stage after the entry into force of this Regulation. In order to enable the design of suitable policies for the collection and treatment of those ashes and soot and to support the review referred to in Annex IV and the monitoring of implementation pursuant to Article 13 of Regulation (EU) 2019/1021, Members States should collect information on the presence of PCDD/PCDF and dl-PCBs in ashes and soot from private households and fly ashes from biomass units for heat and power production. That information should be made available no later than 1 July 2026.* »

The presence of other substances listed in Annex IV of the POPs Regulation is unlikely. Thus, in this study, it is considered that only PCDD/F and PCB-dl are likely to classify ashes and soot from domestic burning and fly ashes from biomass units as POPs waste.

[1] Regulation (EU) 2019/1021 of the European Parliament and of the Council of 20 June 2019 on persistent organic pollutants.
[2] Regulation (EU) 2022/2400 of the European Parliament and of the Council of 23 November 2022 amending Annexes IV and V to Regulation (EU) 2019/1021 on persistent organic pollutants.

2 Context of the study

2.1 The POP regulation

According to the Article 7 of the POPs Regulation, waste consisting of substances listed in the Annex IV of the POPs Regulation, in concentrations above the indicated threshold levels, « *shall be disposed of or recovered, without undue delay and in accordance with Part 1 of Annex V to this Regulation, in such a way as to ensure that the POP content is destroyed or irreversibly transformed so that the remaining waste and releases do not exhibit the characteristics of POPs.* »[3]

In addition, according to the Decision 2014/955/EU[4], POP wastes with a PCDD/F content exceeding the concentration limits fixed in the Annex IV of the POP Regulation are also classified as hazardous waste.

2.2 Substances of concern

2.2.1 Dioxins/furans (PCDD/F)

The group of Polychlorinated Dibenzo-p-dioxins (PCDDs, Dioxins) and Polychlorinated Dibenzofurans (PCDFs, Furans), often referred to as “Dioxins”, consists of 210 congeners. The position and number of chlorines associated with the aromatic rings are specific to each congener. In particular, 17 congeners are considered to be the most toxic (7 PCDDs and 10 PCDFs) and are currently listed in the POPs regulation. Their chemical structures are shown in Figure 1.

The seven PCDDs are:

- 2,3,7,8-Tetra-ChloroDibenzoDioxin (2,3,7,8-TCDD),
- 1,2,3,7,8-Penta-ChloroDibenzoDioxin (1,2,3,7,8-PeCDD),
- 1,2,3,4,7,8-Hexa-ChloroDibenzoDioxin (1,2,3,4,7,8-HxCDD),
- 1,2,3,6,7,8-Hexa-ChloroDibenzoDioxin (1,2,3,6,7,8-HxCDD),
- 1,2,3,7,8,9-Hexa-ChloroDibenzoDioxin (1,2,3,7,8,9-HxCDD),
- 1,2,3,4,6,7,8-Hepta-ChloroDibenzoDioxin (1,2,3,4,6,7,8-HpCDD),
- Octa-ChloroDibenzoDioxin (OCDD).

The 2,3,7,8-TCDD is the most toxic dioxin.

The ten PCDFs are:

- 2,3,7,8-Tetra-ChloroDibenzoFuran (2,3,7,8-TCDF),
- 1,2,3,7,8-Penta-ChloroDibenzoFuran (1,2,3,7,8-PeCDF),
- 2,3,47,8-Penta-ChloroDibenzoFuran (2,3,4,7,8-PeCDF),
- 1,2,3,4,7,8-Hexa-ChloroDibenzoFuran (1,2,3,4,7,8-HxCDF),
- 1,2,3,6,7,8-Hexa-ChloroDibenzoFuran (1,2,3,6,7,8-HxCDF),
- 2,3,4,6,7,8- Hexa-ChloroDibenzoFuran (2,3,4,6,7,8-HxCDF),
- 1,2,3,7,8,9-Hexa-ChloroDibenzoFuran (1,2,3,7,8,9-HxCDF),
- 1,2,3,4,6,7,8-Hepta-ChloroDibenzoFuran (1,2,3,4,6,7,8-HpCDF),
- 1,2,3,4,7,8,9-Hepta-ChloroDibenzoFuran (1,2,3,4,7,8,9-HpCDF),
- Octa-ChloroDibenzoFuran (OCDF).

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[3] The following disposal and recovery operations are permitted, listed in Part 1 of the Annex V:
- Physico-chemical treatment (D9);
- Incineration on land (D10);
- Use principally as a fuel or other means to generate energy, excluding waste containing PCBs (R1);
- Recycling/reclamation of metals and metal compounds, […] (R4).

[4] 2014/955/EU: Commission Decision of 18 December 2014 amending Decision 2000/532/EC on the list of waste pursuant to Directive 2008/98/EC of the European Parliament and of the Council Text with EEA relevance.

These substances are thermally stable, poorly biodegradable, insoluble in water and have a strong affinity for fats. They will therefore accumulate in fatty tissues and persist for long periods of time in the environment [Afssa (2005)].

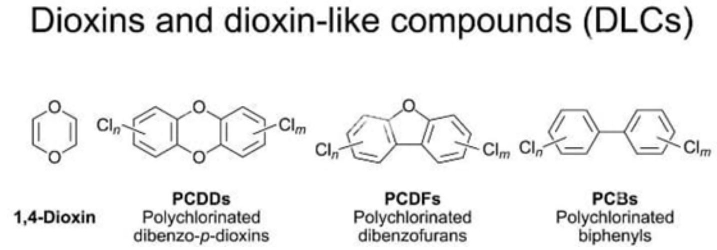


Figure 1 : Chemical structures of PCDD/F and dl-PCB

Dioxins are by-products of incomplete combustion processes, formed unintentionally mainly at low temperatures (< 450°C) in the presence of oxygen, carbon and chlorine. PCDD/Fs are mainly formed during thermal processes such as waste incineration, industrial or domestic activities and accidental processes. The combustion of wood (for domestic heating) or biomass (for the production of heat or electricity) can be source of dioxins formation. The formation of PCDD/Fs depends on several parameters such as the nature of the fuel and its chlorine content, the wood species, its heavy metal content (such as copper, which can act as a reaction catalyst), the presence of chlorinated compounds and the operating conditions of wood-burning appliances (combustion quality, appliance maintenance, flue gas cooling method, etc.) [Référentiels combustibles bois énergie de l'ADEME (2017)].

The production of dioxins is therefore directly linked to the presence of chlorine in the fuel. Natural wood contains no or little chlorine. However, wood or biomass can have significant levels of chlorine in some cases (e.g. high chlorine fixation on bark in general [Collet (2009)] or use of plant protection products) and leads to the formation of dioxins and furans when the combustion conditions are degraded.

It is important to note that dioxins are destroyed at temperatures above 850°C with a residence time of at least 2 seconds, in the presence of oxygen.

2.2.2 Dioxin-like PCBs (dl-PCBs)

Polychlorinated biphenyls (PCBs) are chlorinated aromatic compounds (Figure 1). PCBs are polyhalogenated aromatic hydrocarbons having up to 10 chlorine atoms attached to the biphenyl ring [Afssa (2005)]. There are currently 209 PCB individual chlorinated compounds (congeners) that are classified into two categories: dioxin-like PCBs (dl-PCB) and other PCBs (non-dioxin-like PCBs; ndl - PCB). dl-PCB are flat molecules, similar to dioxins, and represent only a small proportion (< 10% of congeners) of all PCBs. 12 PCB-dl are assessed as very toxic to human health and are included in the POP regulation: 4 ortho (77, 81, 126 and 169) and 8 non-ortho (105, 114, 118, 123, 156, 157, 167 and 189).

Dioxins (PCDDs), furans (PCDFs) and dioxin-like PCBs (dl-PCB) have a similar mechanism of toxicity (binding to the same cellular receptors, known as Ah receptors). Like dioxins, dl-PCBs are not very soluble in water and are very soluble in fat [PCB Fact Sheet].

While PCDD/Fs are unintentional by-products formed during incomplete combustion processes, PCBs are synthetic industrial chemical compounds intentionally added to certain products. PCBs are very stable substances that only decompose at very high temperatures > 1,000°C [Citepa (2023)]. The production and marketing of PCBs has been banned in France since 1987.

It should be noted that the presence of dl-PCB in the waste (ash and soot) studied in has no direct connection with the presence of PCDD/Fs as the origins of these substances are different. The only link that could exist is the possible presence of traces of furans as PCB impurities during their synthesis [Afssa (2005)] or during the dispersion in the environment of PCBs and PCDD/Fs generated during the incineration of industrial waste containing PCBs.

2.3 Summary of the main parameters to be considered for this study

- **Necessary condition: the presence of chlorine**

The concentration and form of chlorine (organo-chlorine compounds or mineral salts) and/or the presence of organic precursors (PCBs, PCP, etc.) are key factors in the formation of dioxins. The presence of chlorine in the initial fuel is therefore a prerequisite. In the case of natural wood burning, few dioxins should be emitted, whatever the combustion conditions. However, some biomasses have high natural chlorine levels. In addition, some natural woods can be highly chlorinated due to sea spray. Finally, wood bark contains a high proportion of inorganic substances, particularly chlorine. The presence of bark therefore promotes the formation of dioxins. It is noted that it is forbidden to place treated wood into a domestic fireplace.

For this study, particular attention will be paid to the geographical origin of the wood burnt, to the introduction of contaminated products or chlorinated waste (plastic packaging, treated wood, leaflets, etc.) and also to the type of wood. The combustion of certain types of wood, such as fir, can emit more dioxins than beech or birch [Collet (2000)]. In addition, people's habits have a non negligeable influence on what is used as combustibles: some practices (combustion of rubbish, household waste (such as PVC) and some materials (such as printed paper) should be banned.

- **Poor combustion quality**

In the case of significant levels of chlorine in the fuel, degraded combustion conditions (low speed operation, old appliances or open fireplaces, slow cooling of flue gases after combustion, the way in which the fire is started, etc.) can lead to the formation of dioxins.

Particular attention will be paid to equipment with inadequate environmental and energy performance, such as open fireplaces.

3 Bibliographic data

A summary of literature data on levels of dioxins (PCDD/F) in ashes and soot from domestic fireplaces and in fly ashes from biomass units is presented below. Foreign studies are also included.

3.1 Method used to calculate the concentration of targeted substances

Dioxins are complex mixtures of congeners. Each congener is associated with a specific degree of toxicity represented by the Toxic Equivalency Factor (TEF). Toxic equivalency factor (TEF) expresses the toxicity of dioxins, furans and PCBs in terms of the most toxic form of dioxin, 2,3,7,8-TCDD.

The overall toxicity of the congeners mixture is calculated by summing the concentrations of each congener, weighted by their respective TEFs.

It is important to note that not all studies use the same Toxic Equivalence Factors (TEF). In fact, two systems of Toxic Equivalence can be used:

- I-TEQ (or I-TEF): the International Toxic Equivalent (I-TEQ) scheme by the North Atlantic Treaty Organisation (NATO);
- WHO-TEQ: set up by the World Health Organization (WHO) and the International Program on Chemical Safety (IPCS).

The POPs regulation uses the WHO/IPCS scheme (WHO-TEQ). Both schemes consider the 17 congeners (7 PCDDs out of 75 and 10 PCDFs out of 135) classified as POPs. The WHO/IPCS system also includes the 12 dl- PCBs.

In the absence of data on the individual concentrations of the dioxins (10 PCDF and 7 PCDD), it is impossible to switch from one scheme to another (I-TEQ or WHO-TEQ). Nevertheless, the data from the I-TEQ system (NATO) are retained in this literature review, for information purposes, as there is generally little difference in the overall result between the two schemes. A more detailed description of the differences between these two schemes is presented in Appendix 1.

3.2 Ashes and soot from domestic burning

A summary of the literature data on dioxin levels in ashes and soot from domestic burnings is presented in Table 1 (ashes) and Table 2 (soot). Only the BiPRO (2005) report and some outdated studies (< 2005) show values above the modified concentration limit (5 µg/kg) for the sum of PCDD/F and PCB-dl.

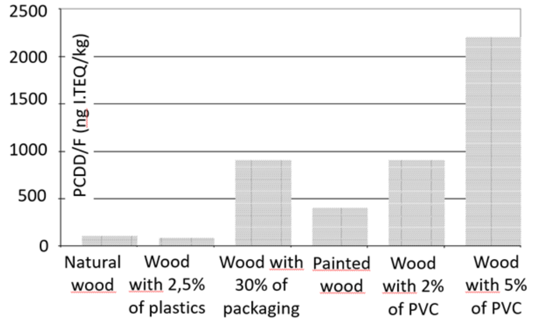
Table 1 : Literature data on PCDD/F levels in domestic burning ashes.

Reference	Domestic burning/ Location	Origin of ashes	Concentration of the sum of PCDD/F
BiPRO (2005)	Domestic burning (Europe)	Ashes (fossil fuel)	Mean= 0.056; Min= 0.00022; Max= 0.15 µg WHO-TEQ /kg
		Ashes (wood)	Mean= 0.11; Min= 0.0001; Max= 0.5 µg WHO-TEQ /kg (PCB: 10 - 20 µg/kg)
Hedman et al. (2006)	Residential Stoves and Boilers 4 types of stoves and boilers with both full and reduced rates of air supply (Sweden)	Ashes (various types of pellets and firewood were combusted)	WHO-TEQ (µg/kg) Between< 0.0009 (modern boiler, birch, full load) and 0.68 (old boiler: birch + paper + plastic; reduced air; slow combustion)

Reference	Domestic burning/ Location	Origin of ashes	Concentration of the sum of PCDD/F
Vandermarken et al. (2016)	Domestic heating systems in Belgium Collection of 22 different wood ash samples The concentration of PCB-dl measured in this study is very low compared with that of dioxins.	Ashes (wood pellets probably treated with chemical preservatives or containing other contaminants, such as glue)	(0.01) BEQ µg TCDD-eq./kg
		Ashes (wood pallets)	(0.0058) BEQ µg TCDD-eq./kg) BEQ: Bio-analytical equivalent
		Solid residues (wood combustion)	0,0006 to 0,0086 µg TEQ/kg

Table 2 : Literature data on PCDD/F levels in domestic burning soot. Values above the new threshold value are shown in red.

Reference	Domestic burning/ Location	Origin of soot	Concentration of the sum of PCDD/F
Bacher et al (1992)	Fireplace in an old farmhouse in the south of Germany	Soot (untreated, wood, natural wood) collected during annual chimney sweeping	755 ng TEQ-WHO_{98}/kg
Dumler-Gradl et al (1995)	Domestic fireplaces in Bavaria (Germany)	81 soot samples from different wood/fireplace type combinations	between 4 and 42 048 ng I.TEQ/kg
Van Oostdam (1995)	British Columbia (Canada)	459 soot samples (natural and treated wood)	86 to 335 ng I.TEQ/kg One fireplace shows high levels of dioxin due to combustion of wood contaminated with sea salt: 7 706 ng I.TEQ/kg Average concentration: 246 ng $_{TEQ\text{-}WHO98}$/kg. Possible contamination of wood by chlorophenol substances used in the wood industry and also present in effluents from pulp mills using chlorine bleaching.

Reference	Domestic burning/ Location	Origin of soot	Concentration of the sum of PCDD/F
Collet (2000) Launhardt (1998)	Tests carried out in Germany in 1998 on stoves and small boilers	Soot (combustion of wood waste containing high levels of chlorine)	
Thoma (1998)	Domestic boilers (combustion of wood, coal, wood/coal or oil) in Bayreuth (Germany)	Soot (wood/coal stoves)	900 ng I.TEQ/kg
		soot (from a wood-fired central heating boiler)	1 500 ng I.TEQ/kg
		soot (from a wood-burning stove)	7 500 ng I.TEQ/kg
Bartet et al (2001)	Domestic burning (country not specified)	soot from wood/coal fireplaces	50 to 10 065 ng/kg I-TEQ
U.S. EPA (2004)	Wood-burning stoves and fireplaces (Western United States)	Soot from domestic wood-burning fireplaces	from 112 to 2 643 ng I-TEQ /kg DM
BiPRO (2005)	Domestic burning (Europe)	Soot (fossil fuel)	Mean=6.15; Min=0.05; Max=10 µg WHO-TEQ /kg
		Soot (wood)	Mean=3.99; Min=0.02; Max=14.4 µg WHO-TEQ /kg (PCB: 0.03 - 0.11 mg/kg)

The studies listed in the Table 1 and Table 2 have not been conducted in France and are not recent, the most recent study dating from 2005. Therefore, these studies are not representative of current consumption (categories and performance of domestic burning technologies) and use (type and origin of wood fuel) in France. The values reported above the POP limit of 5 µg/kg (in red in the tables) are not representative of the current situation, in particular due to the evolution of domestic heating technologies over the last twenty years (improvement of the performance and lowering of the emissions). Collection of additional data in France is therefore necessary. Thus, a national campaign has been conducted in 2024 by Ineris.

3.3 Fly ashes from biomass power plant

A summary of the literature data on dioxin levels in fly ashes from biomass units for heat and power production is presented in Table 3. Some recent studies are listed, such as the studies performed by LECES for ADEME (The French Agency for Ecological Transition) on the assessment of the energy and environmental performance of biomass heating plants located in France. Some studies on other countries are also included, but the list of the studies carried out in other countries is not exhaustive.

Table 3 : Literature data on PCDD/F levels in ashes from biomass plants. Shaded lines correspond to studies performed in France. Values above the new threshold value are shown in red.

Reference	Biomass heating systems / Origin	Fly ashes	PCDD/F concentration
OFEFP (1996)		Cyclone fly ashes (natural wood)	800 ng I.TEQ/kg
		Fly ashes under filter (waste wood)	~ 4 000 ng I.TEQ/kg
LECES (2008)	9 wood boilers (France)	Fly ashes	between 0.7 and 116.5 ng I.TEQ/kg, except for one wood boiler (6 924 ng I.TEQ/kg probably due to the contamination of the wood)
LECES (2014)	10 wood boilers with an output between 360 kW and 15 MW: 4 boilers with an output < 2 MW and 6 boilers between 2 and 10 MW	Two types of ashes analyzed: ashes collected under the furnace often mixed with ashes coming from the multi-cyclone + fly ashes collected from dedusting equipment (fabric filter or electrostatic precipitator) No pesticide (organochlorine compounds) identified in the fuels. Nine out of 10 facilities use wood chips and crushed of wood packaging.	Between 0.05 and 8 505 ng ITEQ/kg DM with a median value of 263 ng ITEQ/kg DM (Dry Matter) and a mean value of 1 425 ng ITEQ/kg DM. The value of 8 505 ng ITEQ/kg, the only one above the POP regulation limit, is linked to poor combustion conditions during the measurements (low loading rate).
LECES (2016)	10 biomass power plants with power range from 300 kW to 21 MW (recent boilers, started between 2012 and 2014): 3 boilers with power range < 2 MW, 6 boilers with a power range between 2	Fly ashes: fine dust from electrostatic precipitator (4 boilers), fine dust from bag filter (4 boilers), fines from a combination of multi-cyclones and an electro filter (1 boiler), fines from a combination of multi-cyclones and a bag filter (1 boiler). In addition, six facilities use wood chips and	Between 5.8 and 4 201 ng ITEQ/kg DM with a median value of 1 156 and an average value of 1 092 ng ITEQ/kg DM. Site 5: 1 065 ng ITEQ/kg DM. This site use wood waste (pulper rejects, sleepers, etc.) and moss.

Reference	Biomass heating systems / Origin	Fly ashes	PCDD/F concentration
	and 10 MW and 1 boiler with an output of 21 MW.	crushed of wood packaging. No organochlorine pesticide-type identified in fuel.	
RECOR 14-0913/1A (2016)	Ashes from collective wood-fired heating systems. Fuels can be forest or woodland chips, wood processing by-products, chips and shreds from urban waste, clean end-of-life wood (pallets).	fly ashes (natural wood)	between 0 and 400 ng I.TEQ/kg
		fly ashes (wood waste containing chlorinated compounds)	> 700 ng I.TEQ/kg
Référentiels combustibles bois énergie de l'ADEME (2017)	Biomass power plants	The French decree of 24 September 2013[5] specifies that fly ashes resulting from the combustion of waste meeting the b(v)[6] criteria of the biomass definition must comply with the following maximum levels of dioxins and furans: 400 ng.I-TEQ/kg.	
Report N° DRC- 18-171115-03897A (2018)	Biomass heating plants located in Haut-Rhin (68): 1 boiler at (output of 8 MW) and 2 biomass boilers at Mulhouse (output of 4 and 8 MW)	Multi-cyclone ashes The biomass burned is wood chips (mainly hardwood).	PCDD/F // PCB-dl concentrations [ng TEQ/kg MS (NATO)] Colmar: 1.93-56.33 // 3.6E-05-0.27; Mulhouse 4 MW: 4.21-11.45 // 0.13-0.36; Mulhouse 8 MW: 18.42-44.7 // 0.45-1.64.
Report Ineris-180235-	National campaign: ashes from biomass	222 samples of bottom ashes, multi-cyclonic and mixed ashes.	between 0.8 and 1 010 ng TEQ_{OMS}/kg DM. PCB-dl not included because of very low levels.

[5] Arrêté du 24 septembre 2013 relatif aux prescriptions généralement applicables aux installations relevant du régime de l'enregistrement au titre de la rubrique 2910-B de la nomenclature des installations classées pour la protection de l'environnement.

[6] Products that can be burned in a 2910B classified facility must comply with definition b)v) of biomass, as defined in the PCI (Classified installations for the protection of the environment) classification: «*wood waste with the exception of wood waste which may contain halogenated organic compounds or heavy metals as a result of treatment with wood-preservatives or coating, and which includes in particular such wood waste originating from construction and demolition waste*».

Reference	Biomass heating systems / Origin	Fly ashes	PCDD/F concentration
07692-v2.0 (2019)	boilers from 30 different sites. Facilities subjected to authorization and declaration (2910 classification of the PCI nomenclature) and facilities subjected to 2910-B classification.		61 samples have dioxin levels below the limits of quantification.
Pohlandt et al. (1994)	wood combustion facilities	fly ashes	121 and 215 ng I.TEQ/kg
	Combustion experiments performed with wood impregnated with inorganic products (boron salts, chromium and copper).	fly ashes (lightly contaminated wood)	52.1 ng I.TEQ/kg
		fly ashes (highly contaminated wood)	89.6 ng I.TEQ/kg
Oehme et al (1995)	3 facilities (between 110 and 850 kW) equipped with high-performance filters (ceramic filters and sleeve filters) in Switzerland.	Fly ashes (natural wood)	between 117 and 372 ng I.TEQ/kg
		Fly ashes (Pentachlorophenol-treated wood)	722 to 7 620 ng I.TEQ/kg
Luthe et al (1997)	Electric boiler (Canada)	Fly ashes under electrostatic precipitator (salt-laden wood waste with a chlorine content ranging from 0.15 to 0.70%).	1 300 to 8 040 ng I.TEQ/kg
Dyke et al (1997)	Industrial plant	fly ash – combustion of treated wood	891 - 1 070 ng I.TEQ/kg
Broekerand al. (1997)	industrial facility (Germany)	fly ashes – combustion of contaminated wood	30 and 23 300 ng I.TEQ/kg

Reference	Biomass heating systems / Origin	Fly ashes	PCDD/F concentration
Yamamura and al. (1999)	industrial waste incinerators: waste wood from demolition waste (Japan)	Fly ashes	6 700 ng I.TEQ/kg
Wunderli and al. (2000)	~ 20 facilities in Switzerland	fly ashes (natural wood)	between 1.5 and 4 ng I.TEQ/kg
		Ashes (wood waste (painted, glued, waste from construction, demolition excluding waste containing PVC and impregnated wood)	between 730 and 21 000 ng I.TEQ/kg
		fly ashes (mechanically processed wood residues)	between 18 and 6 300 ng I.TEQ/kg
BiPRO (2005)	Incineration of non-hazardous waste	Fly ashes	Mean=1.5; min=0.0; max=35 µg WHO-TEQ/kg
	Incineration of hazardous waste		Mean=0.3; min=0.0002; max =2 µg WHO-TEQ/kg
	Biomass power plant (electricity production)		Mean=1,1; min=0,001; max=16 µg WHO-TEQ/kg
Lopes et al. (2020)	4 power plant boilers using forest biomass in Portugal. Three boilers are Bubbling Fluidized-Bed Boilers (BFBs). The fourth is a grate-firing (GF) boiler.	Fly ashes The BFB mainly use residues from forest biomass consisting of bark and branches shredded eucalyptus used in the manufacture of paper and paper sludge. Other residues are also used such as pine residues. GF also use forest biomass residues, pine and eucalyptus residues and sometimes agricultural residues from olive oil production or from the wood industry.	35-1 139 ng TEQ/kg$_{WHO2005}$-TEQ The high levels of chlorine in the biomasses (0.04-0.28%) can lead to the formation of PCDD/Fs.

Regarding the 258 ash samples (fly ash, bottom ash or mixed ash) from French biomass power plants reported in the literature (shaded lines in Table 3), only two ash samples have dioxin values above the new threshold value (values of 6 924 ng I.TEQ/kg and 8 505 ng ITEQ/kg highlighted in red in the table). These two values are exceptional and are linked either to probable contamination of the wood introduced in the boiler, or to poorly controlled combustion conditions (low loading rate). **In the light of these data, fly ashes from biomass power plants are not considered as POPs waste.**

Except for the study performed by Lopes et al (2020), data reported from some foreign countries are not recent (before 2005) and therefore not very representative of current operating conditions. More specifically, the regulatory framework related to biomass power plants has become increasingly restrictive since 1997.

In France, excepted the facilities of less than 2 MW (and less than 1 MW since 2018), all other biomass power plants are regulated and subjected to limit values in terms of atmospheric emissions and element content in the ash [LECES (2016)]. This regulatory framework promotes a low probability of finding high levels (above the POP regulation threshold) of dioxins in the fly ashes. In addition, the biomass introduced in these facilities is closely controlled. The high values observed in the Table 3 correspond either to outdated studies (prior to the 2000s) or to poorly controlled conditions of combustion (incomplete combustion and/or unexpected contamination of the wood). A national campaign for collecting fly ash samples from biomass power plants seems not to be necessary.

3.4 Conclusion on the literature data

Very few data on PCB-dl levels have been reported in the literature: some studies include them, but this is still the exception.

Few data are available on dioxin levels in ashes and soot from domestic burning, and these data are outdated. Additional data are therefore necessary, and a national campaign has been carried out. The corresponding data are presented in the following chapter. It is noted that, it is difficult to guarantee a good representation of all possible cases considering the diversity of household combustion appliances, fuel matrices and possibilities of geographical origins of woods,

A large amount of data is available in the literature on fly ashes from biomass units. For the data collected on units located in France, data on 258 ash samples are available and only 2 samples exceed the POP regulation threshold for the dioxin parameter. These data are therefore considered as representative, and no additional samples were collected. **Fly ashes from biomass units are therefore not considered as POPs waste.**

4 Collection of ash and soot samples from household wood-burning appliances in France

The samples were collected in mainland France. French overseas territories are not included this study.

4.1 Description of samples collected

Ashes and soot samples from domestic fireplaces were collected in 2023 and 2024 in mainland France, for all types of wood-burning appliances. Coal- and oil-fired stoves were excluded from this study. In fact, coal-fired heating appliances are in the minority in France (the use of solid mineral fuels such as coal in the heating, domestic hot water and cooking heating sub-sectors was 4% in 1990 and has almost disappeared since the 2000s [Citepa (2023)]). Moreover, oil- and gas-fired boilers can no longer be sold from July 1, 2022[7].

159 samples were analyzed and are distributed as follows:

- 55 ash samples;
- 96 soot samples;
- 3 "mix" samples from chimney sweep hoover tanks corresponding to open and closed fireplaces;
- 5 "composite" samples made from ash samples with a similar color (see pictures in Appendix 2).

The types of wood-burning appliances considered in this study are: open fireplaces, closed/with an insert fireplaces, wood-burning stoves, pellet-burning stoves, pellet-burning boilers and wood-burning boilers.

Most of the samples were collected by chimney sweeping companies on a voluntary basis. Some samples were collected directly from individual customers.

In general, in the case of dioxins formation, soot concentrates more dioxins than ashes because of its more porous structure enabling to capture a higher level of organic pollutants. As a result, a higher number of soot samples were collected.

Samples were collected all over France in order to take into account the geographical variability of the composition of the wood (assuming that in the case of fireplaces using logs, the wood species used are local), in particular their chlorine content.

The geographical distribution of ash and soot samples and by types of wood-burning appliances are shown in Figure 2 and Figure 3. Almost all regions are covered by this campaign.

[7] Décret n°2022-8 du 5 janvier 2022 relatif au résultat minimal de performance environnementale concernant l'installation d'un équipement de chauffage ou de production d'eau chaude sanitaire dans un bâtiment.

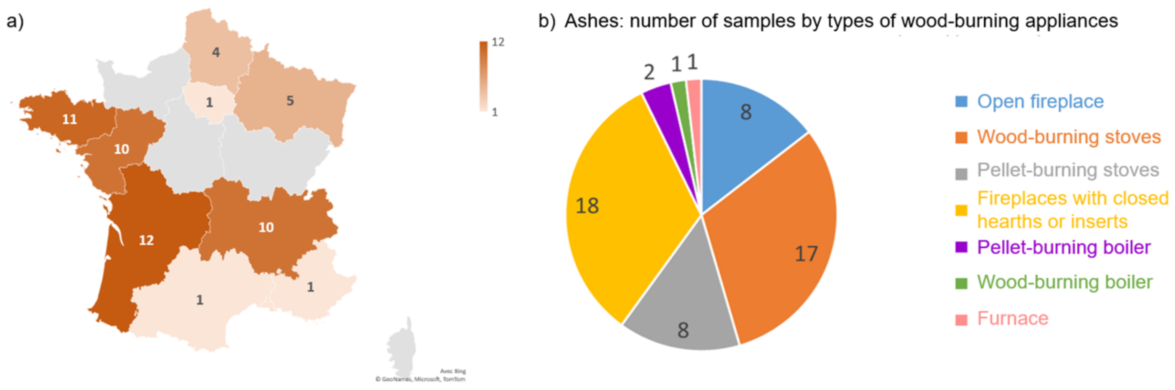


Figure 2 : Information on the 55 ash samples collected: a) geographical distribution b) number of samples by type of wood-burning appliance

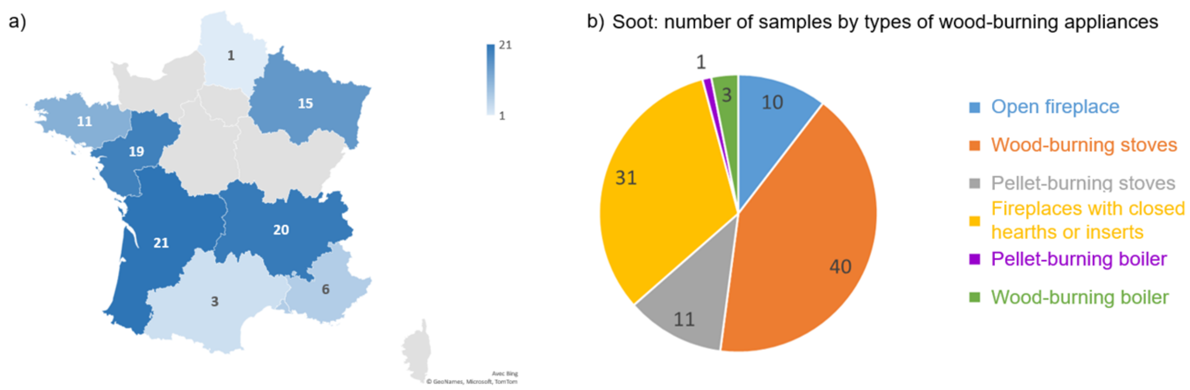


Figure 3 : Information on the 96 soot samples collected: a) geographical distribution b) number of samples by type of wood-burning appliance

In 2021, closed fireplaces (closed hearths fireplaces or inserts) and wood-burning stoves were the main type of domestic burning in France. Among the samples collected, closed fireplaces and wood-burning stoves are indeed the most common (Figure 2b and Figure 3b), which is in line with the actual situation.

The samples were collected in 500-mL polyethylene (PE) jars initially supplied by Ineris. PE jars were chosen rather than glass jars to make it easier for the chimney sweeps to collect the samples (lighter and easier to handle than glass, avoiding breakage, less heavy to transport when collecting several samples in one day). The instruction bas been given to collect cold ashes in order to limit the possibility of dioxin adsorption on the PE jars. All the samples collected have been received by Ineris, weighed and then sent for PCCD/F and PCB-dl analysis. The analyses were subcontracted to MicroPolluant Technologies laboratory.

It should be noted that the representativeness of the sample is not guaranteed in this study for the ash samples collected. The ash samples generally only come from the last combustion cycle(s). As a result, it is impossible to conclude whether or not the concentrations measured are representative of the entire cycle of use of the fireplace by the customers (as the way the fireplace is used may vary). On the other hand, the soot samples collected correspond to approximately one combustion season and a representative quantity of soot during a chimney sweeping is collected and sent for analysis: each soot sample therefore corresponds to approximately one (or half) heating season and is therefore more representative of the conditions in which the fireplace is used.

A questionnaire (presented in Appendix 3) was associated with each sample collected and completed by the customers or chimney sweeps. The aim of this questionnaire was to specify, for each sample, the parameters that could influence the formation of PCCD/F and PCB-dl.

4.2 Results of analysis

4.2.1 General information on the method of analysis

PCCD/F and PCB-dl concentrations are expressed as total WHO-TEQ. In cases where some substances have a concentration below the limit of quantification (LOQ), the value of the concentration of the non-measurable substance is set to the LOQ value.

Concentration values are expressed based on the wet weight (of the waste). The POP regulation does not specify whether the threshold concentrations are to be considered based on the dry weight (of the waste) or on the wet weight. Excepted for 4 samples, all the other dry matter content values are above 90% (and 106/159 samples have a value > 95%). Thus, the impact of expressing the result in terms of wet or dry weight is not significant.

4.2.2 Quality of measurements

The analyses were carried out by the MicroPolluant Technologies laboratory. The analytical uncertainties on the concentrations for each substance as well as the error on the estimation of the recovery rate of the markers are specified below (Table 4). Markers are added to the sample before analysis to ensure that the analysis is quantitative; they are introduced before extraction and follows the entire sample preparation process (extraction, purification, concentration).

Table 4 : Analytical uncertainties

Dioxin substance (PCDD)	Uncertainty (%)	Furan substance (PCDF)	Uncertainty (%)
2, 3, 7, 8 TCDD	15%	2, 3, 7, 8 TCDF	15%
1, 2, 3, 7, 8 PeCDD	15%	1, 2, 3, 7, 8 PeCDF	25%
1, 2, 3, 4, 7, 8 HxCDD	45%	2, 3, 4, 7, 8 PeCDF	25%
1, 2, 3, 6, 7, 8 HxCDD	45%	1, 2, 3, 4, 7, 8 HxCDF	15%
1, 2, 3, 7, 8, 9 HxCDD	25%	1, 2, 3, 6, 7, 8 HxCDF	15%
1,2,3,4,6,7,8 HpCDD	15%	2, 3, 4, 6, 7, 8 HxCDF	20%
OCDD	25%	1, 2, 3, 7, 8, 9 HxCDF	25%
		1,2,3,4,6,7,8 HpCDF	10%
		1,2,3,4,7,8,9 HpCDF	20%
		OCDF	25%
ITEQ	10%		

The concentrations given in the analysis reports are the measured concentrations corrected by the markers recovery rates. Extraction markers (named C13) may be lost during the various stages of sample preparation. The associated recovery rates may therefore be less than 100%. For example, a recovery rate of 50% means that 50% of the dioxin substance has been lost during extraction/analysis. The target range for C13 markers is between:

- 30 and 150% for tetra-, penta- and hexa-chlorosubstituted congeners;
- 20 and 150% for hepta and octa-chlorosubstituted congeners.

Regarding the data from the 159 analysed samples:

- for PCDD/F: 47 samples / 159;

- for PCB-dl: 13 samples / 159

have at least one substance outside these C13 criteria. Although these values do not meet the target range, the impact on the results remains low to moderate, as the concentrations reported are corrected by the recovery rate.

These analyses have not been duplicated.

4.2.3 Samples resulting from a controlled combustion

Among the samples collected, 4 are representative of what can be collected from fireplaces where combustion is carried out under good conditions and with an appropriate fuel (parboiled wood). The results of the analyses are presented in Table 5. The values are very low, in accordance with what is expected.

Table 5 : Soot and ash samples resulting from controlled combustion. The concentrations are expressed based on the wet weight.

Type of fireplace	Type of fuel	Substance/material used for ignition	Type of sample	PCDD/F TOTAL TEQ WHO (ng/kg)	dl-PCB TOTAL TEQ WHO (ng/kg)
Closed fireplace (15 kW)	Parboiled wood (oak, beech, ash tree)	Small woods, firelighters, wood fiber	Soot	8.2	0.6
			Ashes	5.3	0.3
Wood-burning stove (8 kW)		Small woods, firelighters	Soot	8.6	0.9
			Ashes	7.1	0.5

4.2.4 Results obtained on the ash samples

Dioxin/furan concentrations > 500 ng/kg are mainly linked to the combustion of treated wood. According to the Ineris report DRC-12-126318-06147A-V2 (2013), dioxin and furan levels in fly ashes range from 0 to 400 ng I.TEQ/kg for the combustion of natural wood and over 700 ng I.TEQ/kg with the combustion of waste wood containing chlorinated compounds. As a reminder, the limit value of the POP regulation is 5 000 ng/kg.

The TOTAL TEQ WHO-2005 values for PCDD/F and dl-PCB obtained in the 55 ash samples collected are shown in Figure 4. Most of the samples (91% of samples) have low dioxin/furan levels < 100 ng/kg, 4 samples (7% of samples) have a value of between 100 and 500 ng/kg and only 1 sample contains a high level of dioxins (between 1 000 and 5 000 ng/kg). For dl-PCB, all the samples have low values (<50 ng/kg, i.e. less than 1% of the threshold value): the data relating to dl-PCB will therefore not be interpreted in this report as they don't have any influence on the conclusions.

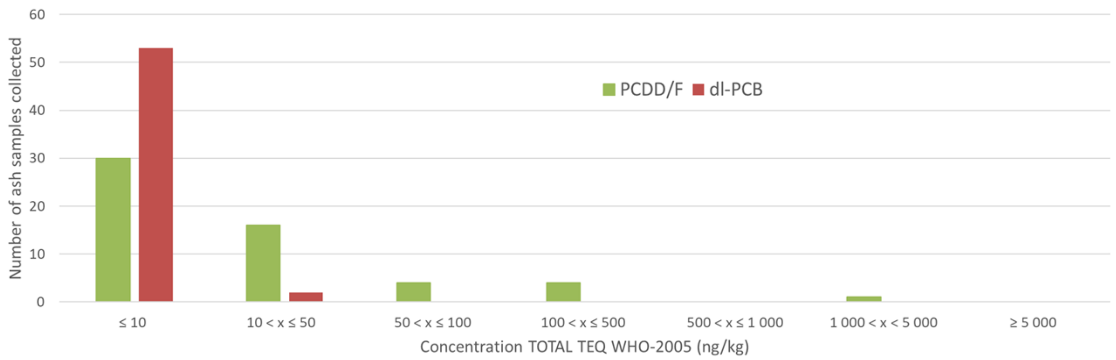


Figure 4 : Distribution of PCDD/F (green) and dl-PCB (red) concentration values in TOTAL TEQ WHO- 2005 for the 55 ash samples

Figure 5 shows the distribution of these Figure 4 data by type of wood-burning appliances. The highest concentrations were observed in pellet stoves (3 samples/11 samples from pellet stoves > 100 ng/kg). One sample from closed fireplace and one sample from a pellet boiler had values > 100 ng/kg.

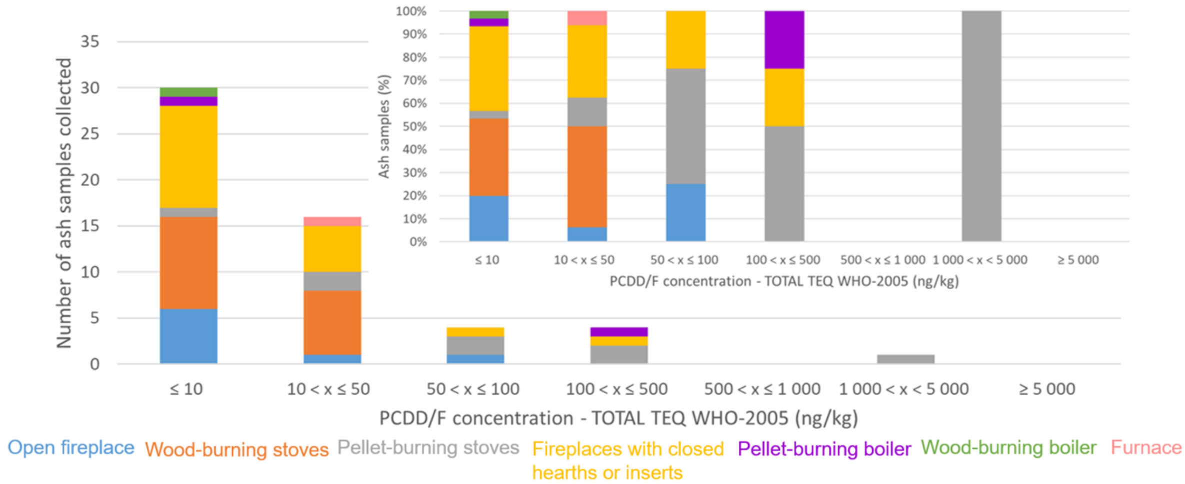


Figure 5 : Distribution of the PCDD/F concentration values for the 55 ash samples by range of values and by type of wood-burning appliance

In conclusion, regarding the dioxin levels measured in the 55 ash samples collected, **none of the ash samples exceeds the POP regulation threshold value of 5 000 ng/kg.**

4.2.5 Results obtained on the soot samples

The TOTAL TEQ WHO-2005 values for PCDD/F and dl-PCB in the 96 soot samples collected are shown in Figure 6. Most of the samples (70% of samples) have dioxin/furan levels < 100 ng/kg, 15 samples (16% of samples) have a value between 100 and 500 ng/kg and 14 samples (15%) have a high level of dioxins (> 500 ng/kg). Only one sample exceeds the POP regulation threshold value of 5 000 ng/kg. For dl-PCB, all samples have values of < 100 ng/kg. The data for dl-PCB are not interpreted in this report as they don't have any influence on the conclusions.

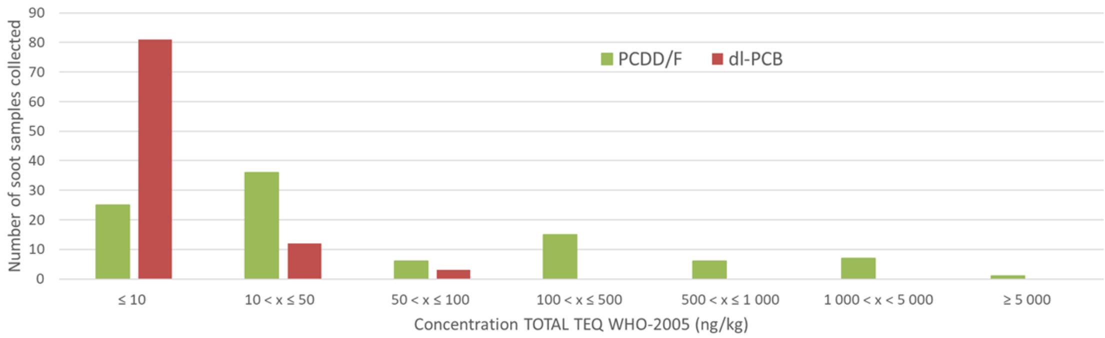


Figure 6 : Distribution of PCDD/F (green) and dl-PCB (red) concentration values in TOTAL TEQ WHO- 2005 for the 96 soot samples

Figure 7 shows the distribution of these Figure 6 data by type of wood-burning appliances. It shows that the types of fireplaces with the highest PCDD/F levels are open fires, wood-burning stoves and pellet-burning stoves.

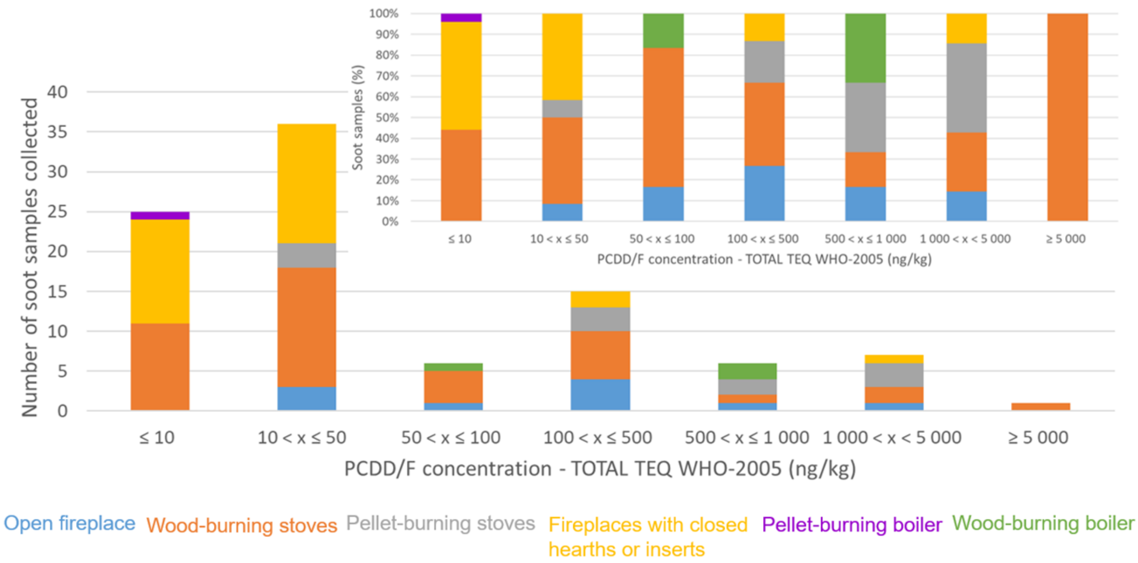


Figure 7 : Distribution of the PCDD/F concentration values for the 96 soot samples by range of values and by type of wood-burning appliance

Thus, regarding the dioxin levels measured in the 96 soot samples collected, **only one soot sample is classified as a POP waste** (value > 5 000 ng/kg). For this sample coming from a wood-burning stove, no additional information (e.g. whether or not waste had been introduced) could be collected via the associated questionnaire.

In order to better characterize the origin of samples with the highest level of dioxins (sum of dioxins > 100 ng/kg), a particular attention has been paid to the questionnaires related to these samples. In most cases, the operating conditions were normal. Some questionnaire reported the presence of waste or materials used for ignition: paper, newspaper/prospectus, kindling, firelighters, pinecones, vegetable, candles, cardboard/cardboard packaging, pallets.

However, it is difficult at this stage to interpret these results in more details, as the level of information found in the questionnaires is different from one sample to another.

4.2.6 "Mix" samples from chimney sweep hoover tanks

Three samples were collected from the tanks of the hoovers used during the annual chimney sweeping. These samples come from the Gironde area and are a mixture of soot/ashes from open and closed fireplaces. The results obtained from these three samples are shown in Table 6 below.

Table 6 : Sum of PCDD/F and dl-PCB in TOTAL TEQ WHO-2005 for the three mixed samples

	PCDD/F TEQ (ng/kg) TOTAL TEQ WHO	dl-PCB TEQ (ng/kg) TOTAL TEQ WHO
Mix 1	5.1	0.38
Mix 2	149.3	0.76
Mix 3	2.6	0.32

These samples are representative of what is usually collected during chimney sweeping. Regarding the values reported in this table, the three mix samples have low PCDD/F and PCB-dl values: they are not classified as POPs.

4.2.7 Ash composites samples

The color of the ashes is an important parameter to consider. Ashes have generally "light grey" color, reflecting a predominantly mineral composition. A darker color (close to black) indicates the presence a significant fraction of organic matter (or perhaps a mixture with soot). The color of the ashes therefore gives an indication of the quality of the combustion.

Therefore, in order to obtain representative values according to combustion quality, five composite ash samples were formed by mixing ashes with similar colors. Pictures of these mixtures are shown in Appendix 2. The samples used to form the five composite samples were those that were available at the time they were made (in April 2024) and in a sufficient quantity (> 100 g) to be able to perform individual analyses and to form the composite sample.

The dl-PCB values for these five samples are low (< 30 ng/kg). The dioxins levels for the five composite samples (reference numbers 257 to 261) are shown in Figure 8. They are very low (< 25 ng/kg). These ash composites samples are therefore not classified as POPs waste.

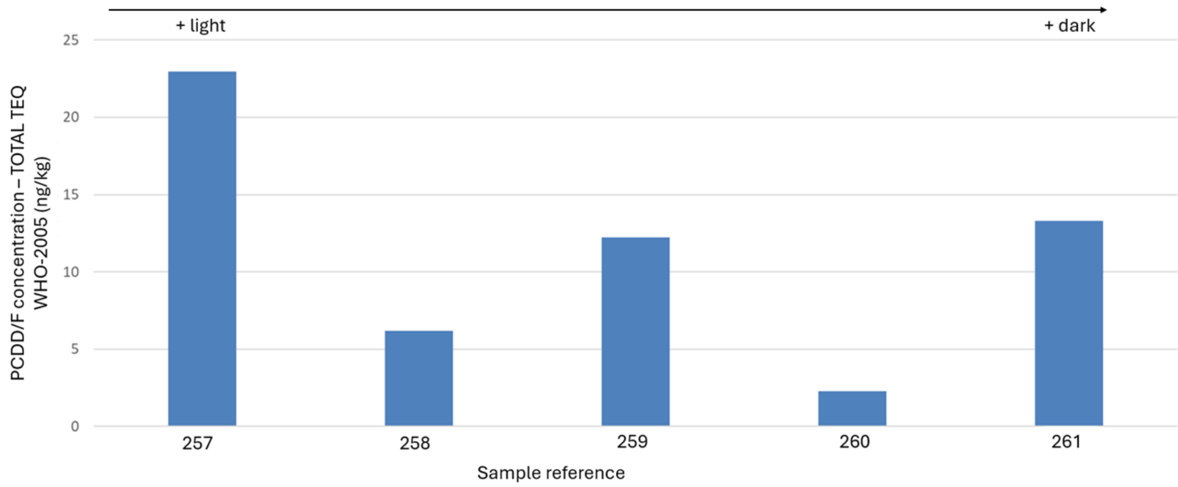


Figure 8 : PCDD/F concentrations in TOTAL TEQ WHO-2005 for the 5 ash composite samples

5 Conclusion

The main parameters leading to the presence of PCDD/F and PCB-dl in ashes and soot from domestic fireplaces and fly ashes from biomass units are the presence of chlorine and poor combustion quality. Therefore, the use of fuels with negligible chlorine content (wood logs, uncontaminated or contaminated by chlorinated products) remains the best way of limiting the production and emission of dioxins during combustion in domestic fireplaces and in the biomass power plants (> 1 MW).

The levels of PCDD/F and dl-PCB in ashes and soot from domestic fireplaces and also in the fly ashes from biomass units in France were investigated in order to compare their values with the threshold value of 5 µg/kg TOTAL TEQ WHO-2005 in waste reported in the POP regulation.

Regarding the residues (soot and ashes) collected from domestic fireplaces, few data on dioxin levels are available in the literature, and most of these data are outdated (< 2006). Given the evolution of the wood-burning technologies over the last twenty years, these data are not representative of the current situation in France. So, new samples have been collected in mainland France, resulting in the collection of 55 ash samples, 96 soot samples and 3 samples from chimney sweep hoover tanks. All types of fireplaces were covered by the national campaign: open fireplaces, closed/insert fireplaces, wood-burning stoves, pellet-burning stoves, pellet-burning boilers and wood-burning boilers. Wood-burning stoves and closed/insert fireplaces were the most widely represented fireplaces. Although each sample was related to a questionnaire on the conditions of use of the corresponding appliance, little information was collected.

Regarding the dioxins levels measured in the 55 ash samples, none of the samples is classified as a POP waste (values below 5 000 ng/kg). Only one sample of ashes from a pellet stove had a high dioxin/furan content (> 500 ng/kg). According to the literature, dioxin/furan concentration values higher than 500 ng/kg are mainly related to the addition of treated wood or waste or to degraded combustion conditions either throughout the combustion process (e.g. in the case of restricted air supply) or during certain stages of the combustion (start-up, power change).

Regarding the 96 soot samples, only one sample was classified as a POP waste (value higher than 5 000 ng/kg). This sample comes from a wood-burning stove, and no information was available in the associated questionnaire. Nevertheless, 15% of the soot samples (i.e. 14 samples) have a high dioxin/furan content (> 500 ng/kg). The types of fireplaces with the highest PCDD/F levels are open fireplaces, wood-burning stoves and pellet stoves.

Lastly, the dioxin-like PCB levels measured in all the samples were very low. Ashes and soot from domestic wood-burning appliances are therefore not POPs waste.

Finally, regarding the biomass plants, their regulatory framework, in particular the emission limit values for atmospheric emissions and for ashes content, limits the presence of pollutants such as dioxins in fly ashes. These facilities must therefore continue to be closely controlled, especially as their number is set to increase over the next few years. Data on the levels of dioxins/furans in fly ashes are available in the literature and come from studies that were carried out over more recent periods. These data are therefore representative and considered as sufficient. Therefore, no fly ash samples have been collected in France. In view of the values presented in the literature, fly ashes from biomass plants are not classified as POPs waste.

6 References

Afssa (2005). Dioxines, furanes et PCB de type dioxine : Evaluation de l'exposition de la population française.

Bacher, Reiner, Max Swerev, and Karlheinz Ballschmiter. "Profile and pattern of monochloro-through octachlorodibenzodioxins and-dibenzofurans in chimney deposits from wood burning." Environmental science & technology 26.8 (1992): 1649-1655.

Bartet, Bernard, Guillaume Pepin, and Michel Nomine. "Dioxine dans les MIOM Teneurs observées et étude préliminaire de leur potentiel de transfert vers l'environnement." Colloque MIOM 2001. Oct 2001, Orléans, France. pp.118-123. ineris-00972239.

BiPRO (2005): Study to facilitate the implementation of certain waste related provisions of the Regulation on Persistent Organic Pollutants (POPs):

https://ec.europa.eu/environment/waste/studies/pdf/pops_waste_full_report.pdf

Björn Hedman, Morgan Näslund, and Stellan Marklund; Emission of PCDD/F, PCB, and HCB from Combustion of Firewood and Pellets in Residential Stoves and Boilers - Environ. Sci. Technol. 2006, 40, 4968-4975.

Quaß, Ulrich, Michael Fermann, and G. Broeker. "Identification of relevant industrial sources of dioxins and furans in Europe (The European Dioxin Inventory). Final report." (1997).

Citepa, 2023. Gaz à effet de serre et polluants atmosphériques. Bilan des émissions en France de 1990 à 2022. Rapport Secten éd. 2023.

Collet Serge. Les émissions de polluants par les foyers domestiques. Pollution Atmosphérique : climat, santé, société, 2009, Numéro special mars, pp.83-90.

Collet Serge (2000) ; Rapport INERIS –DRC-n°00/60-MAPA-SCo-25420 ; Facteurs d'émission - Emissions de dioxines, de furanes et d'autres polluants liés à la combustion de bois naturels et adjuvantés ; MINISTERE DE L'AMENAGEMENT DU TERRITOIRE ET DE L'ENVIRONNEMENT.

Dumler-Gradl, R., H. Thoma, and O. Vierle. "Research program on dioxin/furan concentration in chimney soot from house heating systems in the Bavarian area." Organohalogen Comp 24 (1995): 115-118.

Dyke P. H., Foan C., Wenborn M., Coleman P. J., A review of dioxin releases to land and water in the UK, The science of the total environment, 207, pp 119-131, 1997.

Fact Sheet PCB ; PREFECTURE DE LA REGION RHONE-ALPES. Fiche rédigée par la CIRE Rhône Alpes. Janvier 2010.

Launhardt T, Strehler A, Dumler-Gradl R, Thoma H, Vierle O. PCDD/F – and HAP – emission from house heating systems. Chemosphere 1998 ; 37 : 2013-20.

LECES, Evaluation de performances énergétiques et environnementales de chaufferies biomasse, Etude réalisée pour le compte de l'ADEME, 2008.

LECES, Evaluation des performances énergétiques et environnementales de chaufferies biomasse, Etude réalisée pour le compte de l'ADEME, 2014.

LECES, Evaluation des performances énergétiques et environnementales de chaufferies biomasse, Etude réalisée pour le compte de l'ADEME, 2016.

Lopes, H.; Proença, S. Insights into PCDD/Fs and PAHs in Biomass Boilers Envisaging Risks of Ash Use as Fertilizers. Appl. Sci. 2020, 10, 4951.

Luthe C., Karidio I., Uloh V., Towards controlling dioxins emissions from power boilers fuelled with saltladen wood waste, Chemosphere, Vol. 35, pp 557-574, 1997.

Oehme, M.; Müller, M.D. Levels and congener patterns of polychlorinated Dibenzo-p-dioxins and Dibenzofurans in solid residues from wood-fired boilers. Influence of combustion conditions and fuel type. Chemosphere 1995, 30, 1527–1539.

OFEFP (1996), Incinération de déchets, de bois usagé et des résidus de bois, dans des chauffages au bois et en plein air.

Pohlandt K., Marutzky R., Concentration and distribution of polychlorinated dibenzo-p-dioxin (PCDD) polychlorinates dibenzofuran (PCDF) in wood ash, Chemosphere, Vol. 28, pp 1311-1314, 1994.

Rapport Ineris DRC-12-126318-06147A-v2 - Serge Collet - Note sur l'assimilation d'un produit (bois faiblement adjuvanté) à un combustible de référence et sur la surveillance des installations classées dans la rubrique 2910B (2013).

Rapport Ineris-180235-07692-v2.0– Roseline BONNARD - Eléments pour la fixation d'une valeur limite réglementaire en PCDD/F dans les cendres de biomasse destinées à l'épandage (2019).

Rapport N° DRC-18-171115-03897A – Cécile RAVENTOS - Prélèvement de cendres générées dans des chaufferies biomasse (68) en vue de la caractérisation des cendres (2018).

RECORD 14-0913/1A ; Valorisation des cendres issues de la combustion de biomasse ; Revue des gisements et des procédés associés (2016).

Référentiels combustibles bois énergie de l'ADEME – Définition et exigences (2017) – Blandine ROBERT, Gaëtan REMOND, Rémi GROVEL, Vincent NAUDY, Isabelle ZDANEVITCH, Serge COLLET, Hélène PARTAIX.

Thoma, H. "PCDD/F-concentrations in chimney soot from house heating systems." Chemosphere 17.7 (1988): 1369-1379.

U.S. EPA. 2004. Exposure and Human Health Reassessment of 2,3,7,8-Tetrachlorodibenzo-P-Dioxin (Tcdd) and Related Compounds National Academy Sciences (External Review Draft) (2004). U.S. Environmental Protection Agency, Washington, D.C., EPA/600/P-00/001Cb.

Van Oostdam, Jay C., and J. EH Ward. "Dioxins and furans in the British Columbia environment." (1995).

Vandermarken, Tara & Boonen, Imke & Van Langenhove, Kersten & Goeyens, Leo & Denison, Michael & Croes, Kim & Elskens, Marc. (2016). In vitro reporter gene activity of PCDD/Fs and dl-PCBs in wood ash from domestic heating systems (Belgium) using the H1L7.5c1 CALUX Bioassay - Poster @ Dioxin 2016 Conference at Firenze.

Wunderli S., Zennegg M., Dolezal I., Gujer E., Moser U., Wolfensberger M., Hasler P., Noger D., Studer C., Karlaganis G., Determination of polychlorinated dibenzo-p-dioxins and dibenzo-furans in solid residues from wood combustion by HRGC/HRMS, Chemosphere, Vol. 40, pp 641-649, 2000.

Yamamura K., Ikeguchi T., Uehara H., Study on the emission of dioxins from various industrial wastes incinerators, Organohalogen Compounds, Vol. 41, pp 287-292, 1999.

7 Appendices

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- Annex 1: Toxic Equivalency Systems: I-TEQ (NATO) and WHO-TEQ (WHO)
- Appendix 2: Pictures of the ash “composites” samples
- Appendix 3: Questionnaire

Annex 1: Toxic Equivalency Systems: I-TEQ (NATO) and WHO-TEQ (WHO)

The toxicity of a complex mixture of dioxins is calculated with the sum of the individual concentrations of each congener (7 PCDDs out of 75 and 10 PCDFs out of 135) multiplied by their respective toxic equivalency factors (TEFs). Each TEF value reflects the toxicity of a particular congener. The WHO scheme also includes the 12 dioxin-like PCB congeners (dl-PCB).

The TEF value of the most toxic congener (2,3,7,8-TCDD) is arbitrarily set at 1.

TEF values are frequently re-evaluated by the WHO in line with the level of knowledge about the toxicity of these substances. The latest revision dates from 2005 (WHO-TEQ 2005). The various TEF values depending on the scheme used are listed in the table below.

Table 7 : Toxic equivalency factors (TEFs) for PCDDs, PCDFs and dl-PCB according to the scheme used

	Compounds	I-TEQ NATO (1989)	WHO-TEQ (1998)	WHO-TEQ (2005)
Dioxins (PCDD)	2,3,7,8-TCDD	1	1	1
	1,2,3,7,8-PeCDD	0.5	1	1
	1,2,3,4,7,8-HxCDD	0.1	0.1	0.1
	1,2,3,6,7,8-HxCDD	0.1	0.1	0.1
	1,2,3,7,8,9-HxCDD	0.1	0.1	0.1
	1,2,3,4,6,7,8-HpCDD	0.01	0.01	0.01
	1,2,3,4,6,7,8,9-OCDD	0.001	0.0001	0.0003
Furans (PCDF)	2,3,7,8-TeCDF	0.1	0.1	0.1
	1,2,3,7,8-PeCDF	0.05	0.05	0.03
	2,3,4,7,8-PeCDF	0.5	0.5	0.3
	1,2,3,4,7,8-HxCDF	0.1	0.1	0.1
	1,2,3,6,7,8-HxCDF	0.1	0.1	0.1
	1,2,3,7,8,9-HxCDF	0.1	0.1	0.1
	2,3,4,6,7,8-HxCDF	0.1	0.1	0.1
	1,2,3,4,6,7,8-HpCDF	0.01	0.01	0.01
	1,2,3,4,7,8,9-HpCDF	0.01	0.01	0.01
	1,2,3,4,6,7,8,9-OCDF	0.001	0.0001	0.0003
dl-PCB	PCB 77		0.0001	0.0001
	PCB 81		0.0001	0.0003
	PCB 105		0.0005	0.00003
	PCB 114		0.0005	0.00003
	PCB 118		0.0001	0.00003

	PCB 123		0.0001	0.00003
	PCB 126		0.1	0.1
	PCB 169		0.01	0.03
	PCB 156		0.0005	0.00003
	PCB 157		0.0005	0.00003
	PCB 167		0.00001	0.00003
	PCB 189		0.0001	0.00003

Appendix 2: Photos of composite ash samples

Photographs of the ash samples used to form the composite ash samples are shown below. The samples are sorted from lightest to darkest.

Figure 9 : Sample no. 257.

Figure 10 : Sample no. 258.

Figure 11 : Sample no. 259.

Figure 12 : Sample no. 260.

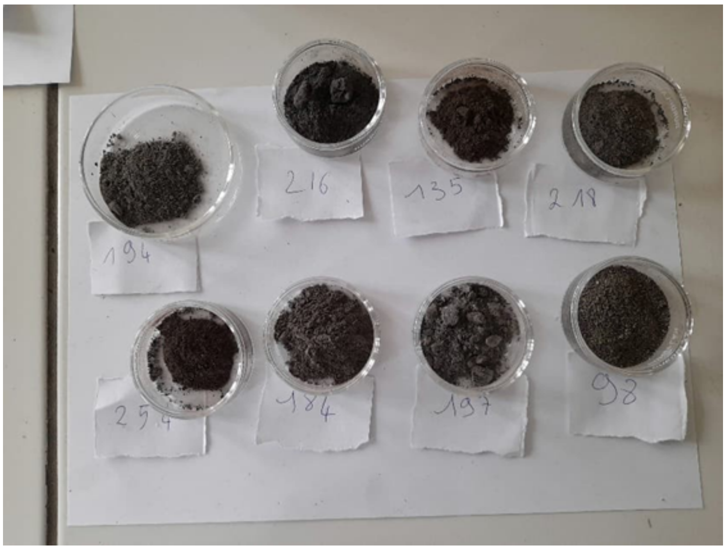

Figure 13 : Sample no. 261.

Appendix 3: Questionnaire

Study of PCDD/PCDF and dl-PCB levels in ashes and soot from domestic fireplaces	
Ashes or soot sample?	
Name of the person or company who collected the sample	
Place (town) of the sample collected	
Sampling date	
Type of fireplace	
Rated power (if known)	
Conditions use of the appliance (main heating, supplementary heating, etc.)	
Chimney sweeping carried out (twice a year, once a year, less than once a year)	
Conditions of Operating conditions (normal or slow combustion, if air supply is restricted, etc.)	
Type of fuel / Types of wood used	
Geographical origin of the wood (if known)	
Humidity (if known)	
Substance/material used for ignition	
Presence of wood waste (paper, cardboard, leaflets, plastic packaging, painted wood, etc.)	
Sampling (from 1 or several combustions)	
Comments	

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