Insights into PCDD/Fs and PAHs in Biomass Boilers Envisaging Risks of Ash Use as Fertilizers

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Abstract: Since ashes are a possible source of Persistent Organic Pollutants (POPs) contamination, their application in soils must be subject to more study and control. In this scope, feed residual forest biomasses and biomass ashes, collected along one year in four biomass power stations, were characterized mainly for their polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs) and Polycyclic Aromatic Hydrocarbons (PAHs) contents. The biomasses present concerning levels of Cl (0.04–0.28%) that may lead to PCDD/Fs formation. The biomasses also contain OCDD (29–260 ng/kg) and 1,2,3,4,6,7,8-HpCDD (35 ng/kg) that may contribute to increased Toxic Equivalents (TEQs) of ashes, possibly involving dechlorination and ash enrichment mechanisms. While the WHO$_{2005}$-TEQs in bottom ashes (14–20 ng TEQ/kg) reaches the proposed limit (20 ng TEQ/kg) for ash use as fertilizers, in fly ashes (35–1139 ng TEQ/kg) the limit is exceeded. PAHs are below 0.02 mg/kg in bottom ashes and 1.5–2.5 mg/kg in fly ashes, complying with the proposed limit of 6 mg/kg. As bottom and fly ash streams may contain different ash flows, a clear definition of ash mixes is required. Correlations between unburned carbon (C), PAHs and PCDD/Fs were not found, which highlights the need for compulsory PCDD/Fs analysis in ashes, independently of their origin, burnout degree or levels of other contaminants. A sensitivity analysis was performed to evaluate the impact of handling non-detected values, which showed more impact for TEQs values close to the proposed regulatory limit of PCDD/Fs. These findings highlight the need to define reporting protocols of analytical results for risk assessments and conformity evaluation.

Keywords: residual forest biomass; combustion; ash; fertilizers; PCDD/Fs; PAHs; TEQs; BaP-EQs; non-detected handling; regulatory limits

1. Introduction

One of the objectives of the United Nations' Sustainable Development Goals (UN SDGs) is the worldwide minimization of release of chemicals to air, water, and soil [1]. The most recent EU Regulation on Persistent Organic Pollutants (POPs) [2], which recast the previous regulation [3] on the EU POPs Implementation Plan, reinforces the need of reduction and elimination of POPs to protect the environment and human life. This regulation aligns with the United Nations (UN) instruments; the Aarhus Protocol on Long-Range Transboundary Air Pollution on POPs (POPs Protocol) [4], the Stockholm Convention on POPs (POPs Convention) [5] and the Basel Convention on the control of transboundary movements of hazardous wastes and disposal [6].

Polycyclic Aromatic Hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), also named as dioxins or PCDD/Fs, are among the dozens of highly toxic POPs envisaged in several regulations. According to annex C of the Stockholm POPs Convention, the PCDD/Fs are considered as "Unintentional" POPs (UPOPs) since they are formed unintentionally in various anthropogenic activities, including "Firing

installations for wood and other biomass fuels". For waste management, the EU POPs Regulation [2] aligns with the Basel Convention; contaminated wastes with levels of POPs above certain limits, "low POPs content" (LPCL), are "POP wastes" and must be disposed or treated. For PCDD/Fs, the provisional LPCL (expressed as Toxicity Equivalents-TEQ), 15,000 ng TEQ/kg, is considered too high and not protective. In fact, practices such as uncontrolled dumping and unaware spread of contaminated residues in soils (sludge, ashes, etc.) [7–9], highlight the need to define more precautionary limits.

The UNEP Standardized Toolkit [10] was developed within the Stockholm Convention on POPs, for identification and quantification of releases of PCDD/Fs and other UPOPs. Five emission (EF) vectors were considered for several activities: EFair, EFsoil, EFwater, EFproducts and EFresidues, revealing that the greatest dissemination routes for PCDD/Fs are air emissions (45%), residues, including ashes (34%), and land accumulation (11%). Several guidelines on "Best Available Technology/Best Environmental Practices" (BAT/BEPs) were also developed in accordance with article 5 and annex C of the POPs Convention, to prevent formation and release of UPOPs [11]. The BAT/BEP "Guidance/Guidelines for Firing Installations for Wood and Other Biomass Fuels" recommends that combustion of contaminated biomass, such as construction wood waste, should be avoided in biomass furnaces to minimize formation of PCDD/Fs and PAHs. It also specifies that fly ashes from biomass combustion have to be properly landfilled. The implementation of technologies to reduce air emissions from industrial installations according to BAT/BEPs and BREFs [12] of the Industrial Emissions Directive [13] is foreseen to increase amounts and hazardousness of ashes contaminated with POPs.

As very Persistent, very Bioaccumulative and Toxic pollutant (PBT), PCDD/Fs were broadly discussed within the EU "Strategy for a Non-Toxic Environment"; a sub-study on very persistent chemicals [14] highlights the risks of their accumulation, concentration and dispersion, namely through reuse/recycling of streams within the Circular Economy. These concerns will be addressed in the upcoming European Green Deal framework [15].

The Community Strategy for PCDD/Fs and PCBs [16] recognized that bioaccumulation via the food chain is the most critical pathway of human exposure to PCDD/Fs and PCBs and that contamination of food processing animals and edible plants occurs mainly via uptake from soils. Given the evidence of environmental legacy and threats, [7,8,17–21], PCDD/Fs and PCBs are included in the group of most relevant soil pollutants, among other POPs. For protection of human health, limits of PCDD/Fs in foodstuffs [22] were pushed down to safer values [23], namely for free-range eggs, which are highly sensitive to dioxin effects. Weber et al. [8] evaluated the sources and influence of soils contamination on food safety, for example, 5 ng TEQ/kg of PCDD/Fs + PCBs in soils induces contents above the safe limits in free-range chickens/eggs, exceeding the Tolerable Daily Intake (TDI). Among identified sources, the application of ashes and sludges are referred to as relevant causes of soils contamination. This highlights the urgent need to update soils regulations, as well as regulations and monitoring of products used as fertilizers and pesticides, with protective limits for POPs.

Between 2010 and 2017, the efforts to control greenhouse gases (GHG) resulted in an increase of 70% and 37% of biomass used for electricity and heat production, respectively [24]. This may increase pressure on the environment since about 90% consists of forest biomass. Hence, sustainable principles to increase bioenergy must include proper ash management and protection of soils, incorporating the Stockholm POPs Convention orientations.

Around 10% of the world primary energy is generated by combustion of biomass, using several combustion technologies, like fluidized bed (FB) systems, grate furnaces (GF) and pulverized combustion (PC) [25]. Combustion processes generate emissions of air pollutants and fine particulate matter (PM), and result in several ash streams like bottom or bed ash, boiler ash, filter ash and electrostatic precipitators (ESP) fly ash. Ash characteristics depend on the biomass used and combustion technology, as well as on air pollution control devices (APCDs) and ash collection strategy. Biomass ashes are essentially composed of inorganic elements contained in the fuels, plus extraneous minerals from adhering soil or sand, minerals used as bed material in the case of FB

systems, and, eventually, additives and sorbents added for pollution control. For clean woody biomass ashes, mostly composed of Si, Ca, Mg, K, P, Na, Al, Fe, Cl and S, only traces of heavy metals are usually present, however, co-combustion with wastes may raise toxic metals to concerning levels [26–30]. Ash may also contain many Products of Incomplete Combustion (PICs), including POPs, of which the most concerning are PCDD/Fs, PAHs, and PCBs [31–35].

The reutilization of ashes is highly attractive for a great variety of purposes, driven by management needs and circular economy [36,37]. Interest of using biomass ashes as soil fertilizers (a traditional practice) has been broadly investigated, mainly concerning physicochemical properties, composition, presence of heavy metals and leachability [38–48]. Some publications address the problem of PAHs [49–53], but usually PCDD/Fs and other organic pollutants are not mentioned or are considered of minor relevance in biomass ashes to be applied in soils. However, the intensive use of biomass ashes may have significant impacts; for example, the application of industrial wood ashes containing 7.4–36 ng TEQ/kg, at 18–38 ton/acre/year, was estimated to increase PCDD/Fs in soils by 0.15–1.53 ng TEQ/kg a year [54]. Bundt et al. [55] also found that wood ash application, containing 16.8 mg/kg of PAHs and 3.4 µg/kg of PCBs, increased by six-fold the concentrations of PAHs in a forest soil. On the other hand, a decrease of PCBs was observed, possibly due to enhanced solubilization, owing to the ash alkalinity. This may indicate that deeper soil levels and water aquifers may become contaminated with PCBs. A previous paper [56] presented the chemical constitution of biomass ashes, revealing low levels of heavy metals and low mineral leachability. Some TEQs and ΣPAHs were also presented to highlight that biomass ash may exhibit POPs contamination, although the EU proposal to regulate the use of ashes as soils fertilizer was not available then.

Despite the low solubility of PCDD/Fs and PAHs, suggesting low environmental availability, it has been shown that leachability of dioxins depends on composition and sorption properties of soils [57]. In fact, Kim and Lee [58] found that the solubility of PCDD/Fs was enhanced by the presence of humic matter. Therefore, the authors concluded that fly ash should not be landfilled with organic wastes in order to prevent leachability of PCDD/Fs [58].

In Europe, some countries have different regulations established for the ash streams that can be applied to soils and different requirements for levels of nutrients and heavy metals allowed, such as the Nord Test Technical Report [59]. POPs are limited in a few countries; in Denmark PAHs control is required only if unburned matter in ashes is higher than 5% with a limit of 3 mg/kg for 9 PAHs [59] and in the Czech Republic the limit is 20 mg/kg [60]. In Sweden there are different limits for carcinogenic and non-carcinogenic PAHs in soils, depending on the soils used sensitivity [61]. In Canada, in addition to the limits for naphthalene and benzo(a)pyrene in wood ashes (4.0 mg/kg for each), PCDD/Fs are also limited to 27 ng TEQ/kg [62]. In Portugal, alternative fertilizers containing sewage sludge and biomass ashes have limits of 6 mg/kg for PAHs, and 100 ng TEQ/kg for PCDD/Fs [63]. In Germany, the regulation for applying fertilizer restricts PCDD/Fs + PCBs to 8 ng TEQ/kg for pasture lands, and 30 ng TEQ/kg for agricultural soils [17]. In Europe, the recent harmonization of EU fertilizers aims at valorizing some wastes as Component Material Categories (CMC) for use as alternative fertilizers [64]. Thermal oxidation materials and derivates, namely ash-based materials, are to be included; in addition to the control of heavy metals, the proposed limit for Σ_{16} PAH is 6 mg/kg and for PCDD/Fs is 20 ng TEQ/kg, respectively [65]. TEQ are the Toxic Equivalents corresponding to the revised WHO_{2005} TEQ [66].

Aware of the perilous nature of ashes, frequently obliviated in many studies concerning ash applications as fertilizers, it is important to initiate further practical investigations to determine the PCDD/Fs and PAHs contents and define if the ashes can be used as fertilizers or need a safe disposal. The purpose of this work is to investigate the presence of PCDD/Fs and PAHs in industrial biomass ashes, to distinguish the degree of contamination of different ash streams and evaluate if they comply with the upcoming European Regulation for use of ashes as fertilizers. Also, we wanted to understand the source of POPs in ashes, namely relating with the composition and contamination of the fired biomasses and constitution of ashes. Furthermore, we conducted a literature survey to provide a

deeper assessment of the fate of PCDD/Fs and PAHs in biomass combustion and compile up-to-date regulations and programs within the subject. In the experimental part we present chemical data of the residual forest biomass used in four biomass power stations and of various biomass ash streams collected over a year. The distribution of the 17 toxic PCDD/Fs and 16 PAHs measured in biomass and in ash blends is interpreted in view of their constitution. The potential toxicity of ashes is evaluated by calculating TEQs and BaP-EQs, according to various protocols. Also, a sensitivity analysis was performed to understand the impact of management of non-detected (ND) congeners on aggregate quantities used in policy regulation, such as TEQs, ΣPCDD/Fs and ΣPAHs. The ND handling can be critical for environmental risk assessment and evaluation of compliance with limit values.

2. Literature Review

2.1. PCDD/Fs and TEQs; PAHs and BaP Equivalents

Of the 210 PCDD/Fs congeners (75 PCDDs and 135 PCDFs), only 10 PCDFs and 7 PCDDs containing 2,3,7,8-Cl substitutions, have been appointed for environmental risk assessment given their high Aromatic Hydrocarbon Receptor (AhR) bioactivity (Table 1) [67]. The toxicity of a complex mixture of PCDD/Fs is usually expressed as Toxic Equivalent (TEQ). TEQ consists of an aggregate measure obtained with the sum of the individual congener concentrations multiplied by their specific Toxic Equivalent Factor (TEF). TEFs correlate each congener's toxicity potency to the most toxic 2,3,7,8-TCDD [18,68].

Table 1. List of 17 polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs) congeners and Toxic Equivalent Factors (TEFs) for Toxic Equivalents (TEQ) calculations.

	PCDD/Fs Congeners	I-TEF [68]	WHO$_{1998}$-TEF [a] [69]	WHO$_{2005}$-TEF [a] [65]
Furans (PCDFs)	2,3,7,8-TCDF	0.1	0.1	0.1
	1,2,3,7,8-PeCDF	0.05	0.05	**0.03 [b]**
	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
	2,3,4,6,7,8-HxCDF	0.1	0.1	0.1
	1,2,3,7,8,9-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
	OCDF	**0.001**	**0.0001**	**0.0003**
Dioxins (PCDDs)	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
	OCDD	**0.001**	**0.0001**	**0.0003**

Notes: [a] dl-PCBs not mentioned in the table. [b] Changed values in bold.

The TEF concept was introduced in 1977 and was adopted internationally, in 1988, as I-TEQ for the 17 PCDD/Fs [69]. The World Health Organization and International Program on Chemical Safety (WHO/IPCS) continually reevaluates the TEF system and later on included the dioxin-like toxicity PCBs (dl-PCB) (12 non-ortho/mono-ortho-substituted polychlorinated biphenyls) in the TEQ protocol, WHO$_{1998}$-TEQ [70]. In the latest revision, WHO$_{2005}$ TEQ [66], modified some TEF values, as shown in Table 1. The possible inclusion of other compounds with dioxin-like effects, such as brominated and mixed halogenated dioxins/furans, is currently under evaluation [66].

Unequivocally, the oldest publications use I-TEQ and subsequently WHO$_{1998}$-TEQ (including or not dl-PCBs), however, they are still in use [10]. Kato and Urano [71] found good correlations between

different TEQ protocols for stack emissions of various incineration facilities, since minor modifications were made in the toxic factors (Table 1).

$$(WHO_{1998}\text{-TEQ(PCDD/F)}) = 1.14 \times (\text{I-TEQ}) \tag{1}$$

$$(WHO_{1998}\text{-TEQ(PCDD/F/dl-PCB)}) = 1.17 \times (\text{I-TEQ}) \tag{2}$$

For wood boilers, the WHO_{1998}-TEQ values were reported to be 10–25% higher than I-TEQ, depending on the congener distribution profile, which is within the measurement uncertainty [72]. From results of Moltó team, two correlations are extracted; Equation (3) [73] and Equation (4) [74].

$$(WHO_{2005}\text{-TEQ(PCDD/F)}) = 0.88 \times (\text{I-TEQ}) \tag{3}$$

$$(WHO_{2005}\text{-TEQ(PCDD/F)}) = 0.99 \times (\text{I-TEQ}) \tag{4}$$

Differences in the correlations may be attributed to the variation of congeners distribution and concentration, given the different magnitude of TEFs.

When reporting WHO-TEQs, reference to the inclusion of dl-PCBs should be made [75]. Nevertheless, the share of dl-PCBs in the WHO_{1998}-TEQ(PCDD/F/dl-PCB) emissions from waste incineration plants was found to be less than 3% [71], and less than 16% for different industrial sources [76]. For biomass combustion emissions, the share of dl-PCBs on WHO_{2005}-TEQ(PCDD/F/dl-PCB) was found to vary from 0.7–22% [73], and 5.8–23% [74]. In municipal solid wastes incineration (MSWI) fly ashes, the contribution of dl-PCBs to WHO_{2005}-TEQ(PCDD/F/dl-PCB) was less than 5% [77]. The share of dl-PCBs on TEQs was found to increase along the flue gas paths equipped with APCDs. This is mainly due to the different adsorptions of PCDD/Fs and dl-PCBs on fly ashes that affect their partition between particle and gas phase [78]. The different volatilities of compounds may also influence the relative proportions of compounds along the exit flue gas path. In another matrix, such as soils and fertilizers, the relevance of dl-PCBs may however be quite different [79].

Also important for TEQ calculation is the strategy to account non-quantified or non-detected (ND) values of individual PCDD/F congeners, as different methodologies can be applied [80–82]. The simplest approach consists of the imputation method; attribution of fractions of the Estimated Quantification Level (EQL) for each congener: the Upper Bound (UB) with ND = EQL, the Medium Bound (MB) with ND = EQL/2, and the Lower Bound (LB) with ND = 0. Different options might lead to different TEQ values, which can hamper accurate risk assessment and evaluation of compliance with regulations [83]. Delistraty and Singleton [84] also evaluated the influence of TEQ schemes and ND handling on TEQs of wood ashes. They verified that the impact of ND handling on TEQs increased with the number of non-detected congeners in wood ash. It was also shown that the ND options had higher influence than the TEQ scheme, for the lower concentrations of PCDD/Fs. Hence, accuracy of small concentrations is of prime importance, even for the evaluation of ash application in soils, for example, use of wood ashes with 1.4–840 ng TEQ/kg was estimated to increase soil's PCDD/F concentrations by 0.038–23 ng TEQ/kg a year [84].

EU regulations on the measurement of PCDD/Fs and PCBs in feed [85] and foodstuff [86] specifies that analytical reports must contain the levels of individual congeners measured, the TEQ values must be reported as LB, MB and UB and differences between LB and UB must be lower than 20%. Different approaches are in use, while the NCASI report [87] computes TEQ for wood boilers emissions assuming ND as zero, other studies [75,88,89] use the MB option. In the previous paper [56], the TEQ results presented were those provided by the analytical laboratory, which assumed the UB option. Reporting the ND handling and quantification/detection levels is frequently absent in the literature, which misleads the interpretation of results. Given the complexity of PCDD/Fs analysis, analytical sensibility may vary widely, depending on the sample characteristics and performance/focus of the laboratory (e.g., food control, environmental or waste analysis) [90]. The BAT/BEP guidelines [11]

also mention that the reporting of PCDD/Fs and dl-PCBs should use LB and UB approaches for ND, and the required quantification levels should be a least 1/5 of the regulatory limits or levels of interest.

PAHs are ubiquitous pollutants, comprising hundreds of lipophilic compounds with fused aromatic rings. They may have natural or anthropogenic origin, existing in many commonly used goods [91]. The United States Environmental Protection Agency (US-EPA) listed 16 PAHs compounds as priority pollutants for environmental risk assessment due to their toxic effects [92]. Table 2 presents the US-EPA 16 PAHs list and the acronyms used in this work. PAHs can be divided in two classes: Low Molecular Weight PAHs (LPAHs) with two and three benzenoid rings (Nap, Acy, Ace, FL, Phe and Ant), and High Molecular Weight PAHs (HPAHs) with four or more benzenoid rings (Flut, Pyr, BaA, Chry, BbFA, BkFA, BaP, DahA, BghiP and IP).

Table 2. List of Polycyclic Aromatic Hydrocarbons (PAHs), Carcinogenicity Classification and Toxicity Factors for BaP-EQ calculations.

	PAHs Compounds	Acronym	Number Rings	IARC [a] [96]	RPF US-EPA [101]	RPF N&L [98]
LPAHs	Naphthalene	NaP	2	2 B	-	0.001
	Acenaphthylene	Acy	3	-	-	0.001
	Acenaphthene	Ace	3	3	-	0.001
	Fluorene	FL	3	3	-	0.001
	Phenanthrene	Phe	3	3	-	0.001
	Anthracene	Ant	3	3	-	0.01
HPAHs	Fluoranthene	Flut	4	3	-	0.001
	Pyrene	Pyr	4	3	-	0.001
	Benzo[a]anthracene	BaA	4	2 B	0.1	0.1
	Chrysene	Chry	4	2 B	**0.001** [c]	**0.01**
	Benzo[b]fluoranthene [b]	BbFA	5	2 B	0.1	0.1
	Benzo[k]fluoranthene [b]	BkFA	5	2 B	**0.01**	**0.1**
	Benzo[a]pyrene [b]	BaP	5	1	1	1
	Dibenzo[a,h]anthracene	DahA	5	2 A	**1**	**5**
	Benzo[g,h,i]perylene	BghiP	6	3	-	**0.01**
	Indeno [1,2,3-c,d]pyrene [b]	IP	6	2 B	0.1	0.1

Notes: [a] IARC classification: 1-Carcinogenic, 2 A-Probably carcinogenic, 2 B-Possibly carcinogenic, 3- Not classifiable as carcinogenicity. [b] PAHs used by Persistent Organic Pollutants (POPs) Protocol. [c] Different values in bold.

LPAHs such as NaP, are usually present in larger quantities in the air phase, and considered acutely toxic to aquatic organisms since they are more water-soluble than HPAHs [93]. Other organizations selected diverse PAHs compounds, and still no worldwide consensus exists. The POPs Protocol [4] uses four PAHs (BaP, BbFA, BkFA and IP) for emissions inventory. In the EU [94], also 16 PAHs are contemplated, although less may be considered. The Directive 2004 on air quality [95] includes BaP, BaA, BbFA, BjFA, BkFa, DahA and IP. Only eight PAHs match the EU and US-EPA PAHs list; BaP, BaA, Chry, BbFA, BkFA, DahA, BghiP and IP. Excluding BghiP, the other PAHs in common are classified as carcinogenic, both by International Agency for Research on Cancer (IARC) [96] and US EPA [97] (Table 2). IARC classifies PAHs in different categories, according to carcinogenic potency (Table 2); BaP is classified in group 1- Carcinogenic to humans, and the others are 2 A and 2 B. NaP is classified as carcinogenic by IARC, but usually is not considered for risk assessment. Flut has been suspected to be carcinogenic, although not confirmed by IARC [94].

Since the eighties, correlations of PAHs toxicities with the most toxic BaP have been pursued [94,98–100]. The equivalence factors of Nisbet and Lagoy (N&L) [98] have been broadly used. US-EPA proposes similar Relative Potency Factors (RPF) (Table 2) [101]. While US-EPA considers DahA as carcinogenic as BaP, Nisbet and Lagoy attributed a factor of five to DahA, for its carcinogenicity proved to be higher than BaP in low doses. Jung et al. [102] used the factor of five for DahA for assessment of the urban air toxicity exposures of young children. Other equivalence systems are used worldwide, as those used by Ramirez et al. [103]. Owing to the PAHs complex toxicity mechanisms,

and assorted PAHs lists, the BaP toxic equivalence system is yet far from general consensus [99,100]. Since this equivalence system is not compatible with the TEQ protocol of PCDD/Fs and dl-PCBs, to discern them, the PAHs factors are herein called RPF and not TEF, and BaP-EQ should be used instead of TEQ-BaP. BaP alone is frequently used as a surrogate for PAHs control [95] and, in fact, there are correlations found between BaP and ΣPAHs produced in wood combustion [104,105].

2.2. Origin, Generation and Fate of PCDD/Fs and PAHs in Combustion Processes

Several tragic historical events like the Agent Orange in Vietnam and Seveso accident [106–108], and more recently animal feed contamination with biodiesel sub-products [109], brought the PCDD/Fs issue to worldwide research focus, regulation, and continuous surveillance. The formation of PCDD/Fs in the combustion process was firstly reported in 1977 for waste incineration systems [110]. Since then, PCDD/Fs have been broadly investigated, despite the complexity and high costs associated with their characterization.

Pre-existing PCDD/Fs in materials used as fuels, such as PCDD/F contaminated PCP treated wood, may be a source of emissions, for complete destruction is achieved only in high efficient combustion systems, with long residence times, typically above 1000 °C, and dedicated flue gas treatment.

In combustion processes, however, PCDDs and PCDFs can also be formed through two pathways: primary formation by the precursor's mechanism, and secondary formation by de novo synthesis. The two mechanisms operate simultaneously and independently, in different zones of the combustion systems, and depend on various parameters like fuel composition (mainly Cl, Cu and S) and presence of organic contaminants, furnace conditions and flue gas treatment applied [111–117]. In the hottest furnace zones (>650 °C) and low O_2, PCDD/Fs originate from precursors like lignin of biomass, waste wood preservative additives containing pentachlorophenol (PCP), PCBs, and other compounds, such as chlorobenzenes, chlorophenols and PAHs, which may be also formed during poor combustion [115,118]. In the post combustion zones, like ESP and baghouse filters, de novo synthesis involves catalyzed chlorination of carbonaceous structures present in fly ashes, between 250–500 °C or higher, with a peak at 300 °C, Cu being the more relevant catalyzer [111,119–123]. Studies on combustion of salty laden wood revealed that 99% of total PCDD/Fs were associated to cyclone and ESP fly ashes, and their main formation was suggested to be de novo synthesis over fly ashes [124]. Tests performed between 260–430 °C, revealed that PCDD/Fs formation decreases for lower temperatures and shorter residence times [125,126]. Accordingly, the operation of ESP at low temperatures, preferably at 140–200 °C, is a key procedure to reduce PCDD/Fs formation by de novo synthesis, allowing simultaneously adsorption on fly ash to decrease emissions with flue gases [124,127–129].

Efforts have been dedicated to characterizing PCDD/Fs fingerprints, and to find congener's surrogate for TEQ estimation, which could allow faster and cheaper diagnostics of emission sources [130]. In combustion systems, PCDFs/PCDDs ratios (F/D) larger than one are interpreted as a preponderance of de novo synthesis that yields more PCDFs, while the precursor mechanism is believed to generate PCDDs preferentially [129,131,132]. F/D ratios have also been correlated with Cl availability; low concentrations appear to be mostly used for chlorination of phenols, forming preferentially PCDDs at high temperatures. High Cl in fuels is often associated with the worst combustion conditions, producing more PICs that are further cracked and chlorinated to form PCDFs in the post-combustion zones [133]. Therefore, the F/D ratio increases for higher Cl contents. Amounts of Cu in fuels also increase F/D ratios, due to higher PCDFs formation in the post-combustion zones [134]. On the other hand, the presence of moisture in the gas phase has been found to increase PCDDs formation over PCDFs, at low temperatures [135].

All PCDD/Fs congeners can be found in solid discharges from incinerators [136–139], in increasing concentrations from the furnace bottom to the flue gas exit (bottom-ash < boiler-ash < ESPash < filter-cake-ash < fly-dust); PCDD/Fs contents in wood fly ashes were reported to be 10 times higher than in corresponding bottom ashes [140]. The PCDDs concentrations generally increase with the

increasing degree of chlorination (nCl) of the congeners; OCDD is usually present in higher amounts, followed by 1,2,3,4,6,7,8-HpCDD. A more random distribution occurs for PCDFs; the hepta, hexa and penta PCDFs, being more prevalent than OCDF [35,124,129,131,141–148]. Moreover, in MSWI bottom ashes lower PCDD/Fs concentrations were found in larger particles [149,150], which suggest that ash separation may provide less contaminated fractions.

Cl is the limiting reactant for PCDD/Fs formation; however, the relation between PCDD/Fs yields and Cl amounts (and its speciation) is not completely understood [124,151,152]. Variations within low Cl contents appear to make little difference, while high concentrations strongly increase PCDD/Fs [87,153,154]. During combustion, Cl is released from the inorganic or organic matrix, generating predominantly HCl, although metal chlorides might also form. HCl can be converted to gaseous Cl_2 through the catalyzed Deacon reaction, which is maximized at about 300 °C, in the presence of O_2 and Cu. Cl_2 is believed to be more active as a chlorinating agent than HCl, owing to the faster production of highly reactive Cl radicals [121,155–158]. Simultaneously, metal chlorides eventually present in fly ashes, such as $CuCl_2$, might behave as Cl donors, chlorinating the carbon structures directly, in the presence of O_2 [118,119,151]. Moreover, the chlorination of dibenzofuran (DF) has been found to be favored over chlorination of dibenzo-p-dioxin (DD), corroborating that higher Cl correlates with higher F/D ratios in waste incinerators [159].

Woody biomass with low Cl contents usually produces low PCDD/Fs, while co-combustion with streams containing Cl and metals (salty wood biomass, bleached kraft mill waste water sludges, straw and cereal residues, treated wood with PCP base preservatives or other metal base preservatives, sewage sludge, etc.), enhances PCDD/F production [27,72,124,143,146,152,160,161]. In the past, biomass co-combustion with paper bleaching sludge generated cyclone fly ashes with PCDD/Fs concentrations attaining 210 ng TEQ/kg [162]. Tame et al. [115] verified that the firing of waste wood, impregnated with Cu base preservatives, increased the basal PCDD/Fs levels of clean wood ash by two to three orders of magnitude and the F/D increased because of preferential formation of PCDFs. Oehme and Muller [140] also revealed that TEQs in filter ash from waste wood incineration may be three orders of magnitude higher (100–10,000 ng TEQ/kg) than for clean wood combustion. Studies performed in waste wood chips incinerators in Taiwan have shown that PCDD/Fs in baghouse fly ashes were extremely high; 38,060 ng I-TEQ/kg in the boiler operating at 850–925 °C and 98,570 ng I-TEQ/kg in the boiler operating at lower temperatures, 500–850 °C [146].

Duo et al. [163] reported that combustion of salt-laden wood with 0.1–2% NaCl, in coastal boilers, resulted in PCDD/Fs emissions two to three orders of magnitude higher than those burning wood with lower Cl. More research in coastal boilers, burning salty wood, revealed that the decrease of PCDD/Fs concentrations in ESP fly ashes was influenced not only by the decrease of Cl concentrations, but was also due to working at lower furnace loads, 65%, that might have promoted better combustion [152]. Someshwar [27] verified that the PCDD/F contents in ESP fly ashes were higher in European boilers, burning forest biomass, than in similar USA boilers, possibly due to higher Cl levels present in the European forest biomass harvest near the Ocean's coasts.

Sulphur has been broadly described as decreasing Cl activity to produce PCDD/Fs [27,72,152,155,158,164–173]. At high S concentrations (S/Cl > 10), in the presence of H_2O, inhibition of de novo synthesis is due to SO_2 oxidation to SO_3 reverting Cl_2 to HCl [174]. The same effect was found for lower S/Cl; below 2.5 [175], and also below 0.64 [166]. Another inhibition mechanism consists in the poisoning of Cu catalyst by formation of $CuSO_4$ (stable until about 800 °C) [158,165,166,176–178]. Gullet et al. [177] pointed out that the higher stability of $CuSO_4$ favors its retention in furnace bottom zones; thus, lower Cu contents in fly ash are available for de novo synthesis. They also suggested that sulfonation of the phenolic precursors prevents their conversion to PCDD/Fs. Therefore, the presence of S may affect the F/D ratios, given the lower formation of PCDFs [172]. Thomas and McCreight [176] proposed a positive correlation of PCDD/Fs emissions on Cl and Cu, and inverse on S for several fuels. Since natural biomass usually contains low S concentrations, the increase of S may be achieved by co-combustion with other fuels containing higher S or use of

S-base additives. Other chemical inhibitors may be used [120,155,179,180], such as the addition of N-S containing compounds, for example, $(NH_4)_2 SO_4$ (ChlorOut technique) and urea [171,181–186].

Similarly, to Cu, other metals present in fuels, namely Fe, Ni, Cr, Zn, Pb and Al, catalyze PCDD/Fs formation, chlorination and dechlorination [116,120,122,156,187–191]. For metal chlorides Zhang et al. [189] consider two functions; as catalysts and as Cl donors, $CuCl_2$ being the most active, followed by $CrCl_3$, $NiCl_2$, and $ZnCl_2$. Addink and Altwicker [192] verified that CuCl and $CuCl_2$ were better as Cl donors than as catalyzers, at 353 °C, in the presence of O_2. Meanwhile, earth alkaline metals, Ca and Mg, have shown a depressor effect on PCDD/Fs formation [116,193]. $CaSO_4$ is formed in the bottom zones of FB systems, consuming SO_3, which converts Cl_2 back to HCl. Ca may also capture HCl forming liquid $CaCl_2$ in the FB bottom zones [169], and/or absorb HCl in the post-combustion zones, preventing formation of Cl_2 [194]. This effect was found to be maximized at 350 °C [195] and 310 °C [196]. Moreover, NaOH and KOH have shown similar effects [197]. However, ashes are mainly composed by aluminas and aluminosilicates, which may serve as active catalytic surfaces for PCDD/Fs formation in the post-flame zones [198].

PCDD/Fs congeners, and other PICs, results from balances of formation, destruction, and dechlorination/hydrogenation [116,132,145,199–206]. Weber and co-workers [207,208] observed increasing dechlorination of OCDD and OCDF, from 260 to 380 °C, under poor O_2. At lower temperatures, the catalytic dechlorination by Cu was more efficient than with other metals, while Ca seemed to preferentially promote destruction. It was also verified a preferential dechlorination in the 1,4,6-positions than in the 2,3,7,8-positions. Thus, elimination of the most toxic PCDD/Fs was not effective at low temperatures. Vogg et al. [120] verified that formation of PCDD/Fs in ESP fly ashes, annealed at 300 °C, substantially increased with O_2 availability. However, in the presence of moisture, the nCl degree of PCDDs decreased from 6.85 to 5.65, and nCl of PCDFs decreased from 5.21 to 4.96, which was attributed to dechlorination. Stieglitz et al. [135] confirmed the influence of water vapor on dechlorination and observed a decrease of F/D ratios. Experiments of the Hagenmaier group [188,209] have shown that, even at temperatures as low as 120 °C, in the presence of $H_2 O$ vapor and absence of O_2, dechlorination and decomposition of PCDD/Fs occur very rapidly. Yasuhara et al. [210] found out that metals present in waste paper combustion decreased PCDD/Fs emissions in the order of Cu > Mg > Mn > Fe > Ni > Co, probably involving dechlorination and oxidation. Hasselriis [127] also revealed that Cu catalyze the dechlorination of PCDD/Fs between 150–280 °C, in the presence of O_2, forming the more toxic penta and hexa PCDDs and PCDFs from the octa forms. Modeling of PCDD/Fs formation [211], under low O_2 atmospheres, showed that the dechlorination takes place in the presence of CaO and Na-silicates as Cl scavengers. The calculated Gibbs energy for dechlorination of various congeners, using different oxides and silicates, led to conclude that the dechlorination of OCDF and OCDD is thermodynamically favored than that of TCDF and TCDD.

Chen et al. [212] evaluated combustion of wood chips from furniture shredding, with Cl below 0.001%, but containing 8.4 ng/kg PCDD/Fs; more than 80% were OCDD + 1,2,3,4,6,7,8-HpCDD and F/D = 0.15. About 80% of the total PCDD/Fs output remained in various ash streams, and 20% was emitted with the flue gases. The output/input ratio of the grate furnace revealed that half of the PCDD/Fs mass entered with the biomass was destroyed in the furnace. However, the I-TEQ output/input was 6.9 because more of the lower chlorinated PCDD/Fs were formed. The F/D ratio increased from 0.14 in biomass to 1.5 in ashes, indicating possible formation of low chlorinated PCDFs. There was also an increase of low chlorinated PCDDs, attributed to formation by precursor mechanism or dechlorination of OCDD and HpCDD contained in the wood chips. Iino et al. [200] suggested that dechlorination might be even more important for OCDF than for PCDDs. Wehrmeier et al. [213] also highlighted the importance of hydrodechlorination reactions of OCDD in fly ash (at 350 °C), in producing varied congeners, including the 2,3,7,8 TCDD and others substituted in non 2,3,7,8 positions. In fact, ashes may contain many of the 210 PCDD/Fs, as well as various PICs and products of dechlorination involved in PCDD/Fs chemistry, such as DD, DF and PAHs [201,214]. A deeper understanding of mechanisms

involved in PCDD/Fs formation requires a more exhaustive analysis than the target list compounds normally used for risk assessment [215].

PAHs compounds are formed by complex mechanisms involving cyclization and aromatization of carbonaceous matter in the pyrolysis phase of combustion process, at temperatures typically higher than 400 °C, with optimum temperature in the 700–900 °C range [216–218]. The thermal destruction of PAHs requires higher temperatures and oxidant conditions [219,220]. Therefore, the yield of PAHs depends on fuel composition and contamination, combustion conditions (temperature, oxygen, residence time and turbulence) and also flue gas treatment [34,50]. Fuel contaminants, such as creosote (a wood preservative), can be important sources of PAHs in combustion systems [61]. PAHs formed in biomass combustion appear to be mostly associated with gas emissions and soot deposits; while LPAHs (two to three rings) are preferentially present in gas phase emissions, HPAHs (more than three rings) are more associated with ashes [33,221,222]. Johansson and Bavel [61] detected PAHs contents as high as 77 mg/kg, of which 11 mg/kg were carcinogenic, in ashes from a biomass boiler. Masto et al. [50] found 0.18–2.61 mg/kg of PAHs in bottom ashes, and 3.59–193 mg/kg in fly ashes from combustion of several biomass residues. LPAHs were preponderant, with NaP accounting for 50–90% in fly ashes, while in bottom ashes more of the three, four and five rings were detected. BaP and other carcinogenic PAHs were found below 0.51 mg/kg in both ashes. Straka and Havelcová [53] detected 6.16 mg/kg of PAHs in a biomass ash containing unburned matter (14.5%), and thus suggested the need to measure PAHs in ashes for soil application, when unburned matter exceeds 9%. However, high PAHs, including the carcinogenic ones, were found in porous fly ash particles from rice husk combustion, independently of their unburned content [223]. Sarenbo [51] detected high contents of PAHs, 91–300 mg/kg, in biomass fly ashes of winter seasons, containing 25–45% unburned carbon. NaP was prevalent (44–120 mg/kg), followed by Acy, Phe, Pyr and Flut, and the carcinogenic IP and BaP reached 7.7 and 3.9 mg/kg, respectively. Rey-Salgueiro et al. [49] found relatively low levels of PAHs in biomass ashes, although 0.4 mg/kg were present in bottom ashes containing 26% organic matter. Correlation of PAHs contents in ash with their unburned carbon content are commonly referred [26]. Košnář et al. [60] found exponential correlations of PAHs with unburned matter (loss in ignition-LOI) for wood fly ashes containing 3.8–148 mg/kg of PAHs. However, the levels of LOI were unusually high, reaching 55%.

Benfenati et al. [224] showed straight correlations between PAHs, PCNs and PCDD/Fs contents in waste incineration, suggesting formation by common reactions. Schoonenboom and Olie [225] showed that PCDDs and PCDFs may be generated from anthracene and 2-chloroanthracene, at 250–300 °C, in the presence of KCl and $CuCl_2$, over alumina. Moreover, Iino et al. [226] revealed that some PAHs compounds produce PCDFs and PCNs, at 200–400 °C, in the presence of O_2. Also, it was demonstrated that PCDD/Fs with a high F/D ratio can be produced by heating various PAHs at 300 °C, with $CuCl_2$ as a catalyst; perylene being the most efficient [227]. Weber et al. [228] suggested that the different patterns of PCDF isomers observed for stoker furnaces and fluidized bed systems could be attributed to their formation from PAHs with perylene structures. Wilhelm et al. [229] also found that some PAHs usually present in fly ash; fluorene, fluoranthene, phenanthrene and anthracene, originate PCDD/Fs at 250 °C, preferentially PCDFs.

To effectively decrease yields of PCDD/Fs in biomass boilers, in addition to optimization of combustion conditions and use of adequate flue gas treatment, the composition of fuels is of prime interest. Besides controlling contents of metals and Cl (and other halogens), the pre-existence of PCDD/Fs in fuels must be avoided, as well as the absence of chemicals used as wood preservatives, pesticides and fertilizers that may serve as PCDD/Fs precursors. Hence, inclusion of treated waste wood and other wastes in biomass boilers should be avoided to prevent formation of very toxic unintentional POPs, such as PCDD/Ds, PCBs and carcinogenic PAHs.

3. Experimental Part

3.1. Materials and Methods

Experiments were performed within the scope of a project dedicated to the study of biomass ash quality in view of its application in soils. Four boilers of biomass power stations located in Portugal, near the Atlantic coast, were involved. Three boilers consist of Bubbling Fluidized Bed systems (BFB) located in pulp & paper plants. They consume mainly forest biomass residues (FBR), composed of shredded bark and branches of eucalyptus trees used for pulp making and paper sludge (from primary and secondary wastewater treatment). Variable quantities of other forest residues are used, such as pine remains and weed trees. Some of these boilers are allowed to consume till 10% of MSW and other non-contaminated biomass residues. The fourth boiler is a grate furnace (GF) also consuming FBR, pine and eucalyptus residues from wildfires and plague control, and occasionally agricultural residues from olive oil production or wood industries. All boilers are equipped with ESPs to reduce particulate emissions. The study was developed during 2011–2013 under the normal and steady operation of boilers.

Sampling campaigns lasted a year, during which four or five biomass composed samples were collected, by increments, in the conveyer belts of the furnace's feeding systems of each boiler. In total, 18 biomass samples were prepared for individual chemical analysis; the extraneous mineral matter (rocks, sand, and loosely attached soil) was previously separated by sieving below 2 mm and manual separation. The samples were dried and milled below 0.63 mm and the analyses were performed according to ASTM, EPA, ISO and CEN/TS standards for biomass analysis or equivalent methods in LNEG installations, as described previously [230].

For PCDD/Fs analyses, representative biomass blends of each boiler, containing the individual samples collected for one year, were prepared. Also, sludge from pulp & paper wastewater treatment (mix of 70% primary and 30% secondary sludge) was analyzed for chemical composition and PCDD/Fs. A soil sample collected in the experimental forest campus, used in the project to test ash fertilization, was also tested for PCDD/Fs.

Ash samples were collected in the four boilers: monthly in BFB1 and BFB3 ($n = 12$), bimonthly in GF ($n = 6$) and three times a year in BFB4 ($n = 4$). The nature of ash streams collected varies depending on the furnace assembling, ash removal systems installed and ash management strategy. In each boiler, the ash flows are combined in two streams; bottom ash (BA) and fly ash (FA), as described in Table 3. In unit BFB4, BA includes bottom bed ashes and ashes from the economizer (EC), superheater (SH), thus, FABFB4 corresponds only to fly ash from the ESP. For the other three units, BA corresponds only to bottom or grate ashes, therefore, FA are mixes of EC, SH, and ESP ashes.

In total, 60 ash samples (30 BA and 30 FA) were prepared for individually chemical analysis. The extraneous matter, above 2 mm, was sieved out. Samples were analyzed following adequate ASTM, EPA, ISO and CEN/TS standards or equivalent methods in LNEG, as described previously [56,230]. For each boiler, representative ash blends (4 BA and 4 FA) containing the ashes collected during a year were prepared for PCDD/Fs and PAHs analysis. The bulk chemical analysis, leachability, TEQs and ΣPAHs of some of these ash blends were previously presented [56] but additional and more detailed results are provided herein.

The PCDD/Fs and PAHs analysis were subcontracted to the Portuguese Reference Laboratory of Agência Portuguesa do Ambiente (APA). PAHs were analyzed using an APA internal method (MMA 98 - SPE-SOX, HPLC/DAD-FLD), based on US EPA method 550.1. PCDD/Fs were analyzed using an APA internal method (MMA 123-LLE-SOX, HRGC/HRMS), based on US EPA method 1613.

Table 3. Identification of biomass ash streams.

	Ash Stream	Combustion Technology	Ash Flows Included
BA (Bottom Ash)	BABFB1	BFB	Bottom bed
	BABFB3	BFB	Bottom bed
	BABFB4	BFB	Bottom bed + EC + SH
	BAGF	GF	Grate ash
FA (Fly Ash)	FABFB1	BFB	Fly ash ESP + EC + SH
	FABFB3	BFB	Fly ash ESP + EC + SH
	FABFB4	BFB	Fly ash ESP
	FAGF	Grate Furnace	Fly ash ESP + EC

Notes: BFB—Bubbling Fluidized Bed, GF—Grate Furnace, SH—Superheater, EC—Economizer, ESP—Electrostatic Precipitator.

The lists of 17 PCDD/Fs and 16 PAHs analyzed correspond to those normally used for environmental risk assessment, as presented in Tables 1 and 2. For calculation of TEQs of PCDD/Fs, several protocols were used, as described previously; I-TEQ, WHO_{1998}-TEQ and WHO_{2005}-TEQ, using TEFs mentioned in Table 1. For PAHs, BaP-EQs were calculated using the equivalence factors of Nisbet and Lagoy [98] and US-EPA [101], presented in Table 2.

Also, a sensitivity analysis was applied in the calculation of ΣPCDD/Fs, ΣPAHs, TEQs and BaP-EQs, using the imputation approach to non-detect (ND) values, based on the estimated quantification levels (EQLs) reported by the analytical laboratory: Low Bound (LB) with ND = 0, Medium Bound (MB) with ND = EQL/2 and Upper Bound (UB) with ND = EQL.

3.2. Results and Discussion

3.2.1. Chemical Composition and PCDD/F in Biomass, Sludge and Soil

Table 4 presents the ranges of mineral composition of the individual biomass samples collected in each boiler, plus the sludge mix.

The composition of biomass samples is typical of woody biomass [231]. The wide ranges of ash concentrations and major ash forming elements, like Si and Ca, may be due to seasonal fluctuations, mainly because of higher soil adhesion to biomass in the raining seasons. Since the extraneous mineral fractions of biomass were excluded from analysis, higher quantities of these materials can be found in produced ashes than the analysis would lead on. The results obtained suggest that co-combustion of sludge might also increase ash production in the boilers, given their high contents of ash forming elements, such as Ca (23%). In addition, the sand used as a fluidizing bed agent in BFB systems also contributes to ash amounts. Scatter of other elements concentrations may reflect natural biologic cycles, although interpretation of variations can be misled due to dilution effects of major elements. In addition to Si (0.169–2.44%), Ca is the main ash-forming element of biomasses (0.21–1.83%), followed by K, Na, Al, Fe, Mg and P. Of the heavy metals measured, Mn is preponderant, as usually found in woody biomass [231]. Cu, Ni, Cr, Pb, Zn and Cd are found in trace levels, below 140 mg/kg, and Hg does not exceed 0.05 mg/kg. One biomass sample collected in BFB3 is responsible for the extreme values of Cu, Zn, Pb, and Cd levels (Table 4). Concentrations of S (0.01–0.16%) are low, as for similar biomass [231]. However, the Cl contents show a wider range, 0.04–0.28% (77% of which are above 0.15%) which is above the common Cl levels found in woody biomass (0.01–0.05%) [231]. The higher concentrations of Cl might be explained in light of the constitution of the residual forest biomass consumed in the studied boilers; mainly eucalyptus barks from pulp & paper industries. Wood barks originated from trees harvested in oceanic´s coasts regions are usually more contaminated with dust deposits and salty mist coming from the sea, mainly containing NaCl [27]. Indeed, the overview of biomass constitution of Vassilev et al. [231] refers to a eucalyptus bark having 0.26% of Cl. Other works [152,163] report the same issue, and established correlations between Cl and PCDD/Fs formation in wood boilers. Many of the Cl contents of the residual forest biomass samples approach the guide limit, Cl < 0.3%, advised to minimize PCDD/Fs formation during combustion of cereal residues [232]. As aforementioned, high S/Cl ratios are important for inhibiting PCDD/F formation. For the biomass samples analyzed,

except one case (1.3), the S/Cl ratios (0.02–1) were possibly too low for effective PCDD/Fs inhibition. Co-combustion of sludge similar to the one analyzed could increase S in the system, however given its high Cl content, the S/Cl would not be significantly improved.

Table 4. Chemical composition of biomass (min–max) and sludge, in dry base.

	Sludge Mix (1°/2°–70/30)	Biomass BFB1 (*n* = 5)	Biomass BFB3 (*n* = 5)	Biomass BFB4 (*n* = 4)	Biomass GF (*n* = 4)
Ash%	74	2.4–8.3	1.5–6.5	4.2–10.6	4.3–6.7
N%	1.29	0.22–0.35	0.32–0.71	0.26–0.43	0.22–0.32
S%	0.31	0.01–0.08	0.02–0.07	0.03–0.16	0.02–0.03
S%, avg	-	0.04	0.05	0.08	0.03
Cl%	0.60	0.08–0.28	0.04–0.19	0.10–0.12	0.15–0.24
Cl%, avg	-	0.22	0.13	0.11	0.19
Cu mg/kg	12	3–5	3–55	6–11	6–9
Ni mg/kg	17	2–9	1–16	17–36	2–32
Cr mg/kg	9	9–17	2–22	28–58	21–60
Zn mg/kg	25	7–11	10–139	17–37	11–24
Pb mg/kg	12	1–3	1–34	2–6	2–5
Cd mg/kg	<3	<0.2	<0.2–0.3	<0.3	<0.3
Hg mg/kg	0.061	0.007–0.021	0.012–0.030	0.012–0.026	0.015–0.047
Mn mg/kg	512	172–434	70–232	145–321	361–802
Fe%	0.18	0.04–0.14	0.03–0.33	0.08–0.32	0.10–0.31
Al%	0.49	0.07–0.36	0.07–0.33	0.15–0.70	0.20–0.53
Ca%	23.2	0.34–1.83	0.21–0.98	0.72–1.56	0.58–0.82
Na%	0.61	0.05–0.21	0.03–0.14	0.04–0.08	0.07–0.12
K%	0.50	0.17–0.39	0.11–0.34	0.28–0.47	0.40–0.66
Mg%	0.39	0.06–0.20	0.05–0.12	0.12–0.16	0.10–0.20
P%	0.35	0.03–0.07	0.02–0.47	0.08–0.18	0.09–0.13
Si%	1.6	0.16–1.56	0.17–1.07	0.59–2.44	0.53–1.54
S/Cl ratio	0.5	0.02–1.0	0.3–0.6	0.2–1.3	0.1–0.2
S/Cl ratio, avg	-	0.29	0.4	0.7	0.1

Notes: n—number of individual samples analyzed, avg—average.

Table 5 presents the contents of PCDD/Fs of three biomass blends from BFB3, BFB4 and GF, plus the sludge mix and the soil sample tested. PCDD/Fs congeners are not detected in this sludge. The soil contains 43 ng/kg of OCDD, which is comparable to other forest soils in Germany [233]. Other congeners might be present, though in lower concentrations than the EQLs reported. In the biomass blends, only OCDD was detected, below 260 ng/kg, except in the case of BFB3 that also contains 1,2,3,4,6,7,8-HpCDD above the detection limit. Interestingly, this biomass blend includes the biomass sample showing the extreme concentrations of heavy metals (Table 4). The PCDD/Fs concentrations found in biomasses are consistent with levels found in natural sinks, for example, 5.4–330 ng/kg in pine needles from rural to higher industrialized areas [234].

Combustion/incineration systems are among the possible emission sources of PCDD/Fs found in soils and vegetation; however, they emit a broad range of PCDD/Fs congeners (preferentially PCDFs) which does not match the environmental profiles enriched in OCDD. Baker and Hites [235] realized that PCDD/Fs sources/deposition mass balances were inconsistent because of excessive OCDD and hepta-PCDD deposition. The excessive OCDD inventory was explained in light of the historical worldwide use of huge quantities of wood preservatives/fungicides containing PCP. In fact, OCDD was a contaminant of PCP preservatives fabrication, thus, it contributed directly to environmental PCDD/Fs sinks, namely soils and vegetation, essentially nearby production plants and application of PCP in agriculture. In addition, deposited PCP volatilizes forming OCDD in the atmosphere water droplets under UV light, spreading contamination all over the world. Notwithstanding PCP pesticide discontinuation, the legacy to the environment contamination is enormous. Still, great concerns on the use of chemicals in soils prevail, since by 2006, about 161 other pesticides were suspected to contain

PCDD/Fs [236]. Cammenzuli et al. [237] evidenced that OCDD contamination of agricultural soils in Australia is mainly due to the former use of pesticides, in particular PCP, and that resuspension to air and periodic burning of agricultural wastes contribute to disperse OCDD over non-agricultural fields. Additionally, PCDD/Fs may originate by photolytic formation from other precursors like chlorophenols, polychlorinated phenoxyphenols and polychlorinated diphenylethers with origin in pesticides production or their progressive degradation, as well as other chemicals such as the widely used biocide triclosan [238]. Forest fires, which are suspected to produce PCDD/Fs [160], also appear to have mainly a dispersive effect of OCDD and precursors existing in vegetation and soils [239]. Predominance of OCDD in the environment may also be enhanced by aging due to preferential degradation of the lower chlorinated PCDD/Fs by natural UV photolysis [240–242].

Table 5. PCDD/Fs and TEQs of biomass blends, sludge and soil, in dry base.

(ng/kg)	Sludge Mix (1°/2° = 70/30)	Soil	Biomass Blend BFB3	Biomass Blend BFB4	Biomass Blend GF
2,3,7,8-TCDF	ND(2.0) [1]	ND(2.0)	ND(2.0)	ND(2.0)	ND(2.0)
1,2,3,7,8-PeCDF	ND(12)	ND(12)	ND(12)	ND(12)	ND(12)
2,3,4,7,8-PeCDF	ND(12)	ND(12)	ND(12)	ND(12)	ND(12)
1,2,3,4,7,8-HxCDF	ND(12)	ND(12)	ND(12)	ND(12)	ND(12)
1,2,3,6,7,8-HxCDF	ND(12)	ND(12)	ND(12)	ND(12)	ND(12)
2,3,4,6,7,8-HxCDF	ND(12)	ND(12)	ND(12)	ND(12)	ND(12)
1,2,3,7,8,9-HxCDF	ND(12)	ND(12)	ND(12)	ND(12)	ND(12)
1,2,3,4,6,7,8-HpCDF	ND(12)	ND(12)	ND(12)	ND(12)	ND(12)
1,2,3,4,7,8,9-HpCDF	ND(12)	ND(12)	ND(12)	ND(12)	ND(12)
OCDF	ND(24)	ND(24)	ND(24)	ND(24)	ND(24)
2,3,7,8-TCDD	ND(2.0)	ND(2.0)	ND(2.0)	ND(2.0)	ND(2.0)
1,2,3,7,8-PeCDD	ND(12)	ND(12)	ND(12)	ND(12)	ND(12)
1,2,3,4,7,8-HxCDD	ND(12)	ND(12)	ND(12)	ND(12)	ND(12)
1,2,3,6,7,8-HxCDD	ND(12)	ND(12)	ND(12)	ND(12)	ND(12)
1,2,3,7,8,9-HxCDD	ND(12)	ND(12)	ND(12)	ND(12)	ND(12)
1,2,3,4,6,7,8-HpCDD	ND(12)	ND(12)	35	ND(12)	ND(12)
OCDD	ND(25)	43	260	67	29
Σ PCDD/F MB [2]	105	135	382	160	122
LB/UB [2]	0/210	43/228	295/468	67/252	29/214
I-TEQ MB	11.8	11.8	12.3	11.9	11.8
WHO$_{1998}$-TEQ MB	14.8	14.8	15.1	14.8	14.8
WHO$_{2005}$-TEQ MB	13.5	13.5	13.8	13.5	13.5
LB/UB	0/26.9	0.01/26.9	0.43/27.2	0.02/26.9	0.009/26.9

Notes: [1] ND—non-detected, (EQL)—Estimated Quantification Level, [2] LB—Lower-Bound (ND = 0), MB—Medium-Bound (ND = EQL/2), UB—Upper Bound (ND = EQL).

The calculated ΣPCDD/Fs and TEQs using UB, MD and LB approaches for ND, are presented in Table 5. The differences between LB and UB reveal how discrepant the reported ΣPCDD/Fs and TEQs can be, for each sample, depending on the ND attribution option. The quantification levels (EQLs), i.e., the sensitivity of the analytical methodology, have a great influence on ΣPCDD/Fs and TEQs. The sludge is an extreme case of this influence; ΣPCDD/Fs may be assumed as 0, or 105, or 210 ng/kg, and TEQ as 0, or 13.5, or 26.9 ng WHO$_{2005}$-TEQ/kg, depending on the ND option. Independently of samples having detectable congeners or ND for all, TEQ values using the MB option are similar for the various samples, 14 ng WHO$_{2005}$-TEQ/kg, 15 ng WHO$_{1998}$-TEQ/kg and 12 ng I-TEQ/kg. Using the UB option, TEQs are also identical among samples. For the LB option, TEQs of biomass blends vary from 0.009–0.43 ng WHO$_{2005}$-TEQ/kg. Similar TEQs were obtained by Moltó et al. [74] in pine needles and cones, 0.66 and 0.33 ng I-TEQ/kg, with preponderance of OCDD, followed by 1,2,3,4,6,7,8-HpCDD and 1,2,3,4,6,7,8-HpCDF, and some other congeners, generally in low quantities.

The TEQs calculated with different protocols are very similar; WHO$_{2005}$-TEQs are about 10% higher than I-TEQs, and about 10% lower than the WHO$_{1998}$-TEQs, in accordance with van den Berg et al. [66].

3.2.2. Chemical Composition, PCDD/Fs and PAHs in Ashes

Table 6 presents the ranges of mineral composition of the individual ash samples collected in each boiler.

Table 6. Chemical composition of biomass ash samples (min–max), in dry base.

| | BFB1 | | BFB3 | | BFB4 | | GF | |
| | BA | FA | BA | FA | BA | FA | BA | FA |
	(*n* = 12)	(*n* = 12)	(*n* = 12)	(*n* = 12)	(*n* = 4)	(*n* = 4)	(*n* = 6)	(*n* = 6)
C%	0.1–0.5	1.4–5.6	<0.1–0.4	0.9–1.7	0.1–0.3	1.2–3.8	0.7–4.2	5.1–12
S%	0.01–0.07	0.3–1.4	<0.01–0.01	0.2–1.3	<0.01	0.2–1.2	<0.01	0.1–0.8
Cl%	0.01–0.22	1.3–8.1	0.004–0.02	0.14–2.2	0.006–0.03	0.31–0.66	0.007–0.01	0.23–1.4
Cu mg/kg	13–36	35–90	19–51	49–85	<10–575	30–167	33–43	38–92
Ni mg/kg	<10	24–65	<10	16–83	<10	13–21	11–21	14–28
Cr mg/kg	11–30	33–95	11–21	40–125	<10–24	38–70	47–73	41–60
Zn mg/kg	25–194	22–249	28–186	159–357	32–244	82–358	27–45	115–765
Pb mg/kg	<10–12	22–135	<10–23	39–173	<10–58	31–133	<10	14–75
Cd mg/kg	<4	<4	<4	<4	<4	<4–5	<4	<4
Hg mg/kg	<0.001	0.01–0.22	<0.002	0.10–0.31	<0.001	0.08–0.16	<0.005	0.05–0.52
Mn mg/kg	581–1160	2671–6482	125–830	914–3282	229–433	1016–1526	1452–2094	1648–4264
Fe%	0.4–1.6	0.9–3.5	0.4–1.1	1.6–3.9	0.4–0.7	1.3–1.7	2.6–4.6	2.3–4.1
Al%	0.6–3.3	1.9–6.6	0.7–2.7	3.5–8.2	1.8–2.3	3.8–6.0	5.6–8.1	5.1–8.5
Ca%	1.5–5.7	8.2–31	0.8–4.8	3.0–15	0.5–3.2	3.9–17	3.4–6.7	3.0–8.2
Na%	0.2–2.7	0.8–2.3	0.1–0.6	0.6–1.6	0.1–0.3	0.6–1.2	0.5–0.8	0.6–0.9
K%	0.5–2.8	3.9–7.5	0.5–2.2	2.5–4.5	1.6–1.9	3.4–3.7	3.0–3.5	3.1–4.8
Mg%	0.2–2.5	1.3–2.8	0.1–0.5	0.7–1.6	0.1–0.2	0.7–1.1	0.8–1.2	0.9–1.6
P%	0.1–0.3	0.3–0.7	0.02–0.1	0.3–1.1	0.04–0.1	0.4–3.8	0.2–0.3	0.3–0.5
Si%	33–40	7.5–23	32–37	16–27	39–40	21–29	25–30	19–25

Notes: n—number of individual samples analyzed, BA—bottom ash (Table 3), FA—fly ash (Table 3).

Ashes contain mainly Si, variable quantities of Ca, K, Fe, Al, Mg, Na, Ti, P, Cl and S, and trace quantities of heavy metals. Except Si, most inorganic elements are in higher quantities in FA than BA. Due to the use of sand in BFB systems, Si is higher in all BABFB than in BAGF, while concentrations are more similar in BAGF and FAGF. In BFB, the C contents are generally lower in FA than BA [26]. The GF ashes contain much higher C contents, revealing serious efficiency problems of the boiler. This GF boiler was retrofitted afterward. Ashes of BFB1 show some extreme values of Cl, Ca, Na and Mg, which may be correlated with their higher contents in the biomass consumed in that boiler, or/and eventual co-combustion of sludge (Table 4). Cl retention in solid phases may persist until about 800 °C, depending mainly on the presence of S, Ca, and alkaline metals, and also on combustion conditions [243,244]. As BFB boilers operate within 750–850 °C [230], there may be instability of Cl retention by Ca in the furnace core, releasing some Cl that may contribute to the generation of PCDD/Fs.

As can be observed in Table 7, PCDD/Fs levels are higher in FA than in BA, except in the case of BFB1. Interpretation of results might be hampered due to the different composition of streams (Table 3), and the presence of several ND congeners. The F/D ratios of FA varies from 0.17–1.1; PCDDs account for 41–86% of ΣPCDD/Fs, which means there is no prevalence of PCDFs, contrary to what is reported for other combustion systems [128,129]. The analyzed ashes contain mostly OCDD and 1,2,3,4,6,7,8-HpCDD, as in other biomass boilers [140], representing 40–70% of total PCDD/Fs identified. However, also the more toxic 2,3,7,8-PCDD and 1,2,3,7,8-PeCDD were found in all FA. Chlorination degrees (nCl) of PCDD/Fs in FA vary between 6.0–7.3; slightly lower for PCDFs (6.0–6.4) than for PCDDs (7.2–7.3), similarly to other results [129]. These results suggest that perhaps de novo synthesis was not preponderant, although FA contains unburned matter and Cl. The presence of Ca and alkaline elements might have captured Cl, reducing chlorination to form PCDFs. Also, the low Cu contents of biomasses may have limited PCDD/Fs formation in the post-combustion zones. However, the

dechlorination of the original OCDD and HpCDD contained in biomass might have occurred [120,209], giving rise to several congeners, including the more toxic tetra and penta PCDDs.

Table 7. PCDD/Fs and TEQs of biomass ash Blends, in dry base.

ng/kg	BFB1 Ash Blend		BFB3 Ash Blend		BFB4 Ash Blend		GF Ash Blend	
	BA	FA	BA	FA	BA	FA	BA	FA
2,3,7,8-TCDF	ND(2.0)[1]	30	ND(2.0)	121	ND(2.0)	88	ND(2.0)	447
1,2,3,7,8-PeCDF	ND(12)	14	ND(12)	43	ND(12)	93	ND(12)	386
2,3,4,7,8-PeCDF	ND(12)	19	ND(12)	49	ND(12)	191	ND(12)	620
1,2,3,4,7,8-HxCDF	ND(12)	ND(12)	ND(12)	23	ND(12)	111	ND(12)	386
1,2,3,6,7,8-HxCDF	ND(12)	ND(12)	ND(12)	26	ND(12)	131	ND(12)	468
2,3,4,6,7,8-HxCDF	ND(12)	ND(12)	ND(12)	27	ND(12)	202	ND(12)	640
1,2,3,7,8,9-HxCDF	ND(12)	ND(12)	ND(12)	ND(12)	ND(12)	64	ND(12)	183
1,2,3,4,6,7,8-HpCDF	28	ND(12)	ND(12)	35	ND(12)	333	ND(12)	976
1,2,3,4,7,8,9-HpCDF	ND(12)	ND(12)	ND(12)	ND(12)	ND(12)	93	ND(12)	244
OCDF	101	ND(25)	ND(24)	27	ND(24)	333	ND(24)	366
2,3,7,8-TCDD	5.8	6.0	ND(2.0)	26	ND(2.0)	11	ND(2.0)	122
1,2,3,7,8-PeCDD	ND(12)	ND(12)	ND(12)	18	ND(12)	48	ND(12)	264
1,2,3,4,7,8-HxCDD	ND(12)	17	ND(12)	ND(12)	ND(12)	48	ND(12)	366
1,2,3,6,7,8-HxCDD	ND(12)	33	ND(12)	21	ND(12)	83	ND(12)	1220
1,2,3,7,8,9-HxCDD	ND(12)	23	ND(12)	13	ND(12)	45	ND(12)	793
1,2,3,4,6,7,8-HpCDD	98	315	ND(12)	121	ND(12)	584	20	9048
OCDD	523	274	33	161	ND(24)	685	121	7523
Σ PCDD/F MB [2]	823	789	126	731	105	3141	228	24052
LB/UB [2]	755/890	733/844	33/219	713/749	0/209		141/315	
I-TEQ MB	18.4	35.9	11.9	88.3	11.9	224	12.2	1144
WHO$_{1998}$-TEQ MB	20.9	38.6	14.9	97.2	14.9	247	15.1	1270
WHO$_{2005}$-TEQ MB	19.7	34.6	13.5	86.5	13.5	207	13.8	1139
LB/UB	7.3/32.1	25.9/43.2	0.01/27.1	85.2/87.8	0/27.1	same	0.2/27.3	same

Notes: [1] ND—non-detected, (EQL)—Estimated Quantification Level [2] LB—Lower-Bound (ND = 0), MB—Medium-Bound (ND = EQL/2), UB—Upper Bound (ND = EQL). BA—bottom ash (Table 3), FA—fly ash (Table 3).

PCDD/Fs contents of FABFB4 being higher than those of other BFB boilers appears to be consistent with its constitution (only ESP ashes). In the case of FAGF, although it is a mix of ESP+EC ashes, the levels of PCDD/Fs are even higher, which can be related to the higher C (5.1–12%), possibly enhancing PCDD/Fs formation and/or higher adsorption [128,143]. In the BA blends only OCDD and H$_7$CDD were detected, with the exception of BABFB1 that also contains 2,3,7,8-TCDD, OCDF and one H$_7$CDF isomer. The corresponding FABFB1 contains more congeners, resulting in a higher TEQ than in BABFB1, despite its slightly lower ΣPCDD/F. The similar FABFB3 contains even more congeners, including TCDD and P$_5$CDD, thus, although having similar ΣPCDD/Fs, its TEQ is more than twice that of BABFB1.

Similar to what is observed for biomass and other samples (Table 4), different assumptions for ND have significant impacts on ΣPCDD/Fs and TEQs of ashes, as can be seen in Table 7.

Comparing with published results [143], TEQs in the studied BA match those of bottom ash from combustion of native wood, or waste wood, depending on the ND option. As for FA, TEQs obtained are more similar to those of fly ash from residual wood combustion (18–6300 ng I-TEQ/kg), than from native wood (1.5–4.0 ng I-TEQ/kg). The higher TEQ of FAGF also matches the I-TEQ range of fly ash from waste wood combustion (730–21,000 ng I-TEQ/kg). The higher levels of PCDD/Fs in ashes were correlated with poor burnout of ashes, which resembles the case of FAGF.

In general, results show that WHO_{1998}-TEQs are higher than I-TEQs, and WHO_{2005}-TEQs are lower than WHO_{1998}-TEQs, and also lower than I-TEQs. Taking in account that dl-PCB are not included in the study and considering only FA blends, the correlations obtained are as follows:

$$(WHO_{1998}\text{-TEQ(PCDD/F)}) = 1.11 \times (\text{I-TEQ}) \tag{5}$$

$$(WHO_{2005}\text{-TEQ(PCDD/F)}) = 0.99 \times (\text{I-TEQ}) \tag{6}$$

$$(WHO_{2005}\text{-TEQ(PCDD/F)}) = 0.90 \times (WHO_{1998}\text{-TEQ(PCDD/F)}) \tag{7}$$

The correlation (6) of WHO_{2005}-TEQ with I-TEQ is similar to the correlation (4) obtained from Molto et al. [74].

Analogous to the fate of heavy metals that are not destroyed in combustion systems and concentrate/enrich in fly ash [245], pre-existing PCDD/Fs in fuels may also enrich in fly ashes. Only under proper combustion conditions they can be destroyed or removed from flue gases [246]. In addition, they may suffer transformations, like dechlorination of the high chlorinated congeners to the lower substituted and more toxic hexa, penta, and tetra PCDD/Fs. As an example, one can calculate the possible magnification of a pre-existing quantity of PCDD/F in biomass, as follows: considering that 100 ng/kg of OCDD present in biomass are not destroyed, and that 80% of the OCDD is transferred to ESP fly ashes [247] (which may represent about 0.5% of the fuel biomass), the levels of OCDD in ESP fly ashes would reach 16,000 ng/kg, corresponding to about 5 ng WHO_{2005}-TEQ/kg. However, if some 10% of this OCDD dechlorinates and forms 1,2,3,7,8-PeCDD or 2,3,7,8-TCDD, the corresponding TEQ could reach 1600 ng WHO_{2005}-TEQ/kg in ash. This shows that even relatively low PCDD/Fs contents present in the forest biomass, or any other fuel, may produce fly ashes with high TEQs. Highly efficient ESP systems may keep PCDD/Fs air emissions below emission limit values (ELVs), however the collected ashes may become contaminated with PCDD/Fs.

Concentrations of PAHs of ash blends of the units BFB1, BFB3 and GF are presented in Table 8. Most PAHs compounds were non-detected (ND) and many are close to EQLs of PAHs. Levels are relatively low, compared with the 16.8 mg/kg of PAHs found in wood ash tested as soil fertilizer [55]. Individual concentration of PAHs and Σ_{16} PAH of all BA are lower than those of FA blends. Only FABFB3, which also contains significant PCDD/Fs, reveals the presence of carcinogenic Cry and also BghiP, in low concentrations. LPAHs constitute 79–100% of total PAHs detected, of which the most prevalent is NaP, 52–93% of ΣPAHs, except in BABFB3. Flut and Pyr were reported as the two most abundant HPAHs in wood combustion [72], however, they are present only in FA blends, accounting for less than 24% of ΣPAH. Presence of the highly volatile NaP in ashes, similar to other works [61], might be a result of relevant generation, and/or its fate during and after combustion. NaP can be originated by several pathways, including sequential dechlorination/destruction of PCDD/Fs [248]. Presence of PAHs is usually correlated with unburned matter in ashes and PCDD/Fs, however, this trend was not found in this study; FAGF has similar PAH contents as other FA blends that contain much less C. Some PAHs formed might have been converted to PCDD/Fs, especially PCDF, by cracking and chlorination in the post-combustion zones [229].

The BaP-EQs obtained according to the US-EPA RPFs are about a third lower than those using the factors of Nisbet and Lagoy. This is expected, since RFPs do not cover the non-carcinogenic PAHs, and some RFPs are lower than those of Nisbet and Lagoy, namely for BkFA, DahA, and Chry. Differences between LB and UB of Σ_{16} PAH are low, indicating that ND handling has low impact for the PAHs results obtained. The same occurs when accounting for carcinogenics, Σ7Carc., since the concentration of Chry is close to its EQL.

Table 8. PAHs, BaP-EQs of biomass ash blends, in dry base.

mg/kg	BFB1 Ash Blends		BFB3 Ash Blends		GF Ash Blends	
	BA	FA	BA	FA	BA	FA
NaP	0.016	1.727	ND(0.005)	0.776	0.060	2.338
Acy	ND(0.005) [1]	0.075	0.008	0.100	ND(0.005)	0.066
Ace	ND(0.005)	0.006	ND(0.005)	0.006	0.006	ND(0.005)
FL	ND(0.005)	ND(0.005)	ND(0.005)	ND(0.005)	ND(0.005)	ND(0.005)
Phe	0.009	0.163	0.011	0.232	ND(0.005)	0.061
Ant	ND(0.005)	0.006	ND(0.005)	0.011	ND(0.005)	ND(0.005)
Flut	ND(0.005)	0.025	0.005	0.171	ND(0.005)	0.023
Pyr	ND(0.005)	0.020	ND(0.005)	0.181	ND(0.005)	0.022
BaA *	ND(0.005)	ND(0.005)	ND(0.005)	ND(0.005)	ND(0.005)	ND(0.005)
Chry *	ND(0.005)	ND(0.005)	ND(0.005)	0.006	ND(0.005)	ND(0.005)
BbFA *	ND(0.005)	ND(0.005)	ND(0.005)	ND(0.005)	ND(0.005)	ND(0.005)
BkFA *	ND(0.005)	ND(0.005)	ND(0.005)	ND(0.005)	ND(0.005)	ND(0.005)
BaP ***	ND(0.005)	ND(0.005)	ND(0.005)	ND(0.005)	ND(0.005)	ND(0.005)
DahA **	ND(0.005)	ND(0.005)	ND(0.005)	ND(0.005)	ND(0.005)	ND(0.005)
BghiP	ND(0.005)	ND(0.005)	ND(0.005)	0.006	ND(0.005)	ND(0.005)
IP *	ND(0.005)	ND(0.005)	ND(0.005)	ND(0.005)	ND(0.005)	ND(0.005)
Σ_{16} PAH MB [2]	0.060	2.045	0.057	1.507	0.101	2.539
LB/UB [2]	0.02/0.10	1.90/2.07	0.02/0.09	1.49/1.52	0.07/0.14	2.51/2.57
Σ 7 Carc. MB	0.018	0.018	0.018	0.021	0.018	0.018
LB/UB	0/0.04	0/0.04	0/0.04	0.006/0.04	0/0.04	0/0.04
BaP-EQ US-EPA [3] MB	0.006	0.006	0.006	0.006	0.006	0.006
BaP-EQ N&L [4] MB	0.016	0.018	0.016	0.018	0.016	0.019

Notes: *—carcinogenic 2 B, **—carcinogenic 2 A, ***—carcinogenic 1. [1] ND—non-detected, (EQL)—Estimated Quantification Level. [2] LB—Lower-Bound (ND = 0), MB—Medium-Bound (ND = EQL/2), UB—Upper Bound (ND = EQL). [3] [101], [4] [98], BA—bottom ash (Table 3), FA—fly ash (Table 3).

3.3. Conformity of PCDD/Fs and PAHs in Ashes with the Proposed Limits for Fertilizers

In view of the proposed limits of contamination in ashes to be used as fertilizers [65], there are some concerns regarding the studied ashes.

While content of Cl in bottom ashes (BA) varies from 0.004–0.22%, fly ash (FA) streams present 0.14–8.1% Cl, exceeding the recommended Cl limit of 3% in some cases.

The Σ_{16} PAHs of fly ashes (1.5–2.5 mg/kg) and bottom ashes (0.06–0.1 mg/kg) comply with the proposed limit of 6 mg/kg. In this case, the handling of ND data has no significant impact on the conformity evaluation.

Regarding PCDD/Fs, the fly ashes present contents between 789–24,052 ng/kg, corresponding to 35–1139 ng WHO$_{2005}$-TEQ/kg, assuming the MB option for ND values. Even assuming the LB option for ND, the values vary from 26–1139 ng WHO$_{2005}$-TEQ/kg. This means that the fly ashes unequivocally exceed the proposed limit of 20 ng WHO$_{2005}$-TEQ/kg. In the case of bottom ashes, judgment on whether TEQs exceed the limit depends on the option used for ND. While for the MB option the TEQs range, 14–20 ng WHO$_{2005}$-TEQ/kg, indicate that bottom ashes may reach the limit; considering LB option (0–7.3 ng WHO$_{2005}$-TEQ/kg) they comply, but considering the UB option (27–32 ng WHO$_{2005}$-TEQ/kg) all bottom ashes exceed the limit. This highlights the need for the requirement of low detection limits for such measurements.

The sensitivity analysis reveals that when there are left-censored data, the chosen options for handling ND results affect the judgment of compliance with limit values. When there are many ND cases, as in this study, the assignment of EQL fractions to ND is perhaps questionable [249]. Given the special case of PCDD/Fs, choice of another analytical methodology or laboratory could be advisable, in view of the target values and sample matrix. It becomes evident that any regulation of contaminants must detail requirements of analytical methodologies, namely sensitivity/detection limit and criteria to present results, including how to handle ND values. This is especially important when limit values are aggregated quantities such as TEQs and sum (Σ). Other ND handling methods could be

used, for example, involving statistical approaches, although this would require a deep knowledge of characteristic distribution of congeners/compounds, for each matrix/source based in data analysis. While there are no specifications, the MB attribution to ND appears to be an acceptable choice as a mid-term approach. Similar to the control of PCDDs/Fs in food, the less conservative (LB) or more precautionary (UB) results should be included in reports, as well as criteria for differences between LB and UB. Research activities and risk assessment works should also observe these critical issues, so that experimental results may represent valuable sources of data to support regulation activities and protect the environment and human life.

Although contents of Cl, C and PAHs in ashes are important for PCDD/Fs formation, other mechanisms may be important, such as the presence of precursors and pre-existing PCDD/Fs. Thus, neither C, Cl or any other parameter, should be assumed as pre-indicators for PCDD/Fs analysis. This analysis of PCDD/Fs must be mandatory and the same applies for dl-PCBs already incorporated in TEQs, or other highly toxic POPs. However, a balance between frequency of measurements and the cost of monitoring requirements need to be considered. One option might be the use of accredited effect-based bioassays used for monitoring PCDD/Fs, such as DRCALUX or CALUX® Bioassay, which are considerably cheaper. The selectivity of these assays for dioxin-like compounds and interference of PAHs can be overcome by appropriate clean-up, and by this can be used for soils and sediments [250] and ashes [251].

The contamination of ashes is affected by mixes: bottom ashes and fly ashes may contain other flows produced in different zones, such as superheaters, economizers, cyclones, baghouses and ESP, which was also highlighted elsewhere [143]. This is another important subject to be addressed in fertilizer regulations, for example, the definition of the constitution of ash streams that may be used as fertilizers.

The provenience of ashes must also be better defined; the simple designation as "biomass ashes" as a corollary for safe use appears to be inadequate. Ashes from residual biomass originated in field plague control, wood and food industries, agriculture, farming, or other types of biomass/bio-residues, such as sludges, compost and organic fractions of MSW, may exhibit much higher contamination than natural biomass ashes. Besides POPs and their precursors, possible contamination of fuels with toxic and bioaccumulative metals (Cd, Pb, Hg, As, etc.) results in higher contents of these metals in ashes. Furthermore, metals like Cu may have a memory effect along the furnace systems, catalyzing PCDD/Fs formation for prolonged periods.

4. Conclusions

This work aimed at contributing to a deeper understanding and knowledge on the risks of using biomass ashes as fertilizers, and the need to incorporate sustainable principles in renewable bioenergy, namely preservation of forest ecosystems. This aim is within the scope of Circular Bioeconomy, and aligns with objectives of the incoming Roadmap on Chemicals Strategy for Sustainability of the European Green Deal, which highlights the need to strengthen regulations for greater protection of humans and wildlife from chemical mixtures, including the use of fertilizers.

Results obtained show that some ashes, in particular fly ashes, from combustion of residual forest biomass contain PCDD/Fs levels exceeding proposed limits for ash use as fertilizer. Hence, the fertilizer regulations must address these concerns, establishing safe limit for POPs values and detailing which ashes can be used. Also, definitions of analytical methodologies, frequency of measurements and reporting data are essential and should be specified in regulations.

Due to the complexity of formation and fate of PCDD/Fs and PAHs, more research is required to get a deeper understanding of the fate of PCDD/Fs and PAHs during residual biomass combustion, using different technologies. However, it became clear that either the nature of residual forest biomass, for example, containing concerning levels of Cl, or presence of background levels of PCDD/Fs may originate contaminated ashes.

The current Basel Convention "low POPs" content of 15,000 ng TEQ/kg is orders of magnitudes too high and could mislead the management of ashes. Even the proposed lower value of 1000 ng TEQ/kg is far too high for the use of ashes in soils [7,8,252]. Due to the increasing generation and use of ashes from biomass combustion/incineration, this should be clarified in Basel Convention not to mislead policy makers and owners of ashes to select the wrong end of life disposal options and contaminate soils with associated exposure risk.

The safety of utilization of ashes is a global issue since the use of biomass residues for energy production is growing worldwide. In many developing countries in Asia, Africa and South America, poor regulation of impacted waste wood and poor combustion technology may result in contaminated ashes that are spread in agricultural soils, with associated long term risk for human health from accumulation in livestock, including chicken/eggs. Also, the intensive household biomass combustion, if impacted wood or plastic is involved, can result in contaminated ashes, and if spread in the garden results in the contamination of soils with risks for chicken/eggs frequently kept around houses in developing countries. The Stockholm and Basel Conventions should therefore reinforce frameworks for developing regions to develop regulations for treated waste wood and facilitate clean biomass combustion, and effectively prevent dissemination and indiscriminate use of contaminated ashes as fertilizers. For this, appropriate PCDD/F limits, similarly to the recently developed limits in the EU or Germany, should also be promoted as a frame for a circular economy for this increasingly generated waste/material flow.

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