

Dioxins from Biomass Combustion: An Overview

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Abstract Biomass combustion originating both from human activities and behaviour and from natural causes, has caused considerable concern as a result of the numerous pollutants emitted into the atmosphere, including polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans and polychlorinated biphenyls, or in brief *dioxins*. The contribution of dioxins emissions from biomass combustion becomes more and more important, especially since evident guided emissions—principally from waste incineration and metallurgy—have been curtailed drastically. Different types of biofuels feature different chemical components, including cellulose, lignin, and proteins, and accompanying organic and inorganic compositions, thus showing different characteristics of dioxins generation. Combustion modes, either flaming or smouldering combustion, also show considerable influence on the amounts of dioxins emitted from the system and they may host distinct processes for forming dioxins. Lean in chlorine and catalytic copper, native biomass materials usually produce low emission factors. However, various contaminants are inevitably mixed into biofuels during combustion and significantly promote the dioxins generation. Emission factor data from a wide range of biomass burning sources are collated in the present review, suggesting that dioxins emissions are substantially influenced by the facilities used, their operating conditions and combustion processes, fuel composition, accidental addition of contaminants, etc.

Their roles in biomass combustion and dioxins formation pathways, however, remain difficult to quantify, resulting in emission factor values stretching over several orders of magnitude and complicating the efforts to build a comprehensive global estimation of dioxins emissions from biomass burning.

Keywords Biomass combustion · Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) · Dioxin-like polychlorinated biphenyls (dl-PCBs) · Incineration · Products of incomplete combustion · Open burning

Abbreviations

2,4-D	2,4-Dichlorophenoxyacetic acid
ACQ	Ammoniacal copper quaternary
APCD	Air pollution control devices
ar	As-received
BFRs	Brominated flame retardants
BTEX-aromatics	Benzene, toluene, ethylbenzene, xylenes
CBA	Copper boron azole
CBz	Chlorobenzenes
CCA	Chromated copper arsenate
CH ₄	Methane
CO	Carbon monoxide
CO ₂	Carbon dioxide
CP	Chlorophenols
daf	Dry-ash-free
dl-PCBs	Dioxin-like polychlorinated biphenyls
DSC	Differential scanning calorimetry
EFs	Emission factors
EPA	U.S. Environmental Protection Agency
FC	Fixed carbon
HCBz	Hexachlorobenzene

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I-TEQ	International toxic equivalence quantity
MSWIs	Municipal solid waste incinerators
NMOC	Non-methane organic compounds
O ₃	Photochemical ozone
OBTF	Open Burning Test Facility
P	Poly-
PAHs	Polycyclic aromatic hydrocarbons
PCBs	Polychlorinated biphenyls
PCDD/Fs	Polychlorinated dibenzo-p-dioxins and dibenzofurans
PCDDs	Polychlorinated dibenzo-p-dioxins
PCDFs	Polychlorinated dibenzofurans
PE	Polyethylene
PICs	Products of incomplete combustion
PM	Particulate matter
PVC	Polyvinylchloride
REP	Relative effect potency
SOA	Secondary organic aerosol
TCDD	Tetrachlorinated dibenzo-p-dioxin
TEFs	Toxic equivalency factors
TEQ	Toxic equivalency
UNEP	United Nations Environment Programme
VM	Volatile matter
WHO-TEQ	World Health Organization toxic equivalence quantity

Introduction

In modern society the usage as a fuel of biomass has become marginal. Conversely, it is still an important source of energy in developing countries or in countries with considerable reserves of biomass [1–4]. Deliberately set fires and natural wildfires have been blamed for injecting large amounts of particulate matter (PM) and trace gases into the atmosphere and significantly impacts local or regional air quality, visibility and health [5–8]. Thus, it is important to analyse the environmental consequences attached to biomass burning and optimise its usage and management.

At a global scale, biomass burning is thought to be the largest source of aerosol PM in the atmosphere and the second largest source of total trace gases [9, 10]. Aerosol PM leads to adverse effects on human health and global climate [1, 11, 12]. Primary trace gases from biomass burning are, in order of abundance, carbon dioxide (CO₂), carbon monoxide (CO), and methane (CH₄) [13] and include the two major greenhouse gases CO₂ and CH₄. Other significant gas-phase emissions relate to non-methane organic compounds (NMOC), responsible for rapid formation of secondary organic aerosol (SOA) and

photochemical ozone (O₃) [14–16]. After biogenic emissions (~1000 Tg/year), biomass burning is the second source of gas-phase NMOC in the global atmosphere, contributing some 400–700 Tg/year [9, 15, 17, 18]. Compared with these emissions (usually stated by their emission factors in g/kg biomass), those of dioxins from biomass burning (in ng/kg biomass) are a factor 10⁹ lower. However, they are far from minor, because of their toxicity at low levels, their ability to persist in the environment for decades, lipophilicity, mutagenicity and tendency to bioaccumulation [19–22].

The term ‘dioxins’ is used differently by different authors. It comprises up to three distinct classes of polychlorinated aromatic compounds, namely 75 polychlorinated dibenzo-p-dioxins (PCDDs), 135 polychlorinated dibenzofurans (PCDFs) and (rarely) 209 polychlorinated biphenyls (PCBs) (Fig. 1). The possible positions of chlorine atoms on the benzene rings are designated by numbering the carbon atoms. Traditionally, waste incineration and iron ore sintering are the largest traditional sources of dioxins [23]. However, biomass burning is becoming increasingly more significant [24–26] as a source, as regulatory interventions as well as technological advances lead to reductions in these customary contributions and forest fires and other wildfires seem still expanding.

Two temperature windows have been reported for fast dioxins formation: between 500 and 800 °C “homogeneous” pyrogenic routes proceed in the gas phase and the “heterogeneous” catalytic gas/solid reactions take place between 200 and 400 °C [27–30]. The dioxins amounts formed from high-temperature homogeneous routes are much lower than those arising from low-temperature heterogeneous mechanisms [30, 31], which are further subdivided into (a) de novo synthesis and (b) precursor pathways. High temperature combustion of biomass tends to sufficiently decompose both the fuel and its organic

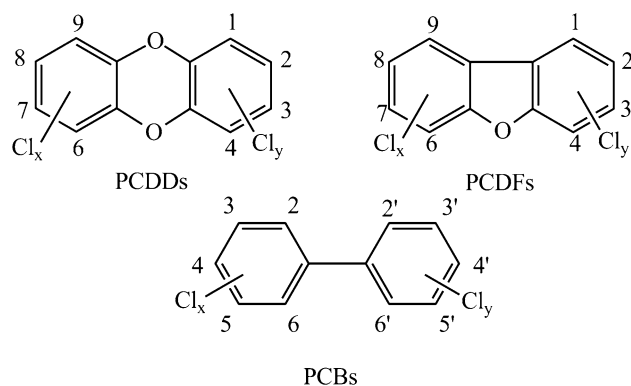


Fig. 1 Chemical structure of PCDDs, PCDFs and PCBs, showing the linking of two aromatic rings by two ether bridges (PCDDs), one ether bridge and a C–C bond (PCDFs) or a single C–C bond (PCBs)

contaminants, including dioxins, with new dioxins being re-formed in the cooler post-combustion zone [26, 32, 33]. Equipped with flue gas cleaning systems, such sources become less problematic. However, small scale stoves, fireplaces, house heating systems, usually operate at more ideal conditions for dioxins formation and are seldom equipped with air pollution control devices (APCD) [26, 34, 35]. Much fiercer are open fires of biomass, either initiated spontaneously as wildfires or ignited artificially for reasons of land management and disposal of residues: a plethora of products of incomplete combustion (PICs), dioxins included, are formed and emitted as a result of poor, uncontrolled combustion conditions. Undesirable impacts on the local atmospheric environment or even at global scale are always detected during or after large-scale biomass burning events [36–38].

Generally, biogenic matter (except straw [39]) usually is lean in chlorine, one of the key factors for dioxins formation. However, anthropogenic waste or other synthetic substances, as well as their additives and coatings (e.g., wood preservatives, paint, pesticides, etc.) are often present in biomass, raising dioxins emissions to levels several orders of magnitude over those from combustion of pure biomass [24, 40–45]. Possible reasons are (1) the added substances bring in copper and/or chlorinated materials into the system, largely facilitating dioxins synthesis, and (2) polymers or metals contained in these anthropogenic matters aggravating the combustion conditions, promoting incomplete combustion and providing the required temperature for dioxins formation [24, 41, 42]. It indicates also that more attention and proper measures should be paid to the burning of ‘impure’ biomass materials.

The present review tries to outline the importance of dioxins from biomass combustion, its potential pathways and reaction steps in the formation of dioxins, followed by collecting and analysing reported dioxins emission data from a wide range of biomass burning sources. The various influencing factors are analysed and the underlying formation mechanisms are explored. Motivated by acquiring relatively accurate data on emission levels of dioxins from biomass combustion, similarities and distinctions in emission factors (EFs) between various sources are assessed and highlighted. Estimating global dioxins release from biomass burning sources is proposed, as well as countermeasures to mitigate these emissions.

This paper relates a keynote presentation prepared for the 6th International Conference on Engineering for Waste and Biomass Valorisation, held at Albi, May 23–26, 2016. This meeting brought a wide variety of contributions dealing with thermal and biochemical conversion or treatment of both waste and biomass.

Biomass Combustion

Introduction to Biomass

Woody biomass is commonly composed of carbohydrates (cellulose and hemicellulose) and lignin, along with small amounts of extractives and inorganic fractions [46]. Typical fractions of these components are shown in Table 1 for some common type of biomass.

It is noticed that the inorganic fraction (ash) in straw is much higher than for other types of biomass. Softwood is wood from gymnosperm trees such as conifers, as opposed to hardwood, which is from angiosperm deciduous leaves trees. Most of the production of timber or of pulp and paper is from softwood. The actual contents of these components vary with plant species, geographic locations and ages [24].

Worldwide, cellulose is the most common organic polymer. It is a polysaccharide involving a linear chain of several hundreds to many thousands of anhydro-glucose units (Fig. 2), with chemical formula $(C_6H_{10}O_5)_n$ [48, 49] and n ranging typically from 7000 to 15,000 [50], yet depending on source and treatment. Different types of biomass have highly variable cellulose content and its mean value decreases in the order [46]: contaminated biomass > herbaceous/agricultural biomass > wood and woody biomass > animal biomass.

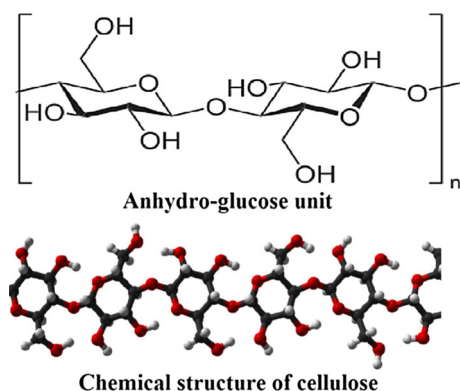
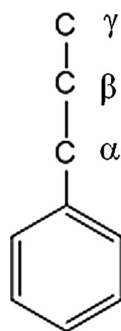
Hemicellulose is also a polysaccharide, composed from several sugars [46, 49]. Its structure is branched and consists of fewer (typically between 500 and 3000) units [50]. Hemicellulose comprises about 20 % of the biomass of most plants and its mean content decreases in the order [46]: wood and woody biomass > herbaceous and agricultural biomass > animal biomass > contaminated biomass.

Lignins are cross-linked phenolic polymers of four or more substituted phenylpropane units (Fig. 3) based upon different building blocks [24, 46, 51], serving to maintain the structural integrity of plant cells and provides mechanical support and strength. Composition varies from species to species, e.g. aspen: 63.4 % carbon, 5.9 % hydrogen, 0.7 % ash, and (by difference) 30 % oxygen, corresponding to a formula $(C_{31}H_{34}O_{11})_n$ [52]. Its mean biomass content decreases in the order [46]: animal biomass > wood and woody biomass > herbaceous and agricultural biomass > contaminated biomass. Composed of phenols, lignins are a source of potential precursors of PCDDs and (less so) of PCDFs.

Another approach to characterising and analysing biomass is considering chemical composition. Proximate analysis and elemental analysis of various types of biomass are given in Table 2, with data on lignin and cellulose for comparison. Biomass has a high content of volatiles,

Table 1 Biochemical components of several common types of biomass [24, 47]

Species	Ash (%)	Extractives (%)		Lignin (%)	Hemicellulose (%)	Cellulose (%)
		Solvent soluble	Water soluble			
Softwood	0.4	2.0	–	28	24	41
Hardwood	0.3	3.1	–	20	35	39
Wheat	6.6	3.7	7.4	17	28	40
Rice straw	16	4.6	13	12	25	30
Bamboo	1.6	0.3	–	20	39	38

**Fig. 2** Anhydro-glucose unit and chemical structure of cellulose**Fig. 3** Phenylpropane, the basis of biomass lignin by connecting substitutes situated on the α , β and γ carbons [24]

typically around 80 %, which burn promptly after ignition and contribute to about 70 % of the heat released [4].

A higher content of chlorine is observed for wheat straw as well as sugar cane bagasse (Table 2), implying that these upon combustion could lead to large chloroaromatics emissions [53, 54]. The stoves burning salt-laden wood in a coastal area, which is rich in content of chlorine, were found to lead to 20 or 90 times greater TEQ concentration in soot than the stoves burning wood from inland sources [55].

Moisture also plays a significant role in the combustion process: a high content of moisture requires substantial drying/heating before de-volatilisation, ignition and real combustion can start, significantly affecting the temperature of the fire and the stability of the flame [4].

Biomass Combustion

Biomass combustion comprises several steps: (1) drying, (2) heating-up, (3) devolatilisation, yielding volatiles (tars and gases) and char, (4) flaming combustion of volatiles and (5) glowing or smouldering combustion of char [4]. The heating and drying converts wet biomass into an ignitable, dry fuel. Pyrolytic decomposition and

Table 2 Chemical composition of typical varieties of biomass based on proximate (ar) and ultimate (daf) analyses (wt%) [4]

Biomass	Proximate analysis, ar				Ultimate analysis, daf				S	Cl
	Moisture	VM	FC	Ash	C	H	O	N		
Wood pine chips	4.0	81.3	14.6	0.1	52.0	6.2	41.6	0.12	0.08	0.01
Willow	6.96	75.7	16.3	1.03	51.6	5.54	42.4	0.38	0.03	0.01
Miscanthus	14.2	70.4	14.1	1.3	49.1	6.4	44.0	0.26	0.13	0.13
Switch Grass	7.17	73.1	15.2	4.62	49.4	5.70	44.3	0.45	0.1	0.1
Wheat straw	7.78	68.8	17.1	6.30	49.2	5.78	44.0	0.64	0.1	0.26
Rice husks	9.4	74	13.2	12.8	42.3	6.1	50.6	1.1	0.1	0.04
Sugar cane bagasse	10.4	76.7	14.7	2.2	49.9	6	43.2	0.4	0.04	0.51
Lignin	9.0	73.5	1.5	16	72.0	6.6	21.3	0	0	0
Cellulose	4.1	94.0	0.2	1.7	44.4	6.17	49.3	0	0	0

ar as-received, daf dry-ash-free, VM volatile matter, FC fixed carbon

devolatilisation of biomass starts at about 160–250 °C [4, 56, 57] and plays an important role in the early stages of the combustion of biomass, since some 80 % (Table 2) of the original fuel is transformed into volatile matter.

Thermal decomposition of carbohydrates starts at temperatures well lower than 300 °C, involving initial dehydration, decarboxylation, and decarbonylation producing water, CO₂ and CO [24]. As temperature rises, the depolymerisation of cellulose and hemicellulose yields monosaccharide monomers, such as levoglucosan, galactosan and mannosan, etc. [24]. These monosaccharides then polymerise, generating heat as well as secondary char, or undergo further thermal decomposition yielding low molecular weight volatiles [24, 58].

Comparatively, lignin decomposes over a wider temperature range (120–500 °C), resulting from the chemical functionality in the lignin macromolecule. The first reaction period occurs between 120 and 300 °C, involving dehydration and generation of gaseous and light liquid compounds from carbonyl groups [24]. The second period proceeds and lasts from 300 to 500 °C, releasing substituted phenolic species [59], which are considered to be potential precursors for dioxins formation.

The combustion process can be split into two types of phenomena: *flaming* versus *smouldering combustion*. Thus, combustion of solid fuel can be represented by a sequence of events (Fig. 4).

Flaming combustion implicates escaping volatiles as fuel, mixing and reacting these with air oxygen, releasing heat and light, while producing a variety of combustion products (e.g., CO₂, CO, H₂O, etc.) as well as smoke [60]. Conversely, smouldering is slow and at times a low-temperature, flameless form of combustion, substantially sustained by the heat evolving when oxygen directly attacks the surface of a condensed-phase fuel [61]. Typically, it remains incomplete, since reaction rates slow down while fuel materials situated in a fire are cooling down; moreover, residual combustible often remains occluded in ash. Smouldering combustion starts at the solid surface, where oxygen meets char and then progressively moves inside (the shrinking core model), while flaming combustion only occurs in the gas phase [62, 63]. Both combustion modes may host distinct processes for forming dioxins, yet obviously, operating in a different physical context and time-

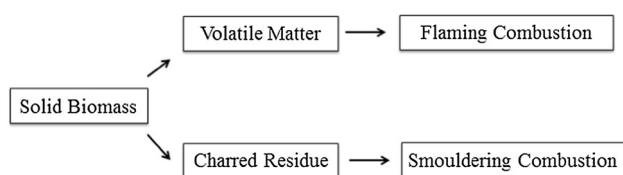


Fig. 4 Combustion of biomass fuel, showing both flaming and smouldering combustion

scale: smouldering combustion continues long after flaming combustion ceased.

Formation of Dioxins from Biomass Burning

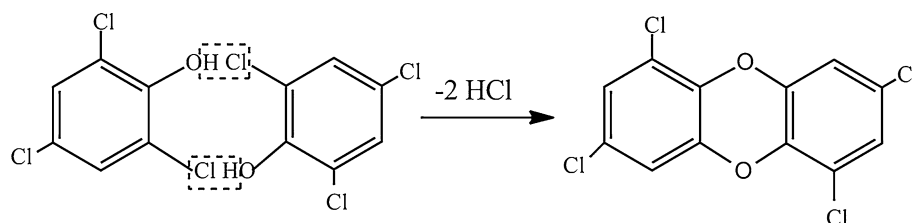
Precursor Route and De Novo Synthesis

Enormous efforts have been made to describe, prevent, and abate the formation of dioxins, ever since their discovery in fly-ash and flue gas from municipal solid waste incineration (in 1977) [64]. Any thermal process proceeding in the presence of carbon, chlorine, oxygen, and metal catalyst has the potential to generate dioxins. During well-controlled combustion processes, the high-temperature (500–800 °C) homogeneous routes produce much lower dioxins amounts than the subsequent low-temperature (200–400 °C) heterogeneous pathways [30, 31]: at high temperature complete combustion prevails, the trace chemistries of fire remaining restricted to anoxic clouds. According to low-temperature heterogeneous mechanisms, the PCDD/Fs form via the two commonly investigated routes: (a) de novo synthesis, starting from macro-molecular carbon or from polycyclic aromatic hydrocarbons (PAHs) and (b) precursor pathways starting from organic molecules similar to PCDD/Fs, including e.g. chlorophenols (CP), chlorobenzenes (CBz) and PCBs. Both pathways proceed at the surface of solid carbon (soot, charred materials), catalysed by certain metal ions (with copper as strongest representative) [29]. The second seems much faster [65, 66] than the first.

Precursors are compounds, structurally similar to dioxins, and that form these by relatively straightforward reactions involving, e.g., the condensation of CP, or oxidation and chlorination reactions, followed by ring closure, leading to PCDD/Fs [30]. Most frequently cited are CP, CBz, PCBs, PAHs and other oxygenated compounds; in particular, the CP pathway is among the most important for the formation of PCDD/Fs [67]. Figure 5 shows how two CP-molecules could condense to one PCDD-molecule. Strong structural similarities allow an easy conversion from precursors into PCDD/Fs [27, 28], which not only is thermodynamically favoured at low temperature, but also occurs at appreciable reaction rates. The large amounts of phenols released from thermal decomposition of lignin are potentially promote the precursor route of dioxins formation [68] (Fig. 5).

De novo synthesis comprises carbon chlorination, namely the transfer of chlorine into the carbon matrix, followed by oxidative degradation of this chlorinated carbon matrix. Pure charcoal oxidation occurs at 550 °C. In the presence of CuCl₂, this temperature reduces to 300–350 °C as shown by differential scanning calorimetry

Fig. 5 Formation of 1,3,6,8-PCDD from condensation of chlorophenols (CP)



(DSC) [69, 70]. The temperature window considered for de novo formation of PCDD/Fs is 250–450 °C [30], yet time influences also upon optimal conditions. De novo synthesis gives rise to numerous product classes, often in an order of prominence [28, 71]:

CBz > CP > PCDFs > PCDDs > dl-PCBs

Both de novo synthesis and precursor routes were repeatedly reviewed [28, 30, 72, 73]. The ratio of PCDF to PCDD has been associated with the respective importance of the de novo and the precursor routes: when PCDF/PCDD ratio is >1, de novo synthesis is supposed to be the dominant mechanism in dioxins formation; otherwise, the precursor pathway predominates [28, 74].

The characteristics and mechanisms of dioxins formation and their resulting signature patterns, which have been used to identify and prioritize dioxins emissions from different thermal sources [75, 76], could also be applied in analysing the emission data derived from biomass burning sources. In this perspective, smouldering combustion could seem a carrier of de novo processes since it is based on slow combustion of carbonised matter; flaming combustion involves fumes full of precursors (such as phenols derived from lignin) and aerosol particles favouring the alternative precursor route. At present, there is only minimal evidence available to support such conjecture [44, 77].

Biomass Burning and Dioxins

Large amounts of aromatic volatiles are generated during the pyrolytic and oxidative decomposition of solid biomass, supplying highly reactive intermediates that polymerise to cyclic compounds, i.e. aromatics, PAHs, and soot. Incomplete combustion will occur whenever oxygen is no longer in adequate supply, or else, the absence of one or more of the three T's (temperature, time and turbulence) fail to completely convert all evolving Volatile Matter (VM) into their principal products of combustion, i.e., CO₂ and H₂O. Figure 6 describes the pathway starting from reactive aliphatic compounds (e.g., ethene, ethyne), leading to soot under oxygen-lean conditions, after passing over

simple BTEX-aromatics (e.g., benzene, toluene, ethylbenzene, xylenes) and PAHs. With the presence of organic/inorganic chlorine and metal catalyst, the generated PAHs and PAH-embodied soot can subsequently be converted into PCDD/Fs at relatively high yield (a fraction of 1 %), through both precursor and de novo pathways [78–81]. Other important volatiles in biomass combustion smoke are dibenzofuran and dibenzo-p-dioxin, the parent molecules of PCDD/Fs, which can form PCDD/Fs via direct chlorination [24, 68].

Different components of biomass (carbohydrate and lignin) show different characteristics for PCDD/Fs formation. Tame et al. [82] experimentally studied the formation from cellulose, hemicellulose and lignin, respectively. Due to the complex functional heterogeneity of lignin, model compounds (vanillin, hydroxybenzaldehyde, syringol, and catechol, Fig. 7a) were used to simulate the thermal decomposition of lignin. All samples were reacted on a surrogate ash, containing CuO, NaCl and SiO₂, in flow gas of 10 % O₂/90 % N₂ at 350 °C. A preference for the formation of PCDFs over PCDDs was observed in all experiments. The ratio of PCDFs to PCDDs varied according to the chemical structure of the feed, with carbohydrates demonstrating greater relative propensity for PCDFs (ratio-PCDFs/PCDDs: 11.9–18.2) than lignin (ratio-PCDFs/PCDDs: 3.0–5.8; with syringol as exception, 16.7). However, this statement is on the contrary in their following experiments [68], pyrolysing cellulose, hemicellulose and a representative wood lignin in pure N₂: lignin showed greater propensity for forming PCDFs (ratio-PCDFs/PCDDs: 34.4 and 41.7 at 320 and 400 °C, respectively) than cellulose and hemicellulose (ratio-PCDFs/PCDDs at 320 °C: 3.9 and 5.6, respectively). The inconsistency of the results from these two series of experiments could be attributed to the various chemical structures of the lignin used and the different experimental conditions. In both of their studies [68, 82], lignin produced considerably more PCDD/Fs than cellulose and hemicellulose.

The formation potential of dioxins varies throughout the combustion process. Tame et al. [77] estimated the PCDD/Fs formed in flaming combustion, smouldering, and

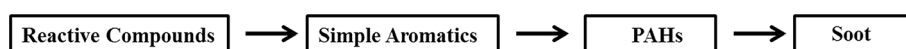
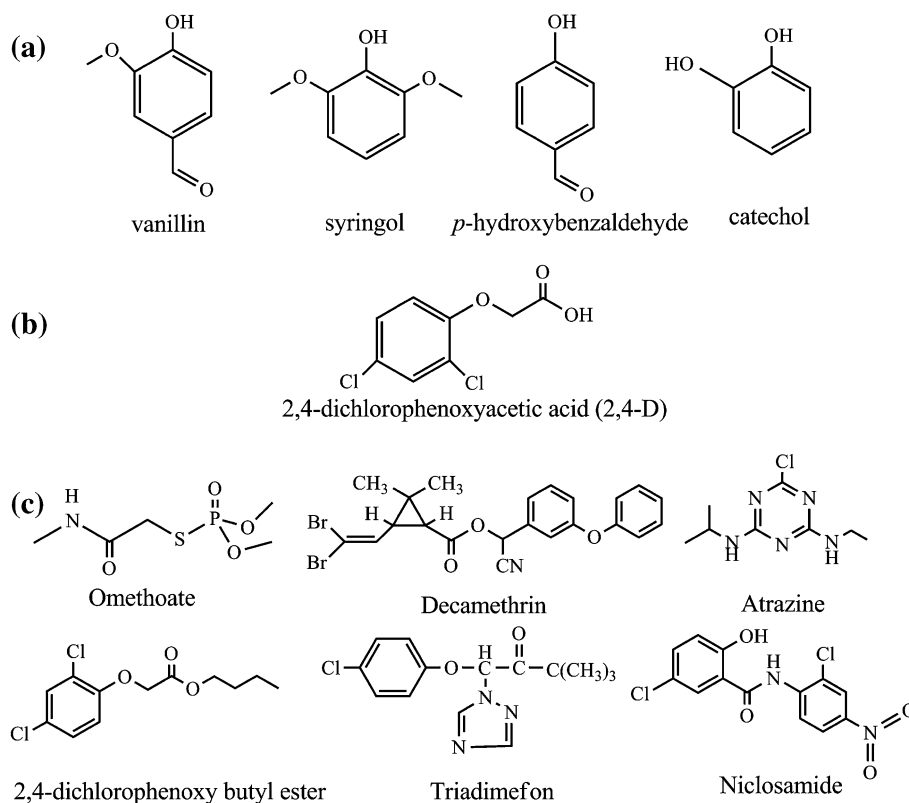


Fig. 6 Formation pathway of monocyclic and polycyclic aromatic hydrocarbons as products of incomplete combustion (PICs)

Fig. 7 Molecular structures of **a** the model compounds for lignin examined in the study of Tame et al. [82], **b** 2,4-dichlorophenoxyacetic acid (2,4-D) and **c** six investigated pesticides in the research of Zhang et al. [42]



oxidative pyrolysis of wood impregnated with two preservatives, ammoniacal copper quaternary (ACQ) and copper boron azole (CBA), by using a cone calorimeter. For the initial pyrolysis of the CBA-treated wood in air, 310 ng/Nm³ (7.5 ng TEQ/Nm³) of tetra to octa-CDD/Fs was detected. During the smouldering period following the pyrolytic release of volatiles, the exhaust gases were found to contain 22 ng/Nm³ (0.57 ng TEQ/Nm³). In a dramatic contrast, the product gases from flaming combustion contained concentrations 2–3 orders of magnitude lower than those from oxidative pyrolysis and smouldering combustion. The concentrations were quantified as 3.5 and 5.2 pg TEQ/Nm³ for the ACQ and CBA timber samples, showing no reasonable increase over that resulting from similar combustion of untreated wood, 3.7 pg TEQ/Nm³. It suggests that low temperature thermal treatment of biomass should be avoided during common combustion processes, especially for the biomass contaminated by preservatives, pesticides and other waste.

Numerous studies relating to the various factors influencing upon dioxins formation concentrate either on municipal solid waste incinerators (MSWIs) [29, 30, 83], or on iron ore sintering [71, 84], the most important industrial source. However, these factors and their effects were rather seldom discussed for biomass incineration and uncontrolled combustion, especially in open fires. It has

generally been accepted that fuel composition (characterised by its source, and amount of carbon, chlorine, and transition metal catalysts), temperature of combustion, reaction atmosphere (oxygen, moisture, hydrogen chloride and sulphur dioxide), the presence of suppressants and other operational parameters significantly impact upon dioxins formation/destruction from bio-burning sources, but the relationships between such parameters are difficult to quantitative.

Roles of Contaminants

Contaminants, such as pesticides, wood preservatives, paint, or general waste, are often present and even mixed into biomass fuel. Since native biomass generally contains only traces amounts of chlorine (Table 2) and even less copper [39], the chlorination of carbon may be the limiting PCDD/Fs formation step during the combustion of biomass [24]. However, these contaminants are most likely to bring in more chlorine, metal catalysts and even organic additives which thermally decompose to provide precursors for dioxins synthesis, boosting the emission of dioxins. Even worse is uncontrolled and open burning of biomass: the added high heating value contaminants require times higher oxygen than native biomass, which will devastate

local combustion condition, prolong smouldering combustion and lead to more PICs generation, including soot, precursor compounds and dioxins.

Most of the common used pesticides are either containing chlorine (e.g., atrazine, 2,4-dichlorophenoxyacetic acid, pentachlorophenol dichlorprop, etc.) and/or embedded with dioxins precursor structures (e.g., dichlorprop, decamethrin, niclosamide, etc.). Their involvement in e.g. forest fires or agricultural residues' burning has been experimentally proved to stimulate the formation of PCDD/Fs and PCBs [42, 85–88]. Furthermore, dioxins present as impurities in some pesticides could volatilise and be emitted due to their incomplete destruction, which constitutes a potentially sizeable supplemental source of dioxins emissions [89, 90]. The influence of various pesticides will be discussed in detail in “[Pesticides-Contaminated Biofuel Burning](#)” section.

Metal-based solutions applied for preserving wood have provided the most popular method for protecting timber. Commonly used are chromated copper arsenate (CCA), CBA, ACQ, etc. These preservatives cause concerns for their promoting effect on dioxins formation during the combustion of impregnated wood, resulting from their copper-based and chlorine-contained constituents, and the prolonging effect on smouldering of wood char following cessation of flaming combustion [24, 44, 77]. The influence of the presence of some preservatives has previously been considered for processes of wood incineration [45, 91] as well as for open fires [92], however, observing no substantially greater PCDD/Fs emissions under good/flaming combustion conditions of preservative-treated timber than for untreated wood.

Anthropogenic waste is inevitably involved into some forms of biomass burning, such as household waste in yard fires of garden waste and plastic film in agricultural residues burning, potentially bringing in not only chlorine and metal catalysts, but also flame-retardants materials complicating deliberate efforts to burn them adequately. Polyvinylchloride (PVC) is a typical plastic which is extensively used and widespread in anthropogenic waste. However, with its high content of chlorine, PVC is frequently branded as a major chlorine donor and spitefully leads to substantial formation of dioxins during poorly controlled or uncontrolled combustion and open fires [93]. Hedman et al. [41] measured the emissions of PCDD/Fs and dl-PCBs from the poorly controlled domestic combustion of yard waste in a barrel and in open fires. The tested waste was composed of garden waste added with other miscellaneous wastes, e.g. paper pack, plastic pack, refuse-derived fuel, polyethylene (PE), waste motor oil and PVC. The test using garden waste and PVC as fuels produced 2–4 orders of magnitude higher emission factor than that from other tests.

Brominated flame retardants (BFRs) are always used in plastics, textiles, mattresses, electrical and electronic equipment and other products, effectively preventing accidental fires [94]. However, the emission of PCDD/Fs will be considerably stimulated if BFRs-contained materials are co-combusted with biomass fuel [95]. Except for the flame-retardant effect of BFRs, which lower the temperature and promote incomplete combustion, the added bromine should also be blamed for enhancing the formation of PCDD/Fs. The possible mechanisms were discussed by Zhang et al. [95].

The influence of contaminants in bio-fuel incineration equipped with flue gas cleaning system is not seriously problematic, compared with other factors, e.g. the type of incinerator/combustor, the nature of bio-fuel and operating parameters. However, the presence contaminates should be avoided in poorly-controlled and uncontrolled combustion of biomass, such as domestic bio-fuel combustion and open fires, as indicated by the discussion in the following chapter.

Dioxins Toxicity Based Units

Thermal processes produce a thermal fingerprint featuring all possible dioxins congeners and their complete analysis is often not necessary. Analysis is frequently further restricted to the seventeen 2,3,7,8-substituted PCDD/Fs required by the international toxic equivalence quantity (I-TEQ) system. Only those PCDD/F-congeners show strong toxicity, with the most toxic 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) as conventional unity. The World Health Organization toxic equivalence quantity (WHO-TEQ) system also includes the twelve dl-PCB congeners. The toxic equivalency factors (TEFs) of the 17 2,3,7,8-substituted PCDD/Fs congeners and the 12 dl-PCBs were determined by the relative effect potency (REP) values of these toxic PCDD/Fs and PCBs compounds compared with 2,3,7,8-TCDD as a reference compound [96]. These TEFs have been developed to facilitate risk assessment of exposure to these PCDD/Fs and PCBs [97, 98]. Thus, a dioxins analysis can be expressed in weight, TEQ-weighted, or molar units.

Emissions of Dioxins from Biomass Combustion

As opposed to fossil fuels, biogenic fuels, such as firewood and dried animal dung, are still used by a large part of the rural population in developing nations. Biomass burning is at the center of several categories of fire: intentionally burned as source of energy or as a way to dispose the residues, or fired for agricultural and forestry purposes (prescribed burning, or converting natural land into arable

land) or unintentionally burned during wildfires. Incineration under controlled conditions combined with air pollution control devices is considered a favourable destruction procedure for many biomass wastes [26], largely reducing the volume of waste and emitting lower pollutants (per unit mass) than uncontrolled combustion and open fires. Conversely, the incomplete combustion in uncontrolled biomass combustion and open burning result in numerous additional PICs being emitted, including CO, hydrocarbons (methane, ethane, ethene, ethyne, higher alkanes and alkenes, dienes, aromatics, PAHs), and oxygenated compounds (organic acids, aldehydes, ketones). In addition, nitrogen containing compounds (e.g., NO₂, NO, N₂O, HCN, NH₃, amines), sulfur compounds (e.g., SO₂, SO₃, H₂S, COS, thiols) and halogen-containing compounds (e.g., methylchloride, methylene chloride..., but also PCDD/Fs, PCBs) are released in substantial amounts [99].

Published emission factors of dioxins still span several orders of magnitude and may even vary with the study method used, e.g., laboratory versus field experiments [100]. Possible explanations for such wide deviations are the disparity of fuel composition (ash, metal and chloride content), of combustion conditions and characteristics, and of amount and quality of ash and char and their contacting in fumes and fire.

Bio-fuel Incineration

Bio-fuels available in the form of wood chips, pellets and pieces, wheat straw, rice husk, and contaminated waste wood, etc., are often combusted for energy generation or/and waste disposal. The capacity of biomass incinerators, rarely exceeding 10 MW, is lower than that of MSWIs. Equipped with APCDs, most well-organised biomass incinerators can also meet the dioxins emission limit value for MSWIs of only 0.1 ng TEQ/Nm³ [26, 32, 33, 101].

Lavric et al. [26] comprehensively reviewed the available data about the levels of dioxins in both gases and ashes produced in combustion of varieties of biomass fuels and co-combustion of biomass with other fuels. The concentration of dioxins in stack gases from incineration of various uncontaminated biomass fuels vary from 0.002 to 1.1 ng TEQ/Nm³, with hay burned in a 50 kW automatically charged multi-fuel furnace ranking the highest [102] and wood chips burned in a 6.3 MW district heating incinerator ranking the lowest [33]. Emission factors based on unit mass are within the range of 0.026 to 5.1 ng TEQ/kg of dry bio-fuel. Launhardt and Thoma [102] tested kinds of herbaceous biofuels (straw, whole plant cereals and set aside hay) and spruce wood for their potential to form chlorinated aromatic compounds during incineration in an automatically charged multi-fuel furnace (50 kW). The emissions of PCDD/Fs from the combustion of these bio-

fuels were ranked as: hay > straw > whole plant cereals ≈ spruce wood. The highest formation ability of hay should be attributed to its highest contents of chlorine (2890 mg/kg, dry base) and copper (4.5 mg/kg, dry mass) among the four types of bio-fuels.

Twenty-seven publications concerning incineration of waste biomass and co-combustion of biomass with other fuels were reviewed by Lavric et al. [26], with incineration facilities varying from lab-scale burners [103, 104] to power and district heating incinerator (95 MW) [33]. The reported dioxins emission factors vary between 0.64 and 170.7 ng TEQ/kg of dry bio-fuel, from multicycle-equipped quad-cell boilers (burning waste wood and sawdust from non-industrial logging operations) [105] and a 150 kW automatic chip furnace (burning waste wood chips from demolition of building) [106], respectively.

Seven wood-burning plants were selected for gas analyses by Kolenda et al. [107]; two of them (9.6 MW fuel injection incinerator and 234 kW stoker incinerator) were tested and compared in order to clarify the influence of the input material (block, briquet, chops, dust), of special organic compounds (PVC-coating) and the inorganic hardener (ammonium sulphate, ammonium chloride) of plywood on PCDD/Fs emission. Emission concentrations in all tests ranged from 0.004 to 9.82 TEQ/Nm³, with highest concentration occurring after the addition of halogenated materials (ammonium chloride hardened plywood or PVC-coated plywood) to the input of the 234 kW stoker incinerator. The comparison of emissions from large and small facilities shows that the facility size tends to have a significant influence due to the corresponding combustion conditions. For the large facilities (>1 MW), even when processing materials containing high halogen quantities, the concentrations remained below those obtained from small facilities using natural wood [26].

The EPA's (U.S. Environmental Protection Agency) inventory of dioxin-like compounds sources uses emission factors of 0.6 ng WHO-TEQ/kg (or 0.56 ng I-TEQ/kg) and 15 ng WHO-TEQ/(kg ash) (or 13 ng I-TEQ/kg ash) as air releases for emissions of dioxins from industrial incineration of nonsalt-laden wood and salt-laden wood, respectively [108]. All solid residues (ashes) are assumed to be landfilled and, therefore, are not considered to be an environmental release [108].

Domestic Stove and Fireplace

The formation of dioxins is inherent to the under-ventilated, low temperature conditions present in fires. It has been concluded that smoke from domestic sources—stove and fireplace contains much higher concentration of dioxins than that from well-organised and APCDs-equipped furnace [26, 33, 106].

Gullett et al. [34] measured emission factors for PCDD/Fs, PCBs, hexachlorobenzene (HCBz) and other pollutants from fireplace and woodstove combustion; using two natural wood types (oak and pine) and artificial commercial logs (Table 3). Emission factors ranged from 0.25 to 1.4 ng TEQ/kg for natural wood fuels and 2.4 ng TEQ/kg for artificial logs, showing no statistical distinction by appliance type. In a single woodstove experiment, the weight amount (ng) of PCBs emitted from the woodstove was three orders of magnitude greater than that of PCDD/Fs; the contribution of PCBs to WHO-TEQ, however, was merely 0.5 % of PCDD/Fs.

A Canada study measured organic compounds released from a conventional wood stove and a certified non-catalytic, advanced technology wood stove using two types of wood, hard maple (a common firewood in Canada) and spruce (a common softwood species) [109]. A total of 12 tests were conducted, with 3 replicates for each of the two fuels in each stove. The emission factors of PCDD/Fs from the certified stove (0.49–1.01 ng TEQ/kg of dry wood) were slightly higher than those from conventional stove (0.20–0.33 ng TEQ/kg of dry wood). No substantial difference of emission factors between the two types of wood was observed. The study produced estimated overall emission factor of 0.5 ng TEQ/kg dry wood for wood stove combustion [26].

Except for the combustion of natural wood, special attention should also be paid to that of wood waste, which is produced in large quantities annually and partially emerged from construction activities and house demolition. Wood residues (waste and industrial) often contain various types of contaminants (metal-based preservatives, creosote, adhesives, resins, paint and other surface coatings) [26]. Many of these contaminants are potent to stimulate the formation of dioxins.

Lavric et al. [26] reviewed the experimental data on such emission levels in flue gas, soot and ash. Typically, the combustion of natural, uncontaminated wood leads to much lower emissions than those from contaminated wood. Bhargava et al. [43] measured pollutant emissions from four different wood products in a cone calorimeter. Two

samples of wood chips resulted in most disparate concentrations (<0.001 and 7.2 ng TEQ/m³); yet, two samples of contaminated/waste wood chips resulted in much higher levels (58.9 and 44.4 ng TEQ/m³). Wevers et al. [110]. measured dioxins emissions from domestic wood-burning appliances and reported emission factors of 22.4 ng TEQ/kg for burning untreated wood and ca. 1700 ng TEQ/kg for burning treated wood, a factor 76 times higher. The Swiss Federal Institution BUWAL reviewed data from mainly the nineties in an attempt to pinpoint the emissions related to the (illegal) co-combustion of waste in woodstoves. Adding waste into woodstoves may raise their dioxins emission data over several orders of magnitude than the combustion of clean wood [40].

Dioxins emission factors of 0.5 ng TEQ/(kg fuel) and 10 ng TEQ/(kg ash) are used for air release and solid residue release from indoor residential burners, respectively, in EPA's inventory of dioxin-like compounds sources [108].

Open Fires

Forest Fires

Plenty of evidence indicates that forest fires release substantial amounts of unwanted products, including greenhouse gases, aerosol PM, PAHs, PCDD/Fs and PCBs, to the global environment [111]. Because of the difficulties and dangers of representative and direct gas sampling during forest fires, often dioxins are measured only afterwards in soil and ash samples, as an indirect a posteriori approach. Kim et al. [112] showed some elevated levels as well as differences in homologue profile of the dioxins in soil samples one month after a fire. However, this kind of indirect approach is merely able to be used as a way to assess the influence of forest fires on local environment, rather than a way for estimating the total amount of dioxins emitted or calculating the corresponding emission factor, due to the unknown partitioning of dioxins between air and ash or soil [113].

Table 3 Emissions from wood burning in woodstoves and fireplaces [34]

Fuel	Appliance	PCDD/Fs		PCBs		HCBz
		Total (ng/kg)	TEQ (ng TEQ/kg)	Total (ng/kg)	TEQ (ng TEQ/kg)	Total (ng/kg)
Oak	Woodstove	7.44	0.25	8370	0.0014	13
Oak	Fireplace	9.62	0.35	–	–	310
Pine	Fireplace	54.4	1.4	–	–	380
Log	Fireplace	75.8	2.4	–	–	990

Fire simulation in burning chambers, as well as field measurement, are the two other methods used for acquiring emission factors for forest fires. Collet and Fiani [114] simulated 10 different kinds of forest fuel fires using an 80 m³ combustion chamber. Table 4 lists the emission factors for PCDD/Fs and dioxins-like PCBs.

Gullett and Touati [115] burned a composition of live shoot and litter biomass originating from Oregon and North Carolina in the EPA's Open Burning Test Facility (Table 4) [116]. The average emission factor of these tests on samples from two widely different places was 19 ng TEQ/(kg fuel). PCBs represented a minor (<2 %) fraction of the total WHO-TEQ value.

In the same facility, Gullett et al. [117] conducted burning tests on two grass and five forest samples sourced throughout the USA. The resulting dioxins emission factors spanned from 0.3 to 26.3 ng TEQ/kg of carbon burned, with an average of 5.8 ng TEQ/kg of carbon burned (Table 4). A major distinction between the two studies is that the first study conducted pile burns, the second standing tree burns.

Black et al. [118] compared the results from field measurements and simulations in a test burn facility, with the purpose of evaluating the effect of the experimental methods on the resulting emission factors. There was very good agreement in the emission factors from the field, brick hearth, and burn facility experiments (Table 4), so that the difference between laboratory simulation and field sampling seemed minor [118].

These studies still show a wide range (ca. 0.2–56 ng TEQ/kg fuel) of emission factors for forest fires. Some believe that chamber tests could have overestimated dioxins emissions, due to longer residence times in the temperature window of dioxins formation, compared with field measurements [53]. In order to study these influencing

factors Grandesso et al. [119] fired pine branches and twigs in an open burning facility, varying the moisture, charge size and chlorine concentration of the feed. The resulting TEQ and total PCDD/Fs (P: poly-, P = 4 to 8) emission factors were independent of both charge size (1–10 kg) and moisture content (7–50 %). However, the mono- to tri-CDD/Fs (that are rarely measured) obviously augmented during poor combustion conditions. The escalation of fuel chlorine from 0.04 to 0.8 wt% resulted in an about 100-fold increase of PCDD/Fs emissions.

Recently EPA [108] summarised these emission factors for dioxins and worked out averages of 0.8 ng TEQ/(kg fuel) and 5.9 ng TEQ/(kg fuel) for field tests and chamber tests, respectively. Finally, 3 ng TEQ/(kg fuel) was selected as a conservative value. Black et al. [100] reassessed the emission factors for release of dioxins and dioxin-like or dl-PCB to land and air, resulting in geometric mean emission factors attaining 1.0 ng TEQ/(kg fuel) and 1.1 ng TEQ/(kg ash), respectively. The factor for dl-PCBs releases to air amounts to a relatively high 0.09 ng TEQ/(kg fuel), or 9 % of the dioxins value.

Savannah and Grassland Fires

Fires in savannah and grassland cause substantial financial losses, and largely devastate local ecological and atmospheric environment in a period of time. Both laboratory and field test burns were designed to measure the emissions from savannah and grassland fires.

Gullett et al. [117] proposed an average dioxins emission factor of 0.32 (0.40 and 0.22) ng TEQ/kg C_{burned} derived from testing two grasses in EPA's open burning facility.

Environment Australia (2002) [120] selected 0.5–10 ng TEQ/(kg fuel) as best emission estimates for fires in

Table 4 Emission factors for PCDD/Fs from forest fires

Source	Experimental approach	n	Mean emission factor (ng TEQ/kg fuel)	Range (ng TEQ/kg fuel)	Reference
Forest biomass, France	Chamber tests	5	10.5	1.02–25.9	[114]
Forest biomass, France	Chamber tests	5	0.8 (dl-PCBs)	0.23–2.34	[114]
Forest biomass, Oregon	EPA's OBTF	3	15	1–56	[115]
Forest biomass, North Carolina	EPA's OBTF	4	25	14–47	[115]
Forest biomass, USA	EPA's OBTF	27	2.9 ^a	0.2–13.2 ^a	[117]
Duke forest	Field	4	0.52	0.4–0.79	[118]
Duke forest	Field, over brick hearth	4	0.59	0.18–1.2	[118]
Duke forest	EPA's OBTF	6	0.75	0.27–1.2	[118]

n number of tests, OBTF Open Burning Test Facility

^a These values originally were reported on a carbon basis and converted to total biomass by multiplying with 1/2 (biomass on a moisture and ash-free basis roughly contains 50 % Carbon)

savannah and grasslands. These values were derived from laboratory tests. In Australia Meyer et al. [53] sampled 19 laboratory and 21 field burns, to measure dioxins. The four fires in tropical savannah woodlands led to a median emission factor of 1.2 ng TEQ/(kg fuel).

Black et al. [118] reported emission factors to air of 0.40, 0.26 and 0.56 ng TEQ/(kg fuel) for grass fires burning by in-field, brick hearth and burn facility experiments, respectively. No significant difference was found between the results from different experimental approaches. The geometric mean emission factor for releases of PCDD/Fs to air for savannah/grass was 0.4 ng TEQ/(kg fuel). The corresponding emission factor for release of PCDD/Fs to land was 0.67 ng TEQ/(kg ash). For dl-PCB an emission factor to air of 0.01 ng TEQ/(kg fuel) was proposed.

The United Nations Environment Programme (UNEP) Toolkit recommends 0.5 and 0.15 ng TEQ/(kg fuel) to air and to land, respectively, as dioxins emission factors for grassland and savannah fires; that of dl-PCB is 0.03 ng WHO-TEQ/(kg fuel) either to air or to land [121].

Agricultural Residues Burning

Because of transportation cost, it is uneconomic to use agricultural residues as fuel for power generation. Therefore, open burning is often applied as an inexpensive and effective way to dispose of crop waste, especially in

developing countries [122, 123]. However, this post-harvest burning behavior has been reported numerously causing serious atmospheric pollution locally [6, 122, 124]. In Taiwan, Shih et al. [36] reported that the total PCDD/Fs concentration in ambient air averaged 9–16 times higher in areas with agricultural residue fires than in those without this burning, during the two weeks after harvesting. Table 5 summarises emission factors derived from experiments using various agricultural residues, together with the experimental approach used.

Gullett and Touati [125] recorded emissions of PCDD/Fs from firing wheat and rice straw samples. Their results did not vary much (Table 5); therefore, an emission factor of 0.5 ng TEQ/kg was settled for both sources.

Gullett et al. [54] combusted sugarcane leaves sourced from Hawaii and Florida. The PCDFs/PCDDs-ratio was 5.3 and 3.9, respectively, suggesting de novo formation. The emission factors from sugarcane were 3–243 times higher than those from straw samples studied before (Table 5) [125].

In Australia Meyer et al. [53] conducted both laboratory experiments and field tests on a variety of fires, including agricultural residues. Sorghum, wheat straw and sugarcane samples were used as fuel for chamber experiments. Field tests were conducted on sugarcane. The dioxins from laboratory experiments on sugarcane were 4.6 times higher than for field tests (Table 5).

Table 5 Emission factors for PCDD/Fs from agricultural residues, following different experimental approaches

Biomass	Experimental approach	Mean emission factor (ng TEQ/kg fuel)	n	Reference
Sorghum, Australia	Lab burn tunnel	35	3	[53]
Rice straw, USA	EPA's OBTF	0.73	1	[125]
Wheat straw, USA	EPA's OBTF	0.47	6	[125]
Wheat straw, Australia	Lab burn tunnel	17	7	[53]
Sugarcane, Australia	Field	0.95	2	[53]
Sugarcane, Australia	Lab burn tunnel	4.4	4	[53]
Sugarcane HI, USA	EPA's OBTF	114 ^a	2	[54]
Sugarcane FL, USA	EPA's OBTF	11 ^a	4	[54]
Sugarcane FL, USA	EPA's OBTF	2 ^a	2	[54]
Sugarcane standing FL, USA	EPA's OBTF	2.3	2	[118]
Sugarcane pile FL, USA	EPA's OBTF	0.34	2	[118]
Sugarcane FL, USA	Field	1.39	4	[118]
Sugarcane FL, USA	Field	1.9	2	[118]
Range of values (all)		0.34–114 ^b		
Range of values (sugarcane)		0.34–114 ^b		
Range of values (other)		0.47–35 ^b		

n number of tests, OBTF Open Burning Test Facility

^a These values were originally reported on a carbon basis and then converted to a total biomass basis, by multiplying by 45 %

^b These ranges do not demonstrate any sizeable difference between different crops and sugarcane

Table 6 Emission factors for agricultural residues burning (ng TEQ/kg material burned) [121]

Classification	Emissions to air		Emissions to land	
	PCDD/Fs	dl-PCB	PCDD/Fs	dl-PCB
Agricultural residue in the field, impacted, poor burning conditions	30	3	10	0.3
Agricultural residue burning in the field, not impacted	0.5	0.05	0.05	0.01
Sugarcane burning	4	0.05	0.05	0.01

Emission factors from field measurements and their simulations in laboratory were examined by Black et al. [118] and compared while using the same type of biomass, yet different sampling methodologies. Experiments with sugarcane showed no significant differences in emission factors when using these two different sampling systems (Table 5). From twenty-four experiments involving different types of biomass, the authors concluded that the distinction of dioxins emission factors and congener patterns between laboratory simulation and field sampling results was only minor across the same fuel type.

The UNEP Toolkit [121] proposes emission factors for estimating PCDD/Fs and dl-PCBs from agricultural residues and sugarcane burning (Table 6) based on the assessment of Black et al. [100].

Pesticides-Contaminated Biomass Burning

Pesticides have found multiple applications in agriculture, becoming ubiquitous as traces in most vegetation. In spite of their benefits in terms of increased productivity, pesticides potentially ordain new threats to people and ecosystems. In Japan, pesticides practicing was a foremost source of dioxins [126, 127]. Their involvement in biomass combustion has caused concern for promoting the formation of dioxins.

Muñoz et al. [86] conducted combustion experiments on pine needles and branches in an Open Burning Test Facility, simulating the firing of forest materials contaminated with pesticides. 2,4-dichlorophenoxyacetic acid (2,4-D, Fig. 7b) was sprayed onto biofuel at 1 and 10 times the manufacturer's recommended concentration. Emission samples were collected and compared against the emissions derived from firing untreated biomass. The average PCDD/Fs emission factors for runs without this pesticide added and with 1-time and 10-times the recommended dosage were 0.22, 0.06, and 1.14 ng TEQ/kg C_{burned} , respectively. The corresponding total PCDD/Fs emissions were 52, 940, 7800 ng/kg C_{burned} . Addition of 2,4-D obviously stimulated the total PCDD/Fs emissions, in spite of the minor influence on TEQ-values. The resulting increases can be attributed to the chlorinated character and the phenoxy-structure of this pesticide.

Zhang et al. [42] conducted field tests on corn straw, doped with six different pesticides (omethoate, decamethrin, atrazine, 2,4-dichlorophenoxy butyl ester, triadimefon and niclosamide, shown in Fig. 7c) at the concentration recommended for crop planting, to evaluate the influence of pesticides on the emission of PCDD/Fs to land from open burning of crop residues. After combustion, the TEQ concentration of PCDD/Fs in residual ash without any pesticide contamination remained at only 0.021 ng TEQ/(kg ash). However, the residual ash from pesticide contaminated straw was much higher, ranging from 0.73 to 5.72 ng TEQ/(kg ash), and averaging 2.34 ng TEQ/(kg ash). Adding pesticides caused 35–270 times higher PCDD/Fs emissions.

The PCDD/Fs formation ability of different pesticides were compared by Vikelsøe and Johansen [88], by combusting 13 types of pesticides (Fig. 8) in a laboratory scale horizontal tubular reactor in air. Most of the tested pesticides are chlorinated, with only two are non-chlorinated. Generally, higher yields are found for aromatic substances. No general correlation can be found between yield of PCDD/Fs and chlorine content, indicating that other factors (structural features of compounds, possible impurities in pesticides, etc.) play a role as well.

Yard Fires

Yard fires embrace firing garden waste with any household waste added; available emission data vary with waste composition, burning conditions, and differences in experimental, burning, and sampling methods [108].

Ikeguchi and Tanaka [128] simulated open burning using a large furnace operating with open doors. One test conducted with tree and leaf materials resulted in an emission factor of 4.6 ng TEQ/kg of waste. This value is 1–3 orders of magnitude lower than for other types of waste burned in the same furnace, e.g. PVC, electric wire tube, scrap tire, wood waste, crops, etc.

Wevers et al. [129] measured dioxins emissions from the firing garden waste in barrels and in open fires as well as burning household waste in an empty oil drum. The concentrations of dioxins in undiluted smoke as well as the calculated emission factors are listed in Table 7. The authors developed emission factors of 4.5 ng TEQ/kg for

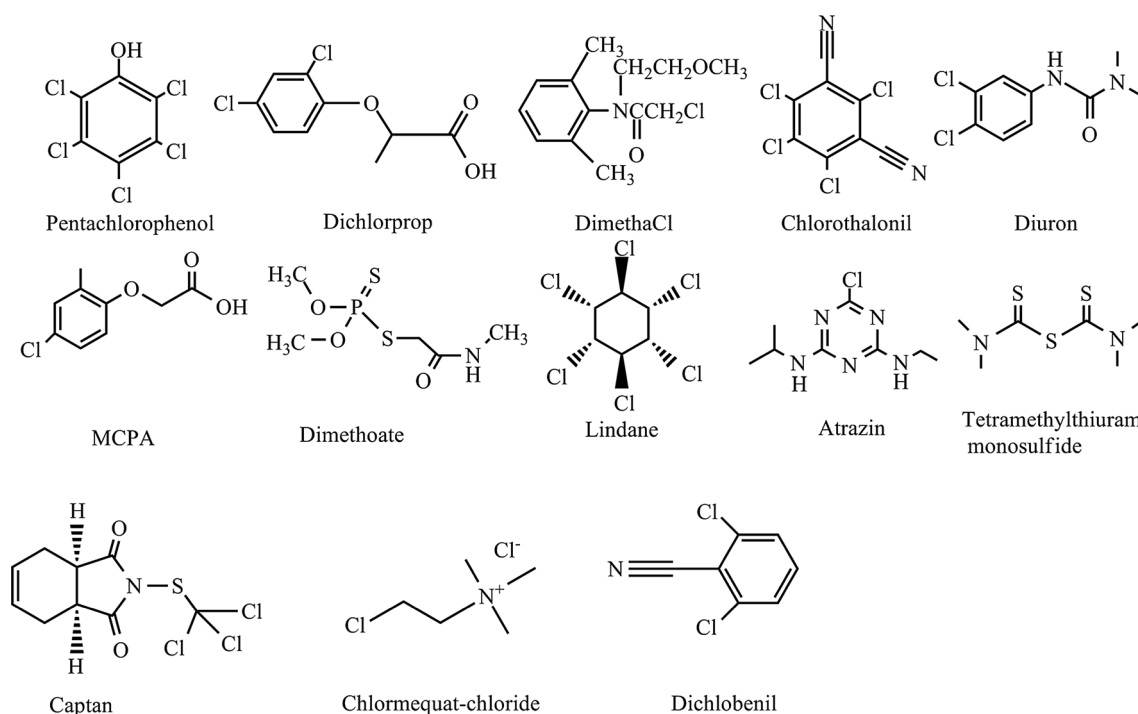


Fig. 8 Chemical formulas of thirteen investigated pesticides in the research of Vikelsøe and Johansen [88]

garden waste and 35 ng TEQ/kg for household waste, respectively. It suggests that co-combustion of wood and leaves with anthropogenic waste would produce higher emission factor than firing pure biomass.

Hedman et al. [41] measured emissions of PCDD/Fs and dl-PCBs from poorly controlled domestic combustion of yard waste in barrel or in open fires. The emission factors of dioxins from twelve tests added with garden waste ranged from 2.2 to 13,000 ng WHO-TEQ/kg, with the test co-combusting garden waste and PVC ranking the highest. Runs burning only garden waste or mixed with other miscellaneous waste yielded almost the same magnitude, no matter whether in barrels or in open fires. In most tests the contribution of toxic dl-PCB to the total WHO-TEQ value was between 1 and 10 %. An emission factor range of 4–72 ng TEQ/kg was suggested by the author for estimating emissions from backyard burning of garden waste and other lightly or moderately chlorine-contaminated waste, with a median value of 20 ng TEQ/kg.

The EPA's inventory of dioxin-like compounds sources uses emission factors of 10 ng WHO-TEQ/kg (air releases) and 0.02 ng WHO-TEQ/kg (solid residue releases) for material burned from residential yard waste burning [108].

Summary

Selected emission factors from different biomass burning sources are summarised and compared in Table 8, including data from recent studies as well as from the UNEP Toolkit [121] and the US EPA inventory [108]. Generally, recent research fills in some data gaps, and also provides a wider reference range than these two comprehensive sources. It is noticed that emission factors of dioxins from the same biomass source still span several orders of magnitude and may even vary with the study method used, e.g., laboratory versus field experiments. No unanimous conclusion can be drawn on whether great discrepancy exists

Table 7 Dioxins concentrations in undiluted smoke (referred to 9 % CO₂) and emission factors [129]

Experiment	Description of waste	Dioxins concentration (ng TEQ/m ³)	Emission factor (ngTEQ/kg waste)
Barrel 1	Garden waste: 139.4 kg (74 % wood, 26 % leaves)	3.5	20
Barrel 2	Garden waste: 149.2 kg (74 % wood, 26 % leaves)	0.84	4.7
Open fire	Garden waste: 3712 kg (96.5 % wood, 3.5 % leaves)	0.79	4.4
Barrel 3	Household waste: 48 kg wood (to lit the fire), then 323 kg household waste loaded on this base fire	3.6	35

Table 8 Some emission factors of dioxins from biomass burning sources (ng TEQ/kg feedstock, unless stated otherwise)

Type of combustion	Specification	PCDD/Fs		dl-PCBs		Refs.
		Air	Land	Air	Land	
	Range	0.026–171	0.05–10	0.0014–3	0.005–0.3	
Bio-fuel incineration	Uncontaminated biomass	0.026–5.1				[26]
	Contaminated biomass	0.64–171				[26]
Stove and fireplace	Untreated wood	0.25–2.4		0.0014		[34]
	Indoor residential burners	0.5	10 ^a			[108]
Forest fires		3		0.2		[108]
		1	1.1 ^a	0.09	0.19 ^a	[100]
Savannah and		0.4	0.67 ^a	0.01	0.19 ^a	[100]
Grassland fires		0.5	0.15	0.03	0.03	[121]
Agricultural residues	Sugarcane	1.6	3 ^a	0.03	0.19 ^a	[100]
	Cereal	0.49	1.1 ^a		0.19 ^a	[100]
	In the field, impacted	30	10	3	0.3	[121]
	In the field, not impacted	0.5	0.05	0.05	0.01	[121]
	Sugarcane	4	0.05	0.05	0.01	[121]
Pesticides		0.06–1.14				[86]
Contaminated biofuel			0.73–5.72 ^a			[42]
Yard fires		4–72	0.1–1.8	0.2–3.6	0.005–0.09	[41]

^a In ng TEQ/(kg ash)

between emission factor data resulting from the two different sampling methodologies [53, 118].

Numerous factors (e.g., fuel composition, combustion conditions, combusting facilities, fuel loading, etc.) contribute to the significant differences in emission data of dioxins even between similar sources. Generally, large, well-organised and APCDs-equipped bio-fuel incinerators tend to emit much lower concentrations of dioxins in stack gas than those small, batch-operated and APCDs-absent furnaces and domestic stoves and fireplaces. Burning contaminated biomass is more problematic than firing native biofuel, no matter in large-scale incineration or in poorly controlled combustion. Contaminants which largely promote dioxins formation during biomass combustion and merit attention are PVC, pesticides, preservatives, paints, etc.

Large parts of PCDD/Fs and PCBs produced are emitted into the flue gas; those found in residues represent typically less than 10 % of the total TEQ generated. PCBs-emissions surpass PCDD/Fs-emissions, when expressed in ng generated per kg of material burned; however, the contributions from dl-PCBs to total WHO-TEQ remains rather marginal, accounting for less than 10 % of total WHO-TEQ. The precursor route operates in parallel with the de novo pathway, producing PCDFs/PCDDs-ratios varying from 0.5 to 2, depending on biomass species and experimental

conditions or approach used (e.g. fire simulation in chamber and field measurements).

Global Emission Estimates

Quantifying global emissions of dioxins is a complex undertaking, because of the vast number of potential dioxins emission sources, the difficulty of quantifying the contribution of each source and the large variability in the experimental values for the emission factors from specific sources. A recent EPA inventory identifies more than 80 distinct sources and estimates their environmental releases of dioxins-like compounds in the US [108]. By 2011, already 68 national dioxins release inventories were made available (reference years: 1999–2009), all applying the UNEP Toolkit methodology. The total release of dioxins globally accounted for 58,700 g TEQ per year [25]. In this inventory, open burning of biomass or waste was identified as one of the major sources of dioxins, accounting for some 48 % for the total global dioxins emissions. Akagi et al. [9] reported a global estimate of combusted biomass (dry matter) for different fire types, based on data collected from 1987 to 2000 (Table 9). However, due to the considerable uncertainty in estimating emission factors from each source precisely, an accurate global estimation of the

amount of dioxins from biomass combustion cannot be given in this study. Moreover, major fires, such as those devastating the forests in South-East Asia at the end of the previous century, influence such data and their atmospheric consequences.

Conclusions

Each year, biomass burning releases large amounts of pollutants, such as PM, greenhouse gases, NMOC, etc. into the environment. These emissions are thought to significantly influence the Earth's atmosphere and climate. Another group of trace pollutants, which should not be ignored for their exceptional toxicity, lipophilicity, mutagenicity and bioaccumulation, are dioxins (PCDDs, PCDFs, and dl-PCBs).

Biomass is a complex heterogeneous mixture of organic matter and, to a lesser extent, extractives and inorganic fractions. The main structural organic components in biomass are carbohydrates (cellulose and hemicellulose) and lignin. Their contents vary with different types of biomass. Characterised by distinct chemical structures, these components go through different ways of decomposition during combustion and result in diverse products. Composed of phenylpropane units based on different building blocks, lignin thermally decomposes and releases amounts of phenolic species at temperature 300–500 °C; with the presence of chlorine, these phenolic species are potential precursors for PCDD/Fs formation. The different characteristics for PCDD/Fs formation were observed and discussed for the different components.

Combustion process of biomass is further classified as flaming combustion and smouldering combustion, with dioxins formation behavior varying with the two different stages. Reported experiments suggest that the formation pathways of dioxins from the two types of combustion indeed differ: smouldering combustion could form dioxins via de novo route, while flaming combustion tends to produce dioxins through precursor synthesis, due to the presence of massive precursors in the fumes. However, there is minimal evidence available to clarify the mechanisms and prove the hypothesis at present.

Published emission factors of dioxins are collected and collated from a wide range of biomass burning sources. Equipped with advanced APCDs, well-organised and continuously operated biomass incinerators can emit rather low concentration of dioxins in the stack gas and meet the emission limit value of 0.1 ng TEQ/Nm³. However, older, batch-operated furnaces, with very little air pollution and combustion control, inevitably lead to high dioxins emission factors. Characterised as under-ventilated, low temperature and APCDs-absent, domestic stove and fireplace lead to smoke containing high concentration of dioxins, contributing to an important of proportion of dioxins emissions from biomass burning sources. Open fires of biomass, featuring poor aeration, local lack of oxygen and intervention, and materials burned in uncontrolled settings, can emit considerable amounts of PICs. Dioxins emission factors from open burning are more difficult to estimate and determine, because of the numerous uncontrollable factors existing in open fire conditions.

Contaminants in biomass, in form of pesticides, wood preservatives, paint, or general waste, etc., can introduce

Table 9 Global estimates of biomass combustion in units of mass of dry matter burned (Tg) per year [9]

Year measured Reference	1990's [130]	Mid 1990's [10]	2000 [131]	1993/1995 [132]	1985 [133]	Others	Average
Savannah	3160	3572	–	–	–	–	3366
Forest	1970	1939	–	–	–	–	1955
Tropical forest	1330	–	–	–	–	–	1330
Extratropical forest	640	–	–	–	–	–	640
Biofuel	2897	–	2458	–	2447	–	2601
Cooking stoves	–	–	1351	–	–	–	1351
Open cooking (fuelwood)	–	–	–	1062	1714	–	1388
Charcoal burning	38	–	39	24	–	–	39
Charcoal making	43	–	–	–	–	–	43
Crop residue (for biofuel)	–	–	495	–	597	–	546
Dung	–	–	75	–	136	–	106
Industrial	–	–	498	–	–	–	498
Peat	–	–	–	–	–	3400 [134]	3400
Pasture maintenance	–	–	–	–	–	240 [18]	240
Crop residue (field burning)	540	475	–	–	451	–	489
Garbage burning	–	–	–	–	–	1000 [135]	1000

more chlorine, metal catalysts, and even precursors into the combustion systems and show a stimulative effect for dioxins formation. Therefore, their presence should be strictly avoided within biofuels which are to be combusted.

In order to curtail the global emissions of dioxins from biomass burning, countermeasures could target:

- Updating the combustion technology, operating conditions and APCDs of old/problematic biomass furnaces;
- A reduction of frequency of residential biomass combustion and occurrence of open fires;
- Avoiding the combustion of biomass mixed with other contaminants;
- The development of additives that allow reducing dioxins, without too much enhancing other relevant emissions.

Dioxins data biomass combustion are abundant, yet unusually variable, stretching over several orders of magnitude; the resulting emission factors are poorly reproducible, even during carefully controlled combustion experiments, using synthetically composed fuels fired in a well-designed test rig. Therefore, further studies could be paid to quantitative the influence of various parameters on dioxins formation from biomass burning, identify emission factors from each source and build a comprehensive inventory of global dioxins emission from biomass combustion.

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