2nd International Online Seminar about Persistent Organic Pollutants¹ Experiences in Best Available Techniques & Best Environmental Practices

BAT/BEP control of PCDD/PCDF from Biomass Boilers and Sustainable Management Issues

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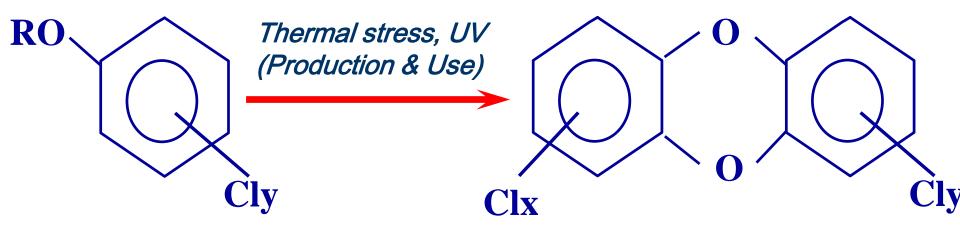
Content of Presentation

- PCDD/F release from pesticide use and increase in release from biomass impacted by pesticides.
- Some basic information on parameters relevant for formation of PCDD/Fs in incinerators.
- National strategies and national situation on biomass residue/waste management.
- Technologies used for thermal recovery of biomass residues
- PCDD/F formation and emission from biomass boilers.
- BAT/BEP to reduce PCDD/F formation and release
- Ash management considering PCDD/F, heavy metals & nutrients
- Utilizing options of ashes from biomass combustion.

PCDD/F release from pesticide use and increase in release from biomass impacted by pesticides

PCDD/PCDF formation from precursors

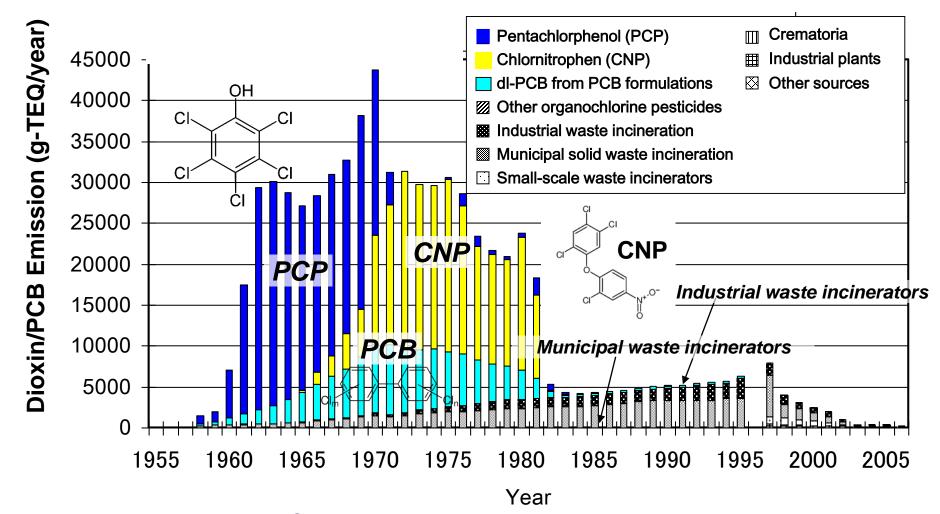
The history of polychlorinated dibenzo-p-dioxins & dibenzofurans (PCDD/Fs) is closely related to the production of chlorinated aromatic chemicals (chlorophenols, PCBs, chlorobenzenes).



e.g. Pentachlorophenol (PCP) 2,4-D a major used pesticide (2,4,5-T; Agent Orange Seveso) The total TEQ of PCP treated wood in Sweden was estimated to 205-250 kg TEQ. (Swedish EPA 2005)

The global dioxin inventory today is approx. 100 kg TEQ. (Wang et al. 2016)

Example for Impact of Application of Chlorinated Aromatics -Historical PCDD/PCDF Input into the Japanese Environment



Approximately 460 kg TEQ has been released into the Japanese environment from pesticide use and approx. 120 kg TEQ from the use of PCBs. This can be compared to the total global dioxin inventory today is approx. 100 kg TEQ. Masunaga 1999; Weber et al. (2008) Env Sci Pollut Res 15, 363-393; Wang et al. (2016) Chemosphere 151 303-309 High PCDD/F contamination in PCP treated & recycled wood ⁶

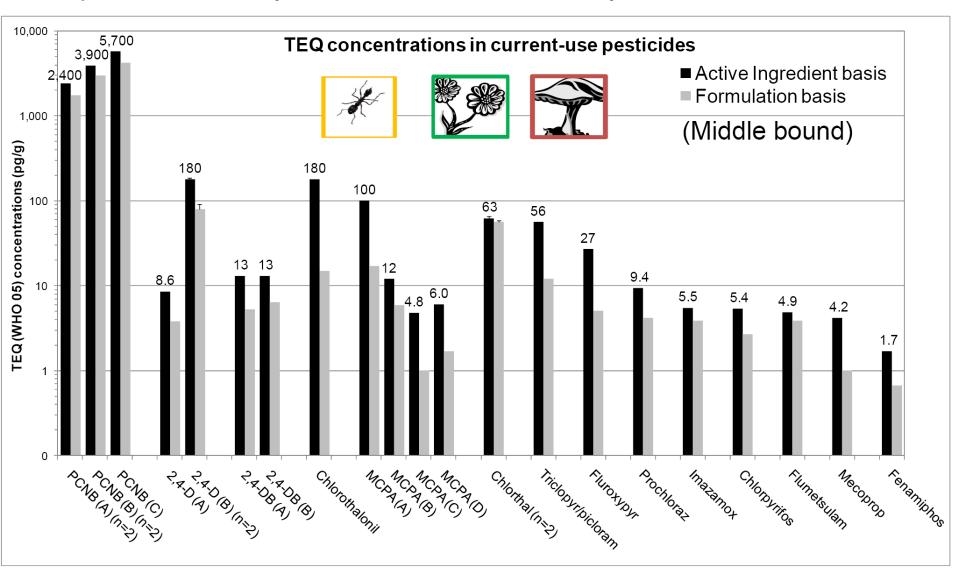
- A large share of PCP was used for treatment of construction wood, utility poles and railway sleepers with high PCDD/F contamination. A share of treated wood of the past 70 years is still in use and can enter recycling or contaminate food by use in smoking of meat or fish or drying of fooder.
- The use of PCP is still exempted for wood treatment (poles & cross arms).

Waste type	PCDD/F	dl-PCB	Country	Reference
Wood at animal prod. facilities	n.d91 620	-	USA	Huwe et al., 2004
Sleepers	21 000	0.93	Japan	Asari et al., 2004
Waste wood chips	0.94	0.51	"	"
Untreated wood	0.006	0.30	"	"
Litter	0-0.86	0.19-240	"	"
PCP treated wood	11-315 000	-	-	Fries et al., 2002
Impregnated wood	67- 38 000	-	various	SEPA, 2009
Wood litter	50ª	-	Italy	Brambilla et al., 2009

n.d.; not detected, ^a the concentration was published as 50 000 ng WHO-TEQ kg⁻¹ but was corrected to 50 ng WHO-TEQ kg⁻¹ after correspondence with the author; PCP: *penta*-chlorophenol Swedish EPA (2011) Low POP Content Limit of PCDD/F in Waste What is the situation of wood treatment in Columbia and what wood treatment has been used in the past?

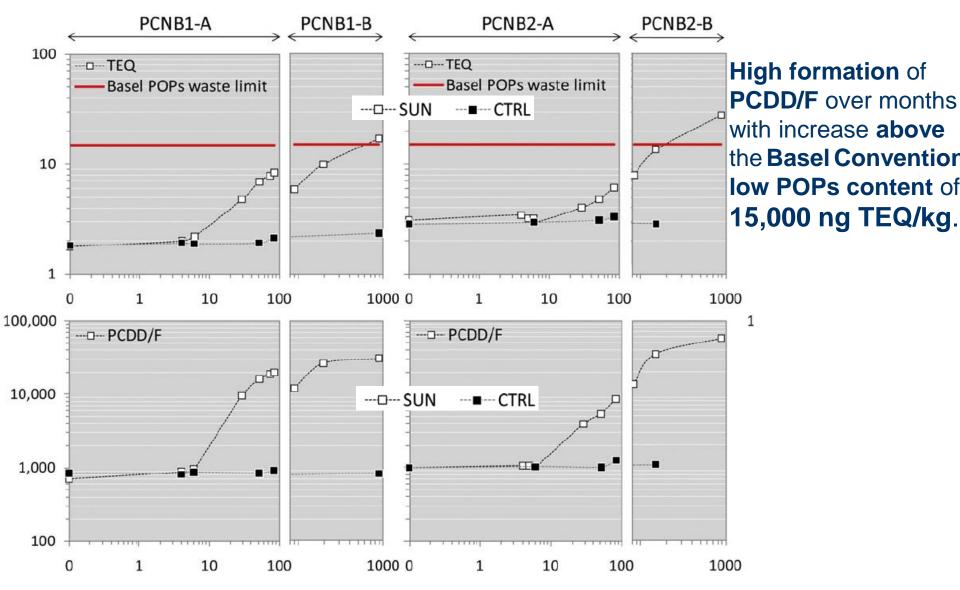
PCDD/Fs in some Pesticides used in Australia

In all pesticides analysed in an Australian study, PCDD/F were detected.



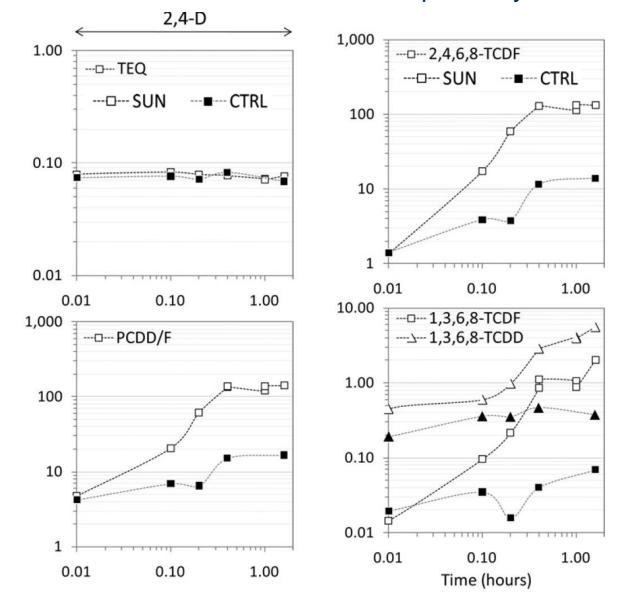
Holt, Weber et al Environ Sci Technol. 2010, 44(14):5409-5415 DOI: 10.1021/es903915k

Some pesticides form PCDD/Fs under sunlight[®] PCDD/F formation from Pentachloronitrobenzene (PCNB) under sunlight



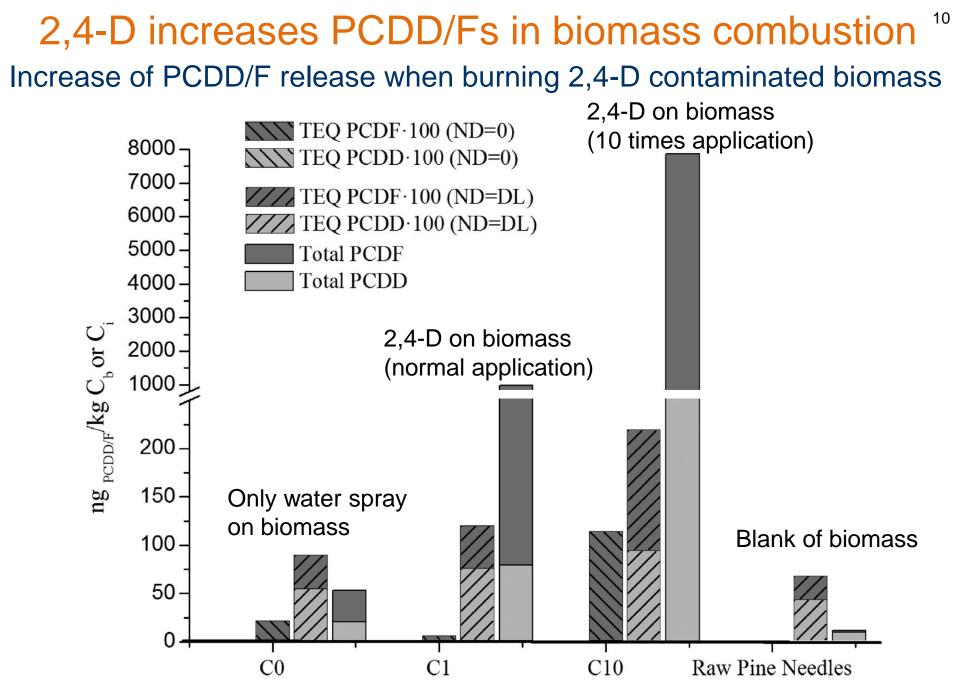
Holt et al. (2012) Chemosphere. 88,364-370 https://doi.org/10.1016/j.chemosphere.2012.03.058

Some pesticides form PCDD/Fs under sunlight⁹ PCDD/F formation from 2,4-Dichlorophenoxyacetic acid (2,4-D) under sunlight



Only non-dioxin-like PCDD/Fs were formed from 2,4-D under sunlight. Therefore no TEQ increase was observed.

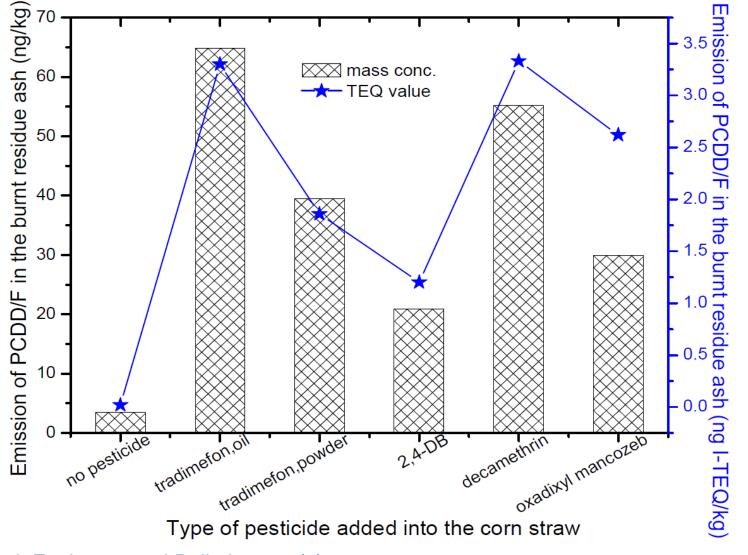
Holt et al. (2012) Chemosphere. 88,364-370 https://doi.org/10.1016/j.chemosphere.2012.03.058



Munoz et al. Environ. Sci. Technol. 2012, 46, 9308-9314

Pesticides increase PCDD/Fs in biomass combustion

PCDD/Fs increased by ca. one order of magnitude in residue ash from open burning of corn straw when pesticides were added.



Zhang et al. Environmental Pollution 159(6):1744-1748.

6a Open Biomass Burning

New Emission Factors UNEP Toolkit 2013

Emission Factors µg TEQ/t biomass

	Air	Land
Agricultural residue burning, impacted*	30	10
Agricultural residue burning, not impacted	0.5	0.05
Sugarcane burning	4	0.05
Forest fires	1	0.15
Grassland and savannah fires	5	4

*"Impacted" is considered when pesticides have been used.

UNEP Toolkit PCDD/PCDF Emission Factors

- Emission Factors in the UNEP Toolkit for biomass combustion are orders of magnitude lower compared to waste incineration.
- If clean biomass is combusted levels are very low. However increase by an order of magnitude if treated waste biomass is co-incinerated ("mixed biomass" misleading – it should be considered "treated").

3k	b Biomass Power Plants	Emission Factors (µg TEQ/TJ biomass burned)						
Classification		Air	Water	Land	Product	Residue*		
1	Mixed biomass fired power boilers	500	ND	NA	NA	ND (500)		
2	Clean wood fired power boilers	50	ND	NA	NA	15		
3	Straw fired boilers	50	ND	NA	NA	70		
4	Boilers fired with bagasse, rice husk, etc.	50**	ND	NA	NA	50		

* Total of bottom ash and fly ash.

** Estimate based on straw combustion, Thailand: Installation with APC: ca. 20 μ g TEQ/TJ.

Some basic information on parameters relevant for the formation of PCDD/Fs in an incinerator

"Trace Chemistry of Fire"

Complete combustion $C_xH_y + O_2 ----> CO_2 + H_2O$

Incomplete combustion (all real processes!!)

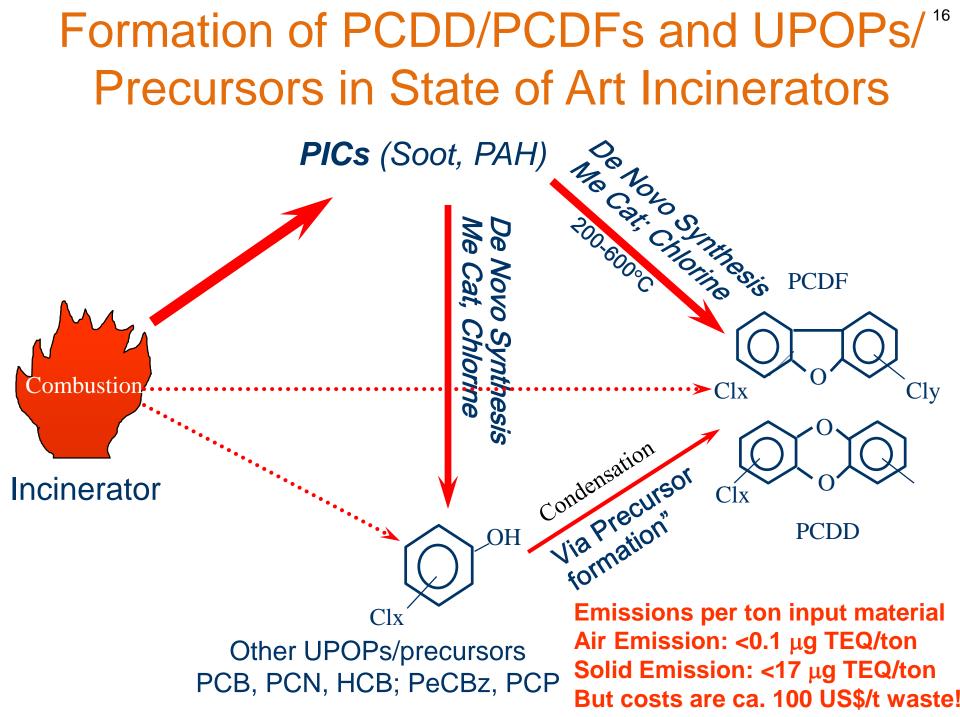
 $C_x H_y + O_2 = ----> CO2 + CO + H_2O$

----> C_xH_yO_z (incl. Aromatics PAH) +H₂O (Products of incomplete combustion (PIC))

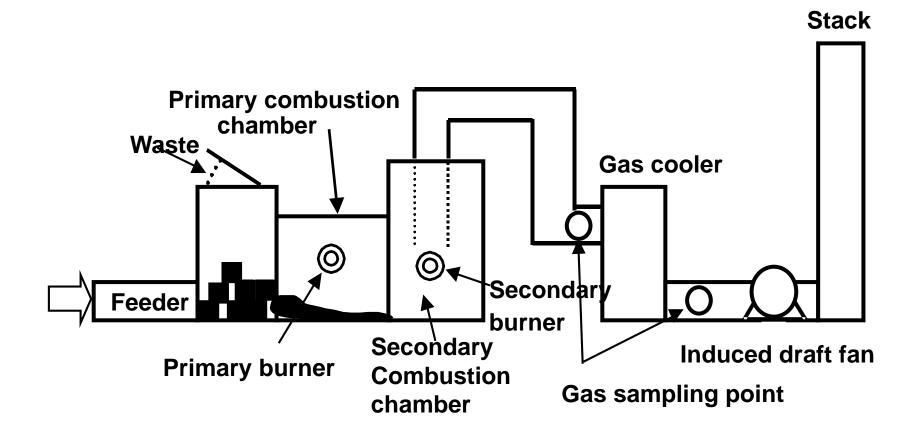
If chlorine is present in combustion process

 $C_xH_y + O_2 + CI \text{ source} ----> C_xH_yO_z + C_xH_yO_zCI_m + CI-Aromatic + PCDD/F$

(Trace Chemistry of Fire; Bumb et al. 1980)



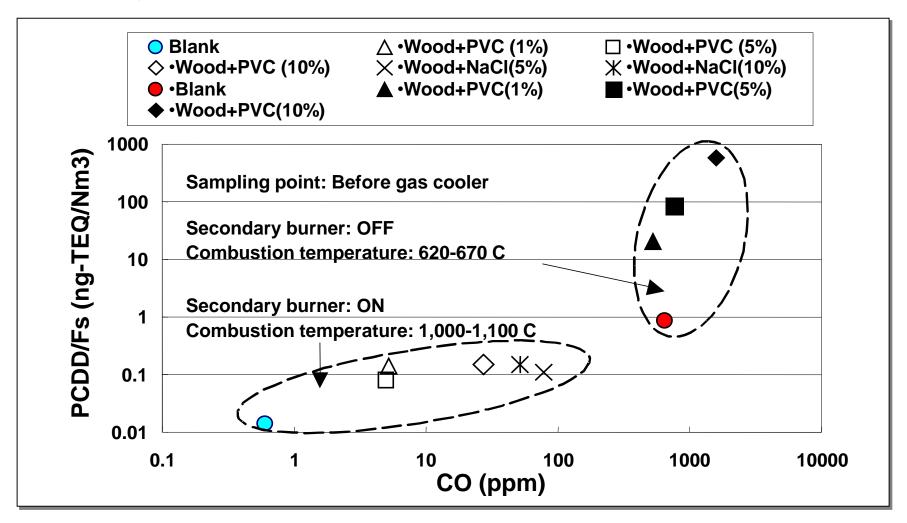
Key Parameters of PCDD/F Formation in Incineration



Ikeguchi & Tanaka, (2001) Organohalogen Compound 50, 390-393. http://dioxin20xx.org/wp-content/uploads/pdfs/2001/01-198.pdf

Key parameter for PCDD/Fs: Combustion Quality¹⁸

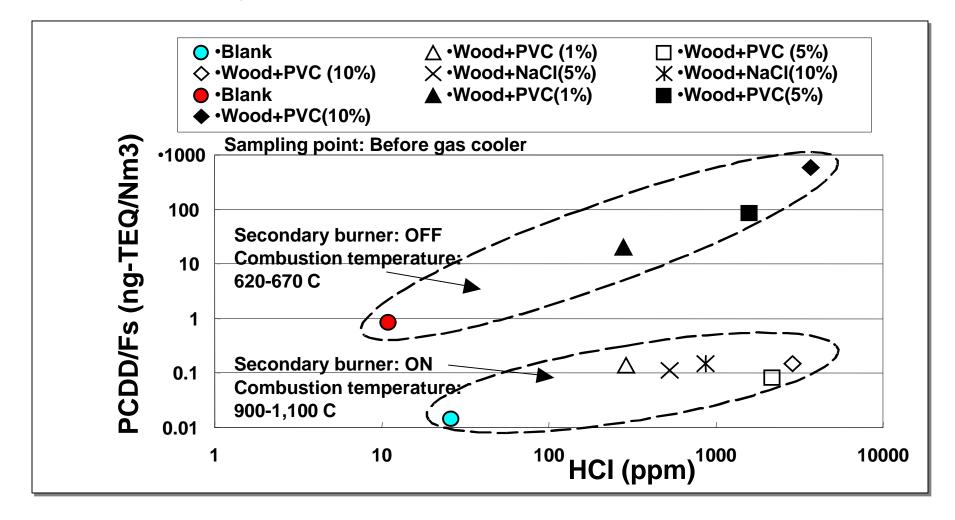
Low PCDD/F levels in all experiments with good good combustion quality (secondary combustion burner on with temperature above 1000°C)



Ikeguchi & Tanaka, (2001) Organohalogen Compound 50, 390-393. http://dioxin20xx.org/wp-content/uploads/pdfs/2001/01-198.pdf

Key parameter for PCDD/Fs: Chlorine Content

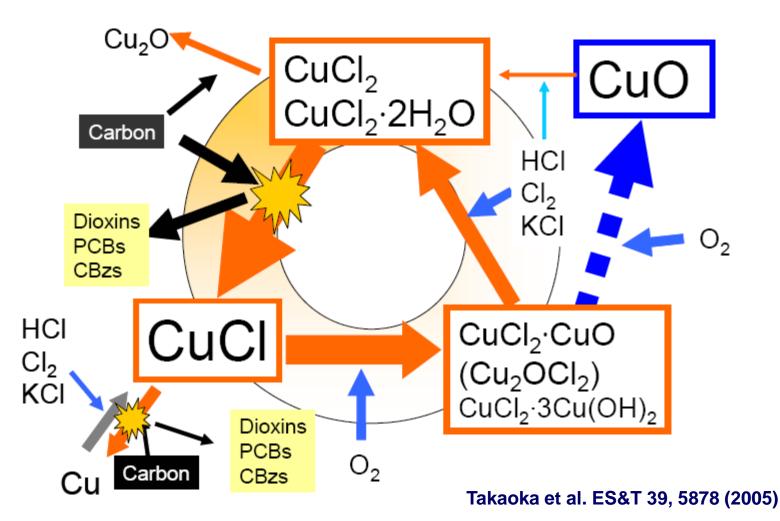
For low combustion quality, PCDD/F levels linearly increase with Cl/ PVC content. For good combustion quality no impact of Cl/PVC content.



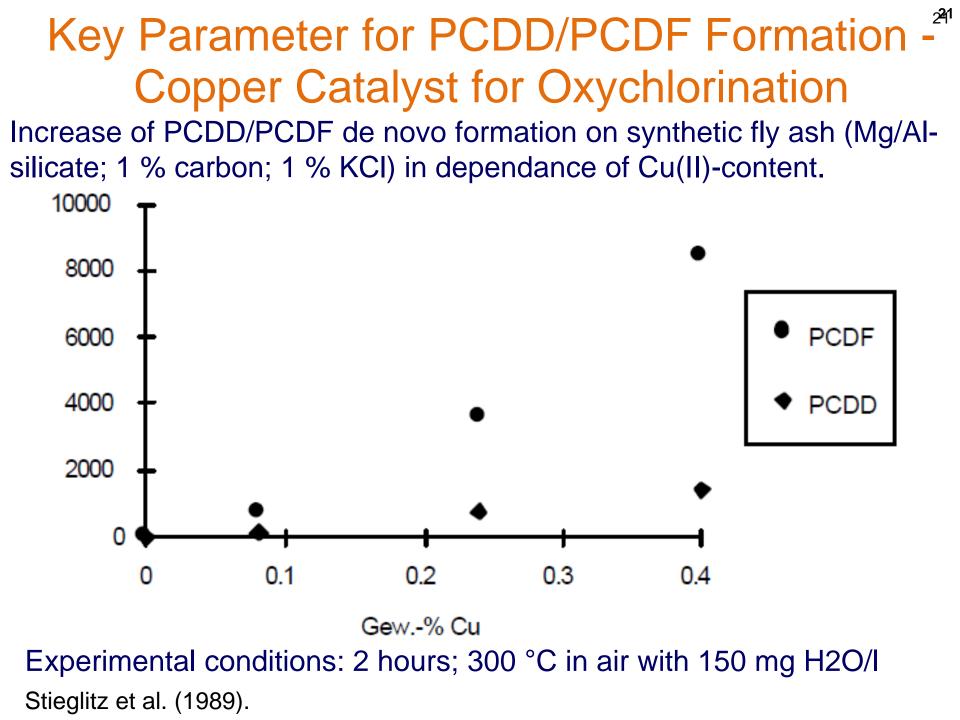
Ikeguchi & Tanaka, (2001) Organohalogen Compound 50, 390-393. http://dioxin20xx.org/wp-content/uploads/pdfs/2001/01-198.pdf

Key Parameter for PCDD/PCDF Formation -Copper Catalyst for Oxychlorination

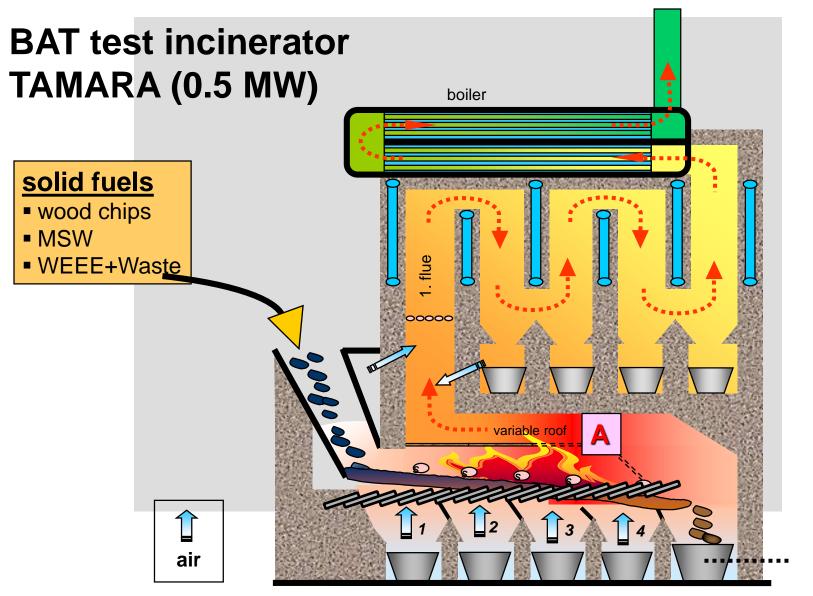
De novo formation of PCDD/PCDF is best catalysed by copper present in waste (including waste wood) (and less by other metals Cr, Fe, Ni).



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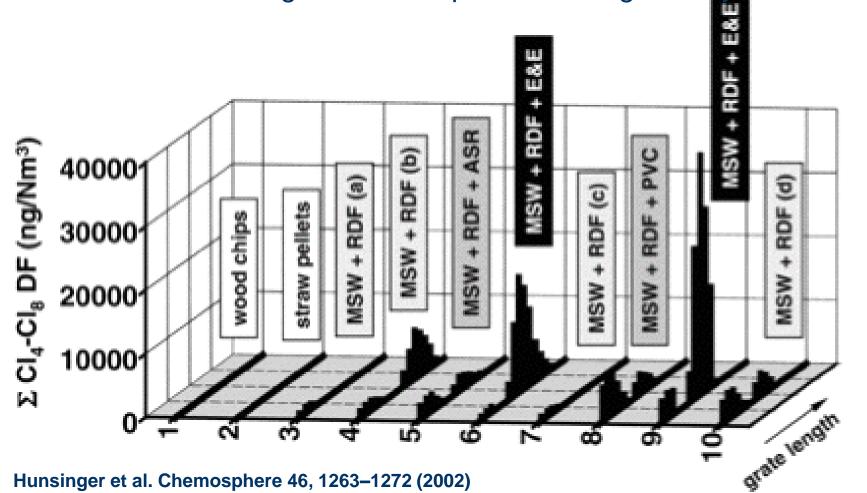


PCDD/PCDF Formation in the 1st Combustion Zone ²²
 ~ Uncontrolled/non-BAT Incinerators and Gasification



Hunsinger et al. Chemosphere 46, 1263–1272 (2002)

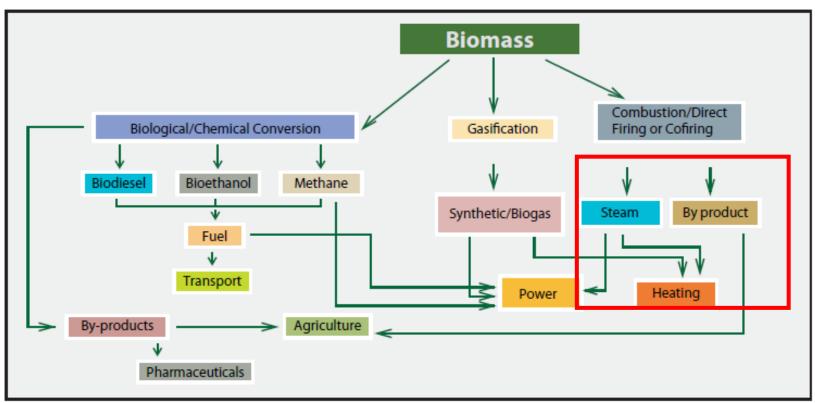
PCDD/PCDF Formation in the 1st Combustion Zone - ²³
 Primitive Technology & Uncontrolled Combustion
 PCDF emission from first combustion zone – strong dependence on the waste composition (biofuel, MSW, ASR; or E-waste)
 Clean biomass has low PCDD/F formation potential (low metal content).
 While e-waste has high formation potential – high catalytic metal content.



National strategies and national situation on biomass residue/waste management

Biomass – combustion, gasification & fuel production

- Countries with high biomass residues should make a biomass strategy.
- E.g. under the Philippine renewable energy plans and programs is implementing biomass use. Combustion of biomass is one focal area
 ⇒ Therefore increase of biomass combustion.
- The 10th million t of biomass result in 100,000 t of ashes.



Source: Philippine Department of Energy

Estimated biomass energy potential in Colombia²⁹

- Agricultural residues are increasing biomass generated in Columbia
- Wood and wood waste are other major biomass in Columbia.

 Also animal & mu 	Bic	mass categories		Preliminary technical potential					
have biomass fractions and materials for thermal recovery.						Mean (T			ce interval pability)
			Ag	ricultural residues		25642	-67	%	76%
 Different types of 	biomas	ses	Animal waste			23202	-37	%	41%
including waste wood might end				dForestry			-73	%	92%
up in biomass power plants.				oan waste	6722		-46	%	60%
	tal		78607	-36	%	39%			
Biomass categories	-			•			retical potential excluding bove-ground biomass		
	Mean (EJ	(EJ) Confidence interval Me (95% probability)			Me	an (EJ)	n (EJ) Confidence interval (95% probability)		
Agricultural residues	0.40	-14.9	9%	17.4%	0.40	כ	-14.9%	17.4	4%
Animal waste	0.15	-31.:	1%	40.5%	0.1	5	-31.1%	40.5	5%
Forestry	219.32	-45.4	4%	46.3%	0.19	Э	-48.7%	61.2	1%
Urban waste	0.01	-35.7	7%	40.4%	0.0 2	1	-35.7%	40.4	4%
Total	219.88	-45.5		46.0%	0.7	5	-17.0%	19.3	3%

Gonzalez-Salazar MA et al. (2014) Applied Energy 136:781-796

Biomass residues increasing in Columbia³⁰

Columbia has high volume of biomass residues available from 4 major agricultural production: Sugar cane, banana, coffee & palm oil (>50 Mt).

Estimated biomass potential from agricultural waste

Crop Year: 2010	Residue type	Amount of residue (million tonnes/yr)
Palm oil	Residues	1.7
Sugar cane	Bagasse	7.0
	Leaves	8.5
Panela sugar cane	Bagasse	5.7
	Leaves	3.8
Banana	Trunks	3.0
	Fibre	6.8
Coffee residue	Husk	13.6

• Biomass production is growing resulting in growing residue volumes.

 Government supports waste to energy (benefits established by Law 1715, e.g., accelerated depreciation of assets & income tax exemption).
 Netherlands Agency Ministry of Foreign Affairs (2013) Biomass Opportunities in Colombia.

Assessment of suitability - which thermal use?³¹

- Palm kernel shell (PKS) is the biomass with the highest content of fixed carbon (22.78 wt % daf) and lignin (58.30 wt %); its hard structure, low ash content (2.67 wt %), and high lignin content make it most suitable for high-temperature processes like combustion & gasification processes.
- Sugar cane bagasse (SCB) has high volatile material (87.41 wt % daf), lignocellulosic composition high in hemicellulose (29.68 wt % daf) and cellulose (39.81 wt. daf), high alkali index (4.07), and soft morphology; this make it a good candidate for fast pyrolysis to produce bio-oil and gas.
- Rice husk (RH), despite having a lignocellulosic composition similar to SCB, has slightly less volatile matter than SCB (75.73 wt % daf), a soft morphological structure, and high ash content (19.33 wt %) mainly of non-catalytic species, which make RH unattractive for pyrolysis; however, its carbon content makes it interesting for combustion and gasification.
- Wt (weight); daf (dry and ash free)

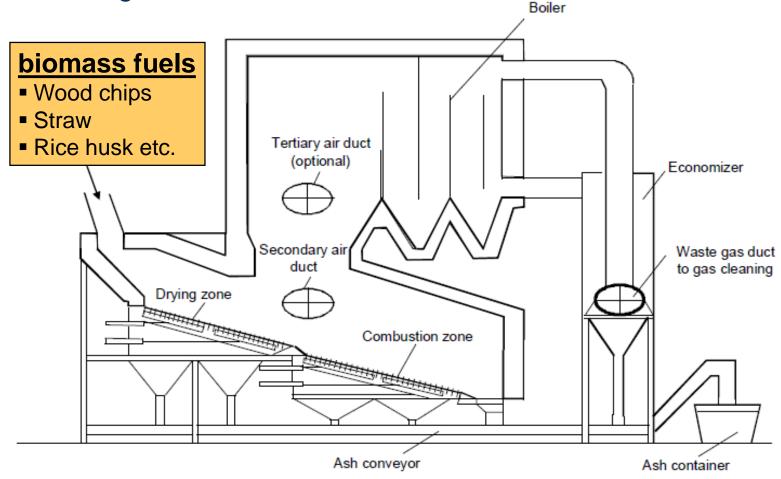
Marrugo et al. (2016) Energy Fuels 30 (10), 8386-8398.

Technologies used for thermal recovery of biomass residues

Technologies used for Biomass Boilers

- If a country start to develop a thermal biomass use concept, then technologies need to be evaluated, selected and supervised.
- The Stockholm Convention BAT/BEP guidance has an own chapter on BAT/BEP for biomass boilers.
- Large-scale installations for firing wood and other biomass fuels mainly use fluidized bed combustion and grate furnaces.
- Technologies for small-scale plants include underfeed furnaces and cyclone suspension furnaces.
- Recovery boilers in the pulp and paper industry apply specific combustion conditions.
- Technology selection is related to fuel properties and required thermal capacity.

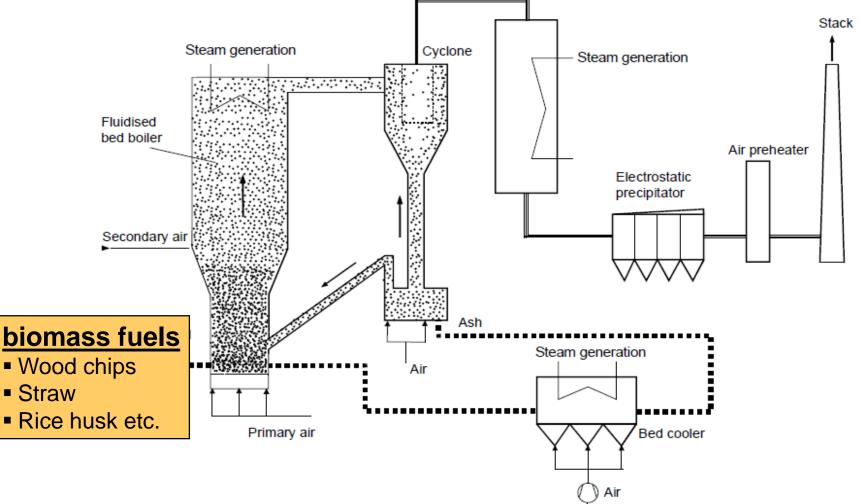
Secretariat of the Stockholm Convention (2008) BAT/BEP Guidelines Annex C POPs http://www.pops.int/Implementation/BATBEP/BATBEPGuidelinesArticle5/tabid/187/Default.aspx ³⁵ Biomass fuel is moved through the combustion chamber using moving grates, traveling grates, stationary sloping grates, or vibrating grates. Fine particle fuels, as pulverized wood or fine straw/rice husk, may be injected through additional burner lances.



Secretariat of the Stockholm Convention (2008) BAT/BEP Guidelines Annex C POPs http://www.pops.int/Implementation/BATBEP/BATBEPGuidelinesArticle5/tabid/187/Default.aspx

BAT/BEP Technologies used for Biomass Boilers ³⁶

Fluidized bed combustion technologies: Two technologies are primarily used for wood combustion. Atmospheric bubbling fluidized bed combustion (FBC) and atmospheric circulating FBC.



Secretariat of the Stockholm Convention (2008) BAT/BEP Guidelines Annex C POPs http://www.pops.int/Implementation/BATBEP/BATBEPGuidelinesArticle5/tabid/187/Default.aspx

Technologies used for Biomass Boilers

Technology selection: Due to fuel properties and thermal capacity.

Application Type		Typical size range ^a	Fuels	Ash	Water content
Manual	Log wood boilers	5 kW-50 kW	Log wood, sticky wood residues	< 2%	5-30%
Automatic	Understoker furnaces	20 kW–2.5 MW	Woodchips, wood residues	< 2%	5-50%
	Moving grate furnaces	150 kW–15 MW	All wood fuels and most biomass	< 50%	5-60%
	Pre-oven with grate	20 kW-1.5 MW	Dry wood (residues)	< 5%	5-35%
	Understoker with rotating grate	2 MW-5 MW	Woodchips, high water content	< 50%	40-65%
	Cigar burner	3 MW-5 MW	Straw bales	< 5%	20%
	Whole bale furnaces	3 MW-5 MW	Whole bales	< 5%	20%
	Straw furnaces	100 kW-5 MW	Straw bales with bale cutter	< 5%	20%
	Stationary fluidized bed	5 MW-15 MW	Various biomass d < 10 mm	< 50%	5-60%
	Circulating fluidized bed	15 MW-100 MW	Various biomass d < 10 mm	< 50%	5-60%
	Dust combustor, entrained flow	5 MW-10 MW	Various biomass d < 5 mm	< 5%	< 20%

Secretariat of the Stockholm Convention (2008) BAT/BEP Guidelines Annex C POPs

European BAT Reference (BREF) Document for³⁹ large combustion plants and waste incineration

The European BAT Reference documents for large combustion plants and waste incineration contain information on techniques which can be used for wood and other biomass combustion.



JRC SCIENCE FOR POLICY REPORT

Best Available Techniques (BAT) Reference Document for Waste Incineration

> Industrial Emissions Directive 2010/75/EU (Integrated Pollution Prevention and Control)

Frederik Neuwahl, Gianluca Cusano, Jorge Gómez Benavides, Simon Holbrook, Serge Roudier

2019





JRC SCIENCE FOR POLICY REPORT

Best Available Techniques (BAT) Reference Document for Large Combustion Plants

> Industrial Emissions Directive 2010/75/EU (Integrated Pollution Prevention and Control)

Thierry Lecomte, José Félix Ferrería de la Fuente, Frederik Neuwahl, Michele Canova, Antoine Pinasseau, Ivan Jankov, Thomas Brinkmann, Serge Roudier, Luis Delgado Sancho

2017



https://eippcb.jrc.ec.europa.eu/reference

PCDD/F levels in biomass incinerators and major factors

UNEP Toolkit PCDD/PCDF Emission Factors

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- Emission Factors in the UNEP Toolkit for biomass combustion are orders of magnitude lower compared to waste incineration.
- If clean biomass is combusted levels are quite low. However, increase by an order of magnitude if treated waste biomass is co-incinerated ("mixed biomass").

3b	Biomass Power Plants	Emission Factors (µg TEQ/TJ biomass burned)						
Classification		Air	Water	Land	Product	Residue*		
1	Mixed biomass fired power boilers	500	ND	NA	NA	ND (500)		
2	Clean wood fired power boilers	50	ND	NA	NA	15		
3	Straw fired boilers	50	ND	NA	NA	70		
4	Boilers fired with bagasse, rice husk, etc.	50**	ND	NA	NA	50		

* Total of bottom ash and fly ash.

** Estimate based on straw combustion, Thailand: Installation with APC: ca. 20 μ g TEQ/ TJ.

UNEP PCDD/PCDF Emission Factors

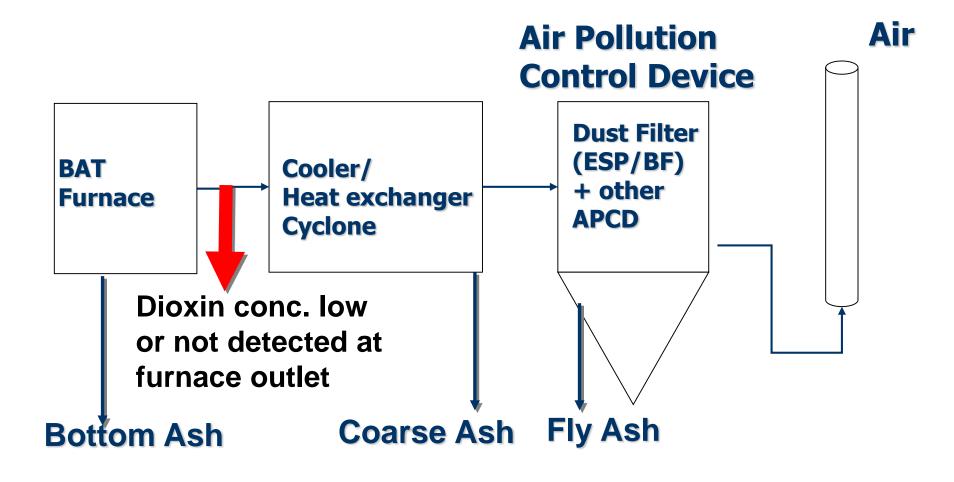
Emission Factors UNEP Toolkit for waste biomass combustion

1f	Waste Wood and Waste Biomass Incinerators	Emission Factors (µg TEQ/t biomass burned) (recalculated)		
Clas	sification	Air	Residues (fly ash)	
1	Older furnaces, batch type operation, no or very little APCS	100	1,000	
2	Updated, continuously operated and controlled facilities, some APCS	10	10	
3	Modern state-of-the-art facilities, continuous, controlled operation, full APCS	1	0.2	

High emission from waste wood combustion in old/small furnaces.

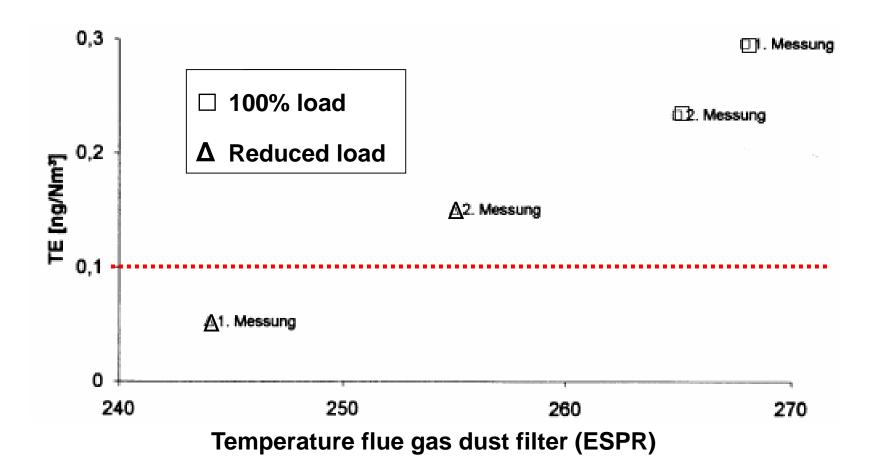
http://toolkit.pops.int/Publish/Main/II_01_Waste.html

PCDD/PCDF Formation in BAT Biomass Boilers



PCDD/Fs Formation in the Cooling Zone

Operation temperature of dust filter (ESP) of a wood boiler and PCDD/F concentration in flue gas.



Strecker (1994) WKI-Bericht 30, Fraunhofer Arbeitsgruppe für Holzforschung, Braunschweig 1994, 91–100

PCDD/F release from biomass boilers

 The use of herbaceous biofuels (straw, whole plant cereals and setaside hay) has higher chlorine content with associated **somewhat** higher PCDD/F emission in biomass boilers.

Fuel type	PCDD/PCDF ng I-TEQ/m ³
Wood (spruce)	0.052
Straw (wheat)	0.656
Hay	0.891
Triticale	0.052
Canola pellets	0.245

Secretariat of the Stockholm Convention (2008) BAT/BEP Guidelines Annex C POPs; LFU 2002

PCDD/F release from biomass boilers

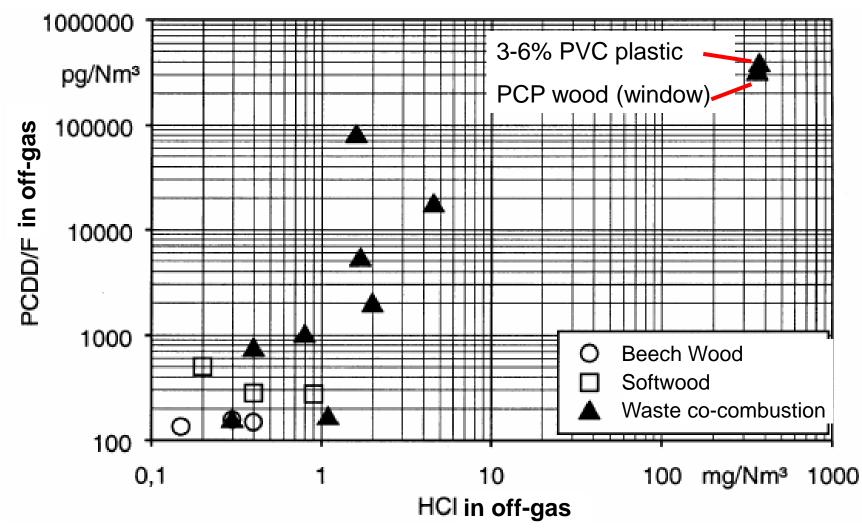
 The use of waste wood with high chlorine content or other waste containing chlorine can increase the emission from biomass boilers by several orders of magnitude.

Type of wood	PCDD/PCDF min. ng I-TEQ/m³ (at 11% O ₂) ^a	PCDD/PCDF max. ng I-TEQ/m³ (at 11% O ₂)
Lump wood (natural)	0.02	0.13
Woodchips (natural)	0.004	0.88
Wood waste	0.03	18.0
Chlorine/heavy metal-free particle board	0.03	0.10
Particle board with PVC or ammonium chloride (NH ₄ Cl)	0.05	12.28
Particle board with pentachlorophenol	0.21	5.14

Secretariat of the Stockholm Convention (2008) BAT/BEP Guidelines Annex C POPs

Factors in Biomass combustion influencing PCDD/PCDF release

Chlorine is a limiting factor for PCDD/PCDF formation from biomass.

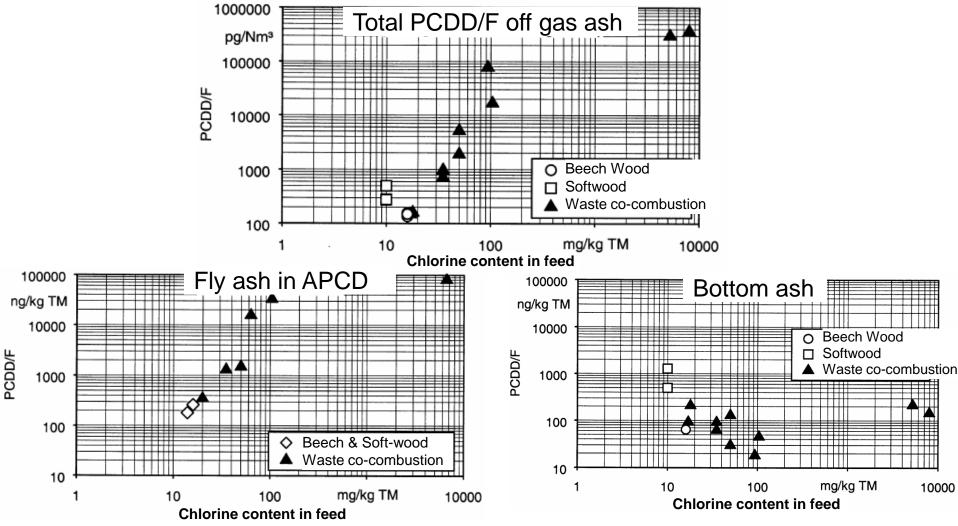


Launhardt et al. (1998) Schriftenreihe StMLU, Materialien Band 142, München 1998).

Factors in Biomass combustion influencing PCDD/PCDF release

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Also resulting fly ashes are contaminated with PCDD/PCDF depending on chlorine fuel input. However bottom ashes have similar levels.



Launhardt et al. (1998) Schriftenreihe StMLU, Materialien Band 142, München 1998).

High PCDD/F levels in ash from waste wood boilers

- Two wood boilers in Taiwan incinerating wood chips from waste wood were assessed for PCDD/F formation and release.
- PCDD/F and dI-PCB concentrations in the raw gas of Plant A were significantly higher than that of Plant B due to the lower combustion temperature in Plant A (500-850°C) compared to Plant B (850-925°C).
- PCDD/Fs levels in Bag Filter ash of Plants A & B during normal operation were 98.6 and 38.1 ng I-TEQ/g, This is higher than ashes from MSWI and the limit promulgated by Taiwan EPA (1.0 ng I-TEQ/g) and even higher than the Basel low POPs content of 15 ng TEQ/g.
- In addition, PCDD/F and dI-PCB concentrations during the start-up period were much higher than those measured during normal operation and shut-down periods due to unstable combustion.

Bai et al. (2017) Chemosphere 189, 284-290.

Contaminated biomass as PCDD/F source

 Contaminated wood and other contaminated biomass can result from many anthropogenic activities, particularly wood processing industries (e.g. building materials, furniture, packing materials, toys, shipbuilding and general construction).

(Secretariat of the Stockholm Convention (2008) BAT/BEP Guidelines Annex C POPs)

- Wood/biomass waste may contain pesticides/PCP, paints, coatings, preservatives, antifouling agents and many other contaminants.
 These are often sources of chlorine and heavy metals. PCP is an excellent PCDD/F precursors.
- Copper compounds are used (Chromated copper arsenate (CCA), alkaline copper quaternary, copper azole) which are the best catalysts for PCDD/F formation. These materials can enhance the formation of PCDD/F by order(s) of magnitude.
- Such biomass should be incinerated in dedicated waste wood incinerators or waste incinerators or co-incinerated (cement kiln).

Impact of Copper Content on PCDD/F Formation for Biomass Combustion

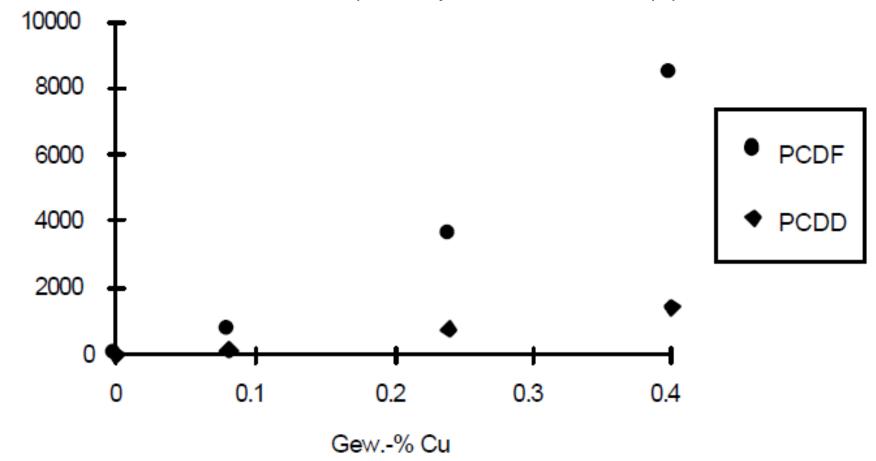
- The catalyst content is another major limiting factor for PCDD/F formation in virgin biomass combustion.
- The presence of catalytic metals in biomass combustion can increase the PCDD/F formation by several orders of magnitude.
- Key sources of catalytic metals e.g.
 - Cu-Arsenate treated wood (used in Columbia?)
 - Waste wood containing other copper salts or other metals.
 - Co-combusted waste fractions.

 \Rightarrow Keep copper/other heavy metals out of biomass combustion!

What is the status of the use of CCA and other copper compounds in wood treatment in Columbia?

Impact of Copper Content on PCDD/F Formation

Increase of PCDD/PCDF de novo formation on synthetic fly ash (Mg/Alsilicate; 1 % carbon; 1 % KCI) in dependance of Cu(II)-content.



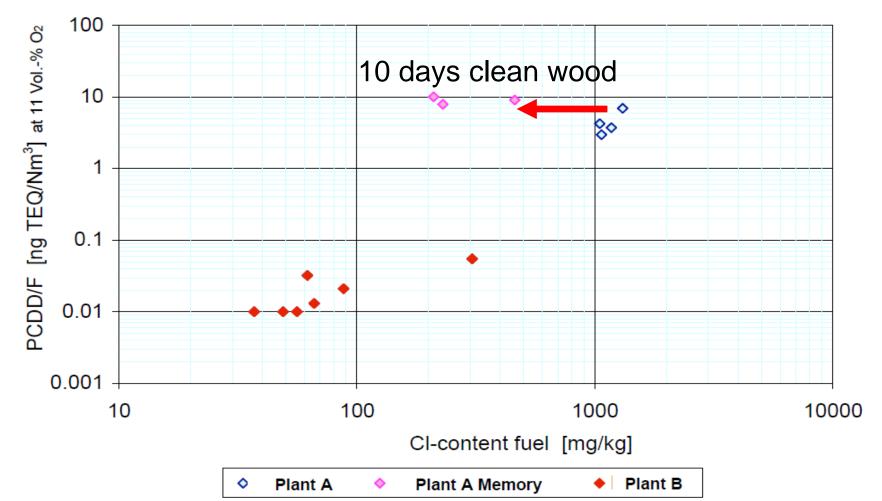
Experimental conditions: 2 hours; 300 °C in air with 150 mg H2O/I Stieglitz et al. (1989).

PCDD/Fs long term formation – Memory effect chlorine and catalytic metal

- Waste wood or waste with high chlorine content and catalytic metals increase emission from boilers by orders of magnitude.
- The heavy metal and chloride contaminate the surface of the boiler and cooling line including the *de novo* area and result in the long term contamination of biomass boiler. After changing to virgin wood, the levels do not decrease for some time since heavy metal catalysts & chloride stay as active surface in *de novo* area.
- Such a "memory effect" can last for long time (weeks) after contaminate waste/wood has been fed into the biomass boiler.
- ⇒ Therefore care need to be taken that facilities are continuously operated with virgin biomass. No waste should be co-combusted. Waste wood or waste should be incinerated in dedicated facilities with specific abatement technology.
- Note: In incinerators a "carbon memory effect" only take hours/day(s).

PCDD/Fs long term formation – Memory effect chlorine & catalytic metal

The use of waste wood with high chlorine & catalytic metal content results in long term contamination and release of biomass boiler.



Fastenaekel (2003) Dioxinmessungen an Holzfeuerungen. In BUWAL (2004) UMWELT-MATERIALIEN NR. 172.

BAT/BEP to reduce PCDD/F formation & release from biomass incineration

BAT/BEP Biomass Boilers: Selection and separation of fuels

- **Treated wood** and other wastes can significantly increase the formation of PCDD/PCDFs during combustion.
- As such, the use of treated wood in firing installations for energy production and ash recovery should be avoided and they should only be burnt in dedicated waste incinerators with flue gas treatment and ash disposal.
- Among the primary measures, control of fuel quality is a key issue (including exclusion of treated wood) for biomass combustion where ashes are recycled to land.

Secretariat of the Stockholm Convention (2008) BAT/BEP Guidelines Annex C POPs

Key BEP is a regulatory frame: Definition and ⁶⁰ management of waste wood categories

- The different waste wood (and waste biomass) contamination/risk levels are best reflected in a regulation with categorization.
- Example of waste wood categorization (regulation Germany):
- a) Waste wood category A I: Waste wood in its natural state or only mechanically worked which, or was during use not contaminated with hazardous substances;,
- b) Waste wood category A II: Bonded, painted, coated, lacquered or otherwise treated waste wood with no halogenated organic compounds in the coating and no wood preservatives;
- c) Waste wood category A III: Waste wood with halogenated organic compounds in the coating, **with no wood preservatives**,
- d) Waste wood category A IV: Waste wood treated with wood preservatives, such as railway sleepers, telephone masts, hop poles, vine poles as well as other waste wood which, due to its contamination, cannot be assigned to waste wood categories A I, A II or A III. With the exception of waste wood containing PCBs falling under PCB waste.

Waste hierarchy to manage waste wood

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Wood Waste Grade	Typical Markets	Typical Source of Raw Material for Recycling	Materials Within Wood Waste Grade	Typical Non – Wood Content Prior Processing
Grade A "Clean" Recycled Wood	Manufacture of products such as animal bedding, horticultural mulches, and the panelboard sector. Fuel in non WID installations, or manufacture of pellets/briquettes.	Distribution Retailing Packaging Secondary manufacture e.g. Joinery Pallets	Solid softwood and hardwood, packaging waste, scrap pallets, packing cases, and cable drums. Process off-cuts from joinery	Nails and metal fixings. Minor amounts of paint, and surface coatings.
Grade B Industrial Feedstock Grade	A feedstock for industrial wood processing operations such as the manufacture of panel products, including chipboard and medium density fibreboard.	As Grade A, plus construction and demolition operations, and Transfer Stations.	May contain up to 60% Grade Amaterial as above, plus building and Demolition materials and domestic furniture made from solid wood.	Nails/metal fixings. Some paints, plastics, glass, grit, coatings, binders and glues. Limits on treated or coated materials as defined by WID.
Grade C Fuel Grade	Biomass fuel for use in the generation of electricity and/or heat in WID compliant installations.	All above, plus Municipal Collections Recycling Centres/sites Transfer Stations, And Civic Amenity	All of the above, Plus fencing, flat pack furniture made from board products and DIY materials High content of panel products: chipboard, MDF, plywood, OSB and fibreboard.	Nails and metal fixings. Paints coatings and glues, paper, plastics and rubber, glass, grit. Coated and treated timber (non CCA or creosote).
Grade D Hazardous Waste	Requires disposal at special facilities.	All of the above plus fencing, track work and transmission pole contractors.	Fencing, Transmission Poles Railway sleepers Cooling towers	Treatment with Copper/ Chrome/ Arsenic CCA Creosote, PCP, chlorinated fungicide

UK Defra (2012) Wood waste: A short review of recent research. July 2012 (with additions)

Eu	Iropean Waste Catalogue – Wood	Waste	62
03	WASTES FROM WOOD PROCESSING AND THE PRODUCTION OF PANELS AND FURNITURE, PULP, PAPER AND CARDBOARD		
03 01	wastes from wood processing and the production of panels and furniture		
03 01 01	waste bark and cork	AN	
03 01 04*	sawdust, shavings, cuttings, wood, particle board and veneer containing hazardous substances	MH	
03 01 05	sawdust, shavings, cuttings, wood, particle board and veneer other than those mentioned in 03 01 04	MN	
03 01 99	wastes not otherwise specified	AN	
03 02	wastes from wood preservation		
03 02 01*	non-halogenated organic wood preservatives	AH	
03 02 02*	organochlorinated wood preservatives	AH	
03 02 03*	organometallic wood preservatives	AH	
03 02 04*	inorganic wood preservatives	AH	
03 02 05*	other wood preservatives containing hazardous substances	MH	
03 02 99	wood preservatives not otherwise specified	MN	
Absolute I	Hazardous AH; Mirror hazardous MH;		

Absolute Non-Hazardous AN; Mirror Non-hazardous MN

European Waste Catalogue Wood waste:

BAT/BEP PCDD/F control Biomass Boilers

- **Control** of **fuel quality** (e.g. calorific value, water content, contaminants); contaminated wood should be limited to waste wood (co-)combustion;
- Optimized combustion technology: Improved burnout of gases and fly ash and reduction of dust content: a) Optimize excess air ratio to < 1.5–2 (burn-out versus energy efficiency), b) Good mixing quality of gas and air (high turbulence); Sufficient residence time in the hot zone; Minimal disturbance of the glow bed and homogeneous distribution of primary air;
- Measures in the boiler: Minimal residence time in the temperature range 180°C and 500°C and minimal dust deposition ability;
- Optimized plant operation:
 - Advanced combustion control technologies;
 - Continuous operation (24 h) prevention of rapid changes;
 - Cleaning of the hot zone of flue gases at regular intervals.

Secretariat of the Stockholm Convention (2008) BAT/BEP Guidelines Annex C POPs (Nussbaumer and Hasler 1998).

BEP: Environment Management System (EMS) for fuel and operation

- Define acceptance criteria and procedures;
- Define refusal criteria;
- Define appropriate fuel conditions;
- Define an Environmental Management System:
 - Mangement system for operation;
 - Management for maintenance;
 - Management for monitoring.



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Overview BAT/BEP PCDD/F Biomass Boilers

Management options	Emission level (%)	Estimated costs				
Primary measures						
Control of fuel quality (e.g. calorific value, water content, contaminants)	Resulting emission level not quantified	Higher fuel price				
Optimized burnout (e.g. reduction of excess air)		No additional cost for new installations				
Sufficient residence time of flue gases in the hot zone of the furnace						
Secondary measures						
Efficient dust abatement	Medium efficiency					

Secretariat of the Stockholm Convention (2008) BAT/BEP Guidelines Annex C POPs

 Adsorbtion (or catalytic abatement) technologies are normally not used for virgin biomass. However are needed for waste wood.

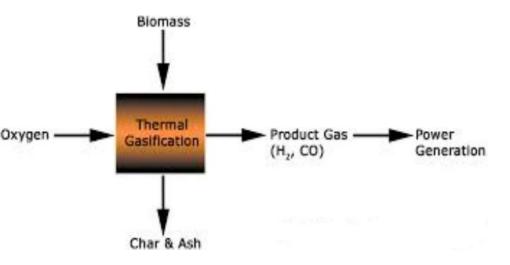
Co-combustion of waste wood as BAT

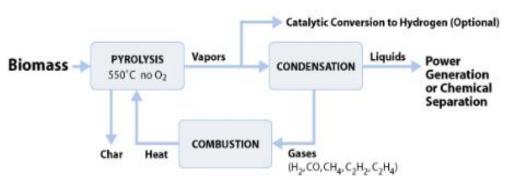
- Co-combustion means the burning of wood wastes and wood residues together with other waste materials or with fossil fuels.
- For wood waste and wood residues, relevant practices include co-combustion in cement furnaces, co-combustion in coal-fired power plants, co-gasification with fossil fuels and waste and co-incineration in waste incineration plants (CSTB 2000).
- The objective is to realize synergy effects between two combustion processes. Benefits include savings in operating costs through the use of cheaper secondary fuels.

Secretariat of the Stockholm Convention (2008) BAT/BEP Guidelines Annex C POPs

 The destruction of contaminated waste wood in facilities with high combustion efficiency of larger facilities (cement kilns; large power plants) results in lower overall emission compared to use of these materials in small wood boilers.

Gasification/Pyrolysis of Biomass





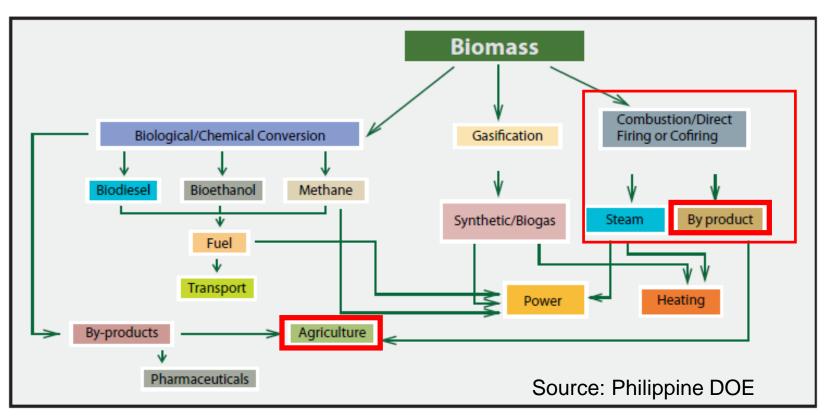
PCDD/F are not a relevant pollutant in biomass gasification/ pyrolysis. However very high PAHs levels in residues !

Gas cleaning is a crucial challenge. **Problem** associated with the **gas cleaning process** include **process control**, the **residue disposal**, and the **high investment** and **operating costs** of the gas cleaning unit itself (CSTB 2000). (Secretariat of the Stockholm Convention (2008) BAT/BEP Guidelines Annex C POPs)

BAT/BEP: Management of ashes considering PCDD/F, heavy metals and nutrients

Management of residues from biomass boilers

- The management of residues from biomass boilers is one key for the sustainable use of biomass.
- With the increased capacity of biomass the ash volume and related challenges in their management increases.
- The biomass concept of Philippines includes residue management.
- The main approach is bringing back residues/ash to agriculture/soil.



Need of concepts for ash management

- Large ash volumes can be generated from biomass incineration.
- E.g. the Philippines generated 2010 from thermal recovery of biomass approximately 161,000 tonnes of ashes which needed management.
- The levels of PCDD/PCDFs, heavy metals & PAHs determine, if the ashes can be used as fertilizers and be brought back to agricultural soil or forest soil or if it need to be disposed of or used otherwise!

	Ash Generation Activity Rate				
Biomass	Fuel Consumption in tons	Ash Content (%)	Ash Generated (tons)		
Fuel wood	8,472,979	1%	84,730		
Charcoal	689,783	8%	55,183		
Agricultural wastes	842,541	2.5%	21,064		
Total	10,005,303		160,977		

Innogy Solutions, Inc. (2013) 3rd national PCDD/PCDF inventory of the Philippines

BAT/BEP considerations for utilization of ashes from biomass combustion

BAT/BEP considerations for utilization of ashes from biomass

- Ash from biomass fuels contains valuable plant nutrients such as K, P, Mg and Ca,
- Depending on waste wood or other wastes used (chlorine/copper) these ashes might contain problematic levels of PCDD/Fs.
- Some of these ashes also contain significant amounts of heavy metals, which have also to be considered for the use strategy.
- Only the nutrient rich and rather heavy metal poor fractions (bottom ash and coarse fly ash) shall be used for fertilizing and soil improvement purposes.
- The heavy metal rich fine fly ash fraction, which represents the smallest fraction, should be industrially utilized or disposed of.
- Netherlands: Ashes from Biomass combustion are disposed and only if they are proven "clean" used in agriculture.

Problematic PCB and PCDD/F levels in soil for ⁷³ chicken egg and meat production

What are critical soil levels for contaminating eggs above regulatory limit?

- With a total uptake of 25 pg (50 pg) TEQ/day a chicken reaches the current EU-limit of 2.5 pg for PCDD/F TEQ/g fat in egg.
- Free range chicken which spend a lot of time outdoor have a soil uptake of 10 to 30% of their feed which translates to approx. 11-31 g soil/day.
- Considering a soil uptake of 20% and a carry over of approx. 50% for TEQ-relevant PCDD/Fs, the problematic soil level is ca 2.8 ng TEQ/kg.
- These problematic soil levels are extremely low and are exceeded in many areas of industrial emissions and can also be exceeded in cities or residential areas (ashes; open burning). In the Netherlands 50% of private chicken herds above limit (former ash use).
- Therefore PCDD/F levels in ash, bio-solids and other fertilizer amended to soils need to be controlled and restricted to below a certain limit.

Weber et al. Environ Sci Eur. 30:42. https://rdcu.be/bax79; Weber et al. (2019) Environ Pollut. 249, 703-715



National PCDD/F limits for soils

 Levels of contamination in the soil which result in contamination of chicken meat/egg above EU limits are below the current regulatory soil limits. Therefore an update is needed considering sensitive uses.

Canadian Environmental Quality Guidelines							
4 ng/kg TEQ	Alert level	ССМЕ, 2005а	a				
New Zealand Interim Acceptance Crit	New Zealand Interim Acceptance Criteria						
10 ng/kg TEQ	Agricultural	МоЕ, 1997	Ь				
1,500 ng/kg TEQ	Residential	МоЕ, 1997	Ь				
18,000 ng/kg TEQ	Industrial	МоЕ, 1997	Ь				
Germany Federal and Lander Minister	s of the Environment recommendations						
5-40 ng/kg TEQ	Agriculture	EU, 1999	с				
100 ng/kg TEQ	Playgrounds	EU, 1999	с				
1,000 ng/kg TEQ	Residential areas	EU, 1999	с				
10,000 ng/kg TEQ	Industrial areas	EU, 1999	с				
The Netherlands Guidelines							
1,000 ng/kg TEQ	Residential and agricultural areas	EU, 1999	с				
10 ng/kg TEQ	Dairy farming	EU, 1999	с				

• To keep the soil below 3 ng TEQ, the PCDD/F levels in ash or other fertilizer need to be restricted. In particular considering long term application and accumulation of the persistent PCDD/Fs over time.

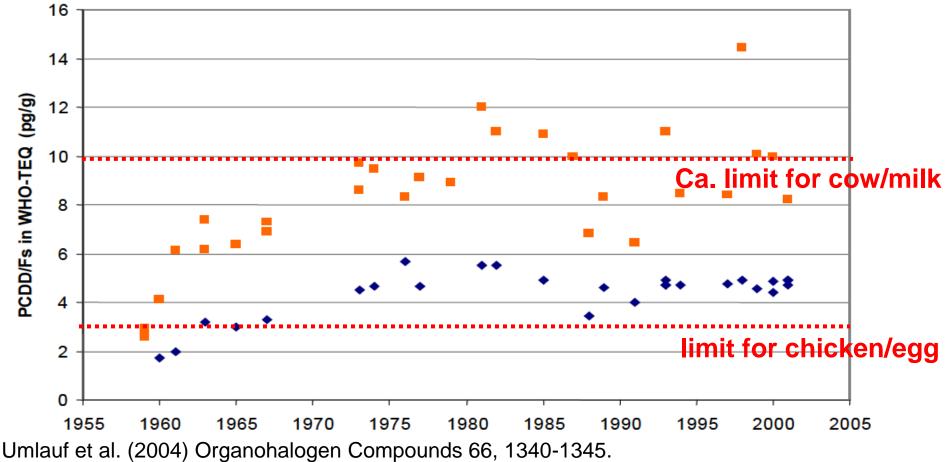
11 ng/kg & 39 ng/kg TEQ PCDD & PCDF soil guideline level

d

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PCDD/F levels in soil can increase with long term[®] application of sewage sludge

• PCDD/Fs levels in soils slowly increased with sewage sludge application and even fertilizer application over 50 years.



• Similar PCDD/F increase can result from application of ashes from combustion if PCDD/F levels are not controlled.

BAT/BEP considerations for utilization of ash from biomass combustion – PCDD/F limits

Regulation for agricultural use of ashes from biomass combustion

- E.g. German regulation for fertilizers (DMG 2020) includes limits for PCDD/s & dI-PCBs; also a proposal for a fertilizer regulation in the EU.
- The **"Basel low POP content" (15,000 ng TEQ/kg) is somewhat misleading** and has also been derived with wrong assumptions (see Swedish EPA 2011; Lopez & Proença 2020; Wu et al. 2020; Weber et al. 2019).

Regulation	Pollutant	Limit value (/kg)	Application/remark
Germany	a) PCDD/F + dl-PCB	30 ng TEQ/kg	All with exemption of b)
Germany	b) PCDD/F + dl-PCB		pasture land and production of feed. & farmland without plowing
EU (2019)	PCDD/F	20 ng TEQ/kg	Fertilizer to land (JRC proposal)
Basel low POP content			Misleading for further use; was wrongly derived!

JRC report EU fertilizer; ISBN 978-92-76-09888-1, doi:10.2760/186684, JRC117856 Swedish EPA (2011). *Low POP Content Limit of PCDD/F in Waste*. Report 6418; ISBN 978-91-620-6418. Lopes H, Proença S (2020) Appl. Sci. 2020, 10, 4951 https://doi.org/10.3390/app10144951; Wu et al. Emerg. Contam. 6, 235-249. https://doi.org/10.1016/j.emcon.2020.07.001; Weber et al. (2019) Environ Pollut. 249, 703-715.

Comparison of PCDD/F concentration in ashes ⁷⁷ from Biomass Combustion with limits for fertilizer

TEQ ng/kg PAH mg/kg	Ash b	BFB1 blend (n=5)	BFB3 Ash blend (n=5)		BFB4 Ash blend (n=4)		GF Ash blend (n=4)	
	BA	FA	BA	FA	BA	FA	BA	FA
Σ PCDD/F MB ²⁾ LB / UB ²⁾	823 755 / 890	789 733 / 844	126 33 / 219	731 713 / 749	105 0 / 209	3141	228 141 / 315	24052
WHO ₂₀₀₅ -TEQ MB LB / UB	19.7 7.3 / 32.1	34.6 25.9 / 43.2	13.5 0.01 / 27.1	86.5 85.2 / 87.8	13.5 0 / 27.1	207 207	13.8 0.2 / 27.3	1139 1139
Σ ₁₆ PAH MB ²⁾ LB / UB ²⁾	0.060 0.02 / 0.10	2.045 1.90 / 2.07	0.057 0.02 / 0.09	1.507 1.49 / 1.52			0.101 0.07/ 0.14	2.539 2.51/2.57

Fly ashes exceeded TEQ limit of fertilizer regulations of Germany (&EU).

- Bottom ashes were below TEQ limit of these fertilizer regulations.
- PAHs in bottom ashes (below 0.1 mg/kg) are and 1.5–2.5 mg/kg in fly ashes, complying with the proposed EU limit of 6 mg/kg.

Lopes H, Proença S (2020) Appl. Sci. 2020, 10, 4951 https://doi.org/10.3390/app10144951

EU Joint Research Center. Technical Proposals for Selected New Fertilising Materials under the Fertilising Products Regulation (Regulation (EU) 2019/1009)—Process and Quality Criteria, and Assessment of Environmental and Market Impacts for Precipitated Phosphate Salts & Derivates, Thermal Oxidation Materials & Derivates and Pyrolysis & Gasification Materials; EUR 29841 EN; Publications Office of the European Union: Luxembourg 2019: ISBN 978-92-76-09888-1 doi:10.2760/186684_IBC117856

BAT/BEP considerations for utilization of ash from biomass combustion – nutrients heavy metals

Generally, following principles apply for biomass combustion:

- The content of volatile heavy metals such as Zn, Pb and Cd increases from bottom ash coarse fly ash fine fly ash.
- The contents of Cadmium (Cd) and to a lesser extent Zink (Zn) are usually the most problematic in terms of environmental impacts. About 35 to 65% of the total amount of Cd and 35 to 55% of Zn in the ash is in the fine fly ash fraction, which accounts for only 5 to 10% of the amount of ash generated in a biomass combustion plant.
- Also the arsenate content can be relevant in particular if Copper-Cr-Arsenate is used in wood treatment in the country/region.
- Mixture of bottom & coarse fly ash accounts to approx. 80 to 95% of the total amount of nutrients (Ca, Mg, K, P) in the fuel/ash.

BAT/BEP considerations for utilization of ash from biomass combustion – nutrients & heavy metals

Some country have regulations on the use of biomass ashes.

	Germany	Austria	Denmark	Sweden	Finland
	-	in g/kg (r	utrients) and mg/kg	(heavy metals)	
Nutrients	(min.)				
Са				125	80/60
Κ				30	K+P 20/10
Mg				15	
Р				7	K+P 20/10
Zn				0.5	
Heavy Me	etals (max.)				
As	40	20		30	25/30
В				800	
Cd	1.5	8	5/15	30	1.5/17.5
Cr _(tot.)		250	100	100	300
Cu	70	250		400	600/700
Hg	1.0		0.8	3.0	1.0
Ni	80	100	30/60	70	100/150
Pb	150	100	120	300	100/150
Tl	1.0				
V		100		70	
Zn	1,000	1,500		7,000	4,500
_	_				

Ornberger & Supancic (2009) Proceedings 17th European Biomass Conference

BAT/BEP considerations for utilization of ash from biomass combustion – nutrients & heavy metals

Content of heavy metals in biomass boiler ashes (bottom ash, coarse fly ash ad fine fly ash) as factor for further use.

Ashes from wood chip combustion

Explanations: BA... bottom ash, CFA coarse fly-ash, FFA ... fine fly CFA Parameter BA FFA CaO 18.1 [% TS] 46.8 46.0 MgO 7.6 7.1 2.8[% TS] K_2O [% TS] 6.1 6.2 22.0 P_2O_5 2.2 [% TS] 2.5 04Cu [mg/kg] 147.7 195.4 174.6 5,849.8 Zn [mg/kg] 452.9 2.464.3 5.8 9.2 31.5 [mg/kg] As Ni [mg/kg] 56.6 89.1 67.8 168.3 116.0 Cr [mg/kg] 140.7 Pb [mg/kg] 15.4 70.5 258.8 2.020.932.9 Cd [mg/kg]

Ashes from straw combustion

v ash	<u>Explanat</u>	tions: BA botto	tom ash, CFA coarse fly-ash, FFA fine fly ash			
	Parame	eter	BA	CFA	FFA	
	CaO	[% TS]	7.9	3.7	1.2	
	MgO	[% TS]	4.4	1.9	0.7	
	K_2O	[% TS]	14.3	10.1	48.2	
	P_2O_5	[% TS]	2.2	1.4	1.2	
_	Cu	[mg/kg]	17.0	13.6	44.0	
1	Zn	[mg/kg]	75.0	77.0	520.0	
	As	[mg/kg]	<5.0	27.9	22.0	
	Ni	[mg/kg]	4.0	11.9	<2.5	
	Cr	[mg/kg]	13.5	9.1	6.8	
	Pb	[mg/kg]	5.1	11.4	80.0	
	Cd	[mg/kg]	0.2	0.8	5.2	

BAT/BEP considerations for utilization of ashes from biomass combustion

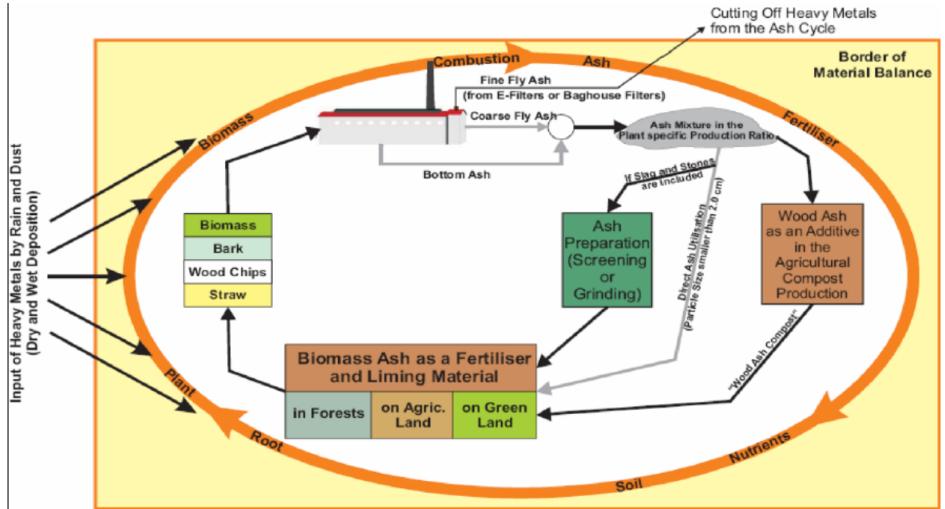
Suggested general principles for sustainable ash utilisation :

- Bottom ash or a mixture of bottom and coarse fly ash shall be recycled to agricultural or forest land in order to contribute to a closure of the mineral cycle (best on same cultivation type soil).
- Fine fly ash, which represents the smallest and heavy metal richest ash fraction, shall be utilised in industrial processes (e.g. heavy metal recovery) or disposed of.
- Therefore, modern biomass combustion/CHP plants shall be equipped with a two-stage dust precipitation system (cyclone and filter) and an applicable ash handling system to allow the separate collection of the different fly ash fractions.
- Only ash from the combustion of virgin biomass should be used for fertilizing. Ashes from the combustion of waste wood or treated wood must not be applied on soils due to their heavy metal contents.

BIOS Austria (2014)

BAT/BEP considerations for utilization of ashes from biomass combustion

Sustainable ash utilisation from biomass combustion:



Ornberger & Supancic (2009) Proceedings 17th European Biomass Conference.

Practical considerations for utilization of ashes from biomass combustion

- The application of ashes on agricultural or forest land requires an appropriate ash treatment in order to meet the requirements of the ash application process selected. Following tasks:
- Proper mixture of the usable ash fractions.
- Preferably dust free ash handling. Avoidance or minimisation of dust formation during ash handling.
- Appropriate dimensioning of the ash storage facilities is usually necessary (main application period ?).
- The ash must be provided in a spreadable particle size (i.e. free of slag and other particles >1.5 to 2 cm) if direct ash application on soils.
- Preparation of the ash for transport (big bags, silo wagon etc.).
- Ash application option: direct (land) or indirect (mix with compost).

Utilizing options of biomass ashes (ECN)⁸⁵

A range of options for the use of biomass are available or tested:

No	Application	Function	Sector
1	Binders alternative for standard cement	Component	Building industry and
2	C-fix	Filler	civil engineering
3	Concrete (products) low quality	Reactive filler	
6	Road Construction material	Binder/Raw material	
7	Sand-lime bricks	Filler	
8	infrastructural works (embankments, fillings)	Filling material	
9	Soil stabilization	Binder	
10	Synthetic aggregates ¹	Raw material	-
11	Fuel	Combustion	Energy production ²
12	Back-filling mining	Filler	Mining
13	Polymers	Filler	Industry
14	Metals	Filler	https://publications.tps
15	Phosphor production	Raw material	https://publications.tnc nl/publication/3463072
16	Zeolites	Raw material	2/4a9uc7/l15079.pdf
17	Metals recovery	Raw material	-
18	Mineral fibers	Raw material	-
19	Soil improvement and fertilizer	Product/Raw material	Agriculture
20	Neutralisation of waste acids	Product	Environmental
21	Adsorption material	Raw material	technology
22	Impermeable layer	Raw material	www.ecn.nl

For the assessment of biomass ash applications in soil and cement mortars see also Tosti et al. Chemosphere 2019, 223, 425-437.

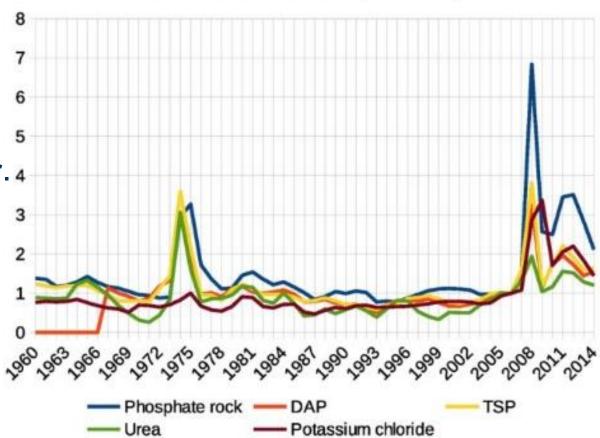
Remarks on biomass ash use as "fertilizers"

Some remarks on biomass ash use as fertilizer:

- Ashes are incomplete fertilizer (no nitrogen, minor-soluble P)
- Low nutrient content compared to heavy metal content (e.g Cd, As, Zn)
- Consistency in quality and quantity needed (relative high variability).

 Fertilizer interest depends on P and K raw material prices.

• World P shortage will 5 become a primary driver. 4



Real Price Relative to 2006 (World Bank)

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Some Conclusions

- Large and growing amount of biomass residues available in Colombia.
- Thermal recovery is one option for treatment with energy recovery.
- Thermal recovery of clean biomass has low PCDD/F release and (most of) the ashes can be used as co-fertilizer. Also other use options.
- If even a small amount of waste wood containing wood preservatives are co-incinerated or other wastes increasing chlorine or heavy metal content, then PCDD/F levels can increase several ordes of magnitude.
- Pesticides on biomass can significantly increase PCDD/F formation.
- The use of ash from contaminated biomass combustion is a risk.
- Regulatory frame for waste wood and ash management needed.
- Columbia might consider a PCDD/F monitoring study of ashes from biomass combustion if used on soils/in agriculture.

EU Project Sweden on recycling wood ash back to forest: http://lifevideos.eu/videos/?id=LIFE03_ENV_SE_000598_01_EN_WASTE.flv

Food for thought – Evaluate investments! *

- Risk that investments in energy from biomass can result in deforestation
- Also the production of agrofuel competes with food production and can result in logging of forests (https://en.wikipedia.org/wiki/Deforestation_in_Colombia).
- Michael Moore documents in his new film that this happens large scale.



https://www.youtube.com/watch?v=Zk11vI-7czE

Interview with Michael Moore: https://www.youtube.com/watch?v=qcqSTX2yDNc

Thank you for your attention ! Questions?⁸⁹

More Information

- Basel Convention: www.basel.int
- Rotterdam Convention: www.pic.int
- Stockholm Convention: http://chm.pops.int/





- Montreal Protocol/Vienna Convention: http://ozone.unep.org
- SAICM: www.saicm.org/ FAO: www.fao.org/ WHO: www.who.int/
- POPs phase out & alternatives http://poppub.bcrc.cn/
- OECD: http://www.oecd.org/chemicalsafety/
- Science: www.ipcp.ch; http://greensciencepolicy.org/
- NGO: www.ipen.org; www.chemsec.org; www.ihpa.info; www.ban.org Better-world-links: http://www.betterworldlinks.org/

