Experiences of BAT/BEP implementation in the metallurgical industry

Dr. Heidelore Fiedler
Örebro University, Sweden

Content

- Stockholm Convention on POPs
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  - Guidance
  - Examples
- PCDD/PCDF formation, prevention and reduction
- BAT/BEP in metallurgical sector
  (ferrous vs. non-ferrous metal industries)
- Dioxin measurements

Obligations (Stockholm Convention)

1) Intentional releases from production and use (Article 3, Annexes A and B)

- Elimination of the production and use of substances listed in Annex A (possibility of specific production /use exemptions for up to 5 years)
- Limitation of the production and use of the substances listed in Annex B (possibility of specific exemptions or acceptable purposes)
- Trade control of the substances listed in Annexes A and B
  - import: OK if for ESM ($\Rightarrow$ BC) or if for permitted use
  - export: OK if permitted use or for ESM (special rule if export to a non-Party)

2) Unintentional releases (Article 5, Annex C)

- Parties to adopt specific measures to reduce unintentional releases, including a national action plan, the promotion of best available techniques (BAT) and best environmental practices (BEP).

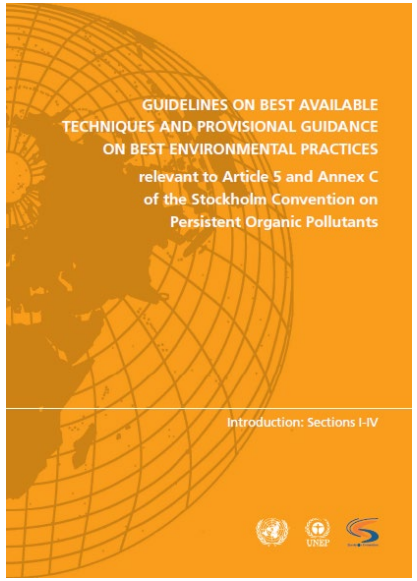
3) **Stockpiles and wastes** (Article 6)

- Parties to manage stockpiles and wastes containing listed chemicals in a manner protective of human health and the environment

BAT/BEP metallurgical industry

Legal mandatory

Guidance



Article 5, annex C: Release inventories, release reduction through BAT/BEP application, updating every five years

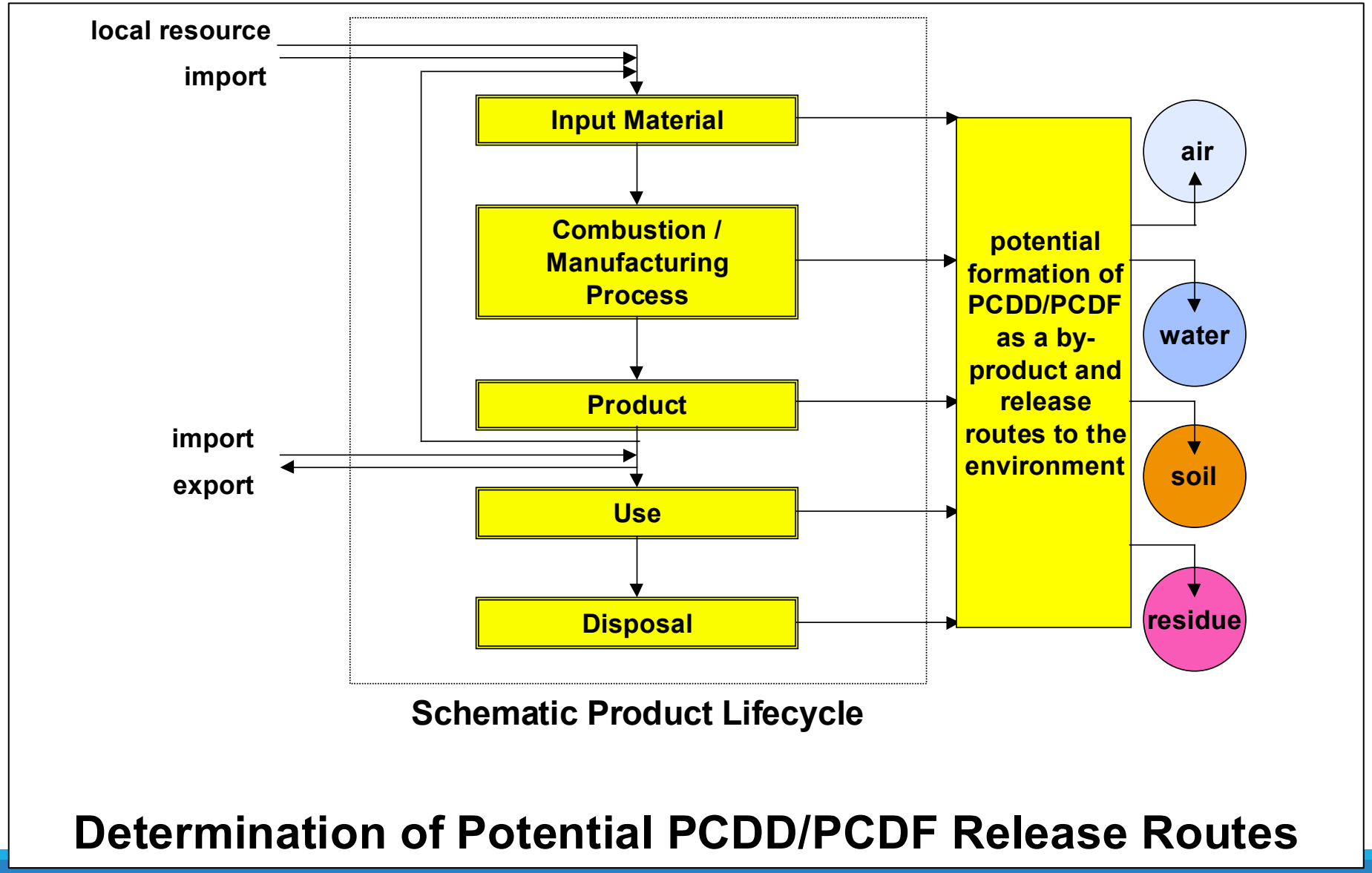
Legal mandatory

Country	Source Group	20xx (g TEQ/year)				
		Air	Water	Land	Product	Residue
	Waste incineration					
	Ferrous and non-ferrous metal production					
	Heat and power generation					
	Production of mineral products					
	Transportation					
	Open burning processes					
	Production of chemicals and consumer goods					
	Miscellaneous					
	Waste disposal					

Country	Source Group	20xx + 5 years (g TEQ/year)				
		Air	Water	Land	Product	Residue
	Waste incineration					
	Ferrous and non-ferrous metal production					
	Heat and power generation					
	Production of mineral products					
	Transportation					
	Open burning processes					
	Production of chemicals and consumer goods					
	Miscellaneous					
	Waste disposal					

National reporting, every four year

PCDD/PCDF release routes



Determination of Potential PCDD/PCDF Release Routes

SG 2 – Ferrous and non-ferrous metal production

Source categories			Potential Release Route (µg TEQ/t)				
Group	Cat.		Air	Water	Land	Product	Residue
2	a	**Iron ore sintering**	X	ND	ND	ND	X
	b	Coke production	X	X	ND	ND	X
	c	Iron and steel production plants and foundries	X	ND	NA	NA	X
		Iron and steel plants	X	ND	NA	NA	X
		Foundries	X	ND	NA	NA	X
		Hot-dip galvanizing plants	X	NA	NA	NA	X
	d	**Copper production**	X	X	NA	NA	X
	e	**Aluminum production**	X	ND	NA	NA	X
	f	Lead production	X	ND	NA	NA	X
	g	**Zinc production**	X	ND	NA	NA	X
	h	Brass and bronze production	X	NA	NA	NA	X
	i	Magnesium production	X	X	NA	NA	X
	j	Thermal non-ferrous metal production (e.g., Ni)	X	ND	NA	NA	ND
	k	Shredders	X	NA	NA	ND	X
	l	Thermal wire reclamation and e-waste recycling	X	ND	ND	ND	ND

ND – Not determined
NA – Not applicable
X – Emission factor, release for quantification

Annex C Part II source categories:
i. Secondary copper production;
ii. Sinter plants in the iron and steel industry;
iii. Secondary aluminium production;
iv. Secondary zinc production

Annex C Part III source categories:
(b) Thermal processes in the metallurgical industry" (open list)
(k) Shredder plants for the treatment of end-of-life vehicles
(l) Smouldering of copper cables

Source: Dioxin Toolkit (2013)

SG 2 – Emission factors

			Source categories	Potential Release Route (µg TEQ/t)				
Group	Cat.	Class		Air	Water	Land	Product	Residue
	a		**Iron ore sintering**					
		1	High waste recycling, incl. oil contaminated materials, no air pollution control	20	ND	ND	ND	0.003
		2	Low waste use, well controlled plant	5	ND	ND	ND	1
		3	High technology, emission reduction	0.3	ND	ND	ND	2
	b		**Coke production**					
		1	No gas cleaning	3	0.06	ND	ND	ND
		2	Afterburner/ dust removal	0.03	0.06	ND	ND	ND
	c		**Iron and steel production plants and foundries**					
			Iron and steel plants					
		1	Dirty scrap, scrap preheating, limited controls	10	ND	NA	NA	15
		2	Clean scrap/virgin iron or dirty scrap, afterburner, fabric filter	3	ND	NA	NA	15
		3	Clean scrap/virgin iron or dirty scrap, EAF equipped with APC designed for low PCDD/PCDF emission, BOF furnaces	0.1	ND	NA	NA	0.1
		4	Blast furnaces with APCS	0.01	ND	NA	NA	ND
			Foundries					
		1	Cold air cupola or hot air cupola or rotary drum, no APCS	10	ND	NA	NA	ND
		2	Rotary drum - fabric filter or wet scribber	4.3	ND	NA	NA	0.2
		3	Cold air cupola, fabric filter or wet scrubber	1	ND	NA	NA	8
		4	Hot air cupola or induction furnace, fabric filter or wet scrubber	0.03	ND	NA	NA	0.5
			Hot-dip galvanizing plants					
		1	Facilities without APCS	0.06	NA	NA	NA	0.01
		2	Facilties without degreasing step, good APCS	0.05	NA	NA	NA	2
		3	Facilities with degreasing step, good APCS	0.02	NA	NA	NA	1

SG 2 – Emission factors (2)

			Source categories	Potential Release Route (µg TEQ/t)				
Group	Cat.	Class		Air	Water	Land	Product	Residue
	d		**Copper production**					
		1	Sec. Cu - Basic technology	800	0.5	NA	NA	630
		2	Sec. Cu - Well controlled	50	0.5	NA	NA	630
		3	Sec. Cu - Optimized for PCDD/PCDF control	5	0.5	NA	NA	300
		4	Smelting and casting of Cu/Cu alloys	0.03	0.5	NA	NA	ND
		5	Prim. Cu, well-controlled, with some secondary feed materials	0.01	0.5	NA	NA	ND
		6	Pure prim. Cu smelters with no secondary feed	ND	0.5	NA	NA	NA
	e		**Aluminum production**					
		1	Processing scrap Al, minimal treatment of inputs, simple dust removal	100	ND	NA	NA	200
		2	Scrap treatment, well-controlled, fabric filter, lime injection	4	ND	NA	NA	400
		3	Optimized proces for PCDD/PPCDF abatement	0.5	ND	NA	NA	100
		4	Shavings/turnings drying (simple plants)	5.0	NA	NA	NA	NA
		5	Thermal de-oiling, rotary furnaces, afterburners, fabric filters	0.3	NA	NA	NA	NA
		6	Primary Al plants	ND	NA	NA	NA	ND
	f		**Lead production**					
		1	Lead production from scrap containing PVC	80	ND	NA	NA	ND
		2	Lead production from PVC/Cl2 free scrap, some APCS	8	ND	NA	NA	50
		3	Lead production from PVC/Cl2 free scrap in highly efficient furnaces, with APC including scrubbers	0.05	ND	NA	NA	ND
		4	Pure primary lead production	0.4	ND	NA	NA	ND

SG 2 – Emission factors (3)

			Source categories	Potential Release Route (µg TEQ/t)				
Group	Cat.	Class		Air	Water	Land	Product	Residue
	g		**Zinc production**					
		1	Kiln with no dust control	1,000	ND	NA	NA	0.02
		2	Hot briquetting/rotary furnaces, basic control	100	ND	NA	NA	1
		3	Comprehensive control	5	ND	NA	NA	1
		4	Zinc melting and primary zinc production	0.1	ND	NA	NA	ND
	h		**Brass and bronze production**					
		1	Thermal de-oiling of turnings	2.5	NA	NA	NA	NA
		2	Simple melting furnaces	10	NA	ND	NA	ND
		3	Mixed scarp, induction furnace, bagfilter	3.5	ND	ND	NA	125
		4	Sophisticated equipment, clean inputs, good APCS	0.1	ND	ND	NA	ND
	i		**Magnesium production**					
		1	Using MgO/C thermal treatment in Cl2, no effluent treatment, poor APCS	250	9,000	NA	NA	0
		2	Using MgO/C thermal treatment in Cl2, comprehensive pollution control	50	30	NA	NA	9,000
		3	Thermal reduction process	3	ND	NA	NA	NA
	j		**Thermal Non-ferrous metal production (e.g., Ni)**					
		1	Contaminated scrap, simple or no APCS	100	ND	NA	NA	ND
		2	Clean scrap, good APCS	2	ND	NA	NA	ND
	k		**Shredders**					
		1	Metal shredding plants	0.2	NA	NA	ND	5
	l		**Thermal wire reclamation and e-waste recycling**					
		1	Open burning of cable	12,000	ND	ND	ND	ND
		2	Open burning of circuit boards	100	ND	ND	ND	ND
		3	Basic furnace with after burner, wet scrubber	40	ND	NA	ND	ND
		4	Burning electric motors, brake shoes, etc., afterburner	3.3	ND	NA	ND	ND

NIP had 435.6 g/yr from open burning

Article 15 – Colombia (4th report)

Parties to the Stockholm Convention submit information on the implementation of the convention, as per by Article 15, every four years through their National Reports.

Country	Source Group	2002 (kg/year)					
		Air	Water	Land	Product	Residue	Subtotal
Colombia	Waste incineration	103.1	0.0	0.0	0.0	21.3	**124.4**
Colombia	Ferrous and non-ferrous metal production	18.7	18.0	0.0	0.0	11.5	**48.2**
Colombia	Heat and power generation	24.6	0.0	0.0	0.0	3.3	**27.9**
Colombia	Production of mineral products	3.8	0.0	0.0	0.1	0.0	**3.9**
Colombia	Transportation	1.6	0.0	0.0	0.0	0.0	**1.6**
Colombia	Open burning processes	156.8	0.0	86.7	0.0	0.0	**243.5**
Colombia	Production of chemicals and consumer goods	0.3	0.5	0.0	41.4	0.7	**42.9**
Colombia	Miscellaneous	0.4	0.0	0.0	0.4	79.4	**80.2**
Colombia	Waste disposal	0.0	3.2	0.0	2.5	5.2	**10.9**
	Total per vector	**309.3**	**21.7**	**86.7**	**44.4**	**121.4**	**583.5**
	Grand total	**583.50**					

12-2

http://www.pops.int/Countries/Reporting/ReportingDatabase/tabid/7477/Default.aspx
http://ers.pops.int/eRSodataReports2/ReportSC_UPOPsInv-Full.htm

2nd National report

10. Please provide the information on estimation of annual releases of Annex C chemicals in your country (refer to annexes: estimations, updating, revisions and projections and Source Categorization)
Please indicate the information sources used to elaborate the release estimates (Please specify all that apply)

SOURCE CATAGORY	YEAR	NR	ND	AIR	WATER	LAND	PRODUCT	RESIDUE
Ferrous and non-ferrous metal production	2006			7.95	18.00	0.00	0.00	4.90
Heat and power generation	2006			10.79	0.00	0.00	0.00	50.70
Miscellaneous	2006			45.40	0.00	0.00	2.27	0.00
Open buming processes	2006			255.94	0.00	209.95	0.00	188.60
Production of chemicals and consumer goods	2006			0.02	0.26	0.00	25.98	0.40
Production of mineral products	2006			2.17	0.00	0.00	0.00	0.00
Transportation	2006			1.99	0.00	0.00	0.00	0.00
Waste disposal	2006			0.00	1.27	0.00	8.81	0.00
Waste incineration	2006			21.30	0.00	0.00	0.00	32.20

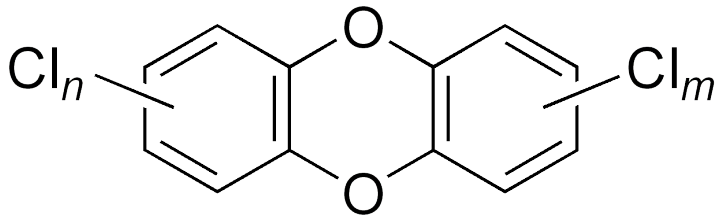
Article 5 - Unintentionally Produced POPs

Each Party shall at a minimum take the following measures to reduce the total releases derived from anthropogenic sources of each of the chemicals listed in Annex C, with the goal of their continuing minimization and, where feasible, ultimate elimination.

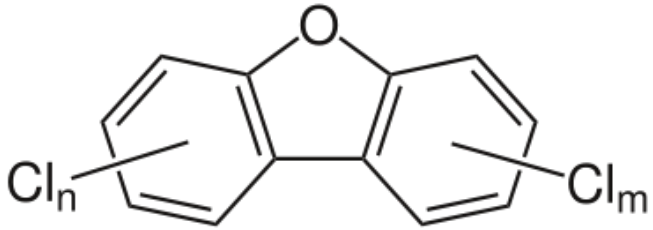
(a) Develop an action plan or, where appropriate, a regional or subregional action plan within two years of the date of entry into force of this Convention for it, and subsequently implement it as part of its implementation plan specified in Article 7, designed **to identify, characterize and address the releases of these chemicals listed in Annex C** and to facilitate implementation of subparagraphs (b) to (e). The action plan shall include the following elements:

Compounds included (Annex C):
PCDD/PCDF (as TEQ); PCB and HCB,
PeCBz (COP4), PCN (COP7), HCBD (COP8)

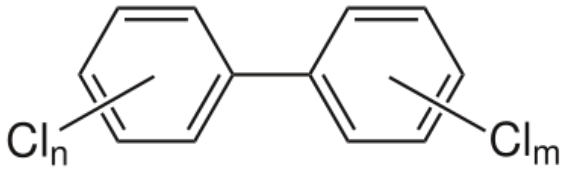
Unintentional POPs listed in Annex C



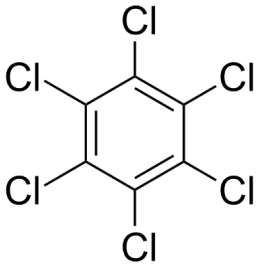
Polychlorinated dibenzo-*para*-dioxins



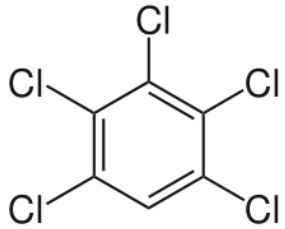
Polychlorinated dibenzofurans



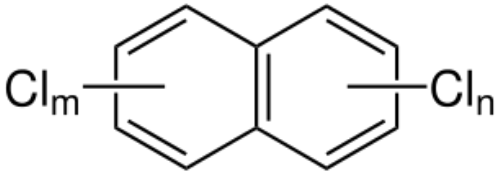
Polychlorinated biphenyls



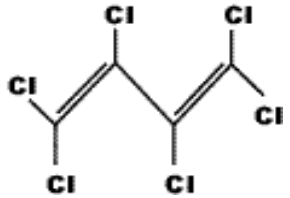
Hexachlorobenzene



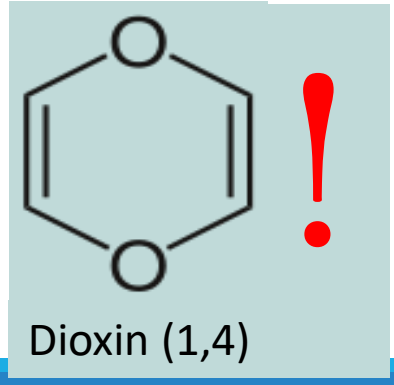
Pentachlorobenzene



Polychlorinated naphthalenes



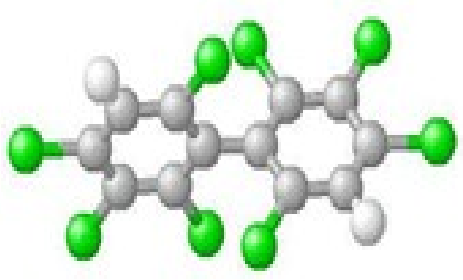
Hexachlorobutadiene



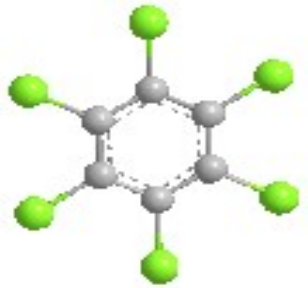
Dioxin (1,4)

Research project

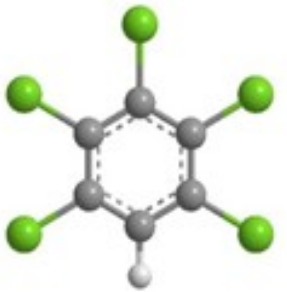
- Project "Inventory Methodology of Unintentionally Produced POPs"
- Donor: National Natural Science Foundation China
  NSFC No. B07, 21561142001
- Project managements:
  - Prof. Gang Yu (School of Environment, Tsinghua University)
  - Prof. Heidelore Fiedler (School of Science and Technology, Örebro University)



Polychlorinated biphenyls



Hexachlorobenzene (HCB)



Pentachlorobenzene (PeCBz)

Publications on emission factors and inventory

Science of the Total Environment 605–606 (2017) 498–506

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Reassessment and update of emission factors for unintentional dioxin-like polychlorinated biphenyls

Wenwen Gong [a], Heidelore Fiedler [a,b], Xiaotu Liu [a], Bin Wang [a], Gang Yu [a,*]

[a] School of Environment, Beijing Key Laboratory for Emerging Organic Contaminants Control, State Key Joint Laboratory of Environment Simulation and Pollution Control (SKLESPC), Tsinghua University, Beijing 100084, China
[b] MTM Research Centre, School of Science and Technology, Örebro University, SE-701 82 Örebro, Sweden

Environmental Pollution 230 (2017) 516–522

Contents lists available at ScienceDirect

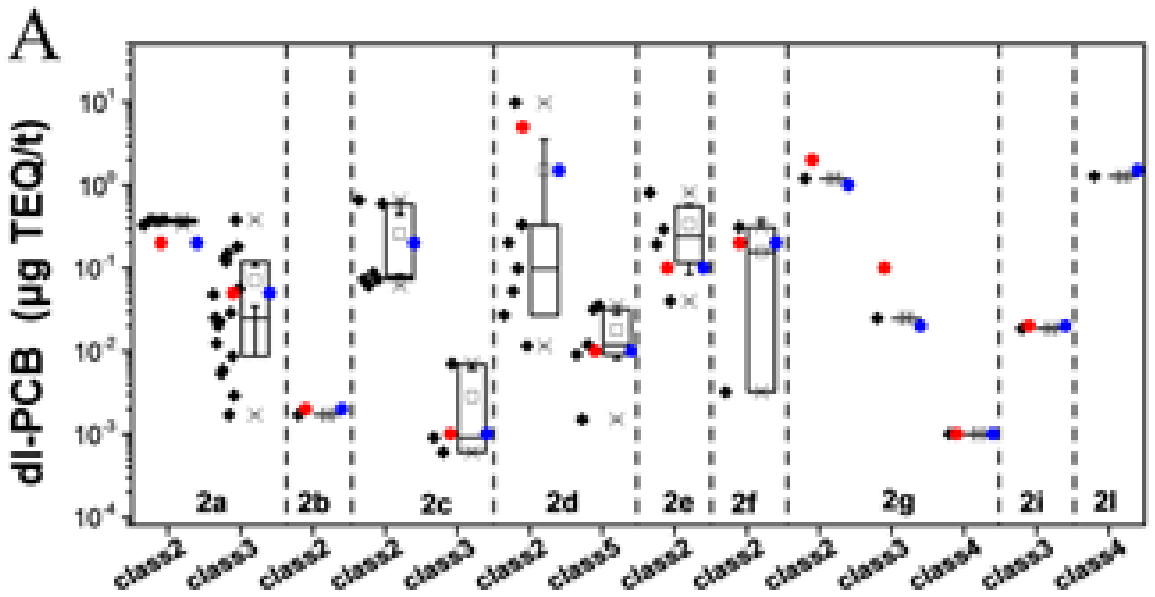
Environmental Pollution

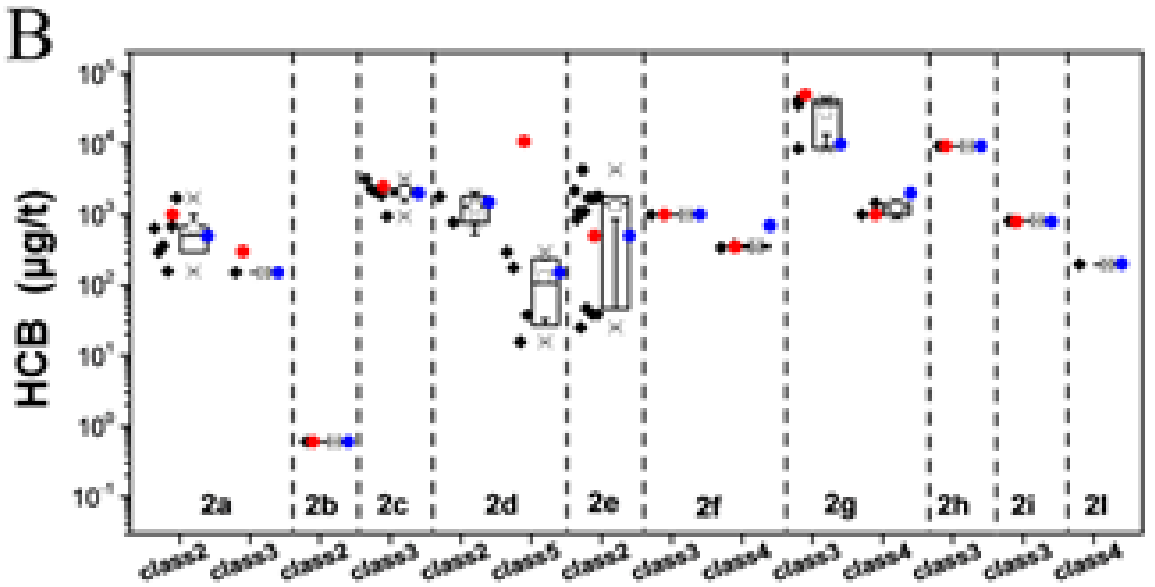
journal homepage: www.elsevier.com/locate/envpol

Emission factors of unintentional HCB and PeCBz and their correlation with PCDD/PCDF☆

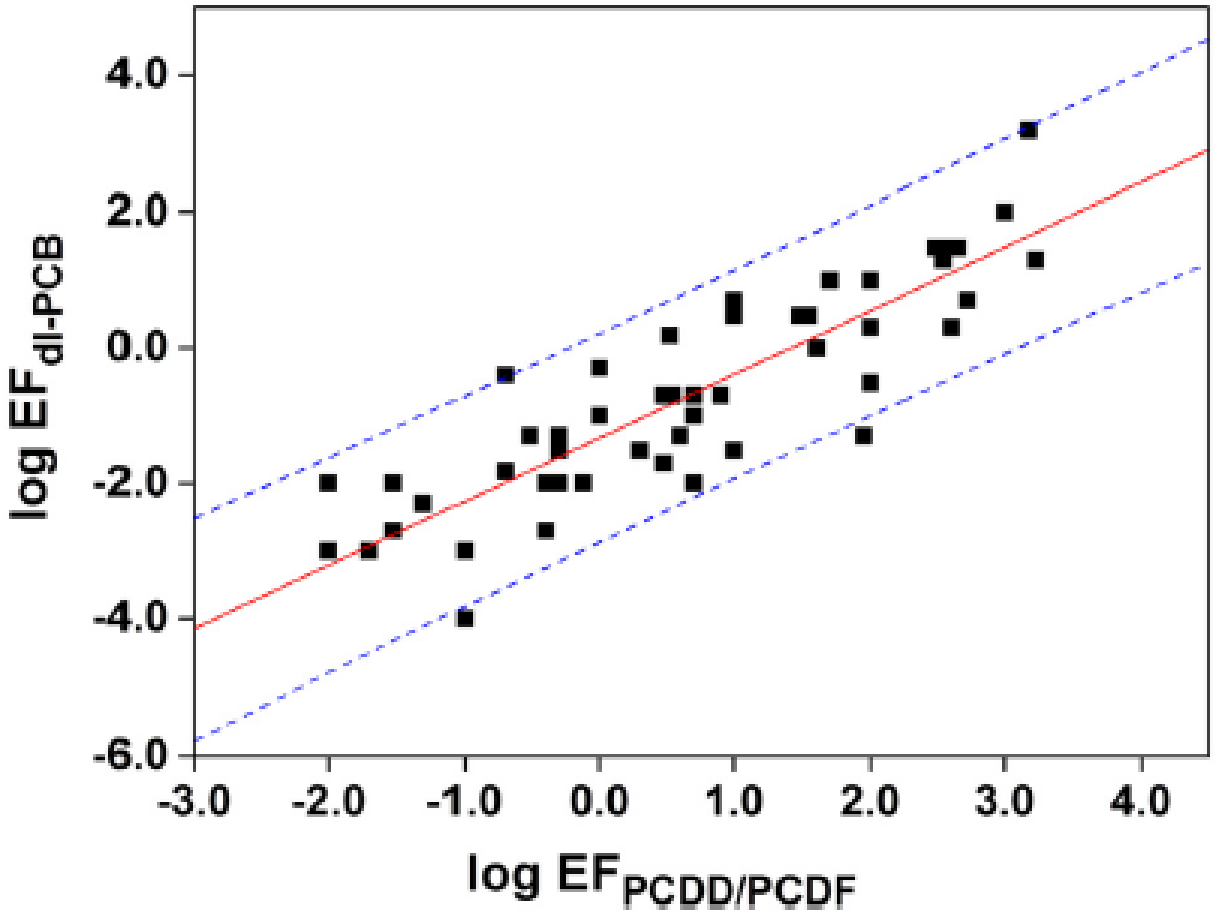
Wenwen Gong [a], Heidelore Fiedler [a, b], Xiaotu Liu [a], Bin Wang [a], Gang Yu [a, *]

[a] School of Environment, Beijing Key Laboratory for Emerging Organic Contaminants Control, State Key Joint Laboratory of Environment Simulation and Pollution Control (SKLESPC), Tsinghua University, Beijing 100084, China
[b] MTM Research Centre, School of Science and Technology, Örebro University, Örebro SE-701 82, Sweden





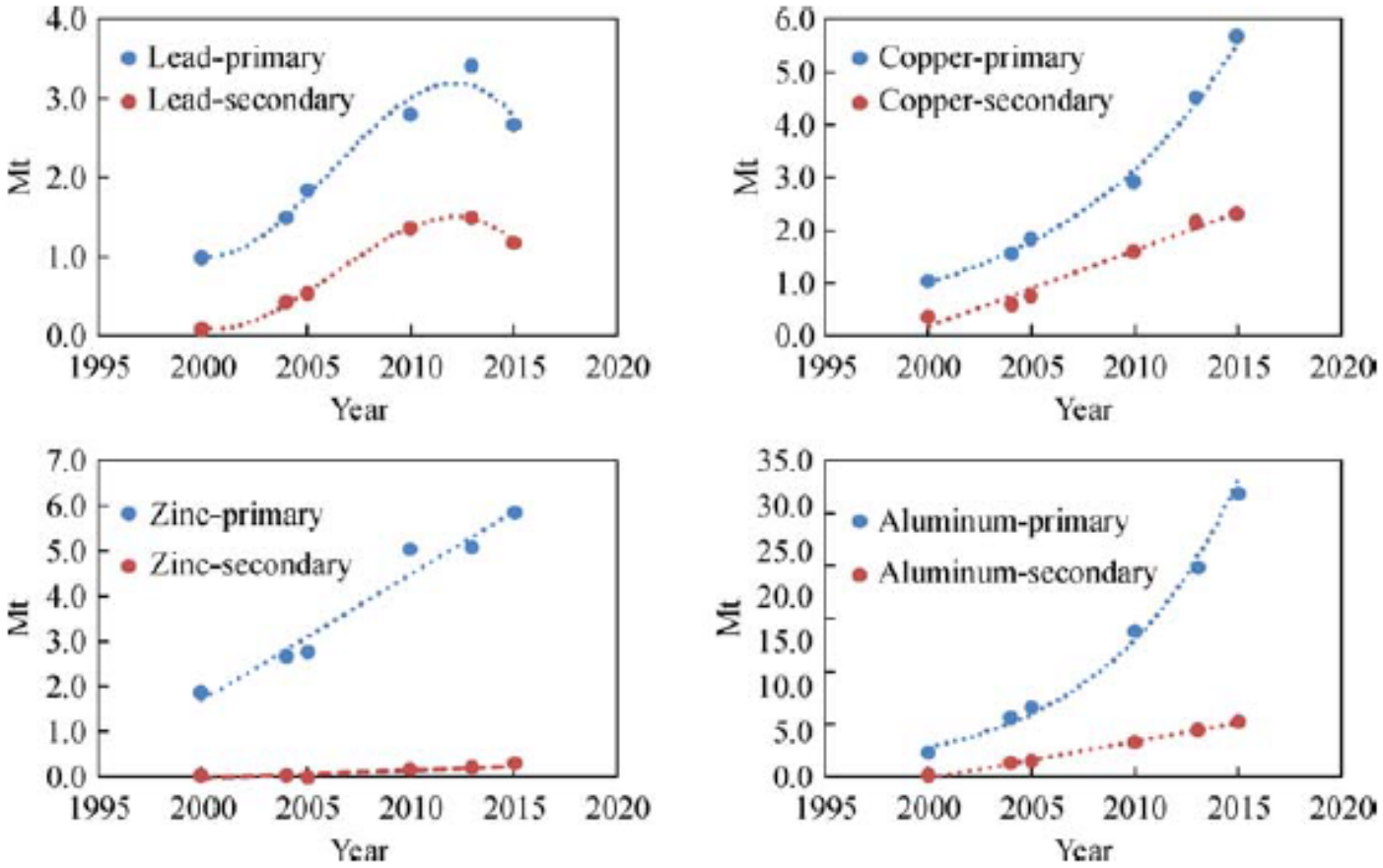
Correlation between $TEQ_{(PCDD/PCDF)}$ and $TEQ_{(PCB)}$



- A significant relationship was observed between EF_{Air} of dl-PCB and PCDD/PCDF for SGs 1, 2 and 6 (R2 from 0.74 to 0.85, p 0.01).
- For other SGs, the correlation was not significant (Pearson correlation coefficient quite high (p 0.05)

Recommendation from COP: Develop and maintain PCDD/PCDF release inventory with 5 vectors (air, water, land, product, residue), using the Toolkit and update every five years

Dynamics - Economic activities in China



Comparisons of production volumes (and increasing trends) between primary and secondary non-ferrous metal production

Liu et al. (2018), Front. Environ. Sci. Eng. **12(6)**, 1-14

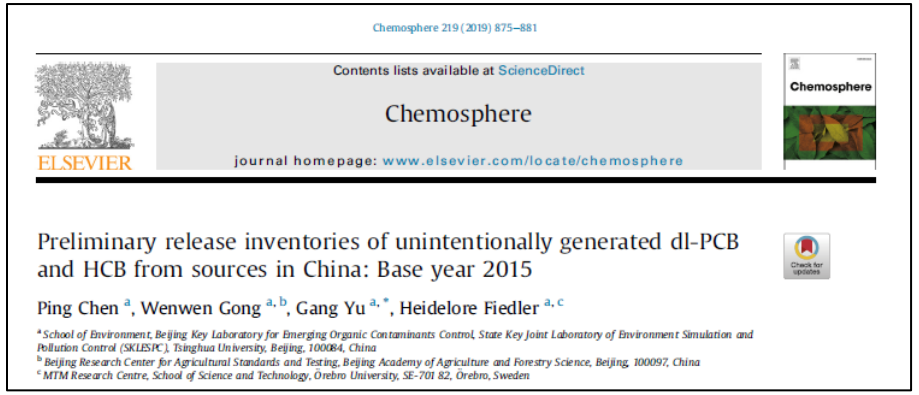
Front. Environ. Sci. Eng. 2018, 12(6): 1
https://doi.org/10.1007/s11783-018-1036-9

OVERVIEW

Potential sources of unintentionally produced PCB, HCB, and PeCBz in China: A preliminary overview

Xiaotu Liu[1,2], Heidelore Fiedler[1,3], Wenwen Gong[1,4], Bin Wang[1], Gang Yu (✉)[1]

1 School of Environment, Beijing Key Laboratory for Emerging Organic Contaminants Control, State Key Joint Laboratory of Environment Simulation and Pollution Control (SKLESPC), Tsinghua University, Beijing 100084, China
2 School of Environment, Guangzhou Key Laboratory of Environmental Exposure and Health, and Guangdong Key Laboratory of Environmental Pollution and Health, Jinan University, Guangzhou 510632, China
3 MTM Research Centre, School of Science and Technology, Örebro University, SE-701 82 Örebro, Sweden
4 Beijing Research Center for Agriculture Standards and Testing, Beijing 100097, China



Chemosphere 219 (2019) 875–881

Contents lists available at ScienceDirect

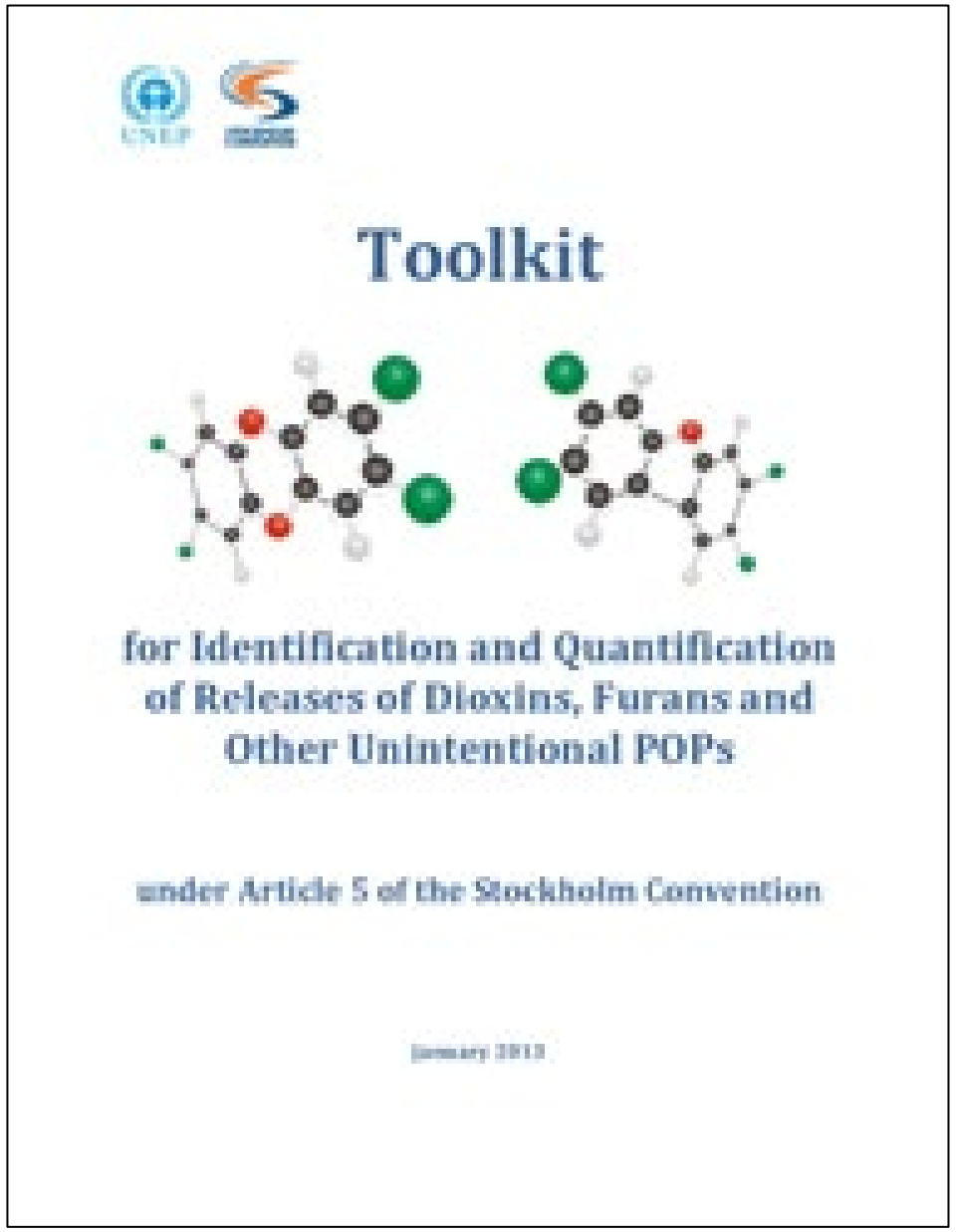
Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Preliminary release inventories of unintentionally generated dl-PCB and HCB from sources in China: Base year 2015

Ping Chen [a], Wenwen Gong [a, b], Gang Yu [a, *], Heidelore Fiedler [a, c]

[a] School of Environment, Beijing Key Laboratory for Emerging Organic Contaminants Control, State Key Joint Laboratory of Environment Simulation and Pollution Control (SKLESPC), Tsinghua University, Beijing, 100084, China
[b] Beijing Research Center for Agricultural Standards and Testing, Beijing Academy of Agriculture and Forestry Science, Beijing, 100097, China
[c] MTM Research Centre, School of Science and Technology, Örebro University, SE-701 82, Örebro, Sweden



Release inventories under article 5 of the Stockholm Convention

Report (narrative for all source groups)
http://toolkit.pops.int/Publish/Downloads/UNEP-POPS-TOOLKIT-2012-En.pdf
and an EXCEL file to calculate the releases
http://toolkit.pops.int/Publish/Downloads/UNEP-POPS-TOOLKIT-PCDD-PCDF-EFs.En.xls

Toolkit methodology (2013)

Toolkit Methodology

Harmonized framework for elaboration of comparable release inventories of Annex C chemicals

Pollutants release inventories are necessary to identify, characterize and quantify sources of these releases; set priorities; elaborate strategies and action plans to reduce these releases; and to evaluate effectiveness of these strategies by establishing release trends through inventory updates.

Release inventories should be:

- Complete (no important source category should be omitted)
- Transparent (use of particular activity data and emission factors should be clearly described, justified and referenced)
- Reliable (best available scientifically sound information should be used)
- Comparable between countries and
- Consistent over time

The Toolkit

Toolkit for Identification and Quantification Releases of Dioxins, Furans and Other Unintentional POPs

Click here to access the electronic Toolkit.

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Arabic | Chinese | English | French | Russian | Spanish

Toolkit
PCDD/PCDF Emission Factors
(revised in 2013)

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Toolkit
Emission Factors for other unintentional POPs
(English only)

Download (Excel)
HCB | PCB | PeCBz

Download from:
http://www.pops.int/Implementation/UnintentionalPOPs/ToolkitforUPOPs/ToolkitMethodology/tabid/196/Default.aspx

Decision SC-9/7 (COP-9, May 2019)

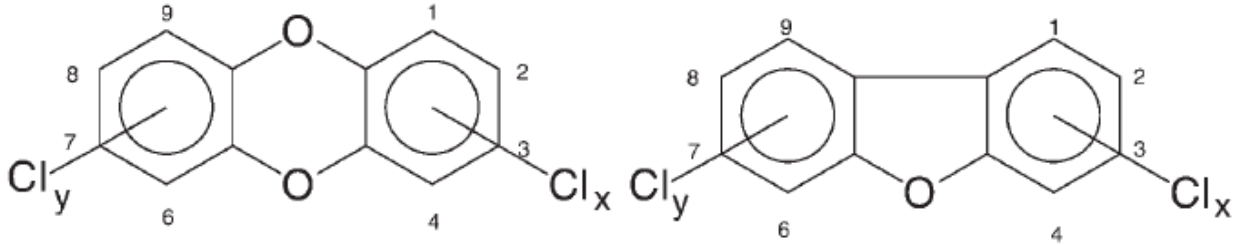
- Encourages Parties to **develop source inventories and release estimates for dioxins and furans and update them every five years** … accordance with Article 5 of the Stockholm Convention, and to report the estimated releases under Article 15.
- For unintentional POPs listed in Annex C other than PCDD/PCDF, emission factors for dioxin-like polychlorinated biphenyls (PCB), hexachlorobenzene (HCB) and pentachlorobenzene (PeCBz) were developed and made available in Toolkit MsExcel files.
- For dl-PCB, HCB, PeCBz the correlation with PCDD/PCDF releases was confirmed;
- For polychlorinated naphthalenes (PCNs) correlation with PCDD/PCDF is assumed (mainly due to structural similarity and assumed formation mechanisms);
- With regards to hexachlorobutadiene (HCBD), it was recommended that there is no need to develop emission factors (and detailed inventories).

Example of BAT/BEP application in Toolkit

Group	Cat.	Class	Source categories	Potential Release Route (µg TEQ/t) Air	Water	Land	Product	Residue	Production t/a	Annual release g TEQ/a Air	g TEQ/a Water	g TEQ/a Land	g TEQ/a Product	g TEQ/a Residue
2			**Ferrous and Non-Ferrous Metal Production**											
	a		**Iron ore sintering**						**200,000**	**0.530**	**0**	**0**	**0**	**0.3**
		1	High waste recycling, incl. oil contaminated ma	20	ND	ND	ND	0.003		**0.000**				**0.000**
		2	Low waste use, well controlled plant	5	ND	ND	ND	1	100,000	**0.500**				**0.100**
		3	High technology, emission reduction	0.3	ND	ND	ND	2	100,000	**0.030**				**0.200**
	b		**Coke production**						**0**	**0.000**	**0**	**0**	**0**	**0**
		1	No gas cleaning	3	0.06	ND	ND	ND		**0.000**	**0.000**			
		2	Afterburner/ dust removal	0.03	0.06	ND	ND	ND		**0.000**	**0.000**			
	c		**Iron and steel production plants and foundries**						**400,000**	**1**	**0**	**0**	**0**	**3**
			Iron and steel plants						*400,000*	*1*	*0*	*0*	*0*	*3.010*
		1	Dirty scrap, scrap preheating, limited controls	10	ND	NA	NA	15	100,000	**1.000**				**1.500**
		2	Clean scrap/virgin iron or dirty scrap, afterburn	3	ND	NA	NA	15	100,000	**0.300**				**1.500**
		3	Clean scrap/virgin iron or dirty scrap, EAF equipped with APC designed for low PCDD/PCDF emission, BOF furnaces	0.1	ND	NA	NA	0.1	100,000	**0.010**				**0.010**
		4	Blast furnaces with APCS	0.01	ND	NA	NA	ND	100,000	**0.001**				
	d		**Copper production**						**500,000**	**85.504**	**0**	**0**	**0**	**156.0**
		1	Sec. Cu - Basic technology	800	0.5	NA	NA	630	100,000	**80.000**	**0.050**			**63.000**
		2	Sec. Cu - Well controlled	50	0.5	NA	NA	630	100,000	**5.000**	**0.050**			**63.000**
		3	Sec. Cu - Optimized for PCDD/PCDF control	5	0.5	NA	NA	300	100,000	**0.500**	**0.050**			**30.000**
		4	Smelting and casting of Cu/Cu alloys	0.03	0.5	NA	NA	ND	100,000	**0.003**	**0.050**			
		5	Prim. Cu, well-controlled, with some secondary feed materials	0.01	0.5	NA	NA	ND	100,000	**0.001**	**0.050**			
		6	Pure prim. Cu smelters with no secondary feed	ND	0.5	NA	NA	NA			**0.000**			

PCDD/PCDF as unintentional POPs

- Formation of PCDD/PCDF needs presence of carbon, chlorine and oxygen;
- There are measures to **prevent formation** of PCDD/PCDF; or
- **reduce emissions/releases** (= primbyproducts in many chemical industrial and all combustion-related processes;
- PCDD/PCDF cannot be eliminated ary measures), and
- **destroy PCDD/PCDF** once formed (= secondary and tertiary measures)



Polychlorinated Dibenzo-para-dioxins (PCDD)	Polychlorinated Dibenzofurans (PCDF)
– 75 possible congeners – 7 have chlorine (Cl) in positions 2, 3, 7 and 8	– 135 possible congeners – 10 have chlorine (Cl) positions 2, 3, 7 and 8
⇒ **17 PCDD/PCDF have been assigned a toxicity equivalency factor (TEF) to form the toxic equivalent (TEQ)**	

Prevention of formation (rules of thumb)

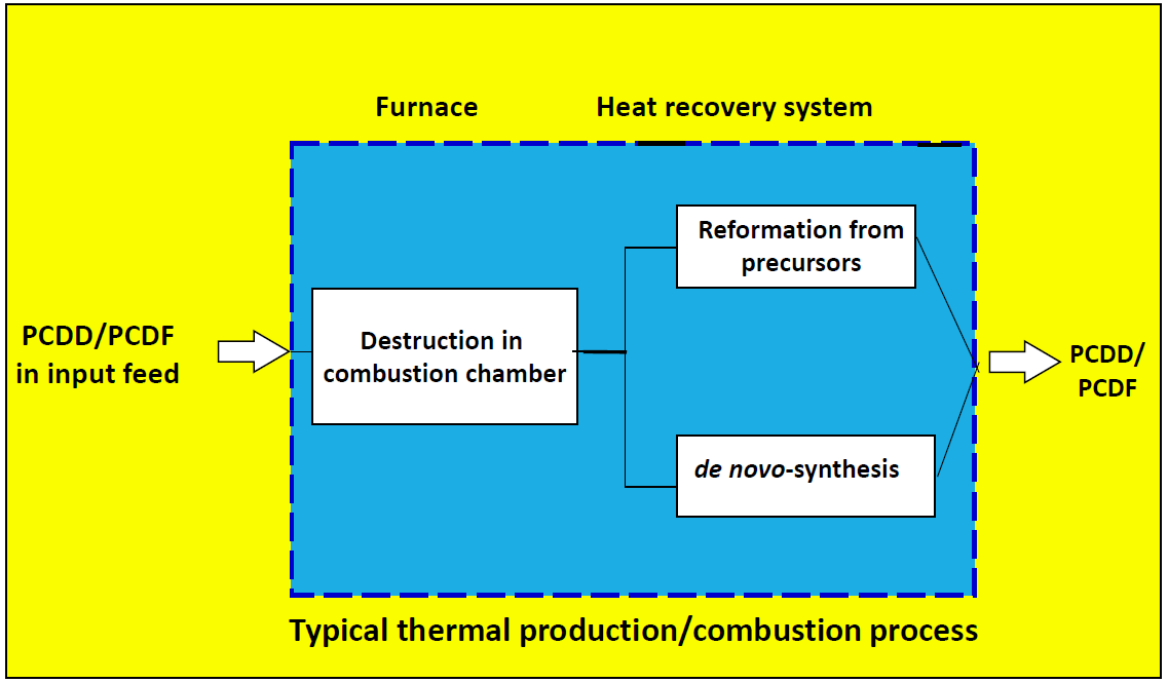
- Chemical processes: No Temp >130 °C
  No uv light
  No alkaline extraction steps
  No radicals
- Pulp and paper: Substitute free chlorine; Split the chlorine multiple
- Thermal formation: Adequate equipment design
  - 3 Ts (temperature, time, turbulence)
  - no ash/soot deposits

  Adequate operation and maintenance
  - good combustion practice, operation as designed, rapid cool-down of gases
  - continuous >> batch-wise/semi-continuous

  Feed/input material
  - Sulfur >> chlorine (Deacon reaction)
  - Metals content (copper, iron, aluminum)

Formation in thermal processes

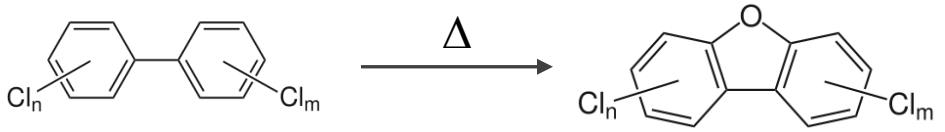
- PCDD/PCDF formation in gas-phase
  - homogeneous phase, fast reactions
- PCDD/PCDF formation on particles
  - heterogeneous phase, slow reactions
- Atmosphere: air/oxygen
  pyrolytic (without oxygen)

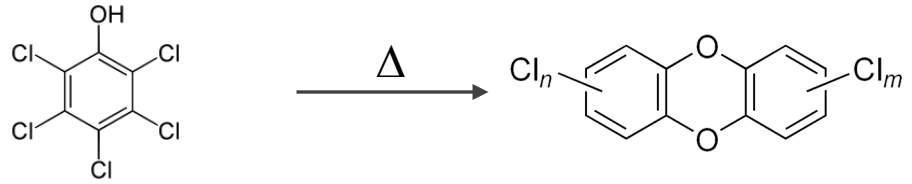


- Re-formation of PCDD/PCDF takes place at temperatures 200 °C-450 °C

Most important formation pathways

1. Chlorinated aromatic precursors



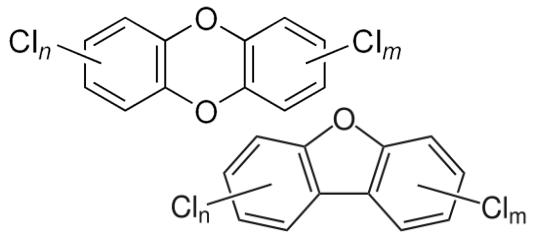


2. Chloroaliphatic precursors

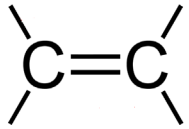
Polychlorinated aromatics

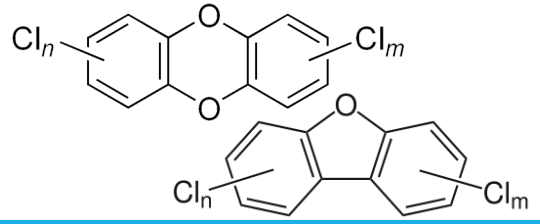
3. Pyrolysis and chlorination of natural precursors

Lignin

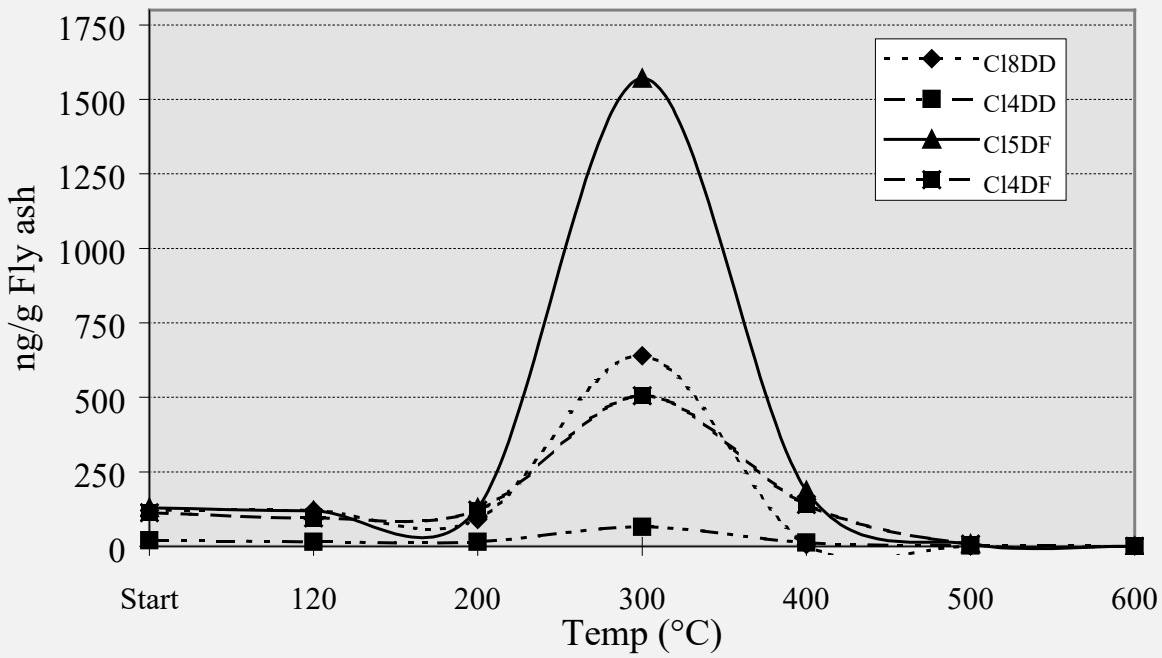


4. Formation from C_2 units





Role of Temperature (annealing, 2 h)



Role of sulfur – Deacon reaction

Reaction 1 – surplus of chlorine:

$$CuCl_2 + \tfrac{1}{2} O_2 \rightarrow CuO + Cl_2$$

$$CuO + 2\ HCl \rightarrow CuCl_2 + H_2O$$

$$2\ HCl + \tfrac{1}{2} O_2 \rightarrow H_2O + Cl_2$$

Reaction 2 - Surplus of sulfur (over chlorine, 0.64):

$$Cl_2 + SO_2 + H_2O \rightarrow SO_3 + 2\ HCl$$

Chemicals containing sulphur and nitrogen have the potential to inhibit the formation of PCDD/PCDF in certain conditions, but may give give rise to other undesirable byproducts (Toolkit (2013)

Role and importance of chlorine

- Hydrogen chloride – HCl:
  - predominant gas-phase chlorine species. Weak chlorinating agent due to strong H-Cl bond;
- Chlorine – Cl_2:
  - gas-phase from chlorine-containing fuels; rapidly transformed to HCl;
- Chlorine radicals – Cl•:
  - most reactive species; important for PCDD/PCDF formation in *de novo* synthesis.

Flue gas cleaning devices (APCS)

- Sufficient oxygen: to allow oxidation of organic pollutants
- Rapid quenching to temperatures below 200 °C (250 °C) (observe temperature profile!);
- Efficient dust removal: to remove active surfaces and catalytic metals to avoid (re)-formation of PCDD/PCDF;
  - Includes fabric filters, wet/dry scrubbers, efficient electrostatic precipitators (caution: temperature range!), ceramic filters
  - Note: collected dust is heavily loaden with organic and other pollutants; needs further treatment
- Activated carbon treatment of flue gases: to adsorb/absorb PCDD/PCDF and other pollutants (incl. Hg)
  - Note: collected active carbon is heavily loaden with organic and other pollutants; needs further treatment
- Selective catalytic reaction: SCR (oxidation) to destroy PCDD/PCDF in gas-phase (and reduce NO_x)

Stockholm Convention Annex C – Reduction measures

(i) Use of improved methods for flue-gas cleaning such as thermal or catalytic oxidation, dust precipitation, or adsorption;

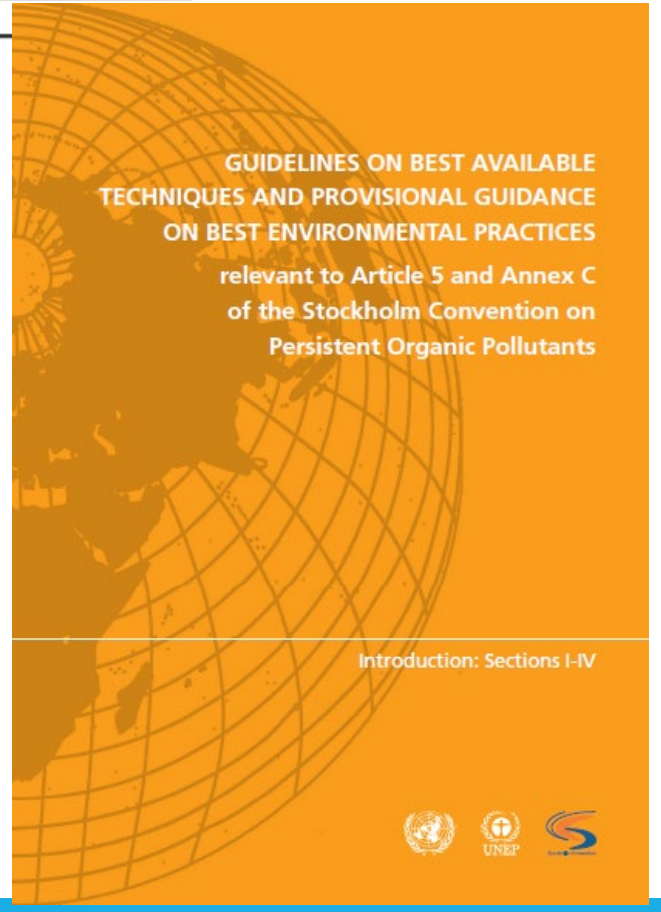
(ii) Treatment of residuals, wastewater, wastes and sewage sludge by, for example, thermal treatment or rendering them inert or chemical processes that detoxify them;

(iii) Process changes that lead to the reduction or elimination of releases, such as moving to closed systems;

(iv) Modification of process designs to improve combustion and prevent formation of the chemicals listed in this Annex, through the control of parameters such as incineration temperature or residence time.

To address all source groups and categories listed in Annex C of the Stockholm Convention

Download from:
http://www.pops.int/Implementation/BATandBEP/BATBEPGuidelinesArticle5/tabid/187/Default.aspx



Updated chapters for BAT/BEP guide

Guidelines on best available techniques and guidance on best environmental practices (2019 updates)

Note: Language versions will be made available subject to the availability of resources.

Arabic | Chinese | English | French | Russian | Spanish

Chapter	Section title	Download
I.IV	INTRODUCTION	
V.B	CEMENT KILNS FIRING HAZARDOUS WASTE	
V.D	THERMAL PROCESSES IN THE METALLURGICAL INDUSTRY	
VI.B	THERMAL PROCESSES IN THE METALLURGICAL INDUSTRY NOT MENTIONED IN ANNEX C PART II	
VI.D	FOSSIL FUEL-FIRED UTILITY AND INDUSTRIAL BOILERS	
VI.E	FIRING INSTALLATIONS FOR WOOD AND OTHER BIOMASS FUELS	
Items: 6		Files: 12

Includes the following changes:

- Make consistent with "Dioxin Toolkit, 2013"
- Include information from EU BREFs (after 2006) and others

Updating underway by "Group of experts on Toolkit and BAT/BEP"

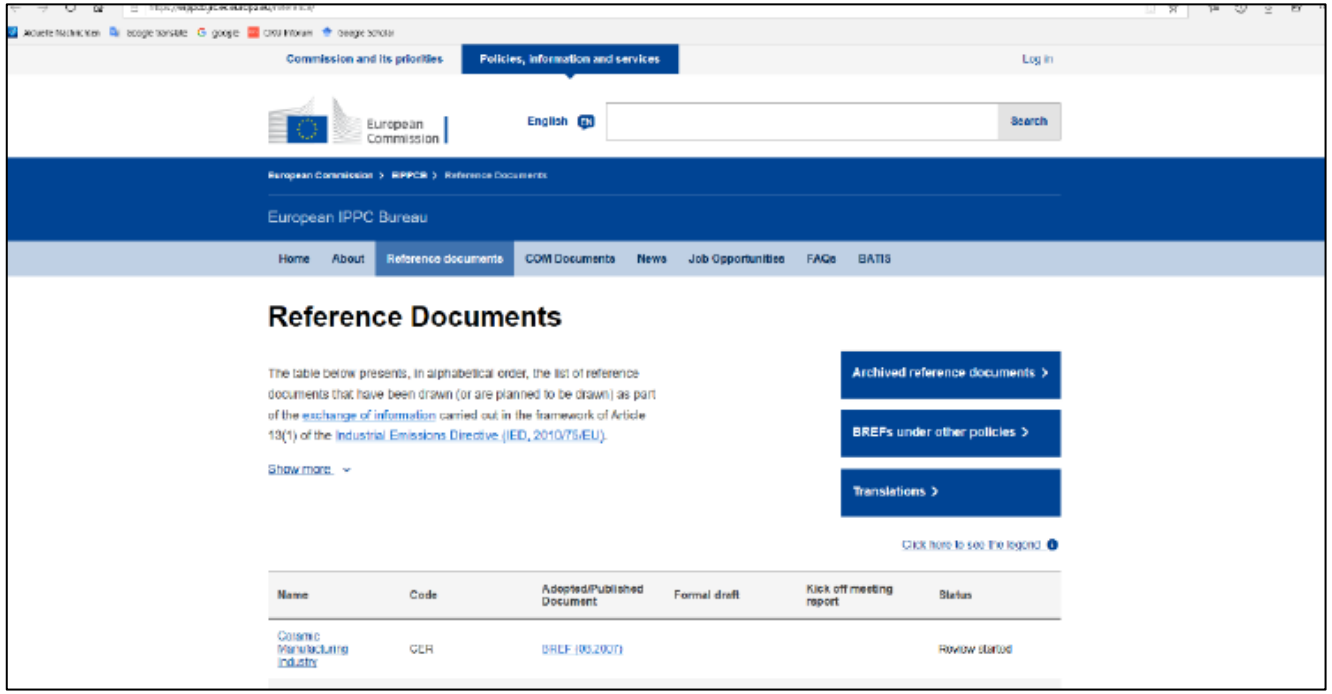
Recommendations to minimize PCDD/PCDF formation

- General: Presorting of feed and fuel materials; removal of oils, plastics, Cl-containing materials (no thermal pretreatment to avoid volatilization of pollutants incl. PCB, PCDD/PCDF or only when followed by afterburner and APCS);
- Afterburners or regenerative thermal oxidizers should be used at temperatures >950 °C to ensure full combustion of organic compounds, followed by rapid quenching of hot gases to temperatures below 250 °C;
- Reduction of diffuse emissions: enclosed converters, short tapping times, enclosed charging. Ventilation systems
- Sinter plants: PCDD/PCDF are formed in the sinter bed itself, probably just ahead of the flame front as the hot gases are drawn through the bed. Disruptions to the flame front (i.e., non-steady-state conditions) have been shown to result in higher PCDD/PCDF emissions. Sinter strands should be operated to maintain consistent and stable process conditions, minimization of oil content in mill scale to a consistent level of <0.5 %.

EU Commission, reference documents BREFs

Reference documents under the IPPC Directive and the IED

- part of the exchange of information carried out in the framework of Article 13(1) of the Industrial Emissions Directive (IED, 2010/75/EU).
- Table contains the Best Available Techniques (BAT) reference documents that have been adopted under both the IPPC Directive (2008/1/EC) and the IED.
- The "BAT conclusions" is a document containing the parts of a BAT reference document laying down the conclusions on best available techniques.
- According to Article 14(3) of the IED, BAT conclusions shall be the reference for setting the permit conditions to installations covered by the Directive.



L 174/32 EN Official Journal of the European Union 30.6.2016

COMMISSION IMPLEMENTING DECISION (EU) 2016/1032

of 13 June 2016

establishing best available techniques (BAT) conclusions, under Directive 2010/75/EU of the European Parliament and of the Council, for the non-ferrous metals industries

(notified under document C(2016) 3563)

Source: http://eippcb.jrc.ec.europa.eu/reference/

BREFs related to metallurgical industry

Name	Code	Adopted/Published Document	Formal draft	Kick off meeting report	Status
Iron and Steel Production	IS	BREF BATC (03.2012)			Published
Ferrous Metals Processing Industry	FMP	BREF (12.2001)	D1 (03.2019)	MR (11.2016)	Document formally adopted
Monitoring of Emissions to Air and Water from IED Installations	ROM	REF (07.2018)			Published
Non-ferrous Metals Industries	NFM	BREF BATC (06.2016)			Published
Smitheries and Foundries Industry	SF	BREF (05.2005)		MR (10.2019)	Review started
Surface Treatment Of Metals and Plastics	STM	BREF (08.2006)			Document formally adopted

General BAT/BEP measures (smitheries and foundries)

- In melting processes, PCDD/PCDF may be produced if the conditions that give rise to such pollutants are present at the same location and time in the process. These conditions are:
  - the presence of chloride ions – these can arise from contaminated scrap, from the use of coal, coke, fuel oil or from certain fluxes
  - the presence of organic carbon – this may arise from contaminated scrap and from coal, coke or oil used as a fuel
  - temperature conditions between 250 °C and 450 °C , with a sufficient gas residence time in this temperature interval
  - the presence of a catalyst such as copper
  - the presence of oxygen.

Iron and steel production (2013) (627 pp)

BREF covers production of iron and steel in **integrated works** as well as the **production of steel in electric arc furnace steelworks**. The main operations covered are:

- loading, unloading and handling of bulk raw materials
- blending and mixing of raw materials
- coke production
- sintering and pelletisation of iron ore
- the production of molten iron by the blast furnace route, including slag processing
- the production and refining of steel using the basic oxygen process, including upstream ladle desulphurisation, downstream ladle metallurgy and slag processing
- the production of steel by electric arc furnaces, including downstream ladle metallurgy and slag processing
- continuous casting.

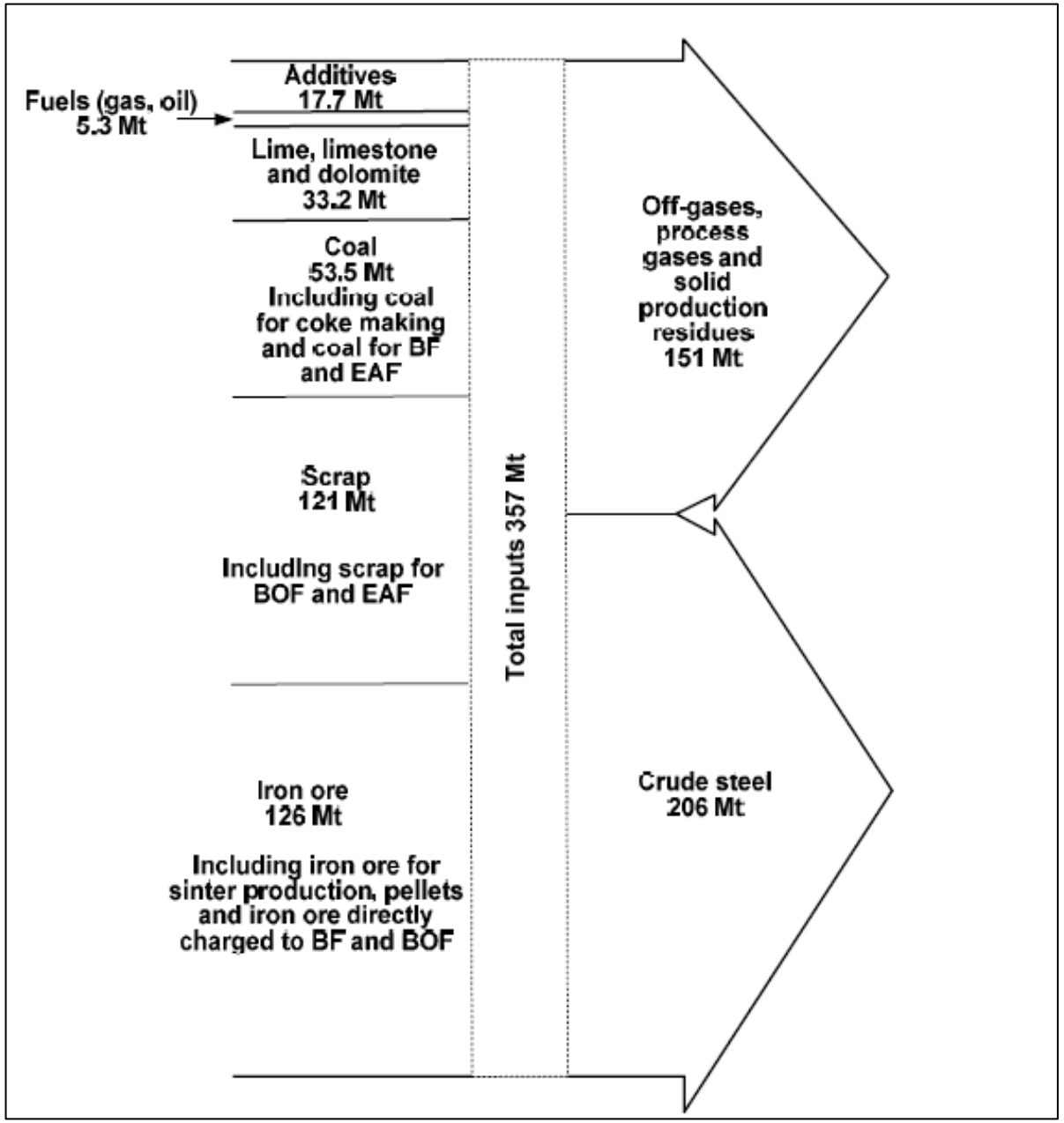
Downstream metal processing activities are covered by BREFs:
(a) Ferrous Metals Processing Industry and (b) Smitheries and Foundries Industry

Overview input/ output of iron and steel industry (EU27, in 2006)

Abbreviations:
BF: blast furnace
BOF: basic oxygen furnace
EAF: electric arc furnace

Two most important steelmaking process routes:

- **Sinter** → pellet plant → coke oven → **blast furnace** → basic oxygen converter, and
- electric arc furnace (direct smelting)



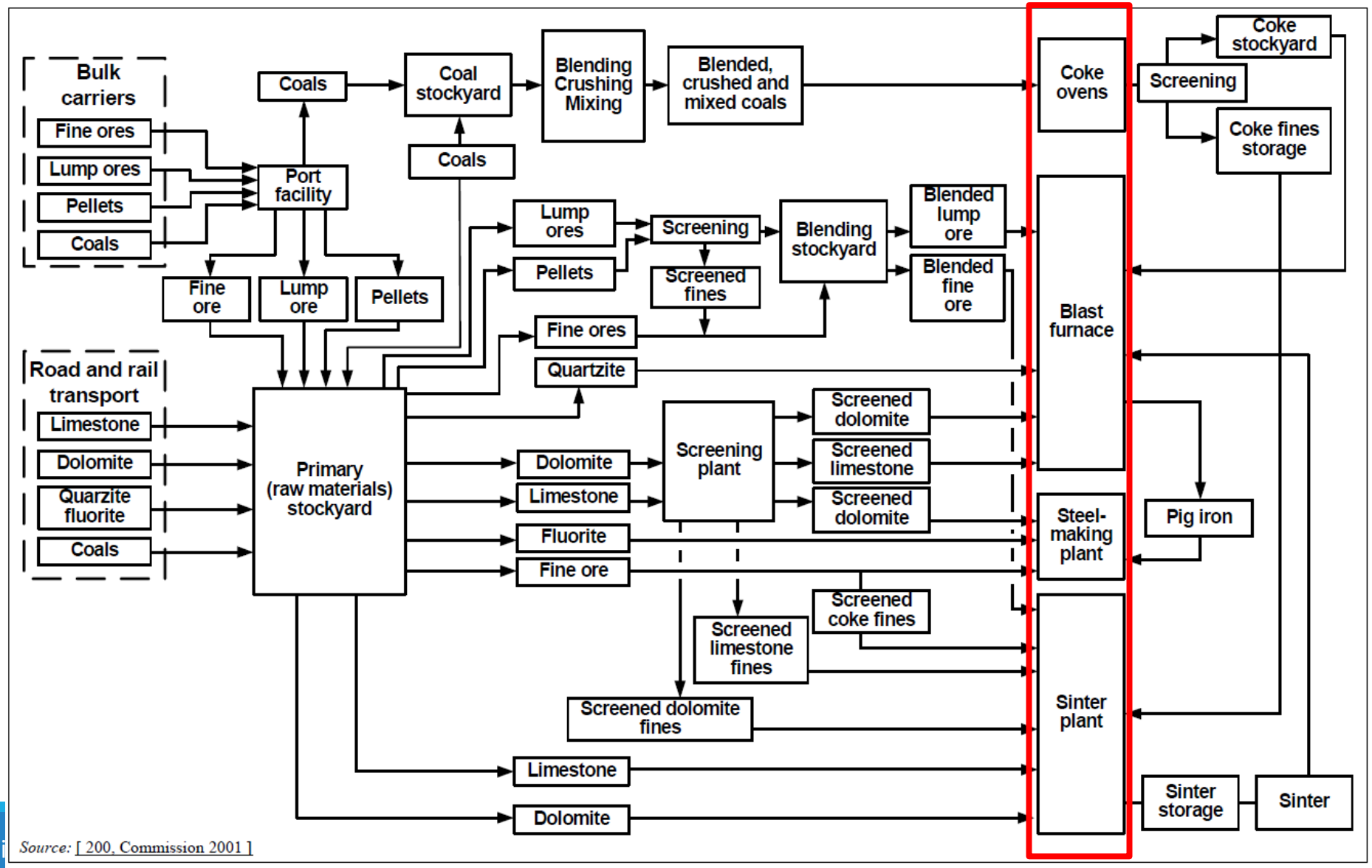
Potential release routes

Releases to (MAJOR/minor)
A/a = air; W/w = water; L/l = land

SOURCES → / RELEASES ↓	Raw material handling	Sinter plant: flue-gas cleaning	Sinter plant: secondary emissions	Pellet plants	Coal pulverisation	Hot blast stoves	Stockhouse	Blast furnace primary gas cleaning	Cast-house	Desulphurisation	BOF: blowing (primary emissions)	BOF: charging/tapping (secondary emissions)	EAF: charging	EAF: melting and refining	EAF: steel and slag tapping
Oxides of sulphur		A		A		A			A	A	A		A	A	
Oxides of nitrogen		A		A		A							A	A	
Carbon dioxide		A		A		A		A		A	A	A	A	A	
Carbon monoxide		A		A		A		A		A	A		A	A	
Hydrogen chloride		A		A								A	A		
Hydrogen fluoride		A		A										A	
Hydrogen sulphide								A							
Ammonia								w							
Oxides of iron	Aw	A	A	A			A	A	A	A	A	A	A	A	A
Alkali metals		A	A	A				A	A	AL	A	A			
Alkaline earth metals		A	A	A			A	A	A	AL	A	A			
Metal oxide particulates	Aw	A	A	A			A	A	A	A	A	A			
Non-metallic particulates	Aw	A	A	A	A		A	A	A	A	A	A			
Metallic iron												A			
Inorganic fluorides			A	A				A			A	A			
Hydrogen cyanide								w							
Cadmium and cadmium oxide	W	A		A				A			A	A	A	A	
Zinc, lead and their oxides	w	A		A				A			A	A	A	A	
Other metals and their oxides	Aw		A	A									A	A	A
Phosphorus compounds								wl			Awl				
Sulphur										l	A				
Carbon								A				A			
Other inorganic chemicals	A W												A	A	
Oils and greases	w														
Slag								Ll			Ll			Ll	Ll
Sludges								wLl		Ll	wLl				
Refractory waste	Aw														
PCDD/F		A		a								A	A	A	
PAH		A												A	
PCB		A												A	
Volatile organic compounds		A		a				A				A		A	

SOURCES → / RELEASES ↓	EAF: furnace and ladle lining repairs	Alloying	Ladle treatment	Reladling and recarburisation	Degassing	Decarburisation	Electroslag remelting	Vacuum induction melting	Induction melting	Ferrous alloy powders	Continuous casting	Ingot casting	Scarfing	Slag processing	Skull burning
Oxides of sulphur		A	A						A					A	
Oxides of nitrogen			A						A						
Carbon dioxide			A	A		A			A				A		
Carbon monoxide			A	A		A			A						
Hydrogen chloride															
Hydrogen fluoride			A				A								
Hydrogen sulphide														A	
Ammonia															
Oxides of iron	Al	A	A	A		A	l		A		Awl	Al	Awl	wl	Al
Alkali metals														wL	AL
Alkaline earth metals														wL	AL
Metal oxide particulates											Awl	Al	Awl	wl	Al
Non-metallic particulates														wl	
Metallic iron	Al									A				wl	
Inorganic fluorides	Al	A													
Hydrogen cyanide	ALl	A													
Cadmium and Cadmium oxide					Wl	A	l								
Zinc, lead and their oxides					wl	A	l				Awl	Al	Awl		Al
Other metals and their oxides			A	A	wLl	A	Ll			A	Awl		Awl		ALl
Phosphorus compounds			A												
Sulphur														wl	
Carbon															
Other inorganic chemicals	Al	ALl	A												
Oils and greases											w				
Slag waste	Al		Ll	ALl	l	Ll		Ll	Ll		Ll	Ll		Ll	Ll
Sludges													wl		
Refractory waste	ALl				l	Ll	Ll	Ll	Ll		Ll	Ll		Ll	
PCDD/F															
Volatile organic compounds															

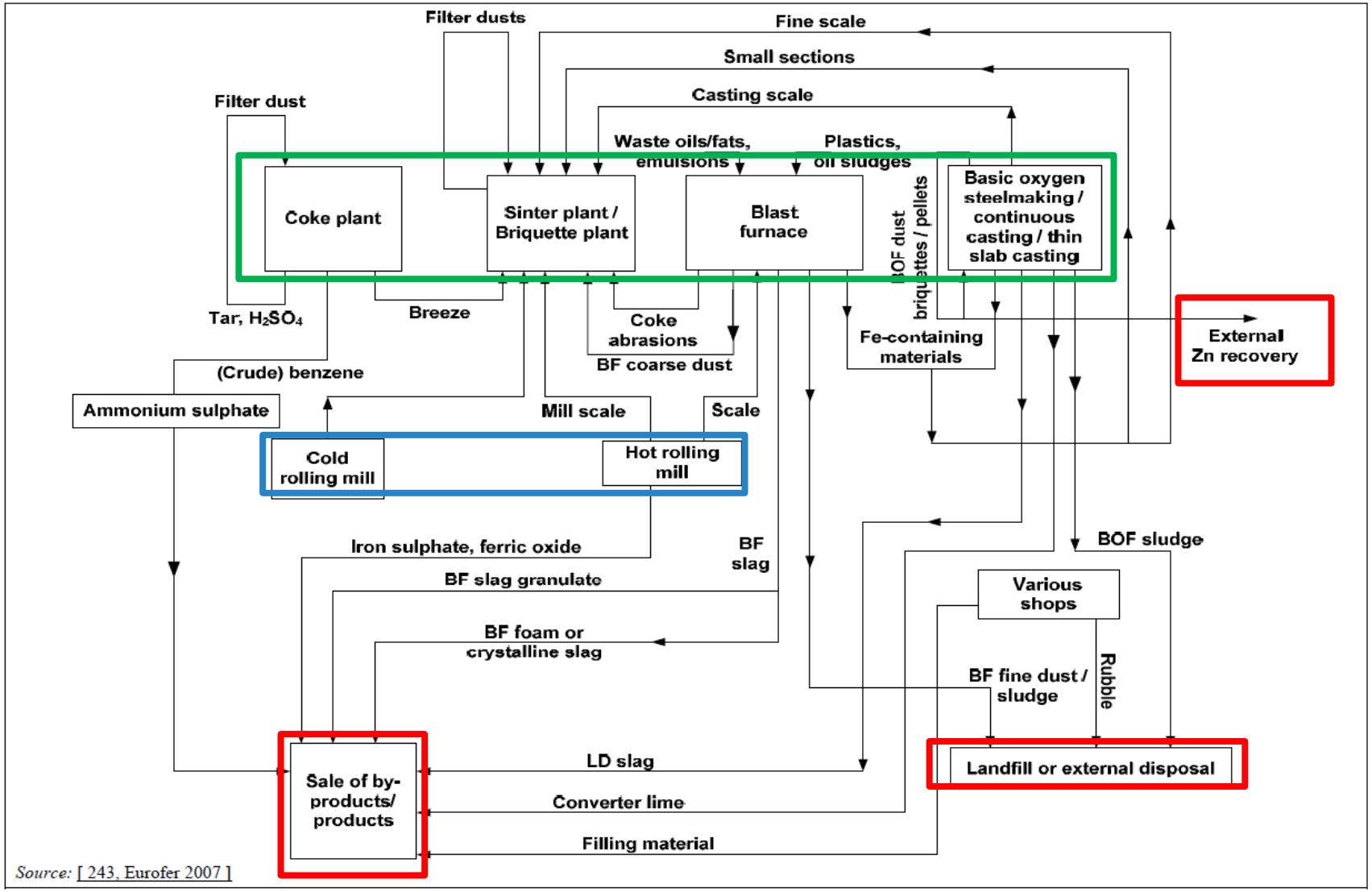
Flow diagram for material handling in integrated steels works



Integrated coke, sinter and hot metal production

Figure 2.10; BREF Iron and steel (2013)

Management of production residues in integrated steelworks



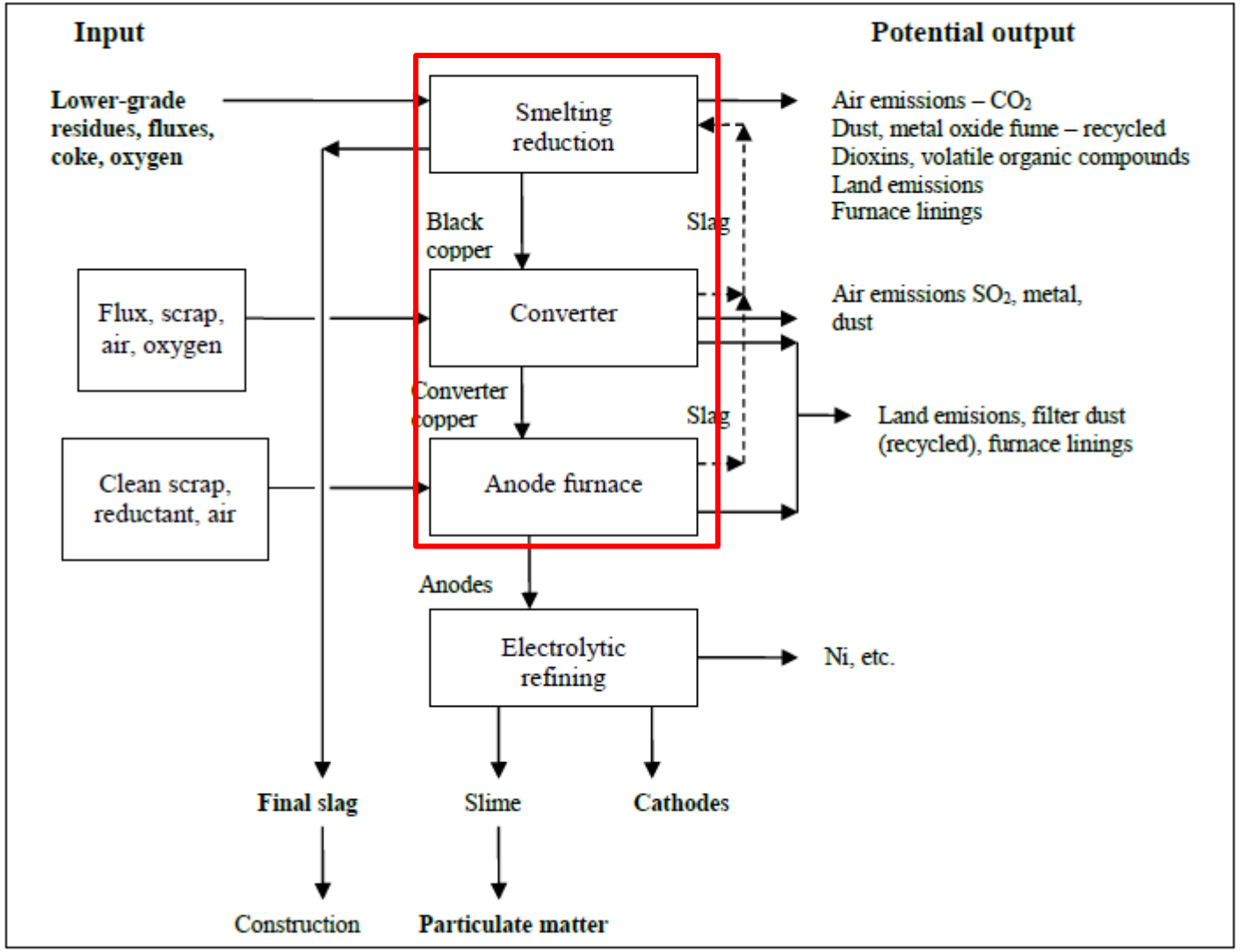
e 2.11: Example for the management of production residues such as by-products and wastes in an integrated steelworks

Secondary copper smelting

Three thermal steps depending on input.

- Copper is the best known catalyst for PCDD/PCDF formation, especially
  - When precursor compounds containing chlorine are present in temperature range 200 °C – 450 °C
  - For reformation/de novo formation if flue gases are not cooled down rapidly

Figure 1. Secondary copper smelting



Source: European Commission 2014, p. 224.

Ferrous metal furnaces in foundries:

- **Cupola furnaces:** massive surplus of chlorine is always present from coke. Enough carbon is present from coke too, but an additional input of carbon may be needed the event of caused by poor scrap qualities. Under specific operational conditions, the conditions for dioxin formation could occur. Since *de novo* synthesis mainly occurs during cooling of the flue-gas, this applies to both hot blast and cold blast cupolas. Average value was 0.54 ng TEQ/Nm^3 for cold blast and 0.75 ng TEQ/Nm^3 for hot blast cupola.
- **Rotary furnaces**: input to rotary kilns generally consists of clean material. High flame temperature, the hot gases leave the furnace at temperatures of between 1000 °C and 1300 °C . Post combustion occurs inside the furnace volume. *De novo* synthesis is possible if flue-gases cool slowly. Reported data range from 0.004 ng TEQ/Nm^3– 0.61 ng TEQ/Nm^3.
- **Induction furnaces**: input to induction furnaces generally consists of clean material. Furthermore the furnace does not produce a ducted high temperature flue-gas stream that cools down slowly.
- **Electric arc furnaces**: EAF furnaces allow melt treatment and alloying if operated in basic lining practice; thus, dirty scrap can be used as a raw material for melting. If scrap containing organic and/or chlorinated compounds is charged, PCDD/PCDF may be formed during cooling of the flue-gas stream. The EAF in acid lining practice does not allow metal treatment and therefore the possibility for feeding contaminated scrap is reduced and the risk of PCDD/PCDF formation is reduced as well.

Furnaces in non-ferrous metal industries

Table 13.2: Drying, roasting, sintering and calcining furnaces

Furnace	Metals used	Material used	Comment
Steam coil dryer Fluidised bed dryer Flash dryer	Copper and some others	Concentrates	
Rotary kiln	Most metals for drying; Fuming ZnO; Calcining alumina, nickel and ferro-alloys; Burning film in precious metals; De-oiling copper and aluminium scrap Mercury removed from gas-cleaning precipitates.	Ores, concentrates and various scrap and residues	Drying, calcining and fuming applications
Shaft	Ferro-alloys (FeCr)	Lumpy furnace charge	Drying, devolatilising and preheating the furnace charge
Fluidised bed reactor	Copper, nickel, cobalt, precious metals, zinc and Al_2O_3	Concentrates and $Al(OH)_3$	Calcining and roasting
Updraught sintering machine	Zinc and lead	Concentrates and secondary raw materials	Sintering
Downdraught sintering machine	Zinc and lead	Concentrates and secondary raw materials	Sintering
Steel belt sintering machine	Ferro-alloys, manganese, chromium and niobium	Concentrates and fines	Other applications possible
Travelling grate Sintering machine	Ferro-alloys	Manganese fines	Sintering
Herreshoff	Refractory metals and molybdenum	Ores and concentrates	Roasting, calcining

Table 13.3: Smelting and converting furnaces

Furnace	Metals used	Material used	Comment
Enclosed refractory-lined crucibles	Refractory metals and special ferro-alloys	Metal oxides	
Open pit	Refractory metals and special ferro-alloys	Metal oxides	
Pusher	Refractory metals	Oxides	
Batch	Refractory metals	Metals	
Vacuum	Lead, tin and refractory metals	Secondary raw materials, carbon	
Baiyin	Copper	Concentrates	
Electric arc	Ferro-alloys	Concentrates, ores, secondary materials	
Contop/cyclone	Copper	Concentrates, ores	
Submerged electric arc	Precious metals, copper and ferro-alloys	Slag, secondary materials, concentrates, ores	For the production of ferro-alloys, the open, semi-closed and closed types are used
Rotary	Aluminium, lead and precious metals	Scrap and other secondary raw materials	Oxidation and reaction with substrate
Tilting rotary	Aluminium Lead	Scrap and other secondary raw materials. Flue-dusts that contain lead and secondary material	Minimises salt flux use Flue-dust from primary copper production. Battery recovery
Rotary/rocking	Lead	Smelting of secondary lead	Also called the Doerschel furnace
Reverberatory and hearth/closed well	Aluminium, copper, lead and others	Scrap and other secondary raw materials	Smelting of oxidic copper material, refining
Vanyukov	Copper	Concentrates	
Ausmelt/ISASMELT/KRS	Copper and lead	Intermediates, concentrates and secondary raw materials	
QSL	Lead	Concentrates and secondary raw materials	
Kivcet	Lead and copper	Concentrates and secondary raw materials	
Noranda	Copper	Concentrates	
El Teniente	Copper	Concentrates	
TBRC (KALDO) and TROF	Copper, lead, tin and precious metals	Most secondary raw materials including slimes	
Mini smelter	Copper/lead/tin	Scrap	
Blast and ISF	Lead, lead-zinc, copper, precious metals, HC FeMn	Concentrates, most secondary	
INCO flash	Copper and nickel	Concentrates	
Outotec flash furnace	Copper and nickel	Concentrates	
Mitsubishi process	Copper	Concentrates and anode scrap	
Peirce-Smith	Copper (converter), ferro-alloys, metal oxide production	Matte and anode scrap	
Hoboken	Copper (converter)	Matte and anode scrap	
Outotec flash converter	Copper (converter)	Matte	
Noranda	Copper (converter)	Matte	
Mitsubishi	Copper (converter)	Matte	

Table 13.4: Melting furnaces

Furnace	Metals used	Material used	Comment
Induction	Most	Clean metal and scrap	Induced stirring assists alloying. Vacuum can be applied for some metals
Electron beam	Refractory metals	Clean metal and scrap	
Rotary	Aluminium and lead	Various scrap grades	Fluxes and salts used for complex matrices
Reverberatory (also known as hearth or closed well)	Aluminium (primary and secondary)	Various scrap grades. (An additional side-well can be used for fine metal particles)	Bath or hearth configurations can vary. Melting or holding metal
Contimelt	Copper		Integrated furnace system
Shaft	Copper	Copper cathode and clean scrap	Reducing conditions
Drum (Thomas)	Copper	Clean copper scrap	Melting and fire refining
Heated crucibles (indirectly heated kettles)	Lead and zinc	Clean scrap and raw metal	Melting, refining and alloying
Directly heated crucibles	Precious metals	Clean metal	Melting and alloying
Submerged electric arc	Ferro-alloys (FeCr, FeMn, SiMn)	Lumpy ore, pellets, sinter, slag and secondary materials	

Different types of scrap (block vs. pieces with higher surface areas; oxygen content, degree of contamination) require different furnaces.
Fuel-heated vs. electrically heated furnaces

Source: Annex BREF NFM

Discontinuous emission monitoring (iron and steel)

Table 2.18: Examples of measuring methods for discontinuous emission monitoring

Component in the flue-gas	Measuring method
Dust	EN 13284-1 (<50 mg/m^3) or ISO 9096 (>20 mg/m^3) VDI 2066 part 1 for low and high concentrations Ö-NORM M 5861 NF X 44-052
SO_2	EN 14791 identical to VDI 2462 part 3 VDI 2462 part 1
NO_x as NO_2	EN 14972 VDI 2456, manual method
CO	EN 15058 VDI 2459, manual method
Metals (As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sb, Se, Tl, V, Zn)	EN 14385 identical to VDI 3868 part 1
TOC	EN 12619 for low concentrations, EN 13526 for high concentrations, VDI 3481 part 1, manual method
Hg	EN 13211
H_2S	VDI 3486 US EPA Method 11
HCl	EN 1911
HF	VDI 2470 part 1 ISO 15713
NH_3	VDI 3496, based on EN 14791
PCDD/F and PCB	EN 1948 VDI 3499, additional for higher concentrations
PAH	VDI 3873 part 1 ISO 11338
Source: [200, Commission 2001] [277, Wiesenberger 2007].	

BREF, Iron and steel (2013)

Dioxin measurements in the EU

- For manual sampling, EN 1948 is the European standard guideline to determine the mass concentration of PCDD/PCDF and dioxin-like PCB from stationary sources.
- Guideline is developed and validated for waste incineration plants to check the compliance to the emission limit value of 0.1 ng I-TEQ/Nm³.
- In many European countries, EN 1948 is the basis for national standard guidelines for the determination of dioxin emissions (e.g. CSN EN 1948; DIN EN 1948 and VDI of 3499, etc.).
- The guideline describes two measurement procedures:
  - Part A is an example for the application of DIN EN 1948 for PCDD/PCDF emissions at about 0.1 ng I-TEQ/Nm³
  - Part B, the measurement method is modified for PCDD/PCDF concentrations in excess of 0.1 ng I-TEO/Nm³. (Only the determination of PCDD/PCDF is validated).
- There are further standardised sampling methods which are used in the EU:
  - EPA 23 A which is a manual sampling method valid in the US, has been developed for the determination of the dioxin emissions from stationary sources of waste incineration plants.

Costs and frequency for PCDD/PCDF measurements

Table 2.19: Total cost for a PCDD/F measurement according to EN 1948

Method	Cost range (EUR)
Manual sampling according to EN 1948 – one sample (one day) inclusive PCDD/F analysis without travel cost	1800 – 3500
Manual sampling according to EN 1948 – three samples (three days) inclusive PCDD/F analysis without travel costs	4000 – 6500
PCDD/F – analysis (EN 1948)	450 – 800
Dioxin-like PCB – WHO PCB (EN 1948)	110 – 600

COMMISSION IMPLEMENTING DECISION (EU) 2016/1032 of 13 June 2016 establishing best available techniques (BAT) conclusions, under Directive 2010/75/EU of the European Parliament and of the Council, for the non-ferrous metals industries

Parameter	Monitoring associated with	Minimum monitoring frequency	Standard(s)
PCDD/F	**Copper**: BAT 48 **Aluminium**: BAT 83 **Lead, Tin**: BAT 99 **Zinc, Cadmium**: BAT 123 **Precious metals**: BAT 146 **Ferro-alloys**: BAT 159 **Other non-ferrous metals** (5) (7)	Once per year	EN 1948 parts 1, 2 and 3

Muchas gracias – Thank you