Unintentionally produced POPs (UPOPs) inventories

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Iskenderun Anemon Hotel, Turkey, 23 March, 2017

Unintentional POPs inventory

Emission inventories principles
Emission factors
Parameters influencing the quality of emissions
Uncertainty of emissions estimations
Overview of inventory tools - UNEP Dioxin Toolkit, Inventory tools of the EU, EEA, CRLTAP
UNEP Dioxin Toolkit - lectures + practical exercise
(Inventories of old and new POPs in products, materials, wastes. Problems of OCPs and PCBs inventories)

Emission inventories

IP and UP POPs

- Unintentionally produced (UP): Dioxins/furans (byproducts in thermal processes)
- Intentionally produced (IP): Polychlorinated pesticides, transformer/capacitor oils (PCB), polybrominated flame retardants, …

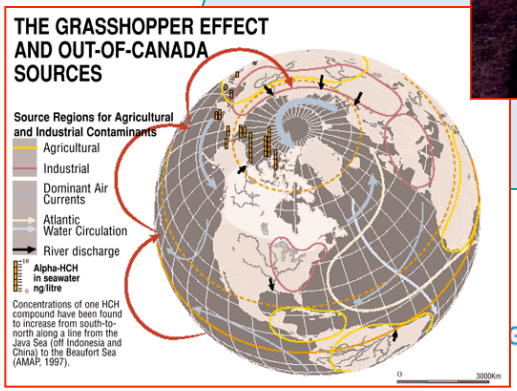
Elimination of stockpiles (IP) - destruction (conservation)

Elimination of byproducts (UP) - prevention and destruction

Decontamination (IP + UP) - remediation of soils, sludges, water, sediments, …

Production, application, disposal

POPs



GANIZATION

Why study emissions?

Support policy development

- Complete coverage of sources (control strategies)
- Complete coverage of parties (e.g. domain of SC)

Support science

- Complete spatial coverage (geographical domain, spatial scale)
- Complete temporal coverage (persistence, primary vs secondary)
- Complete compound coverage (congener/isomer basis)
- Complete media coverage (multimedia pollutants)

Common

- Accuracy
- Uncertainty

If we are to understand and control POPs, knowledge about the sources is essential

Emission inventory principles

An atmospheric emission inventory is a database of information on:

- emission measurements
- emission factors
- individual emission sources
- activity statistics
- emission estimates derived from the above data

Emission inventory principles

Emission inventories are never completely accurate, because unsurveyed or inadequately described sources are always present and society moves ever on, building new sources of emissions, controlling the emissions of others, and ceasing the operation of still others.

Emission inventory principles

The initial steps of emission determination include the selection of:

- substances to be inventoried
- source categories
- determination procedures
- source resolution
- source activity data

POP emission inventory

- POP emission inventory is a basic element of POP environmental regulation.
- Parties of the Protocol to the 1979 Convention on Long-Range Transboundary Air Pollution on Persistent Organic Pollutants are obliged to present information about national emissions meeting the requirements of EMEP in regard to completeness and structure.
- In particular, in the annual information Parties submit data on national annual emissions of selected POPs – PAHs, OCPs, PCBs, PCDDs/Fs.
- It is recommended to present the information in SNAP source-sector split.
- Stockholm Convention – Dioxin only – Dioxin Toolkit, now more

POP emission inventory

The following methodological principles make the ground for estimates of POPs (PCBs, PCDDs/Fs, PAHs, HCB) emissions:

- use of official statistical information on product output and amount of fuel combustion and waste incineration on the regional level (in case such information is not available expert estimates and assumptions are used);

- for the acquisition of the information required for the estimation of emission factors various data and methods are used: literature data, contacts with national experts, own experimental investigations;

POP emission inventory

- estimates are made for the maximum possible sources; in those cases when it was impossible to make quantitative estimates we made qualitative ranging of sources;

- a special attention is focused on reliable spatial distribution of emissions and on the identification of point sources.

Emission factors

- Emission factors are one method used to estimate the emission of air toxins from sources.

- Inputs required to calculate emissions using emission factors include:

1) Activity information about sources (amount of product produced, fuel used, etc.);
2) Emission factors to translate activity information into "uncontrolled" emission estimates; and
3) Control device efficiency information to provide the basis for estimation of emissions to the atmosphere after passage through a control device.

Emission factors

The algorithm for estimating emissions is given by:

$$E = R \times EF \times (1 - C/100)$$

where:

E = emission estimate for source

R = activity level

EF = emission factor

C = control device efficiency

Thus the accuracy of the emission estimate (E) depends upon the accuracy of R, EF, and C.

Errors introduced by any one of these quantities will affect the final emission estimate.

Emission factors

Several variables affect the value of the emission factor.

These include:

(1) Time, because the state of the art of technology changes, e.g., the change of emission factors for vehicles;
(2) Location, because of the variation of technical parameters from one plant to the next, or one country to another, e.g., fuel used, technology used, plant age, etc., and
(3) Knowledge, because on going results can be used to improve measurements techniques.

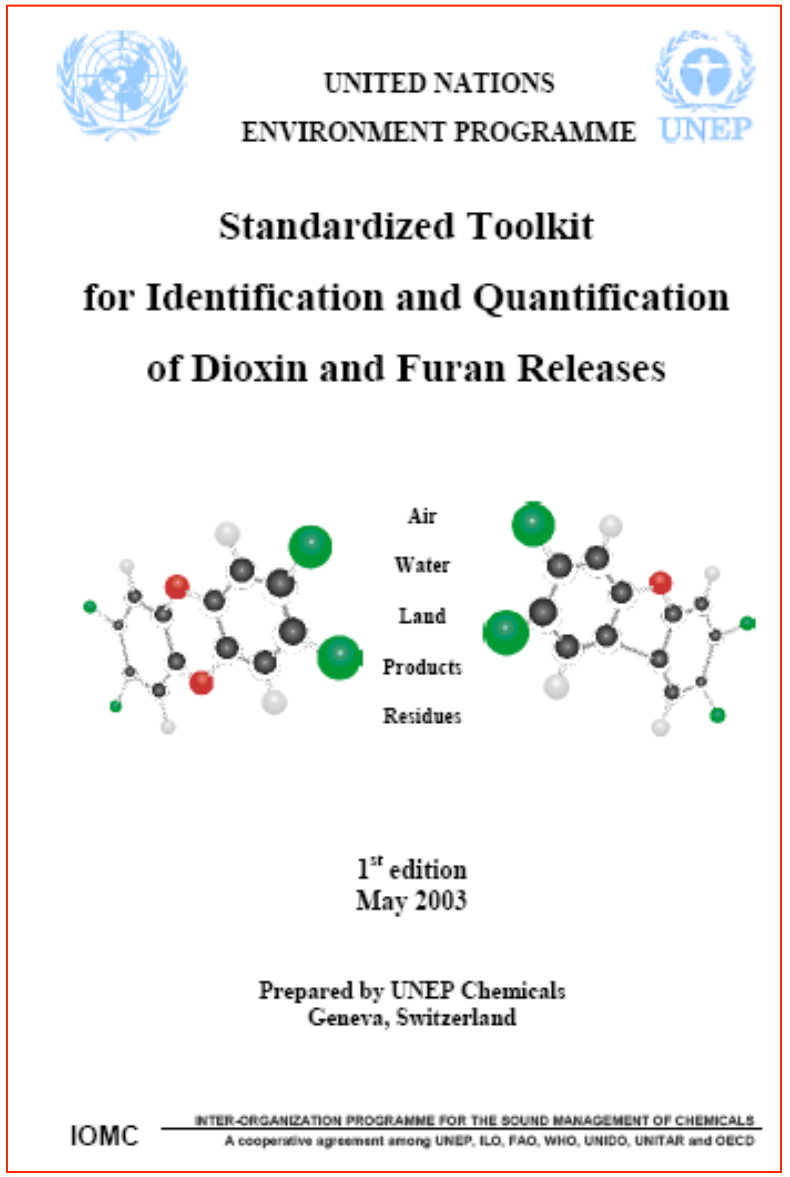
The main sources of persistent organic pollutants

(a) Combustion processes;
(b) Industrial processes;
(c) Diffusing sources (mobile sources, open burning etc.);
(d) Secondary sources (volatilisation from landfills etc.); and
(e) Accidental sources (industrial accident, transport accident etc.).

Dioxin Toolkit 1st edition, May 2003

The United Nations Environment Programme UNEP Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases is designed to cover all source categories and processes that are listed in Annex C, Parts II and III of the Stockholm Convention.

The Toolkit can be used where there are no measured data available and provides default emission factors for all source categories.



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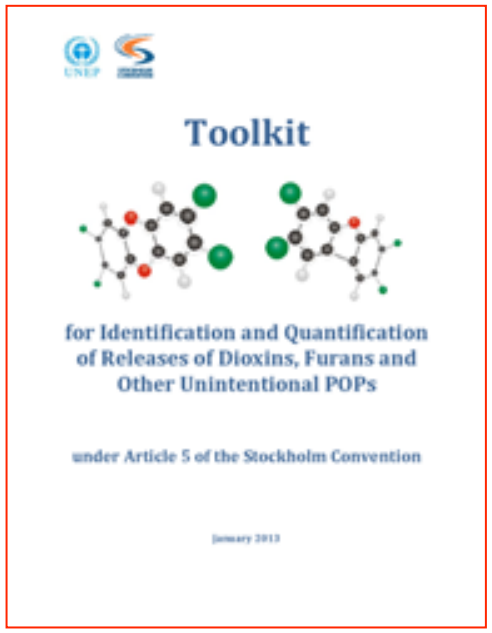
Dioxin Toolkit 2nd edition, May 2013

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

under Article 5 of the Stockholm Convention on Persistent Organic Pollutants

http://toolkit.pops.int/



uPOPs inventory

Pursuant to Article 5 of the Convention, the following unintentional POPs are listed in Annex C:

- Polychlorinated dibenzo-p-dioxins (PCDD)
- Polychlorinated dibenzofurans (PCDF),
- Polychlorinated biphenyls (PCB),
- Hexachlorobenzene (HCB), and
- Pentachlorobenzene (PeCBz)

In addition to emission factors for PCDD/PCDF, the Toolkit also contains emission factors for other POPs when such information is available.

Typically, emission factors are provided for the five release vectors, i.e., air (EFAir), water (EFWater), land (EFLand), product (EFProduct), and residue (EFResidue).

Methodology

- Classification and Emission Factors from "Dioxin Toolkit"
- National Data for Activity Rates
  - National Statistics
  - Annual Activity Reports
  - Sector Associations
  - Questionnaires
  - Scientific Papers and Reports
  - Personal Communications
  - Emission Reports
  - Web-Sites
  - etc...

Parameters influencing the quantity of emissions

(1) Factors which characterise the "production" technology or process

(a) Use pattern

(b) Tonnage

(c) Type of technology or process (closed, opened etc.)

(d) Technology processes - composition of

- reaction mixtures
- combusted mixtures and
- use mixtures (application, disposal etc.)

(e) Technology conditions

- recommended parameters (temperature, pressure etc.)
- composition and types of fuels or reaction mixture
- age of technology
- state of technology
- technology discipline

Parameters influencing the quantity of emissions

(2) Factors, which characterise the pollutants:

- (a) Quantity
- (b) Physical-chemical properties
- (c) Environmental-chemical properties
- (d) Composition of chemical mixtures or wastes

(3) Factors, which characterise the environmental conditions:

- (a) Ambient temperature
- (b) Wind
- (c) Sunlight
- (d) Processes of atmospheric deposition

Specific sources of POPs and the various factors, which can influence the emission factors

(1) Public power, co-generation and district heating plants, commercial, institutional and residential combustion plants, industrial combustion plants and other processes with combustion:

(a) type of fuel
(b) size of furnace
(c) ambient temperature
(d) composition, mixture content, size and shape of the debris burned
(e) compactness of the pile incinerated
(f) age of technology

(2) Non-combustion processes:

(a) type of process
(b) age of technology

Specific sources of POPs and the various factors, which can influence the emission factors

(3) Extraction and distribution of fossil fuels:

(a) fuel properties
(b) air temperature changes
(c) type of storage site

(4) Solvent use:

(a) solvent properties
(b) solvent content of product
(c) air temperature changes
(d) type of depot tank (fixed/floating roof)

Specific sources of POPs and the various factors, which can influence the emission factors

(5) Transportation:

(a) type of fuel
(b) size of engine
(c) vehicle weight and category (private/commercial)
(d) engine design
- two/four stroke (Otto engines)
- type of fuel injection and chamber design (Diesel engines)
- according to EEC/ECE regulations

(e) control devices used for exhaust and evaporative emissions
(f) operating conditions according to driving pattern, average speed and road type
(g) average trip length
(h) ambient temperature
(i) vehicle age
(j) inspection and maintenance of vehicles

Specific sources of POPs and the various factors, which can influence the emission factors

(6) Waste treatment and disposal:

(a) type of fuel
(b) size of furnace
(c) ambient temperature
(d) composition, moisture content, size and shape of the debris burned
(e) compactness of the pile incinerated
(f) processes during waste water treatment
(g) amount of active biomass
(h) type, composition, form and amounts of used sludge
(i) amount of rainfall
(j) ambient temperature

pecific sources of PCDD/F and the variables factors, which can influence the emission factors

(b) type, composition, form and amounts of applied sludge
(c) soil properties
(d) amount of active biomass
(e) amount of rainfall

(g) amount of solar radiation
(f) ambient temperature
(g) amount of solar radiation

Specific sources of POPs and the various factors, which can influence the emission factors

(8) Natural sources:

(a) soil and sediment composition
(b) amount of active biomass
(c) amount of rainfall
(d) ambient temperature
(e) amount of solar radiation

(9) Forest and prairie fires:

(a) type of species
(b) natural conditions (ambient temperature, rainfall etc.)

Uncertainty of emission estimates (PCBs)

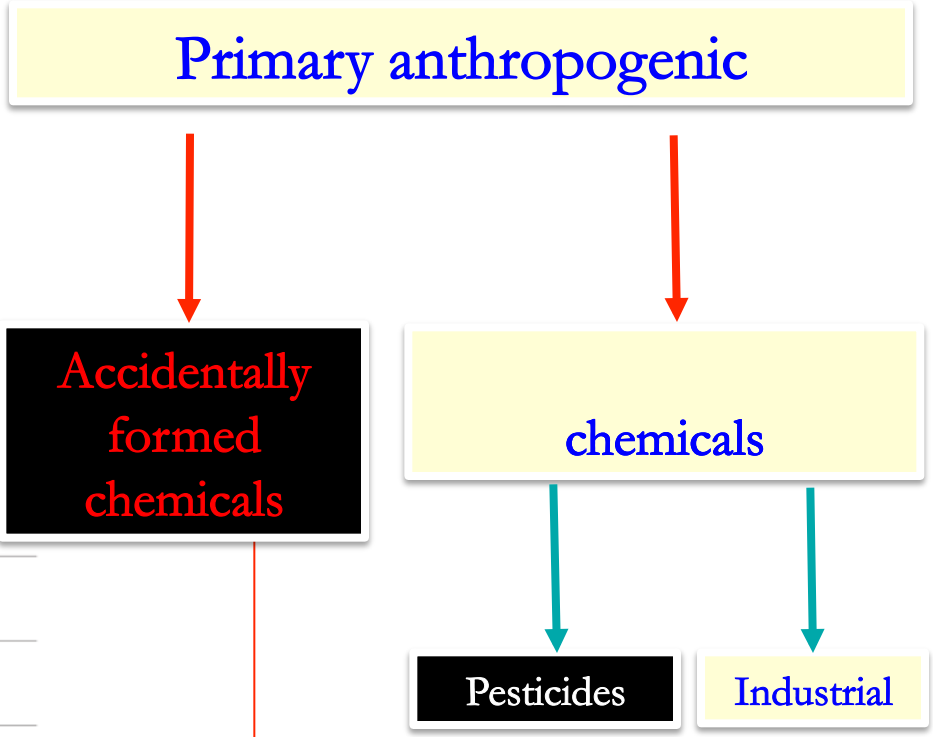
Uncertainty of calculations of PCB emissions distributed over territories is connected with a combination of factors.

They may be divided to some groups:

Uncertainties in estimates of PCB used:

- PCB was produced during decades, consumers of products contained PCB were hundreds of enterprises and organizations.
- This group of factors includes the accuracy of identification of all modern and previous PCB emission sources (manufacturers, consumers, houses, store, landfills).

POPs and iPOPs (industrial POPs)



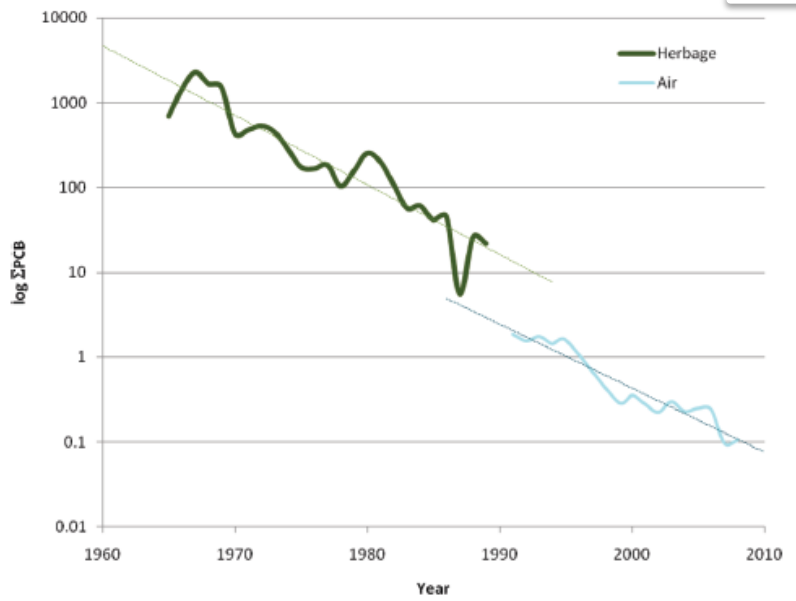


FIGURE 5. ∑PCB for herbage samples from Rothamsted (1965–1989) [herbage in ng/g dry weight for ∑PCB (28, 52, 101, 118, 138, 153)] (*17*) and ∑PCB for atmospheric samples from LON and MAN (1991–2008) [air in ng/m^3 for ∑PCB (28, 52, 101, 118, 138, 153, 180)].

Atmospheric burdens of PCBs and PBDEs are generally decreasing in Europe and Northern America – problem solved?

Schuster et al 2010 ES&T

Unintentionally Produced POPs

Convention Goal = "continuing minimization and, where feasible, ultimate elimination of the total releases of chemicals in Annex C derived from anthropogenic sources"

Annex C, Part I

Chemical
Dioxins and furans (PCDD/PCDF)
Hexachlorobenzene (HCB)
Polychlorinated biphenyls (PCB)

What are POPs by-products

PCDDs/Fs, HCB, PeCB, PCBs (and other POPs) are unintentionally formed and released from thermal processes involving organic matter and chlorine as a result of incomplete combustion or chemical reactions

- Sources
- Stockholm Convention provisions
- Release reduction possibilities
  - Alternative processes

PCDDs/Fs, HCB, PeCB, PCBs (and other POPs)

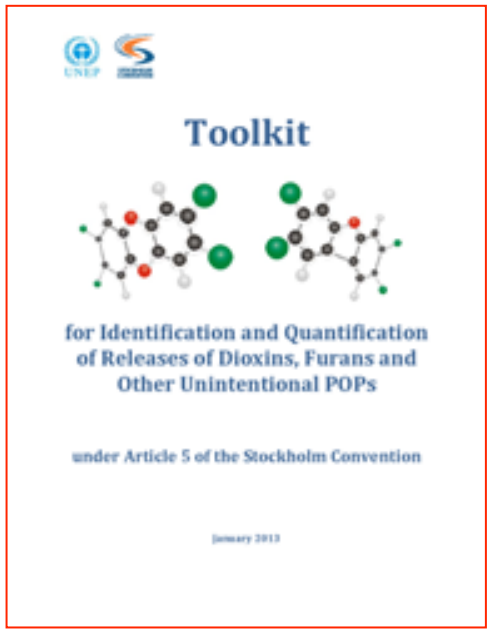
Emission inventories Guidelines

Dioxin Toolkit 2nd edition, May 2013

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

under Article 5 of the Stockholm Convention on Persistent Organic Pollutants

http://toolkit.pops.int/



Dioxin Toolkit – Part I

Part I General Guidance

The *Toolkit for Identification and Quantification of Releases of Dioxins, Furans and Other Unintentional POPs* is divided into three parts.

Part I includes general guidance for inventory development, update and revision, guidance on data quality and quality assurance and quality control of inventory results, guidance to determine activity rates, and others aspects.

http://toolkit.pops.int/

Dioxin Toolkit – Part II

Part II of the *Toolkit for Identification and Quantification of Releases of Dioxins, Furans and Other Unintentional POPs* includes information on default emission factors for source categories grouped in ten source groups within the Toolkit, the levels of confidence assigned to each emission factor value, guidance on estimating activity rates, classifying sources and assigning the appropriate emission factors.

For the purpose of the PCDD/PCDF inventory development, Parts I and II of the Toolkit provide all necessary guidance.

http://toolkit.pops.int/

Dioxin Toolkit – Part III

Part III Annexes and Example Inventories

Part III of the *Toolkit for Identification and Quantification of Releases of Dioxins, Furans and Other Unintentional POPs* includes annexes containing detailed technical complementary information on the derivation of dioxin emission factors for the ten source groups, along with emission factors for other unintentional POPs.

Part III also includes example inventories for each source group illustrating the process of inventory development, update and revision, and providing useful insights into estimating activity rates and/or applying expert judgment for a number of source categories.

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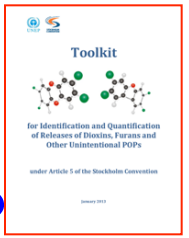
Dioxin Toolkit – Chapter 1.1

Chemicals Listed in Annex C



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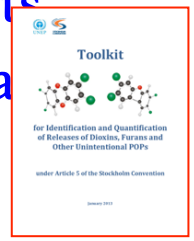
- Pentachlorobenzene (PeCBz).

http://toolkit.pops.int/

Dioxin Toolkit – Chapter 1.1

Among these, PCDD and PCDF (also collectively referred to as PCDD/PCDF) have never been used as commercial products nor were intentionally manufactured for any reason other tha laboratory purposes.

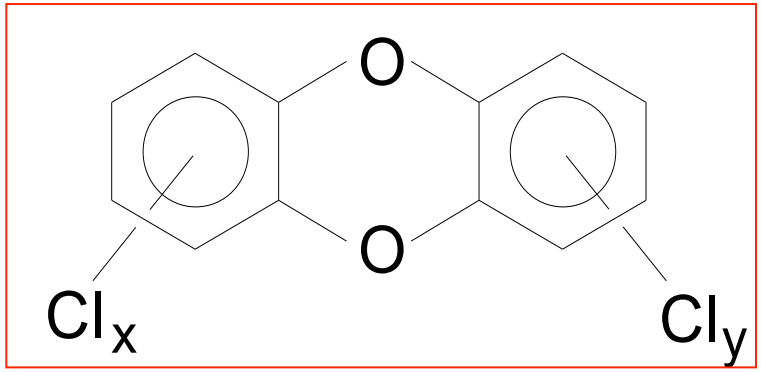


PCB, HCB and PeCBz are also unintentionally formed, usually from the same sources that produce PCDD/PCDF.

However, unlike PCDD/PCDF, they have also been manufactured and used for specific purposes, their intentional production and use being by far higher than the unintentional formation and release.

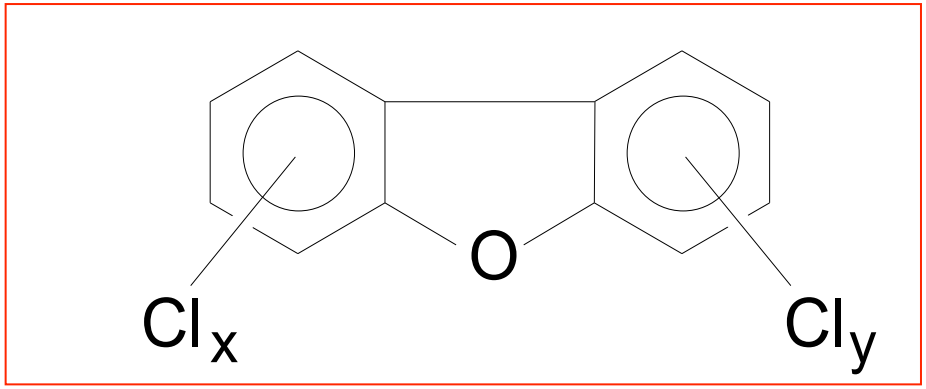
http://toolkit.pops.int/

PCDDs/Fs



Polychlorinated dibenzo-p-dioxins (PCDDs)

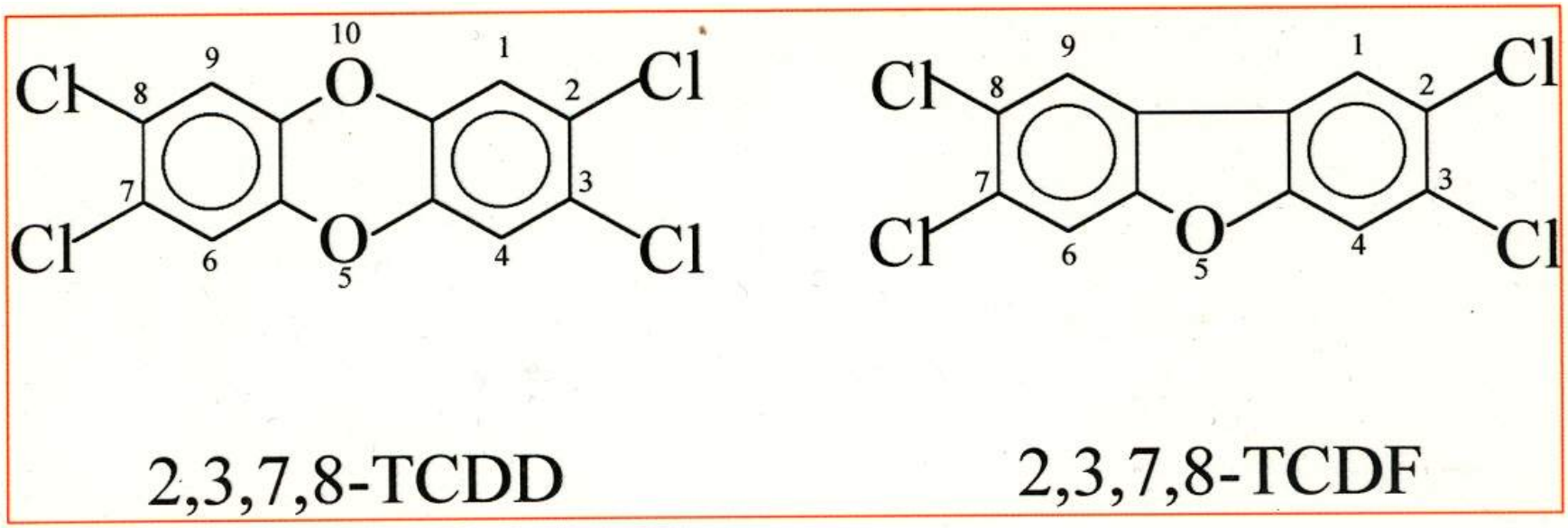
75 congeners



Polychlorinated dibenzofurans (PCDFs)

135 congeners

Dioxins



2,3,7,8-tetrachloro dibenzo[b,e][1,4]dioxin
2,3,7,8-tetrachloro dibenzofuran
Usual term: „dioxins„

Harmfull effects of dioxins

- Very high toxicity for many live beings
- Very high persistent – half time in earth from 10 to 12 years
- Persistent in strong acidic and alkaline media
- Persistent in oxidative and in reductive conditions to 700 °C
- Low solubility in water, good solubility in lipids
- Volatility – spreading into environment
- High biological concentration factors

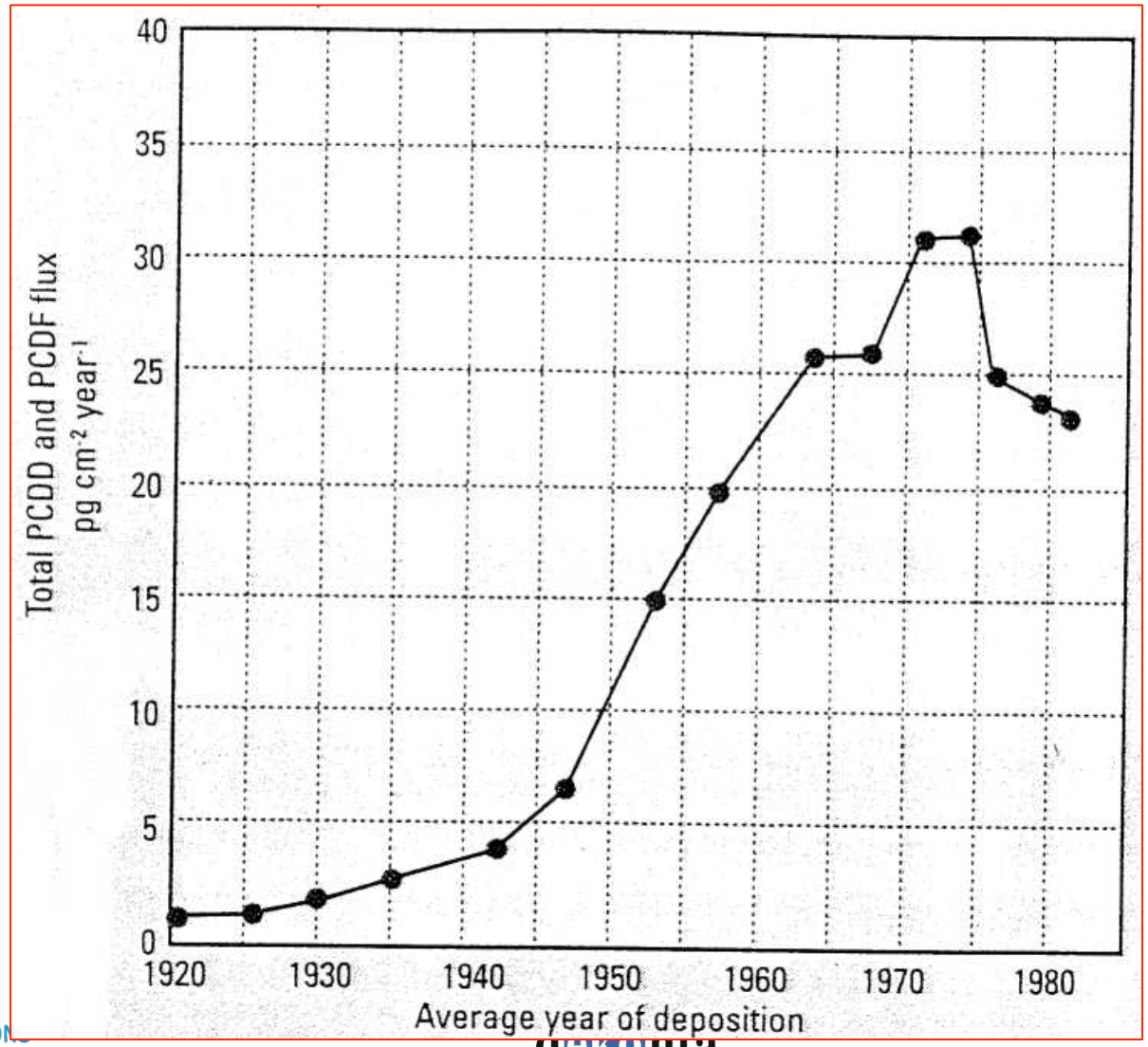
Chloracne

The Seveso accident

Chloracne

Viktor Yushchenko - before and after

Historical trends of PCDDs/Fs environmental levels



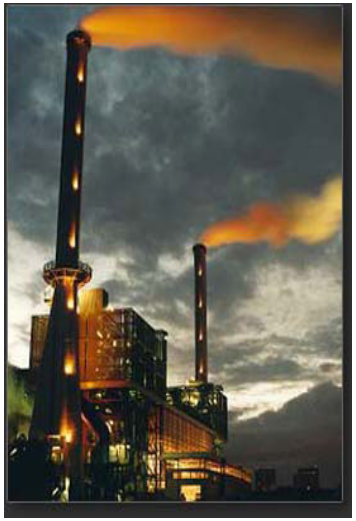
Release sources

- Industrial source categories having a potential for comparatively high formation and release of POPs to the environment: [Annex C, Part II]

- Industrial source categories have the potential for formation and release of POPs to the environment: [Annex C, Part III]

Sources of UPOPs (PCDDs/Fs, PAHs)

- Combustion
- Metal Smelting, Refining, and Processing
- Chemical Manufacturing
- Biological and Photochemical Processes
- Reservoir Sources
- Chemical Accidents



Source categories

The following industrial source categories have the potential for comparatively high formation and release of POPs to the environment: [Annex C, Part II]

- waste incinerators
  - municipal, hazardous or medical wastes
  - sewage sludge
- cement kilns firing hazardous wastes
- pulp production involving elemental chlorine
- thermal processes used in metallurgical industry
  - secondary production of aluminum, copper or zinc
  - sinter plants in iron and steel industry

Source categories

The following industrial source categories have the potential for formation and release of POPs to the environment: [Annex C, Part III]

- open burning of wastes (including landfill sites)
- thermal processes in the metallurgical industry not specified in Part II
- residential combustion sources
- fossil-fuel fired utility and industrial boilers
- firing installations for wood and other biomass fuels
- motor vehicles, especially those burning leaded gasoline

Source categories

The following industrial source categories have the potential for formation and release of POPs to the environment (continued): [Annex C, Part III]

- chemical production processes releasing unintentionally produced POPs (e.g. production of chlorophenols and chloranil)
- textile and leather dying and finishing
- shredder plants for the treatment of end-of life vehicles
- destruction of animal carcasses
- smoldering of copper cables
- waste oil refineries
- crematoria

Formation of PCDD/F's

PCDD/Fs are formed as unintentional by-products in certain processes and activities and may also be introduced into processes as contaminants in raw materials.

PCDD/Fs formation routes can be divided into two broad categories:

(a) formation in thermal processes and

(b) formation in wet-chemical processes.

Combustion Processes

PCDD/PCDF and other unintentional POPs can be formed in combustion processes when their component elements – carbon, oxygen, hydrogen, and chlorine – are present and combustion temperatures range between 200°C and 900°C (De Fre and Rymen 1989).

Combustion processes

Burning in modern incineration plants with "best available technology"can be performed only when all other posibillities of reciclation are exhausted.

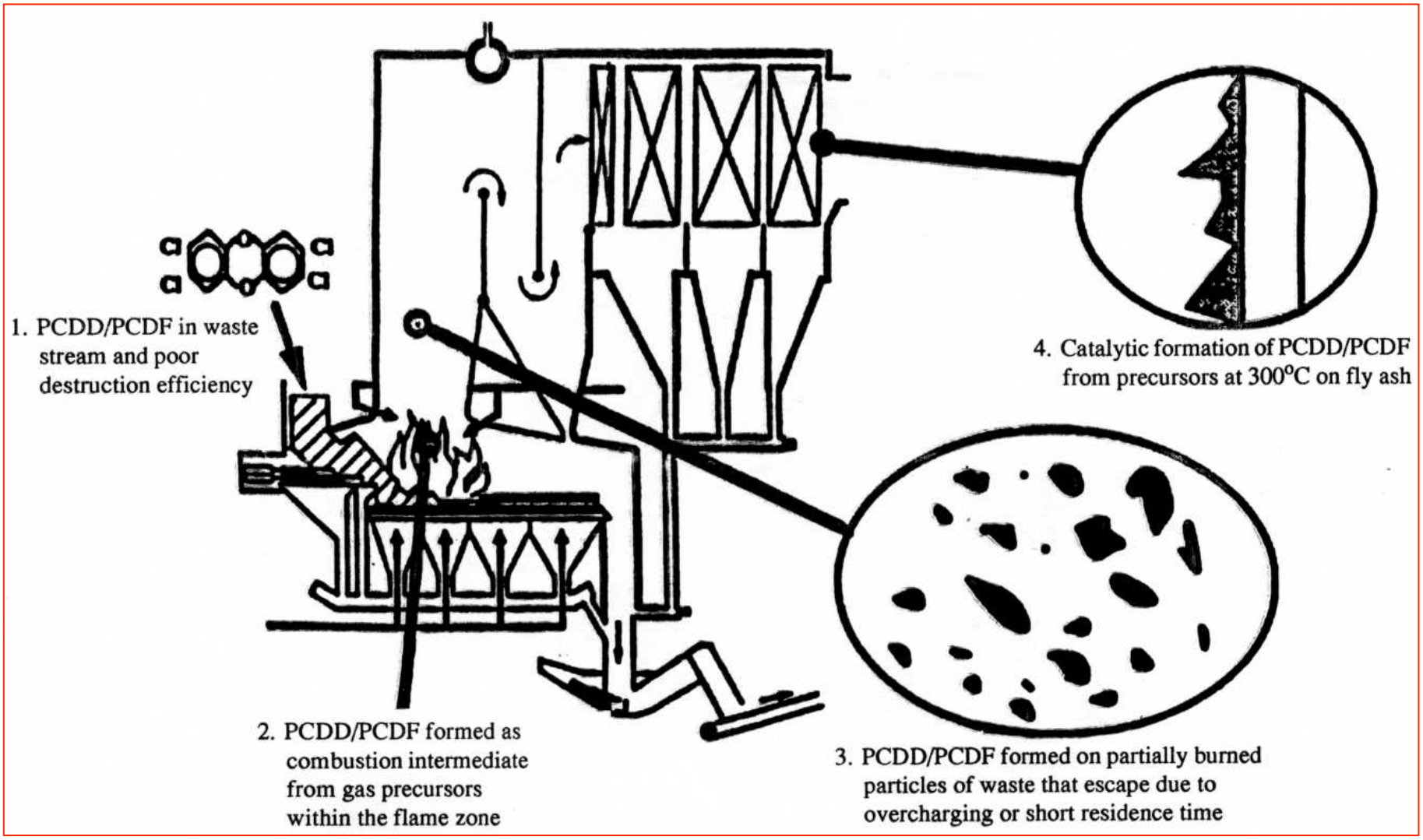
Dioxin Toolkit – Chapter 1.4

Two primary mechanisms for PCDD/PCDF formation during combustion have been proposed:

- *De novo* formation, in which non-extractable carbon-based structures that fundamentally differ from the PCDD/PCDF undergo transformations and reactions to form PCDD/PCDF; and

- Precursor formation/reactions in which hydrocarbon fragments undergo cyclization or incomplete oxidation to form chemicals that share structural similarities with PCDD/PCDF and that undergo further reactions to finally form PCDD/PCDF.

PCDD/F's formation in thermal processes



Dioxin Toolkit – Chapter 1.4

PCDD/PCDF formation via these mechanisms can take place homogeneously (molecules react entirely in the gas phase or in the solid phase) or heterogeneously (the reactions take place between gas phase molecules and surfaces).

PCDD/PCDF can also be destroyed during combustion when temperatures are sufficiently high, residence times are adequate and mixing in the combustion zone is sufficiently thorough.

However, combustion gases must also be rapidly cooled in the post-combustion zone in order to minimize the formation of new PCDD/PCDF in this phase.

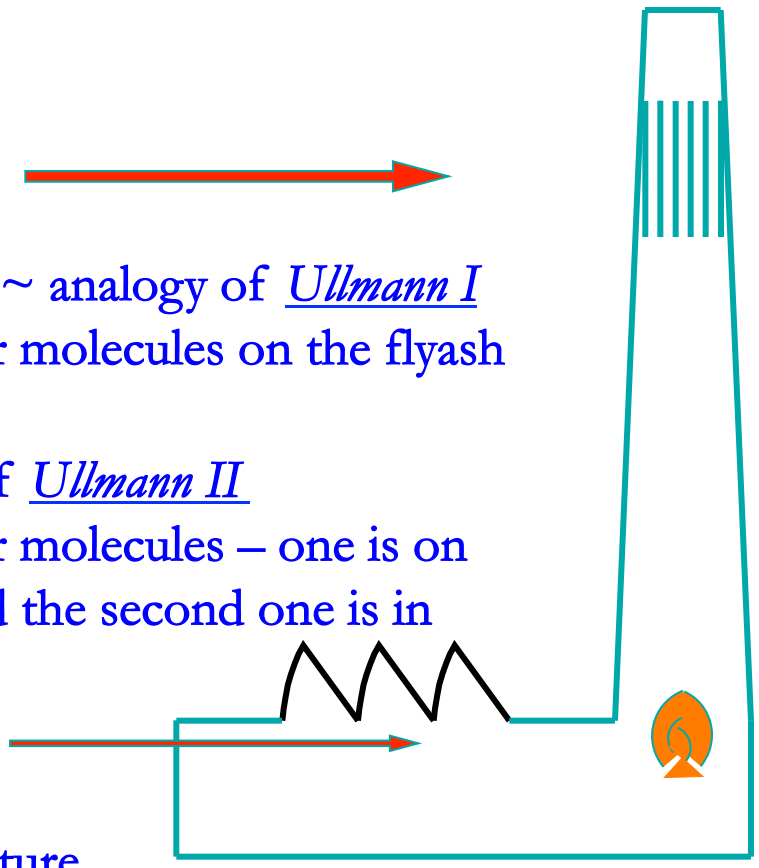
The most important termic processes

- Heterogenous reaction → 250 – 400 °C

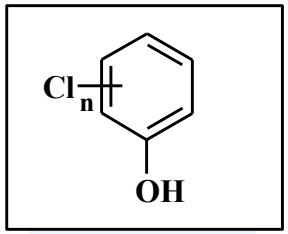
  Langmuir-Hinshelwood type ~ analogy of *Ullmann I*
  (connection of two precurspr molecules on the flyash particle surface)
  Eley-Rideal type ~ analogy of *Ullmann II*
  (connection of two precurspr molecules – one is on the flyash particle surface and the second one is in gaseous phase)

- Homogenous reaction → > 1100 °C

  (gaseous phase, high temperature, $C_1 – C_4$, radicales)



Precursor reactions

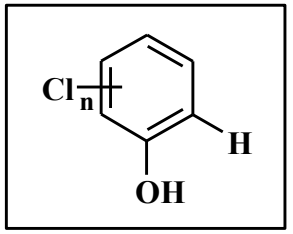


Phenols

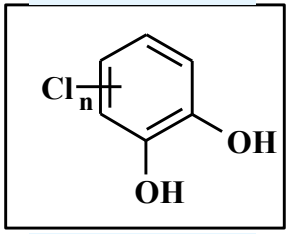
Adsorption

Desorption

Dechlorination

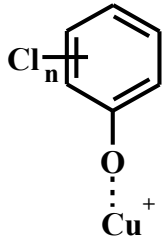


Phenols

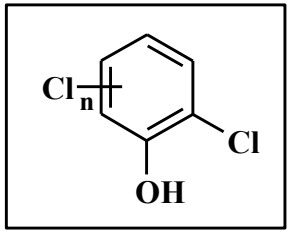


Catechols

Hydroxylation



Chlorination

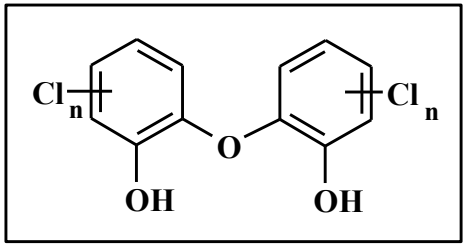


Phenols

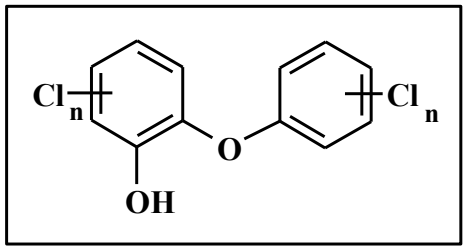
Condensation

Ullmann II

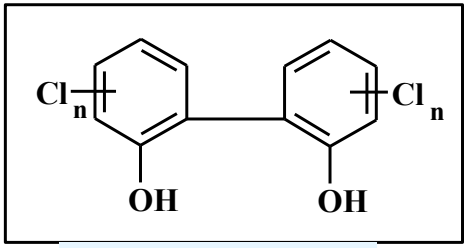
Ullmann I



Diphenylethers



Diphenylethers

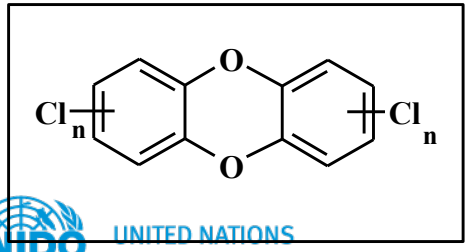


Biphenyls

Cyclization

Cyclization

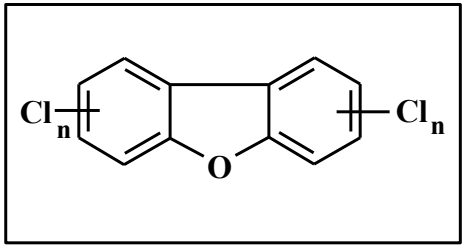
Cyclization



PCDDs

-HCl

- H_2O



PCDFs

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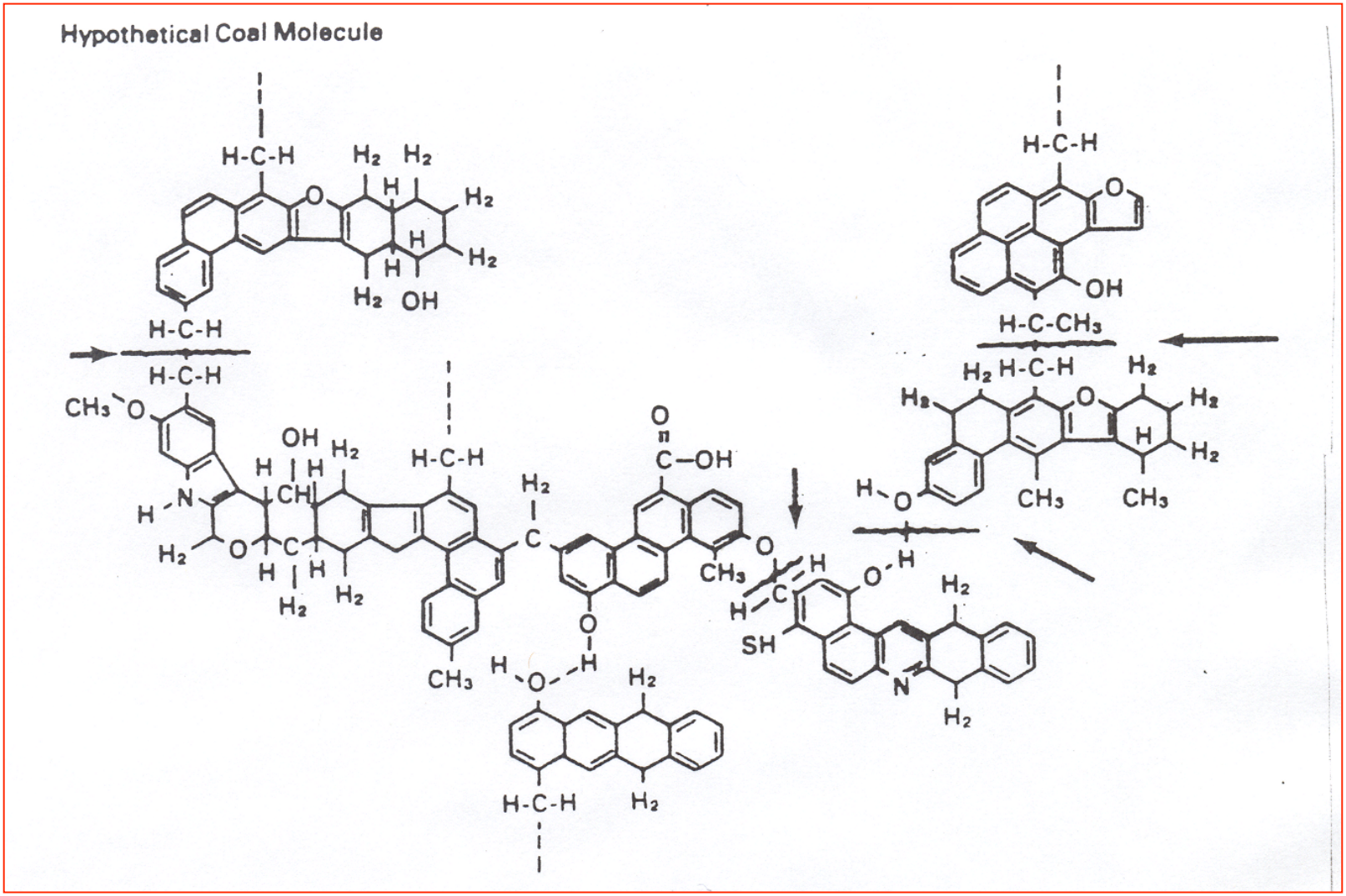
Formation of PCDDs/Fs during combustion processes - summary

- Destruction of PCDDs/Fs in combustion chambers round 900 °C and higher, but they can be produced again after the combustion zone – secondary production

  - Temperature window - 250 – 400 °C
  - Oxidative atmosphere
  - Matrix (flyash)
    - Destructed carbon structures
    - Cu compounds
    - Hydrogen donors
    - Sources of chlorine

Natural sources of PAHs - coal



PAHs formation during combustion processes

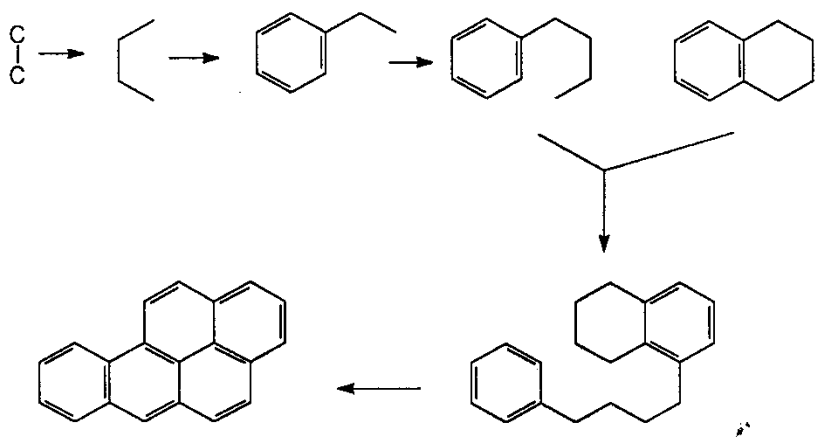
When a mixture of organic compounds containing carbon and hydrogen is exposed to temperatures higher than 700 °C, it means to the pyrolysis conditions, ev. to the conditions of incomplete combustion, non-stable small molecul - precurzors of PAHs are produced. And in the presence of heteroatoms O, N, S – the relevant heteroaromatics compounds are produced, too.

These fragments – mainly radicals - recombining at high temperatures (500-800 ° C) to give relatively stable aromatic hydrocarbons.

PAHs formation during combustion processes

Highly reactive fragments are stabilized by cyclization, condensation, dehdrogenation, Diels – Alder reactions (dien synthesis), it can leads to the closing of ring and other ways under production various polycyclic aromatic systems.

Mechanism of BaP formation by pyrosynthesis



(Badger et al., 196

European Environment Agency (EEA)

The European Environment Agency (EEA) (www.eea.europa.eu) is an agency of the European Union. Its task is to provide sound, independent information on the environment. EEA is a major information source for those involved in developing, adopting, implementing and evaluating environmental policy, and also the general public. The multi-annual strategy and annual work plans of the EEA are publicly available.

EEA's mandate is:

- to help the Community and member countries make informed decisions about improving the environment, integrating environmental considerations into economic policies and moving towards sustainability;
- to coordinate the European environment information and observation network (Eionet).

EMEP/CORINAIR Emission Inventory Guidebook

European Environment Agency
Information for improving Europe's environment

The Emission Inventory Guidebook was prepared by the UNECE/EMEP Task Force on Emissions Inventories and Projections.

The Guidebook is designed to provide a comprehensive guide to the state-of-the-art of atmospheric emissions inventory methodology for each of the emission-generating activities listed in the current versions of the Selected Nomenclature for Air Pollution (SNAP97) but includes cross references to both the NFR and IPPC coding formats.

http://www.aeat.co.uk/netcen/airqual/TFEI/unece.htm

EMEP/CORINAIR Emission Inventory Guidebook

Group 1: Combustion in energy and transformation industries

Group 2: Non-industrial combustion plants

Group 3: Combustion in manufacturing industry

Group 4: Production processes

Group 5: Extraction & distribution of fossil fuels and geothermal energy

Group 6: Solvent and other product use

Group 7: Road transport

Group 8: Other mobile sources and machinery

Group 9: Waste treatment and disposal

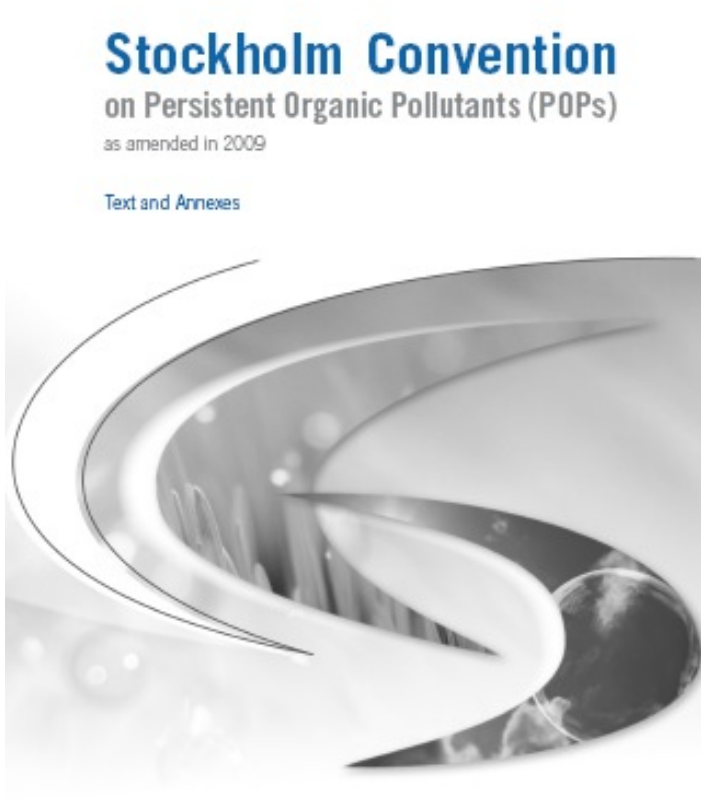
Group 10: Agriculture

Group 11: Other sources and sinks

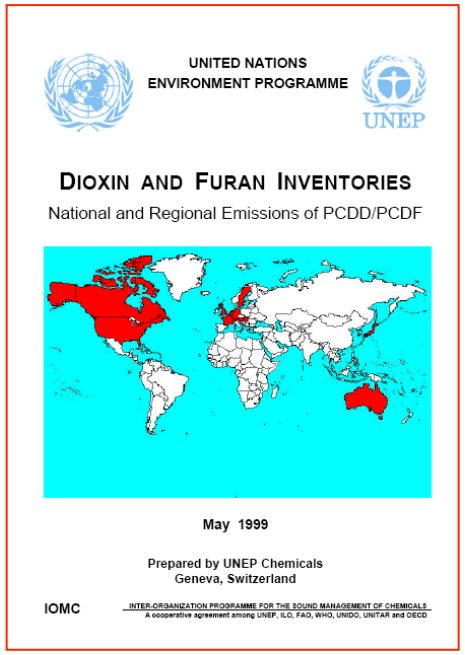
Non-SNAP Chapters

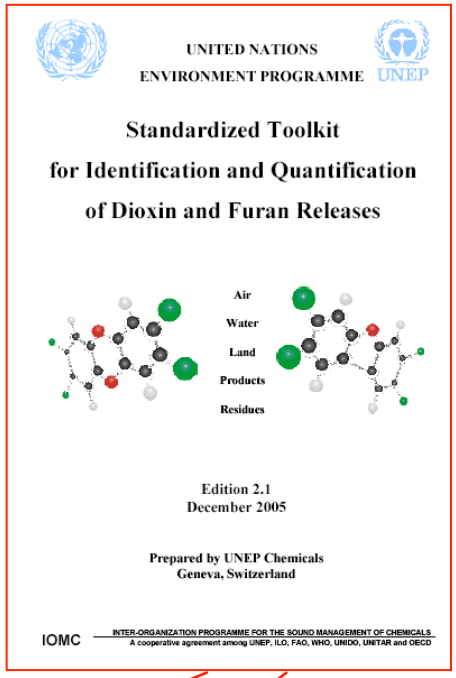
DIOXIN Toolkit
Chapter by chapter

Stockholm Convention on Persistent Organic Pollutants (POPs)



>10 years of unintentional POPs





SC-2/5, SC-3/6
SC-4/7
COP.5/11
COP.5/INF44

Toolkit update and review process (SSC+CB)

Draft

v1

v2

1999 INC-3

2001 INC-5

2003 INC-7

2005 COP-1

2006 COP-2

2011

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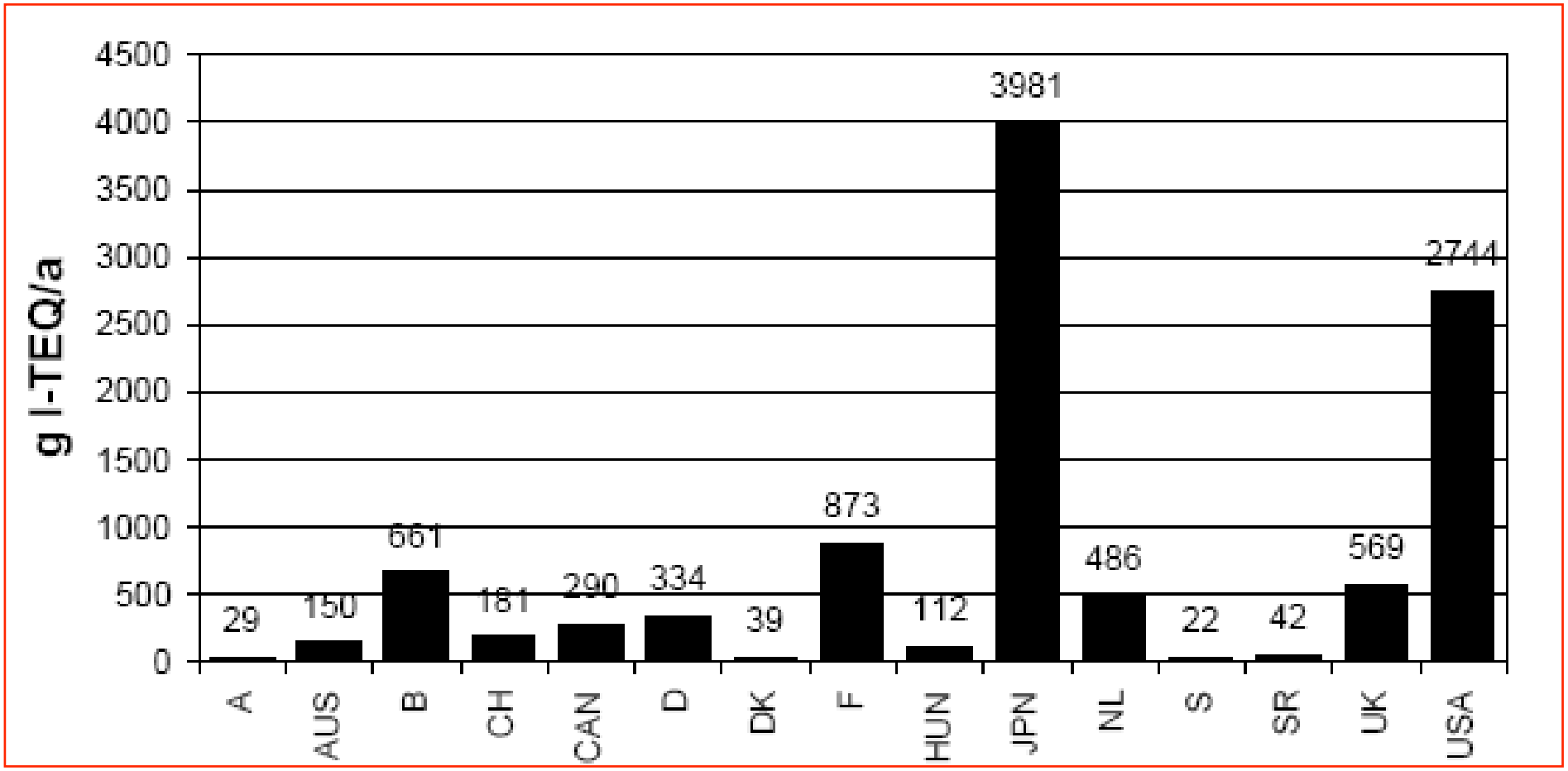
Dioxin Inventories: 1995 vs. 2007

- 1995 emissions:
  - 15 developed countries = *ca.* 10 500 g TEQ per year
  - Emissions to air predominantly
- 2007/2009 releases:
  - *ca.* 20 developed countries - 800 million population
    - *ca.* 14 700 g TEQ per year to air
    - *ca.* 16 500 g TEQ per year in total
  - 62 (most) developing countries - 2.6 billion population
    - *ca.* 22 700 g TEQ per year to air
    - *ca.* 48 500 g TEQ per year in total

Dioxin Inventories: 1995

- 15 developed countries = 10 500 g TEQ per year
- Emissions to air predominantly

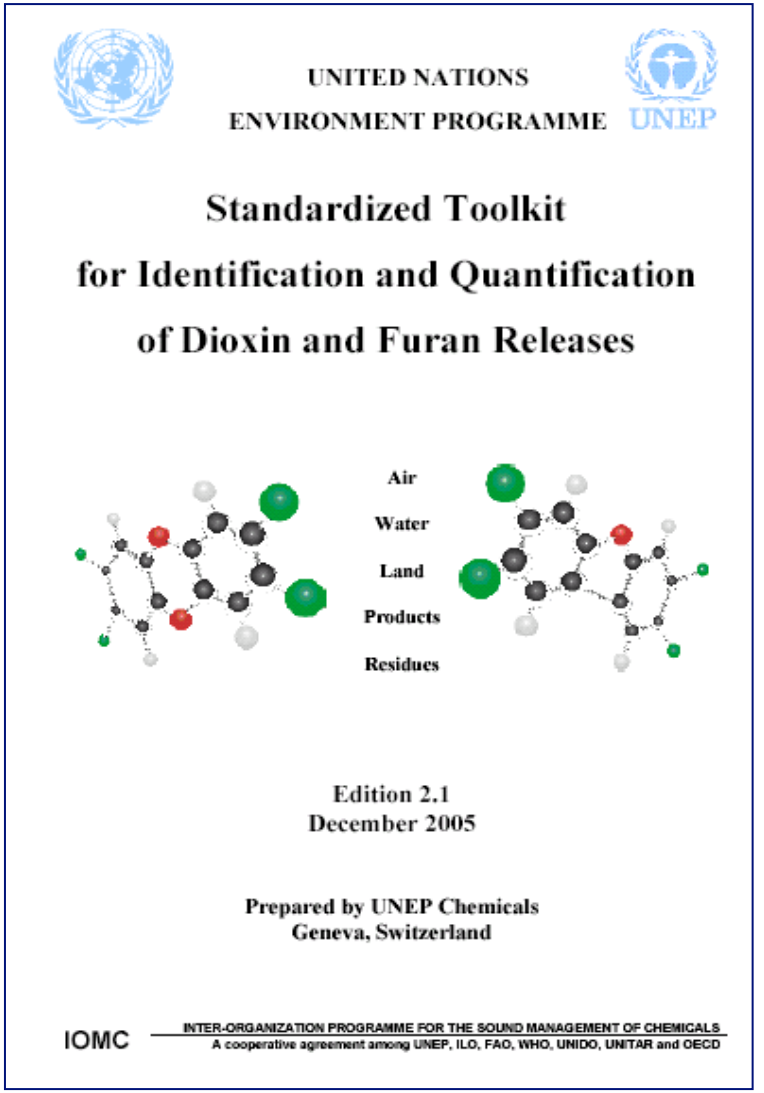


Methodology to establish complete, comparable PCDD/PCDF Inventories

(250 pages + EXCEL file)

Updating and review process mandated by Conference of the Parties, started in 2006

some new emission factors adopted at COP-5 (April 2011)
Electronic version under development

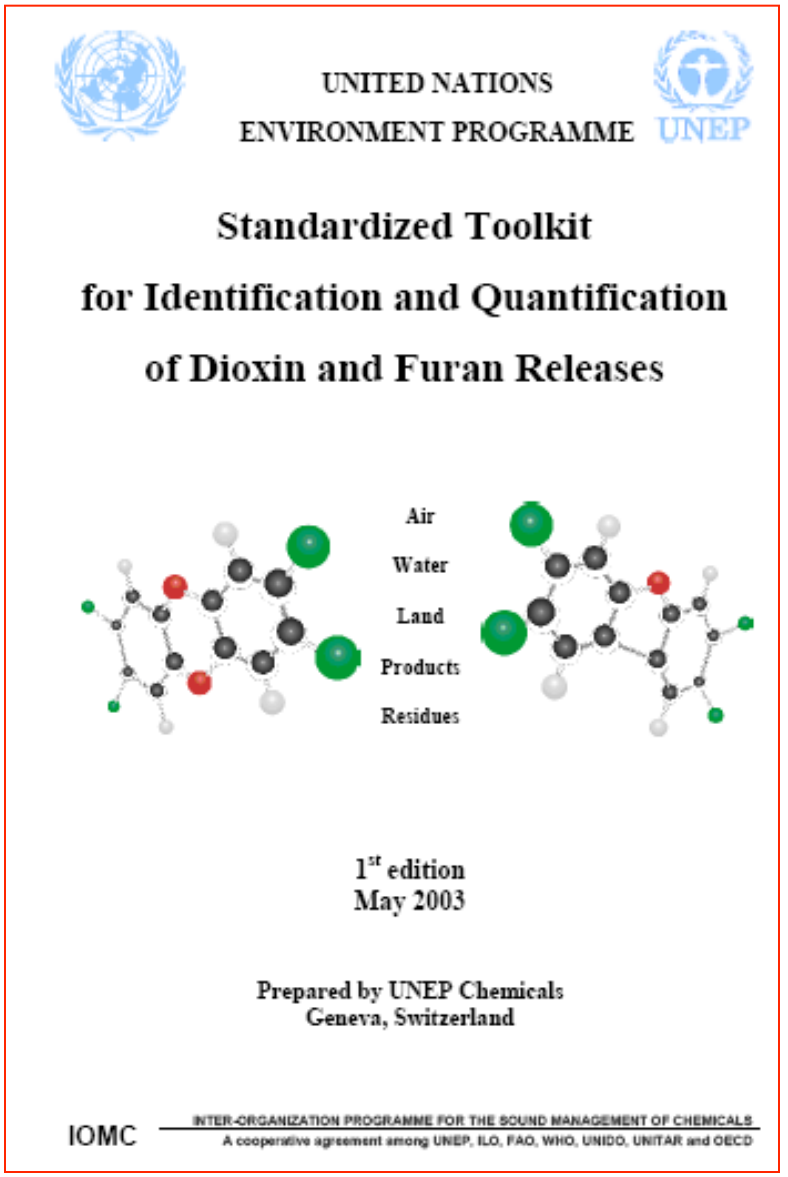


http://www.chem.unep.ch/pops/pcdd_activities/default.htm

Dioxin Toolkit 1st edition, May 2003

The United Nations Environment Programme UNEP Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases is designed to cover all source categories and processes that are listed in Annex C, Parts II and III of the Stockholm Convention.

The Toolkit can be used where there are no measured data available and provides default emission factors for all source categories.



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Revised inventory reporting format

Group	Source Groups	Annual Releases (g TEQ/a)				
		Air	Water	Land	Product	Residue
1	Waste Incineration	0.0	0.0	0.0	0.0	0.0
2	Ferrous and Non-Ferrous Metal Production	0.0	0.0	0.0	0.0	0.0
3	Heat and Power Generation	0.0	0.0	0.0	0.0	0.0
4	Production of Mineral Products	0.0	0.0	0.0	0.0	0.0
5	Transportation	0.0	0.0	0.0	0.0	0.0
6	Open Burning Processes	0.0	0.0	0.0	0.0	0.0
7	Production of Chemicals and Consumer Goods	0.0	0.0	0.0	0.0	0.0
8	Miscellaneous	0.0	0.0	0.0	0.0	0.0
9	Disposal	0.0	0.0	0.0	0.0	0.0
10	Identification of Potential Hot-Spots				0.0	0.0
1-10	**Total**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**
	Grand Total			**0**		

- Updated reporting format
  (under article 15; proposed and adopted at COP-5, INF.44)
- Identical with Toolkit summary table from Excel Files

Toolkit Summary 2010 (n=62)

62 (most) developing countries = 2.6 billion population

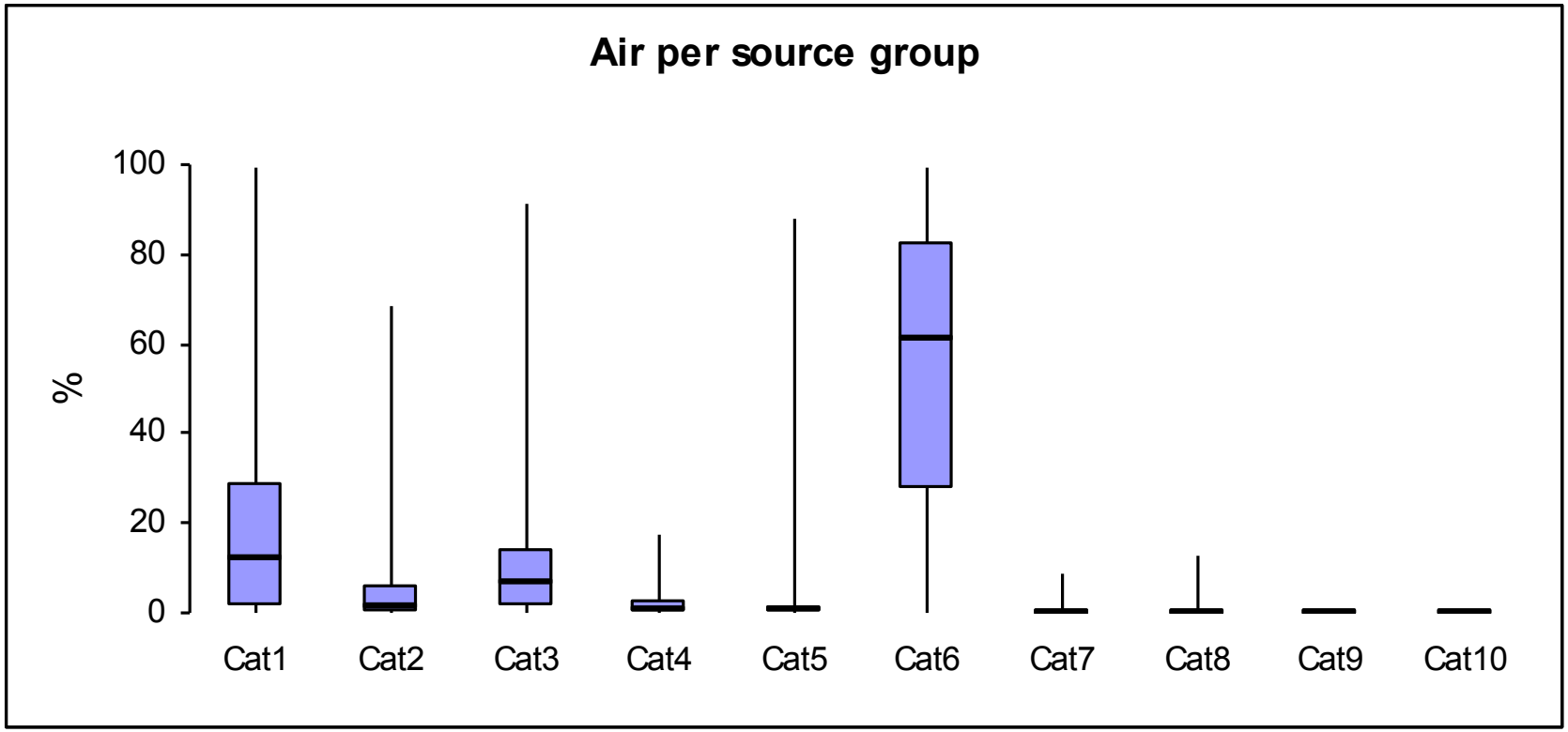
Releases (g TEQ per year)

Air	Water	Land	Product	Residue
22 700	1 130	5 860	4 880	13 900
47%	2%	10%	12%	29%
Grand total (ca.)			48 500	

- Most dioxins go to air ⇒ LRT
- Least dioxins go to water (directly)

Status: Dec 2010

What are the important sources?



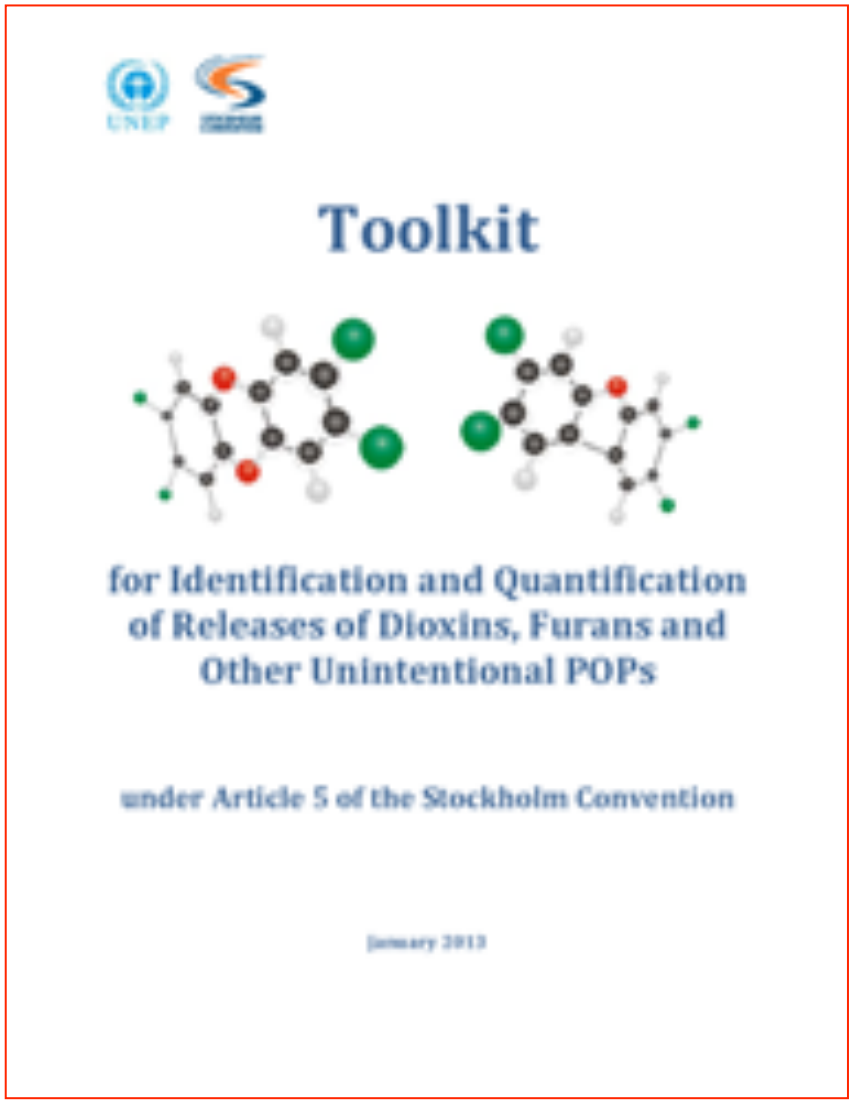
1. Open burning of biomass and waste – Cat 6 = 61% of air emissions
2. Incineration of (medical) waste – Cat 1 = 12%
3. Energy conversion-heating, cooking – Cat 3 = 6.9% n=60

Status: Dec 2010

Dioxin Toolkit 2nd edition, May 2013

Toolkit for Identification and Quantification of Releases of Dioxins, Furans and Other Unintentional POPs *under Article 5 of the Stockholm Convention on Persistent Organic Pollutants*

http://toolkit.pops.int/



Dioxin Toolkit – Part I

Part I General Guidance

The *Toolkit for Identification and Quantification of Releases of Dioxins, Furans and Other Unintentional POPs* is divided into three parts.

Part I includes general guidance for inventory development, update and revision, guidance on data quality and quality assurance and quality control of inventory results, guidance to determine activity rates, and others aspects.

http://toolkit.pops.int/

Dioxin Toolkit – Part II

Part II Default Emission Factors

Part II of the *Toolkit for Identification and Quantification of Releases of Dioxins, Furans and Other Unintentional POPs* includes information on default emission factors for source categories grouped in ten source groups within the Toolkit, the levels of confidence assigned to each emission factor value, guidance on estimating activity rates, classifying sources and assigning the appropriate emission factors.

For the purpose of the PCDD/PCDF inventory development, Parts I and II of the Toolkit provide all necessary guidance.

http://toolkit.pops.int/

Dioxin Toolkit – Part II

Part III Annexes and Example Inventories

Part III of the *Toolkit for Identification and Quantification of Releases of Dioxins, Furans and Other Unintentional POPs* includes annexes containing detailed technical complementary information on the derivation of dioxin emission factors for the ten source groups, along with emission factors for other unintentional POPs.

Part III also includes example inventories for each source group illustrating the process of inventory development, update and revision, and providing useful insights into estimating activity rates and/or applying expert judgment for a number of source categories.

http://toolkit.pops.int/

Dioxin Toolkit – Chapter 1.1

Chemicals Listed in Annex C

Pursuant to Article 5 of the Convention, the following unintentic
POPs are listed in Annex C:

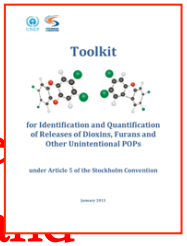
- Polychlorinated dibenzo-*p*-dioxins (PCDD),
- Polychlorinated dibenzofurans (PCDF),
- Polychlorinated biphenyls (PCB),
- Hexachlorobenzene (HCB), and
- Pentachlorobenzene (PeCBz).

http://toolkit.pops.int/

Dioxin Toolkit – Chapter 1.1

Among these, PCDD and PCDF (also collectively referred to as PCDD/PCDF) have never been used as commercial products, nor were intentionally manufactured for any reason other than laboratory purposes.

PCB, HCB and PeCBz are also unintentionally formed, usually from the same sources that produce PCDD/PCDF.



However, unlike PCDD/PCDF, they have also been manufactured and used for specific purposes, their intentional production and use being by far higher than the unintentional formation and release.

http://toolkit.pops.int/

Dioxin Toolkit – Chapter 1.1

PCDD/PCDF releases are accompanied by releases of other unintentional POPs, which can be minimized or eliminated by the same measures that are used to address PCDD/PCDF releases.

When a comprehensive inventory of PCDD/PCDF is elaborat
allows to identify priority sources, set measures and develo
action plans to minimize releases of all unintentional POPs.

http://toolkit.pops.int/

Dioxin Toolkit – Chapter 1.1

It is thus recommended, for practical reasons, that inventory activities be focused on PCDD/PCDF, as these substances are indicative of the presence of other unintentional POPs.

They are considered to constitute a sufficient basis for identifying and prioritizing sources of all such substances as well as for devising applicable control measures for all Annex C POPs and for evaluating their efficacy.

http://toolkit.pops.int/

Dioxin Toolkit – Chapter 1.1

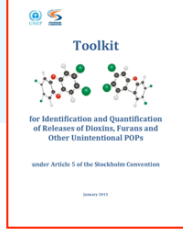
Only in the context of research or other projects it is advisable to analyze emissions of all unintentional POPs listed in Annex C in order to produce useful information for the purpose of deriving emission factors.

In addition to emission factors for PCDD/PCDF, the Toolkit also contains emission factors for other POPs when such information is available.

Typically, emission factors are provided for the five release vectors, *i.e.*, air (EF_{Air}), water (EF_{Water}), land (EF_{Land}), product ($EF_{Product}$), and residue ($EF_{Residue}$)

http://toolkit.pops.int/

Dioxin Toolkit – Chapter 1.2

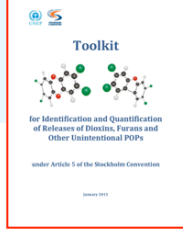


1.2 Purpose

The purpose of the "Toolkit for Identification and Quantification of Releases of Dioxins, Furans and Other Unintentional POPs" is to support Parties in preparing PCDD/PCDF inventories that are consistent in format and content, ensuring that it is possible to compare results, identify priorities, mark progress and follow changes over time at the country level, and at the regional and global levels.

http://toolkit.pops.int/

Dioxin Toolkit – Chapter 1.2



Towards this end, the Toolkit provides the following "tools":

- A simple but comprehensive procedure for identifying sources of PCDD/PCDF, including but not limited to the source categories listed in Annex C, Parts II and III;

- Guidance on gathering basic information on the design, operation and/or expected performance of sources that supports their classification and the assignment of appropriate default emission factors;

http://toolkit.pops.int/

Dioxin Toolkit – Chapter 1.2

- Default emission factors – values for the quantity of PCDD/PCDF, expressed as TEQ, released to each vector per unit of activity (*e.g.*, µg TEQ per ton of material produced, per ton of fuel burned, etc.) that have been assigned for each class within the source categories. For the other unintentional POPs, mass concentrations will be assigned as appropriate;

- Guidance on acquiring data and related information to estimate national values for annual activity rates for source categories and/or classes within source categories, *e.g.*, tons per year of waste burned, tons per year of feed material processed, tons per year of product produced, etc.; and

http://toolkit.pops.int/

Dioxin Toolkit – Chapter 1.2

- A spreadsheet to list all source groups, source categories and their associated classes and emission factors, for the five release vectors. This spreadsheet will automatically calculate annual PCDD/PCDF releases from all source categories in a given country or region where national activity data are entered.

The emission factors can be modified in the spreadsheet, *i.e.*, countries may use their own emission factors instead of the default ones, preferably using the same units to ensure comparability of results.

Countries can also insert new source categories or classes by adding extra lines into the worksheet to better reflect national circumstances.

http://toolkit.pops.int/

Dioxin Toolkit – Chapter 1.3

1.3 Structure and Use of the Toolkit

The Toolkit is divided into three parts:

- Part I contains four chapters providing general guidance,
- Part II contains default emission factors for nine of the ten source groups, and
- Part III provides complementary information, including 53 annexes and 11 example inventories.

http://toolkit.pops.int/

Dioxin Toolkit – Chapter 1.3

Part I

Chapter 1 - Introduction and Overview summarizes the obligations of Parties under Article 5 and Annex C of the Stockholm Convention, describes the purpose and structure of the Toolkit and the chemicals listed in Annex C, including a brief overview of their formation and sources.

Chapter 2 - Identification of PCDD/PCDF Sources and Estimation of Releases addresses the identification of sources and provides general guidance on gathering information that will allow for 1) sources to be identified and catalogued according to the source category and class to facilitate the selection of the most appropriate default emission factors, and 2) guidance to determine activity rates for each of the classes within each source category.

Chapter 3 - Reporting of Releases explains how to undertake inventory updates and revisions as well as projections of future releases. Finally, the reporting format under Article 15 of the Convention is described.

Chapter 4 - Data Quality provides information on the inventory data quality criteria along with guidance on possible quality assurance and quality control measures and a simple approach to characterize the quality of the inventory results.

Dioxin Toolkit – Chapter 1.3

Part II

1 – **Waste Incineration** addresses seven source categories of waste incinerators, the classes within each category and the default emission factors for each class.

2 – **Ferrous and Non-Ferrous Metal Production** addresses twelve source categories for the production of metals and metal alloys including recycling operations, the classes within each category and the default emission factors for each class.

3 – **Heat and Power Generation** addresses five source categories of large and small installations using fossil fuels, biomass or gas, the classes within each category and the default emission factors for each class.

4 – **Production of Mineral Products** addresses seven source categories of processes to manufacture mineral products, the classes within each category and the default emission factors for each class.

5 – **Transport** addresses four source categories including road and ship transport, the classes within each category and the default emission factors for each class.

http://toolkit.pops.int/

Dioxin Toolkit – Chapter 1.3

6 – Open Burning Processes addresses two source categories of burning biomass or waste without technical equipment, the classes within each category and the default emission factors for each class.

7 – Production and Use of Chemicals and Consumer Goods addresses five source categories of various industrial activities, the classes within each category and the default emission factors for each class.

8 – Miscellaneous addresses an array of five source categories that do not match the description of any other source group, the classes within each category and the default emission factors for each class.

9 – Disposal addresses five source categories related to waste disposal, the classes within each category and the default emission factors for each class.

10 – Hot Spots addresses thirteen source categories that should only be noted in the inventory, where possible, since these categories cannot be further classified and no default emission factors can be designated.

http://toolkit.pops.int/

Dioxin Toolkit – Chapter 1.3

Part III

The following annexes provide complementary information:

- Annex 1 - Table of TEFs
- Annex 2 - Guidance on identifying sources of PCDD/PCDF
- Annex 3 - Questionnaires
- Annex 4 - Compilation of all emission factors
- Annex 5 - Reporting of releases
- Annex 6 - Usage of units in air emissions
- Annex 7 - Per capita/GDP emissions
- Annex 8 - Data quality

Annexes 9 to 53 provide complementary information to source groups 1-10 and the source categories included in the respective groups.

Eleven example inventories are also included in Part III to illustrate the process of update and revision of inventories, as well as specific examples of inventories for source groups 1-10.

Dioxin Toolkit – Chapter 1.3

The Toolkit (current version updating and amending edition 2, which was published in 2005) is presented in an electronic version (web-based and CD-ROM).

The electronic version of the Toolkit has been developed to increase the availability, portability and storage of information.

It delivers the Toolkit's content in an interactive and dynamic manner.

http://toolkit.pops.int/

Dioxin Toolkit – Chapter 1.3

The information is organized in a user-friendly multi-layer structure according to the level of complexity, where information elements are arranged according to the relevance for the inventory process:

- The first layer contains key elements of the Toolkit and essential information for the development of the inventory;
- The second layer of complementary information or additional explanatory material is included in annexes and example inventories accessible via hyperlinks;
- Further complementary information is accessible via pop-up windows;
- Cross-referencing within the Toolkit sections is done via internal links; and
- External links are used to reference outside resources.

Among other features, the web-based tool also offers access to interactive features including a search tool and Excel files for calculating releases. The user is therefore given flexibility in accessing the content of the Toolkit to meet specific information requirements.

1.4 POPs Releases from Sources

The Toolkit has been assembled for the purpose of assisting each country in identifying and quantifying sources of unintentional POPs that are located within the country's borders and estimating releases from those sources.

Dioxin Toolkit – Chapter 1.4

Sources of POPs releases are of four general types, three of which are active, ongoing processes, and one is a legacy of historic activities:

- Chemical production processes, *e.g.*, facilities or production units that produce chlorinated phenols or in which certain other chlorinated chemicals are manufactured, or that produce pulp and paper using elemental chlorine for chemical bleaching;
- Thermal and combustion processes, *e.g.*, waste incineration, combustion of solid and liquid fuels, or production of metals in thermal processes;
- Thermal and combustion processes, *e.g.*, waste incineration, combustion of solid and liquid fuels, or production of metals in thermal processes;
- Biogenic processes in which PCDD/PCDF may be formed from precursors – manufactured chemicals such as pentachlorophenol that are structurally closely related precursors of PCDD/PCDF.

Dioxin Toolkit – Chapter 1.4

Reservoir sources such as historic dumps containing PCDD/PCDF and other POPs-contaminated wastes, and soils and sediments in which POPs have accumulated over time.

The Toolkit presents information on each of the unintentional POPs source categories listed in Annex C, some additional source categories, and a strategy for identifying new source categories.

It describes a step-by-step process to estimate PCDD/PCDF releases from each source category to the following environmental media:

- Air,
- Water (surface and ground water, including marine and estuarine water), and
- Land (surface soils),

and to these process outputs:

Products (such as chemical formulations, including pesticides or consumer goods such as paper, textiles, etc.);

Residues (including certain liquid wastes, sludge, and solid residues, which are handled and disposed of as waste or may be recycled).

Dioxin Toolkit – Chapter 1.4

Variables known to influence PCDD/PCDF formation in combustion processes include the following:

Technology: Poor combustion, poor mixing in the combustion chamber, poorly designed and managed post-combustion chambers, and inadequate air pollution control devices are associated with increased PCDD/PCDF formation.

Temperature: Formation has been reported in post-combustion zones and air pollution control devices at temperatures ranging from 200°C to 650°C, with the greatest formation occurring between 200°C and 450°C and peaking at about 300°C;

Dioxin Toolkit – Chapter 1.4

Variables known to influence PCDD/PCDF formation in combustion processes include the following/II:

Metals: Formation is catalyzed by metals including copper, iron, zinc, aluminum, chromium, and manganese;

Sulphur and nitrogen: Chemicals containing sulphur and nitrogen have the potential to inhibit the formation of PCDD/PCDF in certain conditions, but may give rise to other undesirable by-products;

Chlorine: Chlorine must be present. Whether chlorine is present as organic, inorganic or elemental in the materials combusted is relatively negligible. However, its presence in fly ash or in its elemental form in the gas phase may be especially important.

Application of Toxic Equivalents (TEQ)

Taken as a whole, PCDD and PCDF are a group of 210 tricyclic, chlorine-containing aromatic chemicals; there are 75 congeners of PCDD and 135 congeners of PCDF possible. PCDD and PCDF typically occur as mixtures.

Concept of toxicity equivalence factors (TEFs)

- Problems of human risk assessment – complex environmental mixtures of polychlorinated dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs) a biphenyls (PCBs).

- Concept of toxicity equivalence factor (TEF) – for more simple risk determination and intensity exposure control of those environmental mixtures.

- Values of TEF for single congeners in combination with their chemical concentartions can be used for calculation of total concentrations of toxic equivalents of 2,3,7,8-TCDD (TEQ) and all dioxin-like compounts present in the mixture.

Dioxin Toolkit – Chapter 1.4

To determine the TEQ of a mixture, the mass concentration of each congener is analytically determined, multiplied with the assigned TEF, and the products summed.

The first scheme, derived by the Committee on the Challenges of Modern Society of the North Atlantic Treaty Organization in 1988 and called I-TEFs, covered 17 PCDD/PCDF.

Subsequent revisions of TEFs have been coordinated by the World Health Organization (WHO) in 1997 and 2005.

These revisions also included 12 dioxin-like polychlorinated biphenyls (dl-PCB).

For PCB, the compounds having the highest toxicity are those in which the molecule can assume a planar configuration, analogous to that of PCDD/PCDF.

Calculation of toxicity equivalence factors (TEFs)

$$\text{Total TEQ} = \Sigma\, C_{congener} * TEF_{congener}$$

PCDDs/Fs

+

coplanar PCBs

=

Toxic equivalent of 2,3,7,8-tetrachlor-dibenzo-p-dioxin

Calculation of toxicity equivalence factors (TEFs)

- Equation is based on the additivity approach of total toxicity (antagonistic or synergistic relationships are nor included):

$$TEQ = \Sigma\, n_1\, (PCDDs_i * TEFi) + \Sigma\, n_2\, (PCDFs_i * TEF_i) + \Sigma\, n_3\, (PCBs_i * TEF_i)$$

- Majority of experimental studies of toxic interactions of PCDDs, PCDFs and PCBs congeners in binary and complex mixtures confirm additive caracter of these interactions (study of vertebrates – fish, birds and mammals and study of environmental mixtures).

- TEF are valid only for effects on AhR.

Concept of TEQ

Conditions, when dioxin-like substances, have to cover for this concept include:

- Structure similar with PCDDs and PCDFs,
- Binding on Ah receptor,
- Promotion of biochemical and toxic reactions through the mediation of Ah receptor,
- persistence and accumulation in food chains.

Dioxin Toolkit – Chapter 1.4

To estimate PCDD/PCDF releases in inventories, the Convention requires that the most advanced TEFs are used. These are, at present, the WHO-TEFs established by a WHO/IPCS expert meeting in 2005 (van den Berg *et al.* 2006).

However, these have not yet been recognized or adopted by the Conference of the Parties.

For the purpose of the Toolkit and its "order-of-magnitude" estimates of emission factors, the differences between the WHO-TEFs (either from 1998 or 2005) and the international TEFs (I-TEFs) previously established by the Committee on the Challenges of Modern Society of the North Atlantic Treaty Organization in 1988 are negligible.

Therefore, the TEF-scheme accompanying the emission factors is not specified in the Toolkit.

When reference is made to measured values, the TEF scheme used should be included.

Toxicity equivalence factors determined by WHO for human risk assessment WHO 1997/2005

PCDDs	TEF 1997	TEF 2005	PCDFs	TEF 1997	TEF 2005	Coplanar PCBs
2378-TCDD	1,0	1,0	2378-TCDF	0,1	0,1	33´44´-TCB(77)
12378-PeCDD	0,5	0,5	12378-PeCDF	0,05	0,03	344´5-TCB (81)
123478-HxCDD	0,1	0,1	23478-PCDF	0,5	0,3	33´44´5-PeCB (126)
123678-HxCDD	0,1	0,1	123478-HxCDF	0,1	0,1	33´44´55´-HxCB (169)
123789-HxCDD	0,1	0,1	123678-HxCDF	0,1	0,1	233´44´-PeCB (105)
1234678-HpCDD	0,01	0,01	123789-HxCDF	0,1	0,1	23´44´5-PeCB (118)
12346789-OCDD	0,001	0,003	234678-HxCDF	0,1	0,1	2´344´5-PeCB (123)
			1234678-HpCDF	0,01	0,01	2344´5-PeCB (114)
			1234789-HpCDF	0,01	0,01	233´44´5-HxCB (156)
			12346789-OCDF	0,001	0,001	233´44´5´-HxCB (157)
						23´44´55´-HxCB (167)
						22´33´44´5-HpCB (170)
						22´344´55´-HpCB (180)
						233´44´55´-HpCB (189)
Σ TCDD			Σ TCDF			
Σ PeCDD			Σ PeCDF			
Σ HxCDD			Σ HxCDF			
Σ HpCDD			Σ HpCDF			
Σ PCDD			Σ PCDF			
Σ PCDDs/Fs						

Toxicity equivalence factors determined by WHO for human risk assessment 2005

The 2005 World Health Organization Re-evaluation of Human and Mammalian Toxic Equivalency Factors for Dioxins and Dioxin-like Compounds

Martin van den Berg [1] *, Linda S. Birnbaum [2], Michael Denison [3], Mike De Vito [2], William Farland [4], Mark Feeley [5], Heidelore Fiedler [6], Helen Hakansson [7], Annika Hanberg [7], Laurie Haws [8], Martin Rose [9], Stephen Safe [10], Dieter Schrenk [11], Chiharu Tohyama [12], Angelika Tritscher [13], Jouko Tuomisto [14], Mats Tysklind [15], Nigel Walker [16], and Richard E. Peterson [17]

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[3] University of California Davis, Dept of Environmental Toxicology, One Shields Avenue 4241 Meyer Hall, Davis, CA 95616-8501, USA

[4] Office of Research and Development, US Environmental Protection Agency (EPA), 1200 Pennsylvania Ave., NW, Washington DC 20460, USA

[5] Chemical Health Hazard Assessment Division, Bureau of Chemical Safety, Health Canada, Sir Frederick Banting, Bldg. Postal Locator: 2204D1, Tunney's Pasture, Ottawa, ON K1A OL2, Canada

[6] UNEP Chemicals, International Environment House, 11-13, chemin des Anémones, CH-1219 Châtelaine (GE), Switzerland

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[16] National Institute of Environmental Health Sciences, 111 TW Alexander Drive, P.O. Box 12233 Mail Drop EC-34, Research Triangle Park, NC 27709, USA

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Dioxin Toolkit – Chapter 1.4

The most toxic compounds have chlorines in the 2, 3, 7 and 8 positions; they have been assigned a toxicity equivalency factor (TEF) based on the relative potency of each congener in comparison to the most toxic congener, 2,3,7,8-tetrachlorodibenzo-p-dioxin.

In total, there are 17 congeners in which chlorine atoms occur at the 2, 3, 7, and 8 positions.

Mixtures of these congeners are often evaluated and reported as a single number called toxic equivalent (TEQ).

Dioxin Toolkit – Chapter 1.5

1.5 Limitations

An inventory can provide valuable information on the magnitude of releases to each environmental medium and in products and residues.

It can highlight sources for possible impacts but it cannot provide an accurate guide to the relative impact of these releases on human or ecosystem exposure since the fate of PCDD/ PCDF varies considerably from one release source to another.

The main purpose is to identify sources of unintentional POPs, prioritize them and undertake measures to prevent the formation and reduce or eliminate releases of unintentional POPs.

Furthermore, measures taken to address PCDD/PCDF releases are equally suitable for other unintentional POPs.

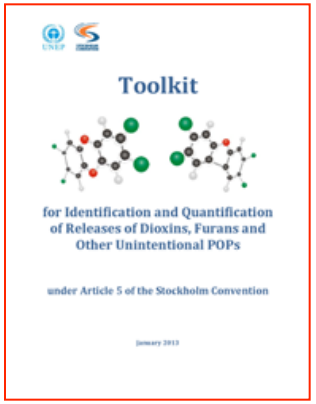
Dioxin Toolkit – Chapter 1.5

The default emission factors presented in the Toolkit are best estimates derived from experimental results at well-documented sources (*i.e.*, taking into account technology, process characteristics and operating practices) or otherwise based on expert judgment.

The results obtained for processes with similar characteristics are then aggregated into one emission factor representing "order of magnitude" release estimates, which do not describe accurately PCDD/PCDF releases from individual plants/facilities.

Dioxin Toolkit new version, May 2013

2.1 Identifying Sources



To assist Parties in identifying PCDD/PCDF sources at the national level, the Toolkit includes source categories as described in Annex C of the Stockholm Convention, Parts II and III.

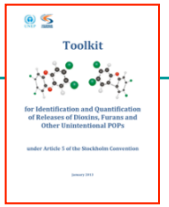
Since the list in Part III is indicative and open for additions, the Toolkit also contains further source categories that have been identified in existing inventories, national assessments, scientific studies, etc.

In addition, it provides a simple screening process for identifying other sources not yet listed in the Toolkit.

http://toolkit.pops.int/

Dioxin Toolkit new version, May 2013

Table I.2.1 – Source Groups and Associated Source Categories						
Source Group		1 - Waste Incineration	2 - Metal Production	3 - Heat and Power Generation	4 - Production of Mineral Products	5 - Transport
Source Categories	a	Municipal solid waste incineration	Iron ore sintering	Fossil fuel power plants	Cement production	4-Stroke engines
	b	Hazardous waste incineration	Coke production	Biomass power plants	Lime production	2-Stroke engines
	c	Medical waste incineration	Iron and steel production and foundries	Landfill Biogas combustion	Brick production	Diesel engines
	d	Light-fraction shredder waste incineration	Copper production	Household heating and cooking (biomass)	Glass production	Heavy oil fired engines
	e	Sewage sludge incineration	Aluminum production	Domestic heating (fossil fuels)	Ceramics production	
	f	Waste wood and waste biomass incineration	Lead production		Asphalt Mixing	
	g	Destruction of animal carcasses	Zinc production		Oil shale processing	
	h		Brass and bronze production			
	i		Magnesium production			
	j		Other non-ferrous metal production			
	k		Shredders			
	l		Thermal wire reclamation			



UNIDO UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION

http://toolkit.pops.int/

dekonta

Dioxin Toolkit new version, May 2013

Table I.2.1 – Source Groups and Associated Source Categories						
Source Group		6 - Open Burning Processes	7 - Chemicals and Consumer Goods	8 - Miscellaneous	9 - Disposal	10 - Hot Spots
Source Categories	a	Biomass burning	Pulp and paper production	Drying of biomass	Landfills, waste dumps and landfill mining	Sites used for the production of chlorine
	b	Waste burning and accidental fires	Chlorinated inorganic chemicals	Crematoria	Sewage/ sewage treatment	Production sites of chlorinated organics
	c		Chlorinated aliphatic chemicals	Smoke houses	Open water dumping	Application sites of PCDD/PCDF containing pesticides and chemicals
	d		Chlorinated aromatic chemicals	Dry cleaning	Composting	Timber manufacture and treatment sites
	e		Other chlorinated and non-chlorinated chemicals	Tobacco smoking	Waste oil treatment(non-thermal)	Textile and leather factories
	f		Petroleum industry			Use of PCB
	g		Textile production			Use of chlorine for production of metals and inorganic chemicals
	h		Leather refining			Waste incinerators
	i					Metal industries
	j					Fire accidents
	k					Dredging of sediments and contaminated flood plains
	l					Dumps of wastes/residues from source groups 1-9
	m					Kaolin or ball clay sites

2.2 Emission Factors

For each source category and/or source, it is necessary to obtain basic information about the design, operation, and other related factors that can substantially influence the magnitude of PCDD/PCDF releases.

Based on this information, each source will be classified and placed in one of the several classes to which default emission factors are assigned.

Dioxin Toolkit – Chapter 2.2

Example questionnaires provided in Annex 3 may be useful in obtaining the information needed to classify source categories and so select appropriate emission factors.

More specific suggestions on the information needed and potential avenues for obtaining such information for a source category may be found in Part II, in the chapters concerning source groups 1 through 10.

2.3 Activity Rates

Activity rates are values in unit per year of product manufactured (*e.g.*, steel, sinter, cement, pulp, compost, etc.) or feed material processed (*e.g.*, municipal waste, hazardous waste, coal, diesel fuel, bodies cremated, etc.), or annual quantities of material released (*e.g.*, m^3 of flue gas, liters of wastewater, kilograms or tons of sludge generated, etc.).

Dioxin Toolkit – Chapter 2.3

Values for activity rates may be found in centralized statistical information assembled by state, provincial, national or international agencies, and they may be obtained from trade associations and owner/operators of facilities.

Potential sources of information on activity rates include the following:

- National statistics;
- National energy balance;
- Regional economic activity records including national production and import/export data;
- International statistics such as EUROSTAT, OECD, FAO, World Bank etc.
- Local operating and permitting records of industrial facilities;
- Industry association data;
- Historical production and industry data;
- Other release inventories such as the inventory of criteria pollutants and or greenhouse gases;
- Questionnaires;
- Pollution Release and Transfer Registers (PRTRs).

Dioxin Toolkit – Chapter 2.3

When the activity rate for an industrial source category is not available but the nameplate capacity is known, an activity rate can be estimated by multiplying capacity by the domestic capacity utilization factor (CUF).

If no domestic CUF is available, a regional or global CUF may be used and, if neither regional nor global CUF is available, the Toolkit Expert Group may provide an appropriate value.

Activity rates for diffuse source categories, such as traffic, open burning of domestic waste, agricultural residues, etc., are best characterized by drawing from centrally available data.

2.4 Release Estimates

Once PCDD/PCDF sources are identified and classified, emission factors selected and national or regional activity rates determined, the estimation of the total annual releases by source group, source category and class is relatively simple and straightforward.

Dioxin Toolkit – Chapter 2.4

For a source class, PCDD/PCDF releases per year are calculated according to the equation below.

The activity rate is multiplied by each of the five emission factors and the sum of the five resulting values represents the quantity of PCDD/PCDF released annually from the source class.

Dioxin Toolkit – Chapter 2.4

PCDD/PCDF released, grams TEQ/year =

$$\text{Activity Rate} * \text{Emission Factor}_{\text{Air}}$$
$$+$$
$$\text{Activity Rate} * \text{Emission Factor}_{\text{Water}}$$
$$+$$
$$\text{Activity Rate} * \text{Emission Factor}_{\text{Land}}$$
$$+$$
$$\text{Activity Rate} * \text{Emission Factor}_{\text{Product}}$$
$$+$$
$$\text{Activity Rate} * \text{Emission Factor}_{\text{Residue}}$$

2.5 Compilation of PCDD/PCDF Inventory

The Toolkit simplifies and expedites the calculations described above by providing an Excel spreadsheet that includes a list of the source categories addressed in the Toolkit, along with their associated classes and accompanying default emission factors.

Once the activity rates for all classes within the source categories that have been determined to be present within a country or region are entered into the spreadsheet, annual PCDD/PCDF releases are automatically calculated for each source category.

A summarizing worksheet provides an overview of all releases according to vectors (air, water, land, product, residue) and source groups.

Dioxin Toolkit – Part II

Part II Default Emission Factors

Part II contains a compilation of PCDD/PCDF emission factors for all source categories listed in Annex C Part II and III of the Stockholm Convention.

Emission factors for certain other unintentional POPs sources are presented in Part III of the Toolkit.

The source categories are grouped into 10 source groups.

Neither the sequence of the groups, nor the sequence of the source categories within the groups implies any ranking of the importance of each group within a country's unintentional POPs inventory.

Dioxin Toolkit – Part II

Emission factors are provided for five release vectors, *i.e.*, air, water, land, product, residue.

Individual source categories included in one source group are addressed by the following sub-chapters:

- Brief description of the source category and potential unintentional POPs releases, linked to the BAT&BEP Guidelines where appropriate;
- PCDD/PCDF emission factors for the particular classes along with detailed information needed for the classification of the sources and selection of most appropriate emission factors;
- If available, emission factors for other unintentional POPs are provided in Annexes;
- Useful guidance facilitating the assessment of relevant activity rates;
- Assessment of the level of confidence associated with emission factors by assigning data quality rating;
- Detailed information on how the emission factors were derived is also provided in Annexes, along with an overview of all recent revisions performed by the Toolkit expert group; and
- Example inventories for every source group are included in Part III.

Chapter 4 Data Quality

Source inventories and release estimates reported under Article 15 should be:

- Reliable,
- Consistent over time,
- Comparable between countries,
- Transparent, and
- Complete.

Dioxin Toolkit – Chapter 4

Reliable inventories entail coherent application of internationally acknowledged methodologies such as the Toolkit and the use of best available national information.

To achieve consistency over time, the same approach should be used over time to establish consistent time trends.

To ensure comparability between countries, all countries should report according to the same source groups and source categorization.

For transparent estimates, the approach, methodology, information, and assumptions used should be clearly described, documented and archived to facilitate inventory updates in the future.

For complete release inventories, all relevant source categories, all sources within those categories and all relevant release vectors have to be considered in the whole country.

The inventory should also include information on source categories that do not exist or are not operational in the country during the reference year.

4.1 Quality Assurance and Quality Control (QA/QC)

The following quality assurance and quality control measures (QA/QC) should be applied to ensure that the source inventory and release estimates meet the quality criteria described above:

Activity Rates

- Align the unit of the activity rate with the unit of the emission factor.
- Pay attention to orders of magnitude while recalculating the activity rates and applying the emission factors.
- Explain clearly and completely all assumptions made in filling gaps in activity rates (see also "completeness").
- Explain clearly and completely the process of classification of sources and the way activity rates were derived.

Emission Factors

- The Toolkit expert group is mandated to evaluate all emission factors that are or will be included in the Toolkit to determine that they are scientifically sound.
- National emission factors should only be derived from measured data of adequate quality *e.g.* the application of standard sampling and analytical methods; proven laboratory experience and good documentation are pre-requisites of high quality data.
- The classification of sources and choice of emission factors have to be explained, documented and archived.
- Consideration has to be given to units and orders of magnitude.

Completeness of Data

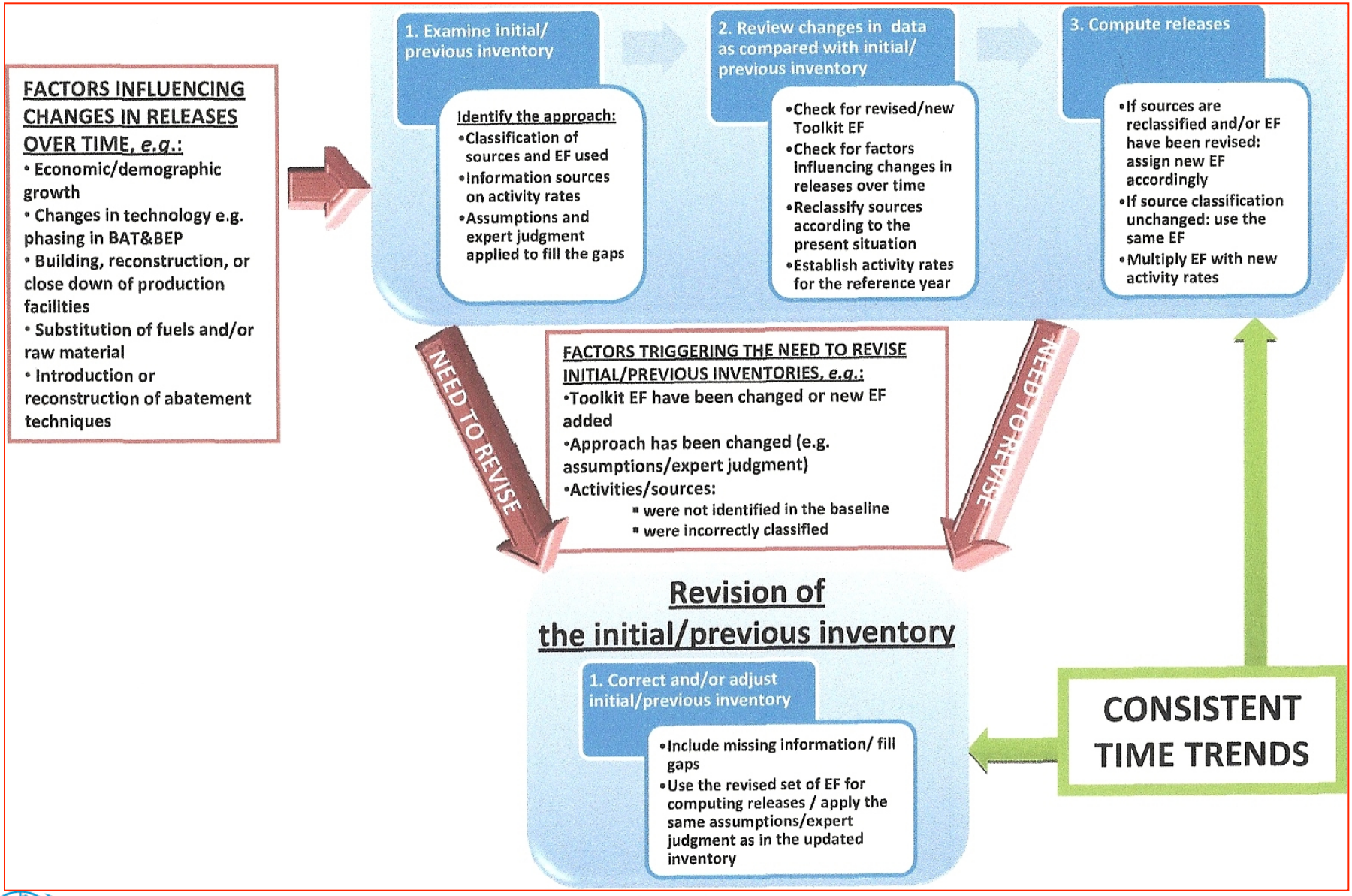
- Whenever practical and appropriate, individual plant questionnaires may be used to gather information for large point sources.
- Questionnaires provide useful information for the classification of plants and selection of emission factors. Since the return rate of the questionnaires is likely to be low, incomplete information-data gaps- will need to be covered by making assumptions about certain sources, where no specific information can be collected. Approaches will vary, but all assumptions should be clearly described in order to facilitate inventory updates in the following years or revisions in light of improved information.
- To determine complete activity rates, a combination of questionnaires (for large point sources) and national statistics should be used.
- When reporting the inventory results, it should be distinguished between "not applicable" *e.g.* the source category does not exist or is not operational in the country, and "not estimated" *e.g.* the source category is relevant but there was no sufficient information to estimate the releases.

4.2 Data Quality

Possibilities of indicating the confidence in the data used to generate emissions estimates may be as follows:

- Reporting of ranges (gives a good indication of confidence in data, however it may create problems while summarizing releases from more countries, therefore suitable only for reporting at the national level);
- Simple qualifiers, *i.e.*, data quality codes "high", "medium", "low" as outlined in Annex 8.

Establishing trends in POPs releases over time



Baseline Inventory – 2006 - Turkey

Group	Source Category	Annual Release (g TEQ/y)				
		Air	Water	Land	Product	Residue
1	Waste Incineration	62.8	NA	NA	NA	1.3
2	Ferrous and Non-Ferrous Metal Production	624.7	ND	NA	NA	675.4
3	Heat and Power Generation	40.6	ND	NA	NA	20.3
4	Production of Mineral Products	10	NA	NA	0.3	0.1
5	Transportation	21.5	NA	NA	NA	NA
6	Open Burning Processes	151	ND	96	NA	NA
7	Production of Chemicals and Consumer Goods	ND	5.3	ND	72.5	23.3
8	Miscellaneous	NA	NA	NA	NA	0.1
9	Disposal	NA	7.5	NA	2.1	212.5
10	Identification of Potential Hot-Spots	NA	NA	NA	NA	NA
1-10	Total	910.6	12.8	96	74.9	933
	Grand Total	2 027				

Summary Data - 2013 - Turkey

Group	Dr. Aykan KARADEMİR, aykan@kocaeli.edu.tr Source Category	Annual Release (g TEQ/y)				
		Air	Water	Land	Product	Residue
1	Waste Incineration	0.2	NA	NA	NA	7.0
2	Ferrous and Non-Ferrous Metal Production	156.2	0.1	NA	NA	567.4
3	Heat and Power Generation	60.5	ND	NA	NA	31.2
4	Production of Mineral Products	11.2	NA	NA	0.2	2.7
5	Transportation	2.6	NA	NA	NA	NA
6	Open Burning Processes	78.4	ND	76.8	NA	NA
7	Production of Chemicals and Consumer Goods	0.3	7.5	ND	87.4	15.3
8	Miscellaneous	NA	NA	NA	NA	0.1
9	Disposal	NA	6.1	NA	1.6	193.2
10	Identification of Potential Hot-Spots	NA	NA	NA	NA	NA
	Total	309.2	13.7	76.8	89.2	816.9
	Grand Total			1 306		

Summary Data - 2013 - Turkey

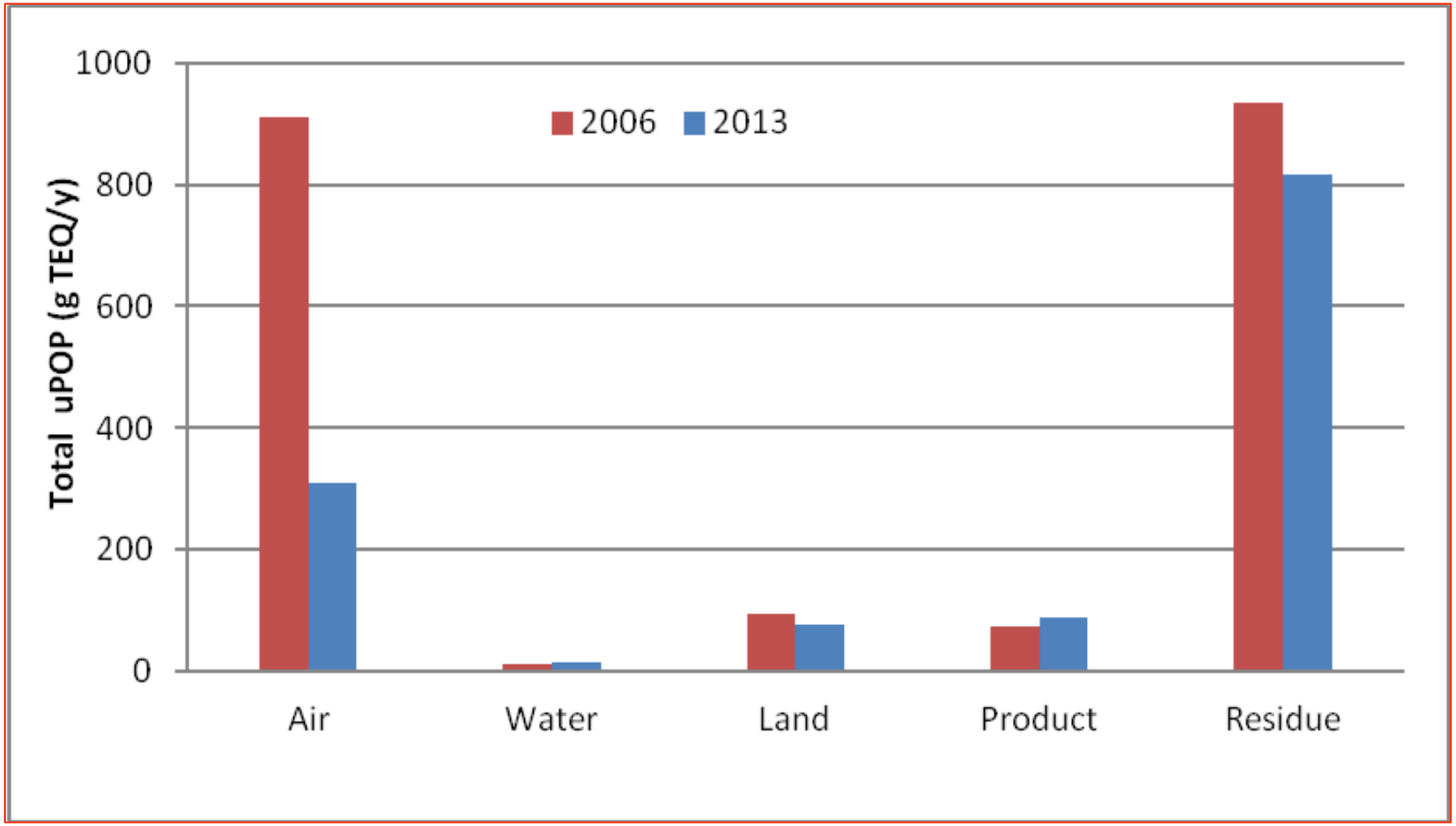
Total UPOP releases:

- 63 % in the residues
- 24 % in the atmospheric emissions
- 7 % in the products
- 6 % in the land
- 1 % in the wastewater discharges.

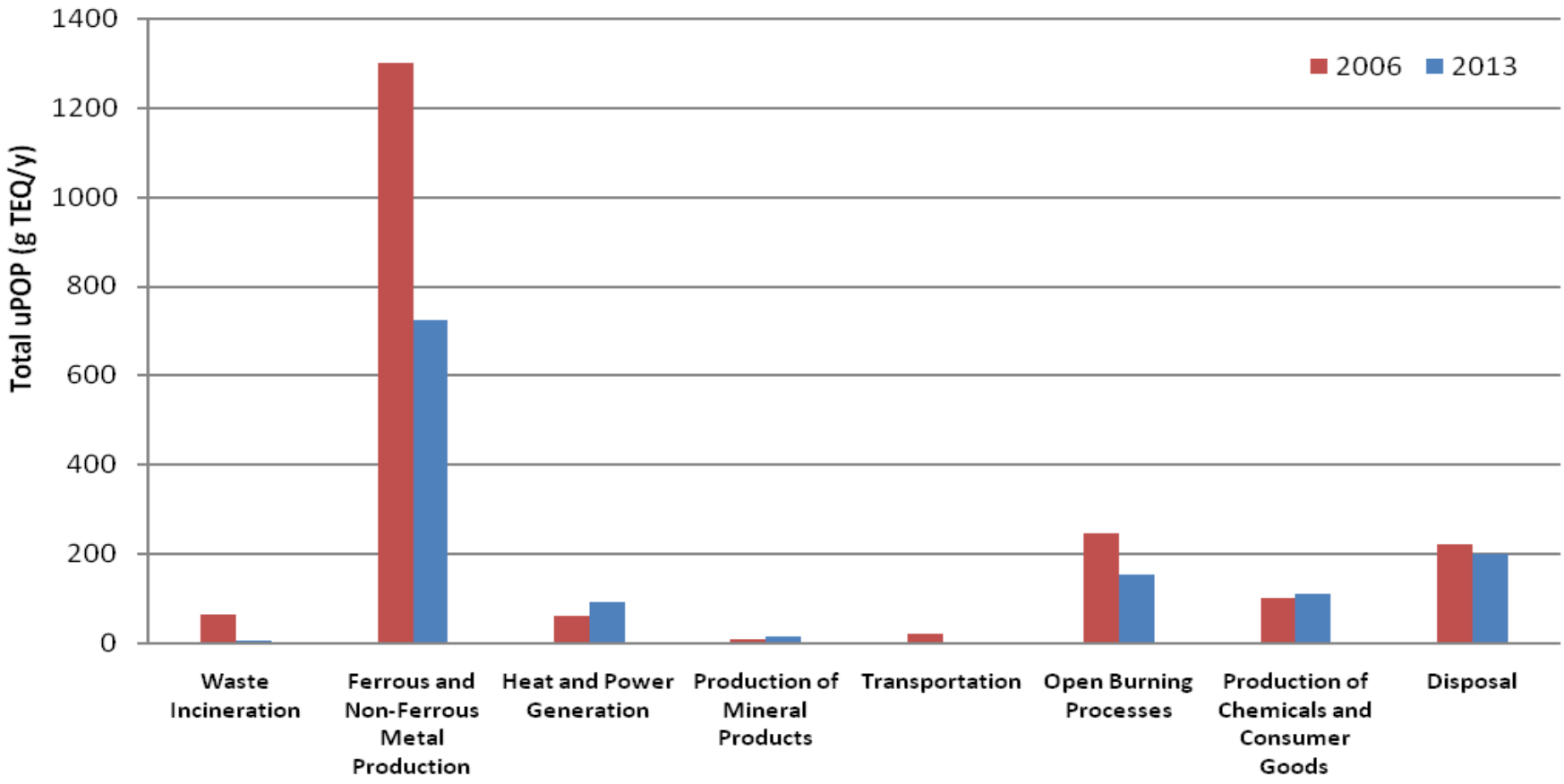
For the UPOP releases in residues, ferrous and non-ferrous metal production and facilities are the most important source groups. disposal

Iron and steel production and copper production have the highest contribution within the ferrous and non-ferrous metal production processes.

Comparison 2006-2013 (36 % decrease) - Turkey



Comparison 2006-2013 (Sources) - Turkey



Comparison 2006-2013 - Turkey

- The significant decrease in the air emissions (about 67 %) explains the difference between two inventories to a large extent.

- Moreover, uPOP releases to land and residues display some decreases about 20 % and 12 %, respectively. On the other hand, uPOP releases in the wastewaters and products increase about 20 % from previous to current inventory.

Uncertainty Problems

- Uncertainty in activity rates of some sources (secondary metal production, open burning processes, fire accidents etc.)
- Uncertainty in some illegal activities (use of waste oils, open burning of agricultural residues and wastes)

- Uncertainty in some emission factors (lack of national data)
- Uncertainty in national statistics

- Lack of recent data

Teşekkür Ederim

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