Dioxins & PCBs concerns

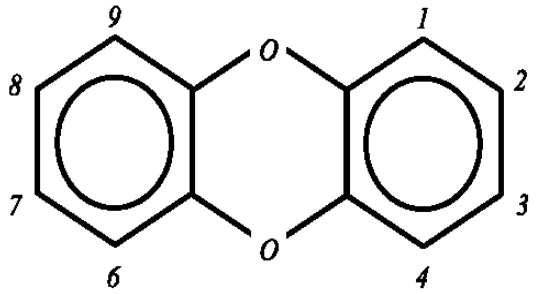
Properties, Sources and Formation

Program

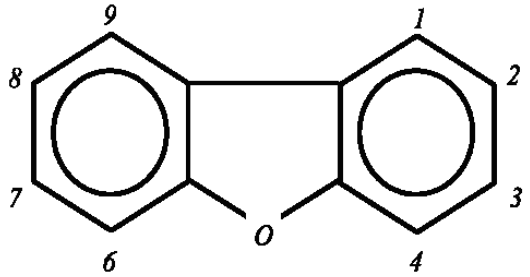
- Introduction to dioxins and PCBs
- Sources and formation
- Fate in environmental media
- Exposure pathways

Dioxins – What are they ?

- "Dioxins" are a group of highly toxic, closely related compounds which exhibit similar chemical and biological characteristics.



Polychlorinated dibenzo-p-dioxins (PCDDs)

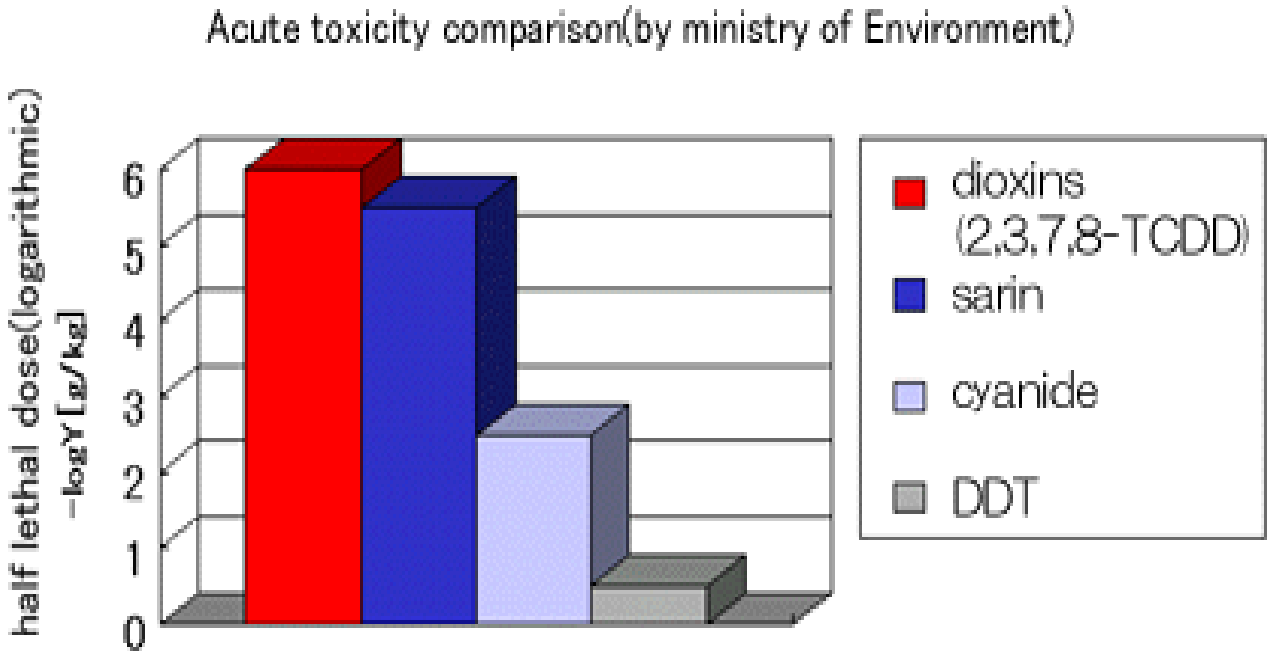


Polychlorinated dibenzofurans (PCDFs)

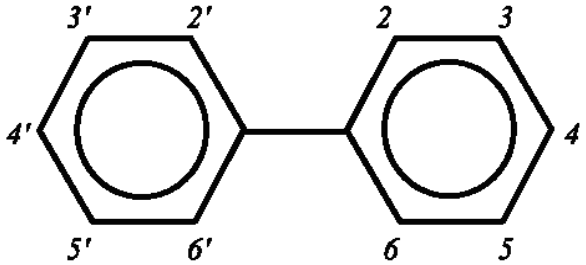
- Polychlorinated dibenzo-p-dioxins (PCDDs) and Polychlorinated dibenzofurans (PCDFs) are generally grouped together as "Dioxins". There are 210 of these compounds.

Dioxins – What are they ?

- **2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)** is the dioxin congener with the highest acute toxicity. It is considered the most toxic man-made substance and the fifth most toxic naturally occurring compound known to man.



Polychlorinated biphenyls (PCBs)



Polychlorinated biphenyls (PCBs)

- Polychlorinated biphenyls (PCBs) are a complex group of compounds, some of which show dioxin-like toxic effects. There are 209 PCB congeners.

Polychlorinated biphenyls (PCBs)

- Polychlorinated biphenyls (PCBs) were used for different applications, taking advantage from their properties

✓ Additives in oils in electrical equipment, hydraulic machinery

✓ Used for applications where chemical stability has been required for safety, operation or durability (waxes, inks, paints, adhesives, plasticizers, joint glues, etc.)

PCDD/F and PCBs possible congeners

Chlorine substitution	PCDDs			PCDFs			PCB	
Mono	2	-	-	4	-	-	3	-
Di	10	-	-	16	-	-	12	-
Tri	14	-	-	28	-	-	24	-
Tetra	-	22	1	-	38	1	40	2
Penta	-	14	1	-	28	2	41	5
Hexa	-	10	3	-	16	4	38	4
Hepta	-	2	1	-	4	2	23	1
Octa	-	1	1	-	1	1	12	-
Nona	-	-	-	-	-	-	3	-
Deca	-	-	-	-	-	-	1	-
Total	26	49	7	48	87	10	197	12
Total PCDD/F and PCBs	75			135			209	

Total number of non-reported isomers in homologue group

Total number of determinated isomers in homologue group

Number of reported 2,3,7,8 - PCDD/F or dioxin-like PCBs in homologue group

Total number of PCDDs and PCDFs (210)

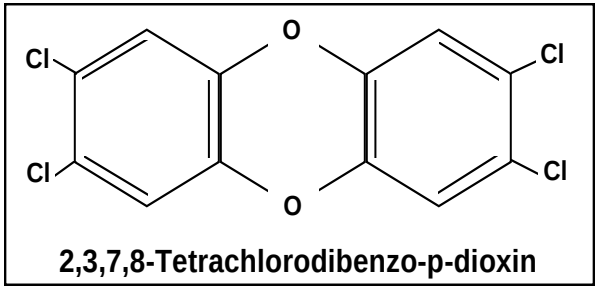
Total number of PCBs (209)

Properties of Dioxins/PCBs

- High Toxicity
- High persistence
  - difficult degradation
- Bioaccumulation
- Ubiquity
  - long range atmospheric transport and deposition

➢ ***Persistent Organic Pollutants***

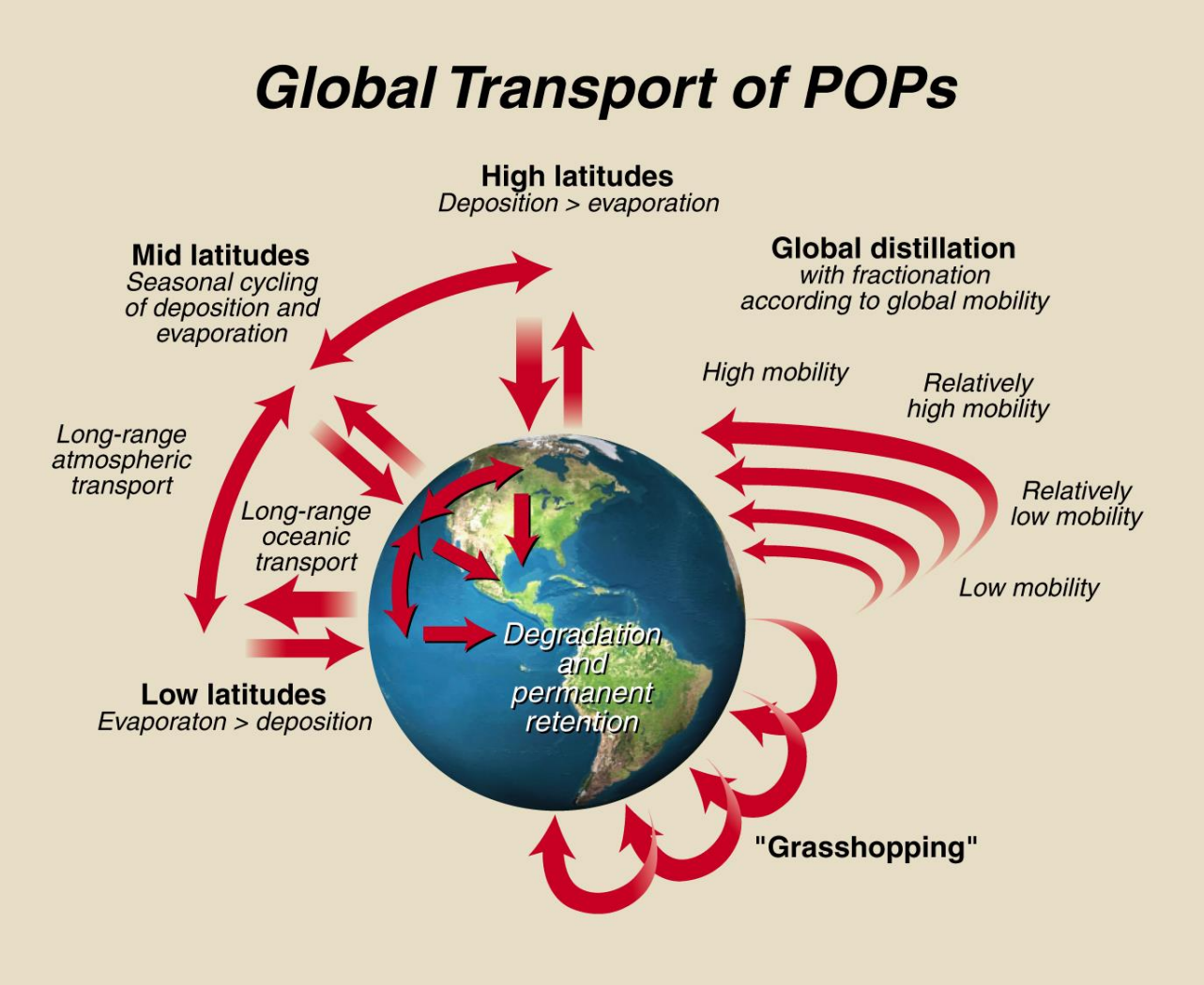
A look on 2378 TCDD



2,3,7,8-Tetrachlorodibenzo-p-dioxin

Name	2,3,7,8-tetrachlorodibenzo-p-dioxin
Formula	$C_{12}H_4Cl_4O_2$
Molecular weight	321,98
Melting point	305°C
Water solubility	20 ng/L at 22°C
Log Kow	6,80 at 25°C

Global mobility of POPs



Dioxins – Why are they of concern ?

- Dioxins are highly fat soluble, difficult to metabolise and tend to accumulate in the fatty tissues of food-producing animals.
- This leads to bioaccumulation in the food chain, increasing human exposure levels.
- Dioxins have been found in meat, dairy and fish products and also in human breast milk.

Dioxins – Why are they of concern ?

- Dioxin and related compounds bind to aryl hydrocarbon (Ah) receptor proteins of cells, causing a toxic response.
- TCDD is classified by IARC as carcinogenic to humans
- Adverse effect to dioxin acute exposure is chloracne
- Acute exposure may cause nausea, vomiting, diarrhoea, hepatic damages and neurological effects.
- Chronic exposure to dioxins may also cause liver disease, alterations of thyroid function, impared immune function, cardiovascular disease, decreased performance in tests of learning and intelligence, etc.

Most toxic compounds

- In total, 7 PCDDs, 10 PCDFs and 12 PCBs exhibit this form of toxicity to varying degrees. These compounds are assigned "Toxic Equivalence Factors" (TEFs) based on their toxicity relative to 2,3,7,8-TCDD.

Chlorine substitution	PCDDs			PCDFs			PCB	
Mono	2	-	-	4	-	-	3	-
Di	10	-	-	16	-	-	12	-
Tri	14	-	-	28	-	-	24	-
Tetra	-	22	1	-	38	1	40	2
Penta	-	14	1	-	28	2	41	5
Hexa	-	10	3	-	16	4	38	4
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Octa	-	1	1	-	1	1	12	-
Nona	-	-	-	-	-	-	3	-
Deca	-	-	-	-	-	-	1	-
Total	26	49	7	48	87	10	197	12
Total PCDD/F and PCBs	75			135			209	

Total number of non-reported isomers in homologous group

Total number of determinated isomers in homologous group

Number of reported 2,3,7,8 - PCDD/F or dioxin-like PCBs in homologous group

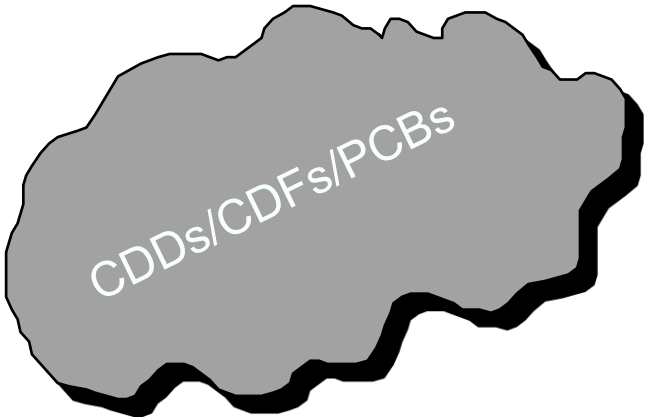
Total number of PCDDs and PCDFs (210)

Total number of PCBs (209)

TEF approach

- Toxicity Equivalent Factors
- Based on acute toxicity values from in vitro studies
- Based on the comparison of toxicity of specific PCDD/F or PCBs to the most toxic
- The most toxic has factor 1 : TCDD
- Administrative tool for conversion of all data in one number

$$\text{Total TEQ} = C_{congener} \times TEF_{congener}$$



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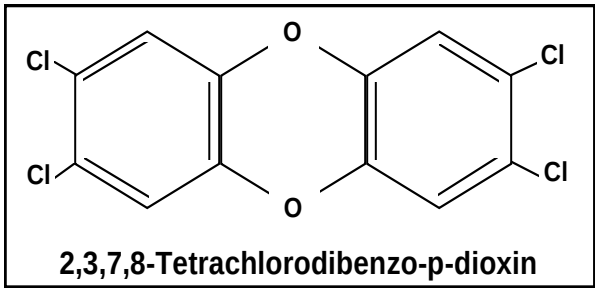
Toxicity Equivalence of



WHO and International TEF

Congener	WHO-TEF		I-TEF (1988)
	1997	2005	
2,3,7,8-TCDD	1	1	1
1,2,3,7,8-PeCDD	1	1	0,5
1,2,3,4,7,8-HxCDD	0,1	0,1	0,1
1,2,3,6,7,8-HxCDD	0,1	0,1	0,1
1,2,3,7,8,9-HxCDD	0,1	0,1	0,1
1,2,3,4,6,7,8-HpCDD	0,01	0,01	0,01
OCDD	0,0001	0,0003	0,001
2,3,7,8-TCDF	0,1	0,1	0,1
1,2,3,7,8-PeCDF	0,05	0,03	0,05
2,3,4,7,8-PeCDF	0,5	0,3	0,5
1,2,3,4,7,8-HxCDF	0,1	0,1	0,1
1,2,3,6,7,8-HxCDF	0,1	0,1	0,1
1,2,3,7,8,9-HxCDF	0,1	0,1	0,1
2,3,4,6,7,8-HxCDF	0,1	0,1	0,1
1,2,3,4,6,7,8-HpCDF	0,01	0,01	0,01
1,2,3,4,7,8,9-HpCDF	0,01	0,01	0,01
OCDF	0,0001	0,0003	0,001

Program

- Sources and formation

Sources and Formation of Dioxins

Dioxins are not produced commercially but exist as byproducts of combustion and certain industrial processes.

- Primary Sources (industrial or combustion processes)

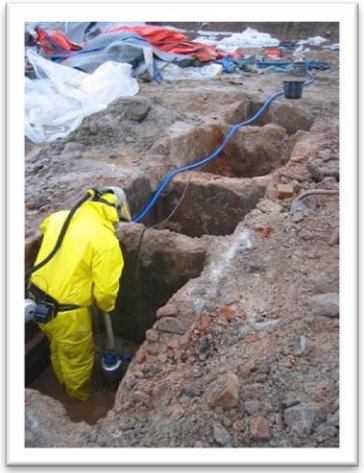
  Stationery Sources

  Diffuse Sources

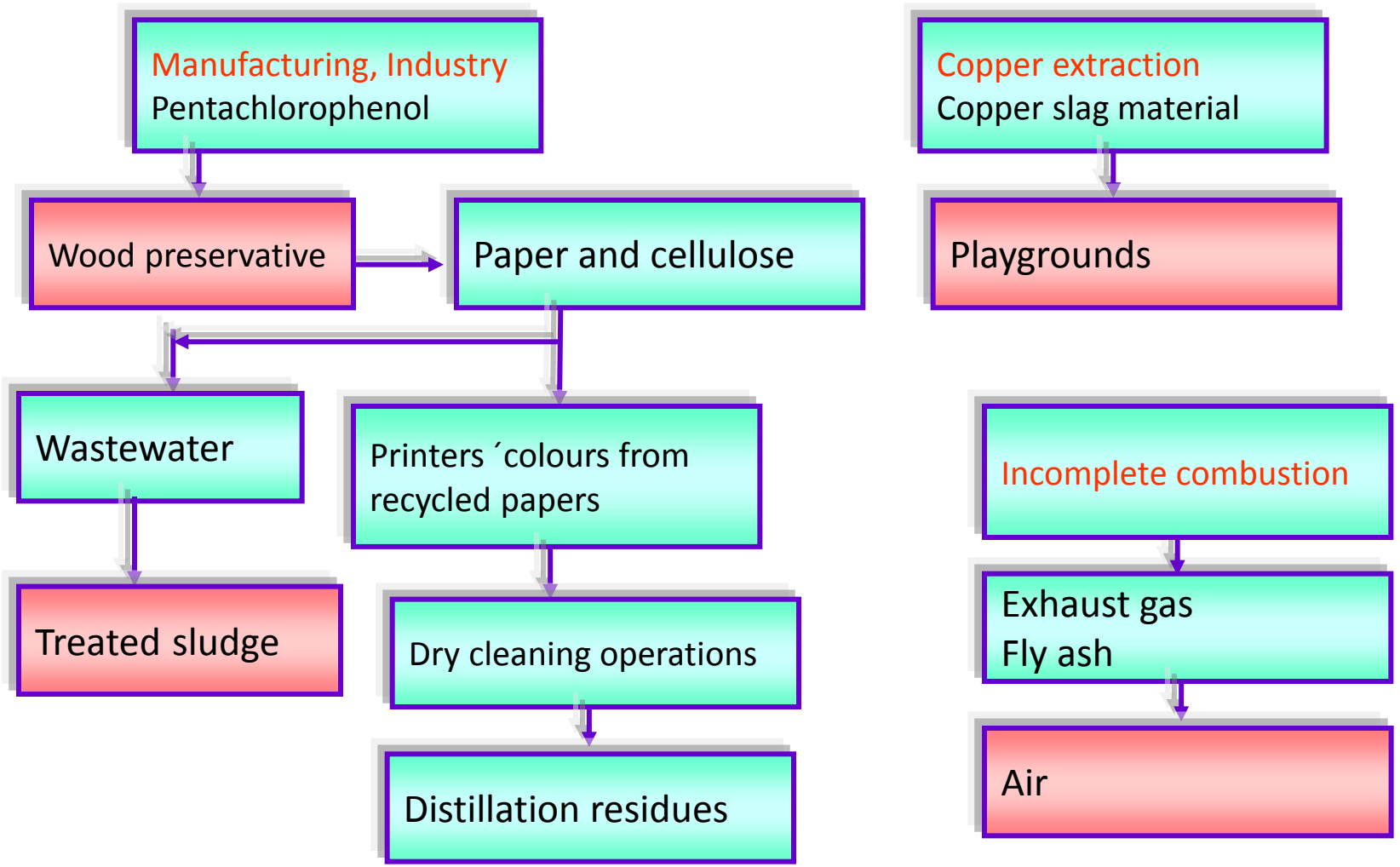
Sources

- **In the past**
  - Chemical industry
  - Pulp and paper industry
- **Nowadays**
  - Thermal processes

- Secondary Sources (sewage sludge / biosludge, compost, contaminated areas)

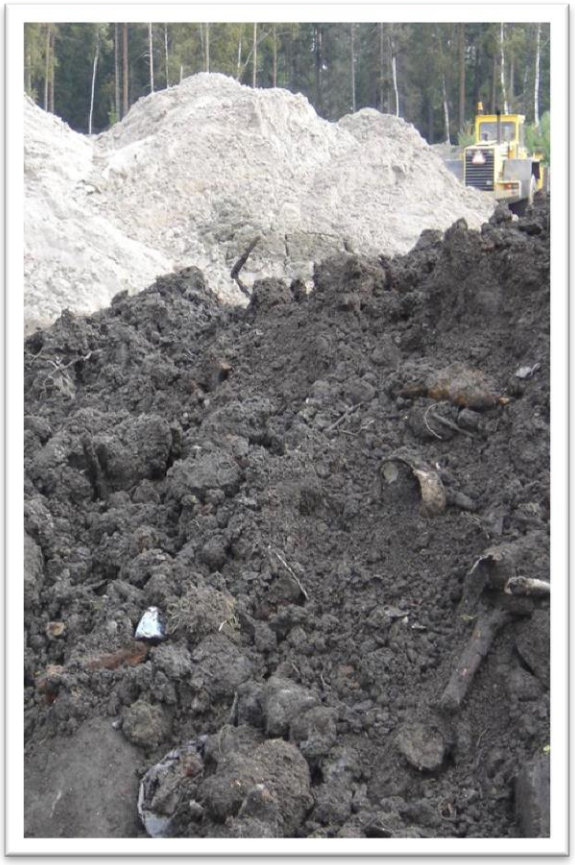


Examples of PCDD/F sources



Secondary Sources

- Reservoir of PCDD/F with possible release to the environment



– PCP treated wood

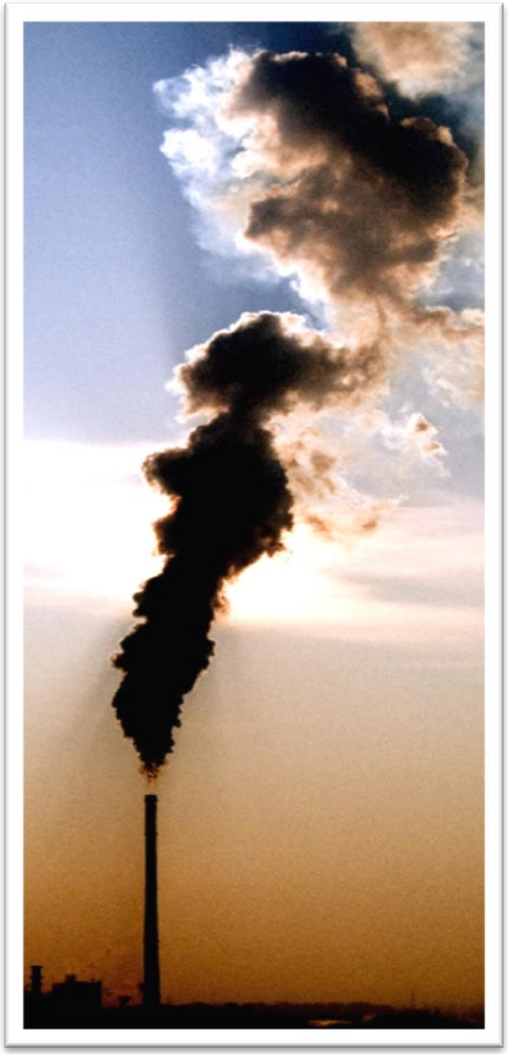
– PCB from transformers, sewage sludge

– Landfills and waste dumps

– Contaminated sites

– Contaminated products such as 2,4,5-T

Process of formation during incineration



- PCDD/F are already present in the incoming waste
- PCDD/F are formed from chlorinated precursors
  - PCB, PCP, ChlBz
- PCDD/F are formed *via de novo synthesis*

Program

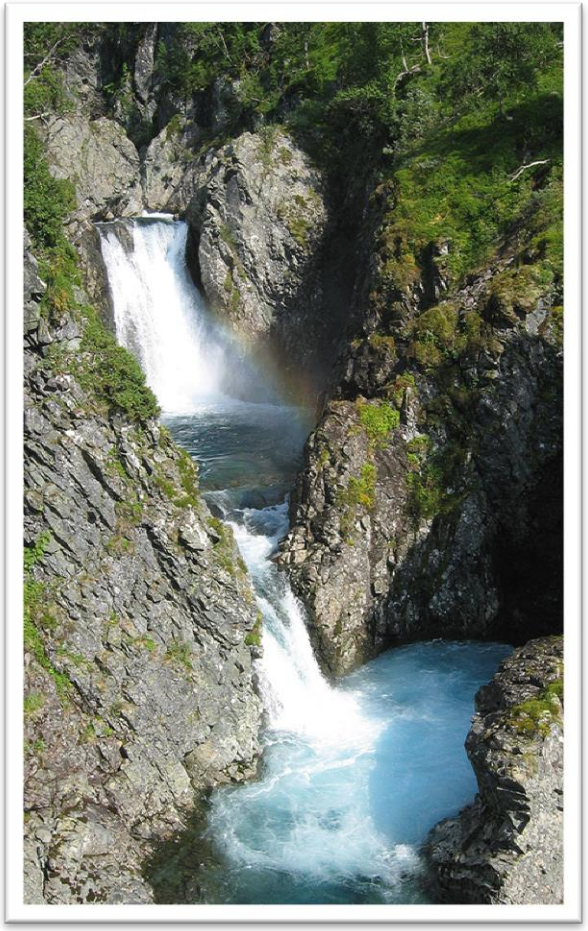
- Fate in environmental media

Environmental Fate

- **Dioxins and Furans, PCBs are found in all media: air, water, soil, sediments, plants, animals, food.**

- Hardly identified in water
- Strong affinity for soil and sediment
- High potential of bioaccumulate in plants, animals and fat

Fate: Aquatic compartment - Sediment

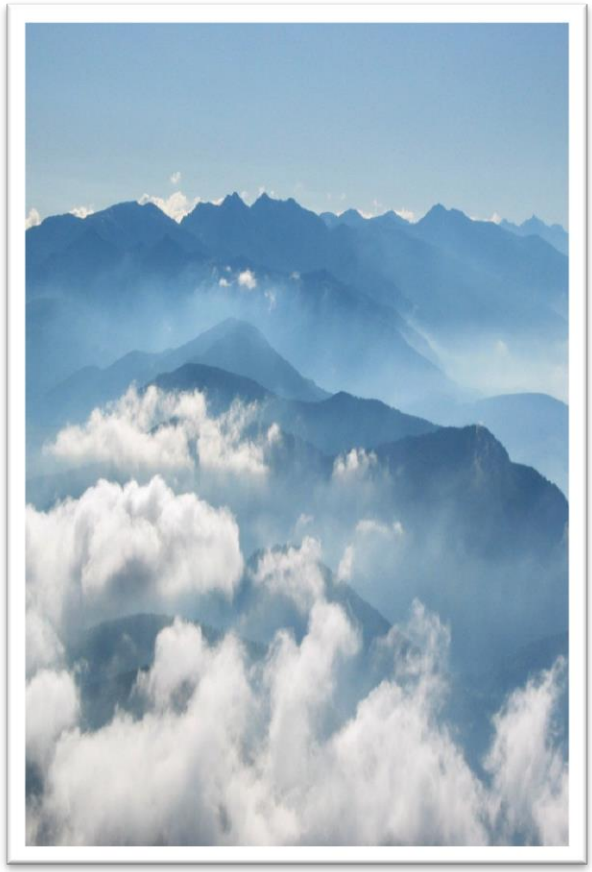


- Dioxins are resistant to oxidation and hydrolysis
  - low efficiciency of these processes
- Photodegradation and microbial transformations are the most important routes

Fate: Soil compartment

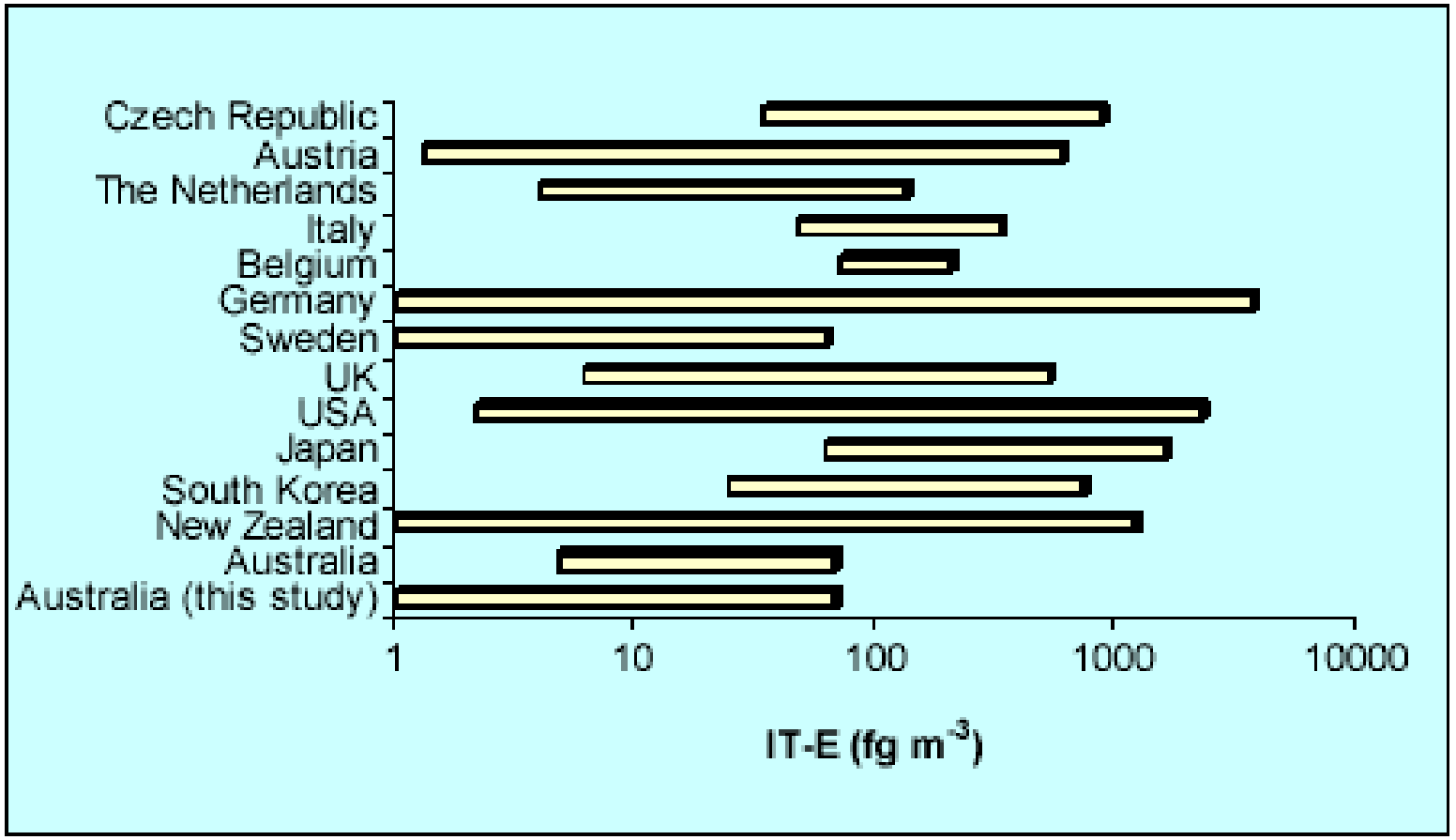
- Absorption on organic carbon in soil
  - Immobilisation
- Mobilization if
  - Presence of lipophilic solvents
  - Erosion, rains
- Soil does not play the main role in environmental contamination and population exposition, but is an excellent indicator of contamination

Air compartment is the most significant for environmental distribution and fate



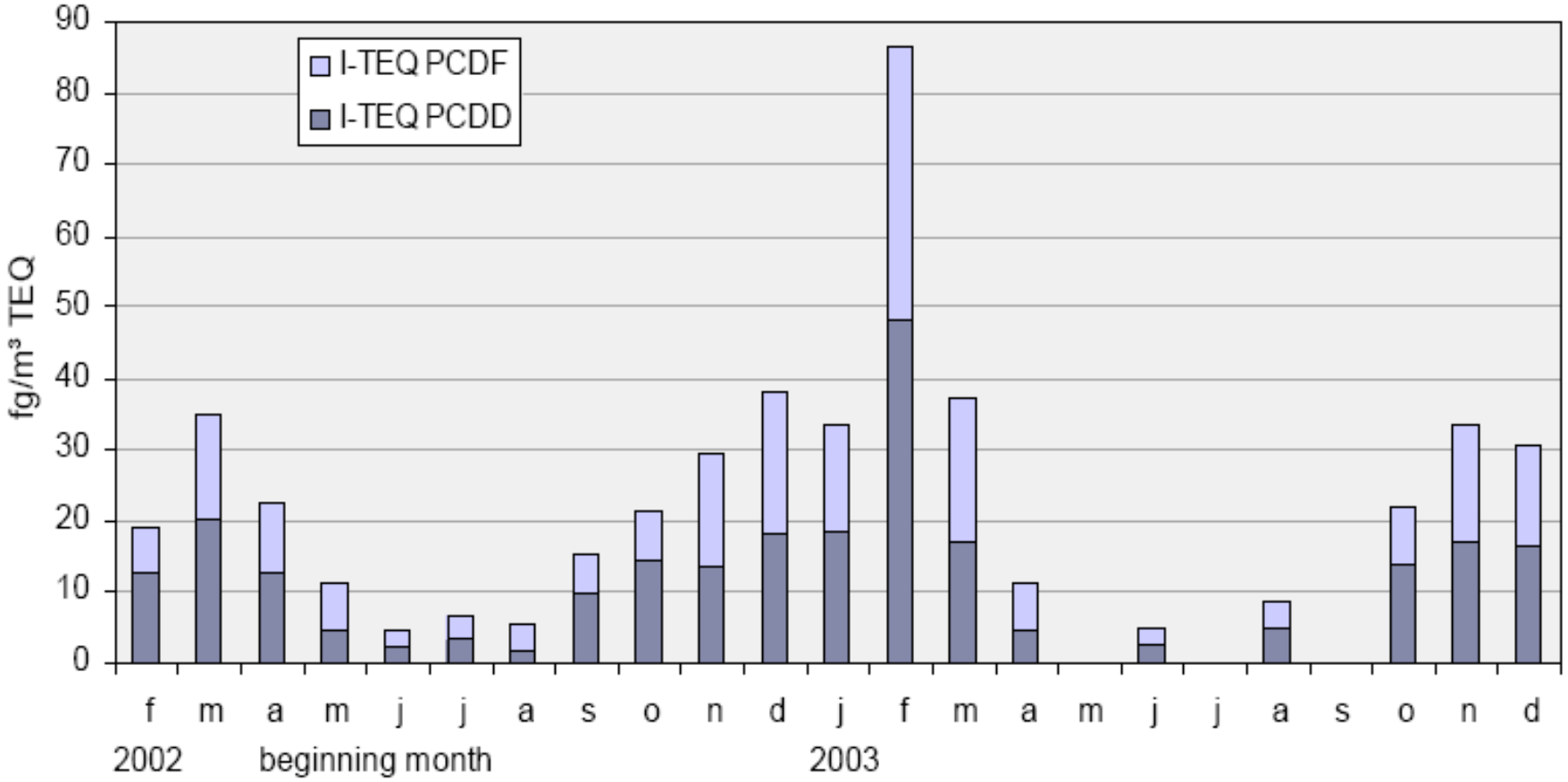
- **Part of Dioxins in gazeous state**
  - Removal processes include chemical and photochemical degradation
- **Part of Dioxins bound to particles**
  - Transport range depends on ion particle size

PCDDs/Fs – Average/country in atmosphere I-TEQ fg/m3



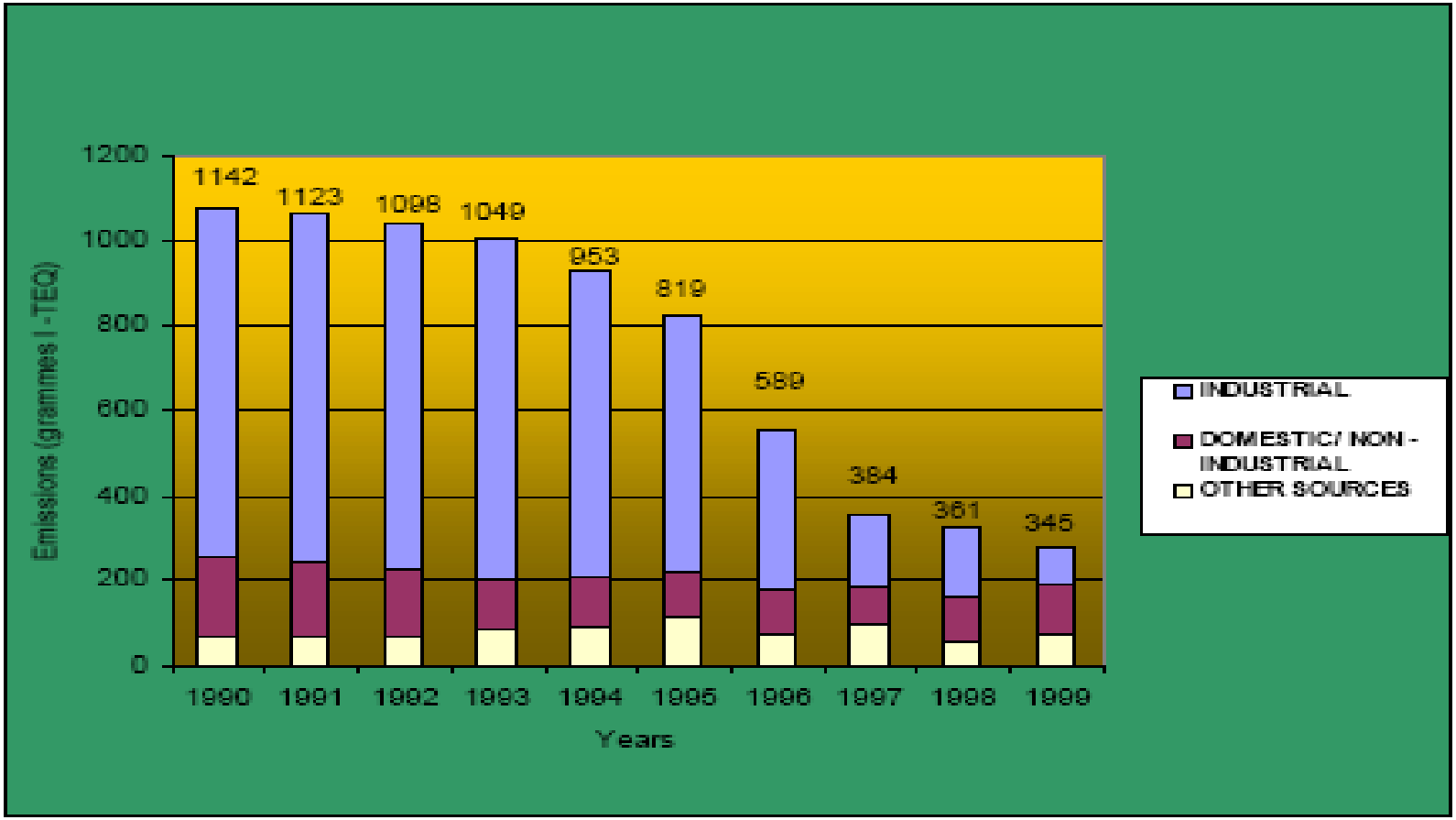
Source: National dioxins program – Australia, May 2004

Monitoring of dioxins in atmosphere



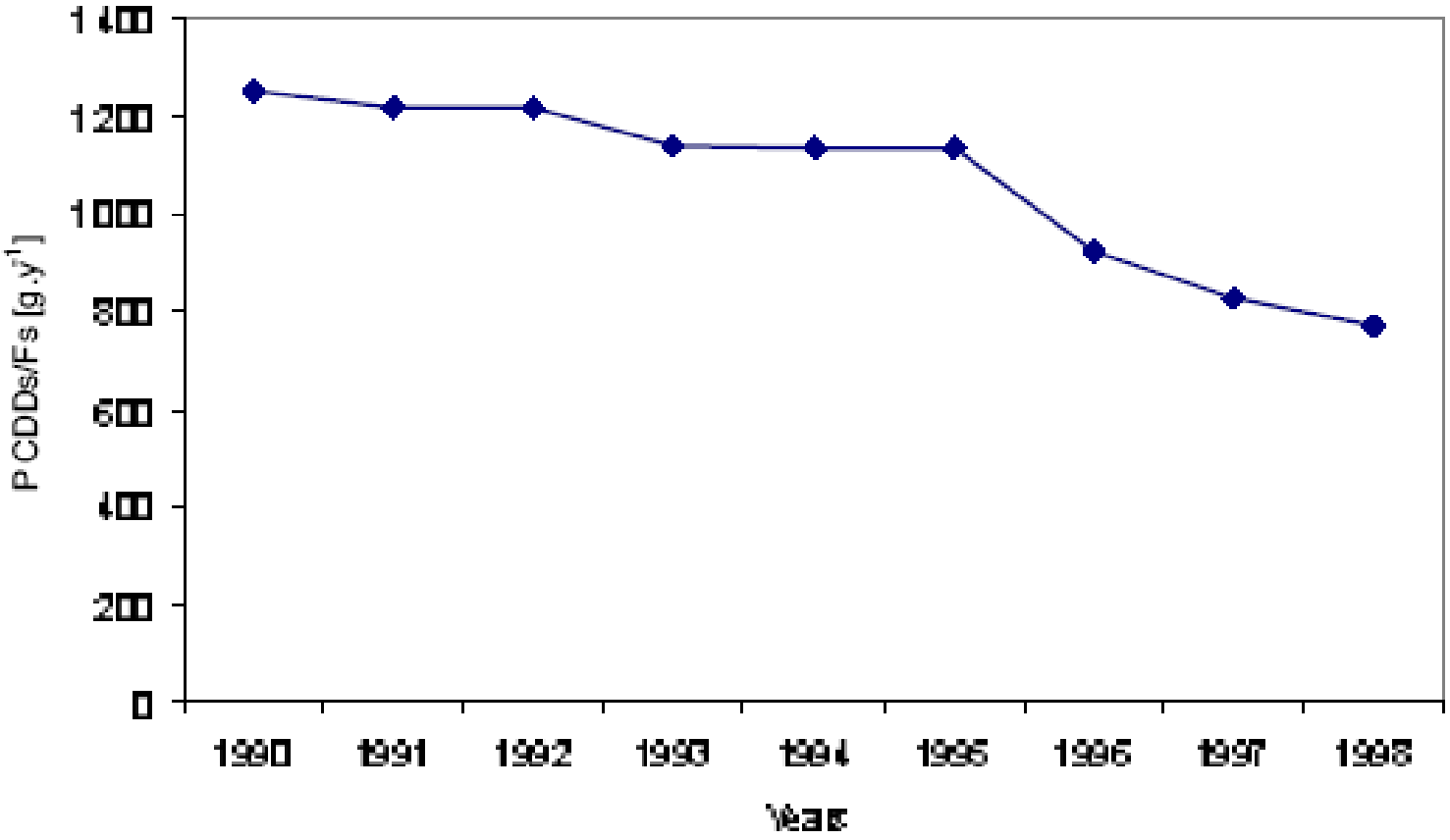
Source: Dioxin in Danish air – NERI 2004

Atmosphere - Time trends of PCDD/F - UK



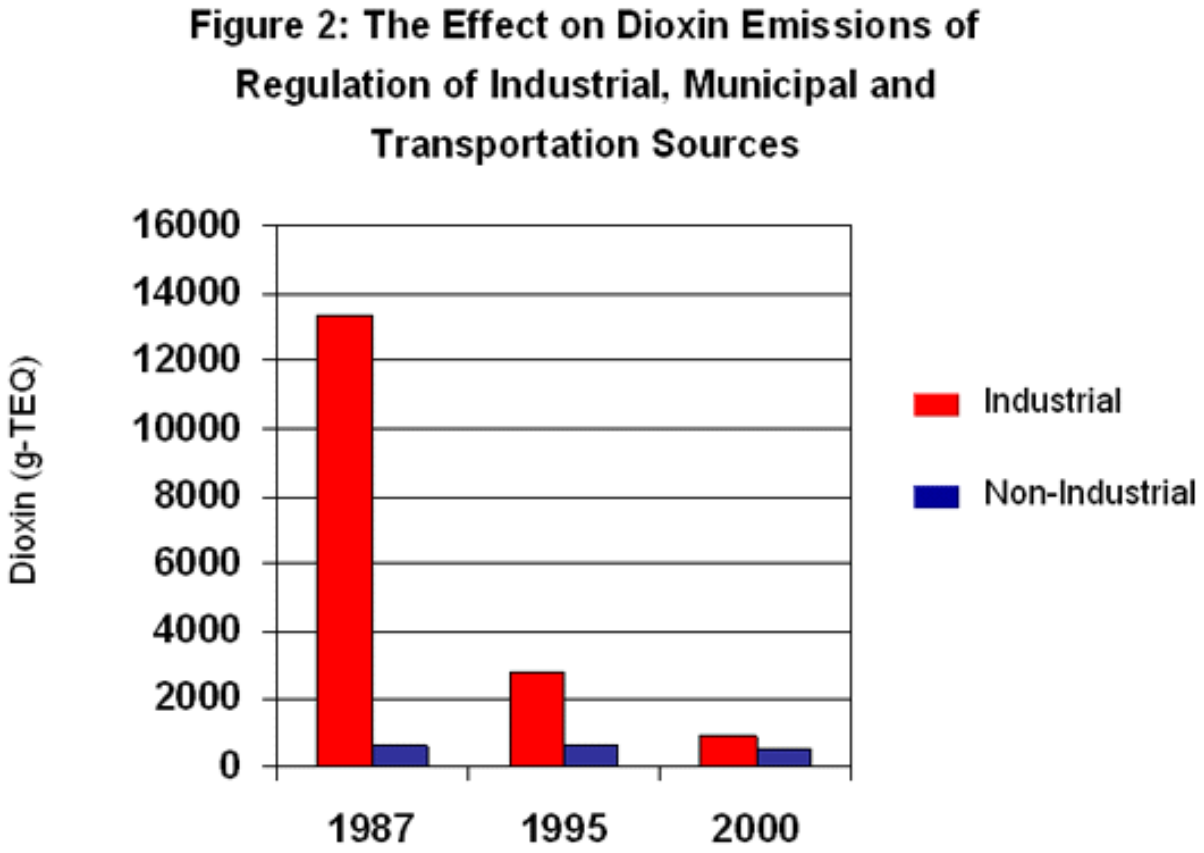
Source: Trends in dioxins emissions (1990 – 1999), Partial Regulatory Impact Assessment – Dioxins and Dioxin-like PCBs in the UK Environment

Atmosphere - Time trends of PCDD/F - CR



Source: Emission of PCDD/F (gram/year) – Czech Republic – Holoubek et al.

Trends in USA PCDD/F Emission 1987-2000



Source: U.S. EPA (Environmental Protection Agency). 2006. An inventory of sources and environmental releases of dioxin-like compounds in the United States for the years 1987, 1995, and 2000. National Center for Environmental Assessment, Washington, DC; EPA/600/P-03/002F

Program

- Exposure pathways

Exposure pathways

- In the past : Occupational exposures

– Chlorophenols production

– Chlorphenoxy herbicides

– Metal production and recycling

– Accidents

Nowadays : Food chain contamination

- Foodstuffs from animal origin
- Other fatty foodstuffs
- Accidental contamination of food