DANCEE - Danish Cooperation for Environment in Eastern Europe

Ministry of Environment Poland

# Inventory of Dioxin and Furan Releases in Poland

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### **Preface**

Background

Dioxins and furans have during recent years attracted national and international attention, as the compounds are very toxic, lipophilic and persistent organic pollutants (POPs), which accumulate in organisms and biomagnify in the natural food chains. Dioxins and furans remain in the environment for a long time, are transported over long distances, and pose risks to the global environment and human health. For this reason, dioxins and furans are selected for immediate actions by a number of intergovernmental organizations, among others UNEP, UNECE and HELCOM.

Health effects

Acute dioxin exposures to humans are associated with severe skin lesions, altered liver function and lipid metabolism, general weakness associated with drastic weight loss, depression of immune system and endocrine and nervous system abnormalities. Long-term exposure means increasing levels in fatty tissues and may result in developmental effects in children, cancer and other diseases.

**Inventories** 

Inventories of emission of dioxins and furans to air in Poland have for nearly a decade been compiled by the Institute of Environmental Protection (IEP). The Inventories have been used for annual reporting to UN ECE/EMEP and used by the Ministry of Environment for considerations regarding reduction of emissions of dioxins to the air. In 2000, the inventory work was taken over by the National Emission Centre (NEC) established at IEP. The establishment of NEC was the result of an agreement between the Minister of Environment, Head of the National Fund of Environmental Protection and the head of IEP.

The reporting of the inventories has in general not included a detailed description of the sources and measures for reduction of formation and emission of dioxins and furans. In order to establish a more detailed overview of the sources of dioxin and furan releases the Ministry of the Environment, Poland has initiated the present study. The study forms part of the preparatory work for development of a National Implementation Plan for implementation of the Stockholm Convention on Persistent Organic Pollutants (POPs).

Recently, another project on persistent organic pollutants 'POPs enabling activities to facilitate early action on the implementation of the Stockholm Convention on Persistent Organic Pollutants (POPs Convention) in Poland' was initiated. The project is funded by Global Environmental Facility (GEF) and the executing agency is IEP.

The inventory has been carried out under a DANCEE financed project: 'Survey of anthropogenic sources of dioxins in the Baltic Region'. Within the project inventories have been drawn up in Estonia, Latvia, Lithuania and Poland in 2001/2002.

UNEP toolkit

The inventory has been undertaken, and the sources are categorized in accordance with the toolkit for identification and quantification of dioxin and furan releases developed by UNEP Chemicals (UNEP 2001). The inventory has

been based partly on actual measurements of dioxin releases from sources in Poland, partly on emission factors derived from experience from other countries.

The present inventory should be considered the first step, and a recommendation for further development of the inventory will be provided.

#### **Steering Committee**

The inventory has been followed by a Steering Committee consisting of:

- Mr. Stanisław Kamiński, Ministry of Environment, (head of Committee);
- Ms. Maria Kłokocka, Ministry of Environment;
- Mr. Carsten Lassen, COWI AS;
- Mr. Krzysztof Olendrzyński, National Emission Centre (NEC).

#### Inventory team

This report has been prepared by Dr. Carsten Lassen and Erik Hansen, COWI A/S (Denmark), Krzysztof Olendrzyński (coordinator of the following group of Polish experts), Wiesław Kołsut, Dr. Janusz Żurek, Dr. Iwona Kargulewicz, Prof. Mariusz Holtzer, Dr. Adam Grochowalski, Bogusław Dębski and Jacek Skośkiewicz.

### **Abbreviations and Acronyms**

APC(s) Air pollution control (system)

BOF Basic oxygen furnaces

BF Blast furnaces

DANCEE Danish Cooperation for Environment in Eastern Europe

EF Emission factor

EMEP Co-operative programme for monitoring and evaluation of the

long-range transmission of air pollutants in Europe

GUS Główny Urząd Statystyczny - Main Statistical Office, in War-

saw

HELCOM The Convention for the Protection of the Marine Environment

of the Baltic Sea

I-TEF International toxicity equivalency factor (see Annex 1)

NEC National Emission Centre - emission inventory group at the

Institute of Environmental Protection in Warsaw

OSPAR The Convention for the Protection of the Marine Environment

of the North-East Atlantic

PCDD Polychlorinated dibenzo(*p*)dioxins

PCDF Polychlorinated dibenzofurans

PCB Polychlorinated biphenyl

PCP Pentachlorophenol
PM Particulate matter

POPs Persistent organic pollutants

PVC Polyvinyl chloride

SNAP97 Selected Nomenclature for sources of Air Pollution 1997

UNEP United Nations Environment Programme

UNECE United Nations Economic Commission for Europe

### **Units**

I-TEQ International dioxin toxicity equivalent (see Annex 1)

t metric ton 1,000 kg = 1 Mg

 $\mu$ g microgram  $10^{-6}$  g ng nanogram  $10^{-9}$  g pg picogram  $10^{-12}$  g

mln. t million t

## **Summary and Recommendations**

The inventory

The following inventory of dioxin and furan releases from Poland has been prepared in accordance with the recommendation of UNEP Chemicals concerning identification and quantification of dioxin and furan releases. Until now, few measurements of dioxin releases have been carried out in Poland, and for most source categories the releases have been estimated by multiplying actual activity rates for each source category by emission factors derived in other countries. For the medium estimates default process specific emission factors from the toolkit for inventories of dioxins and furans prepared by UNEP Chemicals have been applied, unless something else is mentioned in the report. Uncertainty ranges for activity data have been determined by the authors of the report.

Potential releases

The potential releases of dioxins and furans from sources in Poland in 2000 are summarized in Table 1. Sources of releases are grouped into ten main categories: From category 1, 'Waste incineration' to category 10, 'Hot spots'. The releases are estimated separately to five media: To air, water, land, products and residues. The releases are shown as medium estimates and corresponding ranges, within which the "true" value most likely will be. The medium estimate is considered a "best estimate".

Emission to air

The main release route for dioxins and furans is emission to air. The total emission to air is summarised in Table 1 and further illustrated in Figure 1.

Total dioxin and furan emissions to air is estimated at 490g I-TEQ (International toxic equivalents) with a range of 86-1,300 g I-TEQ. Considering the medium estimates, largest emission to air occurred in the categories 'Uncontrolled combustion processes' (37%), 'Waste incineration' (29%), 'Ferrous and non-ferrous metal production' (16%) and 'Power generation and heating' (13%).

The major sources within 'Uncontrolled combustion processes' are uncontrolled waste burnings at households and landfill fires. The former is the source of many other pollutants e.g. PAHs, and is widespread especially in southern Poland. Of 'Waste incineration' major contributions came from the subcategories hazardous and industrial waste incineration, especially at plants with minimal or no air pollution control systems (APCS). Within the category 'Metal production' most releases came from iron ore sintering and secondary aluminium production. Relatively lower contributions came from: Category 3. 'Power generation' 62 g I-TEQ - mainly from household cooking/heating with biomass combustion and category 4. 'Production of mineral products' - 18 g I-TEQ (4%) - mainly from lime and cement production. Total contribution from the remaining categories: 5. Transportation', 7. 'Production of chemicals and 8. 'Miscellaneous' was below 6 g I-TEQ.

10 Hot spots

Total

?

530 ?

Ma	in Category	Potential release in g I-TEQ/year								
		Air		Water		Land	Product		Residues	
		Medium	Range	Medium	Range	Medium	Medium	Range	Medium	
1	Waste incineration	140	15-220						89	
2	Ferrous and non-ferrous metal production	80	21-190	0.05 ?	0.05-0.09	?	?		140 ?	
3	Power generation and heating	62	22-310						55	
4	Production of mineral products	18	3.3-31	?		?	?		0.63 ?	
5	Transport	3.6	2.5-4.7						?	
6	Uncontrolled combustion processes	180	22-530	?		6.6 ?			210 ?	
7	Production and use of chemicals and consumer products	0.07	0.01-0.15	0.04 ?	0.01-0.08		11	0.9-46	1.1 ?	
8	Miscellaneous	1.7	0.5-3			?	0.14 ?	0.01-0.29	0.1 ?	
9	Disposal and wastewater			1.1 ?	0.5-2.0		0.03	0.001-0.1	35	
_										

?

1.2 ?

?

490

86-1300

Table 1. Potential releases of dioxins and furans from all sources in Poland in 2000 by main source categories

0.57-2.2

?

6.6 ?

?

11?

0.91-47

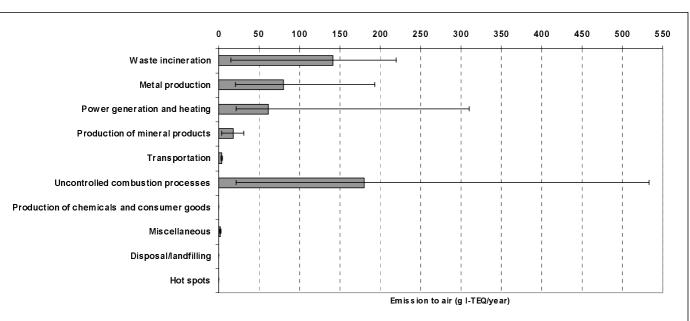


Figure 1. Potential emission of dioxins and furans to air from all sources in Poland in 2000. Medium estimated (bars) with uncertainty ranges (lines)

<sup>\*</sup> An empty cell indicates that the release route is considered insignificant. '?' indicates that the release route may be significant, but no emission factors have been determined. A "?" after a number indicates that the number may be underestimated, as some subcategories have not been quantified due to lack of emission factors.

Whereas the potential emissions to air are relatively well represented by contributions from various main and subcategories of sources, the release to the other four media are - in general - much less investigated. This is caused by an inadequate amount of release measurements that could justify selection of respective emission factors (EF). No actual measurements of dioxins releases to the other media in Poland have been undertaken, and default emission factors are missing for a number of sources. The calculated total releases to residues must thus be expected to significantly underestimate the actual releases. Because of the lack of data for a number of categories and very few measurements for most of the other categories, no attempt has been made to estimate uncertainty ranges for the releases to land and residues. Potential releases where no default emission factors are available, are indicated by a question mark in Table 2. For categories where some subcategories for this reason are not included in the total, a question mark is added to the total. It is, however, estimated that none of the subcategories not included can be assumed to be of major significance.

Releases to water

The main contributions to releases to water came from municipal sewage and coke production subcategories. For some categories emission factors are missing, but the release from these sources is deemed to be of less significance than the quantified sources. Free chlorine is not used for bleaching of pulp and paper in Poland - this source has traditionally been the major source to release to water in many countries.

Releases to land

The only noted category for direct release to land is fires and burning of biomass. It should be noted that a significant part of the release to residues may ultimately end up at land - in particular residues from uncontrolled burning of waste and sewage sludge applied on agricultural soils.

Releases to products

The major sources of releases to products are production of recycled paper and production of chlorinated pesticides. Concerning recycled paper the dioxin content of the products may be present in the paper disposed of for recycling.

Releases to residues

The potential releases to residues are of the same magnitude as the releases to air. The dioxins are in general produced by the same processes, and the dioxins and furans end up in the residues from the air pollution control systems. Residues are mainly disposed of to landfills, but residues from households and sewage plants may ultimately end up at land and account actually for the main releases to land. Dioxins and furans in residues may in the future be released from landfills and waste dumps.

Comparison to previous inventories

The current study brings a little higher value for the total release to air compared to earlier estimates made according to SNAP97 nomenclature for source types (see point 1.2 below). As demonstrated in this inventory the uncertainty of inventories based on default emission factors is quite high, and the differences between the inventories is mostly due to differences in the applied emission factors and a different categorisation with respect to domestic heating and cooking with the use of coal and co-combustion of waste in households. The present study, however, demonstrates that releases associated with landfill fires - not included in previous inventories - may be a major contributor to the national total releases.

Further development of the inventory

The present inventory should be considered the first step, and a number of recommendations for further development of the inventory is provided in the report.

This study showed that more information and data in particular are needed on hazardous and industrial waste incineration, sintering processes and secondary ferrous and non-ferrous metal production. For these processes more disaggregation of activity data and information on conditions of processes and APC systems applied may decrease the uncertainty. However, actual measurements of dioxin emission from a large number of facilities are necessary for obtaining a more profound basis for prioritizing of measures for emission reduction. Facilities with minimal or no APCS seem to contribute most significantly to the national totals, therefore it would be justified to carry out dioxin measurements at these facilities in the first hand. A special study should be devoted to collection of activity data from small plants poorly equipped with APCS, as small facilities are generally not covered by public statistical surveys.

It is deemed very difficult to reduce the uncertainty of the emission factors used for estimating the emission from uncontrolled burning processes, but the uncertainty of the emission estimate may be reduced by obtaining more certain estimates of the amount of waste actually burned in households and by landfill fires.

Measures for release reduction

The report provides for each source category a list of measures for reducing the formation and release of dioxins and furans. For the major source categories measures are already implemented in the most modern of the facilities, and a very significant reduction in the total emission can be obtained by upgrading all facilities to the technological level of the facilities with the best available technology. For diffuse sources promotion of waste collection, waste minimisation, sorting and recycling as well as decreased use of chlorinated plastics could reduce the formation of dioxins and furans significantly.

Main conclusions

- It is the first comprehensive inventory of dioxin and furan release to environment (air, water, land, residues) and products in Poland carried out using a unified methodology developed by UNEP Chemicals;
- An estimation of releases to air agrees fairly well with earlier estimates based on source type disaggregation according to SNAP97 codes and a set of emission factors developed jointly under EMEP/CORINAIR programmes;
- Due to numerous uncertainties in both activity rates and corresponding emission factors, all release estimates including emissions to air should be interpreted as first order estimates;
- Emission factors are missing in the UNEP toolkit for some source categories (especially for releases to land and residues) and therefore the respective release estimations might be underestimated;
- Options for release reductions have been identified in key sectors contributing most to total releases

Table 2. Potential releases of dioxins and furans from all sources in Poland 2000 by category

Main Category	Potential release in g I-TEQ/year								
	Air		Water		Land	Product		Residues	
	Medium	Range	Medium	Range	Medium	Medium	Range	Medium	
Waste incineration	140	15-220						89	
Municipal solid waste incineration	0.001	<0.002						0.05	
Industrial waste incineration	53	5.2-120						26	
Hazardous waste incineration	77	1-81						41	
Medical/hospital waste incineration	12	9-16						22	
Sewage sludge incineration	0.02	0.006-0.06						0.003	
Metal production	80	21-190	0.05 ?	0.05-0.09	?	?		140 ?	
Iron ore sintering	40	8.1-81	?		?	?		0.02	
Coke production	2.7	1.4-7.3	0.05	0.05-0.09	?	?		?	
Iron and steel plants	11	2.4-34	?		?			60	
Foundries	3.9	2-5.9	?		?	?		0.03	
Copper production	2.3	0.46-4.5	?		?	?		29	
Aluminium production	19	6.2-56	?		?	?		49	
Lead production	0.29	0.07-0.92	?		?	?		?	
Zinc production	1.5	0.46-4.6	?		?	?		?	
Brass production	0.024	0.008-0.072	?		?	?		?	
Thermal wire reclamation									
Power generation and heating	62	22-310						55	
Fossil fuel power plants	16	8.1-49						23	
Biomass power plants	0.18	0.04-0.36						0.004	
Landfill and biogas combustion	0.01	0.005-0.03							
Household heating and cooking - biomass	29	6.7-41						30	
Domestic heating - fossil fuels	16	6.8-220						2.5	
Production of mineral products	18	3.3-31	?		?	?		0.63 ?	
Cement production	5	2.5-12			?	?		0.63	
Lime production	12	0.68-18	?		?	?		?	
Brick production	0.24	0.06-0.49			?	?		?	
Glass production	0.31	0.06-0.62				?		?	
Ceramics production	0.15	0.04-0.28			?	?		?	
Asphalt mixing	0.04	0.01-0.07			?	?		?	
Transportation	3.6	2.5-4.7						?	
Uncontrolled combustion processes	180	22-530	?		6.6 ?			210 ?	

Main Category	Potential release in g I-TEQ/year									
	Air		Water		Land	Product		Residues		
	Medium	Range	Medium	Range	Medium	Medium	Range	Medium		
Fires/burnings - biomass	14	0.6-47	?		6.6			?		
Landfill fires	49	8-120								
Uncontrolled waste burning	100	8.4-330	?		?			200		
Accidental fires in vehicles and houses	17	4.8-34	?					14		
Production of chemicals and consumer goods	0.07	0.01-0.15	0.04 ?	0.01-0.08		11	0.9-46	1.1 ?		
Primary pulp and paper production	0.07	0.01-0.15	0.03	0.006-0.08		0.61	0.12-1.2	1.0		
Secondary paper production			?			7.1	0.71-11	?		
Chemical industry	0.00008	<0.0001	0.008	0.008		2.8	0.06-28	0.06		
Petroleum refineries								?		
Textile production			?			0.06	0.006-6.4	?		
Miscellaneous	1.7	0.5-3			?	0.14 ?	0.01-0.29	0.1 ?		
Drying of biomass	0.009	0.009-0.01			?	0.14	0.01-0.29	?		
Crematoria	0.06	0.05-0.07						0.02		
Smoke houses	1.6	0.48-2.9			?	?		0.09		
Tobacco smoking	0.008	0.008								
Disposal/landfilling			1.1 ?	0.5-2		0.03	0.001-0.1	35		
Landfill leachate			?							
Sewage/sewage treatment			1.1	0.5-2				35		
Composting			?			0.03	0.001-0.1			
Hot spots										
Total	490	86-1,300	1.2 ?	0.57-2.2	6.6 ?	11 ?	0.91-47	530 ?		

<sup>\*</sup> An empty cell indicates that the release route is considered insignificant. '?' indicates that the release route may be significant, but no emission factors have been determined. A "?" after a number indicates that the number may be underestimated, as some subcategories have not been quantified due to lack of emission factors.

### 1 Introduction

In order to assist counties in carrying out inventories of dioxin and furan releases, UNEP Chemicals has recently developed a toolkit for dioxin and furan inventories (UNEP 2001). The toolkit includes inventory methodology and default emission factors to be used, if no actual measurements are available.

The toolkit has been applied for this inventory. The methodology is described in more detail in section 1.3 after a short introduction to dioxins and furans.

#### 1.1 Introduction to Dioxins and Furans

#### 1.1.1 What are Dioxins and Furans?

The phrase 'dioxins and furans' is typically used as a short designation of two groups of tri-cyclic, halogenated, organic compounds, of which some chlorinated compounds have been demonstrated to be extremely toxic.

The first group covers the polychlorinated dibenzo-p-dioxins (PCDDs) and the polybrominated dibenzo-p-dioxins. The number of halogen substituents may range from one to eight, and the sub-group of chlorinated dioxins consists of 75 compounds with different combinations of substituents - so-called congeners.

The second group covers the polychlorinated dibenzofurans (PCDFs) and the polybrominated dibenzofurans. Again the number of halogens may range from one to eight bringing the number of congeners for the sub-group of PCDFs up to 135.

To these groups of substances should be added the large groups of mixed brominated/chlorinated dibenzo-*p*-dioxins (PXDDs) and dibenzofurans (PXDFs) that consist of 1,550 and 3,050 different congeners respectively /IPCS 1998/.

In this study only the chlorinated compounds, the PCDDs and PCDFs, are included. These compounds are at present the only dioxins and furans covered by the Stockholm Convention. For convenience, however, the terms dioxins and furans are still used in the report. Most are known about the chlorinated compounds, which are also in general formed and released in larger quantities than the brominated dioxins and furans.

Dioxins are always found in samples as a mixture of various congeners. The toxicity of the dioxins is very congener-specific, ranging from the most toxic 2,3,7,8 TCDD (tetra chloro dibenzo-*p*-dioxin) to congeners more than 10,000 times less toxic. Today only congeners with chlorine atoms in the 2,3,7,8-positions are considered to have toxic properties as TCDD. Over the years a number of toxicity equivalency factor systems have been developed. The equivalency factor systems are described further in Annex 1.

In the *Standardized toolkit* used for this study all emission factors are represented by international toxicity equivalents I-TEQ.

The chemical structure of two dioxins and furans are shown in figure 1.1.

Figure 1.1 Chemical structure of 2,3,7,8-TCDD and 2,3,7,8-TCDF (TC for tetra chloro, which means that there are four chlorine atoms)

2,3,7,8-TCDD

#### 1.1.2 Formation of Dioxins and Furans

Dioxins are not produced intentionally, but are formed as unwanted byproducts of some chemical and thermal processes; among those virtually all combustion processes.

Thermal processes

By thermal processes e.g. waste incineration or combustion of gasoline, the compounds may be formed by two mechanisms:

#### • "De novo synthesis"

By 'de novo synthesis' dioxins and furans are formed from its basic elements - carbon, hydrogen, oxygen and chlorine. The process is taking place at temperatures between approximately 250 and 500°C on catalytically active surfaces. In particular copper compounds are regarded as effective catalysts.

#### • Formation from precursors

Dioxins and furans are formed from chlorinated organic compounds, such as chlorinated phenols that serve as precursors for the process. Similarly, these reactions may take place at temperatures between approximately 200 and 500°C on catalytically active surfaces, but also spontaneously at the relevant temperatures.

Whereas dioxins are likely to be decomposed at very high temperatures (above 800-1000°C) assuming adequate residence time at this temperature level, for-

mation of dioxins may take place again at lower temperatures in the flue gas or on active surfaces by "de novo synthesis". This sets the focus on all kinds of high temperature processes. The source of chlorine could be the material itself, or it could be the fuel.

For all thermal processes the presence of precursors may be anticipated to increase the probability of dioxin formation, and may reduce the need for catalytically active surfaces.

Chemical reactions at lower temperatures

Chemical reactions at lower temperatures include:

- Chemical reactions below 300°C
  - Dioxins and furans may be formed by chemical processes involving specific chemical compounds regarded as precursors for dioxin formation. Typical examples include chlorination of phenols and manufacturing of other chemical compounds from halogenated phenols.
- Exposure of organic matters to active chlorine Dioxins and furans may be formed by the use of active chlorine for bleaching and other purposes. Dioxin formation has been observed by the use of chlorine as bleaching agents in pulp and paper manufacturing and by use of chlorine for disinfecting, e.g. drinking water, but also in cork production. In addition, the chlorine production using graphite electrodes has been shown to result in high contamination of residues by dioxins and in particular furans.
- Photochemical reactions

Exposure of dioxin precursors to UV-light may lead to dioxin and furan formation. Relevant precursors in this context may include halogenated phenols and benzenes as well as polyhalogenated biphenyls and polyhalogenated diphenylethers.

Biological formation

Formation of dioxins by biological processes from precursors - at least from chlorophenols - seems to be possible. Dioxin formation from chlorophenols has been observed at composting processes.

#### 1.1.3 Release of Dioxins and Furans

In the inventory it is distinguished between releases to five media:

- Air:
- Water (aquatic environments);
- Land (soil);
- Products;
- Residues.

By the releases to the media air, water and land the dioxin and furan are released directly to the environment.

Dioxins and furans are persistent and degrade under normal conditions only very slowly. Dioxins and furans released to products or residues may therefore be considered as potential, delayed releases to the environment, unless the products or residues are treated in a way where the dioxins are destructed.

Dioxins in pentachlorophenol for wood preservation may for example be released to the soil or air from the treated wood. Dioxins in residues that are land filled may later be released to air, water (with percolate) or soil (when the landfill e.g. is converted to forest).

#### 1.2 Previous Inventories

Table 1.2 and Figure 1.1 illustrate the results of an earlier PCDD/PCDF inventory for Poland for the year 2000. This inventory was carried out according to SNAP97 nomenclature for source types. This kind of inventory data have been compiled for the period: 1988-2000. The data are reported by the Polish Ministry of Environment to UN ECE, EMEP and European Environment Agency through EIONET network. The applied emission factors are mostly based on the TNO study (Berdowski et al. 1997), and some are based on emission factors derived from other sources (e.g. EMEP/CORINAIR Atmospheric Emission Inventory Guidebook) (see also Olendrzynski et al. 2001).

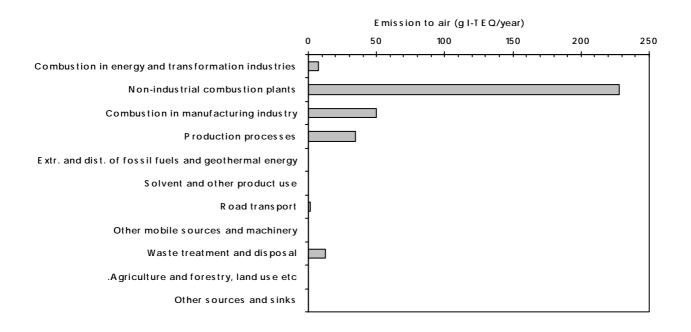
The major source category is residential burning of coal. The category includes co-combustion of coal and waste. In the present inventory based on the *Standardised toolkit* this activity is represented in two categories - the burning of coal is included in section 2.3.2, whereas uncontrolled burning of waste is included in section 2.6.3.

Table 1.2. Releases to air of dioxins and furans from all sources in Poland, 2000 by sector according to SNAP97 nomenclature. Data reported officially to UN ECE/EMEP.

Emission source	Activity	Emission factor	Emission
	Gg	mg I-TEQ/Gg	g I-TEQ
	(1000 t)	(μg I-TEQ/t)	
TOTAL			333.433
01. Combustion in energy and transformation industries			7.198
0101 Public power plants			
Hard coal	42006	0.06	2.520
Brown coal	58755	0.06	3.525
Fuel oil	175	1	0.175
0102 District heating plants			
Hard coal	871	0.06	0.052
Fuel oil	98	1	0.098
0103 Petroleum refining plants			
Hard coal	9	0.06	0.001
Fuel oil	697	1	0.697
0104 Solid fuel transformation plants			
Hard coal	120	0.06	0.007
Fuel oil	2	1	0.002
0105 Coal mining, oil/ gas extraction, pipeline compressors			
Hard coal	1490	0.06	0.089
Brown coal	354	0.06	0.021
Fuel oil	9	1	0.009
Fuel wood	0	1	0.000
02. Non-industrial combustion plants			227.671
0201 Commercial and institutional plants			
Hard coal	5723	0.06	0.343
Brown coal	35	0.06	0.002
Fuel oil	31	1	0.031
Fuel wood	10	1	0.010
0202 Residential plants			
Hard coal	8103	18	145.850
Brown coal	141	10	1.405
Fuel oil	710	1	0.710
Fuel wood	8555	5	42.774
0203 Plants in agriculture, forestry and aquaculture			
Hard coal	1501	18	27.018
Brown coal	135	10	1.351
Fuel oil	1110	1	1.110
Fuel wood	1413	5	7.066
03. Combustion in manufacturing industry	1410	J	50.137
0301 Combustion in boilers, gas turbines and stationery engines			00.107
Hard coal	3079	0.06	0.185
Brown coal	6	0.06	0.000
Fuel wood	283	1	0.283
Fuel wood	9	1	0.009

Emission source	Activity	Emission factor	Emission
	Gg	mg I-TEQ/Gg	g I-TEQ
	(1000 t)	(μg I-TEQ/t)	
0302 Process furnaces without contact			
Hard coal	6485	0.06	0.389
Brown coal	42	0.06	0.003
Fuel oil	852	1	0.852
Fuel wood	2156	1	2.156
0303 Processes with contact			
Hard coal	3230	0.06	0.194
Brown coal	7	0.06	0.000
Fuel oil	14	1	0.014
Fuel wood	2	1	0.002
030301 Sinter and pelletizing plants	8079	5	40.394
030309 Secondary copper production	68	50	3.400
030311 Cement	15046	0.15	2.257
04. Production processes			34.074
040203 Pig iron tapping	6492	2	12.984
040205 Open hearth furnace steel plants	415	2	0.829
040206 Basic oxygen furnace steel plants	6794	2	13.588
040207 Electric furnace steel plants	3290	2	6.580
040301 Aluminium production (electrolysis)	47	2	0.094
07. Road transport			1.452
Motor gasoline	371	2.2	0.817
Unleaded motor gasoline	4560	0.104	0.474
Diesel oil	3745	0.043	0.161
08. Other mobile sources and machinery			0.211
Motor gasoline	68	2.2	0.150
Diesel oil	1426	0.043	0.061
09. Waste treatment and disposal			12.690
090207 Incineration of hospital wastes (incinerators complying with hazardous waste directive)	4	1.38	0.006
090207 Incineration of hospital wastes (incinerators with less efficient abatement systems)	23	83	1.903
090207 Incineration of hospital wastes (incineration facilities without any abatement)	24	453.3	10.780

Figure 1.2 Potential emission of dioxins and furans to air from all sources in Poland, 2000. The same data as in Table 1.1.



### 1.3 Inventory Methodology

The present inventory is based on the methodology of the toolkit for identification and quantification of dioxin and furan releases developed by UNEP Chemicals in the following designated "*Standardized toolkit*" (UNEP 2001).

Categories

In the *Standardized toolkit*, the sources are categorized into 10 Main Categories. The categorization is reflected in the organization of chapter 2 of this report and appears directly from the Table of Contents.

It should be noted that this categorization is different from the SNAP categorization used by EMEP/CORINAIR for the reporting of air emissions in Europe (EMEP/CORINAIR 1999).

The inventory follows the categorization of the UNEP toolkit apart from a few instances where the UNEP subcategories are subdivided into more categories. In each instance the changed categorization is specifically mentioned.

Calculation of releases

Annual releases to the media air, water, land, products and residues for each process identified are estimated by this basic equation:

Dioxin/furan emissions per year = emission factor \* activity rate

The emission factors in unit toxicity equivalency factor per unit of feed material processed or products produced (e.g. µg I-TEQ per tonnes cement pro-

duced) may be derived from actual measurements of releases from the process or derived from experience with similar processes in other countries.

Releases to products concern chemical production processes where dioxins may be formed as by-products in significant amounts, e.g. production of chlorophenols or halogenated biphenyls.

The activity may be represented by the total feed material processed per year or total production of products per year (e.g. tonnes cement produced per year).

The releases per year are all calculated and presented in grams of toxic equivalents, I-TEQ per year.

Hot spots

Beside the identification of releases from processes, potential 'hot spots' where dioxin containing chemicals is stored or dumped are identified to the extent possible. The hot spots have been identified through contact to relevant governmental institutions. Within the limits of the project it has not been possible to make any estimates on potential releases from hot spots.

Process specific data

Process specific data have been obtained by direct inquiries to enterprises and research institutions or from Provincial Environmental Inspectorates. The assessment of the used techniques and technology has only included parameters of significance as regards dioxin formation and emission, among others feed material and flue gas cleaning technology.

Activity data

Activity data for a number of sources have been derived from national statistics obtained mainly from data of the GUS - Main Statistical Office. For other sources, e.g. combustion of hospital waste, the activities have been roughly estimated by the authors.

Uncertainty

Dioxin formation is extremely process specific. This means that the conditions of the individual source with respect to actual feed materials and process conditions, flue gas cleaning and in particular temperature patterns in the flue gas cleaning system and chimneys highly influence the amount of dioxins and furans created. Studies of dioxin releases have demonstrated that minor changes in process conditions may increase dioxin emission by several factors of magnitude.

The majority of default emission factors in the UNEP toolkit relate to air emissions measured on well-controlled, identifiable point sources, and are designed to be representative of average emissions of processes within a class. Estimates of emissions from poorly controlled, small-scale or widely dispersed processes are much less available. In addition releases to water, land or residues are based on relatively few studies. The default emission factors for many processes have consequently to be considered highly uncertain.

Sources, which can only be estimated with high uncertainty - e.g. accidental fires - are often excluded from dioxin inventories. In addition, when the inventories are referred to only average release figures are often reported. The uncertainty on total releases is in most inventories, however, quite high. The total

release to air from sources in the European Union (and Norway) in 1993/94 was thus estimated at about 3,200 g I-TEQ/year with a range between upper and lower estimate of 1,300-20,000 g I-TEQ/year (Quass 1997). In the most recent Danish inventory (1998/99) the total emission to the air was estimated at 19-170 g I-TEQ/year, giving a range of a factor 9 between the lower and the upper estimate (Hansen et al. 2000).

This inventory of dioxin and furan releases in Poland is based partly on actual measurements partly on default emission factors. The UNEP toolkit does not provide estimates of the uncertainty on the default emission factors given in the database and does not provide any recommendation regarding the estimation of uncertainties. It is in the toolkit, however, emphasised that the releases should be represented by ranges and not only average values.

The differences between process dependent emission factors used for the same process are presumed to give a rough indication of the uncertainty on each factor.

For the discussion of the principle, default emission factors for steel production are shown in Table 1.3. The emission factor to the air for a process - where dirty scrap is melted with limited control - is 1,000 times higher than the factor for a process where clean scrap is processed in a furnace designed for dioxin emission control.

Process classification Release (g I-TEQ/t liquid steel) to air to residues Dirty scrap (cutting oils, general contamination), 10 15 scrap preheating, limited controls Clean scrap/virgin iron, afterburner and fabric Clean scrap/virgin iron, EAF designed for low 0.1 1.5 PCDD/PCDF emission, BOF furnaces Blast furnaces with air pollution control system 0.01 Insignificant

Table 1.3. Default emission factors for steel industry (UNEP 2001)

Use of ranges

All estimates are in the report represented as ranges with a medium estimate and an upper and a lower estimate. As uncertainty exists, it will not be possible to give ranges within which the "true value" can be found with 100% certainty. In order to avoid making the ranges so wide that they hardly provide any information, all figures are represented with ranges within which the authors estimate the "true value" to be found with 80% certainty. In other words, for 20% of the figures the "true value" may be outside the ranges and in a few instances it may be even quite far from the range.

For sources where no measurements are available, the medium estimate is based on the default emission factor from the UNEP toolkit for the source class, which is closest to the actual process description. The medium estimate is not

considered to represent the median or mean value. The estimated ranges are often asymmetric around the medium estimate, depending on whether the actual process is considered likely to have higher or lower emissions than the process for which the default emission factors are derived.

## 2 Dioxin and Furan Release by Sector

#### 2.1 Waste Incineration

Main Category 1 'Waste incineration', can be categorised into a number of subcategories according to the types of waste burned:

- Municipal solid waste incineration
- Industrial waste incineration
- Hazardous waste incineration
- Medical waste incineration
- Light-fraction shredder waste incineration
- Sewage sludge incineration
- Waste wood and waste biomass incineration
- Combustion of animal carcasses.

Of these subcategories, incineration of municipal solid waste, industrial waste, hazardous waste, and medical waste actually takes place in Poland at present.

Burning of waste wood from wood-processing industries is included in Main Category 3, 'Power generation and heating'in chapter 2.3, whereas residential burning of waste is included in Main Category 6, 'Uncontrolled Combustion Processes' in chapter 2.6.

#### 2.1.1 Municipal Waste Incineration

Feed material

Incineration is a fairly new method of municipal waste management in Poland. In 2000, there was only one incineration plant in operation (in the second half of the year) and another one undergoing final tests.

Applied technology

The incineration plant is new and equipped with modern technology, i.e. heat recovery boiler, non-catalytic reduction of NOx, fabric filters, lime injection and active carbon adsorption. Measurements have demonstrated that the dioxin concentrations in flue gases are below 0.5 ng I-TEQ/m<sup>3</sup>.

Activity

The total amount of waste incinerated in 2000 was approximately 2,900 t (data from *Ochrona Środowiska 2001 – Environment 2001*, Main Statistical Office - GUS 2002). The reason for the small amount was that the incinerator started up during 2000. The amount is expected to grow in the near future.

**Emission factors** 

As the incineration plant is new and equipped with an efficient APC system, the lowest emission factor provided by the *toolkit* is chosen:  $0.5 \mu g$  I-TEQ/t with a range of 0.2- $0.7 \mu g$  I-TEQ/t.

Release of dioxins and furans

The total release from municipal waste incineration is estimated at <0.002 g I-TEQ.

#### 2.1.2 Industrial Waste Incineration

The *Standardized toolkit* does not have a particular category for non-hazardous industrial waste, but includes the incineration of this waste in "Municipal waste incineration". However, it has here been considered convenient to distinguish this waste from the municipal solid waste generated by households.

Feed material

Industrial waste is generated in various industries. There are no detailed data publicly available on the composition and amounts of waste in particular plants or industries, but the waste included here is not defined as hazardous waste. In some cases apart from industrial waste, the same facilities incinerate also sewage sludge and medical waste. The latter ones are accounted for in sections 2.1.4 and 2.1.6 below.

Applied technology and activity

Installations for incineration of industrial waste require permits from regional environmental boards (representing the governor of a voivodeship).

The public statistical data bring the amount of industrial waste treated thermally as 186,900 t (GUS, 2002). It is estimated that 80-90% of that volume is actually incinerated annually, i.e. app. 149,520-177,555 t of waste.

The industrial waste incineration plants (71 in total including 3 plants for sewage sludge only) can be divided into three classes (Wielgosiński 2002):

A: Installations with a bleak chance of modernization (43 installations including 18 of which no data are available, but which probably fall into this class).

B: Installations that\_require modernization in order to comply with the obligations of the 94/67/EC directive (16 installations);

C: Installations that comply with the obligations of the 94/67/EC directive on hazardous waste incineration (12 installations);

The following APC systems are used in the incineration plants:

- Afterburners of flue gases (41 installations)
- Dedusting devices (cyclones or fabric filters) (25)
- Removal of acid gases (absorption) (44)
- Adsorption on active carbon (9)
- Catalytic reactor (2)
- No data (18)

Based on expert estimates the total mass incinerated can be divided into the following fractions based on the APCS in use:

- 32.7% (53,000 t) for class A high tech. combustion, sophisticated APCS;
- 51.4% (84,000 t) for class B controlled comb. good APCS.

Class C is roughly divided into two equal parts (based on expert opinion):

- 7.95% (13,000 t) controlled comb. minimal APCS;
- 7.95% (13,000 t) low tech. combustion, no APCS.

**Emission factors** 

The *Standardized toolkit* does not have a particular category for non-hazardous industrial waste, but uses the same emission factors for non-hazardous industrial waste incineration as for municipal waste incineration. No actual measurements have been undertaken in Poland, and as the default emission factors range from 0.5  $\mu$ g I-TEQ/t for the best technology to 3,500 t  $\mu$ g I-TEQ/t for incineration without any APCS the estimate will be very dependent on where the facilities will be within this range.

The uncertainty on the classes with relatively low emission factors has no influence on the uncertainty on the total emission from the category. The uncertainty on the emission from installations with minimal or no APCS will be very dependent on feed material and the uncertainty is estimated to be relatively high.

Release of dioxins and furans

The applied emission factors and the estimated release of dioxins and furans are summarised in Table 2.3. As shown in the table, the incinerators without APCS account for the major part, but the estimate is very uncertain.

Class	Activity	Emission factor, air		Annual en	Annual release to residues	
	t/year	μg I-TEQ/t		g I-TEQ/year		g I-TEQ/year
	Medium	Medium	Range	Medium	Range	Medium
A, no APCS	13,000	0.5	0.2-0.7	46	3.6-100	0.0
A, minimal APCS	13,000	30	10-50	4.6	0.78-15	6.5
B, good non-complying	84,000	350	150-700	2.5	0.8-4.5	17
C, complying	53,000	3,500	500-5,000	0.03	0.01-0.04	0.8
Total	163,000	_	-	53	5.2-120	24

Table 2.1 Releases from incineration of industrial waste 2000

#### 2.1.3 Hazardous Waste Incineration

Feed material and activity

In 2000, there were 44 installations for thermal neutralization of hazardous waste (excluding medical waste).

Experts from Institute of Waste Management estimated that about 60,000 t of hazardous waste were incinerated in Poland in 2000 (MoE 2001). This amount includes the waste incinerated in all major incineration plants in which hazardous industrial waste is neutralized. About 35% of waste oils (total of 243,000 t - after GUS 2001a) was incinerated and was accounted for in the section on industrial waste. The hazardous waste which was not incinerated was (GUS 2002): Reused (app. 476,883 t), landfilled (96,199 t), temporarily stored (13,791 t), and the rest solidified or neutralized by physical, chemical or biological methods.

The rough estimation of percentage share of hazardous waste incineration under given conditions is based on the data from implementation plan of 94/67/EC directive (MoE 2001):

<sup>\*\*</sup> Emission factors for release with wastewater were not available.

A: 8% (11 small installations) of installations for hazardous waste incineration were not fit for hazardous waste incineration: APCS: After-burning of flue gases, dedusting systems: cyclones, electrostatic precipitators, fabric filters. Five installations had no APC systems.

B: 68% could meet requirements of the directive after some modernization processes. APCS: Acid gases adsorption (dry or wet method), active carbon adsorption (active carbon injection or carbon bed filter – in a few installations).

C 24% of installations for hazardous waste incineration (percentage in terms of total capacity of hazardous waste incineration plants) could meet requirements of the directive without any modernization. APCS: active carbon adsorption (active carbon injection or carbon bed filter), catalytic method (catalytic converters/SCR systems);

**Emission factors** 

No actual measurements of emission from hazardous waste incinerators in Poland has been obtained except medical waste incineration described in the section below.

The default emission factors of the *Standardized toolkit* range from  $0.5~\mu g$  I-TEQ/t for the best technology to  $35,000~t~\mu g$  I-TEQ/t for incineration without any APCS. The estimate will be very dependent on where the facilities are placed within this range.

The uncertainty on the classes with relatively low emission factors is relatively small and has no influence on the uncertainty on the total emission from the category. The uncertainty on the emission from installations with minimal or no APCS will be very dependent on feed material and the uncertainty is estimated to be relatively high. The high emission factor for incinerators without any APCS of 35,000  $\mu g$  I-TEQ/t is estimated to represent a maximum, and it is estimated that the emission from incinerators in this category may well be of the same magnitude as the default value for incinerators with minimal APCS.

Emission factors for releases to residues for the four classes are 9,000 (no APCS), 900 (A), 450 (B) and 35 (C)  $\mu$ g I-TEQ/t, respectively.

Release of dioxins and furans

The applied emission factors for emission to air and the estimated release of dioxins and furans are summarised in Table 2.3. As for industrial waste incineration, the incinerators without APCS account for the major part, but the estimate is also here very uncertain.

Class	Activity	Emission factor, air Annual emission to		mission to air	Annual release to residues	
	t/year	μg I-	μg I-TEQ/t		EQ/year	g I-TEQ/year
	Medium	Medium	Range	Medium	Range	Medium
A, no APCS	1,750	35,000	350-35,000	76	0.46-77	19
A, minimal APCS	2,600	350	150-700	0.92	0.38-1.9	2.4
B, good non-complying	40,800	10	5-50	0.41	0.2-2	18
C, complying	14,400	0.75	0.3-1	0.01	0.004-0.01	0.43
Total	60,000			77	1-81	41

Table 2.2 Releases from incineration of hazardous waste 2000

#### 2.1.4 Medical Waste Incineration

Activity and feed material

Based on Grochowalski (2002) and GUS (GUS 2001b), it is estimated that approximately 51,000 t of hospital waste was incinerated in Poland in 2000. The total amount of waste was calculated as: Total = 190,952 [hospital beds] \* 278 [days - annual occupancy of a hospital bed] \* 1.6 [kg waste/bed\*day] = 84,935 t. About 60% of that waste is incinerated.

The waste consists partly of infectious material, partly of ordinary municipal waste generated in the health care sector.

Applied technology

In total about 430 incinerators and boilers are used for incineration of hospital waste. For the calculation of the annual emission of dioxins and furans, the incinerators and boilers are categorised into three classes, and the total amount of waste is based on expert estimates broken up as follows:

- 23,800 t is incinerated in class A, old incinerators (app. 350) where the APCS is inadequate or missing altogether. The old hospital waste incinerator are mostly oil or gas-heated chamber furnaces equipped only with a cyclone as waste gas cleaning device. Some of the old incinerators are equipped with low efficient spray absorbers using aqueous alkali solutions.
- 22,900 t is incinerated in app. 60 modern incinerators not meeting the EU requirements (**B**, non-complying modern and improved old incinerators). The modern incinerators are typically equipped with a pyrolytic chamber operated at 500 to 800°C, a thermo reactor operated at 1,100 to 1,200°C and a high efficiency heat exchanger which cools down the gases to 300°C. In addition they are equipped either with dry, wet or wet/dry stack gas cleaning devices.
- 4,200 t is incinerated in app. 20 modern incinerators meeting the EU requirements (**C**, **complying modern incinerators**). The incinerators meeting the EU requirements are typically equipped with state-of-the-art stack gas cleaning devices.

<sup>\*\*</sup> Emission factors for release with wastewater were not available.

**Emission factors** 

Polish emission factors have been calculated based on extensive measurements carried out by the Institute of Chemistry and Inorganic Technology of Cracow Technical University. Analytical results from the determination of dioxins and furans in stack gases sampled from 60 hazardous waste incinerators in Poland is shown in Annex 2. Some of the data have previously been reported by Grochowlski (1998) and Quass (2000). Most results were obtained in form of individual measurements in modern incinerators. These measurements were undertaken during start-up of new incinerators or after installation of new equipment in existing incinerators. None of the incinerators have been regularly monitored.

The determination was performed between 1996 and 2001. As it is shown in Annex 2, dioxin concentration in the stack gases was below the 0.1 ng-TEQ/m<sup>3</sup> necessary for meeting the EU requirements for only a few of the modern incinerators.

Based on a part of the dataset it has previously been demonstrated that incinerators equipped with wet dry stack gas cleaning devices in general have higher emission of dioxins and furans than incinerators equipped with dry or dry/wet cleaning devices (Quass 2000).

Emission factors based on the actual measurements of emission from Polish incinerators are significantly lower than the default emission factors of the UNEP toolkit. In Table 2.3 below emission factors calculated on the basis of actual measurements are shown along with the UNEP toolkit emission factors. The resulting emission factors differ by a factor of more than six.

The lower Polish emission factors for incinerators with low efficiency APC or no APC, may be explained by the fact that a large part of the medical waste incinerated is ordinary municipal waste generated in the health care sector. Another explanation of the difference is that the borderline between the different classes may be slightly different. When the differences in emission factors between the different classes are a factor of hundred or more, the medium estimates will be very sensitive to small changes in classification.

Class	Polish air EF µg ∣-TEQ/t *	Corresponding classes of the UNEP toolkit	UNEP toolkit EF (µg  -TEQ/t)	
			Air	Residues
A - Old incinerators	453 (352-555)	Uncontrolled, batch comb., no or minimal APC	30,000	200
		Controlled, batch comb., no or minimal APC	3,000	20
B – Non-complying modern and old improved incinerators	68 (22-114)	Controlled, batch comb., good APC	525	920
C - Complying modern incinerators	1.4 (1.2-1.7)	High technology, sophisticated APC	1	150

Table 2.3 Estimated air emission factors for Polish hospital incinerators and UNEP toolkit emission factors for corresponding classes

Measurements of dioxins and furans in bottom ash from incineration of medical waste in Poland have been reported by Grochowalski (1996). The reported data are represented as  $\mu g$  I-TEQ/kg of ash, and it is not possible on the basis of the data to calculate emission factors in terms of tonnes feed material. In addition, for modern incinerators the bottom ash accounts only for a minor part of the total amount of dioxins and furans ending up in residues. The main part ends up in the fly ash. For these reasons no attempts were made to calculate country-specific emission factors for releases to residues, and the emission factors of the UNEP toolkit were applied.

From modern incinerators equipped with wet stack gas cleaning devices a minor part of the formed dioxins and furans may be discharged with wastewater. No data are available, and the UNEP toolkit does not provide emission factors for this release route.

Release of dioxins and furans

The release of dioxins and furans from incineration of medical waste is summarised in Table 2.4. As shown in the table, the old incinerators accounted for about 80% of the total emission.

<sup>\*</sup> The range represents a 90% confidence level based on all measurements within the class. Each incinerator is represented by one measurement only, and it is assumed that all measurements within each class can be considered independent samples taken from the same normal distribution.

Class	Activity	Emission factor, air Annual emission to air		Annual release to residues		
	t/year	μg I-TEQ/t		g I-TEQ/year		g I-TEQ/year
		Medium	Range ***	Medium	Range	Medium
A - Old incinerators	23,800	453	352-555	10.8	8.4 – 13.2	0.48*
B - Non-complying modern and old im- proved incinerators	22,900	68	22-114	1.6	0.50 - 2.6	21
C - Complying modern incinerators	4,200	1.4	1.2-1.7	0.006	0.005 - 0.007	0.63
Total	50,900			12	8.9 – 16	22

Table 2.4 Releases from incineration of hospital waste 2000

#### 2.1.5 Light Fraction Shredder Waste Incineration

The amount of incinerated light fraction shredder waste is considered to be negligible and accounted for in industrial waste incineration.

#### 2.1.6 Sewage Sludge Incineration

According to GUS (GUS 2002), the following amounts of waste are neutralized thermally: 5,904 t of sewage sludge from municipal sewage treatment plants and 28,196 t of sewage sludge from industrial sewage treatment plants. The latter are accounted for in industrial waste incineration. As concerns the former, it can be assumed that the entire thermal treatment is practically incineration. All installations used for sewage sludge incineration are equipped with wet scrubbers, therefore it is justified to apply the EF for the class 'Updated, continuously fed, some APCS' of 4  $\mu g$  I-TEQ/t to the entire amount of sewage sludge incinerated. The range is roughly estimated at 1-10  $\mu g$  I-TEQ/t. The estimated emission is <0.06 g I-TEQ/year.

#### 2.1.7 Waste Wood and Waste Biomass Incineration

Emissions from this category have been accounted for in category 3. *Power Generation and Heating* in subcategories: Biomass Power Plants and Household heating and cooking - Biomass, and in category 7. *Production of Chemicals, Consumer Goods* under: Bark boilers only.

#### 2.1.8 Animal Carcasses Burning

Before burning dead animals it is necessary to process the bodies to get a bone meal. This is done in special plants. Only the resulting meal can be burned. It appears from information obtained from four plants possessing permits for burning the meal, that in 2000 only negligible amounts of meal were incinerated in one cement plant.

<sup>\*</sup> refers only to bottom ash left in the combustion chamber \*\* Emission factors for release with wastewater were not available. \*\*\*90% confidence level for the mean

#### 2.2 Ferrous and Non-ferrous Metal Production

In Poland this category can be divided into two basic sectors: Metallurgy of iron and steel that includes part of the coking industry, and metallurgy of nonferrous metals that covers metallurgy of copper, aluminium, zinc and lead. Apart from production of prime target metals, both sectors include some foundries, i.e. iron cast, steel cast and iron alloys foundries, aluminium foundries, copper alloys (brass and bronze) foundries and other non-ferrous metal foundries.

No measurements of dioxin and furan emission from metallurgical processes have been obtained in Poland. Within the time frame of this project it has not been possible to make a full assessment of all technological parameters of relevance to a detailed discussion of the uncertainty on the estimated emission from this sector. The uncertainty on the emission factors has been roughly estimated considering the ranges of the default emission factors applied to the different processes without a detailed discussion.

Options for reduction of releases of dioxins from this sector and other sectors were investigated recently by a group of experts headed by Kołsut (Kołsut 2001)

#### 2.2.1 Iron Ore Sintering

Feed material

The basic input in sintering processes are imported iron ores, coke, as a fuel, limestone as a flux, recycled filter dusts from sinter belts, and iron containing inputs from processing of blast furnace slag and rolling processes. Waste products produced outside ironworks are not applied.

Applied technology

In Polish ironworks, ore sintering is done with sintering belts. In Huta Katowice, there are three belts with 312 m² each. One of the belts is a reserve. The flue gases formed during sintering are dedusted in electro-filters (two per belt). Dust-laden air formed during loading the belts is treated with foam scrubbers due to the high concentration of water. In Huta Sendzimira, there are three belts each of an area of 75 m² in operation. Here, the flue gases formed during sintering are also dedusted in electro-filters. Dust-laden air formed during auxiliary operations (ore sorting, batching and loading) is treated with cyclones, multicyclones, fabric filters, wet scrubbers and electro-filters.

Activity

In 2000, the total production of sinter in Katowice Ironworks and Sendzimir Ironworks was 8,078,700 t

**Emission factors** 

The *Standardized toolkit* applies an emission factor of 5  $\mu$ g I-TEQ/t for well controlled plants with low waste use. Here this EF is applied as the best estimate with a range of 1-10  $\mu$ g I-TEQ/t. For processes with high technology emission reduction the toolkit applies a default factor of 0.3 I-TEQ/t. The default EF for releases to residues is 0.003  $\mu$ g I-TEQ/t.

Release of dioxins and furans

The total emission to air is estimated at 40 (8-81) g I-TEQ/year, indicating that sintering is one of the major sources in Poland. Actual measurements are

needed for more certain estimates. The release to residues is estimated at  $0.02~\mathrm{g}$  I-TEQ/year.

#### 2.2.2 Coke Production

## Feed material and activity

Coke production in Poland is based on coking coal extracted in the Upper and Lower Silesia (Wałbrzych) regions. The coke sector includes independent coking plants and plants integrated with ironworks.

Independent coking plants are:

- Coke-chemical Complex "Zabrze" Inc. that includes four cokeries: Jadwiga, Makoszowy (under liquidation), Radlin and Dębieńsko;
- Coking plant "Przyjaźń";
- Coking plant "Wałbrzych" Inc. Cokery Victoria;
- Coking plant "Zdzieszowice" Ltd.

Coking plants integrated with ironworks are:

- Coking plant of T. Sendzimira Ironworks Inc. S.A.;
- Coking plant of Częstochowa Ironworks Inc. S.A.;
- Coking plant of Metallurgy plant Ltd. in Bytom.

There are currently 10 coking plants in operation in Poland with 29 coke oven batteries in 7 economic units.

In recent years, the coking industry undertook a major restructuring combined with closing down plants and significant reduction of coke production (see Table 2.5 below).

Table 2.5 Coke production in 1990-2000 (thousands of tons = Gg)

Years	1990	1995	1996	1997	1999	2000
Coke production in total	13,713	11,579	10,340	10,536	9,847	9,069

Coking plants, apart from coke, also produce coking gas, tar and crude benzol. As there is no relation between formation of dioxins and furans and production of coking gas and liquid products of coking, the respective data for the latter are not given here.

#### Applied technology

Similarly, as in other countries, coke production takes place by classically high temperature pyrolysis of hard coal. Polish coking plants are generally equipped with good APC systems. Approximately 1/3 of the coke batteries are equipped with fabric filers (99% effectiveness for particulate matter, PM). During production coke is cooled by means of the dry method with fabric filters, water curtains, and the flue gases are treated with cellular fillers and treated chemically (Polish and German patents).

#### **Emission factors**

The *Standardized toolkit* applies emission factors to air of 3 and 0.3 I-TEQ/t of coke for production without or with APCS. Polish coking plants are equipped with good APCS, the factor 0.3  $\mu$ g I-TEQ/t of coke is applied with an uncertainty range of  $\pm$  50%.

The entire sewage formed during coke production is cleaned, therefore, with respect to emission to water, the factor  $0.006~(0.001\text{-}0.01)~\mu g$  I-TEQ/t of coke is applied.

## Release of dioxins and furans

The total emission to air is estimated at 2.7 (1.4-7.3) g I-TEQ/year. Actual measurements are needed for more certain estimates. The release to water is estimated at <0.05 g I-TEQ/year.

#### 2.2.3 Iron and Steel Production

#### Pig iron production in blast furnaces

## Feed material and activity

Most of the production of pig iron in blast furnaces takes place in two steel works: Huta Sendzimira in Cracow and in Huta Katowice. Small amounts of various kinds of foundry pig iron are also produced in Huta Szczecin which has two blast furnaces of 483 m³ each. The basic feed materials for pig iron production are: Sinter or pellets, lime, blast furnace coke and sometimes pulverized coal. Coking gas is used as an energy source in addition to blast furnace gas and coke.

In 2000 production of pig iron and ferroalloys in blast furnaces in all three steelworks amounted to 6,491,000 t.

#### Applied technology

The technology used in blast furnaces (BF) does not differ from the methods generally used in iron and steel industry. The main output of a BF is pig iron, and the main waste is slag which is usually further used in cement plants, building of roads, construction and other sectors of economy. The blast furnaces are equipped with good APC systems and heat exchangers.

#### **Emission factors**

Standardized Toolkit" in relation to blast furnaces gives the emission factor of value  $0.01(0.005\text{-}0.02)~\mu g$  I-TEQ/t of fluid pig iron, when good APC systems are installed, which is the case as regards the three steelworks in Poland.

## Release of dioxins and furans

The total release from this activity is 0.065 (0.03-0.13) g I-TEQ. Blast furnaces are not significant sources of dioxin and furan emissions in Poland.

#### Steel production

## Feed material and activity

In Poland similarly to other countries two methods of steel production are used: In basic oxygen furnaces (BOF) and in electric arc furnaces. Basic oxygen furnaces are in operation in Huta Sendzimira and in Huta Katowice, i.e. in the same steelworks where blast furnaces for pig iron production are located, and also in Huta Częstochowa. The process of steel production in electric arc furnaces is carried out in eleven steelworks: Małapanew, Ostrowiec, Stalowa Wola, Lucchini-Warszawa, Łaziska, Częstochowa, Batory, Duo-Stal, Baildon, Jedność, Buczek and Zawiercie.

Pig iron, scrap steel, ferroalloys and oxygen are the main feed materials for BOFs.

For the electric arc furnaces the basic feed materials are: Scrap steel, ferroalloys and sometimes small amounts of other metals depending on the type of steel to be produced.

In 2000 6,793,809 t of steel were produced in basic oxygen furnaces. As the production of steel in Huta Katowice is approximately twice as large as in Huta Sendzimira, the total amount of steel has been divided into two parts: Equal 2/3 and 1/3 of the total. For the electric arc furnaces the respective figure is 3,289,965 t.

## Applied technology

The APC systems of the BOF in Huta Sendzimira include inter alia two stage Venturi scrubber and foam sieve (Polish patent) and can therefore be classified as good. In Huta Katowice the situation is worse, as the flue gases are first cleaned and then burned as flares.

The APC systems in case of blast furnaces include: In Huta Sendzimira - ESP with efficiency 98% or no APCs; in Huta Katowice - the entire process is airtight, fabric filters.

The APC systems in case of electric furnaces usually include fabric filters, cyclones and multi-cyclones and can be classified as good.

#### **Emission factors**

Basic oxygen furnaces for steel making in Europe in general have low dioxin and furan emissions, and the *Standardized toolkit* applies a default emission factor to air for these furnaces of 0.1 µg I-TEQ/t steel.

For electric arc furnaces a wide range of emission factors has been determined in other European countries ranging from 0.07 to 9  $\mu$ g I-TEQ/t. The *toolkit* applies a default emission factor of 3  $\mu$ g I-TEQ/t for electric arc furnaces using clean scrap/virgin iron as feed material and equipped with afterburner and fabric filter. The Polish plants are here categorised into this class, but the emission factor is very uncertain, and a range of 0.5-10  $\mu$ g I-TEQ/t will be applied. Actual measurements are needed for reducing the uncertainty on the emission factors.

Default emission factors for release to residues for BOF and electric arc furnaces are 1.5 and 15  $\mu g$  I-TEQ/t respectively.

## Release of dioxins and furans

The total emission from steel production is estimated at 11 (4-34) g I-TEQ/year Of these electric arc furnaces account for the major part: 10 (3-33) g I-TEQ/year. Total release to residues is estimated at 60 g I-TEQ/year.

## 2.2.4 Iron and Steel Foundries

In 2000 there were 542 foundries in Poland including: 210 iron-cast foundries, 42 steel-cast foundries, 290 non-ferrous metal foundries, and 45 foundries that produced both iron-cast and non-ferrous metal cast. The total amount of cast in

2000 was 753,000 tons. Annex 5 provides a list of the largest iron and steel foundries.

### Iron casting

Feed material and activity

For iron-cast production, own scrap coming from the respective foundry is used. Also scrap from other sources is applied which can contain plastics and various oils. The scrap is neither heated nor cleaned before being fed into a furnace. The scrap can make up 50% of the input to the furnace.

Applied technology

In Poland iron-cast is produced in the following types of furnaces:

- Cold air cupola (with possibility of enrichment of incoming air with oxygen);
- Hot air cupola (with possibility of enrichment of incoming air with oxygen);
- Electric arc furnace;
- Induction furnace;
- Rotary drum.

Activity

Table 2.3 provides statistics on iron-cast production depending on the type of furnace.

Table 2.6 Amount of iron-cast production depending on the type of furnace (Holt-zer 2002)

Furnace type	Cupola	Induction furnace	Electric arc furnace	Rotary drum	Total
Amount of fluid iron-cast in metric tonnes	640,000	200,000	107,700	7,700	955,400
Amount of iron-cast in metric tonnes	415,800	130,000	70,000	5,000	620,800

**Emission factors** 

The *Standardized toolkit* provides emission factors for four classes of foundries for iron and steel casting.

Compared to the *toolkit* several new subcategories have been added to the section on foundries (e.g. hot air cupola or induction furnace with minimal APCS/fabric filter) to reflect specific Polish conditions. For all the new subcategories the corresponding EFs have been selected based on the actual technology and APCS installed and by means of analogy to the EFs from the toolkit (Prof. Mariusz Holtzer, personal communication). The selection of EFs is not based on actual measurements, but merely on an expert opinion.

In most cases cupola furnaces are equipped with installations for wet or dry scrubbing. Only in a few cases fabric filters are used. For the purpose of this inventory the following data were applied. For all emission factors an uncertainty range of  $\pm$  50% has been applied.

- Cold air cupolas produce app. 320,000 t of iron cast including:
  - 96,000 t (30%) with no gas cleaning; EF: 10 μg I-TEQ/t

- 224,000 t (70%) with wet or dry scrubbing; EF: 6 μg I-TEQ/t
- Hot air cupolas produce app. 320,000 t of iron cast including:
  - 64,000 t (20%) with no APCS; EF 4 μg I-TEQ/t
  - 144,000 t (45%) with wet or dry scrubbing; EF 0.6 μg I-TEQ/t
  - 112,000 t (35%) with fabric filters; EF: 0.03 μg I-TEQ/t
- Electric arc furnaces produce app. 107,700 t of iron cast including:
  - 21,600 t with no APCS; EF: 10 μg I-TEQ/t;
  - 86,100 t with fabric filters; EF: 5 μg I-TEQ/t;
- Induction furnaces do not have gas cleaning installations; emission factor in that case is 1 µg I-TEQ/t;
- Rotary drum furnaces are equipped with fabric filters. Emission factor in that case is 4.3 μg I-TEQ/t.

Release of dioxins and furans

The total emission from iron casting is estimated at 3.5 (1.7-5.2) g I-TEQ/year. Cold air cupola with no or minimal APCS accounts for the main part of the total emission.

### Steel casting

Feed material

For steel-cast production, own scrap coming from the respective foundry is used. Also scrap from other sources e.g. automobile industry is applied. This scrap might contain plastics and various oils, and is neither heated nor cleaned before being fed into a furnace. The scrap can make up 50% of the input to the furnace.

Applied technology

In Poland steel-cast is produced in the following types of furnaces:

- Electric arc furnace;
- Induction furnace:
- Basic oxygen furnace (one plant).

Practically all electric arc furnaces are equipped with fabric filters. The effectiveness of these filters with respect to dust is 98-99%. However, the effectiveness of flue gas treatment is only app. 90%. The remaining 10% contributes to diffuse emissions. Induction furnaces have no APCS, but the scrap is preselected and cleaned and does not contain plastic parts.

Activity

Table 2.7 provides statistics on steel-cast production depending on the type of furnace.

Table 2.7 Amount of steel-cast production depending on the type of furnace

Furnace type	Induction furnace	Electric arc furnace	BOF	Total
Amount of fluid iron-cast in metric tonnes	100,000	11,000	2,000	113,000

#### **Emission factors**

Practically all electric arc furnaces are equipped with fabric filters of efficiency between 98-99%. However, the efficiency of capturing the flue gases is merely 90%. The remaining 10% contributes to fugitive emissions. Induction furnaces have no APCS but the scrap is pre-selected and cleaned and does not contain plastic parts. The following emission factors have been applied with an uncertainty range of  $\pm$  50%:

Electric arc furnaces: 5 µg I-TEQ/t
Induction furnaces: 1 µg I-TEQ/t
Basic oxygen furnace: 0.01 µg I-TEQ/t

Release of dioxins and furans

The total emission from steel casting is estimated at 0.44 (0.22-0.66) g I-TEQ/year. Electric arc furnaces account for nearly 100% of the total emission.

## 2.2.5 Aluminium Production and Casting

Aluminium production and casting includes primary aluminium production, secondary aluminium production and aluminium casting

Feed material and activity

Production of primary aluminium (made of aluminium oxide) takes place in Huta "Konin". The activity is app. 46,000 t/year. The *Standardized toolkit* does not provide EF for primary aluminium production, as the formation of dioxins and furans is thought to be low, although low levels of formation have been associated with the use of carbon anodes. The process has not been further assessed.

- secondary produc-

Secondary aluminium is produced inter alia in: Alumetal - Kęty group, Nicromet at Bestwina, Metal Plant "Skawina", PPM "Domet" at Konin. The feed material for the secondary production is aluminium scrap, aluminium waste from steelworks and other metals needed for production of specified alloys. For secondary aluminium production both new and old scrap are used. Most new scrap reaching the secondary industry comes directly from the manufacturing industry, whereas old scrap is discarded products which can contain plastics, paint remains and various oils. For aluminium alloy refinement various gaseous preparations are used, like e.g. hexachloroethane (C<sub>2</sub>Cl<sub>6</sub>), or chlorine in nitrogen or preparation that releases chlorine during melting.

The products of the secondary production are mainly ingots used for aluminium casting. In some cases the aluminium casting may take place at the same facility as the secondary aluminium production.

Production of secondary aluminium is more difficult to assess than production of primary aluminium. It is assumed - after GUS (GUS 2001b) - that the production is equal to 'own use' that is 123,169 t in 2000. Moreover, 50,000 t was accounted for as aluminium casting (assuming 50% losses, i.e. 75,000 t of liquid aluminium).

- casting

The feed material for aluminium casting is mainly ingots of primary or secondary aluminium, but some new scrap of well-defined alloys from the manufacturing industry may be used as well. The total production of cast aluminium in 2000 was 75,000 t.

## Applied technology

Secondary aluminium producers use the following stages of production:

- Aluminium scrap collection in compliance with existing regulations;
- Segregation, washing and other methods of scrap preparation;
- Composition of feed depending on the required quality of the product;
- Melting and refinement of alloys when needed;
- Aluminium or alloy casting into shapes depending on the requirements of the buyer;
- Solid waste management.

In general the secondary aluminium plants are not equipped with afterburners, fabric filters or lime and active carbon injection.

Oil and gas fuelled furnaces and induction furnaces are used for aluminium casting. APCS are not applied for any types of furnaces used for aluminium casting.

#### **Emission factors**

Primary aluminium production is considered insignificant with respect to releases of dioxins and furans.

The emission of dioxins and furans from secondary aluminium production is highly dependent on the used feed material and the applied APCS with default emission factors ranging from 150  $\mu g$  I-TEQ/t for processes with minimal treatment of inputs and simple dust removal to 0.5 for processes with APCS optimised for control of dioxin and furan releases. As there are no good APCS in Polish secondary aluminium production, it is proposed to apply the high EF of 150  $\mu g$  I-TEQ/t of aluminium with an uncertainty range of 50-450  $\mu g$  I-TEQ/t. Actual measurements are necessary for reducing the uncertainty of the emission factor.

The emission factor for release to residues is  $400 \,\mu g$  I-TEQ/t produced aluminium.

The *Standardized toolkit* does not provide any default emission factors for aluminium casting. As pure ingots are used for the production, the emission factors are estimated to be considerably lower than the EF for secondary aluminium production. The toolkit applies an EF of 1  $\mu$ g I-TEQ/t for brass casting in simple melting furnaces without APCS and 0.3 for casting of zinc alloys. The European Dioxin Inventory (Quass 1997) applies emission factors for nonferrous metals (tin, cobalt, chromium, nickel, silver, zinc and aluminium) in the range of 0.15-2.4  $\mu$ g I-TEQ/ton of material. This range will be used here as a first estimate.

## Release of dioxins and furans

The total release of dioxins and furans to air from aluminium production is estimated at 11 (3.7-33) g I-TEQ/year. Of this aluminium casting accounted for app. 1% only.

The release to residues from secondary aluminium production is estimated at 29 g I-TEQ/year.

#### 2.2.6 **Copper Production and Casting**

This section includes primary production, secondary production and casting of copper and copper alloys.

## Feed material and activity

The main producer of primary copper in Poland is the conglomerate: KGHM "Polska Miedź" S.A., which includes two copper mills (HM): Huta "Legnica" and Huta "Głogów". In Głogów, there are two different installations in operation. In HM "Głogów I" and HM "Legnica" there are shaft furnaces, whereas in HM "Głogów II" copper is produced in an anode oven.

The basic feed material for primary copper production are concentrates obtained from copper ores extracted in own copper mines, and as additional feed material is copper scrap added to furnaces. In the furnaces, copper refinement is conducted.

According to GUS (GUS 2001a), in 2000 the total primary copper production was 486,000 t.

- secondary production In secondary copper and copper alloy production, feed materials include: Copper and brass scrap and primary metals (zinc, aluminium) used to obtain special product characteristics. According to GUS (GUS 2001b), in 2000 the total secondary copper production was 45,376 t.

#### - copper alloy casting

In copper alloy casting ingots of primary or secondary copper alloys are commonly used as feed material. The total copper alloy-cast production in 2000 was 24,300 t of liquid metal.

#### Applied technology

Primary copper production includes the following stages:

- Ore extraction;
- Ore refinement in floatation processes;
- Drying and briquetting of concentrate;
- Metallurgy processing in shaft furnaces to obtain socalled copper stone that contains about 60% of pure copper;
- Converting of copper stone (elimination of iron sulphide);
- Copper refinement in anode ovens;
- Electro-refinement of anode copper;
- Utilization of flue gases in sulphuric acid plant.

The primary copper plants in Poland use a rather complex system of flue gas desulphurisation and management. It is associated with the necessity of elimination of large quantities of sulphur dioxide which is formed during processing of sulphuric ores. This has important consequences for emission reduction of emission of dioxins and furans.

- secondary production In the secondary copper production, a great variety of technologies is applied. However, the initial stage is the same for all technologies. It is sorting and cleaning of scrap. Scrap quality is regulated by law in Poland and therefore relatively clean. Most large copper mills are well equipped with APCS, i.e. with electro-filters, quenching and fabric filters.

- copper alloy casting

In Poland copper alloy-cast is done in the following types of furnaces: Induction furnace (mostly), oil-fuelled furnace and gas-fuelled furnace. For any type of furnace used for copper alloy casting there are no APCS.

**Emission factors** 

For all types of primary copper production the factor for emission to air is 0.01  $(0.005-0.02) \mu g I-TEQ/t of copper produced.$ 

The emission of dioxins and furans from secondary copper and copper alloy production is highly dependent on the used feed material and the applied APCS with default emission factors ranging from 800 µg I-TEQ/t for processes with minimal treatment of inputs and simple dust removal to 5 for processes with APCS optimised for control of dioxin and furan releases. As most large copper mills are well equipped with APCS, and because scrap quality is regulated by law in Poland it is proposed to use EF of the class "Well controlled" of 50 µg I-TEQ/t of secondary copper with an uncertainty range of 10-100 µg I-TEQ/t. Actual measurements are necessary for reduction of the uncertainty of the emission factor. The default emission factor for releases to residues from secondary copper production is 630 µg I-TEQ/t of secondary copper produced.

Compared to secondary copper production, the default emission factor for copper alloy casting is rather low: 0.03 (0.01-0.1) µg I-TEQ/t.

The Standardized toolkit is concerning copper alloys somewhat inconsistent, as brass (copper and zinc alloy) is addressed separately; but as no data exist for this production, emission factors for copper and zinc production should be applied. In this report brass is therefore addressed together with copper and other copper alloys.

Release of dioxins and furans

The total release of dioxins and furans to air from copper production and casting is estimated at 2.3 (0.5-4.5) g I-TEQ/year. Secondary production accounted for nearly 100% of the total emission.

The release to residues from secondary copper and copper alloy production is estimated at 29 g I-TEQ/year.

#### 2.2.7 **Lead Production**

Feed material and activity

Emission of dioxins and furans from primary lead production is considered to be insignificant, and the process is not assessed further.

- secondary production Used batteries from automobiles and stationary equipment are the basic feed material for secondary lead production. Scrap lead may come from other sources as well. Dioxin emissions occur in the process of lead recovering from used batteries, as they contain PVC separators, which during smelting provide

organic chlorine - thus leading to dioxin formation. The process of utilization of used batteries is implemented at Mining and Metallurgy plant "Orzeł Biały".

Applied technology

Prior to melting, the lead scrap is shredded, filling (sulphuric acid) is recovered and the remaining shredded elements are sorted into heavy metallic and light plastic (PCV, PP). The plastic parts are then granulated and reused through non-thermal processes, whereas the metallic fraction is melted in rotary furnaces. Coke is used as a fuel. Total production of secondary lead was in 2000 36,682 t (GUS 2001b). Relatively small amounts of scrap lead were reused in 2000, as some old batteries were not collected. The recycling of used batteries is expected to increase after introduction of specific incentives. The export of scrap lead in 2000 was rather small - merely 349 t (GUS 2001b).

APCs in lead production include baghouse filters, and the captured dust is returned to the process.

Emission factors

The emission factor is highly dependent on whether the PVC separators are melted in the furnace together with the metallic part. This is not the fact in Poland, and a default emission factor of 8  $\mu g$  I-TEQ/t is applied with an uncertainty range of 2-25  $\mu g$  I-TEQ/t. Actual measurements are necessary for reducing the uncertainty on the emission factor.

The emission factor for release to residues has not been determined.

Release of dioxins and furans

The total release of dioxins and furans to air from secondary lead production is estimated at 0.29 (0.07-0.92) g I-TEQ/year.

#### 2.2.8 Zinc Production and Casting

Feed material and activity

There are two main primary zinc producers in Poland. These are: Copper mill Huta "Miasteczko Śląskie" (ISP process and shaft furnace) and Mining and Metallurgy Plant ZGH "Bolesław" (electrolytic process - RLE technology). They use different production methodologies and cooperate closely with enterprises that extract zinc and lead-zinc ores. The total production in 2000 was 161,773 t (GUS 2001a). Primary zinc production is not considered a significant source of dioxin and furan emission and has not been assessed further.

- secondary production The secondary production of zinc in 2000 is estimated at 15,155 t (GUS 2001b).

- zinc alloy casting In zinc alloy, scrap is commonly used up to 50% of the input to a furnace.

Applied technology In Poland zinc alloy-cast is produced in the following types of furnaces: Induction furnace (mostly) and resistance furnace.

Activity The total zinc alloy-cast production in 2000 was 9,600t of liquid metal.

Emission factors

The emission of dioxins and furans from secondary zinc and zinc alloy production is highly dependent on the used feed material and the applied APCS with default emission factors ranging from 1,000 µg I-TEQ/t for kilns with no dust

control to 5 for processes with APCS optimized for control of dioxin and furan releases. The actual processes in Poland include APC systems, such as fabric filters, afterburners and baghouse filters. Therefore the medium EF has been selected ( $100 \mu g I-TEQ/t$ ).

For zinc smelting and casting the default emission factor is 0.3 (0.1-1)  $\mu g$  I-TEQ/t for all processes.

Release of dioxins and furans

The total release of dioxins and furans to air from secondary zinc production and zinc casting is estimated at 1.5 (0.46-4.6) g I-TEQ/year.

#### 2.2.9 Thermal Wire Reclamation

In Poland, wires are not burned in order to recover copper or lead. The insulating material is removed mechanically and the remaining wire is further processed as scrap. The recovered insulating material is commonly reused after granulation and non-thermal processing.

## 2.3 Power Generation and Heating

Main Category 3, 'Power generation and heating' can be categorised into a number of subcategories:

- Fossil fuel power plants and boiler houses;
- Biomass power plants and boiler houses;
- Landfill, biogas combustion;
- Household heating and cooking (biomass);
- Domestic heating (fossil fuels).

Activities within all these subcategories take place in Poland at present. The main source of data for this source category is publication of GUS on energy statistics (GUS 2001a). The fuel use data in that publication are given in thousands of tons and in TJ. As the *Standardized toolkit* uses only TJ in connection with emission factors, we also use these units only.

In power generation sector in the *Standardized toolkit*, there is no distinction between the hard and brown coal (lignite). In the following we apply the same principle.

#### 2.3.1 Power Plants and Boiler Houses

Feed material and activity

In this chapter we do not describe technologies used in energy and heat production, or the differences in construction of boilers, turbines and environmental protection systems, as - despite differences in thermal output - all these entities operate on similar principles. In general, those entities are equipped with effective flue gas cleaning systems, and also with dry, semi-dry or wet desulphurisation systems.

Combustion of waste oils - although it is co-combusted in power plants and boiler houses - is included under hazardous waste incineration in section 2.1.3.

In Poland relatively small quantities of residue plant and animal fuels are combusted. The combustion takes place usually at their origin, i.e. in furniture, meat and fat industries. Wood fuel is noted separately in the public statistics. It is used mainly in the timber industry and pulp-and-paper sector.

The power plants in this category combust in total the following amounts of fuels:

•	hard coal	1,111,975.4 TJ
•	brown coal	501,928.1 TJ
•	high-methane natural gas	15,375.4 TJ
•	nitrified natural gas	6,684.5 TJ
•	oil fuel and light fuel oil	2,441.6 TJ
•	heavy fuel oil	22,372.4 TJ
•	coking gas	17,093.4 TJ
•	blast furnace gas	345.3 TJ
•	solid fuels and tars from coal cokin	ıg 1,714.9 TJ
•	residue plant and animal fuels	337.0 TJ
•	wood fuel	233.5 TJ
•	biogas	1,234.0 TJ

Concerning biomass fuels the contributions accounted for in the pulp and paper industry have been subtracted, as this part is included in Section 2.7.1. It is expected that the use of biogas will increase fast in the future.

In total this is

•	solid fossil fuels	1,615,617.5 TJ
•	heavy fuel oil	22,372.4 TJ
•	light fuel oil and gaseous fuels	41,940.2 TJ
•	biomass fuel	1.804.5 TJ

Applied technology

In general, power generation plants are equipped with effective flue gas cleaning systems, and also dry, semi-dry or wet desulphurisation systems.

**Emission factors** 

The applied medium emission factors used for power plants and boiler houses are based on the default emission factors of the *Standardized toolkit*. The default emission factor for coal seems to be quite uncertain and is based on values reported ranging from 7 to 230  $\mu g$  I-TEQ/TJ. For coal-fired power boilers we apply the medium EF of 10  $\mu g$  I-TEQ/ TJ. Polish coal has a relatively high content of chlorine (as discussed in section 2.3.3), and the actual emission factors may be higher than this. It is further doubtful, however, if the same value should represent both hard coal and lignite.

The reported ranges for the other fuels seem to be significantly narrower. As the emission from other power plants and boiler houses is not a major source, the uncertainty of the other emission factors has been roughly estimated by the authors and will not be discussed further.

The following emission factors have been applied (uncertainty ranges indicated in brackets):

Coal-fired power boilers: 10 (5-30) µg I-TEQ/TJ of burnt fuel; Heavy fuel-oil power boilers 2.5 (1.5-5.5) µg I-TEQ/TJ; Light fuel-oil and natural gas-fired power boilers 0.5 (0.25-1.5) µg I-TEQ/TJ; Wood and peat-fired power boilers 50 (25-100) µg I-TEQ/TJ; Oil-shale gas, generator gas and biogas boilers 8 (4-20) µg I-TEQ/TJ.

Wood and peat are included in class 2 (emission factor 50), as pure wood or peat is used for heat generation (not mixed with waste, straw, etc). The wood used is not chemically treated.

Emission factors for releases to residues were applied in case of coal-fired power boilers (14  $\mu g$  I-TEQ/TJ) and wood and peat-fired power boilers (15  $\mu g$  I-TEQ/TJ).

Release of dioxins and furans

In spite of the large uncertainty it is evident from Table 2.8 that the main emission source within this category is coal-fired power plants.

	Activity TJ/year Medium		factor, air	Annual emission to air g I-TEQ/year		Annual release to residues
	iviedium	Medium	Range	Medium	Range	Medium
Fossil fuel power plants	1,679,930			16	8.1-49	23
Fossil fuel/waste co-fired power boilers	0	35	-	-	-	-
Coal-fired power boilers	1,615,618	10	5-30	16	8.1-48	23
Heavy fuel-fired power boilers	22,372	2.5	1.5-3.5	0.06	0.03-0.08	ND
Light fuel oil/natural gas-fired power boilers	41,940	0.5	0.25-1.5	0.02	0.01-0.06	ND
Biomass power plants	571			0.18	0.04-0.36	0.004
Other biomass-fired power boilers	337	500	100-1,000	0.17	0.03-0.34	ND
Wood-fired power boilers	234	50	25-100	0.01	0.006-0.02	0.004
Landfill gas and biogas combustion	1,234	8.0	4-20	0.01	0.005-0.02	0.0
Total	1,681,501			16	8.2-49	23

Table 2.8 Potential releases of dioxins and furans from power plants and boiler houses in Poland, 2000

ND: No emission factors have been determined; releases may be of significance.

## Applied technology

## 2.3.2 Household and Domestic Heating and Cooking - Biomass

In Poland, combustion of wood in households takes place generally in simple kitchen stoves or heating boilers. However, more modern and - from an energy point of view - more efficient stoves, become increasingly common, especially in recreation houses. In contrast to West European states, the fraction of wood burned in fireplaces is low, but has been growing in recent years.

Activity

Co-combustion of wood and wastes takes place in rural and suburban areas located close to forests and in recreation houses. The public statistics data give the value of 95,000 TJ for combined combustion of wood and peat. The contribution of the latter is considered to be small. According to expert estimates, about 15% of the total amount of wood is contaminated. Considering the uncertainty on this estimate the total amount of contaminated wood is estimated at 9,500-19,000 TJ. During the combustion apart from gaseous pollutants, also solid pollutants containing dioxins and furans are formed and generally dumped to land (soils).

- virgin wood

A large number of studies exist on the emission of dioxins and furans from burning of clean wood in wood stoves and open furnaces of households. The actual emission will depend on several factors, but the analyses consistently find relatively low emissions from burning of clean wood. There seems to be no clear correlation between operating conditions and dioxin emission. For example it has been found in Danish experiments that the optimal operating con-

dition in several experiments led to significantly higher dioxin emissions than sub-optimal conditions (Vikelsøe et al. 1993, Schleicher et al. 2001). The UNEP toolkit uses a value of 1.5 µg I-TEQ/t wood (100 µg I-TEQ/TJ) as default. The most recent inventory of dioxin emission from the USA applies a value of 2 µg I-TEQ/t wood as best estimate (U.S. EPA 2000). Considering the variation in published results the emission factor is estimated to be within the range of 50-150 µg I-TEQ/MJ. Same emission factor is applied for peat and uncontaminated waste wood from wood processing industries.

The UNEP toolkit applies a default concentration of dioxins and furans in residues at 10 ng I-TEQ/kg ash for virgin wood. With the assumption that 30 kg of ash is generated for each tonne fuel and a heating value for wood of 12-15 MJ/kg, the emission factor is in the toolkit estimated to be  $20 \mu g$  I-TEQ/TJ.

- contaminated wood

Concerning the combustion of contaminated wood and waste in wood stoves more uncertainty exists. As residential burning of waste and contaminated wood may be a major dioxin source in Poland, the background for the applied emission factors will be presented in more detail.

Burning of contaminated wood in general generates more dioxins than burning of clean wood. The reason may be that the contaminated wood

- provides catalytic active surfaces (e.g. copper and iron);
- provides precursors for dioxin formation (e.g. PCP);
- otherwise serves as chlorine donor (e.g. other chlorinated preservatives);
- changes the burning process (e.g. lowering the temperature).

In the studies performed the composition of the waste is in general not analysed in detail, and the mechanism of increased dioxin formation is not clear except for the effect of the presence of PCP as precursor.

The UNEP toolkit applies a value of around 25  $\mu g$  I-TEQ/t (1,500  $\mu g$  I-TEQ/MJ) for contaminated wood. The European Dioxin Inventory (Quass 1997) applies 50  $\mu g$  I-TEQ/t as a medium estimate of slightly contaminated wood (not containing PCP) and 500  $\mu g$  I-TEQ/t for wood preserved with PCP.

It is not quite clear how much contamination is necessary to result in increased formation. If the mechanism is that the contaminated wood provides precursors, only small amount of contaminants may be enough. The significant effect of burning contaminated wood and household waste is clear from the results of Chatowitz et al. (1993), who measured emissions from stoves and furnaces burning different types of wood. It should be noticed that burning of uncoated chipboard chips did not result in significant increases, which have recently been confirmed by Danish results (Schleicher et al. 2001).

#### **Stoves:**

Open door burn of beech wood sticks: 0.77 µg I-TEQ/t Closed door burn of beech wood sticks: 1.25 µg I-TEQ/t Closed door burn of household waste: 3,230 µg I-TEQ/t

## Automatic chip furnaces:

Natural wood chips: 0.8 to 2.6 µg I-TEQ/t

Chipboard chips (uncoated): 0.29 to 0.91 µg I-TEQ/t

Waste wood chips from building demolition: 26 to 173 µg I-TEQ/t DF (Scha-

towitz et al., 1993 quoted by U.S. EPA 2000)

In one study focusing on the effect of adding paper/cartons or chlorine-free plastic waste to the clean wood, the emission increased a factor of 5-10 by addition of 30% paper waste, whereas chlorine-free plastics (2.5 and 25 %) did not show any significant effect (quoted by Quass 1997; Germany Inventory).

There is no use of PCP for wood preservation in Poland today, but PCP was produced until 1995, and the total amount used is estimated at approximately 3,000 t.

All wood from buildings will here be considered contaminated. The UNEP default emission factor of 1,500  $\mu g$  I-TEQ/TJ (25  $\mu g$  I-TEQ/t) for contaminated waste will be applied with an uncertainty range of 500-5,000  $\mu g$  I-TEQ/t.

The UNEP toolkit applies a default emission factor of 2,000 µg I-TEQ/TJ for releases to residues by burning of contaminated waste.

Release of dioxins and furans

Potential releases are summarised in Table 2.9 in the following section.

## 2.3.3 Household and Domestic Heating - Fossil Fuels

Feed material

Hard coal is the basic fossil fuel burned in households not only for heating, but also for cooking. However, the public statistics note systematic growth of natural gas (cooking and nitrified) consumption. For heating purposes also light fuel oil - the so-called domestic type - is used.

Activity

Polish statistics provide the following consumption figures:

•	hard coal	174,338	TJ
•	lignite	980	TJ
•	high methane natural gas	110,658	TJ
•	nitrified natural gas	16,953	TJ
•	LPG	20,812	TJ
•	light fuel oil	17,496	TJ

By grouping the fuels according to type (solid, liquid, gaseous) we get the following figures:

•	coal	175,318 TJ
•	oil	17,496 TJ
•	natural gas	148,423 TJ

Gaseous fuels are used almost exclusively for cooking purposes in urban areas. For the three added categories the following activity are assumed (GUS 2001a)

There is a significant co-combustion of waste in coal-fired stoves. In order to distinguish between heating purposes and waste disposal the emission from burning of the waste is here included in section 0, 'Uncontrolled waste burning', where this issue is further discussed. In the annual inventories carried out according to SNAP97 nomenclature (section 1.2) the co-combustion of coal and waste is included in the category covering residential coal combustion.

**Emission factors** 

Domestic heating using coal is one of the major source categories, and for this reason the applied emission factors are discussed in more detail in the following.

Medium emission factor to air applied for oil and natural gas-fired stoves is according to the UNEP toolkit 10 and 1.5  $\mu g$  I-TEQ/TJ respectively. The uncertainty range is roughly estimated at  $\pm 50\%$ . These fuels only account for a very small part of the total, and the emission factors will not be discussed further.

The Standardized toolkit applies an emission factor for burning of coal in residential heating systems of 70  $\mu g$  I-TEQ/TJ corresponding to approximately 2  $\mu g$  I-TEQ/t. The default emission factor was derived from mean values reported between 1.6 and 50  $\mu g$  I-TEQ/t of coal burned.

Several recent measurements indicate that the emission from the residential burning of Polish coal may be much higher (app.  $4.7~\mu g$  I-TEQ/t; Grochowalski 2002).

In 1998 the Austrian Umweltbundesamt presented unexpectedly high emission factors ranging from 108 to 663 µg I-TEQ/t fuel (at 0% O<sub>2</sub>) for combustion of hard coal from Poland in a simply constructed single heating stove (Moche & Thanner 1998). As mentioned above, measurements made in Poland do not confirm these very high estimates.

High emission of dioxins and furans from burning of Polish coal was confirmed by Quass et al. (2000) who found significant fuel-derived differences in dioxin emission dependent on the fuel. In the study different types of coal (anthracite, hard coal briquettes, lignite, etc.) were burned in two types of domestic heating stoves. Burning of hard coal from Poland in the two stoves resulted in average emission factors of 27 and 88  $\mu$ g I-TEQ/t respectively (n=3x2). These emission factors were about ten times higher than the emission factors for the other types of coal used for the test.

The Austrian findings have recently been reassessed with emission measurements using three different types of solid fuel stoves (Thanner & Moche 2001). The average emission from all appliances using coal as fuel was 7,700  $\mu$ g I-TEQ/TJ (n=8) corresponding to approximately 220  $\mu$ g I-TEQ/t.

The formation of dioxins and furans seems to be dependent on the chlorine content of the coal. Thuss et al. (1995) measured flue gas concentrations of dioxins and furans from a household heating system in Germany, fired either with salt lignite coal (total chlorine content of 2,000 ppm) or normal lignite coal (total chlorine content of 300 ppm). Emissions were seven times higher for the "salt"

lignite (2.74  $\mu$ g I-TEQ/t) than for the "normal" lignite (0.34  $\mu$ g I-TEQ/t). The relationship between the dioxin content of the bottom ashes and the chlorine content of the lignite was less distinct.

The results indicate that the emission factor for residential burning of coal - even though the coal is not co-combusted with waste - may be significantly higher than the default emission factor of the *Standardized toolkit*. The default emission factor is still used as a medium estimate, but it is estimated that the real average emission factor is likely to be higher rather than lower, and a range of 35-1,000 µg I-TEQ/t will be applied.

A default concentration of dioxins and furans in residues is according to the UNEP toolkit 5,000 ng I-TEQ/kg ash. In lack of data on the amount of ash and soot produced per tonne used fuel, an emission factor resembling the release of dioxins and furans to residues from coal-fired power plants of 14 µg I-TEQ/TJ has been applied. This factor may actually be significantly higher.

Release of dioxins and furans

The potential releases from all household heating activities are summarised in the following section. Burning of coal, virgin wood and contaminated wood makes up a significant part of the total. The uncertainty on the emission from burning of coal is very high, and the emission should be further investigated by actual measurements.

Table 2.9 Potential releases of dioxins and furans from household heating an, cooking and domestic heating in Poland, 2000\*

	Activity TJ/year			Annual emission to air		Annual release to residues
	Medium	μg I-	TEQ/t	g I-TEQ/year		g I-TEQ/year
		Medium	Range	Medium	Range	Medium
Household heating and cooking - biomass	95,000			29	6.7-41	30
Contaminated wood/biomass-fired stoves	14,250	1,500	300-1.500	21	2.9-29	29
Virgin wood/biomass-fired stoves	80,750	100	50-150	8.1	3.8-13	1.6
Domestic heating - fossil fuels	385,403			16	6.8-220	2.5
Coal-fired stoves	219,484	70	30-1,000	15	6.6-220	2.5
Oil-fired stoves	17,496	10	5-15		0.09-0.26	ND
Natural gas-fired stoves	148,423	1.5	0.75-2.15	0.22	0.11-0.32	ND
Total	480,403			45	13-260	33

Emission from co-combustion of waste is not included

#### 2.4 Production of Mineral Products

Main Category 4, 'Production of mineral products. These are high-temperature processes for melting (glass, asphalt), baking (brick, ceramics) or thermally in-

ND No emission factor has been determined

duced chemical transformation (lime, cement). In them, fuel combustion generates dioxins and furans as unwanted by-products. Additionally, formation of them may be linked to the process raw materials used. Cement and lime kilns are large-volume processes which often add wastes as a low/no cost fuel. Where effective controls are installed, the use of waste materials like tires, waste oil, sludge, etc. is not problematic; low emissions have been measured.

The category can be categorised into a number of subcategories:

- Cement production;
- Lime production;
- Brick production;
- Glass production;
- Ceramics production;
- Asphalt mixing.

Of these subcategories, only the first two yield emissions exceeding 1 g I-TEQ. Therefore, cement and lime production is treated separately, whereas the remaining categories are described jointly.

#### 2.4.1 Cement Production

#### Feed material

Waste materials make up app. 5% of total feed material in cement production in rotary hearths. The generally inorganic waste materials include: Slag from metallurgy and ash from power generation. Toxic organic wastes are not treated in cement production, so waste management in cement plants should not affect emissions of persistent organic pollutants. Cement plant Górażdże has recently obtained a permit to burn used automobile tires in clinker furnaces.

Cement plants in Poland are:

- LAFARGE Cement plants: "Małogoszcz" S.A., "Kujawy" S.A., "Wierzbica" S.A.;
- CBR/Heidelberger Cement plants: "Górażdże" S.A., "Strzelce Opolskie" S.A., "Groszowice" S.A., "Wiek" S.A.;
- CRH Cement plants: "Ożarów" S.A., "Rejowiec" S.A.;
- Dyckerhoff Cement plants: "Nowiny" S.A., "Warszawa" S.A.;
- Miebach Cement plant "Odra" S.A.;
- Polen Cement/Miebach Cement plant "Warta" S.A.;
- Readymix Cement plants "Rudniki" S.A., "Chełm" S.A.;
- Rumeli Cement plant "Nowa Huta" S.A.;
- State owned Cement plant "Wejcherowo".

### Applied technology

Approximately 60% of clinker is produced with dry method and the rest with wet method. The observed tendency in recent years is an increase of the dry method share.

In Polish cement industry, the APC systems apply to dust (PM) only. There are no special methods for reduction of gaseous pollutants  $(SO_2, NO_x)$ . Electrostatic precipitators are the most used dedusting installations. The only fabric

filters are in "Rudniki" cement plant, while in some case also cyclones are used. The age of the APCS varies between 30+ and a few months for the latest modern installations. Devices that fulfil the condition of PM emissions less than 50 mg/m³ make up app. 65% of the total. The average emission factor for PM emissions in Polish cement sector is app. 0.7 kg/t of clinker.

Activity

Clinker production (Table 2.10.) shows an increasing trend during the last 10 years.

Table 2.10 Clinker production during the period 1990, 1995-2000

Year	1990	1995	1996	1997	1998	1999	2000
Clinker production [1000 t]	10,309	12,602	11,756	12,739	11,974	11,678	11,558

The cement production in 2000 was 15,046,400 t.

**Emission factors** 

For the dry method a default emission factor of 0.15 (0.075-0.3)  $\mu$ g I-TEQ/t of cement is applied.

For the wet method the emission is highly dependent on the temperature over the precipitator with default emission factors of 0.15 (>300°C), 0.6 (200-300°C) and 5 (<200°C)  $\mu g$  I-TEQ/t. The temperature in Polish cement kilns is typically in the range 200-300°C, and the EF of 0.6  $\mu g$  I-TEQ/t cement is applied as medium with a range of 0.3-1.5  $\mu g$  I-TEQ/t.

Practically all residues are taken back into the process.

Release of dioxins and furans

The total emission of dioxins and furans is estimated at 5.0 (2.5-12) g I-TEQ/year.

### 2.4.2 Lime Production

Feed material

The basic feed material for lime production are limestone and coke as a primary fuel. Sometimes instead of coke, natural gas and liquid fuels are used.

Applied technology

Lime burning takes place in various types of kilns:

- Type 100c most common;
- Mearz kilns and;
- GOPEX kilns.

Mearz kilns are fitted with APC devices with fabric filters, while 100c kilns with the exception of cement plant at Bukowa are without any APCS.

Activity

Total lime production in 2000 was 2,376,000 t. About 50% of that figure can be attributed to kilns fitted with good dust abatement devices.

**Emission factors** 

The default emission factors of the *Standardized toolkit* for lime production is 10 µg I-TEQ/t for the case of cyclone/no dust control and 0.07 µg I-TEQ/t of

lime for kilns of high efficiency and with fabric filters. The high emission factor for facilities without any APCS is based on relatively few measurements and should be considered highly uncertain, and a range of  $0.5\text{-}15\mu\mathrm{g}$  I-TEQ/t will be applied.

Release of dioxins and furans

The total emission of dioxins and furans is estimated at 12 (0.68-18) g I-TEQ/year. Lime production may be a significant source, but more certain estimates can only be obtained by actual measurements.

## 2.4.3 Other Mineral Products: Bricks, Glass, Ceramics, Asphalt Mixing

Production of other mineral products is of minor significance to the total emission of dioxins and furans in Poland, and the activities and applied technologies have only been assessed briefly.

Activity and applied technology

The production of bricks amounted to 2,600,000 t. There is a great variety of brick plants ranging from large modern plants to very small plants with primitive technology. Approximately 60% of bricks are produced under good dust abatement conditions.

In total 649,938 t ceramics were produced from clay, sand and inorganic chemicals. The production is roughly divided 50% to 50% between plants with good and no dust control devices (expert estimate).

In total 1,549,600 t glass was produced in 2000 from sand and inorganic chemicals with natural gas as energy source. As for ceramics the activity is divided 50% to 50% between plants with good and no dust control devices (expert estimate).

In total 1,041,600 t asphalt was produced from dried rock chips, sand and various fillers (e.g. fly ash from power plant) bound together in bitumen. In Poland, there are both large modern asphalt producing installations, and very small plants with primitive devices and no APCS. The modern installations are usually based on German technologies.

**Emission factors** 

Production of other mineral products is not a major source of dioxins and furans, and sophisticated APCs for reducing the emission are usually not applied. The emission factors are very dependent on whether the plants are equipped with good APCS (ESP and fabric filter) or no APCS, and the total emission from the source category will be very dependent on the split between the different classes. The total uncertainty may be reduced by further assessing of the disaggregation of activities on the different activities. The uncertainty on the applied emission factors is roughly estimated and shown in Table 2.11.

Release of dioxins and furan

The applied emission factors and the release of dioxins and furans are summarised in Table 2.11. Even when the highest emission factors within the range are applied, these activities are not major sources of dioxins and furans emission in Poland.

Category	Activity (t/year)	Emission factor µg I-TEQ/t		Total emission to air g I-TEQ/year	
		Medium	Range	Medium	Range
Brick production	2,500,000			0.24	0.06-0.49
- Cyclone/no dust control	1,040,000	0.2	0.04-0.4	0.21	0.04-0.42
- Good dust abatement	1,460,000	0.02	0.01-0.05	0.03	0.01-0.07
Glass production	1,549,600			0.31	0.06-0.62
- Cyclone/no dust control	1,549,600	0.2	0.04-0.4	0.31	0.06-0.62
Ceramics production	646,938			0.15	0.04-0.28
- Cyclone/no dust control	323,469	0.2	0.04-0.4	0.06	0.01-0.13
- Good dust abatement	323,469	0.02	0.01-0.05	0.006	0.003-0.02
Asphalt mixing	1,041,600			0.04	0.01-0.07
- Mixing plant with no gas cleaning	520,800	0.07	0.02-0.12	0.04	0.01-0.06
- Mixing plant with fabric filter, wet scrubber	520,800	0.007	0.003-0.01	0.004	0.002-0.005
Total	11,476,276			1.4	0.32-2.8

Table 2.11 Emission of dioxins and furans to air from asphalt mixing and production of bricks, glass, and ceramics in Poland, 2000

## 2.5 Transport

Emission of dioxins and furans from transport relies heavily on the combustion of gasoline (leaded and unleaded), diesel and other fuels. The category can be categorised into four subcategories dependent on the fuels used:

- 4-stroke engines (gasoline-fuelled cars, motorcycles, light trucks, etc.)
- 2-stroke engines (boats, mopeds, lawn mowers, etc.)
- Diesel engines (diesel-fuelled cars, trucks, ships etc.)
- Heavy oil-fired engines (ships, tanks, stationary power generators, etc.).

For transport, emission to air is the only emission route considered.

Activity

The total consumption of gasoline in Poland in 2000 was according to data of GUS and Institute of Automobile Transport in Warsaw, app. 4,999,000 t. Of these it is estimated that about 4,858,600 t was used for 4-stroke engines whereas 140,400 for 2-stroke engines. Most of the passenger cars and light trucks (<3.5 t) were equipped with catalytic converters. It is roughly estimated that 3,204,200 t of the gasoline used for 4-stroke engines was combusted in engines with catalyst. Passenger cars used 2,821,900 t of unleaded gasoline with catalyst, while light trucks used 382,300 t. The consumption of unleaded gasoline without catalyst was 1,296,390 t. The leaded gasoline consumption amounted to 358,010 t.

Gasoline for 2-stroke engines was used by motorcycles (34,700 t), mopeds (21,400 t) and passenger cars (16,200 t). Of these, unleaded gasoline accounted for 58,910 t while leaded for 13,390 t. Other machinery used 68,100 t of leaded gasoline. The total of leaded gasoline for 2-stroke engines was: 81,490 t.

The total consumption of diesel in 2000 was 5,171,000 for all types of transport. The respective figure for heavy oil used in all types of engines was 460,000 t engines.

4-stroke engines

All combustion engines produce dioxins and furans as unwanted by-products. Higher emissions have been associated with the use of chlorinated or brominated scavengers used in leaded gasoline. In 4-stroke engines, the formation of dioxins and furans is significantly lower when unleaded gasoline is used. If a catalytic converter is installed, the final emission of dioxins is considered negligible.

2-stroke engines

In 2-stroke engines, oil is usually added to the fuel for lubrication, and higher amounts of pollutants may be released from these engines. The default emission factor proposed by UNEP for a 2-stroke engine using unleaded gasoline is 2.5 µg I-TEQ/t, which is actually 25 times higher than the emission factor for a 4-stroke engine without catalyst using unleaded gasoline.

Heavy oil-fired engines The emission factors for heavy oil-fired engines are considered to be relatively high. Based on a limited number of studies with emission factors ranging from 3 to 6 µg I-TEQ/t, UNEP propose a default emission factor of 4 µg I-TEQ/t for steady state conditions.

Total emission

The total emission of dioxins and furans from transport in Poland in 2000 is shown in Table 2.12.

Engines	Fuel con- sumption	Emission factor		Total emission to air	
	(t/year)	(μg I-1	ΓEQ/t)	(g I-	TEQ/year)
		Medium	Range	Medium	Range
4-stroke engines					
Leaded fuel	358,010	2.2	1.6-2.8	0.79	0.57-1
Unleaded fuel without catalyst	3,204,200	0.1	0.05-0.15	0.32	0.16-0.48
Unleaded fuel with catalyst	1,296,390	0.0	-	0.0	-
2-stroke engines					
Leaded fuel	81,490	3.5	3-4	0.29	0.24-0.33
Unleaded fuel without catalyst	58,910	2.5	1.5-3.5	0.15	0.09-0.21
Diesel engines	5,171,000	0.05	0.02-0.08	0.26	0.1-0.41
Heavy oil fired engines	460,000	4.0	3-5	1.8	1.4-2.3
Total (round)	10,630,000			3.6	2.5-4.7

Table 2.12 Emission of dioxins and furans from transport in 2000

## 2.6 Uncontrolled Combustion Processes

The processes within Main Category 6, 'Uncontrolled combustion processes' are typically poor combustion processes, which may be significant sources of dioxin and furans.

The category is in the *Standardized toolkit* categorised into two subcategories conditional on the materials burned, but here will be categorised into four subcategories:

- Clean biomass burning: Forest, grassland & moor fires and agricultural field burning
- Landfill fires
- Uncontrolled waste burning
- Accidental fires in houses, factories and vehicles.

Accidental fires and uncontrolled waste burning are here categorised into three separate subcategories, because different measures may be taken to decrease the releases from sources within the three categories.

## 2.6.1 Clean Biomass Burning

Clean biomass burning includes forest fires, burning of grassland and destruction by fire of agricultural residues (straw) in the field.

Agricultural crops, grassland, etc.

In 2000, according to GUS (GUS 2002), there were 3,360 fires of agricultural crops, grasslands & stubbles and 16,024 fires of waste lands, which covered the areas of 4,679 ha and 24,264 ha respectively. According to literature (Simpson and Winiwarter 1998) the amount of biomass burned per hectare in this case is:

3.6 t/ha. Based on these numbers, it is estimated that the total mass of biomass burned in 2000 was app. 520,000 t. The uncertainty considered, the range is estimated at 200,000-850,000 t.

Forest fires

According to GUS (GUS 2002), there were 12,428 forest fires in 2000 which covered the area of 7,013 ha. In Simpson and Winiwarter (1998) there is an emission factor which correlates amount of burned biomass with the fire area: 37.5 t/ha. On this basis, it is estimated that app. 260,000 t of biomass was burned in Poland in 2000. Considering the uncertainty, the range is estimated at 100,000-500,000 t.

Agricultural residue burning (in field)

The amount of agricultural residue burned in the field was estimated based on the area of agricultural crops (after GUS: 14,129.3 thousands ha) and the respective emission factor (Simpson and Winiwarter 1998) - average amount of burned crops per cultivated area: 0.025 t/ha. On this basis, it is estimated that app. 350,000 t of biomass was burned in Poland in 2000. Considering the uncertainty, the range is estimated at 150,000-550,000 t.

**Emission factors** 

Emission factors for emission from open burning of biomass have only been determined with high uncertainty. The default emission factors for emission to air from burning of agricultural residues are significantly higher because of the possible presence of chlorinated pesticides. To what extent chlorinated pesticides are used in Poland has not been investigated. As this source probably not is a major source, the default emission factors for emission to air will be applied with uncertainty ranges roughly estimated by the authors:

- Forest and grassland fire: 5 (1-10) μg I-TEQ/t of material burnt.
- Agricultural residues: 30 (2-60) µg I-TEQ/t of material burnt.

The default emission factors for release to land are 4  $\mu$ g I-TEQ/t for fires in forests, grassland, etc. and 10  $\mu$ g I-TEQ/t for burning agricultural residues.

Release of dioxins and furans

The total emission to air from clean biomass burning is with a very high uncertainty estimated at 14 (0.6-47) g I-TEQ/year, whereas the release to land is estimated at 6.6 g I-TEQ/year. The major part is from burning of agricultural residues.

#### 2.6.2 Landfill Fires

Burning of stored waste at landfills is prohibited, but landfill fires may unintentionally occur now and then. At present no investigation of the amount of waste burned in landfill fires has been undertaken, but a first rough estimate of the potential releases will in the following be obtained using two different approaches.

For both approaches experience from a detailed Swedish study will be used for the estimate.

The occurrence of landfill fires and the potential emission of dioxin and furans from the fires have been intensively studied in Sweden around 1990 (quoted by

U.S. EPA 2000 that uses Swedish data for estimating the emission from this source in the USA). Based on the results, the total emission from landfill fires in Sweden in 1993 has been estimated at 2.8-30 g Nordic TEQ/year (Bernes 1998) corresponding to 0.3-3.3  $\mu$ g Nordic TEQ/person/year. As congener-specific results were not provided in the study, it is not possible to derive exact emission factors in units of I-TEQ, but the Nordic and the International toxicity equivalency factors are the same except for one congener. The physical conditions for landfill fires (e.g. weather conditions) are deemed to be comparable between Sweden and Poland. Considering that the amount of waste generated per capita in Sweden in 1990 was somewhat higher than the amount generated in Poland, the range is estimated at 0.2-3  $\mu$ g I-TEQ/person/year. The total emission from this source in Poland can on this basis be estimated at 8-120 g I-TEQ/year.

Alternatively the default emission factor from the *Standardized toolkit* can be applied.

According to statistical data of the Fire Department, 960 fires of deep landfills (depth exceeding 5m) and 106 fires of surface landfills were reported in Poland 2000. The amount of burned material in each landfill fire was not reported. Using the Swedish experience about the average waste amount burned in a fire for surface and deep landfills respectively (150 m³ and 500 m³), the total biomass burned in landfill fires in Poland was app. 49,250 t. The average density of waste dumped to Polish landfills is estimated at 250 kg/m³, which is lower than the density reported in the Swedish study. It has to be noted, however, that the Polish data refer to uncompressed waste.

The estimated emission from landfill fires is shown in Table 2.13. The recalculation of the Swedish results using the emission factor of the *Standardized tool-kit* resulted in a total emission somewhat higher than the emission calculated in the study. For Poland this calculation resulted in an emission factor in the middle of the range of 8-120 g I-TEQ/year, and this range will be used as the first rough estimate of the emission from this source.

Landfills fires Average waste Assumed Number Mass of **Emission Emission** density waste burn of fires waste burned factor g I-TEQ per fire kg/m3 μg/t m3 Sweden Surface landfills 700 150 167 17,535 1,000 17.54 Deep landfills 700 500 50 17,500 1,000 17.50 Total 35.04 Poland Surface landfills 250 \* 150 960 36.000 1,000 36.00 Deep landfills 250 \* 500 106 13.250 1.000 13.25 49.25 Total

Table 2.13 Estimated emission from Swedish and Polish landfill fires using the emission factor of the Standardized toolkit

## Activity

## 2.6.3 Uncontrolled Waste Burning

Uncontrolled burning of waste - usually as co-combustion of coal or wood and waste - is quite common in Poland, especially in the southeastern part. It is difficult to quantify the amount of waste burned in that way due to the lack of statistical data.

Uncontrolled burning of domestic waste was estimated at 333,000 t in 2000. The total amount of solid waste generated (by households) in the rural area in 2000 was 3,339,000 (1,713,000) t (MoE 2002). The total amount of solid waste collected and removed in rural areas was 1,097,900 tons. Assuming that the fraction of household waste removed is the same as for the total (1,098/3,339) we obtain 1,149,750 tons of household solid waste that was not removed. The composition of the household solid waste in urban and rural waste is presented in Table 2.14 (after MOE 2002). The fraction of combustible waste can be approximated as 0.29 (by summing up contributions of paper and paper cardboard, plastics and textiles). The approximated total of combustible solid waste generated by households in rural areas  $(0.29 * 1,145,750 t \approx 333,000 t)$  was assumed to be burnt entirely. This is a rough estimate with uncertainty range: 167,000 - 666,000 (factor of two differences).

Household solid waste Waste fraction Urban areas Rural areas 1) Organic waste of plant origin 32% 2) Organic waste of animal origin 2% 1% 3) Other organic waste 2% 2% 4) Paper and paper cardboard 19% 13% 5) Plastics 14% 14% 6) Textiles 4% 3% 7) Glass 8% 8% 8) Metals 4% 4% 5% 10% 9) Mineral waste 10) Small fraction (<10mm) 33% 10% 100% 100% Total

Table 2.14 Estimated composition of household waste in 2000 (MeE 2002)

No data on burning of contaminated wood from demolition have been available.

Measurements

The significance of this source has indirectly been demonstrated by data from the University of Cracow indicateing that co-combustion of waste and coal in residential heating systems is a major source of dioxin emission in Cracow (Grochowalski and Chrząszcz 1997).

In 1996, thorough measurements of dioxin content in suspended particulate matter in air from Cracow during winter months were undertaken. Samples of suspended particulate matter in air of dimensions less than 10  $\mu$ m (PM10) were taken from monitoring points in four quarters of Cracow. Because of strong adsorption of dioxins to surface-active particles of the suspended particulate matter, dioxins are present in air mostly in the form of compounds adsorbed onto the surface of solid particles. In order to make comparison, similar measurements were carried out in June 1996.

The results show that the levels of dioxins in air in Cracow were much higher during winter (Figure 2.1). The results have been confirmed by other measurements. Slightly higher dioxin levels during winter are known from larger cities in Western Europe, but not at the high levels measured in Cracow. The data indicate the presence of a local source during winter - most likely connected with residential heating using coal. It is though still unclear to what extent the burning of waste contributes to the emission, or the main source is the relatively high chloride-containing coal itself.

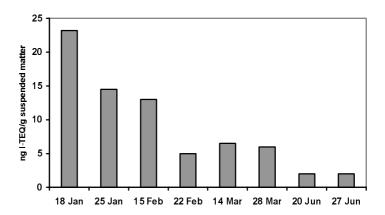


Figure 2.1 Dioxin content of suspended particulate matter in air for the most polluted quarters of Cracow, Podgórze in 1996 (after Grochowalski and Chrzqszcz 1997).

**Emission factors** 

A value of 300  $\mu g$  I-TEQ/t is proposed in the UNEP toolkit for open burning, where a wide range of wastes including items such as household hazardous wastes and chemicals may be burned. Regarding the release to residues an indicative emission factor of 600  $\mu g$  I-TEQ/t is used for open burning of domestic wastes.

Recently the U.S. EPA has reported the results of seven "baseline" waste burning tests (U.S. EPA 2000). Domestic waste burning is widespread in rural areas of the USA. These tests exhibited variation in the emissions of dioxins and furans with a 1-2 order of magnitude spread between the lowest and highest TEQ values. The average emission factor for the seven waste types was 74 µg I-TEQ/t (setting not detected values equal to one half of the detection limit). Variation from the baseline waste chlorine content (0.2% by weight PVC) included testing at three different PVC levels (0, 1.0, and 7.5% by weight PVC). The average emissions from the 0, 1.0, and 7.5 percent PVC were 14, 201 and 4,916 µg I-TEQ/t respectively. In two tests using waste impregnated with inorganic chloride (CaCl<sub>2</sub>) at a 7.5% by weight (and no PVC) emissions averaged 734 µg I-TEQ/t. The tests demonstrated a significant influence of PVC and inorganic chlorine on the total emission of dioxins and furans. Other variations in baseline waste composition included conducting one test with compressed waste, one test with a double load of waste, and one test in which some of the waste paper was wetted to simulate high moisture burns. These tests resulted in a higher mean emission factor of 534 µg I-TEQ/t.

Considering the high uncertainty the emission factor is estimated to be in the range of  $50-500 \mu g$  I-TEQ/t.

- open burning of waste wood

Based on Japanese studies, the UNEP toolkit applies an emission factor of 60  $\mu$ g I-TEQ/t for burning of contaminated wood from demolition. The default emission factor for burning of contaminated wood in stoves is - as discussed in section 2.3.2 - about 25  $\mu$ g I-TEQ/t. When the uncertainty is considered, the

emission factors cannot be considered significantly different. The emission factors for emission to air from open burning of contaminated wood are here estimated at 20-200  $\mu g$  I-TEQ/t. The UNEP toolkit proposes an emission factor for release to residues of 10  $\mu g$  I-TEQ/t.

Release of dioxins and furans

The release of dioxins and furans from uncontrolled waste burning is summarised in Table 2.15. The calculations indicate that uncontrolled burning of waste may be one of the major sources of emission to air in Poland. This is in accordance with the annual inventories carried out according to SNAP97 categories, where the co-combustion of waste and coal is estimated as the major source in Poland. The estimates are, however, very uncertain.

Table 2.15 Potential release of dioxins and furans from uncontrolled burning of waste in Poland, 2000

	Activity t/year	Emission factor, air μg I-TEQ/t		Annual emission to air g I-TEQ/year		Annual release to residues
		Medium	Range	Medium	Medium Range	
Uncontrolled domestic waste burning	167,000-666,000	1,000	400-1.500	100,000	8.4-330	200
Open burning of wood from construction and demolition	-	60	20-200	-	-	-
Landfill fires	20,000-80,000	300	50-500	49	8-120	ND
Total	187,000-750,000			150	16-450	210 ?

ND: No emission factor has been determined

## 2.6.4 Accidental Fires in Vehicles and Houses

Activity

Statistics of the Fire Department indicate that there were 38,305 vehicle fires in Poland in 2000. The same source provides the data shown in Annex 3 on the fires in public buildings, houses and apartments, production plants and warehouses in Poland in 2000.

According to the data collected by the fire Department, app. 10 kg of material is burned on each square meter of area in industrial/production plants. For other types of places (public buildings/facilities, flats/houses/ and warehouses) the respective amount of burned material is usually greater, therefore the so-called multiplication factor is that varies between 15 and 20 kg/m² is introduced.

Based on these data the total amount destroyed by fires in buildings is estimated at 32,377 t/year.

**Emission factors** 

Given the wide range of materials considered under accidental fires and the wide range of possible emission factors the UNEP toolkit proposes an initial default emission factor to air of 400  $\mu g$  I-TEQ/t of material burnt for accidental fires in buildings and emission factor in residues 400  $\mu g$  I-TEQ/t of material burnt. The uncertainty range is here roughly estimated at 100-800  $\mu g$  I-TEQ/t.

Limited testing has been carried out on the release of PCDD/PCDF from fires in vehicles. In this report a medium emission factor to air of 94  $\mu$ g I-TEQ/event is applied (range: 40-200  $\mu$ g I-TEQ/event) and an emission factor for releases to residues of 18  $\mu$ g I-TEQ/event.

Release of dioxins and furans

Emission to air from vehicle fires in Poland is estimated to be 3.6 (1.5-7.6) g I-TEQ/year and in residues 0.7 g I-TEQ/year.

Emission to air from fires in buildings is estimated to be 13 (3.2-26) g I-TEQ/year, whereas app. 13 g I-TEQ/year may end up in residues.

The emission can alternatively be estimated using the default emission factors of 1  $\mu$ g I-TEQ/year/person used in the European Dioxin Inventory (Quass 1997). This factor derived from German experience covers all fires including landfills fires. Using this per capita factor, the total emission from all fires in Poland can be estimated at 40 g I-TEQ/year.

# 2.7 Production and Use of Chemicals and Consumer Products

Dioxin and furan releases from production of chemicals and consumer goods may be due to dioxin and furan input with the raw materials themselves or formation in the production process.

The Main Category 7, 'Production and use of chemicals and consumer products' can be categorised into a number of subcategories:

- Primary pulp and paper mills
- Secondary paper production
- Chemical industry
- Petroleum industry
- Textile plants
- Leather plants

The first two and the last two subcategories are discussed in individual sections at the beginning and at the end of the chapter.

## 2.7.1 Pulp and Paper Production

Feed material and activity

There are three plants in Poland that are integrated pulp mills. These are plants in Świecie, Ostrołęka and Kwidzyń. All of them produce pulp using the Kraft (sulphate) process. Other Polish paper plants use primary or secondary feed materials either produced in Poland or imported. Pulp bleaching (300,600 t in 2000) is done only in Kwidzyń plant. The applied method (ECE) is based on ClO<sub>2</sub> use. The other two integrated plants do not use bleaching. In total, 840,700 t of pulp was produced in 2000 of which 450,400 t was unbleached, while 89,800 t of pulp was obtained through mechanical pulping (TMP method). Sulphite process for pulp production is not used in Poland.

In order to produce over 840,000 t of pulp it was necessary to use app. 2,000,000 t of timber (app. 45% yield) of which 5% is bark then burned in bark boilers. Approximately 0.2% of mass of burned bark is retained by precipitators as sludge (200 t). During production of pulp by the Kraft process, for each tonne of pulp about 1.5 t of black liquor is formed. 35% of the black liquor mass consists of organic substances that incinerated in boilers (840,700 - 89,800 = 750,900 t x 1.5 = 1 126 350 t x 0.35 = 394,222 t) i.e. 394,222 t. During the combustion in boilers, approximately 2 kg of residues are generated per 1 t of sludge burned (in total 788.5 t).

According to GUS (GUS 2001b), total paper production in 2000 was 1,934,000 t, of which 1,223,000 t was from primary production and 711,000 t was from secondary production.

Release of dioxins and furans

Traditionally pulp and paper mills have been the major source of direct releases of dioxins and furans to water because of the use of elemental chlorine for bleaching. Changing from elemental chlorine bleaching to bleaching using ClO2 reduces the default emission factor for emission to water from 4.5 to 0.06  $\mu$ g I-TEQ/ADt (air dried tons pulp). The following emission factors have been applied (with uncertainty ranges in brackets):

#### To air:

- Combustion of black liquor sludge: 0.07 (0.02-0.12) µg I-TEQ/t of sludge
- Combustion of bark: 0.4 (0.1-0.7) µg I-TEQ/t of bark

#### To water:

- Kraft process (ClO<sub>2</sub> bleaching): 0.06 (0.02-0.1)µg I-TEQ/t to water
- Unbleached pulp: 0.03 (0-0.1)µg I-TEQ/t to water

#### To products:

- Kraft papers, ClO2, TCF, unbleached papers: 0.5 (0.1-1) µg I-TEQ/t
- Recycled paper: 10 (1-15) µg I-TEQ/t

## To residues:

- Combustion of black liquor sludge: 1000 µg I-TEQ/t of sludge
- Combustion of bark: 1000 μg I-TEQ/t of sludge

Release of dioxins and furans

Total releases of dioxins and furans are estimated as follows:

To air: 0.07 (0.013-0.15) g I-TEQ/year. To residues: 1.0 g I-TEQ/year. To water: 0.03 (0.006-0.075) g I-TEQ/year.

To products: 7.7 (0.8-12) g I-TEQ/year. Secondary paper production accounts for the major part of release to products. The source of the dioxins and furans is the recycled paper where the dioxins and furans may have been generated by former production using elemental chlorine. However, it is very uncertain to what extent the recycled paper actually contains dioxins and furans, and the level can only be determined by measurements.

## 2.7.2 Chemical Industry

Activity, applied technology

Dioxins and furans may be formed as by-product by production of chlorinated chemicals and the *Standardized toolkit* provides default emission factors for a number of chlorinated chemicals.

The inventory has only briefly addressed the chemical industry, and this industry should be further evaluated for development of the inventory.

Among the listed chlorinated pesticides only 2,4-dichlorophenoxy acetic acid (2,4-D) is produced in Poland (4,000 t in 2000) at Chemical Plant Rokita. To the knowledge of the authors no measurements of dioxin and furan concentrations in 2,4-D have been available.

PVC production in 2000 was 273,930 t (GUS 2001b). Production of ECD/VCM/PVC with oxychlorination process takes place in Poland in one plant: "Anwil" in Włocławek. All stages of PVC production are integrated at one production (closed) system, and this is why PCDD/F emission in Excelsheet is estimated based on total production of PVC in Poland. Residues and waste gases generated during ECD/VCM production are combusted/after-burned in modern installation.

Pentachlorophenol (PCP) has been produced at Chemical Plant Rokita at Brzeg Dolny until 1995. The annual production was app. 200 t of PCP. The total production volume was app. 3,000 t. PCP has been banned since 1996. It is on the list - made by the Ministry of Agriculture and Food Management - of substances that pose a special threat to humans, animals and environment. Similarly, production of polychlorinated biphenyls (PCBs) has been banned since 1995. Chloranil has never been produced in or imported to Poland.

**Emission factors** 

The default emission factor of the *Standardized toolkit* for release to products for by production of 2,4-D is 700  $\mu g$  I-TEQ/t. Reported concentrations range from 3  $\mu g$  I-TEQ/t to 200,000  $\mu g$  I-TEQ/t. It has not been possible to obtain any measurements of the content of Polish produced 2,4-D, and the emission factor must be considered highly uncertain. It is estimated that it could be somewhere between 7 and 7,000  $\mu g$  I-TEQ/t. No dioxins and furans were found in measurements of flue gases (Grochowalski 2002), therefore the low EF given in the toolkit was applied.

PVC:  $0.0003 \,\mu g$  I-TEQ/t - to air;  $0.03 \,\mu g$  I-TEQ/t - to water;  $0.1 \,\mu g$  I-TEQ/t - to products;  $0.2 \,\mu g$  I-TEQ/t - to residues.

Release of dioxins and furans

The total release of dioxins and furans to products by production of 2,4 D is roughly estimated at 2.8 (0.028-28)  $\mu$ g I-TEQ/t. The dioxins and furans will ultimately be released to the environment by the use of the pesticides.

## 2.7.3 Petroleum Industry

According to UNEP (2001) so far only one potential source for dioxins and furan emissions within the petroleum refinery industry has been identified: Regeneration of the catalyst used during catalytic cracking of the larger hydrocar-

bon molecules into smaller. Combustion processes may also emit dioxins and furans, but these emissions are included in section 2.3. No emission factor for petroleum industry is available, and the activity has not been assessed further. The petroleum industry is in general not considered a major source of dioxins and furans.

#### 2.7.4 Leather and Textile Plants

Sources of dioxins and furans in final textile products can be due to:

- Use of chlorinated chemicals, especially pentachlorophenol (PCP);
- Use of dioxin-contaminated dye-stuffs, especially dyes-stuff on the basis of chloranil;
- Formation of dioxins and furans during finishing, e.g. by using chlorinated chemicals.

Dioxins and furans in leather products are mainly due to the use of PCP for preservation of the leather.

PCP has not been used for textile or leather production in Poland, neither have dyestuffs based on chloranil. It is difficult, however, to exclude the possibility that dioxins and furans are formed during textile finishing processes, during which imported chlorine containing substances are applied.

Textiles that may have been treated with imported preservation substances containing PCP are canvas covers used in the military. It was not possible to confirm that the canvas has been imported. PCP may further be present in imported textiles and leather, especially from Asia.

Activity, applied technology

In 2000, 63,800 t of textiles were produced in Poland. Of this app. 13% i.e. 8,400 t was used for production of tyres (cord fabric) and canvas covers.

**Emission factors** 

The *Standardized toolkit* does not provide a default medium emission factor for releases of dioxins and furans to textile products. According to the at toolkit the emission factor will be within a lower limit of 0.1  $\mu$ g I-TEQ/t and an upper limit of 100  $\mu$ g I-TEQ/t. As no indication of the use of dioxin containing chemicals for textile and leather production in Poland exists, a range of 0.1-100  $\mu$ g I-TEQ/t with a medium estimate of 1  $\mu$ g I-TEQ/t will be applied.

Release of dioxins and furans

The total release of dioxins and furans to textiles is estimated at 0.06 (0.006-6) g I-TEQ/year. As mentioned above dioxins and furans may be present in imported products.

An indication of the potential turnover with textiles can be obtained using Danish experience. In Denmark in 2000 the total turnover with imported textiles was estimated at about 0.5 g I-TEQ/year (Hansen et al 2000). If dioxins are present at similar concentrations in Poland, it would correspond to some 4 g I-TEQ/year, of which a substantial part would be discharged to the sewage system by laundry.

## 2.8 Miscellaneous

Some sources of dioxin and furan releases do not fit into one of the other categories and are therefore brought together in the Main Category 8, 'Miscellaneous'. The category can be categorised into a number of subcategories:

- Drying of biomass
- Crematoria
- Smoke houses
- Dry cleaning
- Tobacco smoking.

## 2.8.1 Drying of Biomass

Feed material and activity

According to GUS (GUS 2001b), there were 3,391,600 m<sup>3</sup> of sawn wood produced in 2000. This gives app. 1,804,120 t of which 70-80% is dried. Dioxins and furans may be formed by this process as all other fuel burning processes.

Total production of hay in 2000 was 1,674,600 t. According to expert estimates, almost all plants and greens used for green fodder production are dried in natural conditions without using any drying facilities. The formation of dioxins and furans from drying of fodder is estimated to be insignificant.

**Emission factors** 

Using the default emission factor of 0.007  $\mu g$  I-TEQ/t - to air and 0.1  $\mu g$  I-TEQ/t - to products the emission to air is estimated at < 0.01 g I-TEQ/year to air and < 0.3 g I-TEQ/year to products.

## 2.8.2 Crematoria

It is not a common way of burying human corpses in Poland. There are only a handful of small crematoria in operation (not in continuous operation). The total number of corpses burnt in 2000 was app. 6,000. However, it is expected that the number of crematoria will increase in the near future. Default emission factors for crematoria range from 0.4 to 90  $\mu g$  I-TEQ per cremation dependent on the control. Total emission from crematoria is estimated at 0.06 (0.03-0.14) g I-TEQ/year.

#### 2.8.3 Smoke Houses

Smoking of meat and other foodstuffs takes place on a number of facilities. The emission is mainly originating from burning of the wood.

According to GUS (GUS 2001b) 23,415 t of smoked fish were produced in 2000 and 856,600 t of cured meat products, of which 75-80% was smoked. According to expert opinion, app. 1/3 of the smoke house installations are old types without afterburner, and the remaining installations are newer with some APCS. In general, contaminated wood is not used at smoke houses in Poland.

The amount of wood used for smoking of meat is estimated at about 0.1-0.15 t of wood per tonne of smoked meat.

**Emission factor** 

The <code>Standardized toolkit</code> applies a default emission factor of 6 and 0.6  $\mu g$  I-TEQ/t for smoke houses without and with afterburners respectively. The uncertainty is estimated at  $\pm$  70%. The emission factors for release to residues are estimated at 0.125  $\mu g$  I-TEQ/t smoked product, based on an emission factor for burning of wood of 15  $\mu g$  I-TEQ/MJ, app. 15 t/MJ and a wood consumption of 0.1-0.15 t wood per t product.

Release of dioxins and furans

In total the releases to air is estimated at 1.6 (0.5-2.9) g I-TEQ/year, whereas app. 0.1 g is released to residues.

## 2.8.4 Dry Cleaning Residues

Release of dioxins and furans to dry cleaning residues is connected to the occurrence of PCP in textiles and the use of chlorinated solvents. The UNEP toolkit applies default emission factors of 50 and 3,000  $\mu g$  I-TEQ per tonne of dry cleaning residues for normal textiles and PCP treated textiles respectively. It has not been possible to obtain an estimate of the amount of residues generated in Poland, and no data have been identified in inventories from other countries. The amount of dioxins and furans in the residues is considered insignificant compared to residues from the major sources.

## 2.8.5 Bleaching and Disinfection

The formation of dioxins and furans by the use of hypochlorite and chlorine gas for disinfection and bleaching (apart from pulp and paper production) is not included in the UNEP toolkit, but will shortly be addressed here.

There are only a few investigations that have dealt with the issue. Adding 0.3 g chlorine/l to drinking water developed a dioxin concentration equal to 37 pg I-TEQ/L (Rappe et al. 1989). The water samples were chlorinated at a dosage rate, which is considerably higher (by a factor of one to two orders of magnitude) than the range of dosage rates typically used to disinfect drinking water. Adding the same amount of chlorine to two times distilled water developed 8 pg I-TEQ/l, meaning that some dioxin or precursors must have been present in the gas itself.

Under the test conditions examined by the Swedish Naturvårdsverket, dioxins were neither formed during dishwashing and laundry washing nor during bleaching by hypochlorite-containing bleach (quoted by U.S. EPA 2000).

Based on these few data, the total release of dioxins and furans from bleaching and disinfection to sewage in Denmark has been estimated at <0.5 g I-TEQ/year (Hansen et al 2000). No attempt has been made to estimate the potential release of dioxins and furans from this activity in Poland.

#### 2.8.6 Tobacco Smoking

Activity, emission factor

Like any other thermal process, "combustion" of cigarettes and cigars produces dioxins and furans. Investigations in Germany demonstrated emission factors around 0.1 pg I-TEQ per cigarette. There are no results for cigars, but the emis-

sion is by UNEP roughly estimated to be three times higher per item. Only emission to air is considered to be significant. The total amount of cigarettes produced in Poland in 2000 was 83,800,000 cigarettes (GUS 2001b).

With an emission factor of 1 x  $10^{-7}$  µg I-TEQ/piece the total emission to air is estimated at app. 0.008 g I-TEQ/year.

## 2.9 Disposal

Thermal disposal of waste is covered by Main Categories 1 and 6, whereas non-thermal/non-combustion waste disposal practices, which can lead to releases of dioxins and furans predominantly to water and land, are included in Main Category 9, 'Disposal'. The category can be categorised into five subcategories:

- Landfills and water dumps
- Sewage and sewage treatment
- Open water dumping
- Composting
- Waste oil disposal (non-thermal)

Open water dumping does not take place in Poland.

## 2.9.1 Landfills and Waste Dumps

Dioxins disposed of to landfills and waste dumps may slowly be released to the surroundings with percolating water. In Poland only a few landfills with bottom film lining and leachate collection exist, and no data have been obtained on the discharge to surface waters with leachate from the landfills. From other landfills and waste dumps dioxins may diffuse to the surrounding in a more uncontrolled manner. Landfills and waste dumps may serve as reservoirs for potential dioxins releases in the future.

## 2.9.2 Sewage and Sewage Treatment

Dioxins and furans may be present in sewage. Analyses of dioxins and furans in sewage and sewage sludge have not been carried out in Poland.

Activity

According to GUS (GUS 2001c) 1,494,000,000 m³ of municipal sewage was generated in 2000. Of this, 1,243,422,000 m³ was treated including 450,475,000 m³ that was treated with efficient removal of biogenic substances. The density of effluents was assumed to be equal to that of water, i.e. 1t/m³.

In total 354,115 t of dry mass of sludge was produced (GUS 2001c). The sludge is commonly disposed of on agricultural land.

**Emission factor** 

The default emission factors for urban environments are used for all wastewater.

#### Emission to water:

- No sludge removal: 0.002 (0.001-0.003) µg I-TEQ/t of water;
- With sludge removal: 0.0005 (0.0002-0.001) µg I-TEQ/t of water.

#### Release to residues:

• Sludge removed: 100 µg I-TEQ/t of dry matter.

## Release of dioxins and furans

Potential dioxin release from sewage and sewage treatment could be 1.1 (0.5-2) g I-TEQ/year to water and 35 g I-TEQ/year to residues. A part of the dioxins in residues will ultimately end up on agricultural land. To obtain a more exact estimate it will be necessary to obtain actual measurements in effluents and sludge.

According to a recent Danish study (Hansen et al 2000) the main sources of dioxins and furans to sewage in Denmark seem to be atmospheric deposition, human excretions and washing of textile. The observed congener profile for dioxins in sewage sludge was according to Danish investigations correlated better to congener profiles for textiles than to profiles for air deposition. To what extent washing of textiles in Poland could also be a main source of dioxins and furans to wastewater is not known.

## 2.9.3 Composting

#### Activity

In 2000, the total amount of composted municipal waste was 248,300 t and 73,700 t of industrial waste (GUS 2001b). All larger composting plants use technology without prior sorting of waste. All hard parts (remains of glass, metals and plastics) are removed at a later stage of composting.

### **Emission factor**

The *Standardized toolkit* applies an emission factor of 100  $\mu g$  I-TEQ/t to product for 'All organic fraction', whereas an emission factor of 5  $\mu g$  I-TEQ/t is applied for 'Green materials from not impacted environments'. These emission factors are about 1,000 higher than usually observed (referred in Hansen et al. 2000), and it is here assumed that the factors in the *Standardized toolkit* should actually be in ng I-TEQ/t. For this reason an emission factor of 0.1 (0.003-0.3)  $\mu g$  I-TEQ/t is applied.

## Release of dioxins and furans

The total release to compost is estimated at 0.03 (0.001-0.1) g I-TEQ/year.

It should be noted that residues from domestic burning of coal and wood as well as residues from uncontrolled burning of waste may end up in compost e.g. in private gardens, and that the release of dioxins and furans by this route may be much higher than the release with compost of the organic fraction of the waste.

## 2.9.4 Waste Oil Disposal (Non-Thermal)

According to GUS (GUS 2001a) app. 116,100 t of waste oils were produced in 2000. 69% of this was reused (after refinement), 9.7% disposed of thermally (accounted for in section on hazardous waste incineration), 14.4% disposed of

with a non-thermal method, and the rest 10.3% was temporarily stored. Disposal of waste oil to landfills does not seem to take place.

#### 2.10 Potential Hot Spots

Hot spots' are sites with particularly high concentration of dioxins and furans due to release or inadequate disposal of contaminated materials. Release from these sites may already be ongoing or can be expected to begin, if no remedial action is taken.

No data on the actual release of dioxins and furans from hot spots exists, and no attempt has been done to develop models for estimating the potential releases from hot spots.

#### 2.10.1 Production Sites of Chlorine

There are three methods of production of chlorine and sodium lye from sodium chloride through electrolysis. In short, these three methods are termed as: Mercury, diaphragmal and membrane. In Poland, the two first methods have been in use. Dioxins and furans can be formed in the mercury method, when graphite electrodes (anodes) are used.

Graphite anodes are produced from various types of carbon-containing substances held together with various binders. Some oxygen liberates from the anodes with the chlorine and reacts with carbon forming carbon monoxide and carbon dioxide. This is the main cause of graphite electrode wear of 2-4 kg per ton of chlorine produced. The graphite residues (silt) can be contaminated by dioxins and furans which are formed from the reaction between chlorine, oxygen and pitch binder containing polycyclic aromatic hydrocarbons. In such cases, sites of mercury electrolysis should be monitored as well as sites of storing used anodes in order to eliminate any possible incorrect practices.

Graphite electrodes were used in the following chemical plants:

- Zakłady Azotowe (nitrogen plant) in Tarnów
- Chemical Plant "Rokita" (formerly: NZPO Rokita) and
- Chemical Plant Dwory (formerly: Zakłady Chemiczne Oświęcim).

Since 1986 the graphite electrodes have been gradually replaced by titanium electrodes. It seems that the electrolysis in Oświęcim will soon be discontinued, while the other two plants are going to be reconstructed for diaphragmal or membrane electrolysis.

The graphite residues and used electrodes have probably been burnt, but it is necessary to investigate to what extent contaminated residues and electrodes are stored or present in waste dumps and to take any suitable actions.

#### 2.10.2 Production of Chlorinated Organics

In plants and installations where chlorinated organics had been produced, there is a significant probability that there are some residues of these compounds in the buildings and soil on which they stand. High concentrations of dioxins and furans can be expected especially in places where chlorinated phenols or their derivatives were produced. If chlorinated phenols or their derivatives produced in those plants found their way to wastewater, then the sewage pipes in which they flowed can also be contaminated with sludge containing dioxins and furans. Moreover, if wastewater was kept in sediment tanks that were the last stage of sewage treatment or merely reservoirs for averaging the composition of sewage, it is probable that the sludge from these installations is also contaminated with dioxins and furans.

Chlorination of organic compounds have taken place in the following plants:

- Nitrogen Plant Azotowe in Tarnów (Mościcach) production of chlorine derivatives of methane;
- Anwil Plant in Włocławek production of PVC and solvents in processes of chlorination and oxychlorination of ethylene and propylene;
- Chemical Plant Dwory in Oświęcim chlorination of acetylene and benzene;
- Chemical Plant Rokita in Brzeg Dolny chlorination of benzene and phenol;
- Nitrogen Plant in Jaworzno production of hexachlorocyclohexane (lindane);
- Chemical Plant Zachem in Bydgoszcz chlorination of propylene for allyl chloride.

Releases of dioxins and furans could have taken place and probably did in Chemical Plant Rokita with chlorination of phenol for PCP, DCP and MCP (pentachlorophenol, dichlorophenol and monochlorophenol). Trichloroethylene and dichlorobenzenes were produced in the plant as well. However, the main product contaminated by dioxins and furans was pentachlorophenol (PCP).

Another plant where dioxins and furans could have been formed, is "Anwil" in Włocławek, with production of solvents, in which hexachlorobenzene was formed as residue (production of solvents have been discontinued) and in the oxychlorination process of ethylene to form 1,2-dichloroethane (component of for PVC production). There is an efficient system of hydrogen chloride retrieval and incineration of solid residues from production of vinyl chloride (VC) and PVC, so that only the system of sewage drainage and treatment remains to be analyzed to find out if there is formation of dioxins and furans.

Also in Anwil, VC and PVC are produced with the use of dichloroethane (EDC) as input. The formation of dioxins and furans has been registered in production processes with the use of ethylene. The "Anwil" plant makes use of ethylene which is produced in the "Orlen" plant in Płock, and which is transported to Włocławek through a pipeline. Gaseous chlorine is produced in situ in the diaphragmal electrolysis.

The "Anwil" plant has the capacity to produce 200,000 tons of PVC per annum. Capacities of chlorination and EDC cracking installations meet the needs of polymerisation. At this level of production, and using the emission factor recommended by UNEP -  $0.05~\mu g$  I-TEQ/t PVC (total for releases to air, wastewater, residues like silt and sludge, and to final product), the total emission of dioxins and furans would amount to 10~m g I-TEQ/year.

The actual emissions and actual release sites in the Anwil plant are not known. Therefore, options for emission reductions can be identified only after carrying out an analytical inventory of dioxins and furans at PVC complex in Włocławek.

In the other plants listed above, the probability of finding dioxins and furans in residues and sewage is very low. However, there are waste dumps, e.g. at the Chemical Plant Jaworzno, with residues contaminated by chlorinated organic compounds despite the fact that chlorination processes were discontinued a long time ago. The probability of finding similar waste dumps in the other plants is lower. The only feasible option at those plants is to take inventory actions in order to assess the actual state. At the Chemical Plant Jaworzno it seems that the situation is assessed pretty well. However, there exists no action plan to eliminate the threat posed by chloroorganic compounds (HCH) that were stored at waste dumps in the past.

## 2.10.3 Sites of Formulation and Use of Preparations Containing Chlorinated Phenols

As there are no reliable data on all sites in which formulation of preparations containing chlorinated phenols could have taken place, especially sites in which PCP-containing preparations were produced and used, we decided to combine this section with the one on wood processing sites. In the future, an inventory of all such sites needs to be carried out.

On locations where biologically active PCP-containing preparations were produced, there is a probability of contamination of soil and the elements inside of buildings with PCP itself as well as dioxins and furans that appear most often as an addition to PCP. We have a similar situation with the use of preparations containing PCP and also other derivatives of chlorinated phenols, like e.g. 2,4,5-T and 2,4-D as pesticides in agriculture. Contamination could have taken place especially at sites where these preparations were filled into tanks of machinery and devices that were used for spraying plants, or where contaminated agricultural machinery was washed. Analogous situations exist in wood processing plants, e.g. in sawmills where wood preservation was carried out with PCP-containing preparations.

Pentachlorophenol had been produced in Poland only at Chemical Plant Rokita at Brzeg Dolny. The production stopped more than ten years ago. Still produced in that plant are 2,4-dichlorophenol and acid 2,4-D. This acid is then, on the same location, transformed into ready for use products for agriculture. So, if production is concerned, there is only a single site potentially contaminated by chlorinated phenols.

During this study, due to a limited timeframe, it was not possible to carry out a detailed inventory of all sites where chlorinated phenols or chlorinated phenol-containing preparations were used. Such an inventory can be prepared with the participation of Polish Association of Plant Protection, Association of Plant Protection Means Producers and Polish Economic Chamber of Timber Industry. The main obstacle here is the large number of enterprises and organizations in the field and the necessity to obtain approval from of all the companies involved for relevant data collection and consent for making the data public in publicly available report.

Although, the only Polish producer of chlorinated phenols is the Rokita plant, there are a number of western companies operating on the Polish market that offer preparations for use in agriculture and in the timber industry. The data of the Ministry of Agriculture and Rural Development, indicate that no preparations containing PCP or 2,4,5-T were allowed for use in Poland. In the list of pesticides and herbicides allowable for use, there are, however, imported substances that contain 2,4-D as an active substance.

Polish preparations for wood preservation do not contain PCP. The same applies to imported substances. This is confirmed by the fact that all the substances obtained, required in Poland certificates issued by the National Board of Hygiene and technical approvals issued by the Institute of Construction Technology. These means are usually provided by well known West European companies, e.g. BASF that guarantee correct quality of these substances.

#### 2.10.4 Transformers and Capacitors Filled with PCB

In 1994, the Institute of Power Sector, carried out an inventory of the amount of PCB present in electrical and power equipment in the power industry (Kachniarz 1996, Kołsut 2001). The study with questionnaires covered 33 plants that use large transformers and capacitors filled with dielectric fluid representing app. 30% of total number of all such plants. In addition, some samples were taken in selected transformers and analyzed for PCB content.

In accordance with domestic policy, transformers filled with oil used for installations within the power grid and in power stations (at transformer stations of highest voltage, power plants and combined heat and power plants) contained exclusively mineral oil. In eight power distributing plants there are no PCB-containing devices, and in the remaining 25 plants the only such devices are capacitors for voltage range between 50 and 150 kV. The total number of these capacitors is app. 4,300, and the respective amount of sealant is app. 26.5 t. (see Annex 4.). On the basis of this pilot study, it was concluded that the total amount of PCB in the entire power industry does not exceed 100 metric tons.

The amount of PCB contained in devices used in the power industry, was also estimated within the research project "Counteracting PCB contamination of the environment in Poland" carried out at the Institute of Chemistry and Oil and Coal Technology of Wroclaw Technical University. According to preliminary estimates there are about 150,000-200,000 capacitors in use in Poland (excluding power industry) each containing app. 4 litres of sealant. Those capacitors

were produced at the "Elektromontaż" plant in Bydgoszcz, which manufactured in total 80,000 PCB-containing capacitors over the period 1980 - 1990. Their lifetime is expected to be 20 years. The production stopped in 1991. Therefore, it can be estimated that the amount of PCB in electrical equipment outside power industry does not exceed 1,000 t.

Not all capacitors in Poland contain PCB. According to a recent study prepared by the Institute of Chemistry and Oil and Coal Technology, among 34,000 analyzed capacitors, 11,000 contained PCB, and 611 items were scrapped due to poor condition (Kachniarz 1996, Kołsut 2001).

To reduce PCB emission, and indirectly emission of dioxins and furans, it is necessary to

- take firm actions to identify, mark and scrap devices containing more than 19%, of polychlorinated biphenyls of capacity exceeding 5 litres;
- take firm efforts to identify, mark and scrap devices containing more than 0.05% of polychlorinated biphenyls of capacity exceeding 5 litres;
- identify and scrap devices containing more than 0.005% of polychlorinated biphenyls of capacity exceeding 5 litres.

It seems that despite the studies carried out so far, a new inventory work should be carried out in order to identify and assess the actual situation, as scrapping of the capacitors after partly emptying might cause significant emissions of dioxins and furans, PCBs and HCB during thermal processes in the iron and steel industry.

#### 2.10.5 Dumps of Wastes/Residues from Categories 1-9

Dioxins and furans can be also released from dumps of wastes and residues formed during the processes described in the previous sections of this report. Such types of sources have not been inventoried in Poland with respect to possible dioxins and furans releases. Below we present some general information on dumps of waste and residues that can be considered as potential sources of emissions of the substances in question.

High concentrations of dioxins and furans are first of all found in fly-ash and residues from flue gas treatment, in which contaminants in addition are relatively mobile. Bottom-ash and slag contain a relatively low concentration of dioxins and furans.

**Residues from waste incineration.** The residues from waste incineration are in general stored at dumps for waste from the power sector. Official public statistics do not cover that waste as a separate category.

**Residues from thermal processes in metallurgy** (especially slag) are stored at own dumps at steelworks. There are 7 such waste dumps at mills currently in operations, and app. 20 sites near steelworks that had been closed down.

**Residues from fuel combustion for power generation** (mainly slag and ashes) are stored in large quantities all over the country. According to available

statistical data for the year 2000 the amount of ash-slag mixtures stored was app. 4,200,000 t.

Residues and waste from chemicals. These residues and waste include: App. 300 dump sites of pesticides residues and other hazardous waste (in total app. 7,000 t), sludge from chlorine produced with mercury method (5 facilities), dumps of industrial waste containing HCH and PCP (2 facilities), facility sludges from wastewater treatment plants in pulp producing plants (3 facilities) and paper (more than 10 facilities). Some of these facilities have been described earlier (see subsection 2.7).

#### 2.10.6 Sites of Relevant Industrial and Road Transport Accidents

For the last 20 years there has been a system in Poland of inventorying of all kinds of industrial and transport accidents run by National Centre for Coordination of Rescue Work and Protection of Population. All occurrences are registered immediately at the central database of the Centre. The database includes the name of the chemical substance if the accident covered a hazardous substance. Moreover, all fires are registered, including forest, peat land fires, and incidents with burning of grassland in rural areas.

The content of the database is not published. Use of the database for purposes like this study requires a special search (e.g. with respect to transformer fires, or fires of store houses or installations containing chlorinated organics).

An analysis of accidents during the period 1988 - 1992 showed 700 registered incidents of which: 151 posed a significant threat to environment. Those accidents were characterized by leakage or other release to the environment of hazardous substances, 11 concerned explosions and/or fires. 80% of all substances that contaminated the environment, were liquid fuels (in total leaked 3,600 t), 8% - compressed gases, 7% - toxic substances and 5% - caustic substances.

#### 2.10.7 Dredging of Sediments

There is no information on dredging of sediments with a particularly high content of dioxins and furans, e.g. sediments downstream pulp mills in which elemental chlorine have formerly been used for bleaching.

#### 2.10.8 Kaolinitic or Ball Clay Sites

In recent years a number of investigations have demonstrated the presence of dioxins and furans in clays, among others mined ball clay from the USA and kaolinite clay from Germany. Dioxins in clay may end up in feeding stuff, if the clay is used for production of feed pellets. The possible releases of dioxins from mining of clay are discussed in the recent U.S. inventory (US EPA 2000) in which it is concluded that insufficient evidence is available to make even a preliminary estimate of releases.

There are significant resources of silty ceramic substances in Poland. There are 1331 documented sites of which 471 (843,000,000 t) were exploited in 2000.

In 2000, approximately 300,000 t of kaolinitic substances and 200,000 t of ceramic (ball) clay were extracted in Poland. There are no measurements of concentrations in those substances. The kaolinitic substances have similar mineral composition as kaolin which is used for porcelain production. Kaolin itself is not extracted in Poland.

## 3 Further Development of the Inventory

The present inventory should be considered the first step and can be further improved by further assessments of activities and technology and by actual measurements. The further assessments aim at reducing the uncertainty of the estimates and thus provide a more profound basis for a prioritization of the measures for reducing the formation and releases of dioxin and furans.

Measurements

Apart from the category "Medical waste incineration" the inventory is based on emission factors derived from experience in other countries. To obtain very certain estimates on all activities would imply a very comprehensive measurement program. For the next step in developing the inventory and for prioritizing of measures it is recommended to at least carry out measurements within the following categories:

- Hazardous waste incineration and industrial waste incineration. Measurements should be undertaken at all facilities, and programs with regularly monitoring of the emission should be initiated.
- Sintering plants. Measurements should be undertaken at all facilities.
- Steel plants with electric arc furnaces. Measurements should be undertaken at all facilities.
- Plants for secondary production of aluminium, copper, zinc and lead.
   Measurements should be undertaken at all facilities.
- Cement and lime plants. Measurement may be undertaken at representative facilities and the technological parameters for extrapolation of the results to other facilities should be obtained.
- Cold air cupola foundries. Measurement may be undertaken at representative foundries, and the technological parameters for extrapolation of the results to other foundries should be obtained.
- Domestic burning of coal. A measurement program on the burning of different types of Polish coal should be undertaken.
- Chemical products. Measurements of dioxin and furan contamination of selected products e.g. 2,4-D should be undertaken.
- Potential hot spots around chemical plants and installations where chlorinated organics have been produced should be further assessed by actual measurements.

Emission from other sources may be highly relevant at a local level, and the list above only represents the first priority categories.

Further assessments of activities

It is deemed very difficult to reduce the uncertainty on the emission factors used for uncontrolled burning processes, but as the next step the activities and

the mechanisms behind the uncontrolled burning of waste should be further studied. It means that the uncontrolled burning of waste in households and the extent of landfill fires should be assessed in more detail.

The possible formation of dioxins and furans as by-product in the chemical industry - in products, waste and direct releases - should be further assessed.

Further assessments of technology

For a number of the categories the disaggregation of the activities on different technology specific classes highly influences the estimated total emission from the category. The disaggregation can be further improved by obtaining more exact information from all facilities - especially within the categories 'Waste incineration' and 'Ferrous and non-ferrous metal production'. It is, however, recommended to combine further assessment of the technological parameters with actual measurements of emission either from all or from representative facilities.

## 4 Measures for Reducing the Formation and Release of Dioxins and Furans in Poland

A general introduction to measures for reducing the formation and release of dioxins and furans is provided in Annex 6. The Annex describes the techniques for reducing the emission in further detail.

The measures can be divided into measures for **reducing the formation** of dioxins and furans and measures for **reducing the releases** of already formed compounds.

Measures for reducing the formation

Measures for **reducing the formation** addresses the presence of chlorine or chlorinated compounds in raw materials, products and fuels and changes in processes that may lead to formation of dioxins and furans. Examples of these measures are:

- Avoidance of halogenated scavengers in gasoline;
- Changed synthesis pathways in chemical industry and reduced production and use of certain halogenated chemicals;
- Avoidance of chlorine bleaching, e.g. in the paper and pulp industry;
- Avoidance of household burning of waste and contaminated wood;
- Reduction in the use of halogen-containing products especially precursors for dioxin and furan formation - and thereby reduction in the formation of dioxins and furans by waste incineration and accidental fires;
- Increased sorting of waste products for incineration or reprocessing, e.g. avoidance of PVC in scrap for aluminium remelting;
- Modifications of process technology, e.g. increasing the temperature in the combustion chamber and reducing the residence time in the critical region of temperature for dioxin formation in the flue gas system.

Measures for reducing the releases

The measures for reduction of releases may be divided into measures for **destruction of dioxins** and furan already formed and measures for **reducing the direct releases to the environment** by adsorbing the dioxins and furans to the residuals. These measures primarily concern changes in flue gas cleaning systems. Examples of these measures are:

- Destruction of dioxins and furans by selective catalytic reduction;
- Adsorption with activated charcoal and subsequent thermal destruction;
- Adsorption with mixtures of activated charcoal and lime with subsequent deposition of residuals.

## 4.1 Possible Measures for Reducing the Releases in Poland

More specifically the following measures should be considered for reduction of the releases of dioxins and furans in Poland. For the major source categories measures are already implemented in the most modern of the facilities, and a very significant reduction in the total emission can be obtained by upgrading all facilities to the technological level of the facilities with the best available technology. For all categories it will be necessary to carry out more detailed assessments of the actual processes and technology to come up with detailed site specific measures.

#### Waste incineration

 Upgrading APCS in existing incinerators, especially for hazardous waste and industrial waste; better control of technological processes (temperature, oxygen supply). Complying with the requirements of the EU directive on waste incineration will in general reduce the emission of dioxins and furans from waste incineration significantly.

#### Municipal waste:

 The actual emissions will increase with the growing number of incineration plants in operation and growing amount of waste; it is desirable to promote sorting of waste and recycling to decrease the total amount of generated waste for incineration.

#### Industrial waste:

- Improvements in and modernization of existing installations; introduction of modern incineration plants and closing down of old plants;
- Measures aimed at further decrease of generated waste; promotion of recycling.

#### Hazardous waste:

• Improvements in and modernization of existing installations; introduction of modern incineration plants.

#### Medical waste:

- Closing down old hospital waste incinerators with no APC systems;
- Improvements in and modernization of existing installations; introduction of modern incineration plants;
- Measures aimed at further decrease of generated waste; treatment of municipal waste generated in health care system in municipal rather than in medical waste incinerators.

#### Sewage sludge incineration:

- Improvements in and modernization of existing installations; introduction of modern incineration plants,
- As only part of sewage sludge is incinerated, decrease of total amount of sludge does not lead directly to the decrease of emissions; some households in rural areas are not yet covered by the sewage system.

#### Ferrous and non-ferrous metal production

- Decreasing the share of ore sintering for blast furnaces (e.g. closing down an old installation in Huta Częstochowa, reduction of the number of sintering grates in operation in Sendzimira and Katowice Steelworks);
- Redirecting the flue gases into the process (done in Huta Katowice);

- Further use of modern APCS, fitted with e.g. afterburners, fabric filters; use of active carbon and lime injection;
- Further use of wet scrubbers, quenching of flue gases, leaching;
- Scrap pre-treatment and cleaning elimination of oils, fats, paints, plastics; such a process has already been implemented at the metal plant "Skawina".
- Improved implementation of Polish norms with regard to scrap (Law on Waste)
- Improved process control optimizing the flue gas temperature.

#### Power generation

- Fuel switch from coal and lignite to liquid and gaseous fuels;
- Modernization of APCS.

#### Production of mineral products

- Increasing share of the dry method for cement production;
- Implementation of more efficient APCS (yielding PM emission below 50 mg/m³) with fabric filters and temperature of flue gases below 200°C above the filter:
- Decommissioning of old installations and replacing them by modern ones with good APCS (lime production);
- Further introduction of modern technologies of (continuous) brick production;
- Fitting additional APCS in large glass plants.

#### **Transport**

- Total elimination of leaded gasoline;
- Avoiding chlorinated additives to fuels and lubricants.

#### Households/Uncontrolled combustion process:

- Reduced use of coal-fired stoves; promotion of central heating and hot water supply in suburban areas;
- Replacing coal-fired stoves by stoves fired with natural gas in rural areas;
- There seems to be no obvious options to reduction of dioxin emission from burning of pure wood by optimising the operating conditions. As wood is a renewable energy source, decreasing the use of wood for domestic heating is not recommended.
- Reduction of waste co-combusted with coal and wood in households by:
  - Introduction of incentive-based waste collection, sorting and recycling;
  - Educational measures (e.g. leaflets); informing about the need for waste sorting, not combusting PVC containing waste, contaminated wood, etc.
- Reduced use of chlorinated plastics especially for packaging may significantly reduce the formation of dioxins by waste burning in households and by landfill fires.
- Reduced use of chlorinated compounds for preservation of wood and chlorinated plastics in the building sector will reduce future formation of dioxins and furans from burning of demolition waste and accidental fires.
- Avoid landfill fires by improved landfill techniques.

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#### **ANNEX 1**

### **Toxicity Equivalency Factors**

Dioxins and furans are always found in samples as a mixture of various congeners. The most toxic is 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD). The toxicity of other chlorinated dioxins and furans is estimated relatively to 2,3,7,8-TCDD. Today only congeners with chlorine atoms in the 2,3,7,8-positions are considered to have a toxic mechanism similar to TCDD.

Over the years a number of toxicity equivalency factor systems have been developed. The dominating system during the nineties has been the international system that was developed by a NATO-working group in the late eighties. This system replaced more or less the German UBA-system from 1985, the Nordic system from 1988 as well as older systems developed by USEPA.

Recently - in 1998 - a new system was developed by a WHO Working Group (UNEP 1999). In Table A1.1 the factors for the WHO and the international systems are listed. The differences are indicated in bold. In addition, WHO has also developed toxicity equivalency factors for a number of non-*ortho* and mono-*ortho* substituted PCBs (coplanar PCBs).

The knowledge of brominated dioxins is less developed. On an interim basis WHO suggests that the current toxicity equivalency factors for chlorinated dioxin congeners are also applied to similar brominated dioxin congeners /IPCS 1998/.

The toxicity equivalence (TEQ) of a measurement is calculated by multiplying the measured concentration of each congener by the corresponding TEF followed by an addition of the results for each congener.

In the *Standardized toolkit* (UNEP 2001) and this report the international toxicity equivalence system (I-TEQ) is used.

Table A1.1 International and WHO toxicity equivalency factor systems for dioxins and furans (differences indicated by using bold)

Congener **	WHO 1998	International (NATO) 1989
	WHO-TEF *	I-TEF
Dioxins:		
2,3,7,8-TCDD	1	1
Other TCDDs	0	0
1,2,3,7,8-PeCDD	1	0.5
Other PeCDDs	0	0
1 2,3,4,7,8-HxCDD	0.1	0.1
1,2,3,6,7,8-HxCDD	0.1	0.1
1,2,3,7,8,9-HxCDD	0.1	0.1
Other HxCDDs	0	0
1,2,3,4,6,7,8-HpCDD	0.01	0.01
Other HpCDDs	0	0
OCDD	0.0001	0.001
Furans:		
2,3,7,8-TCDF	0.1	0.1
Other TCDFs	0	0
1,2,3,7,8-PeCDF	0.05	0.05
2,3,4,7,8-PeCDF	0.5	0.5
Other PeCDFs	0	0
1 2,3,4,7,8-HxCDF	0.1	0.1
1,2,3,6,7,8-HxCDF	0.1	0.1
2,3,4,6,7,8-HxCDF	0.1	0.1
1,2,3,7,8,9-HxCDF	0.1	0.1
Other HxCDFs	0	0
1,2,3,4,6,7,8-HpCDF	0.01	0.01
1,2,3,4,7,8,9-HpCDF	0.01	0.01
Other HpCDFs	0	0
OCDF	0.0001	0.001

<sup>\*</sup> The TEF-values stated cover exposure to humans and mammals. Separate and slightly different TEF-values have been stated for fish and birds /UNEP 1999/.

<sup>\*\*</sup> The first letters refer to the number of chlorine atoms: T (4), Pe (5), Hx (6), Hp (7) and O (8).

# ANNEX 2 Dioxin and furan emission data from hospital waste incinerators in Poland

Analytical results from the determination of dioxins and furans in stack gases sampled from 60 hazardous waste incinerators in Poland is shown in Table A2.1. In general one measurement was taken only from each incinerator. Determination was performed between 1996 and 2001.

For details about sampling method and analytical techniques please see Grochowalski (1998).

Table A2.1 Dioxin and furan emission data from 60 hospital waste incinerators in Poland, 1996-2001. The measurements are ordered with increasing PCDD/F concentrations in the flue gases.

No.	Class	Stack gas diox- ins concentra- tion ng-TEQ/Nm³	Mass of hospital wastes incinerated t/h	Stack gas emission in Nm³/h	Emission factor μg-TEQ/t
1	Complying New	0.02	0.075	1450	0.39
2	Complying New	0.04	0.15	3200	0.85
3	Complying Improved Old	0.045	0.20	8830	1.99
4	Complying New	0.05	0.08	2850	1.78
5	Complying New	0.05	0.10	4200	2.10
6	Complying Improved Old	0.055	0.05	900	0.99
7	Complying New	0.06	0.26	4300	0.99
8	Complying New	0.065	0.60	3950	0.43
9	Complying New	0.075	0.06	1090	1.36
10	Complying New	0.075	0.05	1200	1.80
11	Complying New	0.075	0.05	1160	1.74
12	Complying Improved Old	0.08	0.085	2150	2.02
13	Complying New	0.10	0.18	2300	1.28
14	Complying New	0.10	0.08	1820	2.28
15	Non-complying New	0.12	0.32	4250	1.59
16	Non-complying New	0.18	0.45	6700	2.68

No.	Class	Stack gas diox- ins concentra-	Mass of hospital wastes inciner-	Stack gas emission in Nm <sup>3</sup> /h	Emission factor μg-TEQ/t
		tion ng-TEQ/Nm <sup>3</sup>	ated t/h		. 0
17	Non-complying New	0.20	0.25	4660	3.73
18	Non-complying Improved Old	0.20	0.05	550	2.20
19	Non-complying New	0.20	0.09	2820	6.27
20	Non-complying New	0.22	0.12	3500	6.42
21	Non-complying New	0.23	0.18	2250	2.88
22	Non-complying New	0.24	0.35	8900	6.10
23	Non-complying Improved Old	0.24	0.185	6700	8.69
24	Non-complying New	0.25	0.045	1530	8.50
25	Non-complying New	0.25	0.08	1600	5.00
26	Non-complying New	0.29	0.075	1470	5.68
27	Non-complying Improved Old	0.32	0.20	4500	7.20
28	Non-complying Improved Old	0.39	0.35	2230	2.48
29	Non-complying New	0.40	0.025	600	9.60
30	Non-complying Improved Old	0.42	0.13	1900	6.14
31	Non-complying Improved Old	0.45	0.70	7320	4.71
32	Non-complying Improved Old	0.48	0.27	2950	5.24
33	Non-complying New	0.88	0.35	4460	11.21
34	Non-complying New	0.98	0.06	1050	17.15
35	Non-complying Improved Old	1.25	0.275	5900	26.82
36	Non-complying Improved Old	1.60	0.075	2800	59.73
37	Non-complying Improved Old	2.0	0.10	3650	73.00
38	Non-complying New	2.2	0.12	2400	44.00
39	Non-complying New	2.5	0.045	700	38.89
40	Non-complying New	2.6	0.85	6125	18.74

No.	Class	Stack gas diox- ins concentra- tion ng-TEQ/Nm³	Mass of hospital wastes incinerated t/h	Stack gas emission in Nm³/h	Emission factor μg-TEQ/t
41	Non-complying Old	3.8	0.10	3470	131.86
42	Non-complying Improved Old	9.7	0.275	4280	150.97
43	Non-complying Old	11.5	0.115	3350	335.00
44	Non-complying Improved Old	12.1	0.30	1560	62.92
45	Non-complying Improved old	15.0	0.48	3725	116.41
46	Non-complying Improved Old	18.5	1.45	11300	144.17
47	Non-complying Old	22	0.45	1700	83.11
48	Non-complying Improved Old	26	0.32	2770	225.06
49	Non-complying Old	29	0.225	4000	515.56
50	Non-complying Old	29	0.12	1525	368.54
51	Non-complying Old	32	0.25	4600	588.80
52	Non-complying Improved Old	33	0.16	1380	284.63
53	Non-complying Old	33	0.056	800	471.43
54	Non-complying Very old	36	0.08	1200	540.00
55	Non-complying Very old	36.5	0.21	3400	590.95
56	Non-complying Very old	38	0.40	5480	520.60
57	Non-complying Old	41	0.125	1650	541.20
58	Non-complying Very old	43	0.33	2050	267.12
59	Non-complying Very old	64	0.075	1100	938.67
60	Non-complying Improved old	82	0.13	1400	883.08

Class A: Very old - older than 1960 – uncontrolled process, no APC - older than 1990

Class B: Non-complying New and Non-complying Improved Old (- old chamber, new thermoreactor and new APC)

Class C: Complying New - new design, construction not older than 1994

# **ANNEX 3**Calculation of Total Amount of Materials Burned in Accidental Fires

Data according to statistics of Fire Department.

	Calculation of total amount of materials burned in accidental fires						
type of object and type of fire	number of fires	average area of fire [m²]	total area of fire [m²]	material amount multi- plication factor [kg/m²]	amount of material burned [kg]	total amount of material [t]	
public buildings						3 706.8	
small	2 917	60	175 020	15	2625 300		
medium	170	250	42 500	15	637 500		
large	28	700	19 600	15	294 000		
very large	4	2500	10 000	15	150 000		
flats and houses						22 682.1	
small	22 088	55	1214 840	15	18222 600		
medium	1 088	250	272 000	15	4080 000		
large	29	700	20 300	15	304 500		
very large	2	2500	5 000	15	75 000		
production plants						2 823.2	
small	2 132	60	127 920	10	1279 200		
medium	338	250	84 500	10	845 000		
large	57	700	39 900	10	399 000		
very large	12	2500	30 000	10	300 000		
warehouses						3 164.5	
small	1 218	60	73 080	20	1461 600		
medium	167	250	41 750	20	835 000		
large	37	700	25 900	20	518 000		
very large	7	2500	17 500	20	350 000		
Total						32 376.7	

### ANNEX 4 List of Power Plants that use Capacitors Containing PCB

List of power plants that use capacitors containing PCB

Plant Num	ber of capacitors	PCB [ kg]
Będzin	24	120
Białystok	325	1769
Częstochowa	207	1185
Elbląg	24	120
Gorzów	126	1008
Jelenia Góra	22	110
Kalisz	96	687
Koszalin	100	515
Kraków	12	60
Legnica	158	1315
Lublin	611	3851
Łódź	24	120
Opole	369	2262
Płock	45	280
Poznań	105	1053
Rzeszów	437	3131
Skarżysko-Kamienna	105	525
Słupsk	17	85
Szczecin	95	480
Tarnów	48	240
Toruń	27	165
Wałbrzych	189	1017
Warszawa	118	809
Zamość	505	3371
Zielona Góra	234	2207
Total	4023	26485

# **Annex 5 Largest Foundries in Poland**

The list of 10 largest **iron-cast foundries** with production output in 2000 includes:

•	CENTROZAP S.A.	– 87 200 t
•	Teksid Poland Skoczów	- 60 000 t
•	KRAKODLEW S.A.	– 42 600 t
•	ZNTK Bydgoszcz	$-20\ 000\ t$
•	METALODLEW S.A.	– 19 150 t
•	Odlewnie Polskie S.A.	– 18 000 t
•	Koneckie Zakłady Odlewnicze S.A.	– 16 100 t
•	WSK PZL Rzeszów	– 15 000 t
•	Electric engine plant "TAMEL" Tarnów	– 13 000 t
•	Industrial equipment plant "ZETKAMA" S.A.	– 10 000 t

The list of ten largest **steel-cast foundries** with production output in 2000 includes:

•	MAŁAPANEW Foundry plant at Ozimek	– 12 300 t
•	Bumar Łabędy	- 6 500 t
•	MISTAL Myszków	- 6 000 t
•	PIOMA – Piotrków Trybunalski	- 6 000 t
•	ALSTOM Power Elblag	- 5 800 t
•	STALCHEMAK Siedlce	- 4 000 t
•	METALODLEW Kraków	- 3 500 t
•	Odlewnie Polskie	- 2 500 t
•	Huta Katowice	- 2 000 t
•	FUGO Konin	- 1 700 t

The list of 10 largest **non-ferrous metal foundries** with production output in 2000 includes:

•	ALSTOM Power Elblag	– 1 500 t (Cu alloys)
•	Fabryka Akcesoriów Meblowych S.A.Chełm	no – 2 700 t (Mg, Zn)
•	Krakowska Fabryka Armatur S.A.	- 3 000 t (Al, Cu, Zn)
•	WSK PZL Rzeszów	- 1 500 t (Al, Mg)
•	ZELMER Rzeszów	– 2 000 t (Al, Zn)
•	Zakłady Mechaniczne PZL-Wola	– 1 000 t (Al, Cu)
•	SPOMEL Lębork	- 400 t (Al)
•	Odlewnia SILUM	- 900 t (Al, Zn)
•	Zakłady Metalowe ALMET, Nisko	- 600 t (Al, Zn)
•	Fabryka Silników Elektrycznych TAMEL	– 450 t (Al).

#### **ANNEX 6**

## Measures for Reducing the Formation and Releases of Dioxins and Furans

A general introduction to measures for control of dioxin and furan emissions has been presented in two annexes to 'Protocol to the 1979 Convention on Long-range Transboundary Air Pollution on Persistent Organic Pollutants'. The following general introduction is to a wide extent based on these.

For the discussion of measures for reducing the formation and release of dioxins and furans it is convenient to distinguish between mobile sources and stationary sources.

#### Stationary sources

There are several approaches to the control or prevention of emissions of dioxins, furans and other POPs from stationary sources. The following list provides a general indication of available measures, which may be implemented either separately or in combination:

- Replacement of feed materials which are POPs or where there is a direct link between the materials and dioxin and furan emissions from the source;
- Best environmental practices, such as good housekeeping, preventive maintenance programmes or process changes, such as closed systems;
- Modification of process design to ensure complete combustion, thus preventing the formation of persistent organic pollutants through the control of parameters such as incineration temperature or residence time;
- Methods for flue-gas cleaning, such as thermal or catalytic incineration or oxidation, dust precipitation, adsorption;
- Treatment of residuals, wastes and sewage sludge by, for example, thermal treatment or rendering them inert.

Cost-efficient considerations may be based on total costs per year per unit of abatement (including capital and operational costs). POP emission reduction costs should also be considered within the framework of the overall process economics, e.g. the impact of control measures and costs of production. Given the many influencing factors, investment and operating cost figures are highly case-specific.

The main control measures for reducing dioxin and furan emissions from waste incineration facilities are:

- Primary measures regarding incinerated wastes;
- Primary measures regarding process techniques;
- Measures to control physical parameters of the combustion process and waste gases (e.g. temperature stages, cooling rate, O2 content, etc.);

- Cleaning of the flue gas;
- Treatment of residuals from the cleaning process.

The primary measures regarding the incinerated wastes, involving the management of feed material by reducing halogenated substances and replacing them by non-halogenated alternatives, are in general not appropriate for municipal or hazardous waste incineration. It is more effective to modify the incineration process and install secondary measures for flue-gas cleaning. The management of feed material is a useful primary measure for waste reduction and has the possible, added benefit of recycling. This may result in indirect reduction of dioxins and furans by decreasing the waste amounts to be incinerated.

The modification of process techniques to optimize combustion conditions is an important and effective measure for the reduction of dioxin and furan emissions (usually 850°C or higher, assessment of oxygen supply depending on the heating value and consistency of the wastes, sufficient residence time - 850°C for about 2 sec - and turbulence of the gas, avoidance of cold gas regions in the incinerator, etc.). Fluidized bed incinerators keep a lower temperature than 850°C with adequate emission results. For existing incinerators this would normally involve redesigning and/or replacing a plant. The carbon content in ashes should be minimised.

Flue gas measures

The following measures are possibilities of lowering reasonably effectively the dioxin and furan content in the flue gas. The de novo synthesis takes place at about 250 to 450°C. These measures are a prerequisite for further reductions to achieve the desired levels at the end of the pipe:

- Quenching the flue gases (very effective and relatively inexpensive);
- Adding inhibitors, such as triethanolamine or triethylamine (can reduce oxides of nitrogen as well), but side-reactions have to be considered for safety reasons;
- Using dust collection systems for temperatures between 800 and 1000°C, e.g. ceramic filters and cyclones;
- Using low-temperature electric discharge systems;
- Avoiding fly ash deposition in the flue gas exhaust system.

Methods for cleaning the flue gas are:

- Conventional dust precipitators for the reduction of particle-bound dioxins and furans;
- Selective catalytic reduction (SCR) or selective non-catalytic reduction (SNCR);
- Adsorption with activated charcoal or coke in fixed or fluidized systems;
- Different types of adsorption methods and optimized scrubbing systems
  with mixtures of activated charcoal, open-hearth coal, lime and limestone
  solutions in fixed bed, moving bed and fluidized bed reactors. The collection efficiency for gaseous dioxins and furans can be improved by the use
  of a suitable pre-coat layer of activated coke on the surface of a bag filter;
- H<sub>2</sub>O<sub>2</sub>-oxidation; and

• Catalytic combustion methods using different types of catalysts (i.e. Pt/Al<sub>2</sub>O<sub>3</sub> or copper-chromite catalysts with different promoters to stabilize the surface area and to reduce ageing of the catalysts).

The methods mentioned above are capable of reaching emission levels of 0.1 ng I-TEQ/m³ dioxins and furans in the flue gas. However, in systems using activated charcoal or coke adsorbers/filters care must be taken to ensure that fugitive carbon dust does not increase dioxins and furans emissions downstream. Also, it should be noted that adsorbers and dedusting installations prior to catalysts (SCR technique) yield dioxins and furans-laden residues, which need to be reprocessed or require proper disposal.

Waste incinerators

A comparison between the different measures to reduce dioxin and furan formation in flue gas is very complex. The resulting matrix includes a wide range of industrial plants with different capacities and configuration. Cost parameters include the reduction measures for minimizing other pollutants as well, such as heavy metals (particle-bound or not particle-bound). Consequently a direct relation for the reduction in dioxins and furans emissions alone cannot be isolated in most cases. A summary of the available data for the various control measures is given in Table A6.1.

Table A6.1 Comparison of different flue-gas cleaning measures and process modifications in waste incineration plants to reduce dioxins and furans emissions

Management options	Emission level (%) <sup>a/</sup>	Estimated costs	Management risks
Primary measures by modification of feed materials:  - Elimination of precursors and chlorine-containing feed materials; and - Management of waste streams.	Resulting emission level not quantified; seems not to be linearly dependent on the amount of the feed material.		Pre-sorting of feed material not effective; only parts could be collected; other chlorine-containing material, for instance kitchen salt, paper, etc., cannot be avoided. For hazardous chemical waste this is not desirable.  Useful primary measures are feasible in special cases (for instance, waste oils, electrical components, etc.) with the possible, added benefit of recycling of the materials.
Modification of process			
technology: - Optimized combustion conditions;			Retrofitting of the whole process needed.
- Avoidance of temperatures below 850°C and cold regions in flue gas;			
- Sufficient oxygen content; control of oxygen input depending on the heating value and consistency of feed material; and			
- Sufficient residence time and turbulence.			
Flue gas measures:			
Avoiding particle deposition by:			
- Soot cleaners, mechanical rappers, sonic or steam soot blowers.			Steam soot blowing can increase PCDD/F formation rates.
- Dust removal, generally in waste incinerators:	< 10	Medium	Removal of PCDD/F adsorbed onto particles. Removal methods of particles in hot flue gas streams used only in pilot plants.
- Fabric filters;	1 - 0.1	Higher	Use at temperatures < 150°C.
- Ceramic filters;	Low efficiency		Use at temperatures 800-1000°C.
- Cyclones	Low efficiency	Medium	
- Electrostatic precipitation.	Medium efficiency		Use at a temperature of 450°C; promotion of the de novo synthesis of PCDD/F possible, higher NOx emissions, reduction of heat recovery.
- Catalytic oxidation.			Use at temperatures of 800- 1000°C. Separate gas phase abatement necessary.



Management options	Emission level (%) <sup>a/</sup>	Estimated costs	Management risks
- Gas quenching.			
High-performance adsorption unit with added activated charcoal particles (electrodynamic venturi).			
Selective catalytic reduction (SCR).		High investment and low operating costs	NOx reduction if NH3 is added; high space demand, spent catalysts and residues of activated carbon (AC) or lignite coke (ALC) may be disposed of, catalysts can be reprocessed by manufacturers in most cases, AC and ALC can be combusted under strictly controlled conditions.
Different types of wet and dry adsorption methods with mixtures of activated charcoal, open-hearth coke, lime and limestone solutions in fixed bed, moving bed and fluidized bed reactors:			
Fixed bed reactor, adsorption with activated charcoal or open-hearth coke; and	< 2 (0.1 ng TE/m³)	High investment, medium operating costs	Removal of residuals, high demand of space.
Entrained flow or circulating fluidized bed reactor with added activated coke/lime or limestone solutions and subsequent fabric filter.	< 10 (0.1 ng TE/m³)	Low investment, medium operating costs	Removal of residuals.
Addition of H <sub>2</sub> O <sub>2</sub> .	< 2 - 5 (0.1 ng TE/m³)	Low investment, low operating costs	

a/ Remaining emission compared to unreduced mode.

Medical waste incinerators may be a major source of dioxins and furans in many countries. Specific medical wastes, such as human anatomical parts, infected waste, needles, blood, plasma and cytostatica are treated as a special form of hazardous waste, whereas other medical wastes are frequently incinerated on-site in a batch operation. Incinerators operating with batch systems can meet the same requirements for dioxins and furans reduction as other waste incinerators.

Parties may wish to consider adopting policies to encourage the incineration of municipal and medical waste in large regional facilities rather than in smaller ones. This approach may make the application of BAT more cost-effective.

Treatment of residuals from the flue-gas cleaning process.

Unlike incinerator ashes, these residuals contain relatively high concentrations of heavy metals, organic pollutants (including dioxins and furans), chlorides and sulphides. Therefore their method of disposal has to be well con-

trolled. Wet scrubber systems in particular produce large quantities of acidic, contaminated liquid waste. Some special treatment methods exist. They include:

- (a) The catalytic treatment of fabric filter dusts under conditions of low temperatures and lack of oxygen;
- (b) The scrubbing of fabric filter dusts by the 3-R process (extraction of heavy metals by acids and combustion for destruction of organic matter);
- (c) The vitrification of fabric filter dusts;
- (d) Further methods of immobilization;
- (e) The application of plasma technology.

Thermal processes in the metallurgical industry Specific processes in the metallurgical industry may be important, remaining sources of dioxins and furans emissions. These are:

- (a) Primary iron and steel industry (e.g. blast furnaces, sinter plants, iron pelletizing);
- (b) Secondary iron and steel industry;
- (c) Primary and secondary non-ferrous metal industry (production of copper).

dioxin and furan emission control measures for the metallurgical industries are summarized in Table A6.2.

Metal production and treatment plants with dioxins and furans emissions can meet a maximum emission concentration of 0.1 ng I-TEQ/m $^3$  (if waste gas volume flow 5000 m $^3$ /h) using control measures.

Management	Emission	Estimated	Management
Management options	level (%) <sup>a/</sup>	costs	risks
Sinter plants			
Primary measures:			
- Optimization/encapsulation of sinter conveying belts;		Low	Not 100% achievable
- Waste gas recirculation, e.g. emission optimized sintering (EOS) reducing waste gas flow by abt 35% (reduced costs of further secondary measures by the reduced waste gas flow), cap. 1 million Nm³/h;	40	Low	
Secondary measures:			
- Electrostatic precipitation + molecular sieve;	Medium efficiency	Medium	
- Addition of limestone/activated carbon mixtures;	High efficiency (0.1 ng TE/m³)	Medium	
- High-performance scrubbers - existing installation: AIRFINE (Voest Alpine Stahl Linz) since 1993 for 600 000 Nm3/h; second installation planned in the Netherlands (Hoogoven) for 1998.	High efficiency emission reduction to 0.2-0.4 ng TE/m <sup>3</sup>	Medium	0.1 ng TE/m³ could be reached with higher energy de- mand; no existing installation
Non-ferrous production (e.g. copper)			
Primary measures:			
- Pre-sorting of scrap, avoidance of feed material like plastics and PVC-contaminated scrap, stripping of coatings and use of chlorine-free insulating materials;		Low	
Secondary measures:			
- Quenching the hot waste gases;	High efficiency	Low	
- Use of oxygen or oxygen-enriched air in firing, oxygen injection in the shaft kiln (providing complete combustion and minimization of waste gas volume);	5 - 7 (1.5-2 TE/m³)	High	
- Fixed bed reactor or fluidized jet stream reactor by adsorption with activated charcoal or open-hearth coal dust;	(0.1 ng TE/m³)	High	
- Catalytic oxidation; and	(0.1 ng TE/m <sup>3</sup> )	High	
- Reduction of residence time in the critical region of temperature in the waste gas system.			
Iron and steel production			
Primary measures:			
- Cleaning of the scrap from oil prior to charging of production vessels;		Low	Cleaning solvents have to be used.
- Elimination of organic tramp materials, such as oils, emulsions, greases, paint and plastics from feedstock cleaning;		Low	
- Lowering of the specific high waste gas volumes;		Medium	
- Separate collection and treatment of emissions from loading and discharging;.		Low	
Secondary measures:			
- Separate collection and treatment of emissions from loading		Low	

and discharging; and			
- Fabric filter in combination with coke injection.	< 1	Medium	
Secondary aluminium production			
Primary measures:			
- Avoidance of halogenated material (hexachloroethane);		Low	
- Avoidance of chlorine-containing lubricants (for instance chlorinated paraffins); and		Low	
<ul> <li>Clean-up and sorting of dirty scrap charges, e.g. by swarf de- coating and drying, swim-sink separation techniques and whirl- ing stream deposition;</li> </ul>			
Secondary measures:			
- Single and multi-stage fabric filter with added activation of limestone/ activated carbon in front of the filter;	< 1 (0.1 ng TE/m³)	Medium/ high	
- Minimization and separate removal and purification of differently contaminated waste gas flows;		Medium/ high	
- Avoidance of particulate deposition from the waste gas and promotion of rapid passing of the critical temperature range; and		Medium/ high	
- Improved pretreatment of aluminium scrap shredders by using swim-sink separation techniques and grading through whirling stream deposition.		Medium/ high	

<sup>&</sup>lt;sup>a/</sup> Remaining emission compared to unreduced mode.

#### Mobile sources

In some countries 1,2-dibromomethane in combination with 1,2-dichloromethane is used as a scavenger in leaded petrol. In order to reduce the formation of dioxin and furans from mobile sources, the addition of halogenated scavengers and other halogenated compounds to petrol and other fuels and to lubricants should be avoided as far as possible.