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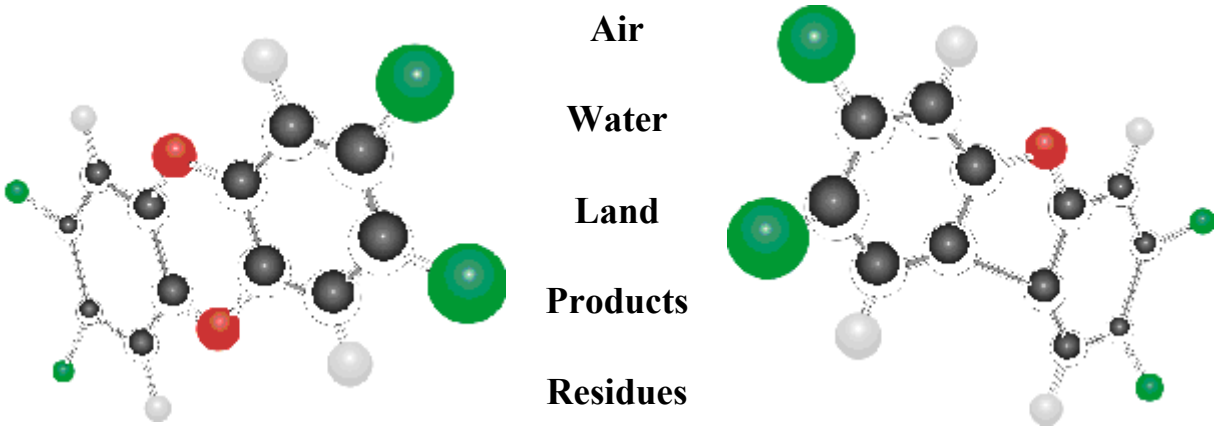
ENVIRONMENT PROGRAMME

Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases



1st edition
May 2003

Prepared by UNEP Chemicals
Geneva, Switzerland

IOMC

INTER-ORGANIZATION PROGRAMME FOR THE SOUND MANAGEMENT OF CHEMICALS
A cooperative agreement among UNEP, ILO, FAO, WHO, UNIDO, UNITAR and OECD

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The publication is intended to assist countries to establish release inventories of polychlorinated dibenzo-*p*-dioxins and dibenzofurans at a national or regional level. The information contained in this report was taken from the published scientific literature, from government reports as well as from the Internet and through personal communication. While the information provided is believed to be accurate, UNEP disclaims any responsibility for possible inaccuracies or omissions and consequences, which may flow from them. Neither UNEP nor any individual involved in the preparation of this report shall be liable for any injury, loss, damage or prejudice of any kind that may be caused by any persons who have acted based on their understanding of the information contained in this publication.

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This publication was updated by UNEP Chemicals based on the draft publication dated January 2001 and on comments from governments and non-governmental organizations according to decision 6/4 taken at the Sixth session of the Intergovernmental Negotiation Committee of the Stockholm Convention.

On the cover: Molecules of 2,3,7,8-tetrachlorodibenzo-p-dioxin and tetrachlorodibenzo-furan, courtesy of Wellington Labs, Guelph, ONT, Canada.

This publication is produced within the framework of the Inter-Organization Programme for the Sound Management of Chemicals (IOMC)

The Inter-Organization Programme for the Sound Management of Chemicals (IOMC), was established in 1995 by UNEP, ILO, FAO, WHO, UNIDO and OECD (Participating Organizations), following recommendations made by the 1992 UN Conference on Environment and Development to strengthen cooperation and increase coordination in the field of chemical safety. In January 1998, UNITAR formally joined the IOMC as a Participating Organization. The purpose of the IOMC is to promote coordination of the policies and activities pursued by the Participating Organizations, jointly or separately, to achieve the sound management of chemicals in relation to human health and the environment.

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UNEP CHEMICALS

May 2003

Preface

The Stockholm Convention on Persistent Organic Pollutants (POPs) requires Parties to reduce the total releases of unintentionally produced POPs such as polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/PCDF) with the goal of their continuing minimization and, where feasible, ultimate elimination. Accordingly, Parties will need to identify their sources of PCDD/PCDF and quantify their releases. The methodology used to assess sources should be consistent in order to assess PCDD/PCDF releases over time and between countries.

This first edition of the "Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases" (Toolkit) presents an update of the draft version, issued by UNEP Chemicals in January 2001. This update was developed in response to decision INC-6/4 taken by the POPs Intergovernmental Negotiating Committee (INC) at its Sixth Session in June 2002, and is based on comments from governments and non-governmental organizations. In its decision, the INC also noted "…that the Standardized Toolkit for the Identification and Quantification of Dioxin and Furan Releases provides a basis for the development of provisional guidance on the evaluation of current and projected releases of chemicals listed in annex C of the Stockholm Convention on Persistent Organic Pollutants".

The Toolkit has been introduced to countries in a series of training workshop and is being field-tested by a number of countries receiving assistance from UNEP. The Toolkit will be used to produce dioxin and furan inventories within the national implementation plans under the Stockholm Convention.

The Toolkit is flexible and can be applied to all countries: Countries with no PCDD/PCDF data at all will find the Toolkit helpful to screen industrial and other activities to make first estimates of the scale of potential PCDD/PCDF sources and releases. Countries with measured data may use the Toolkit to review and update the coverage of their inventory, as well as to seek agreement between their data and data provided in the Toolkit.

As with any methodology, the Toolkit needs live testing and validation. Users of the Toolkit are invited to consult with UNEP Chemicals where problems with application, interpretation and implementation occur or where the system does not seem to apply to the situation found in the country.

Countries are invited to use the Toolkit to submit their inventories to UNEP, which will update the Dioxin and Furan Release Inventory (UNEP Report of May 1999). The inventories received will be published and made available on the POPs Clearinghouse (http://www.chem.unep.ch/pops). UNEP also invites all users of the Toolkit to provide feedback on all aspects of this product.

Geneva, May 2003

James B. Willis
Director
UNEP Chemicals

Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases

Contents

Table of Tables

Table of Figures

Abbreviations and Acronyms

2,4,5-T	2,4,5-Trichlorophenoxyacetic acid
°C	Degrees Celsius
a	Year (annum), 365 days
ADt	Air-dried ton (of pulp)
APC(S)	Air pollution control (system)
BAT	Best available techniques
BF	Blast furnace
BOF	Basic oxygen furnace
BOS	Basic oxygen steel
C	Chlorination bleaching stage using molecular chlorine dispersed dissolved in water (pulp and paper production)
CF	Cupola furnace
CNP	2,4,6-Trichlorophenyl-4'-nitrophenyl ether
CORINAIR	Core inventory of air emissions
CTMP	Chemo-thermo-mechanical pulp
D	Chlorine dioxide bleaching stage using a water solution of chlorine dioxide (ClO_2) (Section on pulp and paper production)
DL	Detection limit
d.m.	Dry matter
E	Extraction bleaching stage using sodium hydroxide (NaOH)
EAF	Electric arc furnace
ECF	Elemental chlorine free (bleaching)
ECVM	European Council of Vinyl Manufacturers
EDC	1,2-Dichloroethane
EMEP	Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air pollutants in Europe
EPA	Environmental Protection Agency
ESP	Electrostatic precipitator
EU	European Union (15 Member States: Austria, Belgium, Denmark, Finland, France, Germany, Greece, Ireland, Italy, Luxembourg, the Netherlands, Portugal, Spain, Sweden, United Kingdom)
GEF	Global Environment Facility
h	Hour(s)
HW	Hazardous waste
I-TEF	International Toxicity Equivalency Factor
I-TEQ	International Toxic Equivalent
IF	Induction furnace
ISO	International Standardization Organization
K	(Degree) Kelvin

kPa	Kilo Pascal (= one thousand Pascal)
L	Liter
LPG	Liquefied petroleum gas
LOI	Loss of ignition (a measure for residual carbon content)
LS	Liquid steel
m	Meter
m^3	Cubic meter (typically under operating conditions without normalization to, *e.g.*, temperature, pressure, humidity)
Mg	Magnesium but see also: megagram (under units)
MSW	Municipal solid waste
NA	Not applicable (not a relevant release vector)
NaOH	Sodium hydroxide
Na_2S	Sodium sulfide
NCASI	National Council (of the Paper Industry) for Air and Steam Improvement, Inc.
N-TEQ	Toxic equivalent using the Nordic scheme (commonly used in the Scandinavian countries)[1]
ND	Not determined/no data (in other words: so far, no mesaurements available)
NFR	Nomenclature For Reporting
NIP	National Implementation Plan (under the Stockholm Convention on Persistent Organic Pollutants)
Nm^3	Normalized (standard) cubic meter; the volume a gas occupies at atmospheric pressure (1,013 mbar) and 273.15 K (0 °C)
O	Oxygen bleaching stage (pulp and paper production)
PARCOM	Paris-Oslo Commission
PCB	Polychlorinated biphenyls
PCDD	Polychlorinated dibenzo-*para*-dioxins
PCDF	Polychlorinated dibenzofurans
PCP	Pentachlorophenol
PCP-Na	Sodium pentachlorophenate
POPs	Persistent organic pollutants
PTS	Persistent toxic substances
PVC	Polyvinylchloride
RDF	Refuse derived fuel
rpm	Revolutions per minute
SI	International system of units
SNAP	Selected Nomenclature for Air Pollution
t	Ton (metric)

[1] For the purpose of the Toolkit, there is no difference if concentrations or emission factors are reported in I-TEQ or N-TEQ or WHO-TEQ (for PCDD/PCDF only)

TCF	Totally chlorine free (bleaching)
TEF	Toxicity Equivalency Factor
TEQ	Toxic Equivalent
UV	Ultra-violet
UNECE	United Nations Economic Commission for Europe
UNEP	United Nations Environment Programme
VCM	Vinyl chloride monomer
WHO	World Health Organization

SI Units

g	gram	10^0 g		
kg	kilogram	10^3 g		
t	ton	10^6 g (1,000 kg)	also: Mg	Megagrams (a million grams)
kt	kilo ton	1,000 t		

g	gram	10^0 g
mg	milligram	10^{-3} g
µg	microgram	10^{-6} g
ng	nanogram	10^{-9} g
pg	picogram	10^{-12} g

kJ	Kilojoule	10^3 Joule
MJ	Megajoule	10^6 Joule
GJ	Gigajoule	10^9 Joule
TJ	Terajoule	10^{12} Joule

MW	Megawatt
MWh	Megawatt hours

Pa	Pascal	
kPa	kiloPascal	10^3 Pascal

Non-SI Units

Gallon	1 gal	=	0.1337 ft³	=	0.0038 m³
pound	1 lb.	=	0.4536 kg		
inch	1 in	=	2.54 cm	=	0.0254 m

Executive Summary

This Toolkit is a methodology to help countries just developing their inventories to estimate releases of PCDD/PCDF and also leads them through the process of how to enhance and refine these inventories. The Toolkit's goal is to guide the inventory makers within a country in the techniques and stages of the inventory development by giving examples and check parameters for classification. The Toolkit also highlights the pathways of the PCDD/PCDF into the environment or other matrices. Finally the Toolkit is robust enough to characterize releases in orders of magnitude and for sectors as a whole.

Worldwide there are only a few national inventories reporting releases of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/PCDF). A review by UNEP Chemicals in 1999 (UNEP Chemicals 1999) identified only 15, nearly all from developed Northern countries. Since that date, only a few more have been completed and published.

The Stockholm Convention on Persistent Organic Pollutants, a global legally binding treaty requests parties to minimize or, where feasible, eliminate the releases of PCDD/PCDF. Therefore, sources of unintentionally generated POPs must be quantified and the methodology used to assess sources must be consistent in order to follow or monitor dioxin releases over time and between countries.

Existing PCDD/PCDF inventories are not satisfactory for these purposes. Many are incomplete, out of date or lack uniform structure. Inventories that do not address potentially important sources of PCDD/PCDF, perhaps due to insufficient national information, suggest, erroneously, that these sources are not significant and do not need effective controls. Further, only a few inventories address releases other than to air.

In order to assist countries as they identify sources and estimate releases of dioxins and furans, UNEP Chemicals has developed a "Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases." In addition, UNEP Chemicals is conducting a capacity building program and training workshops to assist countries in the preparation for the POPs Convention.

The "Toolkit" has been assembled using the accumulated experience of those who have compiled inventories. The framework of source categories was developed by a core team in consultation with end users from countries wanting assistance in compilation of inventories. It is designed as a simple and standardized methodology and accompanying database to enable assembly of consistent national and regional PCDD/PCDF inventories. This Toolkit has been developed for use by countries that do not have their own measured PCDD/PCDF data from their sources; they will utilize the default emission factors provided in this Toolkit. However, this Toolkit is also applicable to countries that have their own measured data and would like to apply their own emission factors.

Compilation of the inventories should be consistent, time-and resource-efficient and accurate enough to identify reliably the major sources and the key data deficiencies. No testing is necessary to apply the Toolkit and to compile an inventory. The process is also designed to be adaptable. The emission factor and process description database may be revised and improved as new measured data emerges and the new figures may be applied to improve the overall inventory.

The key elements of this "Toolkit" are:

- **An effective methodology** for identifying the relevant industrial and non-industrial processes releasing PCDD and PCDF to air, water, land and with products and residues in a country and screening these to identify the most important ones.

- **Guidance on gathering information** about the relevant processes, which will enable classification of the processes into classes with similar releases.

- **A detailed database of emission factors**, which provides suitable default data to be applied which is representative of the class into which processes are grouped. This database can be updated in the future as new data becomes available.

- **Guidance on the assembly and presentation of an inventory** using both the default emission factors and any country specific data so that the resulting inventories will be comparable.

Information on release of PCDD/PCDF is related to the following general five compartments and/or media into which PCDD/PCDF are released or transferred: air, water, land, residues, and products. For a comprehensive approach, all PCDD/PCDF releases from a given source or activity must be considered (although it does not follow that releases to all compartments have an equal impact).

The basic principle is to gather "activity statistics" which describe the amount of a process (*e.g.*, tons of product produced per year), and "emission factors" which describe release of PCDD/PCDF to each medium per unit of activity (*e.g.,* µg I-TEQ/ton). Multiplying the two yields annual releases. The framework is applied and the inventory produced by taking the five steps shown in Figure 2 (on page 20). The screening matrix (Table 1, page 20) indicates the ten major source categories and includes industrial and non-industrial sources as well as reservoirs and contaminated sites. For each main category a listing of subcategories indicates the detailed process activities. Within each process type, key parameters or process characteristics are provided. Thus, releases to all media where data are available can be assigned. Relatively accessible plant and process information or more detailed information by the application of questionnaires can be used to adequately and simply select an appropriate emission factor from the database.

The process of gathering the detailed information on the processes carried out within the country will be tailored to the situation. In many cases, central statistical data will be sufficient. Some might require a plant-by-plant questionnaire, examples of which are provided. Once activity statistics are available, ranges of potential releases can be estimated by applying the highest and lowest emission factors to the overall activity. Such information can help to set priorities for more detailed data gathering.

Guidance is provided on the presentation of the results with the intention that inventories be clear, consistent and comparable. Results can also be updated and improved as activity statistics and emission factors are updated and improved. Where measured data are available or national estimates have been made the Toolkit is designed to allow for their inclusion alongside estimates derived from default emission factors. Data gaps, uncertainties and differences between processes in one country and emission factors generated from the international literature can be seen.

The final country inventories will clearly show that all potential sources have been addressed, even if the activity does not exist or is insignificant in that country. For each source within a country there will be an estimate of releases to all media where data are sufficient and an indication of likely magnitude if full data are unavailable. Additional information such as plans for upgrading of processes or imminent closure of plants can be included. Taken together, this process will help in the interpretation of results and the prioritization of future actions.

1 INTRODUCTION

Dioxins and furans, more precisely polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) are two of the twelve Persistent Organic Pollutants (POPs) covered by the Stockholm Convention on Persistent Organic Pollutants (POPs). PCDD/PCDF, together with polychlorinated biphenyls (PCB) and hexachlorobenzene (HCB) are listed in Annex C of the Stockholm Convention POPs; they are unintentionally generated and are commonly named "by-products". All POPs listed in Annex C require "continuing minimization and, where feasible, ultimate elimination" (SC 2001). Paragraph (a) of Article 5 within the Convention requires the development and implementation of an action plan to "identify, characterize and address the releases of the chemicals listed in Annex C" and sub-paragraph (i) specifies that the action plan shall include "the development and maintenance of source inventories and release estimates".

Decision 18/32 of UNEP's Governing Council taken in Nairobi in May 1995 addresses directly the need for international actions to reduce and eliminate releases and emissions of POPs.

In its decision 19/13 C of February 7, 1997, the Governing Council requested that UNEP develop and share information on the following topics: alternatives to POPs, inventories of PCBs and available destruction capacity, and sources of and management strategies for PCDD/PCDF. Pursuant to these requests, UNEP convened a number of regional and sub-regional Awareness Raising Workshops to inform countries about the POPs and the Stockholm Convention. A frequent request from participants in these workshops was for assistance in assessing releases of PCDD and PCDF within their countries and/or regions. Participants expressed concern about the possible effects of these compounds, which are formed unintentionally as by-products in a number of processes.

UNEP Chemicals (UNEP 1999) reviewed a few national PCDD/PCDF inventories. Unfortunately, these inventories were not compiled in a comparable form. There was no internationally established listing of sources (new sources are still being discovered and different sources are predominant in different countries) and source strengths may change with new information and changes in technology. Several inventories did not address potentially important sources of PCDD/PCDF due to insufficient information, which can lead to an unwarranted conclusion that these sources are not significant. Starting in 1999 and running through the year 2000, UNEP Chemicals conducted a capacity building program and holding training workshops to help countries prepare for the POPs Convention. In January 2001, UNEP Chemicals within the framework of the IOMC (Inter-Organization Programme for the Sound Management of Chemicals) released the "Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases" as a draft. It has been translated into Spanish, French, and Russian. Subsequently, UNEP and others have initiated projects to field-test the Toolkit and several dioxin and furan release inventories have been compiled using the Toolkit. Further inventories are under development.

In June 2002, the Sixth Session of the Intergovernmental Negotiating Committee (INC) of the Stockholm Convention in Decision 6/4

1. "Notes that the "Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases" (Toolkit) of the United Nations Environment Programme provides a basis for the development of provisional guidance on the evaluation of current and projected releases of chemicals listed in annex C of the Stockholm Convention on Persistent Organic Pollutants;

2. Notes further that it may be appropriate to update the Toolkit and to include additional chemicals, emissions factors, levels of detail and other elements to enhance its usefulness;

3. Invites Governments and others to provide the secretariat with comments on how the Toolkit can be updated and expanded before 31 December 2002;

4. Requests the secretariat to develop an updated and expanded version of the Toolkit, taking into consideration the comments received as well as experience in field-testing the Toolkit in countries, for consideration by the Intergovernmental Negotiating Committee at its next session."

The comments from governments and non-governmental organizations received by May 2003, experiences from application of the Toolkit especially in Asia and in Latin America, and the results from a sampling and analysis program in Thailand have been combined into this first edition.

It should be noted that this first edition of the Toolkit only addresses the releases of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans. Separate efforts are needed to develop Toolkits for polychlorinated biphenyls (PCB) and hexachlorobenzene (HCB) as by-products.

The Toolkit is designed to cover at a minimum all source categories and processes that are listed in Annex C, Parts II and III of the Stockholm Convention and that are known to release PCDD/PCDF. The Toolkit can be used where there are no measured data available or where domestic measured data and emission factors have been generated.

The major goals of the Toolkit are:

- To be comprehensive, easy to read, follow, and apply;
- To approach the subject in a logical and pragmatic manner;
- To group and present the classes and emission factors on a reasonable and practical basis;
- To enable the establishment of internationally comparable inventories.

2 AIMS AND LIMITATIONS

2.1 Aims

This Toolkit is a methodology to help countries just developing their inventories to estimate releases of PCDD/PCDF and also leads them through the process of how to enhance and refine these inventories. The Toolkit's goal is to guide the inventory makers within a country in the techniques and stages of the inventory by giving examples and check parameters for classification of sources. The Toolkit also highlights the pathways of the PCDD/PCDF into the environment or other matrices. Finally the Toolkit is robust enough to characterize releases in orders of magnitude and for sectors as a whole.

Whereas other international methodologies that are available have been created for evaluation of impacts on single environmental media, the Toolkit is aimed to provide a methodology and associated emission factors for PCDD/PCDF releases into all media (air, water, land, products and residue). The "Toolkit" is designed to produce a simple and standardized methodology and accompanying database to enable assembly of consistent national and regional PCDD/PCDF inventories. It comprises a UNEP-recommended procedure for the effective compilation of source and release inventories of PCDD/PCDF. Only comparable sets of PCDD/PCDF source release data can provide a clear global picture on the scale of releases as a step in prioritizing actions to control or reduce releases. International comparability is the goal of this process.

Compilation of the inventories should be resource efficient (*i.e.* not too time consuming to assemble) and accurate enough to reliably identify the major sources and the key data deficiencies. Inventories should be presented in a standard form. No emission testing is necessary to apply the Toolkit and to compile an inventory.

The Toolkit is also designed to be adaptable. The emission factor database may be revised and improved in response to the emergence of new emission data or improved processes. It is a screen, not an exhaustive registry, and is designed to ensure the positive identification of the bulk of significant sources. Speed and ease of use have been deemed more relevant for the users of the Toolkit than the unattainable goal of 100 % accuracy.

It includes:

- An effective methodology to identify relevant industrial and non-industrial processes releasing PCDD and PCDF, screen these for importance, and to identify the most important.

- Guidance on the gathering of information about the relevant processes, so as to allocate processes into classes having similar emissions.

- A detailed and dynamic database of emission factors that provides suitable default data representative of process classes.

- Guidance on the assembly of an inventory and presentation of the findings using both the default emission factors and any country specific data so that the resulting inventories will be comparable. The presentation of the data will allow for data gaps and will indicate ranges of emissions where accurate classification cannot be achieved.

The Toolkit is designed to be applicable to all countries. It can accommodate country-specific data to supplement default emissions factors. Different countries will investigate sectors differently depending on the resources available and the local priority for that source. It may be appropriate to carry out additional work on particular sources at some future date as further information or resources become available. The use of default emission factors side-by-side with local measured data will help to refine and improve the Toolkit for use in other countries.

2.2 Limitations

The majority of inventories available are for industrialized and developed countries. A review (UNEP 1999) identified 15 such inventories; however, they are not assembled uniformly or reported for the same reference year. Since than, a few more inventories have been published in other countries (Fiedler 2003 and references therein).

In some cases estimates of releases were only made for a subset of processes (*e.g.*, only industrial processes). Some drew on emission factors from literature to supplement local emissions measurements, but virtually all reflect processes and emission factors derived from developed countries. Comparatively little is known about processes and technologies used in less developed countries, about emissions and releases from locally manufactured equipment such as burners, and region-specific feedstocks or input materials.

An inventory can provide valuable information on the magnitude of releases to each environmental medium and in products and residues. It can only highlight sources for possible impacts but it cannot provide an accurate guide to the relative impact of these releases on human or ecosystem exposure since the fate of PCDD and PCDF varies considerably from one release source to another.

Release or emission inventories have been compiled by countries as a requirement under national regulations or other conventions. However, it has to be noted that these inventories may aggregate information based on needs other than under the Stockholm Convention. Examples are groupings according to industry codes such as SNAP/CORINAIR in the UNECE Aarhus Protocol on POPs or the NFR codes. The Toolkit does follow these groupings since the purpose of such grouping is different from the goal of the Stockholm Convention and the release inventories under this Convention. The Stockholm Convention addresses releases of organic by-products from anthropogenic sources and has global coverage.

The process of assembling inventories is complex and involves many stakeholders. In order to facilitate the use of the Toolkit and enable countries to identify sources of PCDD/PCDF and establish their first dioxin and furan release inventories, UNEP has organized training workshops at a sub-regional level. UNEP also provides other relevant information, and cooperates with the other implementing agencies (UNDP, UNIDO, World Bank) when countries implement their National Implementation Plans (NIPs) under the Stockholm Convention on POPs. The Toolkit is intended to quickly identify the major PCDD/PCDF

sources and thus, provide an overview of the scale of releases and their source processes or activities. Consequently, the derived PCDD/PCDF inventories will assist countries to direct efforts to prioritize their PCDD/PCDF sources for implementation actions to minimize PCDD/PCDF releases. It will also help to indicate the relative importance of dioxins and furans for a country's national action plan.

Although the majority of the measured concentrations have been generated in developed countries and the newer data refers to modern processes and technology, the emission factors presented in this Toolkit take into consideration the circumstances of less sophisticated and controlled processes, older or simpler technology, *etc.* Experiences from OECD countries at early times of PCDD/PCDF measurements have been taken into account when extrapolating results to "create" emission factors for plants, processes and activities with little or no controls. These classes of emission factors – typically class 1 or class 2 factors within each subcategory – may be appropriate when releases from small and simple plants in developing countries are being estimated. The results from a joint UNEP/GTZ/PCD sampling and analysis project in Thailand have shown that state-of-the-art technology exists in developing countries and thus, low emission factors can be applied (UNEP 2001).

Although an abundance of PCDD/PCDF source categories are included in the Toolkit, there may be further processes or activities that are suspected to generate and release PCDD/PCDF or where in single cases PCDD/PCDF were detected. Very often such activities can be covered within one of the listed sub-categories. For example, tire burning, in a first approximation, can be included into the category of open waste burning or classified the same as if a house burns down. Given the frequency that such accidental fires occur compared to the mass of waste openly burned, the total releases within this category of open burning may not change.

2.3 Further Reading

This Toolkit is for the preparation of a release inventory for polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) as requested in subparagraph (a) of the Article 5 in the Stockholm Convention on Persistent Organic Pollutants. It is aimed to cover all release vectors (air, water, land, products, residues) from industrial and domestic activities by identifying the sources and quantifying the releases for two classes of unintentionally generated POPs. Other chemicals' related conventions typically cover more chemicals but are limited in scope, address one release vector only, are targeted on special industrial sectors or only address potential problems within one country. Although different in scope and coverage, much information and expertise can be found in the documentation related to the methodology applied elsewhere. These may also be consulted for further reading and application within the Toolkit. Some examples are given below together with the respective Web Pages:

The UNECE Aarhus Protocol on Persistent Organic Pollutants (1998) under the 1979 UNECE Convention on Long-range Transboundary Air Pollution (LRTAP): This convention is to abate air pollution. The EMEP/CORINAIR Emission Inventory Guidebook has been prepared as a guide to atmospheric inventory methodologies.
URL for the Protocol: http://www.unece.org/env/lrtap/pops_h1.htm
URL for EMEP: http://www.EMEP.int
URL for the Guidebook: http://reports.eea.eu.int/EMEPCORINAIR3/en

The Harmonised Quantification and Reporting Procedures for Hazardous Substances (HARP-HAZ): This project run by the Norwegian Pollution Control Authority (SFT) is a reporting is specific to emissions into the marine environment (and more specifically for northern European countries).
URL: http://www.sft.no/english/harphaz/

Pollutant Release and Transfer Registers (PRTR): They will be established following recommendations contained in UNCED Agenda 21, Chapter 19. Governments and relevant international organizations with the cooperation of industry should [among others] "Improve data bases and information systems on toxic chemicals, such as emission inventory programmes…"
URL of a clearinghouse: http://www.chem.unep.ch/prtr/Default.htm

The IPPC Directive - Integrated Pollution Prevention and Control of the European Union: This directive is about minimizing pollution from various point sources throughout the European Union. All installations covered by an Annex of the Directive are required to obtain an authorization (permit) from the authorities in the EU countries. The permits must be based on the concept of Best Available Techniques (BAT). It has also been decided that policy-makers as well as the public at large need better information about the. The Directive provides for the setting up of a European Pollutant Emission Register (EPER) to inform about the amount of pollution that different installations are responsible for.
URL for IPPC Directive: http://europa.eu.int/comm/environment/ippc/
URL for BAT documents: http://eippcb.jrc.es/
URL for EPER: http://europa.eu.int/comm/environment/ippc/eper/index.htm

OSPAR Commission for the Protection of the Marine Environment: The Commission will develop programs and measures to identify, prioritize, monitor and control (*i.e.,* to prevent and/or reduce and/or eliminate) the emissions, discharges and losses of hazardous substances which reach, or could reach, the marine environment of the North Atlantic.
URL: http://www.ospar.org/eng/html/welcome.html

Baltic Marine Environment Protection Commission (Helsinki Commission – HELCOM): Work of this commission is to protect the marine environment of the Baltic Sea from all sources of pollution through intergovernmental co-operation of member states.
URL: http://www.helcom.fi/helcom.html

Australia's National Pollution Inventory (NPI): Australia has developed a database where emissions are estimated for industrial facilities across the country, and for diffuse sources.
URL: http://www.npi.gov.au/

For further consultation on PCDD/PCDF inventories, information can be found in the international literature (such as Fiedler 2003), the report by UNEP Chemicals (1999), and at Web Pages of regional organizations such as the European Commission (EC - http://europa.eu.int/comm/environment/dioxin/), the Commission for Economic Cooperation (CEC - http://www.cec.org/home/) and several national governments and agencies.

3 FORMATION AND RELEASE OF PCDD AND PCDF

3.1 Formation of PCDD/PCDF

PCDD/PCDF are formed as unintentional by-products in certain processes and activities, Annex C of the Stockholm Convention provides two lists for several of these. Besides being formed as unintentional by-products of manufacturing or disposal processes, PCDD/PCDF may also be introduced into processes as contaminants in raw materials. Consequently, PCDD/PCDF can occur even where the PCDD/PCDF are not formed in the process under consideration. PCDD/PCDF formation routes can be divided into two broad categories: (a) formation in thermal processes and (b) formation in wet-chemical processes (for further details, see UNEP 2003a).

(a) PCDD/PCDF are formed in trace quantities in combustion processes *via* two primary mechanisms:

1. The so-called *de novo* synthesis in which PCDD/PCDF are formed from non-extractable carbon (C) structures that are basically dissimilar to the final product (PCDD/PCDF); and

2. Precursor formation/reactions *via* aryl structures derived from either incomplete aromatic oxidation or cyclization of hydrocarbon fragments.

Four conditions, present either individually or in combination, favor generation of PCDD/PCDF in thermal processes:

- High temperature processes (during cool-down of combustion gases in a temperature range of ca. 200-450 °C) and/or incomplete combustion;
- Organic carbon;
- Chlorine;
- PCDD/PCDF containing products.

(b) For chemical manufacturing processes, the generation of PCDD and PCDF is favored if one or several of the conditions below apply:

- High temperatures (>150 °C)
- Alkaline conditions (especially during purification)
- UV radiation or other radical starters.

Data by Gullett *et al.* from waste burning experiments under uncontrolled conditions have shown that the potential to generate PCDD/PCDF does not depend on a single parameter. High concentrations of PCDD/PCDF have been detected when "normal" household waste has been burned. The concentrations increased when either the chlorine content increased (independently of its origin, organic or inorganic), or the humidity increased, or the load increased, or catalytic metals were present, or in general: the combustion conditions were bad.

PCDD/PCDF are persistent in the environment and transfers can occur between media (*e.g.*, run-off from soil to water). Such transfers may form an important contribution to human exposure to PCDD/PCDF. However, exposures of the environment or humans are not quantified in this Toolkit. This Toolkit is focused on activities under more direct human control and addresses PCDD/PCDF only.

The Toolkit addresses **direct** releases of PCDD/PCDF to the following five release vectors to the following compartments and/or media (Figure 1).

- Air
- Water (fresh, ocean, and estuarine; then subsequently into sediments)
- Land
- Residue (including certain liquid wastes, sludge, and solid residues, which are handled and disposed of as waste or may be recycled)
- Products (such as chemical formulations or consumer goods such as paper, textiles, *etc.*).

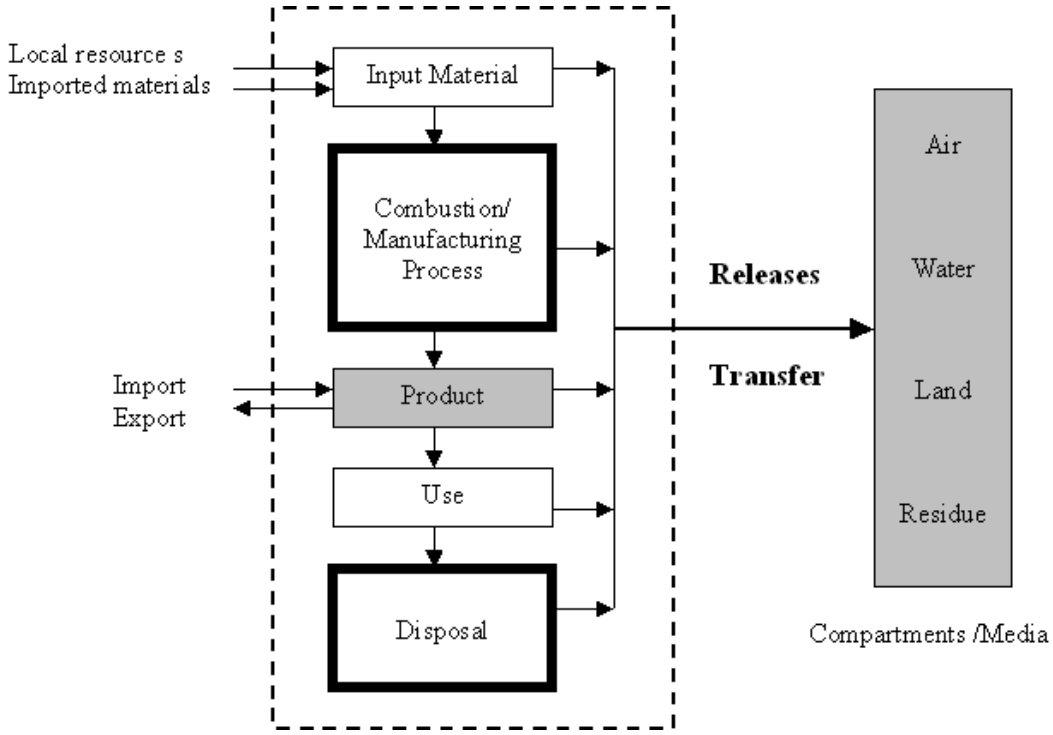

Figure 1: "Life-cycle" of PCDD/PCDF
Boxes in grey represent compartments/media that may contain PCDD/PCDF and should be quantified within the PCDD/PCDF inventory;
Boxes with bold frames represent steps where PCDD/PCDF may be generated;
The dotted line indicates the inventory borders where the data collection will take place.
Note: Reservoirs are not included in this figure but may be present in the compartment "land"

Principally, the releases from given sources to any of the receiving compartments or media may result in the creation of a reservoir of PCDD/PCDF. Highly contaminated reservoir sites have the potential to act as "reservoir" sources, which are addressed as a separate category (Category 10 – Hot Spots).

The Toolkit addresses at a minimum all the sources and activities listed in Part II of Annex C, which require application of best available techniques (BAT) for the release reduction at new sources and all the sources listed under Part III of the same Annex. The Toolkit also goes beyond these named sources since the list in Part III of Annex C).

PCDD and PCDF releases arise from four types of sources. Three are process related:

- Chemical production processes – for example the production of chlorinated phenols and the oxychlorination of mixed feeds to make certain chlorinated solvents, or the production of pulp and paper using elemental chlorine for chemical bleaching;
- Thermal and combustion processes – including incineration of wastes, the combustion of solid and liquid fuels and the thermal processing of metals;
- Biogenic processes, which may form PCDD/PCDF from precursors such as pentachlorophenol.

The fourth is related to previous formation:

- Reservoir sources such as historic dumps of contaminated wastes and soils and sediments, which have accumulated PCDD/PCDF over extended periods.

Minimization or elimination of the formation and releases of PCDD/PCDF are further requirements under the Stockholm Convention on POPs. To achieve this goal, the implementation of best available techniques (BAT) and best environmental practices (BEP) are required to be undertaken or promoted. An Expert Group on BAT and BEP will provide guidelines and guidance for these. Final guidelines and guidance will be adopted by the Conference of the Parties.

3.2 Direct Releases of PCDD/PCDF

3.2.1 Release to Air

Releases of PCDD/PCDF into the atmosphere occur either from stationary sources or diffuse/dispersed sources. Stationary sources are mostly associated with industrial activities such as production and manufacturing, and from diffuse or dispersed sources are mostly related to the use and application of PCDD/PCDF-containing products. PCDD/PCDF emitted from either of these two source categories can undergo long-range transport and thus, PCDD/PCDF can be detected in air at locations far from the origin of its release.

Examples of processes releasing PCDD/PCDF into air include off-gases from:

- Combustion processes;
- Metal processing operations, *e.g.* sintering, metal smelters, *etc.;*
- Drying and baking operations, smoke houses, *etc.;*
- Other industrial thermal processes, *e.g.,* pyrolysis, ash recycling, cracking, *etc.*

Actual dioxin formation potential and actual release will depend on process conditions and air pollution controls applied. Technologies have been developed to reduce formation of PCDD/PCDF and to control emissions to very low levels for many processes.

3.2.2 Release to Water

PCDD/PCDF releases to water can occur with the discharge of wastewater, run-off from contaminated sites, leaching from waste dumps, dumping of wastes, application of dioxin-contaminated chemicals (*e.g.,* application of pesticides) *etc.* PCDD/PCDF may be present in a discharge, if the PCDD/PCDF formed in the industrial production process, entered the industrial process with the feed material, or leached from a repository. Examples are:

- Wastewater discharge from pulp and paper production especially when elemental chlorine is used;
- Wastewater discharge from chemical production processes, especially when elemental chlorine is used;
- Wastewater discharge from the use of dioxin-contaminated preservatives or dyestuffs for textiles, leather, wood, *etc.;*
- Other wastewater discharge from processes identified to be associated with PCDD/PCDF in at least one of the four other environmental compartments and/or media, or
- Wastewater discharge from normal household operations (washing machines, dishwashers, *etc.*) when clothes or other textiles and/or detergents, that contain PCDD/PCDF, are present.

Release of wastewater in form of leachates into surface waters and/or ground water may be deliberate or unintentional. Leaching occurs when rainwater is allowed to migrate through inadequately stored repositories of PCDD/PCDF-containing products, residues and/or wastes. Additional mobilization will occur if co-disposal of organic solvents has taken place. However, it has been shown that phenolic structures in "normal" landfill leachates are capable of mobilizing PCDD/PCDF from wastes. Examples are:

- PCDD/PCDF-contaminated areas such as production or handling sites of chlorophenol herbicides;
- Timber industry sites where pentachlorophenol or other chlorinated aromatic pesticides were used as wood preservatives;
- Waste dumps and junk yards, especially when PCDD/PCDF-contaminated production residues or waste oils have been disposed.

Consequently, the criteria used to identify potential releases of PCDD/PCDF to water include:

1. Wastewater discharge from processes involving chlorine and/or PCDD/PCDF contaminated products or combustion, incineration and other thermal processes where wet scrubbers are used to clean flue gases;
2. Use of PCDD/PCDF contaminated pesticides (especially PCP and 2,4,5-T) and other chemicals (especially PCB);
3. Leachate from storage and/or disposal sites of PCDD/PCDF contaminated materials.

3.2.3 Release to Land

Sources releasing PCDD/PCDF to land can be divided into three classes: PCDD/PCDF contaminated product "applied" to land directly, residues from a process left on or applied to land or PCDD/PCDF deposited onto land *via* environmental processes. In all cases, land serves as a sink for the PCDD/PCDF from which they can be released into the food-chain through uptake by plants and/or animals.

Examples include:

- PCDD/PCDF contaminated product or waste use, *e.g.* pesticides, wood preservatives;
- Application of sewage sludge on farm land or compost in gardens;
- Direct disposal of PCDD/PCDF containing wastes on land; an example would be the ashes that are left from combustion, *e.g.,* open burning on the ground;

Deposition of PCDD/PCDF to land *via* the atmosphere is not addressed in the Toolkit.

It should be noted that in the Toolkit, solid residues from industrial or domestic activities such as bottom ashes, fly ashes, or sludges are classified as residues as they are generated as such within the process. Such residues can be left at the site and later contaminate land, waters, *etc.,* can be disposed of in a landfill (simple dump or sanitary landfill) or used for another application, *e.g.,* bottom ashes in road construction or raw material in, *e.g.,* metal recovering processes. Whenever solid residues are being generated in a process, a country may be interested to learn more about the fate of these residues since they may need to be considered under Article 6 of the Stockholm Convention or need special consideration due to their potential to become a source at a later stage.

3.2.4 Release in Products

Major sources of environmental contamination with PCDD/PCDF in the past were due to production and use of chlorinated organic chemicals and the use of elemental chlorine in the pulp and paper industry.

The highest concentrations of PCDD/PCDF have been found in chlorinated phenols and their derivatives, *e.g.,* pentachlorophenol (PCP and its sodium salt), 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) or polychlorinated biphenyls (PCB). Wastes and residues from production of these and other chlorinated chemicals are also contaminated with PCDD/PCDF (see release vector "Residue").

PCDD/PCDF elimination or reduction comes through

(a) Product substitution through ban of production and use of a product known to be highly contaminated with PCDD/PCDF, so that the process that generates PCDD/PCDF is no longer realized in a country;

(b) Modification of the problematic step of the process, changing of the process conditions, or moving to other feed materials so that PCDD/PCDF are no longer generated or at least minimized.

Source controls such as the above-mentioned affects the PCDD/PCDF at all points in the product life-cycle, including consumer waste. Effective control of the PCDD/PCDF source to the product leads to benefits in several other environmental compartments and media at the same time.

3.2.5 Release in Residues

An almost infinite number of processes can transfer PCDD/PCDF to wastes or (mostly solid) residues. However, the most likely types of wastes can be classified according to their origin, since PCDD/PCDF are always a by-product. Examples include:

- Garbage, trash, and rubbish (municipal, industrial, hazardous, medical, *etc.*);
- By-product waste from combustion and thermal processes (fly ash from flue gas cleaning equipment, bottom ash, soot, *etc.*);
- Production residues and residual products (sludge and residues from chemical production, sewage sludge from wastewater treatment, waste pesticides, waste transformer oil, *etc.*).

PCDD/PCDF concentrate in solid waste streams from combustion and thermal industrial processes such as fly ash, bottom ash, and other dust. Particulate matter from combustion and thermal industrial processes contains unburned carbon where PCDD/PCDF adsorbs. Fine fly-ashes and dusts collected from thermal industrial processes contain by-product PCDD/PCDF in a concentrated form so that they are not emitted to the air.

In general, poor combustion process control and high particle removal efficiency of the air pollution control (APC) system mean higher concentrations of PCDD/PCDF in the solid residue. Iron ore sintering serves as a perfect example. Combustion is virtually uncontrolled inside the sinter bed; fly ash removal by the APC system is very efficient so as to recover the high iron content in the fly ash. Consequently, PCDD/PCDF concentrations in iron ore sintering fly ash can be expected to be significant.

Chemical production involving especially elemental chlorine leads to wastes containing PCDD/PCDF. Whether it is the production of chlorine containing pesticides or the chlorine bleaching during paper production, chemical production processes with or around elemental chlorine produce waste streams. This waste usually contains PCDD/PCDF to some extent. Chapter 6.7 details what causes the PCDD/PCDF to be concentrated in the waste stream.

Effluents from the pulp and paper-making industries as well as municipal sewage waters generate PCDD/PCDF contaminated waste streams. The residues remaining after treatment of the wastewater - being mechanical, biological, or chemical - is sludge. In many cases, these sludges are contaminated with PCDD/PCDF. In general, a higher standard of living gives rise to higher PCDD/PCDF contamination of the sewage sludge with consumer products as the major source.

Importantly, PCDD/PCDF may be associated predominantly with only one of the residue streams from a process while other streams contain low or insignificant levels. For example, thermal processes often concentrate PCDD/PCDF in the residues from flue gas cleaning operations (fly ash) while grate ash has low concentrations of PCDD/PCDF (in processes with an efficient burn-out); however since bottom ash is generated in far larger amounts, the bottom ashes may constitute the largest release vector for PCDD/PCDF.

The potential for residues to cause environmental contamination or exposure to PCDD/PCDF depends to a great degree on how the residue is treated and disposed of. For example whereas contaminated wastes from the chemical industry may be incinerated and effectively destroy any PCDD/PCDF present, dumping of such residue may result in the creation of a reservoir source. Further, residues from one process may be used as a raw material in another process and without adequate controls, PCDD/PCDF releases to air, water or product can occur. Although the mobility of PCDD/PCDF within residues is generally quite low and exposure to airborne PCDD/PCDF typically results in higher impacts on man or the environment, the Stockholm Convention requires assessment of all media/compartments.

3.2.6 Potential Hot Spots

Potential Hot Spots are included as a category for assessment (see Section 4.1). This category 10 differs from the other nine categories as Hot Spots from former operations known to be related to PCDD/PCDF. Hot spots have the potential to become sources in the future. Although Hot Spots are not included in the Dioxin Source Inventory with numeric values, it is important to identify them.

Hot Spots can be sites of former or ongoing production of PCDD/PCDF contaminated products. This can occur from storage of product, disposal of waste or application of the product over a long period. Although the concentrations of PCDD/PCDF in these Hot Spots can be very high, present releases may be negligible or small. Nevertheless, Hot Spots must be identified and registered. In many cases, once catalogued, no other immediate action may be required, if there is no immediate threat of significant release. In such a case of lower urgency the Hot Spot should be assessed and longer term action plan derived.

If a Hot Spot has already started to release large amounts of PCDD/PCDF or it is foreseeable that such a release is imminent, it should be entered into the source inventory, the state of urgency noted and remedial action arranged. In any case, a site-specific assessment and evaluation of the Hot Spot is needed.

Contaminated sites are addressed in Article 6 of the Stockholm Convention on POPs and although the Convention does not require remediation of these sites, it endeavors “to develop appropriate strategies for identifying sites contaminated by chemicals listed in Annex A, B or C; if remediation of those sites is undertaken it shall be performed in an environmentally sound manner”.

4 PROTOCOL FOR THE INVENTORY ASSEMBLY

The basic aim of the Toolkit is to enable an estimate of average annual release to each vector (air, water, land, products, residues) for each process identified. The estimate can be calculated by this basic equation:

Source Strength (Dioxin emissions per year) = Emission Factor x "Activity Rate" (1)

The PCDD/PCDF releases per year will be calculated and presented in grams of toxic equivalents (TEQ) per year. The annual **Source Strength** is calculated by multiplying the release of PCDD/PCDF (*e.g,.* in µg TEQ) per unit of feed material processed or product produced (*e.g.,* ton or liter) – referred to as the **Emission Factor** – for each release vector (air, water, land, product, residue) with the amount of feed material processed or product produced (tons or liters per year) – referred to as the **Activity Rate**. The sum of al these calculations gives the total release for a given source (= source strength) per year (see also Chapter 4.4.2).

The Toolkit is designed to assemble the necessary activity data and to provide a means of classifying processes and activities into classes for which appropriate average emission factors are provided.

The Toolkit consists of a five-step standardized procedure to develop consistent and comparable source inventories (see Figure 2). First, a coarse screening matrix is used to identify the Main PCDD/PCDF Source Categories present in a country. The second step details these Main Source Categories further into Subcategories to identify individual activities, which potentially release PCDD/PCDF.

In the third step, process-specific information is used to characterize, quantify and ultimately classify the identified PCDD/PCDF release sources in a particular country or region. Standardized Questionnaires are provided in the Annex (Chapter 8.2), which may be useful to obtain the necessary information.

In the fourth step, releases are calculated on the basis of information obtained in the previous steps *via* Equation (1). The last step is then the compilation of the standardized PCDD/PCDF inventory using the results generated in steps 1 through 4.

A standardized presentation format is provided to ensure that all sources are considered (even if they cannot be quantified), data gaps are apparent and inventories are comparable and transparent.

1. **Apply Screening Matrix to identify Main Source Categories**
2. **Check subcategories to identify existing activities and sources in the country**
3. **Gather detailed information on the processes and classify processes into similar groups by applying the Standard Questionnaire**
4. **Quantify identified sources with default/measured emission factors**
5. **Apply nation-wide to establish full inventory and report results using guidance given in the standard format**

Figure 2: The recommended five-step approach to establish a national PCDD/PCDF release inventory using the Toolkit

Tables and Figures are provided as worksheets to outline the standardized structure of the Toolkit as well as to obtain all the necessary source data. The Toolkit's list of sources and emissions factors will be updated, improved or amended as more information becomes available.

4.1 Step 1: Screening Matrix: Main Source Categories

The first step in developing a standardized PCDD/PCDF source inventory is identification of Main Source Categories and the main release routes for each category. The coarse screening matrix (Table 1) facilitates preliminary evaluation of activities (industries, product uses, domestic activities, *etc.*), which potentially release PCDD/PCDF into one or more of the five compartments and/or media as defined above.

Table 1: Screening Matrix – Main Source Categories

No.		Main Source Categories	Air	Water	Land	Product	Residue
1		**Waste Incineration**	X				X
2		**Ferrous and Non-Ferrous Metal Production**	X				X
3		**Power Generation and Heating**	X		X		X
4		**Production of Mineral Products**	X				X
5		**Transport**	X				
6		**Uncontrolled Combustion Processes**	X	X	X		X
7		**Production and Use of Chemicals and Consumer Goods**	X	X		X	X
8		**Miscellaneous**	X	X	X	X	X
9		**Disposal**	X	X	X		X
10		**Identification of Potential Hot-Spots**	Probably registration only to be followed by site-specific evaluation				

These Main PCDD/PCDF Source Categories are broad enough to capture the wide variety of industries, processes and/or activities known to potentially cause releases of PCDD/PCDF. The ten Main Source Categories are designed to have common characteristics and manageable complexity. The "X" indicates a main release route for each category on a relative basis although some of these releases may not be well characterized. The "x"

denotes additional release routes that have been identified so far.

The coarse Screening Matrix can be used to provide some guidance on the areas in which information will be required and may influence the composition of a team to collect initial information about possible sources of PCDD/PCDF present in a country. The Screening Matrix will be the starting point for a strategy to seek advice and expertise that will be needed during the more detailed information gathering and data evaluation work.

4.2 Step 2: Subcategories Identification

Next, processes or subcategories within each Main Source Category are identified. For comparability, each of the ten Main Source Categories has been divided into a series of subcategories (described in Sections 4.2.1 to 4.2.10). The list of subcategories gives the summary matrix of the Dioxin Source Inventory, which will be compiled (see Section 5.2).

For each subcategory listed, an investigation shall establish the presence or absence of the activity in the country or region. Easily accessible data is most valuable at this stage (*e.g.* tons per year of waste are incinerated). Centralized statistical information may be most appropriate. Any subcategory, which is reliably known not to be present, can be eliminated from further investigation. However, the fact that the process is absent is to be noted in the inventory.

When basic activity data are available preliminary estimates of potential emissions may be made (see Section 5.1). Even incomplete information can be useful, as it will help to direct subsequent quantification efforts. Further breakdowns for each Main Source Category and main release routes for each subcategory or process are listed. Columns identify the five compartments or media into which significant amounts of PCDD/PCDF are potentially released. The large "X" denotes the release route expected to be predominant, and the small "x" shows additional release routes to be considered.

4.2.1 Subcategories of Waste Incineration

In the Toolkit, waste incineration is categorized according to types of waste burned (Table 3). Incineration in this context means destruction of wastes in a technological furnace of some sort; open burning and domestic burning in barrels and boxes does not belong to these subcategories; they are addressed in Section 4.2.6 – Uncontrolled Combustion.

Table 3: Subcategories of the Inventory Matrix – Main Category 1

			Potential Release Route				
No.		**Subcategories of Main Category**	**Air**	**Water**	**Land**	**Product**	**Residue**
1		**Waste Incineration**	**X**				**X**
	a	Municipal solid waste incineration	X	(x)			x
	b	Hazardous waste incineration	X	(x)			x
	c	Medical waste incineration	X	(x)			x
	d	Light-fraction shredder waste incineration	X				x
	e	Sewage sludge incineration	X	(x)			x
	f	Waste wood and waste biomass incineration	X				x
	g	Destruction of animal carcasses	X				x

Each subcategory represents an entire industry in itself. Wastes differ in composition and combustion characteristics and the combustion equipment typically differs for each of the waste incineration subcategories.

Releases mainly occur into residues, which typically contain the highest concentrations of PCDD/PCDF. Emissions to air may be a much smaller fraction depending on the operational conditions of the incinerator and flue gas cleaning equipment present. However, releases to air are of greatest importance as they may undergo long-range transport and subsequently contaminate the food-chain. Releases to water play only a minor role and only in cases where wet scrubbers are used for flue gas treatment and where discharged ashes are cooled down with water and these waters are released. Adequate wastewater treatment can easily transfer PCDD/PCDF from effluents to residues (from the aqueous phase into the solid phase).

4.2.2 Subcategories of Ferrous and Non-Ferrous Metal Production

Production of ferrous and non-ferrous metals is now the largest source of PCDD/PCDF in many European countries. This source was not recognized until relatively recently, and many countries still ignore it. There are many different processes in this category and many different release points; both make classification and quantification of releases difficult.

In the Toolkit, this Main Source Category has twelve subcategories, each of which refers to a specific process. The important metal production processes are mainly thermal and major releases are to air *via* flue gas and to residue *via* flue-gas-cleaning wastes. In the case of copper reclamation by wire burning, soil and water contamination with PCDD/PCDF are also well known.

Table 4: Subcategories of the Inventory Matrix – Main Category 2

			Potential Release Route				
No.		**Subcategories of Main Category**	**Air**	**Water**	**Land**	**Product**	**Residue**
2		**Ferrous and Non-Ferrous Metal Production**	**X**				**X**
	a	Iron ore sintering	X				x
	b	Coke production	X	x	x	x	x
	c	Iron and steel production and foundries	X				x
	d	Copper production	X				x
	e	Aluminum production	X				x
	f	Lead production	X				x
	g	Zinc production	X				x
	h	Brass and bronze production	X				x
	i	Magnesium production	x	x			x
	j	Other non-ferrous metal production	x	x			x
	k	Shredders	X				x
	l	Thermal wire reclamation	X	(x)	x		x

4.2.3 Subcategories of Power Generation and Heating/Cooking

Power generation and heating as referred to here are limited to combustion processes using fossil fuels and other combustible materials. Fuel cells, solar, wind, hydro-electric, geo-thermal or nuclear generation are not included as no dioxin/furan release associated with them has been identified. Table 5 lists the relevant subcategories.

Table 5: Subcategories of the Inventory Matrix – Main Category 3

			Potential Release Route				
No.		**Subcategories of Main Category**	**Air**	**Water**	**Land**	**Product**	**Residue**
3		**Power Generation and Heating/Cooking**	**x**		**(x)**		**X**
	a	Fossil fuel power plants	x				x
	b	Biomass power plants	x				x
	c	Landfill, biogas combustion	x				x
	d	Household heating and cooking (biomass)	x		(x)		X
	e	Domestic heating (fossil fuels)	x		(x)		X

In large, well-controlled fossil fuel power plants, the formation of PCDD/PCDF is low since the combustion efficiency is usually fairly high, typically they use fuel that contain more sulphur than chlorine and thus inhibit the formation of PCDD/PCDF, and the fuels used are homogeneous. However, significant mass emissions are still possible as large volumes of flue gases are emitted with small concentrations of PCDD/F. Where smaller plants or biomass are used, the fuel may be less homogeneous and burned at lower temperatures or with decreased combustion efficiency. These conditions can result in increased formation of PCDD/PCDF. The same may occur when landfill gas and/or biogas is used as a fuel due to the presence of unwanted and undefined additional constituents.

In the cases of domestic and/or household heating/cooking the quality of the fuel used is often poor and the combustion efficiency very low, resulting in increased formation of

PCDD/PCDF. The predominant release vectors are to air (flue gas emissions) and with residues, fly-ashes and bottom ashes.

4.2.4 Subcategories of Production of Minerals

These are high-temperature processes for melting (glass, asphalt), baking (brick, ceramics), or thermally induced chemical transformation (lime, cement). In them, fuel combustion generates PCDD/PCDF as unwanted byproducts. Additional, formation of PCDD/PCDF 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 in place, use of waste materials like tires, waste oil, sludges, *etc.* is not problematic; low emissions have been found. Table 6 summarizes potentially relevant mineral production processes.

Table 6: Subcategories of the Inventory Matrix – Main Category 4

			Potential Release Route				
No.		**Subcategories of Main Category**	**Air**	**Water**	**Land**	**Product**	**Residue**
4		**Production of Mineral Products**	**X**				**X**
	a	Cement production	X				x
	b	Lime production	X				x
	c	Brick production	X				x
	d	Glass production	X				x
	e	Ceramics production	X				x
	f	Asphalt mixing	X			x	x

4.2.5 Subcategories of Transportation

Transportation relies heavily on the combustion of gasoline (leaded and unleaded), kerosene, 2-stroke mix (typically a 1:25–1:50 mixture of motor oil and gasoline), diesel fuel (also known as light fuel oil), and heavy oil. The sub-categories are shown in Table 7. Higher emissions from leaded gasoline are linked to the presence of halogenated scavengers as additives to the fuel. Poor maintenance, low fuel quality, and poor combustion efficiency are likely to result in increased PCDD/PCDF releases.

In most cases emissions from internal combustion engines lead only to releases to air. Only in a few cases where diesel or heavy oil is fired in low efficiency motors, the soot and coke residues produced contain higher concentrations of PCDD/PCDF.

Table 7: Subcategories of the Inventory Matrix – Main Category 5

			Potential Release Route				
No.		**Subcategories of Main Category**	**Air**	**Water**	**Land**	**Product**	**Residue**
5		**Transport**	**X**				
	a	4-Stroke engines	X				
	b	2-Stroke engines	X				
	c	Diesel engines	X				(x)
	d	Heavy oil fired engines	X				(x)

4.2.6 Subcategories of Uncontrolled Combustion Processes

Uncontrolled combustion processes are typically poor combustion processes, and may be significant sources of PCDD/PCDF. Table 8 differentiates into two categories. Uncontrolled combustion of biomass usually results in lower formation of PCDD/PCDF than combustion of mixed waste from man-made materials. Higher releases result from mixed wastes due to poorer combustion, inhomogeneous and poorly mixed fuel materials, chlorinated precursors, humidity, and catalytically active metals. In all cases the primary release vectors are to air and into the residue; however, releases to water and land are also possible under some circumstances.

Table 8: Subcategories of the Inventory Matrix – Main Category 6

			Potential Release Route				
No.		**Subcategories of Main Category**	**Air**	**Water**	**Land**	**Product**	**Residue**
6		**Uncontrolled Combustion Processes**	**X**				**X**
	a	Biomass burning	X	(x)	X		(x)
	b	Waste burning and accidental fires	X	(x)	X		(X)

4.2.7 Subcategories of Production and Use of Chemicals and Consumer Goods

Dioxin and furan releases from production of chemicals and consumer goods may be due to PCDD/PCDF input with the raw materials themselves or formation in the production process (Table 9).

Indicators of high probability to form PCDD/PCDF in chemical manufacturing processes are ‘high temperature’, ‘alkaline media’, ‘the presence of *UV*-light as an energy source’, and ‘the presence of radicals in the reaction mixture/chemical process’ (see Section 3.1).

Table 9: Subcategories of the Inventory Matrix – Main Category 7

			Potential Release Route				
No.		**Subcategories of Main Category**	**Air**	**Water**	**Land**	**Product**	**Residue**
7		**Production and Use of Chemicals and Consumer Goods**	**X**	**X**		**X**	**X**
	a	Pulp and paper production	x	X		x	X
	b	Chemical industry	x	x	(x)	X	X
	c	Petroleum industry	x				x
	d	Textile production		x		x	
	e	Leather refining		x		x	

During production processes PCDD/PCDF releases can occur along all vectors to environmental media/compartments and into the products. The use of elemental chlorine for bleaching and the use of certain biocides such as PCP and certain dyestuffs (chloranil-based) have been contributors to direct releases of PCDD/PCDF to water. Thus, strong emphasis should be put on the detailed investigation of these few potential sources of major significance of contribution to the overall PCDD/PCDF problem.

4.2.8 Subcategories of Miscellaneous

Table 10 summarizes some miscellaneous categories. Drying processes involve hot gas brought into direct contact with the material to be dried. Formation of PCDD/PCDF occurs mostly when contaminated fuels are being used and due to reaction of the hot gases with the organic matter of the materials to be dried. In case of biomass drying and smoke-houses , wastes such as used/treated wood, textiles, leather or other contaminated materials have been used as fuels.

Crematories may be a source of PCDD/PCDF releases since the combustion process is usually inefficient and the input materials are inhomogeneous. Coffins, embalming fluids, and decoration materials may contain chlorinated chemicals and plastics, metal-based colors and non-combustible materials.

Residues from dry cleaning are another miscellaneous source of PCDD/PCDF, where dioxin-containing chemicals (mainly PCP and dyestuffs) have been concentrated after the dry cleaning process. The sources of PCDD/PCDF are the biocides applied on the textiles and the dyestuffs used for coloring. The dirt deposited onto the textiles and sweat are only minor contributors.

Table 10: Subcategories of the Inventory Matrix – Main Category 8

			Potential Release Route				
No.		**Subcategories of Main Category**	**Air**	**Water**	**Land**	**Product**	**Residue**
8		**Miscellaneous**	**X**	**X**	**X**	**X**	**X**
	a	Drying of biomass	x			x	
	b	Crematoria	x				X
	c	Smoke houses	x			x	X
	d	Dry cleaning		x		x	x
	e	Tobacco smoking	x				

4.2.9 Subcategories of Disposal

Table 12 lists the significant non-thermal/non-combustion waste disposal practices, which can lead to PCDD/PCDF releases predominantly to water and land. These practices include landfilling of any kind of waste including sewage sludge, waste oil dumping and open water dumping of wastes and sludge.

In order to determine the release rate of PCDD/PCDF the amount of waste disposed of and the concentration of available PCDD/PCDF must be determined. Especially the co-disposal of mixed wastes can be a major source of PCDD/PCDF releases. Although there exists only a small database, alternative methods of waste treatment and disposal should be encouraged.

Table 12: Subcategories of the Inventory Matrix – Main Category 9

No.		**Subcategories of Main Category**	**Air**	**Water**	**Land**	**Product**	**Residue**
9		**Disposal**		**X**	**X**		**X**
	a	Landfills and waste dumps		x			
	b	Sewage/ sewage treatment	(x)	x	x	x	x
	c	Open water dumping		x			
	d	Composting			x	x	
	e	Waste oil treatment (non-thermal)	x	x	x	x	x

4.2.10 Subcategories of Hot Spots

Hot Spots exist as the direct result of disposal practices as described in Section 4.2.9 or of 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. Table 13 describes an indicative list of locations where Hot Spots can potentially be found.

In subcategories a-c Hot Spots may be linked to an existing production process. Releases may be ongoing from processes on-site or from historical activities. Subcategories f-i are typically reservoirs where PCDD/PCDF containing materials have been stored, dumped or accumulated over many years. In these cases the release may be ongoing, imminent or only potentially threatening in the future. Identification of these sites may be difficult.

Table 13: Subcategories of the Inventory Matrix – Main Category 10

			Potential Release Route				
No.		**Subcategories of Main Category**	**Air**	**Water**	**Land**	**Product**	**Residue**
10		**Identification of Potential Hot-Spots**	Probably registration only to be followed by site-specific evaluation				
	a	Production sites of chlorinated organics			X		
	b	Production sites of chlorine			X		
	c	Formulation sites of chlorinated phenols			X		
	d	Application sites of chlorinated phenols	x	X	x	x	
	e	Timber manufacture and treatment sites		X	X	x	x
	f	PCB-filled transformers and capacitors				x	x
	g	Dumps of wastes/residues from categories 1-9	x	X	X		x
	h	Sites of relevant accidents		X	x		x
	i	Dredging of sediments					x
	j	Kaolinitic or ball clay sites			x		

Site-specific evaluation of each Hot Spot should determine its current status: immediate threat or potential for releases in the future. In either case the site should be registered.

4.3 Step 3: Information Gathering

The next step is to gather detailed information on processes. Size and scale (*e.g.,* tons of waste burned, tons of copper produced) as well as process information are relevant to the assessment. Within one subcategory to produce the same product, the emissions of PCDD/PCDF can vary considerably depending on technology, performance, *etc.* and in many cases only an estimate is possible. Estimation methods chosen will differ and should reflect local conditions and the available resources. Key parameters used to distinguish high emitting processes from low emitting processes are given in Section 6.

Basic data on the magnitude of activity in each category and basic structure of that sub-category is usually assembled first. A starting point and good sources for such information include:

- National industrial, labor, and tax statistics;
- Regional economic activity records including national production and import/export data;
- Local operating and permitting records of industrial facilities;
- Industry Association data;
- Historical production and industry data.

Subcategories comprised mainly of large plants might be characterized by individual location. Subcategories comprised of diffuse sources should be characterized by aggregating centrally available data. If no information on a certain activity is available, the range of potential releases can be calculated by applying the lowest and the highest emission factors.

The most important information needed to classify processes and sub-categories is included in the Example Questionnaires (see Section 9). These are designed to facilitate selection of appropriate emission factors.

All sources should be characterized. If individual plant questionnaires are used, diligent follow-up may be needed in order to ensure a high return rate of completed questionnaires. Incomplete data collection will impact all subsequent results and reduce the overall quality of the inventory. Independent quality control and quality assurance procedures are recommended for the data-gathering step. Ideally, a complete and highly detailed database containing all activities potentially related to the release of PCDD/PCDF will be established on individual sites for each source.

Incomplete information - data gaps - will result in the need to make assumptions about those sources where no specific information could be collected. Approaches will vary, but all assumptions should be transparent in order to facilitate estimation for future data years and reevaluation in the light of improved information. Two approaches are presented.

A "middle ground" approach assumes that missing data is distributed similarly to available data (*e.g.,* high *vs.* low emitters or state of compliance with technology requirements). A "conservative" approach assumes that missing sources are best described by the highest emission factor in the database or the highest emission factor of those plants providing information. Assumptions should be based on best judgment making use of all available data, presented clearly and reviewed externally. In some cases additional data may be available from trade associations, equipment suppliers, regulators or experts on the industry.

4.4 Step 4: Process Classification and Source Quantification

Releases from processes listed as "subcategories" above can vary by orders of magnitude depending on the process technology or operation. Chapter 6 contains a complete listing of the different subcategories and processes within each subcategory. Each Section also indicates how to classify processes and choose appropriate emission factors.

The Toolkit methodology encourages the use of measured data where available within a country or region. However, to ensure comparability and to provide valuable feedback on the effectiveness of the process, the classification and application of default emission factors should be carried out even where measured data are available. The results of source quantification based on measured data, presented alongside results based on default emission factors, help to indicate how effective the Toolkit is and highlights areas for further improvement.

In nearly all cases some grouping (or classification) of the processes within a country or region will be needed to compile an inventory since it is very unusual to find measured data for every single process within a country or region and some extrapolation will be required.

4.4.1 Process Classification

Section 6 details the classes of processes within each of the subcategories. Each class has a set of emission factors provided (Sections 6.1 through 6.10).

Information gathered in Step 3 by the use of the standard questionnaire or other means should be sufficient to group processes given the technology and process descriptions given in Section 6. Each class is designed to represent a certain level of technology and performance, which will result in similar releases and justify use of the same emission factor.

Within one subcategory, emission factors for two different states of technology may differ for one vector (*e.g.* air) but may be the same for another vector (*e.g.* residue or land). Judgment and assumptions may be required to classify plants finally.

To ensure that all activities are accounted for, the sum of the activity rates for the individual classifications should equal the total amount of material processed within the subcategory. For example in the subcategory "municipal waste incineration" the mass in well-controlled plants added to the mass in poorly controlled plants, *etc.* should add up to the total mass incinerated. This requires that all sources be placed into the most appropriate class, based on their main characteristics. Classification of plants and processes can be difficult and advice may be sought from UNEP.

As an illustration, consider the production of aluminum from scrap (sector 2 subcategory e). Within this subcategory, three classes of process are listed (see Section 6.2.5) relating to three levels of technology/process operation. Each has a distinctly different emission factor. In a hypothetical country, 1 million tons per year of aluminum is produced from scrap. Data gathering has shown that 200,000 t/a arise from plants with simple dust arrestment and 300,000 t/a from plants with fabric filters and lime injection. No information was provided on the remaining 500,000 t/a.

In this case, an assumption must be made to classify the unknown 500,000 t/a production. Advice from the national trade association suggests that the split is likely to be the same as for the plants returning data; this is confirmed by regulators. Consequently the final estimates are as shown in the Table 14. Where assumptions are made they can be improved if new data becomes available.

Table 14: Example of classification – as applied to thermal aluminum production

Aluminum production from scrap – 2e	Activity Rate (t/a)			
Classification	Results from Surveys	Total Production in Country	Final Estimates	Comment
1. Scrap Al, minimal treatment of inputs, simple dust controls	200,000		400,000	Information from trade association and regulators indicates that survey results are a good reflection of total production
2. Scrap treatment, well controlled, fabric filters with lime injection	300,000		600,000	
3. Process optimized for PCDD/PCDF control – afterburners, lime injection, fabric filters and active carbon			0	
4. Total		1,000,000	1,000,000	

The information compiled on individual sources, including the data obtained through the Standard Questionnaires, serves as the basis to classify each individual source (see Chapter 9 for examples). The Standard Questionnaire has a space to assign a classification to each source according to its process and equipment characteristics and by referring to the descriptions of the classes in Section 6.

4.4.2 Source Quantification

In order to quantify the source strength, release rates must be determined as annual mass flow rates of PCDD/PCDF expressed in grams TEQ of PCDD and PCDF released per year. Most concentrations of PCDD/PCDF in the published literature and limit values in legislation, such as in the waste incineration Directive of the European Union (EU 76/2000) and in the United States are presented as I-TEQ (International Toxic Equivalents using the NATO toxicity equivalency factors (= I-TEF) established in 1988 (NATO/CCMS 1988). The Stockholm Convention, however, requires to utilize state-of-the-art Toxic Equivalency Factors, which presently are those established by a WHO/IPCS expert group in 1998, which are the WHO-TEFs (van Leeuwen and Younes 1998). As can be seen in Chapter 11.1, the difference between the I-TEFs and the mammalian WHO-TEFs are minor and insignificant for the purpose of the Toolkit for PCDD/PCDF. As mentioned in Chapter 1 and Chapter 2.2, the emission factors in this Toolkit address the releases of PCDD and PCDF only and do not include the dioxin-like PCB. Further, the emission factors represent order of magnitude release estimates.

The annual releases for all vectors from a source or a source category are calculated as follows:

Source Strength (Dioxin Emissions per year) = Emission Factor x "Activity Rate" ***(1)***

In practical terms this means that per source five calculations have to be performed:

$$\begin{aligned}\text{Source Strength (PCDD/PCDF released per year)} = {} & \Sigma \text{ Emission Factor}_{Air} \text{ x Activity Rate} \\ & + \Sigma \text{ Emission Factor}_{Water} \text{ x Activity Rate} \\ & + \Sigma \text{ Emission Factor}_{Land} \text{ x Activity Rate} \\ & + \Sigma \text{ Emission Factor}_{Product} \text{ x Activity Rate} \\ & + \Sigma \text{ Emission Factor}_{Residue} \text{ x Activity Rate}\end{aligned}$$

The PCDD/PCDF emission is expressed in grams TEQ per year. According to equation (1), the annual **Source Strength** is calculated by multiplying the **Activity Rate** (= the amount of feed material processed or product produced in tons or liters per year) by each of the **Emissions Factors** (Emission Factor$_{Air}$, Emission Factor$_{Water}$, Emission Factor$_{Land}$, Emission Factor$_{Product}$, Emission Factor$_{Residue}$). Each Emission Factor is the amount of PCDD/PCDF (in µg I-TEQ) that is released to any of the five vectors (air, water, land, product, or residue) per unit of feed material processed or product produced (*e.g.,* tons or liter).

However, in some cases, *e.g.,* within Main Category 7 – Consumer Goods and Products - it may be impractical to use a default emission factor for a specific release. In such cases, default **Emission or Release Concentrations** will be applied that are considered to be typical for a given matrix. Such cases occur especially for releases into water (as discharges/effluents; these are given in pg TEQ/L) or for releases in residues (given in ng TEQ/kg of residue). The same approach may be used in cases where measured **Emission Concentration** data from an individual source is available and used rather than the default emission factors as provided by the Toolkit. In such cases, the **Source Strength** is calculated by multiplying measured emissions/releases or those mentioned in the Toolkit as the basis to calculate the emission factor (*e.g.,* in ng I-TEQ/m³) by the **Flux**.

Equation 2 applies:

Source Strength (PCDD/PCDF Releases per year) = Release Concentration x Flux (2)

The annual **Flux** is the mass flow rate of gas, liquid or solid released per year (*e.g.* in m³/a or t/a). It is calculated as the product of the mass or volume flow per hour at full load (*e.g.* m³/h or t/h) times the number of full load operating hours per year (h/a). It is important to adjust the number for the mass or volume flow rate released per hour to the actual load conditions in order to obtain a mass or volume flow rate at full load. Likewise it is equally important to correct the annual load variations of a source to the corresponding hours of full load.

Care must be taken that the units of Source Strength result in g TEQ/a. The Quality Assurance process should include checks of units of measurement and considerations for consistency.

Consequently, the resulting Source Strengths calculated as annual PCDD/PCDF mass flow for all releases are determined by two critical factors:

1. The annual Flux (mass or volume flow rate) or Activity Rate given either as:
   - product produced (*e.g.,* steel, sinter, cement, pulp, compost, *etc.*), or
   - feed material processed (*e.g.,* hazardous waste, coal, diesel, dead body burned, *etc.*) or
   - material emitted (*e.g.,* m³ of flue gas, liters of wastewater, kilograms or tons of sludge generated, *etc.*)
2. The emission factor for the releases of a specific source given either as:
   - the respective default emission factor from this Toolkit;
   - actually measured local data from the respective source as a concentration (*e.g.,* ng TEQ/m³, ng TEQ/liter).

The product of (1) and (2) above determines the Source Strength of each individual source. The result to be obtained at the end of this Step 4 is Source Strength in form of an annual PCDD/PCDF release estimate for each subcategory.

4.4.3 Determination of the Flux or Activity Rate

The Activity Rate or Flux for an individual plant will be taken from the collected data or the responses obtained with the Standard Questionnaire. The Quality Assurance program should validate that respective Activity Rate and/or Flux obtained for each individual source are credible and expressed in appropriate units. The same principle applies to estimates of activity rates applied to subcategories or classes of processes for which questionnaires are not available.

The Activity Rate or Flux can be:

- amount of product produced or feed material processed or consumed per year (*e.g.,* t/a, m³/a, *etc.*);
- mass or volume flow rate released per year (*e.g.*, m³/h released @ full load x full load operating h/a, *etc.*).

4.4.4 Using the Toolkit's Default Emission Factors

For each process within a subcategory, releases are calculated by multiplying the activity rate for the given class by the emission factor provided in the Toolkit for all release vectors, namely air, water, land, product, and residue (see Chapter 6).

Default emission factors provided represent average PCDD/PCDF emissions for each class within each subcategory. Typically, classes have been assigned to describe processes with no or poor controls, simple equipment, *etc*., which present the worst case scenario (class 1); as the class number increases (from class 2 through class 4), the performance of the process/source/activity improves resulting in lower PCDD/PCDF releases. The highest class number would generally represent BAT and BEP. The emission factor for each class represents the best estimate (medians or means) based on measured data at existing sources with similar technology, process characteristics, and operating practices. Although these default emission factors are based on best available information from the literature or other sources they will be amended or classifications expanded as new data becomes available. The vast majority of emission factors are based on published data found in peer-reviewed literature or in governmental or institutional reports. In order to make the emission factors user-friendly, manageable, and robust, it was necessary to aggregate these original data into order of magnitude estimates (for the majority of the classes within the subcategories).

4.4.5 Using Own Emission Data

The Toolkit can be used where there are no measured data available or where domestic measured data and emission factors have been generated. In the first case, the default emission factors are used; in the second case, good quality data measured at individual and preferentially local plants can be applied. However, the extrapolation of measured data to unmeasured plants should only be done if all plants are of the same type and operating under similar conditions. In all cases, plant descriptions should be used to classify the process and the appropriate default emission factors should be applied.

Obtaining PCDD/PCDF data is analytically challenging. Locally obtained data should be used only if it is of adequate quality and is representative and trustworthy. This process includes carefully following the way the data was generated. If necessary, meta-data and other supporting information should be requested and reviewed. Application of standard methods for sampling and analysis, proven laboratory experience and good documentation are pre-requisites for high data quality. If these requirements are not met, then the default emission factors as provided by the Toolkit rather than own measured data of questionable quality should be used. When using emission factors other than those provided in the Toolkit to estimate annual releases, this should be highlighted. In such case, these can be introduced into the respective columns of the EXCEL sheets, which are provided together with the Toolkit.

4.5 Step 5: Compilation of Inventory

To compile the inventory, an estimate for every subcategory has to be completed as described in Step 4. As described in Section 5, the detailed inventory is build up from each estimated release for all subcategories.

Next, the annual emissions of all individual subcategories are added to give the releases across all five potential vectors for the Ten Main Source Categories.

Finally, the releases of all ten Main Source Categories are added up and the national inventory can be calculated, which represents the total estimated releases from all identified and quantified sources in a country. This level usually represents the third and least detailed level, which is being reported.

The release estimates for several countries can be clustered into regional release inventories.

5 PRESENTATION OF THE INVENTORY

The presentation of inventory data is critical and must be harmonized to allow for meaningful comparisons from one country to another.

5.1 Establishment of an Interim Inventory

Early in the process, an interim inventory can be used to:

- Invite comments and review on the initial stages of the study before too much resource is committed;
- Provide valuable initial comparative information at the national, regional and international level;
- Show the potential ranges of releases from the main sources; and
- Focus needs for further data gathering efforts.

The establishment of an interim inventory can take place after Main Source Categories have been identified and the activity statistics for the processes within them have been generated but before completion of detailed information gathering exercises.

The interim inventory is designed to illustrate the potential range of releases from identified processes and thus, for early priority setting. For each source the resulting output will be a range within which the final result, after detailed assessment using the Toolkit, is expected to fall. These ranges can provide valuable comparative information.

An interim inventory will contain the following information:

- a listing of all subcategories that are carried out in the country;
- the activity statistics for each category and a short description of how this was found or estimated;
- the range of emission factors by sub-category and the overall range of potential releases (mass flow multiplied by low and high-end emission factors.
- more precise country estimates, where available, shown separately from the potential range of releases made using the Toolkit default factors, along with an explanation of how the result was achieved.
- potential ranges shown as a bar chart for each source based on default emission factors.
- in-country estimates shown as points or ranges overlaid on the potential range.

The interim report would identify the main potential sources and those sources for which additional information is required and can be used as a guide to where to place most effort in the next stages of the inventory compilation.

5.2 Final Report

The final country inventory of releases of PCDD/PCDF from all activities listed in the Toolkit to all media will result from the application of the full Toolkit methodology.

The Final Report will identify the major activities and processes leading to releases, to provide information on the nature and extent of processes linked to releases and to identify those processes for which there are important data gaps that must be addressed in the future. It will also address releases to air, water, and land, in products and residues to the maximum extent possible while recognizing that there are significant deficiencies in the coverage and quality of data in some areas. Cases where no measured data or where no appropriate activity information (such as statistics) are available should be highlighted for follow-up as financial resources become available.

The guidance provided here is intended to assist in the assembly of reports that contain the crucial outputs from the inventory projects in formats that are immediately useful for the intended audiences.

Key elements of this technology-based final inventory will include:

Summary: Releases to all media for the ten Main Source Categories as identified in the screening matrix. The summary will also include the principal findings and clearly identify major data gaps, main release routes and priority areas for data collection and improvements.

The completed country inventory: Releases to all media calculated at the process subcategory level. Numerical values are preferable; otherwise an indication will be given of the relative magnitude of releases (*i.e.* a ranking). Where no emission factors and no own measured data exist, so that the release can be quantified, this will be identified. Where no release exists this will also be identified. If a process/activity does not exist in a country, a phrase such as "This activity is not realized in the country" should be introduced as to show that the respective activity has been investigated but was not present.

An example of results within subcategories is shown in Section 10.1 and summary tables of national inventories made with the Toolkit in 10.2.

Process by process summary and analysis: The bulk of a country report will consist of sections devoted to each categories investigated and detailed in the subcategories. Each sub-section will provide information on the basic process, the approaches and means used to investigate potential releases from the process and provide the findings.

Each Section is expected to be relatively short to reduce the overall report size. The key information will be included for each Section.

Detailed supporting data: This should not be included in the report to keep it short, however, data should be organized and held at the country level. It is important that at the country level the detailed background data is collected and maintained to be available for review, further assessment and update at a later time.

Incomplete information: Data gaps are common. Where information is incomplete, information obtained should be used to make an estimate for the activity. If information is insufficient to completely classify all processes, a range of relevant releases should be presented. If conservative assumptions result in very high estimates, further investigation is needed.

Example: initial process information indicated all plants operated with pollution controls although the nature of the pollution controls was unclear. In such a case it may be appropriate to take the range of emission factors from the subcategories for plants fitted with pollution controls and exclude the emission factors for plants with no controls. This serves to narrow uncertainty in the inventory and helps show need for additional resources.

Assessment: A short section summarizing:

- principal sources to each medium;
- measures in place to control these releases or expected changes to process/activities that will substantially alter the releases;
- main data gaps and their perceived importance;
- priorities for further assessment, data generation, measurements or policy measures.

6 DEFAULT EMISSION FACTORS

At the beginning of each source category within this chapter, the relevance to the Stockholm Convention will be given. The grouping will be done as follows:

- Annex C, Part II source categories: these are the industrial source categories that have potential for comparatively high formation and release of PCDD/PDCF. Part II includes four source categories.

- Annex C, Part III source categories: these are sources that are also known to unintentionally form and release PCDD/PCDF. Part III includes 13 source categories.

This Section 6 details the default emission factors, which have been determined and how these have been derived. The subcategories within the ten Main Source Categories are listed in sequential order from 1 to 10. Neither the sequence of the Main Source Categories nor the sequence of the subcategories within each Main Source Category implies any ranking of the importance of each sector within a country's dioxin inventory. Further, parameters to characterize the classes within the subcategories in the Sections below may not describe every situation in every country and a given description may not exactly match the actual situation. The next nearest class per subcategory should be used and the estimate of releases made on this basis. As described in Chapter 2 - Aims and Limitations - such cases should be notified to UNEP for inclusion in the next update of the Toolkit. Also, as releases of PCDD/PCDF are known to vary from plant to plant (or activity to activity) and from day to day the emission factors used here are designed to represent average releases from the categories shown. Individual plants may have higher or lower releases.

6.1 Main Category 1 – Waste Incineration

The incineration of waste is the source category the best studied to explain formation of PCDD/PCDF and also to identify and apply measures to prevent formation or minimize releases of PCDD/PCDF. This Chapter 6.1 addresses the incineration of different types of waste using some sort of incinerator. In many instances wastes may be burned in the open – *i.e.* with no technological incinerator at all – such cases are addressed in Section 6.6. Also, the burning of *e.g.,* wood or other clean biomass for the generation of energy, is not addressed here but in Section 6.3.2. The subcategories to be evaluated under this category include (Table 15):

Table 15: Subcategories of Main Category 1 – Waste incineration

			Potential Release Route				
No.		***Subcategories***	***Air***	***Water***	***Land***	***Product***	***Residue***
1		**Waste Incineration**	**X**				**X**
	A	Municipal solid waste incineration	X	(x)			x
	B	Hazardous waste incineration	X	(x)			x
	C	Medical waste incineration	X	(x)			x
	D	Light-fraction shredder waste incineration	X				x
	E	Sewage sludge incineration	X	(x)			x
	F	Waste wood and waste biomass incineration	X				x
	g	Destruction of animal carcasses	X				x

Relevance to Article 5, Annex C

Waste incinerators are listed in sub-paragraph (a) in Part II of Annex C and therefore have to be addressed with priority within the action plan since they may be the first to warrant the implementation of BAT and BEP.

Annex C, Part II source categories include:

	Source category	Section in Toolkit
(a)	Waste incinerators (waste types explicitly mentioned)	6.1.1, 6.1.2, 6.1.3, 6.1.5
(a)	Waste incinerators (not explicitly mentioned)	6.1.4, 6.1.6

Annex C, Part III source categories include:

	Source category	Section in Toolkit
(i)	Destruction of animal carcasses	6.1.7

6.1.1 Municipal Solid Waste

Municipal solid waste includes any type of solid waste generated by households, residential activities, and/or waste material to be disposed of by people during their normal course of living activities. It also includes domestic-like wastes produced in industrial, commercial or agricultural activities. Although the composition of municipal solid waste varies considerably from country to country, it is considered non-hazardous and common constituents are paper and cardboard, plastics, food and kitchen residues, cloth and leather, wood, glass, and metals as well as dirt and rocks and other inert materials. Small quantities of hazardous materials often cannot be eliminated such as batteries, paints, drugs, and some household chemicals.

Municipal solid waste (MSW) may be burned in a wide array of devices ranging from small, batch-type muffle furnaces to large, highly sophisticated mass burn systems with grates, heat recovery boilers for steam generation and air pollution control (APC) plants at the back end.

MSW, however, is also often burned in the open *e.g.,* in piles on the ground or in barrels or drums (200 liter) in an uncontrolled fashion; this issue is addressed in Section 6.6 - Uncontrolled Combustion Processes.

In a typical system, MSW is introduced into the furnace *via* a feed chute either continuously or batch-wise. The furnace consists of some kind of stationary or moving grate on which the MSW ignites and burns out. Combustion air is fed from underneath the grate as well as from the side. More sophisticated systems also provide for secondary air injection to improve the combustion efficiency as well as the gas burnout. Some remaining ash drops of the back end of the grate into an ash collection hopper, from where it is removed frequently and disposed of. The furnace chamber itself is either refractory lined or "water-wall". In either case the hot flue gases are retained for a certain period of time within the combustion zone for burnout and preliminary cooling. After leaving the combustion chamber, the flue gases are either cooled in a heat recovery boiler, quenched by water injection or decrease in temperature by loss of radiant heat. In some cases two stage incinerators or plants with a pyrolysis chamber at the first stage and an air/oxygen-rich afterburner have been used for MSW. These consist of two chambers, in the first waste is pyrolyzed and the gases are burned out in the secondary chamber.

In the worst case the flue gases including all entrained fly ash particles are then released into the atmosphere directly. In better plants, they are passed through a boiler and an APC system, which can consist of at least a particulate matter removal device such as a cyclone, an electrostatic precipitator (ESP), a baghouse or fabric filter, or a wet scrubber, followed by several more stages of more or less efficient gas cleaning devices, *e.g.,* active carbon adsorber or DeDiox/NO_x catalyst. As a rule of thumb, it can be stated that the sophistication and effectiveness of the APC system increases with the number of stages and different types of technologies employed.

PCDD/PCDF can pass through from the incoming waste, be formed in the combustion process or more often are formed after the combustion process is completed and the flue gas cools down. High PCDD/PCDF formation is associated with poor combustion conditions (batch operation, high CO, *etc.*), problematic input materials and dust collectors operated at high temperatures. The operation of electrostatic precipitators (ESP) at elevated temperatures (above 200 °C) can increase releases of PCDD/F to air and in fly ash. Releases from such plants would likely be higher than a similar plant using fabric filters or operating with an ESP at a lower temperature.

A municipal solid waste incinerator was included in the dioxin sampling and analysis project in Thailand (UNEP 2001, Fiedler *et al.* 2002). The plant consisted of one 250 ton per day unit. It had a reciprocating grate, a heat recovery steam boiler, a quench cooler, a dry lime injection system, and baghouse filter.

The PCDD/PCDF emissions to land are negligible and there is no product. Relevant releases to water occur only if wet scrubbers are used for the removal of particulate matter and the water is not recirculated within the process. Releases to water will occur when the effluent is not adequately treated, *e.g.,* to filter out the particles with the PCDD/PCDF adsorbed onto them or water is used to cool down the ashes and the water is not caught. Thus, the most significant release routes are to air and residue. Typically, higher concentrations are found in the fly ash, bottom ash has lower concentrations but the larger volume. If both ashes are mixed, the combined residues will be more contaminated as the bottom ashes alone. In countries with waste management plans in force, fly ashes are typically sent to landfills.

Often, bottom/grate ashes are being used as secondary building materials such as in road construction. The possible range of technologies is divided into four groups of emission factors as given in Table 16.

Table 16: Emission factors for municipal solid waste incineration

	Emission Factors - µg TEQ/t MSW Burned		
	Air	Fly Ash	Bottom Ash
1. Low technology combustion, no APC system	3,500	-	75
2. Controlled combustion, minimal APC	350	500	15
3. Controlled combustion, good APC	30	200	7
4. High technology combustion, sophisticated APC system	0.5	15	1.5

These default emission factors are based on the assumption that the waste burned leads to about 1–2 % of fly ash and 10–25 % bottom ash. Table 16 provides default emission factors for fly ash and bottom ash separately. If residues are combined the emission factor is the sum of the two. The removal efficiency of particulate matter increases with the quality of the plant. Class 1 emission factors should be chosen for very small (< 500 kg/h) and simple furnaces operated in a batch type mode without any APC system attached to the back end. Class 4 should only be used for highly sophisticated MSW incineration plants as found in some Western European countries as well as occasionally in North America. Only, if a regulatory value equivalent to 0.1 ng TEQ/Nm³ (@11 % O_2)[2] is strictly enforced, and the facility in question must be assumed to be in compliance, class 4 should be applied. The vast majority of all MSW incineration plants can be assumed to fall into classes 2 and 3.

6.1.1.1 Release to Air

Emission to air is the vector of most concern for MSW combustion. The default emission factor of 3,500 µg TEQ/t of waste burned as an average emission factor for class 1 was derived from a specific flue gas flow rate of about 10,000 Nm³/t MSW and a concentration of 350 ng I-TEQ/Nm³ (@11 % O_2). Emission factors of 3,230 µg TEQ/t have been reported from Switzerland and 5,000 µg I-TEQ/t from the Netherlands (LUA 1997). Class 2 assumes a reduction in the specific flue gas volume to 7,000 Nm³/t MSW due to better combustion controls and lower excess air. The PCDD/PCDF concentration drops to 50 ng TEQ/Nm³ (@11 % O_2). Plants of this type may be equipped with an ESP, multi-cyclone and/or a simple scrubber. In class 3, the combustion efficiency improves further and the efficiency of the APC system improves (*e.g.,* ESP and multiple scrubbers, spray-dryer and baghouse or similar combinations) resulting in a drop of the PCDD/PCDF concentration to about 5 ng TEQ/Nm³ (@11 % O_2). Also, the specific flue gas volume is reduced to 6,000 Nm³/t MSW. Class 4 represents the current state-of-the-art in MSW incineration and APC technology (*e.g.,* activated carbon adsorption units or SCR/DeDiox). Thus, only 5,000 Nm³/t MSW and a concentration of less than 0.1 ng TEQ/Nm³ (@11 % O_2) will be the norm (LUA 1997, IFEU 1998).

[2] As required for waste incineration plants in EU member states according to EU Directive 2000/76/EC (EC 2000)

The flue gas concentrations @11 % O_2 at the Thai municipal solid waste incinerator ranged from 0.65 to 3.10 ng I-TEQ/Nm³ with an average of 1.71 ng I-TEQ/Nm³ (@11 % O_2). The concentrations of total PCDD/PCDF (Cl_4-Cl_8) were between 41.3 and 239 with a mean of 122 ng/Nm³ (@11 O_2). The measured average concentration of 122 ng PCDD/PCDF/m³ is above the Thai standard for municipal waste incinerators of 30 ng/m³; the mean of 1.7 ng I-TEQ/Nm³ is also above the European standard of 0.1 ng I-TEQ/m³. The measured emissions would result in an emission factor of 6.1 µg TEQ/t of waste burned. The Toolkit would have classified this incinerator into class 3 and would have given an emission factor of 30 µg TEQ/t. Applying the Toolkit's default emission factor, the release would have been over-estimated by a factor of 5 but would have fallen into the anticipated order of magnitude.

6.1.1.2 Release to Water

Releases to water may occur when wet scrubbers are employed for the removal of particulate matter or to cool down ashes. In this case, the amount of PCDD/PCDF released through this vector, can best be estimated using the default emission factors supplied for residue. Normally, concentrations are in the range of a few pg I-TEQ/L and the highest PCDD/PCDF concentration reported in a scrubber effluent before removal of particulate matter was below 200 pg/L. Most of the PCDD/PCDF is associated with the particulate matter and consequently removed during wastewater treatment. Additionally, most of the APC equipment installed at MSW incineration plants operates wastewater free. Presently, such releases cannot be quantified.

6.1.1.3 Release to Land

No release to land is expected unless untreated residue is directly placed onto or mixed with soil. The concentration released in such cases will be covered under "Release in Residues", Chapter 6.1.2.5

6.1.1.4 Release in Products

The process has no product, thus there will be no emission factor.

6.1.1.5 Release in Residues

PCDD/PCDF concentrations in the fly ash are substantial, even though the total mass generated per ton of MSW is typically only around 1–2 %. PCDD/PCDF concentrations in the bottom ash are rather low, however, the amount of bottom ash generated per ton of MSW is around 10–20 % [3]. Fly ash and bottom ash also contain unburned carbon from 1 % (class 4) up to 30 % (class 1). Since unburned carbon in the ash greatly enhances the adsorption of PCDD/PCDF, the concentration is greatest in class 1; here, 500 ng TEQ/kg were chosen for

[3] In some Western European countries, 300 kg of bottom ash per ton of municipal solid waste burned (30 %) were generated when the share of in inerts and glass was higher in the 1960s and 1970s.

bottom ash [4]. As these types of incinerators do not have a collection system for fly ash, there will be no emission factor for fly ash. In class 2 the concentration is assumed to be 30,000 ng TEQ/kg in fly ash and 100 ng TEQ/kg in bottom ash due to greatly improved combustion efficiency resulting in a much lower LOI of the ash. Class 3 cuts these values in half based on further improvements. Class 4 assumes not only high combustion efficiency but also a very high collection efficiency, especially of the very small fly ash particles. These small particles supply a large adsorption surface for PCDD/PCDF and therefore the overall concentration does not decrease further. Thus, the value for the fly ash is set at 1,000 ng I-TEQ/kg and the concentration for the bottom ash drops to 5 ng TEQ/kg.

6.1.2 Hazardous Waste Incineration

Hazardous waste (HW) refers to residues and wastes, which contain hazardous materials in significant quantities. Generally spoken, all materials including consumer goods, which require special precautions and restrictions during handling and use belong to this group. Any consumer goods, which are labeled to such an extent and have entered the waste stream, must be considered hazardous waste. These include solvents and other volatile hydrocarbons, paints and dyes, chemicals including pesticides, herbicides, and other halogenated chemicals, pharmaceutical products, batteries, fuels, oils and other lubricants, as well as goods containing heavy metals. Also, all materials contaminated with these materials such as soaked rags or paper, treated wood, production residues, *etc.,* must be considered hazardous waste.

The term "hazardous waste" as used in the Toolkit does not include hospital waste (see next section 6.1.3) since the location of the waste's origin and the technology where hazardous waste and hospital waste, respectively, are treated are different. Further, for the compilation of a PCDD/PCDF release inventory accessibility of primary data, such as location and rate of waste generation are different for these two types. When looking for data suppliers on the amounts and types of hazardous waste generated and incinerated, Ministries of Industry, associations and/or private companies hat treat such wastes may be the primary contacts. In the case of hospitals wastes, very often information can be found at the Ministry of Health or local health authorities or at individual hospitals known that they operate incinerators.

Typically hazardous waste is burned either in special technology incinerators or in rotary kiln type furnaces. Special technology incinerators include very low technology drum type, grate type, or muffle type furnaces. Also, other technologies such as supercritical water oxidation, electric arc vitrification, *etc.,* which treat hazardous waste can be included in this group (although they are not necessarily classified as "incineration"). Since the classification of hazardous waste is highly dependant on country specific legislation and the number of different technologies used for hazardous waste incineration is almost unlimited. The following brief process description covers only the rotary kiln technology most commonly used at commercial waste incineration plants designed to accept a wide range of wastes.

Solid hazardous waste is introduced into a refractory lined rotary kiln *via* a feed chute. High calorific liquid as well as sludge waste is atomized in a burner or combustion lance located in the front wall of the rotary kiln respectively. The waste ignites and combusts inside the

[4] Extrapolated value: assumed 10-fold above the average measured concentrations from European plants of the 1980s

rotary kiln, which is typically maintained at temperatures above 1,000 °C. In the usually 10–20 meter long rotary kiln, the hazardous waste is converted into flue gas and furnace ashes/molten slag, both of which leave the rotary kiln at the back end. The vitrified ash is quenched in a water bath, separated and disposed of. Due to the fact that in most modern facilities, the bottom ash results from molten slag, the PCDD/PCDF concentrations in these slags are generally low compared to those in the fly ashes. For the older technologies, no data could be obtained. Following the rotary kiln, the flue gas enters a secondary combustion chamber where additional burners burning high calorific hazardous waste maintain a temperature above 1,200 °C. Also, secondary combustion air is injected for additional burnout of the gas. After leaving the 2-stage combustion system, the flue gas is treated the same way as described for MSW incineration. In many cases the solid residues from the furnace of a hazardous waste incinerator is considered as hazardous waste and re-introduced into the furnace. In general, hazardous waste incinerators are operated hotter than MSW incinerators, but with a higher amount of excess air. This leads to overall similar gaseous PCDD/PCDF emissions. However, due to the commonly high content of halogenated organics in the hazardous waste, deficiencies and imperfections in the combustion process make it more susceptible towards higher PCDD/PCDF emissions. The release vectors are identical with the ones outlined for MSW incineration. Thus, four groups of emission factors are given in Table 17.

Table 17: Emission factors for hazardous waste incineration

	Emission Factors - µg TEQ/t HW Burned	
	Air	Residue (Fly Ash Only)
1. Low technology combustion, no APC system	35,000	9,000
2. Controlled combustion, minimal APC	350	900
3. Controlled combustion, good APC	10	450
4. High technology combustion, sophisticated APC system	0.75	30

These default emission factors are based on the assumption that the waste burned leads to about 3 % of fly ash and the PCDD/PCDF release associated with the disposal of bottom ash is negligible in classes 3 and 4. No data exist for classes 1 and 2 for bottom ash concentrations. Also, the removal efficiency of particulate matter increases with the quality of the plant. Class 4 should only be used for highly sophisticated hazardous waste incineration plants as found in some Western European countries and in North America. Only, if a regulatory value of 0.1 ng TEQ/Nm³ (@11 % O_2) - such as in European legislation - is strictly enforced, and the facility in question must be assumed to be in compliance, class 4 should be applied. The vast majority of all hazardous waste incineration plants can be assumed to fall into classes 2 and 3. Class 1 should be chosen mainly for very small (< 500 kg/h) and simple furnaces operated in a batch type mode without any APC system attached to the back end, *e.g.,* muffle ovens.

6.1.2.1 Release to Air

Releases to air are the predominant vector for HW combustion. The default emission factor for class 1 was derived from a specific flue gas volume flow rate of about 17,500 Nm^3/t of hazardous waste and a concentration of about 2,000 ng TEQ/Nm^3. Class 2 assumes a reduction in the specific flue gas volume flow rate to 15,000 Nm^3/t of hazardous waste due to better combustion controls and lower excess air. The PCDD/PCDF concentration drops to 20 ng TEQ/Nm^3 (@11 % O_2) in this case. In class 3, the combustion efficiency improves further and the efficiency of the APC system improves resulting in a drop of the PCDD/PCDF concentration to about 1 ng TEQ/Nm^3 (@11 % O_2). Also, the specific flue gas volume flow rate is reduced to 10,000 Nm^3/t HW. Class 4 represents the current state-of-the-art in HW incineration and APC technology. Thus, only 7,500 Nm^3/t HW and a concentration of significantly less than 0.1 ng TEQ/Nm^3 (@11 % O_2) is realistic (LUA 1997, IFEU 1998, Environment Canada 1999).

6.1.2.2 Release to Water

Releases to water occur when wet scrubbers are employed for the removal of particulate matter. In this case the amount of PCDD/PCDF released through this vector can best be estimated using the default emission factors supplied for residue. The maximum actual PCDD/PCDF concentration found in wet scrubber effluent was below 0.15 µg TEQ/t (LUA 1997). Overall, this release vector is not considered to be important for this source type.

6.1.2.3 Release to Land

No release to land is expected unless untreated residue is directly placed onto or mixed with soil. The concentration released in such cases will be covered under “Release in Residues”, Chapter 6.1.2.5

6.1.2.4 Release in Products

The process has no product, thus no release to product occurs.

6.1.2.5 Release in Residues

To generate emission factors only fly ash has been taken into account for the residue, since no data for bottom ash is available for classes 1 and 2. For classes 3 and 4, in which it must be assumed, that the bottom ash is extracted from the furnace, no substantial contribution to the overall release of PCDD/PCDF occurs. Consequently, only PCDD/PCDF concentrations in the fly ash residue are substantial and will be considered further. The amount of fly ash in hazardous waste is typically around 3 %. Fly ash also contains unburned carbon of 0.5 % (class 4) up to 20 % (class 1). Since unburned carbon in the fly ash greatly enhances the adsorption of PCDD/PCDF, the concentration is greatest in class 1. In class 1 the PCDD/PCDF was assumed to be around 300,000 ng TEQ/kg residue. In class 2 the concentration drops to 30,000 ng TEQ/kg residue due to greatly improved combustion efficiency resulting in a much lower LOI of the fly ash. Class 3 cuts this value down to

15,000 ng TEQ/kg residue based on further improvements. Class 4 assumes not only high combustion efficiency but also very high collection efficiency, especially of the very small fly ash particles. These small particles supply a large adsorption surface for PCDD/PCDF and therefore the overall concentration decreases to about 1,000 ng TEQ/kg residue. If absolutely no fly ash data is available but actual stack emission data exists, it is fair to assume the PCDD/PCDF emissions through the residue vector to be similar and roughly in the same order of magnitude when compared to the air. Thus, the overall emissions can roughly be split equally between the air and the residue vector. However, this provides a much less accurate estimate of the overall PCDD/PCDF emissions due to the different nature and composition of hazardous waste fly ash.

6.1.3 Medical Waste Incineration

Medical waste is considered to be every waste generated from medical activities regardless if these activities take place in a hospital or are performed by a medical doctor, dentist or any other physician. The waste generated during these activities contains in many cases infectious materials, secretes, blood, pharmaceuticals and packaging materials and/or tools used during or for the medical treatment of people or animals. To reliably destroy viruses, bacteria, and pathogens his waste is often thermally treated (by incineration or pyrolysis). Further, due to its origin and its composition, medical waste can contain toxic chemicals, *e.g.,* heavy metals or precursors, which may form dioxins and furans. In many countries, medical waste is a waste that requires special surveillance and it was found that incineration of all wastes generated within a hospital would be the most efficient way to get rid of these wastes. However, it has also been shown, that incineration of medical waste in small and poorly controlled incinerators was a major source of PCDD/PCDF (UNEP 1999). Consequently, these small plants have mainly been closed or sometimes upgraded in developed countries. Based on these experiences, the thermal treatment of medical waste constitutes an own subcategory in the Toolkit. Information on location, volumes of waste generated and incinerated typically can be obtained from Ministries of Health, municipalities, *etc.*, or the private sector charged with the disposal of this type of waste.

Typically, medical waste is incinerated locally at the hospital or any other medical facility in small furnaces in a batch-type mode. In many cases, larger and centralized medical waste incineration facilities are operated only for eight hours a day and five days a week. Large and continuously operated medical waste incinerators are extremely rare and mostly found in Western Europe and North America. Also, waste heat recovery boilers are rare.

Results from a developing country are available from a dioxin/furan measurement program at a hospital waste incinerator in Thailand. The plant consisted of two identical units, which were started-up every morning and operated until all the hospital waste delivered was incinerated. The furnace had a static grate, was equipped with a secondary combustion chamber and two afterburners. It should be noted that not all the equipment with which the facility was originally designed was present. The flue gases passed over an alkaline water bath before being discharged through a flue stack. Overall, the plant appeared poorly designed and poorly maintained (UNEP 2001, Fiedler *et al.* 2002).

The Toolkit defines four classes of emission factors for medical waste incinerators (Table 18). The high emissions of PCDD/PCDF from medical waste incineration are caused by the batch-type operations, which commonly lead to a long warming and cooling phase of the furnace resulting in pyrolytic conditions in the furnace over an extended period of time.

Combined with the high heating value and halogenated plastics in the waste, the PCDD/PCDF formation potential is generally higher than for municipal solid waste. The major release vectors of concern are air and residue (here fly ash only due to the lack of data for bottom ash). Water releases are less important since APC equipment, if present at all, is almost wastewater free.

Table 18: Emission factors for medical waste incineration

	Emission Factors - µg TEQ/t Medical Waste Burned	
	Air	Residue
1. Uncontrolled batch type combustion, no APC system	40,000	200 *
2. Controlled, batch type combustion, no or minimal APC	3,000	20 *
3. Controlled, batch type combustion, good APC	525	920 **
4. High technology, continuous, controlled combustion, sophisticated APC system	1	150 **

* refers only to bottom ash left in the combustion chamber
** refers to the combined bottom and fly ashes

These default emission factors are based on the assumption that the medical waste burned leads to about 3 % of fly ash and the PCDD/PCDF release associated with the disposal of bottom ash is currently unknown, since no measured data are available presently. Also, the removal efficiency of particulate matter increases with the quality of the plant. Class 1 should be chosen for very small and simple, small box type incinerators operated intermittently (in which a load of waste is ignited and left) with no secondary combustion chamber, no temperature controls and no pollution control equipment. Class 2 applies to all medical waste incinerators with controlled combustion and equipped with an afterburner, which, however, are still operated in a batch type mode. Class 3 should be applied for controlled batch-type plants, which have good APC systems in place, *e.g.,* ESPs or preferably baghouse filters. Class 4 should only be used for highly sophisticated medical waste incineration plants as found in some Western European countries as well as occasionally in North America, *e.g.,* if a limit value equivalent to 0.1 ng TEQ/Nm³ (@11 % O_2) is strictly enforced, and the facility can be assumed to be in compliance. In this latter case the question of continuous *versus* batch type operation will become irrelevant, since these facilities are usually preheated with oil or natural gas extensively. Only after the intended furnace operating temperature of usually well above 900 °C is reached, medical waste is introduced into the furnace. The vast majority of medical waste incineration plants can be assumed to fall into class 2. Larger, centralized plants may be grouped into class 3.

6.1.3.1 Release to Air

Release to air is the predominant vector for medical waste incineration. The default emission factor for class 1 was derived from a specific flue gas volume flow rate of about 20,000 Nm³/t medical waste and a concentration of about 2,000 ng TEQ/Nm³ (@11 % O_2). Class 2 assumes a reduction in the specific flue gas volume flow rate to 15,000 Nm³/t medical waste due to better combustion controls and lower excess air. The PCDD/PCDF concentration drops to 200 ng TEQ/Nm³ (@11 % O_2) in this case. Class 3 is based on European data where a concentration of 35 ng I-TEQ/Nm³ (@11 % O_2) with 15,000 Nm³/t has been determined. Class 4 represents the current state-of-the-art in medical waste

incineration and good APC technology. In these cases, only 10,000 Nm³/t of medical waste was generated and a concentration of less than 0.1 ng TEQ/Nm³ (@11 % O_2) was measured (LUA 1997, IFEU 1998, Environment Canada 1999).

The PCDD/PCDF concentrations emitted *via* the stack to air from the hospital waste incinerator in Thailand were – adjusted to 11 % O_2 – between 21.8 and 43 ng I-TEQ/Nm³ for line A and between 10.7 and 45.0 ng I-TEQ/Nm³ for line B; the averages were 33.8 and 28.6 ng I-TEQ/Nm³, respectively. These emissions resulted in an emission factor of approximately 1,200 µg TEQ/t of waste burned, which is between the class 2 (3,000 µg TEQ/t) and class 3 (525 µg TEQ/t) emission factors.

6.1.3.2 Release to Water

Releases to water occur when wet scrubbers are employed for the removal of particulate matter and quench water is used to cool ashes. This is hardly ever the case except in Western Europe where wet scrubbers are occasionally used for acid gas absorption. This would only be applicable to class 4. Measured concentrations of PCDD/PCDF in scrubber water after medical waste incinerators are not available. Where wet scrubbers and quenching of ashes are identified, the water treatment should be noted.

6.1.3.3 Release to Land

No release to land is expected unless untreated residue is directly placed onto or mixed with soil. The concentration released in such cases will be covered under "Release in Residues", Chapter 6.1.3.5

6.1.3.4 Release in Products

The process has no product; thus no release to product occurs.

6.1.3.5 Release in Residues

PCDD/PCDF concentrations in the fly ash are substantial. Due to a lack of data for PCDD/PCDF concentration in bottom ash, default emission factors provided in the residue category only relate to PCDD/PCDF releases *via* fly ash PCDD/PCDF concentrations in the residues can be high, especially where combustion is poor (*e.g.,* in a simple batch-type incinerator). Classes 1 and 2 medical waste incinerators will not generate fly ash due to the lack of dust removal equipment. In these cases, all residues will consist of the residue left in the combustion chamber. The class 1 emission factor is based on the assumption that the 200 kg of residue per ton of medical waste burned is left in the combustion chamber with a concentration of 1,000 ng TEQ/kg. For class 2, combustion is improved, so the bottom ash residue should contain only 100 ng TEQ/kg; resulting in an emission factor of 20 µg TEQ/t of waste.

For classes 3 and 4, fly ash is being collected and mixed with grate ash; the amount of fly ash in medical waste typically is around 3 %. Class 3 assumes 30,000 ng TEQ/kg in the fly ash

and 100 ng TEQ/kg in the grate ash (same as class 2). Class 4 incinerators have high combustion efficiency, resulting in an organic carbon content of about 1 % of unburned carbon but also a very high collection efficiency of the very small fly ash particles. Fly ash is collected (30 kg/t of waste) with a concentration of 5,000 ng TEQ/kg and 10 ng TEQ/kg of grate ash is chosen. These small particles supply a large adsorption surface for PCDD/PCDF and therefore the overall concentration does not decrease any further.

The results from the hospital waste incinerator in Thailand were extremely high due to the poor combustion conditions in the primary chamber and the operation on-site, where the bottom ashes were left overnight in the chamber to slowly cool down. Such conditions create high concentrations of PCDD/PCDF. We found bottom ash concentrations of 1,390 and 1,980 ng TEQ/kg of bottom ash, which is about 20 times higher than was expected for a class 2 bottom ash (UNEP 2001, Fiedler *et al.* 2002).

6.1.4 Light-Fraction Shredder Waste Incineration

Light-fraction shredder waste (LFSW) in the sense used here (also sometimes referred to as shredder "fluff" or light weight aggregate) describes the light fraction derived from shredder. In many countries, large items such as old vehicles, white goods, bulky containers, *etc*. are shredded in order to reduce the volume as well as enable the separation of recoverable materials such as metals from plastics and composites. Typical separation mechanisms include screening, sifting, and fractionation processes, which utilize the weight differences between the materials or the magnetic properties of ferrous metals in order to fractionate the shredder aggregate into ferrous metals, non-ferrous metals, glass, other heavy inerts, and light-weight aggregate fractions. In some cases the light fraction has little use and may be combusted for disposal.

The release vectors of concern are air and residue, since APC equipment, if present at all, maybe wastewater free. Thus, three groups of emission factors are given in Table 19.

Table 19: Emission factors for LFSW incineration

	Emission Factors - µg TEQ/t LFSW Burned	
	Air	Residue
1. Uncontrolled batch type combustion, no APC system	1,000	ND
2. Controlled, batch type combustion, no or minimal APC	50	ND
3. High technology, continuous, controlled combustion, sophisticated APC system	1	150

The default emission factors given are based on the assumption that the LFSW burned leads to about 1 % of fly ash. Class 1 should be chosen for very simple type combustors such as barrels, drums or simple stationary grate furnaces with no combustion controls and no APC equipment attached. Batch type operated furnaces without any APC also fall into class 1. Class 2 should be chosen for all other furnaces with some kind of combustion control technology such as under and/or over fire air, stoker controls, fluidized beds, *etc.* including the facilities with some kind of APC system such as an ESP, baghouse or wet scrubber for dust removal. Class 2 also applies to LFSW incinerators with controlled combustion and adequate APC equipment, which, however, are still operated in a batch type mode. The vast

majority of all LFSW incineration plants can be assumed to fall into classes 1 and 2. Class 3 should only be used for highly sophisticated RDF incineration plants as found in North America and occasionally in Western Europe. Only, if a regulatory value equivalent to 0.1 ng TEQ/Nm³ (@11 % O_2) is enforced, and the facility in question must be assumed to be in compliance, class 3 should be applied.

6.1.4.1 Release to Air

Releases to air are the most important release vector for LWSF combustion. There are not many measured data from this type of activity. The default emission factor for class 1 was derived based on a emission factor of 1,000 ng TEQ/kg as determined by the US EPA during a barrel burn study of selected combustible household waste which closely resembles the composition of fluff. Class 2 uses various emission data from a series of Western European and North American RDF facilities including Japanese fluidized bed combustors with minimal APC equipment. An emission factor of 50 µg TEQ/t was determined. Class 3 represents the current state-of-the-art in LFSW incineration and APC technology. Thus, only 10,000 Nm³/t light-shredder waste and a concentration of less than 0.1 ng TEQ/Nm³ (@11 % O_2) is taken (US EPA 1999, LUA 1997, IFEU 1998, Environment Canada 1999).

6.1.4.2 Release to Water

Measured PCDD/PCDF concentrations found in scrubber effluent after LFSW incinerators are not available. No emission factor can be provided.

6.1.4.3 Release to Land

No release to land is expected unless untreated residue is directly placed onto or mixed with soil. The concentration released in such cases will be covered under “Release in Residues”, Chapter 6.1.4.5

6.1.4.4 Release in Products

The process has no product; thus no release to product occurs.

6.1.4.5 Release in Residues

PCDD/PCDF concentrations in fly ash must be assumed to be high. The amount of fly ash in LFSW is typically around 1 %. Fly ash also contains unburned carbon of 5 % (class 3) up to presumably 30 % (class 1). In class 1, no APC equipment is used and consequently no fly ash is collected but rather most of it is emitted to the atmosphere with the flue gas. Even though no specific collection device for fly ash is installed and the majority of the fly ash is discharged through the stack, some fly ash is expected to collect in the furnace and the ductwork leading to the stack as well as in the stack itself. Since unburned carbon in the fly ash greatly enhances the adsorption of PCDD/PCDF, the concentration is greatest in class 1. However, no accurate data is available. Class 3 assumes not only high combustion efficiency

but also very high collection efficiency, especially for the very small fly ash particles. Thus, a value of 15,000 ng TEQ/kg is chosen. These small particles supply a large adsorption surface for PCDD/PCDF and therefore the overall concentration does not decrease any further (US EPA 1999, LUA 1997, IFEU 1998).

6.1.5 Sewage Sludge Incineration

Sewage sludge is the product of any wastewater treatment processes regardless of its origin (*e.g.,* wastewater from municipal, agricultural or industrial activities). Wastewater always contains solids, which are normally removed during the treatment process. Since PCDD/PCDF are virtually insoluble in water, the bulk of the PCDD/PDCD adsorbs to the solids present in the wastewater. If the solids are not removed, the PCDD/PCDF will be discharged with the wastewater. These solids can be removed by filtration or flocculation, so that the PCDD/PCDF are collected in the wastewater treatment sludges. These sludges can be either incinerated, otherwise treated (co-combustion in power plants or cement kilns, undergo wet oxidation, pyrolysis, gasification, *etc.*) or landfilled. This subsection addresses PCDD/PCDF releases from incineration of sewage sludge in dedicated plants; the latter two issues are addressed in Main Source Category 9 (Section 6.9.2). Incineration of sewage sludge is quite common, especially in industrialized countries. Incineration of sludge from industrial processes such as the pulp and paper industry, where the sewage sludge has a substantial heating value and is used for heat and energy generation purposes, is covered in Main Source Category 7 (Section 6.7.1). Another option for the disposal of sewage sludge is co-incineration in boilers, *e.g.,* fossil fuel power plants (see Main Source Category 3 – Section 6.3.1) or in cement kilns (see Main Source Category 4 - Section 6.4.1).

Sewage sludge is incinerated in either bubbling or circulating fluidized bed furnaces where the formation of PCDD/PCDF is limited due to good combustion conditions. Also, high removal efficiencies of particulate matter, which are critical for the operation of circulating fluidized bed furnaces, reduce PCDD/PCDF emissions. Other furnace types commonly used are vertical rotary stage or open hearth-type furnaces, grate-type furnaces or muffle-type furnaces. All furnace types lead to reasonably low PCDD/PCDF formation depending, however, on the composition of the sludge burned. Incineration of sludge with a high content of halogenated hydrocarbons and/or other organic contaminants as well as heavy metals such as copper can increase the PCDD/PCDF emissions.

The release vectors of concern are mostly air and residue. Releases to water can occur with the use of wet scrubbers. Three groups of emission factors are given in Table 20.

Table 20: Emission factors for sewage sludge incineration

	Emission Factors - µg TEQ/t Sewage Sludge	
	Air	Residue
1. Older furnaces, batch type operation, no or very little APC equipment	50	23
2. Updated, continuously operated and controlled facilities, some APC equipment	4	0.5
3. Modern state-of-the-art facilities, continuous, controlled operation, full APC system	0.4	0.5

6.1.5.1 Release to Air

Releases to air represent the most important vector for sewage sludge combustion. The default emission factor for class 1 was determined based on an average emission concentration of 4 ng TEQ/Nm³ (@11 % O_2) and a specific flue gas volume flow rate of about 12,500 Nm³/t of sewage sludge burned based on a Belgian study as well as value of 77 ng TEQ/kg reported from the UK for a multiple hearth furnace with ESP. Class 2 is an emission factor determined in The Netherlands from fluidized bed plants with scrubbers and ESP. Class 3 is for fluidized bed plants with optimized air pollution control systems consistently meeting the emission limits equivalent to 0.1 ng I-TEQ/Nm³ (@11 % O_2) (from Canadian, German and Swiss measurements) (LUA 1997, IFEU 1998, Environment Canada 1999).

6.1.5.2 Release to Water

PCDD/PCDF concentrations in scrubber effluent from sewage sludge incinerators are not available. However, since wastewater from wet scrubbers is often treated and then reintroduced to the wastewater treatment plant, no PCDD/PCDF are released from the incineration plant to water.

Where plants use wet scrubbers or simple water quench is applied to cool down the off-gases or to quench grate ash this should be noted as well as the treatment and fate of the effluents. The European inventory (EU 1999) reports concentrations between 1.2 and 6.5 pg I-TEQ/L in scrubber effluents from sewage sludge incinerators.

6.1.5.3 Release to Land

No release to land is expected unless untreated residue is directly placed onto or mixed with soil.

6.1.5.4 Release in Products

The process has no product; thus no release to product occurs.

6.1.5.5 Release in Residues

UK testing (Dyke *et al* 1997) of multiple hearth furnaces showed PCDD/PCDF in the grate ash at concentrations of 39 ng TEQ/kg and 470 ng TEQ/kg in fly ash from the ESP. Rates of ash production were 430 kg per ton of grate ash and 13 kg per ton of ESP ash for the multiple hearth plant. Levels in ash (all the ash was collected in the ESP) from fluidized bed combustion were much lower (<1 ng TEQ/kg). 373 kg of ESP ash was produced per ton of sludge combusted in the fluidized bed.

Class 1 releases to residues (combined) are therefore 23 µg TEQ/ton of waste. Class 2 releases are 0.5 µg TEQ/ton of waste. Class 3 releases are estimated the same as class 2.

6.1.6 Waste Wood and Waste Biomass Incineration

This subcategory addresses the combustion of waste wood and waste biomass in furnaces under controlled conditions. This Section deals with the incineration of wood and biomass, which may have been treated or become mixed with treated wood or contaminated biomass. This waste biomass is incinerated in furnaces under conditions ranging from no control to highly controlled. The combustion of clean biomass for generation of energy is addressed in Section 6.3.2. Any "clean" biomass or contaminated biomass burned on land will be discussed in Section 6.6 – Uncontrolled Combustion Processes.

Contaminated wood and other contaminated biomass can result from many anthropogenic activities. The major ones are wood processing industries (*e.g.,* building materials, furniture, packing materials, toys, ship building, general construction, *etc*.). In addition, combustion of construction debris is covered in this category. The wood/biomass waste may contain paints, coatings, pesticides, preservatives, anti-fouling agents, and many other things. These materials, when incinerated together with the biomass, can enhance the formation of PCDD/PCDF during combustion. In many cases, combustion conditions may be poor, which can severely increase the formation and release of PCDD/PCDF.

In modern facilities, biomass is burned in either stationary or circulating fluidized bed furnaces where the formation of PCDD/PCDF is greatly limited due to good combustion conditions. Such plants would likely have effective pollution control systems, especially removal of particulate matter, which is critical for the operation of circulating fluidized bed furnaces. Other furnace types commonly used are vertical rotary stage or open hearth-type furnaces, grate-type furnaces or muffle-type furnaces. All furnace types lead to reasonably low PCDD/PCDF formation depending, however, on the composition of the biomass burned. Biomass with a high content of halogenated hydrocarbons or heavy metals such as copper, lead, tin, or cadmium typically result in higher PCDD/PCDF emissions than the burning of virgin biomass. Three classes of emission factors are given in Table 21.

Table 21: Emission factors for waste wood/biomass incineration

	Emission Factors - µg TEQ/t Biomass Burned	
	Air	Residue (Fly Ash Only)
1. Older furnaces, batch type operation, no APC equipment	100	1,000
2. Updated, continuously operated and controlled facilities, some APC equipment	10	10
3. Modern state-of-the-art facilities, continuous controlled operation, full APCS	1	0.2

6.1.6.1 Release to Air

Releases to air are the predominant vector for waste wood and biomass combustion. The default emission factors for all three categories were determined based on reported emission concentrations between 130 µg TEQ/t (Belgian study) and 1 µg TEQ/t (Canadian and Swedish studies). Thus, for class 1 a default emission factor of 100 µg TEQ/t was chosen for those old uncontrolled facilities. Class 2 represents better controlled newer facilities. A default emission factor of 10 µg TEQ/t was assigned to this class. Finally, class 3 with a selected default emission factor of 1 µg TEQ/t includes all the modern facilities for waste wood and biomass combustion (LUA 1997, IFEU 1998, Environment Canada 1999).

6.1.6.2 Release to Water

This release vector is not considered to be important for this source type.

6.1.6.3 Release to Land

No release to land is expected unless untreated residue is directly placed onto or mixed with soil. The concentration released in such cases will be covered under “Release in Residues”, Chapter 6.1.6.5

6.1.6.4 Release in Products

The process has no product; thus there will be no emission factor.

6.1.6.5 Release in Residues

PCDD/PCDF concentration in the ash will be high since the ash usually contains rather high concentrations of unburned carbon. Especially in older furnaces, higher gaseous emissions clearly indicate lower combustion efficiency resulting in higher concentrations of unburned carbon in the fly ash. Thus, high concentrations of PCDD/PCDF in the ash must be expected. Unfortunately, only very limited data from Canada as well as Germany was found indicating a wide range from as high as 23,000 ng TEQ/kg ash to as low as 3.7 ng TEQ/kg of ash. Based on the fact that the total ash concentration in waste wood and biomass averages

between 3 % and 10 %, an average value of 5 % was chosen. This leads to a default emission factor of about 1,000 µg TEQ/t for class 1 and 0.2 µg TEQ/t for class 3. For class 2, a medium value was chosen due to lack of data (LUA 1997, IFEU 1998, Environment Canada 1999). In class 1, no APC equipment is used and consequently no fly ash is collected but rather most of it is emitted to the atmosphere with the flue gas. Even though no specific collection device for fly ash is installed and the majority of the fly ash is discharged through the stack, some fly ash is expected to collect in the furnace and the ductwork leading to the stack as well as in the stack itself. Measured data for bottom ash could not be obtained, which results in the fact that the default emission factors for residue only consider fly ash.

6.1.7 Destruction of Animal Carcasses

The thermal destruction of animal carcasses can be applied to avoid public health risks resulting from natural decay of carcasses. The combustion process itself is often poorly controlled and incomplete combustion is the norm rather than the exception, since the main purpose is disinfection and complete eradication of all biological activity rather than complete combustion or even energy generation.

Animal carcasses are often burned in simple, low technology furnaces. Thus, it is virtually impossible to describe a typical animal carcass-burning furnace. These furnaces are often not designed to guarantee well-controlled combustion conditions nor a high removal efficiency of particulate matter to keep PCDD/PCDF emissions low.

The release vectors of concern are air and residue. Only where the combustion takes place directly on the soil, a release to land will exist. However, no data is available for such soil contamination. Three classes of emission factors are given in Table 22.

Table 22: Emission factors for destruction of animal carcasses

	Emission Factors - µg TEQ/t Animal Carcasses Burned	
	Air	Residue
1. Older furnaces, batch type operation, no APC equipment	500	ND
2. Updated, continuously operated and controlled facilities, some APC equipment	50	ND
3. Modern state-of-the-art facilities, continuous controlled operation, full APC system	5	ND

6.1.7.1 Release to Air

Release to air is the predominant vector for animal carcass burning. The default emission factors for all three classes were determined based on reported emission concentrations between almost 50 µg TEQ/100 kg body weight (UK study) and less than 0.5 µg TEQ/100 kg body weight (Austrian and German studies). Thus, for class 1 a default emission factor of 500 µg TEQ/t body weight was chosen for those old uncontrolled facilities as well as open burning of animal carcasses. Class 2 represents better-controlled newer facilities. A default emission factor of 5 µg TEQ/100 kg (= 50 µg TEQ/t) body weight was chosen based on data from Switzerland, Germany and the UK for this class. Finally, class 3 with a selected default

emission factor of 5 µg TEQ/t body weight includes all the modern facilities for animal carcass combustion (LUA 1997, IFEU 1998).

6.1.7.2 Release to Water

This release vector is not considered to be significant for this source type.

6.1.7.3 Release to Land

Release to land is only expected the combustion of animal carcasses directly on the ground. This situation is not addressed in this section and would fall into Section 6.6.2.

6.1.7.4 Release in Products

The process has no product; thus no release to product occurs.

6.1.7.5 Release in Residues

PCDD/PCDF concentration in the ash is high since the ash usually contains rather high concentrations of unburned carbon. Especially in older furnaces and in open burning situations higher gaseous emissions clearly indicate lower combustion efficiency resulting in higher concentrations of unburned carbon in the fly ash. Thus, high concentrations of PCDD/PCDF in the ash must be expected. No data was found for assigning default emission factors.

6.2 Main Category 2 – Ferrous and Non-Ferrous Metal Production

The iron and steel industry as well as the non-ferrous metal industry are highly material and energy intensive industries. Considerable amounts of the mass input become outputs in the form of off-gases and residues. The most relevant emissions are those to air. Further, secondary materials and the rate of reuse and recycling of solid residues constitute a large part of the industries activities. Ores and concentrates contain quantities of metals other than the prime target metal and processes are designed to obtain a pure target metal and to recover other valuable metals as well. These other metals tend to concentrate in the residues from the process, and in turn, these residues form the raw material for other metal recovery processes. Lastly, filter dusts can be recycled within the same plant or used for the recovery of other metals at other non-ferrous metal installations, by a third party or for other applications.

In this Toolkit, primary metallurgical processes are understood to be those aimed at obtaining metals such as iron, copper, aluminum, lead, zinc, *etc.,* from their original ores, whether sulfidized or oxidized, through such processes as concentration, smelting, reduction, refining, *etc.* Secondary metallurgical processes utilize scrap metals, often coated with plastics, paints, used batteries (for lead productions), oils, *etc.* and/or slags or fly ashes from metallurgical or other processes. In this chapter, the term "primary" metal production should only be applied when no used or waste material enter into the process as the metal source.

PCDD/PCDF are relevant to the production of metals and particularly the production from secondary raw materials has been recognized as a source of dioxins and furans (LUA 1997, LUA 2000, UNEP 1999). In addition, processes that need chlorination such as the electrolytic production of magnesium from seawater and dolomite may generate PCDD/PCDF (see Section 6.2.9). PCDD/PCDF or their precursors may be present in some raw materials and enter the process or they are newly formed from short-chain hydrocarbons *via de novo* synthesis in furnaces or abatement systems. PCDD/PCDF are easily adsorbed onto solid matter and may be collected and subsequently removed by dust, scrubber solids, and fly ash filter dust (Fiedler 1998, BREF 2001).

The secondary metals´ industry relies on the supply of secondary raw materials from the scrap industry and from other metal-containing wastes. The impurities present - even in high quality scrap - may lead to the formation of PCDD/PCDF during incomplete combustion or by *de novo* synthesis. Oils and other organic materials on scrap or other sources of carbon such as partially burnt fuels and reductants, *e.g.,* coke, can generate PCDD/PCDF when reacting with (inorganic) chlorides or organically bound chlorine in the temperature range of 250 to 450 °C (see Section 3). This process is known as *de novo* synthesis and is catalyzed by the presence of metals such as copper, iron, *etc.* (NATO/CCMS 1992a, Fiedler 1998, BREF 2001).

Although PCDD/PCDF are destroyed at high temperatures (typically above 850 °C) in the presence of oxygen, the process of *de novo* synthesis takes place as the flue gases cool down through the "reformation window". This temperature window can be present in flue gas abatement systems and in cooler parts of the furnace, *e.g.,* the feed area. Therefore, care should be taken in the design of cooling systems to minimize the residence time in the window to prevent *de novo* synthesis. Sufficient oxygen needs to be present in the hot gases and oxygen injection can be used to ensure complete combustion to minimize the PCDD/PCDF formation potential (NATO/CCMS 1992a, Fiedler 1998, BREF 2001).

There are many common features within the ferrous and non-ferrous metal sector. Some of the components or operations may lead to the formation and release of PCDD/PCDF. When estimating PCDD/PCDF releases, within each of the subcategories individual steps have to be evaluated for their potential to be a source of PCDD/PCDF releases. Besides the furnaces used to produce the metal, the pre-treatment steps have a potential to generate PCDD/PCDF, *e.g.,:*

Decoating and deoiling: Applied on secondary raw materials to reduce the organic content of the feed to some main processes. Washing and pyrolysis processes are used. In thermal systems exist the potential to generate PCDD/PCDF. The removal of oil and some coatings is achieved in a specially designed furnace such as a swarf dryer. In most cases a rotary furnace is used at low temperature to volatilize oil and water. Direct and indirect heating of the material is used. Modern plants will have an afterburner operated at high temperature (more than 850 °C) to destroy the organic products produced in the furnace, and will have the gases are filtered in a fabric filter.

Incineration and pyrolysis: Applied to treat photographic film, sweepings, catalysts and other materials and to concentrate the precious metals content. Simple box kilns and rotary furnaces are used for the incineration or pyrolysis stage.

Sulphuric acid plant: It may be present in smelters and serves as a flue gas treatment system. Sulphide minerals entering with the smelter feed upon oxidation generate and emit sulphur oxide. It can be recovered from smelter off-gases and be converted to sulphuric acid in such a plant for use in industrial processes (BREF 2001).

Whereas comparatively high PCDD/PCDF emissions have been detected in metal recycling plants, almost no information is available for base metal smelters. Environment Canada undertakes a dioxin/furan testing program on its base metal smelters to obtain better information and to develop an emission testing protocol (Charles E. Napier 2002).

In this Section, the Toolkit addresses the following sub-categories (Table 23):

Table 23: Subcategories of Main Category 2 – Ferrous and Non-Ferrous Metal Production

			Potential Release Route				
No.		***Main Categories and Subcategories***	***Air***	***Water***	***Land***	***Product***	***Residue***
2		**Ferrous and Non-Ferrous Metal Production**	**X**				**X**
	a	Iron ore sintering	X				x
	b	Coke production	X	x	x	x	x
	c	Iron and steel production and foundries	X				x
	d	Copper production	X				x
	e	Aluminum production	X				x
	f	Lead production	X				x
	g	Zinc production	X				x
	h	Brass and bronze production	X				x
	i	Magnesium production	x	x			x
	j	Other non-ferrous metal production	x	x			x
	k	Shredders	X				x
	l	Thermal wire reclamation	X	(x)	x		x

Relevance to Article 5, Annex C

With relevance to the provisions of Article 5, sources in this category can be classified as follows:

Annex C, Part II source categories include:

	Source category	Section in Toolkit
(d) (i)	Secondary copper production	6.2.4
(d) (ii)	Sinter plants in the iron and steel industry	6.2.1
(d) (iii)	Secondary aluminum production	6.2.5
(d) (iv)	Secondary zinc production	6.2.7

Annex C, Part III source categories include:

	Source category	Section in Toolkit
(b)	Thermal processes in the metallurgical industry not mentioned in Part II	6.2.2, 6.2.6, 6.2.8, 6.2.9, 6.2.10
(k)	Shredder plants for the treatment of end of life vehicles	6.2.11
(l)	Smoldering of copper cables	6.2.12

6.2.1 Iron Ore Sintering

Sinter plants are associated with iron manufacture, often in integrated iron and steel works. The sintering process is a pre-treatment step in the production of iron where fine particles of metal ores are agglomerated by combustion. Agglomeration is necessary to increase the passage for the gases during the blast furnace operation. Typically, sintering plants are large (up to several hundred square meters) grate systems used to prepare iron ore (sometimes in powder form) for use in a blast furnace. In addition to iron ore, there is usually a carbon source (often coke) and other additions such as limestone. In some cases wastes from various parts of the steel making process are present. In the sintering process, burners above the grate belt heat the material to the required temperature (1,100-1,200 °C), which causes the fuel in the mixture to ignite. The flame front passes through the sintering bed as it advances along the grate causing agglomeration. Air is sucked through the bed. The process is finished once the flame front has passed through the entire mixed layer and all fuel has been burned. Cooled sinter is transferred to screens that separate the pieces to be used in the blast furnace (4-10 mm and 20-50 mm) from the pieces to be returned to the sinter process (0-5 mm as "return fines", 10-20 mm as "hearth layer").

The waste gas flow from a sinter plant varies from 350,000 to 1,600,000 Nm^3 /hour[5], depending on the plant size and operating conditions. Typically the specific waste gas flow is between 1,500 and 2,500 Nm^3/t of sinter (BREF 2000c).

[5] Note: in this category, when referring to Nm^3 or m^3, there is no normalization to any content of oxygen; thus, the volumes refer to operational oxygen concentrations

Waste gases are usually treated by dust removal in a cyclone, electrostatic precipitator, wet scrubber or fabric filter. In plants, where high PCDD/PCDF emissions have been identified, high performance scrubbing systems may be installed to reduce emissions, coupled with measures to reduce gas flows.

Extensive research into formation of PCDD/PCDF in the sintering process has shown that they are formed within the sinter bed itself, probably just ahead of the flame front as the hot gases are drawn through the bed. It has also been shown that *de novo* formation of PCDD/PCDF in the gas collectors from reactive fine dust particles is responsible for approximately only 10 % of the total PCDD/PCDF and that primary measure should to prevent PCDD/PCDF formation should be taken in the sinter bed. Besides input-related measures, disruptions to flame front propagation, *i.e.* non-steady state operations, result in higher PCDD/PCDF emissions (Nordsieck *et al.* 2001). Thus, operating the sintering process as consistent as possible in terms of strand speed, bed composition, bed height, use of additives, and keeping the strand, ductwork and ESP air tight to minimize, as far as possible, the amount of air ingress in the operation will result in less dioxin and furan formation.

A mean of 1.0 ng I-TEQ/Nm³ has been achieved from a total of 41 samples at four sites in the UK. However at plants in other EU Member States performing the same or very similar operation conditions such low values could not be achieved. In Germany, usually 2-3 ng I-TEQ/Nm³ was measured. From one plant values between 5 and 6 ng I-TEQ/Nm³ were reported (BREF 2000c).

Three emission factor classes are given Table 24.

Table 24: Emission factors for iron ore sintering plants

Classification	Emission Factors – µg TEQ/t of Sinter Produced				
	Air	Water	Land	Product	Residue
1. High waste recycling including oil contaminated materials	20	ND	ND	NA	0.003
2. Low waste use, well controlled plant	5	ND	ND	NA	0.003
3. High technology emission reduction	0.3	ND	ND	NA	0.003

For plants with high use of waste including cutting oils or other chlorinated contaminants and limited process control class 1 factors should be used. Class 2 should be applied for those plants that can show good combustion control and have little use of waste in particular cutting oils. Emissions factors in class 3 should be used for those plants, which have taken comprehensive measures to control PCDD/PCDF.

Very low technology sintering plants may have higher emissions. Any plants found with poor combustion controls and very limited pollution control systems should be noted for future examination.

6.2.1.1 Release to Air

Iron ore sinter plants have been identified as a major source of PCDD/PCDF to air in some countries. The highest emissions are expected from plants, which have not made comprehensive attempts to reduce PCDD/PCDF emissions and also use waste materials such as cutting oils, dust from the ESP, *etc.* in the sinter production. The emission factor for this class –

20 µg TEQ/t - comes from two inventory studies using a gas volume of 2,000 Nm³ per ton of sinter and a concentration of 10 ng TEQ/Nm³ (HMIP 1995, SCEP 1994). It should be mentioned that at one plant in Germany, an emission factor of nearly 100 µg TEQ/t sinter has been determined; respective stack emissions were 43 ng TEQ/m³ (LUA 1997).

For plants with low waste use, the class 2 emission factor is 5 µg TEQ/t based on studies from Belgium, Sweden, the Netherlands, and Germany.

For the highest technology plants, where PCDD/PCDF emissions addressed and major changes to technology and plant operation were realized, the class 3 emission should be selected. Improvement implemented may include measures to reduce gas flows and multi-stage scrubbing with effluent treatment. An emission factor of 0.3 µg TEQ/t is based on a reduced gas flow of 1,500 Nm³/t and a concentration of 0.2 ng TEQ/Nm³ (Smit *et al.* 1999, HMIP 1995).

Much higher concentrations of PCDD/PCDF have been found in certain instances, possibly linked to the use of chlorinated cutting oils, and generation of measured data is required.

It should also be mentioned that hot sieving and crushing can add an additional 1 µg TEQ/t of sinter and fugitive emissions form the sinter belt another 2 µg TEQ/t sinter according to German data (LUA 1997).

6.2.1.2 Release to Water

A release to water may occur if there is a wet scrubber used in the process with an effluent discharge. No emission factor could be developed for this release route. Any liquid discharge should be noted, its quantity and any treatment will be important factors.

6.2.1.3 Release to Land

No release to land is expected. Any dumping of residues to land should be noted.

6.2.1.4 Release in Products

The product of this process is sinter, which is fed to the blast furnace. Any PCDD/PCDF present in the sinter will enter the blast furnace and are likely to be destroyed. Therefore no release in product is assessed.

6.2.1.5 Release in Residues

The main residue is expected to be in the form of dust collected in the dust control devices. Some of this may be recycled to the process or it may be removed from the process as a waste. Data is available from the UK on the amounts of PCDD/PCDF in dust from sinter plant ESPs giving a range from 29 to 90 ng I-TEQ/kg. Only a small amount of sinter dust is disposed of (*e.g.,* in the UK: 700 t/a from a sinter production of 15.1 million tons of sinter – about 0.05 kg dust per ton of sinter). Data from Germany measured in 1993/94 were in the range from 196 to 488 ng I-TEQ/kg (EC 1999). The emission factor of 0.003 µg TEQ/t is

based on UK plant data (Dyke *et al.* 1997) and is assumed to be unchanged with process type in the absence of other data. It should be noted that up to 2 kg dust per ton of sinter has been suggested (BREF 2000c).

6.2.2 Coke Production

Coke is produced from hard coal or from brown coal by carbonization (heating under vacuum). In "coke ovens", coal is charged into large vessels, which are subjected to external heating to approximately 1,000 °C in the absence of air. Coke is removed and quenched with water. The major users of coke – at least in industrialized countries is the iron and steel industry.

The release of PCDD/PCDF from coke production has not been extensively studied. Emission factors are provided based on a plant that used an afterburner and dust control to treat flue gases from the process. If technology is substantially different from this, emissions may be quite different. Differences in the technology should be noted.

No data are available to estimate releases from the production of charcoal from wood. This process can be carried out in many small units, which taken together may represent a considerable production. Unfortunately, there are no measured data available. For initial estimates of emissions, the emission factors given in this section for simple plants should be applied (class 1).

Three classes are given in Table 25.

Table 25: Emission factors for coke production

Classification	Emission factors – µg TEQ/t of Coke Produced				
	Air	Water	Land	Product	Residue
1. No gas cleaning	3	0.06[1]	NA	ND	ND
2. APC with afterburner/dust removal	0.3	0.06[1]	NA	ND	ND

[1] Use factor of 0.006 µg TEQ/t where water treatment is applied

Class 1 should be applied to facilities where no dust removal device is in use, class 2 for better equipped plants.

6.2.2.1 Release to Air

Emissions to air can occur during charging and discharging of the coal/coke as well as during the heating. As there is no gas conducted to a stack, the emission factors are hard to measure and are therefore subject to uncertainty.

Class 1 emission factor is used as an estimate of releases where no gas cleaning is present. Class 2 emission factor should be used for releases from plants using technology such as afterburner and dust removal equipment (Bremmer *et al.* 1994). This emission factor is approximately equivalent to 0.23 µg TEQ/t of coal processed.

6.2.2.2 Release to Water

A release to water will occur if effluents from quenching or wet scrubbing are discharged. Two emission factors are given: 0.06 µg TEQ/t for untreated water and 0.006 µg TEQ/t for treated water (assumed to be 90 % effective).

6.2.2.3 Release to Land

No release to land is expected.

6.2.2.4 Release in Products

Any PCDD/PCDF present in the coke product is expected to pass to other processes. No data were available to estimate the amount present.

6.2.2.5 Release in Residues

Residues may arise from sludges from water treatment and from any collected solids. No data were available on PCDD/PCDF in the residues.

6.2.3 Iron and Steel Production Plants

The iron and steel industry is a highly material intensive industry with raw materials such as ores, pellets, scrap, coal, lime, limestone (in some cases also heavy oil and plastics) and additives and auxiliaries. It also consumes much energy. More than half of the mass input becomes outputs in the form of off-gases and solid wastes or by-products. The most relevant emissions are those to air with the emissions from sinter plants to dominate the overall emissions for most of the pollutants (see Section 6.2.1).

In this section all processes used in the manufacture of iron and steel should be covered. Four routes are currently used for the production of steel: the classic blast furnace/basic-oxygen furnace route, direct melting of scrap (electric arc furnace), smelting reduction and direct reduction (BREF 2000c). For the purpose of the Toolkit, a categorization can be done either by the type of the input material: in this way, blast furnaces (BF) are used only for the production of pig iron and are fed with iron ores from either sintering plants or pelletizing plants. Blast furnaces do not utilize scrap. Scrap is being used in electric arc furnaces (EAF), Basic Oxygen Furnaces (BOF) as well as in foundries where cupola furnaces (CF) and induction furnaces (IF) are found.

Five types of furnaces are commonly used to melt metals in foundries: cupola, electric arc, induction, reverberatory, and crucible. The last two types are more common in the non-ferrous metal industries and thus will not be considered further in this section dealing with the iron and steel industry. Some foundries operate more than one type of furnace (US-EPA 1998b).

In the following paragraphs, basic description of the various furnace types and processes are given:

In an integrated steel works the **blast furnace (BF)** is the main operational unit, where the primary reduction of iron oxide ores takes place leading to liquid iron (the "hot metal"). Modern high-performance blast furnaces require physical and metallurgical preparation of the burden. The two types of iron ore preparation plants are the sinter plants and the pellet plants. Sinter is generally produced at the ironworks from pre-designed mixtures of fine ores, residues and additives. Until today, the blast furnace remains by far the most important process for the production of pig iron.

Ores containing high percentages of iron oxides are charged together with coke and fluxes to a blast furnace to produce molten iron, slag, and blast furnace gas. The molten iron (= hot metal) contains about 4 % carbon, which is being reduced to less than 1 % to produce steel. The function of the blast furnace is to reduce solid iron oxides to molten iron. The blast furnace, itself is a tall, shaft-type furnace with a vertical stack over a crucible-shaped hearth. A blast furnace is a closed system into which iron bearing materials (iron ore lump, sinter and/or pellets), additives (slag formers such as limestone), and reducing agents (coke) are continuously fed from the top of the furnace shaft through a charging system that prevents escape of blast furnace gas. In a blast furnace, the iron ore is reduced to pig iron by using the reaction of coke [6] and oxygen as an energy source, producing carbon monoxide (CO) as the reducing agent. When the feedstock materials are charged, pressurized air of 900-1,350 °C ("hot blast") is blown just above the hearth [7]. From the furnace liquid iron and slag are collected in the bottom of the furnace, from where they are tapped.

Although a lot of cooling water is recirculating, there are hardly any open aqueous effluents; a major release route for solids is the slag. Waste gas is often cleaned in a dry cyclone-type "dust catcher" to remove coarse material and in 2-stage Venturi scrubbers to remove the fine particulates.

The slag from the blast furnace is granulated, pelletized, or tapped into slag pits. The slag granules or pellets can be sold to cement manufacturing companies. Also, slag from pits can be used in road construction. The liquid iron from the blast furnace (pig iron) is transported to a basic oxygen furnace, where the carbon content (approx. 4 %) is lowered to less than 1 %, thereby resulting in steel. Upstream ladle desulfurization of the pig iron and downstream ladle metallurgy of the steel is generally applied in order to produce steel of the required quality. On leaving the basic oxygen furnace the liquid steel is cast, either into ingots or by means of continuous casting. Casting products, whether ingots, slabs, billets or blooms, are subsequently processed in rolling mills and product finishing lines in order to prepare them for market. The specific quantity of slag mainly depends on the raw materials used, but lies in the range 210-310 kg/t pig iron produced.

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[6] from the coke oven plant. This is the reason why coke ovens are placed into this sector of the ferrous and non-ferrous metal productions

[7] The hot blast for the blast furnace operation is provided by hot stoves (also called "cowpers"). Stoves are auxiliary installations used to heat the blast. Three or four hot stoves are necessary for each blast furnace.

The **basic oxygen furnace (BOF)** became popular when in the 1950s cost-effective oxygen became available on an industrial scale to replace the air. Always, a BOF is followed by a ladle furnace and an argon stirring station or another aggregate for the secondary treatment since the steel from a BOF contains too much oxygen to be casted directly (BSE 2002). In addition, the water-cooled lance technology was developed for introducing the oxygen into the converter. The BOF process and the electric arc furnace (EAF) have since replaced often less energy efficient existing steel making processes such as the Thomas process and open-hearth process (Bessemer, Siemens-Martin). The objective in oxygen steel making is to burn (*i.e.* oxidize) the undesirable impurities contained in the metallic feedstock. The operation of a BOF is semi-continuous. A complete cycle consists of the following phases: charging scrap and molten pig iron, oxygen blowing, sampling and temperature recording and tapping. In a modern steelworks, approximately 300 tons of steel are produced in a 30-40 minute cycle.

Foundries typically use scrap as their primary source of metal; in cases, where scrap is not available, iron ingots may be used. Flux – often chloride or fluorine salts - is added to the furnace charge or to the molten metal to remove impurities. The BOF typically operates with about 20 % of scrap (whereas an EAF can be run on 100 % of scrap metal).

The **cupola** furnace is primarily used to melt gray, malleable, or ductible iron. It is a continuous process, coke and feedstock are alternately stacked *via* a side opening, and the coke burns and melts the metal. Flue gases are typically passed through an afterburner and then treated by scrubbing. Hot air cupolas use preheated air (500-600 °C) whereas cold air cupolas do not preheat the air. The available PCDD/PCDF data are for plants using fabric filters.

Electric arc furnaces (EAFs) are used for the direct melting of iron-containing materials, such as scrap and of cast iron or steel. Electric arc furnaces have the advantage of not requiring incoming steel to be clean. The major feedstock for the EAF is ferrous scrap, which may comprise of scrap from inside the steelworks (*e.g.,* offcuts), cut-offs from steel product manufacturers (*e.g.,* vehicle builders) and post-consumer scrap (*e.g.,* end of life products). Direct-reduced iron (DRI) is also increasingly being used as a feedstock. In the electric steel process, the heat is obtained from an electric or induction or plasma furnace or in energy-efficient plants from oxygen. As in the BOF, a slag is formed from lime to collect undesirable components in the steel. Scrap preheating may result in higher emissions of aromatic organohalogen compounds such as polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/PCDF), chlorobenzenes, polychlorinated biphenyls (PCB) as well as polycyclic aromatic hydrocarbons (PAH) and other partial combustion products from scrap, which is contaminated with paints, plastics, lubricants or other organic compounds. Up to 5-times higher PCDD/PCDF emissions have been found in such cases (LAI 1997). Electric arc furnaces (EAFs) typically have capacities between 60 and 80 tons (range: 25-400 tons) and the tap-to-tap times are from 35 minutes to two hours. Electric arc furnaces operate as a batch process. They melt the charge between 1,600 and 1,670 °C (BSE 2002). Gaseous pollutants are emitted and may be released to a ducting system. In addition, there may be fugitive emissions, which may account for a large portion of overall emissions.

Rotary drum furnaces are operated in a batch process. Usually an oil burner is used to heat drum and charge. Flue gases are typically treated by fabric filter.

Induction furnaces are used to melt ferrous and non-ferrous metals. There are several types of induction furnaces but all create a strong magnetic field by passing an electric current through coils to induce heating currents in the metal charge. Induction furnaces require

cleaner scrap than electric arc furnaces. Flue gases maybe treated in fabric filters.

It should be noted, that filter dusts and sludges from steel making are often recycled within the steel making process or in sinter plants or are sent to the non-ferrous metal industry as they often contain recoverable non-ferrous metals.

Reheating furnaces, which are part of the production of primary and secondary iron and steel, maybe relevant on the national level as they may cause local impact. Presently, no information on PCDD/PCDF emissions could be found.

The following classes of emission factors were developed and are shown in Table 26.

Table 26: Emission factors for the steel industry and iron foundries

Classification	Emission Factors – µg TEQ/t of LS				
	Air	Water	Land	Product	Residue
Iron and Steel making					
1. Dirty scrap (cutting oils, general contamination), scrap preheating, limited controls	10	ND	NA	NA	15
2. Clean scrap/virgin iron, afterburner and fabric filter	3	ND	NA	NA	15
3. Clean scrap/virgin iron, EAF designed for low PCDD/PCDF emission, BOF furnaces	0.1	ND	NA	NA	1.5
4. Blast furnaces with APC	0.01	ND	ND	ND	ND
Iron Foundries					
1. Cold air cupola or rotary drum with no gas cleaning	10	NA	NA	NA	ND
2. Rotary Drum - fabric filter	4.3	NA	NA	NA	0.2
3. Cold air cupola – fabric filter	1	NA	NA	NA	8
4. Hot air cupola, or induction furnace – fabric filter (foundry)	0.03	NA	NA	NA	0.5

6.2.3.1 Release to Air

PCDD/PCDF will be released into gases from the furnaces. It can be difficult to capture all the gases from the process and a large fraction of the gas and the PCDD/PCDF may be present in fugitive emissions rather than in the stack gases. Emissions seem to increase greatly by poor quality mixed scrap feeds, in particular where metal working residues, including cutting oils, are fed. The preheating of scrap to improve energy efficiency can lead to increased emissions as well; concentrations up to 9.2 ng TEQ/Nm³ have been measured (Germany, LAI 1997). In Europe, PCDD/PCDF measurements gave emission factors that ranged 0.07-9 µg I-TEQ/t LS (liquid steel) [8].

Flue gas volumes from hot stoves are between 100,000 and 600,000 Nm³/h per blast furnace. Emission factors determined from measurements from four EU member States were from <0.001 to 0.004 µg I-TEQ/t LS. For the Toolkit, class 4 emission factor should be used for

[8] Based on European data, a conversion factor of 940 kg pig iron/t LS was used

blast furnaces with good APC systems.

In BOFs during oxygen blowing, converter gas is released, which contains small amounts of PCDD/PCDF. Basic oxygen steel making plants in Europe generally have quite low emission factors, slightly higher than blast furnaces (with an upper end of 0.06 µg I-TEQ/t LS based on measured data).

For electric arc furnaces, most measured emission data relate to plants using relatively clean scrap and virgin iron and which are fitted with some after-burners and fabric filters for gas cleaning. Emission factors derived from plants in Sweden, Germany, and Denmark gave emission factors between 0.07 and 9 µg I-TEQ/t LS. For the Toolkit, an emission factor of 3 µg TEQ/t LS is applied (Bremmer *et al.* 1994, SCEP 1994, Charles Napier 1998).

Emissions from EAF plants using dirty scrap containing cutting oils or plastic materials as well as plants with scrap preheating and relatively poor controls were found to have higher concentrations of PCDD/PCDF in stack gases as found in Germany (SCEP 1994). In such cases, an emission factor of 10 µg TEQ/t LS is used (poor plants could emit more).

Where careful controls are placed on the scrap used (excluding cutting oils and heavily contaminated scrap) and efficient gas cleaning is used with secondary combustion and fabric filters (sometimes in combination with a rapid water quench) emissions below 0.1 ng TEQ/Nm³ can be achieved. For these plants an emission factor of 0.1 µg TEQ/t should be used (class 3). The same low concentrations were measured in the flue gases from basic oxygen furnaces; *e.g.* a median concentration of 0.028 ng I-TEQ/Nm³ (LAI 1997); class 3 emission factors should be applied for such plants.

For foundries, there are hardly any data available: testing in Germany (SCEP 1994) showed that hot air cupolas and induction furnaces fitted with fabric filters had low emissions to air, an emission factor of 0.03 µg TEQ/t of product should be used.

Cold air cupolas showed higher emissions and a factor of 1 µg TEQ/t is used for plants with fabric filters.

Limited testing on rotary drum furnaces showed higher levels again and a factor of 4.3 µg TEQ/t is applied to plants with fabric filters for gas cleaning.

Where cold air cupolas or rotary drum furnaces are used which do not have fabric filters or equivalent for gas cleaning a higher emission factor of 10 µg TEQ/t should be used.

If poor quality scrap (high contamination) or poorly controlled furnaces with gas cleaning other than effective fabric filters is found this should be noted.

6.2.3.2 Release to Water

Releases to water could occur where wet scrubbers or quenches are used. No data were available to provide an emission factor. Where an effluent is released this should be noted and information reported.

6.2.3.3 Release to Land

No release to land is expected.

6.2.3.4 Release in Products

No significant release is expected with the product steel from this process, it has been subject to high temperatures and PCDD/PCDF is likely to have been driven off or destroyed.

6.2.3.5 Release in Residues

The principal residues of interest are slag and dust collected in flue gas treatment systems. Other dust deposited from fugitive emissions may also contain PCDD/PCDF.

From blast furnaces, 9-15 kg of dust and sludges per ton of LS are generated from the gas purification system. 280 kg of slag are produced per ton of LS.

In BOF steel making, 12-27 kg of dusts and slags are generated per ton of LS from BOF gas treatment. Converter slag is 99 kg per ton of LS. Electric arc furnaces produce more slags, *e.g.* 129 kg/t LS for carbon steels and 161 kg/t LS for high alloyed and stainless steels.

An average emission factor for PCDD/PCDF in residues can only be given for EAFs: from gas cleaning operations (fabric filter) an emission factor of 15 µg TEQ/t is based on an average of UK data (Dyke *et al.* 1997). This factor assumes similar gas cleaning equipment; the release may be different with other systems. This factor is used for the poorly controlled and average plants. A lower emission factor of 0.15 µg TEQ/t is used for the best plants (Bremmer *et al.* 1994). The fate or use of the residues should be noted (PCDD/PCDF can be introduced into other processes if these residues are used as feedstock in recycling processes).

From foundries, cupolas and EAFs emit particulate matter, which is likely to contain PCDD/PCDF. Induction furnaces emit much less particulates. Data from Germany (SCEP 1994) indicated the emission factors shown in Table 26. Slag can be generated as well as sand casting technologies will generate substantial volumes of sand, which may be reused in the plant or be sent off for use as construction material (US-EPA 1998b).

6.2.4 Copper Production

Thermal copper generation and releases of PCDD/PCDF are of special interest as copper (Cu) is the most efficient metal to catalyze the formation of PCDD/PCDF.

When analyzing the copper production sector for PCDD/PCDF releases, it is important to differentiate between primary and secondary production.

Primary copper

Primary copper may be produced by two different technologies depending on the type of minerals treated, either oxides or sulfides, and may be produced from primary concentrates and other materials either by pyrometallurgical or hydrometallurgical routes (BREF 2001,

CONAMA 2003).

Hydrometallurgical methods are applied to treat oxidized minerals, *i.e.* leaching, solvent extraction, and electrowinning. All these processes are operated at temperatures below 50 °C. It is not expected that formation of PCDD/PCDF will occur.

Typically, sulfurized minerals are treated by the pyrometallurgical route. Sulphidic minerals are first treated in a concentration plant, operated at room temperature, and then the concentrates are pyrometallurgically refined in primary copper smelters. The concentrates to be smelted consist basically of copper and iron sulfides and are low in chlorine (part per million). The stages involved are roasting, smelting, converting, refining, and electro-refining. The smelting process is performed in an oxidizing atmosphere at temperatures between 1,200 °C and 1,300 °C.

There are two basic **smelting processes** in use: **bath smelting**, where the smelting process uses oxygen enrichment to produce (nearly) auto-thermal operation and the **flash smelting**, where generally a lower degree oxygen enrichment occurs.

Bath smelting furnaces include: reverberatory, electric, SIA Smelt, Noranda, Mitsubishi, Teniente, Bayin, Vanyucov furnaces. All of the processes rely on the roasting and smelting process taking place in a molten metal bath with slag and matte separation and tapping taking place in various ways.

Flash smelting is carried out in either Outokumpu or Inco flash smelters or in a cyclone furnace (Contop). Flash smelting relies on the roasting and smelting of dry concentrate in airborne particles.

Two types of **converter** processes are used: the conventional batch process (most common, *e.g.,* Pierce-Smith converter, Hoboken-type converter) and the continuous converting process (*e.g.,* Kennecott/Outukumpu flash furnace, Mitsubishi furnace, and Noranda converter). Top Blown Rotary Converters have been used in the past for batch-wise conversion of primary copper material to blister copper but are not very common any longer.

Purification steps applied to the crude metal (also named "blister copper") after the conversion stage involves the addition of air and then a reductant to reduce any oxygen present. Fire refining and electrolytic refining are typically used.

Secondary copper

Secondary copper is produced by pyro-metallurgical processes and is obtained from scrap or other copper-bearing residues such as slags and ashes. Since used copper can be recycled without loss of quality, secondary copper production is an important sector. An overview of secondary raw materials for copper production can be found in the BAT Reference document of the EU (BREF) on Production of Non-Ferrous Metals (BREF 2001). Since secondary feed material can contain organic materials, de-oiling and de-coating methods are applied, also to minimize the formation of PCDD/PCDF in the subsequent stages of the copper production. The stages used for secondary copper production are generally similar to those for primary production but the raw materials are usually oxidic or metallic and therefore, the smelting of secondary raw materials uses reducing conditions.

Some primary copper smelters are integrated with secondary smelting facilities or production of lead or zinc oxide dust from mixed concentrates, *etc.* (BREF 2001).

Refined copper is produced from primary and secondary raw materials by copper refineries; their product is copper cathode. This is melted, alloyed and further processed to produce rods, profiles, wires, sheets, strips, tubes, *etc.* This step may be integrated with the refinery but is frequently carried out at another site.

Furnaces are used for a variety of purposes in this industry such as roasting or calcining raw materials, melting and refining metals and for smelting ores and concentrates. Furnaces commonly used in the production of copper depending on the raw material and process stage include (BREF 2001):

Furnaces for roasting, calcining, *etc.*: Rotary kilns;

Furnaces for Smelting: Copper Flash Smelting Furnace, Bath Smelting Furnaces, Reverberatory Furnaces [(a) for smelting or calcining or concentrating, (b) for melting or refining], Blast furnaces, Electric Furnaces, Cyclone smelting furnaces;

Converters (to convert copper oxide to copper): Rotary Furnaces or converters;

Melting and Refining Furnaces: Induction Furnaces, Shaft Furnaces, rotary furnaces

Modern plants have gas cleaning using wet scrubbers and wet electrostatic precipitators to clean process gases that undergo sulphur recovery in a sulphuric acid plant (BREF 2001).

So far, there exist only few data on releases of PCDD/PCDF from copper plants. The majority of information is from secondary copper plants, where occasionally high PCDD/PCDF emissions were found in the stack gases. In primary copper production plants, base metal smelters, PCDD/PCDF seem to be very low.

Table 27: Emission factors for the copper industry

Classification	Emission Factors – µg TEQ/t of Copper				
	Air	Water	Land	Product	Residue
1. Sec. Cu - Basic technology	800	ND	NA	NA	630
2. Sec. Cu - Well controlled	50	ND	NA	NA	630
3. Sec. Cu - Optimized for PCDD/PCDF control	5	ND	NA	NA	300
4. Smelting and casting of Cu/Cu alloys	0.03	ND	NA	NA	ND
5. Prim. Cu including thermal steps	0.01	ND	NA	NA	ND

6.2.4.1 Release to Air

Emissions to air from copper production seem to vary considerably depending on the process technology, the nature of the materials processed and the gas cleaning system applied. The occurrence of PCDD/PCDF is principally associated with secondary copper production.

The following data are from secondary copper facilities. A study in the US on a copper production plant using a blast furnace and fitted with afterburners and fabric filters, gave an emission factor of 779 µg TEQ/t of scrap.

Studies in Germany on several plants gave emission concentrations, which varied over a large range from 0.032 to 30 ng TEQ/Nm³ (LUA 1997).

Installations for smelting and casting of copper and its alloys, *e.g.* brass, gave emissions between 0.003 and 1.22 ng I-TQ/Nm³ with a geometric mean of 0.11 ng TEQ/Nm³ (German data, LUA 1997). The compilation for European plants by the IPPC Bureau reported emissions of <0.1 ng I-TEQ/Nm³ (BREF 2001). From these data, an emission factor of 0.03 µg TEQ/t of copper/copper alloy was derived. The data do not allow for further differentiation according to technology or performance.

In the cleaned gases from sulfuric acid plants, emissions between 0.01 and 0.001 ng TEQ/Nm³ have been measured (BREF 2001). The same sources report – without further specification - that processes in the melt shop for the production of semis (semi-manufactures such as alloy cast ingots, foils, sheet, strip) gave emission factors for electric furnaces of <5 µg and for shaft and rotary furnaces of <10 µg TEQ/t, respectively.

Class 1 to class 3 emission factors address secondary copper manufacture. Class 1 emission factor should be applied to thermal processing of mixed materials where furnaces are equipped with simple fabric filters or less effective gas cleaning. Class 2 emission factor is to be used where thermal processing of scrap copper materials is carried out in furnaces that are well controlled and fitted with afterburners and fabric filters. The scrap should undergo some sorting and classification prior to processing to minimize contaminants.

Class 3 should be used for plants where measures have been taken to address releases of PCDD/PCDF such as installation of rapid water quench prior to the fabric filters and activated carbon is used in the flue gas treatment.

Although in most cases, no PCDD/PCDF were measured in the off-gases from primary copper facilities, class 4 is included in this Toolkit, which addresses emissions from primary copper production. Measured data from Germany for primary copper generation in flash smelting furnaces and matte converters gave emissions between 0.0001 and 0.007 ng TEQ/Nm³ resulting in a very narrow range of emission factors from 0.002 and 0.02 µg TEQ/t of copper. The EU Dioxin Inventory report of 1997 (LUA 1997) reports concentrations of 0.005-0.015 ng I-TEQ/m³ in the waste gases from the roasting furnace for ore desulphurization. The volume of the waste gas was 5,000 Nm³ per ton of copper produced. In addition, from a Swedish primary smelter, which produced 2,000 Nm³/t of waste gases, a concentration of 11 ng I-TEQ/m³ was reported. From the results of the measurements given above, emission factors of 0.25 µg I-TEQ/t (from German results) and 22 µg I-TEQ/t (from Swedish results) were derived. An emission factor of 10 µg I-TEQ/t was finally taken to estimate the emissions for Belgium's inventory (LUA 1997). The class 4 emission factor of 0.01 µg TEQ/t should be applied for primary copper production when applying this Toolkit.

There is a need to better characterize primary copper production plants (with no integration of other metals recycling). It is hoped that measured data from such plants, also through the Canada surveys underway, will be obtained soon.

6.2.4.2 Release to Water

No data were available to estimate releases to water. These may occur if effluents are discharged and the concentration is likely to be influenced by any water treatment applied. Any liquid release should be noted along with its source and treatment applied.

6.2.4.3 Release to Land

No release to land is expected.

6.2.4.4 Release in Products

No releases to with the products are expected.

6.2.4.5 Release in Residues

PCDD/PCDF will be found in the solid residues from the process. The principal concern is the residues from the gas treatment equipment. Dusts and sludges collected from gas treatment may be highly enriched in PCDD/PCDF. Concentrations of up to 20,000 ng TEQ/kg have been reported (SCEP 1994).

UK data (Dyke *et al.* 1997) suggests approximately 2,000 t of filter dusts arise from production of 46,000 t of copper. Combined with an average concentration of 14,400 ng TEQ/kg in the dust (SCEP 1994) this gives an emission factor of 630 µg TEQ/t of product. This estimate is highly uncertain. Concentrations and rates of production will vary but there is insufficient information to make a more detailed estimate at this time. For high technology plants a lower emission factor of 300 µg TEQ/t can be used.

It is important to consider the possibility for PCDD/PCDF in residues to be passed to other processes. Many residues from copper production may be used for precious and other metal recovery in other processes.

6.2.5 Aluminum Production

Aluminum ore, most commonly bauxite, is refined into aluminum oxide trihydrate (alumina) and then electrolytically reduced into metallic aluminum. These primary aluminum production facilities are often located in areas where there are abundant supplies of inexpensive energy, such as hydro-electric power. PCDD/PCDF have been associated with the use of the carbon anodes but levels are generally thought to be low and the main interest is in the thermal processing of scrap materials.

Basically all used aluminum can be recycled into aluminum, which has the same quality as primary aluminum. Secondary aluminum is obtained by remelting Al scrap, shavings, and other materials containing aluminum. Secondary aluminum production can be performed in a variety of furnaces, where rotary drum furnaces are used when salt, *e.g.*, cryolite (sodium aluminum fluoride), is added whereas in a variety of furnaces, *e.g.* rotary drum, hearth furnaces or induction furnaces normally do not require salt. Induction furnaces are predominantly used in foundries when oxide-free scrap is fed. The aluminum smelted in the furnaces is run off for refining, alloying,, or keeping warm in converters. Scrap material may be contaminated with oils, plastics, paints and other contaminants. Releases of PCDD/PCDF may occur from scrap melting where organic contaminants and chlorine are present and also from refining (where hexachloroethane or chlorine may be used) and pretreatment such as thermal cleaning of scrap. Smelting furnaces typically have capacities between 0.5 and 0.7 t.

Very often, turnings are thermally treated or dried to reduce the oily processing auxiliaries (*e.g.,* drilling suspensions) adhering to the turnings. Such drying is carried out in rotary drum heating dryers heated by gas or oil. Formation of PCDD/PCDF is possible as the oil-based contaminants can contain certain organic or inorganic chlorine (IFEU 1998, LAI 1997).

The following classes of emission factors have been developed and are shown in Table 28.

Table 28: Emission factors for aluminum industry

Classification	Emission Factors – µg TEQ/t of Aluminum				
	Air	Water	Land	Product	Residue
1. Thermal processing of scrap Al, minimal treatment of inputs and simple dust removal	150	ND	NA	NA	400
2. Thermal Al processing, scrap pre-treatment, good controls, filters with lime injection	35	ND	NA	NA	400
3. Shavings/turning drying	5	NA	NA	NA	NA
4. Thermal Al processing, scrap pre-treatment, well-control, fabric filters with lime injection	3.5	NA	NA	NA	100
5. Optimized for PCDD/PCDF control – afterburners, lime injection, fabric filters and active carbon	0.5	ND	NA	NA	100

Class 1 factors should be used for plants with simple or no dust removal equipment, class 2 factors should be used where plants have afterburners and fabric filters. Class 4 should be used where high efficiency controls are in place consisting of scrap cleaning, afterburners, fabric filters with lime and activated carbon injection.

6.2.5.1 Release to Air

Several steps in the processing of aluminum scrap can lead to the release of PCDD/PCDF to air. Thermal pretreatment of input materials, scrap melting and metal refining using chlorine or hexachloroethane[9] can all lead to releases of PCDD/PCDF to air.

Emissions to air vary greatly depending on the nature of the scrap, pre-cleaning of the feed and the type of furnace and gas cleaning system applied. The majority of information is relatively old. Presently, there are industry activities underway to better characterize the emissions from this subcategory.

Older technology furnaces fitted with fabric filters had emissions of 146 to 233 µg TEQ/t of product. Concentrations and volumes of flue gas vary considerably; concentrations up to 10 ng I-TEQ/m³ were reported (SCEP 1994). Drum furnaces using aluminum turnings seemed to produce high emissions. For systems using contaminated scrap (such as scrap with cutting oils, plastics) with simple controls and gas cleaning consisting of cyclones or basic fabric filters an emission factor of 150 µg TEQ/t of product should be used.

For better-controlled systems using afterburners, scrap pretreatment and gas cleaning with filters and lime injection the class 2 emission factor of 35 µg TEQ/t of product should be used

[9] as a degasifying agent

(LUA 1997). The class 4 emission factor of 3.5 µg TEQ/t is taken from recent measurements at two European plants and are for well-controlled modern plants with scrap treatment, fabric filters, and lime injection (EEA 2003).

Class 3 emission factor of 5 µg TEQ/t applies to the drying of Al shavings and turnings in rotary drums or similar equipment (EAA 2003).

Systems optimized to reduce emissions which might include careful scrap selection and pre-treatment, advanced gas treatment systems including afterburners where high organic gases were released, fabric filters coupled with lime injection and activated carbon showed low emissions and no use of hexachloroethane (SCEP 1994). For these systems, the class 4 an emission factor of 0.5 µg TEQ/t of product is used.

6.2.5.2 Release to Water

Releases to water may result where wet scrubbers or other processes have liquid effluents. There is insufficient information to estimate emission factors. Any liquid effluents should be noted and their source recorded.

6.2.5.3 Release to Land

No release to land is expected.

6.2.5.4 Release in Products

No release into the products is expected.

6.2.5.5 Release in Residues

Residues from the process are expected to contain PCDD/PCDF. The highest contamination is expected to be associated in dusts and sludges from flue gas treatment. The amounts of such dusts and sludges should be recorded and any use in other processes may lead to transfer of PCDD/PCDF.

Melting in rotary drum furnaces generates 300-500 kg salt slag per ton of Al and 10-35 kg filter dust/t Al. Dross generated at ca. 25 kg/t Al can be reused in rotary drum furnaces (UBAVIE 2000).

Concentrations of PCDD/PCDF in filter dusts have been recorded from 3 to 18,000 ng TEQ/kg (SCEP 1994, Bremmer *et al.* 1994). Filter dusts are produced at a rate of approximately 8 % of the metal production (Dyke *et al.* 1997). Combined with an average concentration of 5,000 ng TEQ/kg, this gives an emission factor of 400 µg TEQ/t of product. A single factor is used to make initial estimates for class 1 and class 2 plants; clearly concentrations and rates of production will vary. For class 3, high technology plants, the lower factor of 100 µg TEQ/t should be applied to make initial estimates.

6.2.6 Lead Production

Two main routes for primary lead production from sulfide ores are available – sintering/smelting and direct smelting. Emissions from direct smelting are low (SCEP 1994) and not considered further. No data are available on releases from sintering/smelting for primary lead production.

Considerable quantities of lead are recovered from scrap materials, in particular vehicle batteries. A variety of furnace designs are used including rotary furnaces, reverberatory, crucible, shaft, blast and electric furnaces. Continuous direct smelting processes may be used.

PCDD/PCDF emissions may be linked to high organic matter on scrap materials and the presence of chlorine – in particular a link between the use of PVC separators in vehicle batteries and PCDD/PCDF emissions has been made (EPA 1998).

PCDD/PCDF emissions were determined from a secondary lead smelter within the Thailand Dioxin Sampling and Analysis project (UNEP 2001, Fiedler *et al.* 2002). The plant company operates two rotary kilns for the recovery of lead. The capacity of each furnace is about 3.5-5 t of lead per batch and each batch takes about 2-3 hours. Each line has an after-burning chamber behind the rotary kiln, a cooling tower, a cyclone separator, and a baghouse filter. For one of the lines, the flue gas stream from the smelter is combined with other off gases and large quantities of ventilation air from the work-floor, *e.g.* furnace feed door ventilation hood, slag tap kettle ventilation hood, refinery kettles for casting the final product, raw scrap material processing ventilation hood, ash agglomeration and melting furnace, and the ash melting slag tap kettle.

Table 29: Emission factors for the lead industry

Classification	Emission Factors – µg TEQ/t of Lead				
	Air	Water	Land	Product	Residue
1. Lead production from scrap containing PVC	80	ND	NA	NA	ND
2. Lead production from PVC/Cl_2 free scrap, APC present	8	ND	NA	NA	ND
3. Lead production from PVC/Cl_2 free scrap in highly efficient furnaces, with APC including scrubbers	0.5	ND	NA	NA	ND

6.2.6.1 Release to Air

Test data for production of lead from scrap materials are available from Germany (SCEP 1994, LUA 1997), Sweden, Belgium, the Netherlands (LUA 1997), and the USA (US-EPA 2000). In these countries, typically PVC is separated from batteries and facilities tested had dust abatement by fabric filters and some also had scrubbers. In US tests the addition of a scrubber reduced air emissions by approximately 90 % (US-EPA 2000).

In the USA, the following emission factors were determined for the various types of secondary lead smelters (US-EPA 2000): Blast furnaces = 0.63-8.81 µg TEQ/t lead, reverberatory/co-located furnace = 0.05-0.41 µg TEQ/t lead, and rotary furnace = 0.24-0.66 µg

TEQ/t lead. Emissions to air were about 10-times higher before any scrubber/APCS than in the purified air. The average emissions were 8.31 and 0.63 ng TEQ/m³ for blast furnaces before and after the scrubber, respectively; 0.41 and 0.05 ng TEQ/m³ for reverberatories/co-located furnaces before and after the scrubbers, respectively; and 0.24 and 0.66 ng TEQ/m³ for rotary kilns before and after the scrubbers, respectively (US-EPA 2000).

European measurements gave 5 µg TEQ/t of lead in Belgian blast furnaces and in the Netherlands for a lead smelter, which processed contaminated scrap but was equipped with lime injection and fabric filter (1.3 ng TEQ/m³ were measured). German measurements were 0.14-0.27 ng TEQ/Nm³ at rotary kilns; 0.59 ng TEQ/Nm³ at a shaft furnace, 0.09-0.18 ng TEQ/Nm³ at short rotary kilns and 0.14-0.27 ng TEQ/Nm³ at rotary kilns. A recycling lead smelter for used car batteries had emissions between 0.2 and 0.3 ng TEQ/Nm³. The report, does not give average emission factors for the German secondary lead industry (LUA 1997).

The concentrations measured at the Thai secondary lead smelter (rotary kilns with afterburners, cyclone and bagfilter) ranged from 0.021 to 0.032 ng I-TEQ/m³ with a mean of 0.027 ng I-TEQ/m³ for the line with the combined flue gas streams and from 0.06 to 0.11 ng I-TEQ/m³ with a mean of 0.089 ng I-TEQ/m³ for line, which only operated the rotary kiln at the operational O_2 content of about 19 %. The latter concentration corresponds to an emission factor of 10 g TEQ/t of lead and therefore very well fits into class 2 (EF = 8 µg TEQ/t of lead) as shown in Table 29 (UNEP 2001, Fiedler *et al.* 2002).

An emission factor of 8 µg TEQ/t of lead produced is to be used for furnaces fitted with fabric filters where PVC is excluded from battery separators. An estimated factor of 80 µg TEQ/t is used where PVC may be present and a factor of 0.5 µg TEQ/t for high technology furnaces and sophisticated flue gas cleaning equipment including scrubbers (concentrations around and below 0.1 ng TEQ/m³).

6.2.6.2 Release to Water

A release to water may result where effluents are discharged. There is not enough data to estimate an emissions factor. The presence of any liquid discharge should be noted and its source within the process recorded.

6.2.6.3 Release to Land

No release to land is expected.

6.2.6.4 Release in Products

No PCDD/PCDF is expected in the refined lead.

6.2.6.5 Release in Residues

PCDD/PCDF will be present in flue gas treatment residues. In tests in Germany (SCEP 1994), concentrations between 2,600 and 3,100 ng TEQ/kg were reported in dusts from a shaft furnace. Any use of residues as raw materials in other processes may result in transfer

of PCDD/PCDF.

6.2.7 Zinc Production

Zinc may be recovered from ores by a variety of processes. The occurrence of lead and zinc ores in combination means that there may be considerable overlap between these sectors. Crude zinc may be produced in combination with a lead ore blast furnace (HMIP 1994) or be recovered from the slag from such processes in rotary kilns (LUA 1997). A variety of scrap materials may be used for zinc recovery as well as secondary raw materials such as dusts from copper alloy production, electric arc steel-making (*e.g.*, filter dusts and sludges), residues from steel scrap shredding, scrap from galvanizing processes. The zinc generating process from secondary raw materials can be done in a zinc recovery rotary kiln (Waelz kiln), which is up to 95 m long with internal diameters of around 4.5 m; they are lined with refractory material. The granulated blast-furnace slag is mixed with other zinc intermediates, *e.g.* steel dusts, it travels down the kiln and is heated to reaction temperature by combustion of gases from a burner at the discharge end. In the slag-fuming process, a mixture of coal dust and air is injected into a liquid blast furnace slag at 1,150-1,250 °C in a water-jacketed furnace. The slag is directly delivered to the blast furnace.

The processing of impure scrap such as the non-metallic fraction from shredders is likely to involve production of pollutants including PCDD/PCDF. Relatively low temperatures are used to recover lead and zinc (340 and 440 °C). Melting of zinc may occur with the addition of fluxes including zinc and magnesium chlorides.

Emissions from the production of zinc have not been well studied but may be relevant (LUA 1997).

Table 30: Emission factors for the zinc industry

Classification	Emission Factors – µg TEQ/t of Zinc				
	Air	Water	Land	Product	Residue
1. Kiln with no dust control	1,000	ND	NA	NA	ND
2. Hot briquetting/rotary furnaces, basic dust control; *e.g.*, fabric filters/ESP	100	ND	NA	NA	ND
3. Comprehensive pollution controls, *e.g.*, fabric filters with active carbon/DeDiox technology	5	ND	NA	NA	ND
5. Zinc melting	0.3	ND	NA	NA	NA

6.2.7.1 Release to Air

Emissions to air may arise from smelting processes and melting of mixed scrap. European plants would be fitted with fabric filter systems to control particulate emissions (HMIP 1994, LUA 1997).

In Germany emission factors were provided for hot briquetting (63-379 µg TEQ/t zinc with emissions between 89 and 953 ng TEQ/m³, mean = 521 ng TEQ/m³), a rotating cylinder furnace (62.3 µg TEQ/t with emissions between 10 and 335 ng TEQ/m³; mean = 175 ng TEQ/m³) and for zinc melting (typically under 0.1 ng TEQ/m³ (LUA 1997).

Although this data set is very limited initial estimations of releases may be obtained by applying the emission factor of 100 µg TEQ/t of zinc produced where hot briquetting or rotary furnaces are used. Where furnaces are used feeding scrap materials or filter ashes from the steel industry to recover zinc (Japanese data) and with no dust removal an estimated factor of 1,000 µg TEQ/t can be used. For high technology facilities using comprehensive pollution controls such as fabric filters with lime and active carbon injection an estimated factor of 5 µg TEQ/t can be used.

6.2.7.2 Release to Water

A release may occur if effluents are discharged. The source of any effluent from the process should be noted.

6.2.7.3 Release to Land

No release to land is expected.

6.2.7.4 Release in Products

Levels of PCDD/PCDF in refined zinc are not relevant.

6.2.7.5 Release in Residues

Residues from gas cleaning are expected to contain PCDD/PCDF. Insufficient information was available to estimate an emissions factor.

6.2.8 Brass and Bronze Production

Brass is a hard yellow shiny metal that is an alloy of copper (55 %-90 %) and zinc (10 %-45 %). The properties of brass vary with the proportion of copper and zinc and with the addition of small amounts of other elements, such as aluminum, lead, tin, or nickel. In general, brass can be forged or hammered into various shapes, rolled, *etc.* Brass can be produced by either re-melting the brass scrap or melting stoichiometric amounts of copper and zinc together. In principle, either one or both can be primary or secondary metal.

Bronze is a hard yellowish-brown alloy of copper and tin, phosphorus, and sometimes small amounts of other elements. Bronzes are harder than copper and brasses. Bronze is often cast to make statues. Most bronze is produced by melting the copper and adding the desired amounts of tin, zinc, and other substances. The properties of the alloy depend on the proportions of its components.

Brass and bronze can be produced in simple, relatively small melting pots or in more sophisticated equipment such as induction furnaces equipped with APC systems.

Measured PCDD/PCDF data from brass production are available from the Thailand sampling program (UNEP 2001, Fiedler *et al.* 2002). The plant consisted of a small, batch-type smelter for primary and secondary brass production. The brass from the smelter was cast manually into bars, which were then rolled into coils for different products. The furnace was heated with about 30 L/h low sulfur, heavy fuel oil. The furnace was operated on a 250 kg/batch discontinuous mode during one day shift. The flue gases from the furnace and several surrounding areas pass a wet scrubber and are then discharged through the roof *via* a steel stack.

For a first estimate, the emission factors as chosen for the copper and zinc production should be applied. There will be only two classes of emission factors (Table 31).

Table 31: Emission factors for the brass and bronze industries

Classification	Emission Factors – µg TEQ/t of Brass/Bronze				
	Air	Water	Land	Product	Residue
1. Simple melting furnaces	10	ND	NA	NA	ND
2. Sophisticated equipment, *e.g.* induction ovens with APCS	0.1	ND	NA	NA	ND

6.2.8.1 Release to Air

Emissions to air may arise from smelting processes and melting of mixed scrap. The stack concentrations from the secondary brass smelter in Thailand ranged between 0.13 and 0.21 ng I-TEQ/Nm³ with an average of 0.15 ng I-TEQ/Nm³ at the actual operating O_2 concentration of 19 %. This concentration corresponds to an emission factor of 11 µg I-TEQ/t of brass (11 µg WHO-TEQ/t).

Class 1 emission factor should be used for simple smelting furnaces equipped with some flue gas abatement technology, *e.g.* scrubber or ESP. Class 2 emission factor should be used for more elaborated plants, *e.g.* induction ovens equipped with baghouse filters and wet scrubbers.

6.2.8.2 Release to Water

A release may occur if effluents are discharged. The source of any effluent from the process should be noted.

6.2.8.3 Release to Land

No release to land is expected.

6.2.8.4 Release in Products

Levels of PCDD/PCDF in refined brass are not relevant.

6.2.8.5 Release in Residues

Residues from gas cleaning as well as in sludges from wet scrubbers, if present, are expected to contain PCDD/PCDF. The PCDD/PCDF concentrations in the sludge samples taken from the clarifier of the water treatment system of the wet scrubbers had rather high concentrations of 8,683 and 8,567 ng I-TEQ/kg d.m.; in most countries, residues from such processes or with such concentrations would be classified as hazardous waste. The amount of sludge generated was low but could not be quantified. As expected, the slag sample from the furnace exhibited a low concentration of 13.6 ng I-TEQ/kg (UNEP 2001, Fiedler *et al.* 2002). There is still insufficient information to provide emission factors for solid residues.

6.2.9 Magnesium Production

The production of magnesium from ores is largely based on either the electrolysis of $MgCl_2$ or the chemical reduction of oxidized magnesium compounds. The raw materials used are dolomite, magnesite, carnalite, brines or seawater depending on the process. Magnesium can also be recovered and produced from a variety of magnesium-containing secondary raw materials

The electrolysis process is more widely used. This process seems to be of most interest from the point of view of PCDD/PCDF formation and release. Secondary magnesium production is not addressed in this Section.

In the thermal reduction process calcined dolomite is reacted with ferro-silicon sometimes together with aluminium in a furnace or retort vessel. The calcination process takes place by decarbonization and dehydration of dolomite limestone. For the calcination process for dolime, often a rotate or vertical furnace is used.

Tests from a plant in Norway, which produced electrolytic magnesium from dolomite and brine as raw materials, indicated that the main process causing the formation of PCDD/PCDF was a furnace converting pellets of MgO and coke to $MgCl_2$ by heating in a Cl_2 atmosphere at 700-800 °C (Oehme et al. 1989). It is possible that other process operations may also form PCDD/PCDF such as purification of MgO using HCl and graphite blades ("chloridation") or electrolysis of $MgCl_2$ using graphite electrodes (Bramley 1998). Chlorinated hydrocarbons and PCDD/PCDF are mainly emitted in the chlorination process that is used in the electrolysis of magnesium. These pollutants need to be removed from the off-gas, which can be done by using a wet-cleaning system. This consequently results in polluted washing water that itself needs an efficient wastewater treatment (BREF 2001).

Any PCDD/PCDF formed in the production process may be destroyed in subsequent process steps or may be released to air or water or in residues. The fluxes will depend on the nature of the process; whereby the carbon source may have some influence with coal producing more PCDD/PCDF than coke or pet coke (Musdalslien *et al.* 1998).

In the Norwegian process, the off-gases from the furnace were scrubbed in three stages, dedusted in a wet ESP and passed to an incinerator. Releases to water from the scrubber liquor will depend on water treatment and any recycle/regeneration. With water treatment and the gas treatment described the releases from the Norwegian plant were estimated at

under 2 g Nordic-TEQ[10] to air and 1 g N-TEQ to water each year (Musdalslien *et al.* 1998).

Prior to the installation of the water treatment facilities scrubber effluent was released to water and contained approximately 500 g N-TEQ each year (Oehme 1989).

Table 32: Emission factors in the magnesium industry

Classification	Emission Factors – µg TEQ/t of Magnesium				
	Air	Water	Land	Product	Residue
1. Production using MgO/C thermal treatment in Cl_2 – no treatment on effluent, limited gas treatment	250	9,000	NA	NA	0
2. Production using MgO/C thermal treatment in Cl_2 – comprehensive pollution control	50	30	NA	NA	9,000
3. Thermal reduction process	3	ND	NA	NA	NA

6.2.9.1 Release to Air

Emission factors to air from the production of magnesium by using the chlorination-electrolytic process are quite uncertain. PCDD/PCDF are formed and released from the chlorination furnace where magnesium oxide is converted into magnesium chloride. The following data are reported in the EU BREF document: 0.8 ng TEQ/Nm³ were found from chlorination off-gas treatment (EF = 12 µg TEQ/t); for the vent gases from chlorination, an emission factor of 28 µg TEQ/t was determined and concentrations in the hall from electrolysis and chlorination gave an emission factor of 13 µg TEQ/t (BREF 2001).

An emission factor of 250 µg TEQ/t of production is estimated for electrolytic processes, which do not have afterburners but use wet scrubbers. For processes with multi-stage wet scrubbers and afterburners an emission factor of 50 µg TEQ/t of production.

For plants applying the thermal reduction process, an emission factor of 3 µg TEQ/t will be used (BREF 2001).

Emissions could be much worse if the gas treatment is limited or where a high PCDD/PCDF producing carbon source is used.

6.2.9.2 Release to Water

Releases to water will depend on the amount of PCDD/PCDF formed in the process, the efficiency of the scrubbing systems to remove PCDD/PCDF in gas streams and crucially on the treatment applied to the effluents.

[10] The Nordic TEF system is used by the Scandinavian countries and varies from the I -TEF scheme only in the numeric value for one congener: whereas 1,2,3,7,8-Cl_5DF in the I-TEF is assigned a value of 0.05, only 0.01 is given in the N-TEF scheme. For the Toolkit, the difference is not relevant.

There is insufficient information to estimate releases from processes other than those including a thermal treatment of MgO/coke in Cl_2.

For processes fitted with comprehensive water treatment (including high efficiency solids removal), an emission factor is estimated based on releases reported from the Norwegian plant in the late 1990s or under 1 g TEQ per year. Prior to the installation of the water treatment system releases to water were estimated at 500 g TEQ per year and this is used to estimate an emission factor to be used where no treatment occurs.

An emission factor of 9,000 µg TEQ/t of Mg is used where direct discharge of the untreated effluent occurs. From European plants, an emission factor of 33 µg TEQ/t of Mg metal was reported (BREF 2001).

6.2.9.3 Release to Land

A release to land may occur where part of the water treatment involves release to a lagoon. Quantities are estimated in the residue Section (6.2.9.5).

6.2.9.4 Release in Products

PCDD/PCDF levels in magnesium produced are expected to be negligible.

6.2.9.5 Release in Residues

Residues from scrubbing processes may be expected to contain PCDD/PCDF. A stage in the water treatment may include settling in a lagoon, which would constitute a release of the residue to land. To estimate the release from the electrolytic process, it can be assumed that 0.01 tons of PCDD/PCDF-containing sludges are generated in the water treatment plant (BREF 2001).

Very little information is available on the concentrations of PCDD/PCDF in residues from this process or the amounts of residue produced. Initial estimates only may be made.

It is assumed that where no water treatment is used, no PCDD/PCDF is found in residues (although some may arise from other parts of the process). So the emission factor is zero. Where comprehensive water treatment is applied it is assumed that the difference in the release to water will approximately equal the PCDD/PCDF captured and therefore be present in the residues. An emission factor of about 9,000 µg TEQ/t of production is given to make an initial estimate.

6.2.10 Other Non-Ferrous Metal Production

A variety of processes are undertaken to produce and refine non-ferrous metals. The exact processes used and the propensity to form PCDD/PCDF is complex and not studied in detail.

Work in Norway showed that a process carried out to refine primary nickel, which used a fluidized bed reactor at 800 °C to convert $NiCl_2$ to NiO, had polluted the environment heavily with PCDD/PCDF but no emission factors were given (Oehme *et al.* 1989).

Tests in Germany have identified high emissions from tin smelting (up to 113 µg TEQ/t) but insufficient information is provided to be able to apply this to tin production processes (Bröker *et al.* 1999).

Other thermal metal processes can release PCDD/PCDF and emissions will be influenced by the degree of contamination on the scrap materials and the capture and treatment of the flue gases. Lowest emissions can be expected where the raw materials are clean and gas treatment comprehensive – including dust control by fabric filters, lime injection and possibly activated carbon addition and in some cases an afterburner.

It is important not to miss potentially significant PCDD/PCDF sources simply because there is insufficient data available to provide comprehensive emissions factors. Therefore, to provide an initial indication of potential releases, it is suggested that processes for non-ferrous metal production are examined. Releases may occur to air, water, and in residues. When investigating production processes, it is suggested that thermal processes are noted, the type of gas cleaning system applied is recorded and the levels of contamination found on the input materials is noted. The use of Cl_2 or hexachloroethane for refining and the presence of chlorinated compounds on raw materials should also be noted.

The Questionnaire provide in the Toolkit will assist in identifying and recording these parameters and criteria to follow-up.

Table 33: Emission factors for thermal non-ferrous metal processes

Classification	Emission Factors – µg TEQ/t of Product				
	Air	Water	Land	Product	Residue
1. Thermal non-ferrous metal processes – contaminated scrap, simple or no dust control	100	ND	NA	NA	ND
2. Thermal non-ferrous metal processes – clean scrap, fabric filters/lime injection/afterburners	2	ND	NA	NA	ND

6.2.10.1 Release to Air

Emissions will be high for installations with poor controls on input materials leading to high concentrations. Even if mass flow is small, local contamination may result. The emission factors are estimated based on patchy data on thermal non-ferrous metal recovery, concentrations would vary widely from well under 1 ng/m³ (class 2) to tens of ng/m³ (class 1).

6.2.10.2 Release to Water

Releases to water may occur where effluents are discharged. The presence and source of effluents should be noted.

6.2.10.3 Release to Land

No release is expected except where residues are dumped on land.

6.2.10.4 Release in Products

No PCDD/PCDF is expected in refined metal products.

6.2.10.5 Release in Residues

Residues may contain PCDD/PCDF. Insufficient data were available to estimate emissions factors. The use of a residue as a raw material could lead to contamination of the subsequent process.

6.2.11 Shredders

Shredders are large-scale machines, which use high-powered hammers to fragment scrap materials. Typically a ferrous metal stream is produced, which is relatively clean and consists of small (50 mm) pieces of steel and a "fluff" stream, which contains the fragments of non-ferrous metals and other materials that entered the shredder (also known as fragmentizer). For potential emissions from the thermal treatment, see Section 6.1.4). Often the feed materials would be old cars or consumer goods such as refrigerators, washing machines and cookers.

Few data is available and a single class of emission factors is used for emissions from the shredding process itself. PCDD/PCDF may result from contamination of the input material (for example with PCB) or from localized high temperatures in the system (Table 34).

Table 34: Emission factors for shredders

Classification	Emission Factors – µg TEQ/t of Steel				
	Air	Water	Land	Product	Residue
Metal shredding plants	0.2	NA	NA	ND	ND

6.2.11.1 Release to Air

Emissions arise due to high temperatures in the shredder, which release gases to atmosphere. An emission factor of 0.2 µg TEQ/t (concentration of 0.04-0.4 ng TEQ/m³) is developed based on data provided by SCEP (1994).

6.2.11.2 Release to Water

A release to water could occur where effluents are discharged. No data were available to estimate emission factors. Any liquid discharge should be reported and any treatment applied.

6.2.11.3 Release to Land

No release to land is expected.

6.2.11.4 Release in Products

It is likely that the products will have some level of contamination on them although it is not possible to estimate this.

6.2.11.5 Release in Residues

Residues may be materials from dust removal devices or unsaleable products from the shredding operation (non-metallic materials). PCDD/PCDF are likely to be present at low levels in these but no data were available to make an estimate. The metal recovered is likely to enter a thermal recovery process and releases may occur from these processes.

6.2.12 Thermal Wire Reclamation

Burning of cable is the process in which copper and lead are recovered from wire by burning the insulating material. In its most basic form, this process takes place in the open and consists of scrap wire, which is burned to remove wire coverings. In many countries this would be considered to be an illegal operation. More sophisticated operations would use a furnace with gas clean-up consisting of afterburners and scrubbers. In this process, all ingredients to form PCDD/PCDF are present: carbon (sheath), chlorine (PVC or mould-resistant agents) and a catalyst (copper).

It may be necessary to estimate the amount of wire burned in the open since it is unlikely that statistics will be kept. Sites where this process occurs can usually be identified due to the residue that remains.

The following classes of emission factors were developed (Table 35).

Table 35: Emission factors for thermal wire reclamation

Classification	Emission Factors – µg TEQ/t of Material				
	Air	Water	Land	Product	Residue
1. Open burning of cable	5,000	ND	ND	ND	ND
2. Basic furnace with afterburner and wet scrubber	40	ND	NA	ND	ND
3. Burning electric motors and brake shoes, *etc.* – after burner fitted	3.3	ND	NA	ND	ND

Class 1 factors for open burning of wire, Class 2 factors should be used for controlled operations recovering wire using a furnace with basic gas cleaning, and Class 3 factors for furnaces used to recover electric motor windings, brake shoes and the like with some gas cleaning system fitted.

6.2.12.1 Release to Air

To our knowledge, there are no measured data for emissions from open cable burning and only very few from legal cable burners. Highest concentrations reported for thermal wire reclamation were 254 ng TEQ/m³ (Dutch data) and emission factors up to 500 µg TEQ/t were used in the Dutch and Austrian inventories (LUA 2000); lowest were 3.3 µg TEQ/t. The Swiss inventory applied an emission factor of 2,340 µg TEQ/t (LUA 2003). To provide an estimate for emissions from open burning with no controls an emission factor of 5,000 µg TEQ/t is estimated (class 1).

Class 2 emission factors should be used for cable burning in furnaces fitted with afterburners and wet scrubbers. The concentration of 40 µg TEQ/t for emissions to air was given by Bremmer *et al.* (1994).

For furnaces burning electric motors, brake shoes and the like and fitted with an afterburner an emission factor of 3.3 µg TEQ/t is used (Bremmer *et al.* 1994).

Any similar recovery operations should be looked at and a note made of the controls applied and any gas cleaning in use.

6.2.12.2 Release to Water

Where a furnace is used and a wet scrubber is present a release to water is expected. The presence of wet scrubber systems at such plants should be noted, the fate of effluent and any treatment applied to the effluent noted.

6.2.12.3 Release to Land

Releases to land are expected to occur where open processing takes place, the residues in this case will be on the ground. At illegal burning sites, soil concentrations up to 98,000 ng TEQ/kg have been measured. In other cases where residues are removed these will be considered in the Section on residues. In the case of open cable burning contamination of the land can be significant and sites should be identified as potential hot spots.

6.2.12.4 Release in Products

No release into the copper product is expected.

6.2.12.5 Release in Residues

Residues from the process are expected to contain PCDD/PCDF and levels may be high. No data were available to estimate releases.

6.3 Main Category 3 – Power Generation and Heating

The category of power generation and heating includes power stations, industrial firing places (furnaces) and installations for providing space heating, which are fired with fossil fuels (including the co-combustion of up to 1/3 of waste), biogas including landfill gas, and biomass only. Table 36 outlines the five subcategories within this Main Source Category. The main release vectors are air and residue. Land is considered a release vector only in case of domestic heating and cooking either using biomass (mostly wood) or fossil fuels. Releases to land can occur if residues are dumped on the ground.

Table 36: Subcategories of Main Source Category 3 – Power Generation and Heating/Cooking

No.		Subcategories of Main Category	Air	Water	Land	Product	Residue
3		Power Generation and Heating/Cooking	X		(X)		X
	a	Fossil fuel power plants (coal, oil, gas and co-combustion of waste)	x				x
	b	Biomass power plants (wood, straw, other biomass)	x				x
	c	Landfill, biogas combustion	x				x
	d	Household heating and cooking with biomass (wood, other biomass)	x		(x)		X
	e	Household heating and cooking with fossil fuels (coal, oil, gas)	x		(x)		X

As generation of heat or power is the aim of these plants, in the case of the combustion of biomass or fossil fuels, the amount of PCDD/PCDF cannot easily be equated to masses (in tons) of fuel burned. The preferred basis to report emissions of PCDD/PCDF would be the heating value of the fuel. As the heat or power output is the "product" of the processes in this Section 6.3, this Main Source Category relates the default emission factors derived from the available data back to the heating value of the fuel. Thus, instead of reporting default emission factors in µg I-TEQ/t of fuel, these factors are given in µg I-TEQ/TJ of heat input. The reason for this choice can be explained easily and is based on the extremely wide variety of fuels used for power generation. The range of heating values of various coals from various parts of the world stretches over more than one order of magnitude. To recalculate heating values into masses, tables are provided in the Annex under Section 11.3.

Relevance to Article 5, Annex C

With relevance to the provisions of Article 5, sources in this category can be classified as follows:

Annex C, Part II source categories include:

	Source category	Section in Toolkit
(a)	Co-incinerators of waste	6.3 (as a whole)

Annex C, Part III source categories include:

	Source category	Section in Toolkit
(c)	Residential combustion sources	6.3.4, 6.3.5
(d)	Fossil fuel-fired utility and industrial boilers	Covered within the industrial production process, 6.3.1, 6.3.5
(e)	Firing installations for wood and biomass	6.3.2

6.3.1 Fossil Fuel Power Plants

Fossil fuel fired power plants generate the majority of the electricity consumed in today's world. In most Western countries, fossil fuel based power generation accounts for 50–70 % of the overall power production. In many developing nations as well as countries with economies in transition, fossil fuel based generation accounts for over 90 % of the overall power production in the public and industrial sectors.

Here, four categories are defined within this subcategory according to the types of fuels used, namely coal, heavy fuel oil, light fuel oil and natural gas, as well as any type of fossil fuel in a combination with the co-combustion of any kind of waste or sludges. For all four categories, it is assumed that reasonably well-operated and maintained power steam generators are employed in order to maximize power output. In all cases, air and residue are the only two release vectors under consideration.

Fossil fuel is burned in a wide array of devices for power generation ranging from small stoker fired furnaces to large elaborate highly sophisticated boiler/burner systems with extensive air pollution control (APC) plants at the back end. Coal combustion for power generation takes place in two general types of boilers distinguished by the way the ash is extracted from the system. The so-called dry bottom boilers use stokers or pulverized coal burners arranged in an opposed wall, all wall or corner fired (also referred to as tangentially fired) scheme. All these firing systems burn coal in a highly efficient manner leaving the majority of the ash as a dry residue at the bottom of the boiler. The so-called wet bottom boilers use pulverized burners in a cyclone or U-fired arrangement, which leads to much higher combustion temperatures resulting the ash to melt and collect as a liquid slag at the bottom of the boiler. Especially wet bottom boilers are frequently used for co-combustion of waste, particularly RDF or sludge. The molten slag at the bottom of the boiler provides for high enough temperatures to completely oxidize all the organic constituents within the waste. However, also all the pollutants are released into the flue gas.

Heavy fuel oil is also combusted for power generation purposes. It is usually burned in specially designed burners incorporated in the boiler walls. The formation of PCDD/PCDF is favored during co-combustion of liquid or sludge wastes such as waste oil and/or used solvents.

Light fuel oil and natural gas are always fired in specially designed burners and are not likely to generate large amounts of PCDD/PCDF since both are very high calorific, clean burning fuels with little to no ash. Only if liquid or sludge waste is co-fired higher concentrations of PCDD/PCDDF may be formed.

Like in all combustion processes, PCDD/PCDF are usually formed after the combustion process is completed and the flue gas cools down. The remaining organic fragments and the

chlorine contained in the coal recombine in the presence of the metal-chloride catalysts to form PCDD/PCDF. Releases to water, land and product are normally negligible. Thus, the only important release routes are to air and residue, especially to fly ash. Releases to water may occur at plants where wet scrubbers are installed and the water is not recirculated within the scrubbers. In such cases, releases to water have to be included. Sludges from such scrubbers, when separated from the effluents. will occur under "Residues". Four classes of emission factors were derived from studies done in Belgium, Germany and Switzerland. These are given in Table 37.

Table 37: Emission factors for fossil fuel based power generation and production of heat/energy in industry

	Emission Factors - µg TEQ/TJ of Fossil Fuel Burned		
	Air	Water	Residue
1. Fossil fuel/waste co-fired power boilers	35	ND	ND
2. Coal fired power boilers	10	ND	14
3. Heavy fuel fired power boilers	2.5	ND	ND
4. Light fuel oil/natural gas fired power boilers	0.5	ND	ND

These default emission factors are based on the assumption that the fuels burned lead to PCDD/PCDF releases associated with the disposal of fly ash. Emissions through bottom ash are negligible. Also, the removal efficiency of particulate matter increases with the quality of APC system employed at the plant.

6.3.1.1 Release to Air

Releases to air are the predominant vector for fossil fuel combustion. Typically, measured concentrations from large power plants are far below 0.1 ng TEQ/m³; mostly one to two orders of magnitude for solid and liquid fuels. Whereas Dutch data from large coal-fired power plants gave an emission factor of 0.35 µg TEQ/t, German data were between 0.004 and 0.2 µg TEQ/t (0.09 and 7.1 µg TEQ/TJ) and UK data had a median value of 0.14 µg TEQ/t (range: 0.06-0.32 µg TEQ/t). Swiss sources gave mean emission factors of 230 µg TEQ/TJ for coal-fired power plants. German data report between 0.02 and 0.03 µg TEQ/TJ for natural gas-fired boilers (LUA 1997).

The default emission factor for class 1 was derived from values reported between 0.4 and 118 µg TEQ/TJ. For the Toolkit, a median value of 35 µg TEQ/TJ was chosen. Class 2 emission factor was derived from average values reported between 230 (Swiss data from LUA 1997) and 7 µg TEQ/TJ as a median. Class 3 was derived from average values reported between 1 and 4 µg TEQ/TJ. Class 4 came from average values reported between 0.5 and 1.5 µg TEQ/TJ (LUA 1997, IFEU 1998, Environment Canada 1999).

6.3.1.2 Release to Water

No release to water is expected. However, in cases where wet scrubbers are installed and effluents are generated, this release vector needs to be highlighted. Presently, no numeric value can be provided to estimate this release.

6.3.1.3 Release to Land

No release to land is expected unless untreated residue is directly placed onto or mixed with soil.

6.3.1.4 Release in Products

The process has no product; thus no release to product occurs.

6.3.1.5 Release in Residues

There is a scarcity of measured data for PCDD/PCDF concentrations in fly ash and more data will be needed. It can be assumed that the content of PCDD/PCDF in the fly ash increases with the content of unburned carbon and the amount of waste co-fired.

To make a preliminary estimate UK data on PCDD/PCDF in residues from industrial coal combustion can be used (Dyke *et al* 1997, EC 1999). Concentrations in fly ash were 0.23-8.7 ng TEQ/kg ash and grate ash gave 0.02-13.5 ng TEQ/kg. The concentrations in soot were higher (up to 53 ng TEQ/kg). Taking an average ash production rate of 10 % and average concentration of 4 ng TEQ/kg ash give an emission factor of 0.4 μg TEQ/t (coal input) (approx. 14 μg TEQ/TJ) was derived.

6.3.2 Biomass Power Plants

Many countries and regions rely heavily on the combustion of biomass for power and heat production. Whether it is wood including twigs, bark, saw dust, wood shavings, *etc.*, peat, and/or agricultural residue (*e.g.,* straw, citrus pellets, coconut shells, poultry litter, camel excretes, *etc.*). In most cases, biomass is burned directly and without any addition of fossil fuels in small, continuously operated steam boilers. For the Toolkit, two categories are defined within this subcategory according to the types of biomass fuel used, namely wood fired boilers, and all other types of biomass fired boilers. For both categories, it is assumed that reasonably well-operated and maintained power steam generators are employed in order to maximize power output. In all cases, air and residue are the only two release vectors under consideration. This Section does not address firing of contaminated wood, which is covered in Section 6.1.6.

Biomass is burned in a wide array of devices for power generation ranging from small stoker fired furnaces to large elaborate highly sophisticated boiler/burner systems with extensive air pollution control (APC) plants at the back end. The combustion of biomass for power generation takes place predominantly in two general types of boilers distinguished by the way the fuel is fed to the system.

The so-called stokers fired boilers use a stationary, vibrating, or traveling grate on which the biomass is transported through the furnace while combusted. Primary combustion air is injected through the biomass fuel from the bottom of the grate. All these firing systems burn biomass in a highly efficient manner leaving the majority of the ash as a dry residue at the bottom of the boiler. Only a small fraction of the inerts leaves the boiler as fly ash.

The so-called fluidized bed boilers use a bed of inert material (*e.g.,* sand and/or ash), which is fluidized by injecting primary combustion air. The biomass is shredded and added to the fluidized bed, where it is combusted. The fluidized ash, which is carried out with the flue gas, is commonly collected in a (multi-)cyclone followed by an ESP or baghouse and re-injected into the boiler. No or very little bottom ash leaves the boiler, since all the larger ash particles either remain within the fluidized bed or are collected by the cyclone separator. Thus, almost all the ash is collected as fly ash in the ESP or baghouse.

The presence of PCDD/PCDF in this sub-category is based on the same general rules as is for fossil fuel plants. Two groups of emission factors were derived from studies done in Belgium, Germany, and the UK. These are given in Table 38. Releases to water may occur at plants where wet scrubbers are installed and the water is not recirculated within the scrubbers. In such cases, releases to water have to be included. Sludges from such scrubbers, when separated from the effluents. will occur under "Residues".

Table 38: Emission factors for biomass based power generation

	Emission Factors - µg TEQ/TJ of Biomass Burned		
	Air	Water	Residue
1. Mixed biomass fired power boilers	500	ND	ND
2. Clean wood fired power boilers	50	ND	15

These default emission factors are based on the assumption that the fuels burned lead to PCDD/PCDF releases associated with the disposal of ash. Emissions through bottom ash are negligible since the total amount of ash in biomass is between 0.5 % (wood) and 1 % (other biomass). Also, the removal efficiency of particulate matter increases with the quality of APC system employed at the plant.

6.3.2.1 Release to Air

Releases to air are the predominant vector for biomass combustion. The default emission factor for class 1 was derived from average values for straw combustion reported for the UK ranging between 17 and 54 µg TEQ/t. Data reported from Austria ranges between 2–500 µg TEQ/TJ. Based on an average heating value of about 8–11 MJ/kg a default emission factor of 500 µg TEQ/TJ was chosen as a representative value even though values as high as 5,000 µg TEQ/TJ could be found. Class 2 was derived from mean values reported between 4.7 (Belgian study) and 5.4 (UK study) µg TEQ/t of wood burned. Based on an average heating value of 12–15 MJ/kg, a default emission factor of about 350 ng TEQ/GJ can be calculated. (LUA 1997, IFEU 1998, Environment Canada 1999).

6.3.2.2 Release to Water

No release to water is expected. However, in cases where wet scrubbers are installed and effluents are generated, this release vector needs to be highlighted. Presently, no numeric value can be provided to estimate this release.

6.3.2.3 Release to Land

No release to land is expected unless untreated residue is directly placed onto or mixed with soil.

6.3.2.4 Release in Products

The process has no product; thus no release to product occurs.

6.3.2.5 Release in Residues

PCDD/PCDF in the ash residue can be assumed to be present. However, very limited detailed data regarding the amounts could be found. Based on a German study, typical concentration range from 30–3,000 ng TEQ/kg for bottom ash and 30–23,300 ng TEQ/kg for fly ash. Due to the large overlap in values reported for bottom ash and fly ash, no further differentiation was deemed necessary. Thus, an average value of 3,000 ng TEQ/kg based on an ash content of 0.5 % was chosen as a default emission factor.

No adequate data could be found for other biomass fuels. Thus, further research is still needed.

6.3.3 Landfill/Biogas Combustion

Landfill gas and biogas are both generated from anaerobic digestion of organic matter. The resulting gas is a mixture of carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), and ammonia (NH_3), and smaller fractions of combustible gases as well as a large fraction of water (H_2O). The combustible portion of the gas is usually around 50 % and the heating value is 15–25 MJ/kg depending on the origin of the gas. The combustion of landfill and biogas either occurs in a flare, in gas motors or turbines and or other power generating devices.

The combustion of these gases for power generation takes place predominantly in either gas-fired boilers or gas motors/turbines. Both systems closely resemble their templates firing natural gas. The combustion process is virtually residue free. One single emission factor was derived from studies done in Germany, the Netherlands, and the UK, which is given in Table 39.

Table 39: Emission factors for bio-/landfillgas power generation and flaring

	Emission Factor - µg TEQ/TJ of Gas Burned Air
Boilers, motors/turbines, flaring	8

6.3.3.1 Release to Air

Releases to air are the only vector for landfill gas and biogas combustion. The default emission factor for class 1 was derived from mean values reported between 7.6 and 8.4 µg TEQ/TJ of biogas burned for the German and UK study, respectively (LUA 1997, IFEU 1998, Environment Canada 1999).

6.3.3.2 Release to Water

No release to water is expected.

6.3.3.3 Release to Land

No release to land is expected since landfill gas and biogas burn virtually residue-free.

6.3.3.4 Release in Products

The process has no product, thus no release to product occurs.

6.3.3.5 Release in Residues

No release to residue occurs since landfill gas and biogas burn virtually residue-free.

6.3.4 Household Heating and Cooking with Biomass

Heating and cooking in residential households with biomass is common practice in many countries. In most cases the fuel of preference is wood, however, other biomass fuels may be used. Here, only two individual categories are defined within this subcategory and the main difference between these two categories is the purity of the fuel [11]. Thus, the differentiation is between virgin biomass and contaminated biomass such as treated and/or painted wood, straw heavily impacted by chlorinated pesticides. Air, residue, and in some cases land are the release vectors under consideration.

Biomass for residential heating and cooking is burned in a wide array of devices ranging from small, open pit stoves and fireplaces to large elaborate highly sophisticated wood burning stoves and ovens. The combustion of biomass for household heating and cooking takes place predominantly in devices of increasing combustion efficiency as the gross national product and the state of development of individual countries increase.

PCDD/PCDF are formed as a result of incomplete combustion, typical in these small devices with no or limited combustion controls. Releases to water and product are negligible. Releases to land can occur only if the combustion process takes place directly on the

[11] Such differentiation was not done in the public and industrial sectors for power and energy generation where the use of contaminated biomass, *e.g.* wood, is considered waste wood disposal

ground [12] or residues are disposed of to the land. Thus, the only significant release routes are to air, land, and residue. Two groups of emission factors were derived from studies done in Austria, Belgium, Denmark, Germany, The Netherlands, Sweden, Switzerland, and the UK. These are given in Table 40.

Table 40: Emission factors for biomass based household heating and cooking

	Emission Factors - µg TEQ/TJ of Biomass Burned		Concentration µg TEQ/TJ Residue
	Air	Land	
1. Contaminated wood/biomass fired stoves	1,500	ND	2,000
2. Virgin wood/biomass fired stoves	100	ND	20

Emission factors for releases with residues are given on the basis of measured concentrations in the ash (and not related the heating value of the fuel).

6.3.4.1 Release to Air

Releases to air are the predominant vector for biomass combustion. The default emission factor for class 1 was derived from mean values reported between 2 and 50 µg TEQ/t of wood burned. The values of 2.4–4.7 µg TEQ/kg as reported in the Austrian study seems to be extraordinarily high. The values of 0.2–0.7 µg TEQ/t as reported in the German study seem to represent the lowest end of the spectrum. So does the Swiss value of 24 ng TEQ/GJ. It is important to note that the values reported for clean biomass combustion are consistently one order of magnitude below the values reported for the combustion of contaminated biomass such as treated and/or painted wood. Thus, an average value of 1.5 µg TEQ/t was chosen for clean biomass where as a value of around 25 µg TEQ/t was used for contaminated biomass. Based on an average heating value of 12–15 MJ/kg for wood, default emission factors of about 100 µg TEQ/TJ can be calculated for clean biomass and 1,500 µg TEQ/TJ for contaminated biomass (LUA 1997, IFEU 1998). LUA (1997) gave emission factors of 50 µg TEQ/t for slightly contaminated and 500 µg TEQ/t for highly PCP-treated wood, which would result in emission factors of 3,300 µg TEQ/TJ and 50,000 µg TEQ/TJ, respectively.

6.3.4.2 Release to Water

No release to water is expected.

6.3.4.3 Release to Land

No release to land is expected unless the combustion takes place directly on the soil. Due to a lack of data, no default emission factor could be derived.

[12] This case is dealt with in Sector 6.6 – Uncontrolled Combustion Processes

6.3.4.4 Release in Products

The process has no product, thus no release to product occurs.

6.3.4.5 Release in Residues

PCDD/PCDF in the ash residue range from a few nanograms to several thousand ng TEQ/kg. Combustion of virgin wood will generate lower concentrations in the ash whereas treated wood results in higher concentrations. The mean concentrations determined by Wunderli *et al.* (1996) will be used in the Toolkit as a first estimate: they determined an average of 1,000 ng I-TEQ/kg for contaminated wood and 10 ng I-TEQ/kg for clean wood. The emission factors for the two classes have been calculated on the basis of these two numbers and the assumption that 3 % of ash is generated (normal ranges are 3-5 %; in cases of good burn-out the amount of ash will be lower; for bad burn-outs, the amounts of ash can be much higher).

6.3.5 Domestic Heating and Cooking with Fossil Fuels

Fossil fuel is used extensively for domestic heating, especially in developed countries and in countries with economies in transition. Coal, (light fuel) oil and (natural) gas are the main sources of fossil fuel used for domestic heating, which will constitute the three categories within this subcategory. For all three categories, it is assumed that reasonably well-operated and maintained heating ovens are employed in order to maximize heat output. In all cases air is the release vector under consideration. In case of coal combustion, residue must also be considered as a potential release vector.

Fossil fuel is burned in devices from small stoker fired furnaces to large elaborate highly sophisticated boiler/burner systems for central heat generation in large multi unit residential buildings.

Combustion for domestic heating takes place in two general types of boilers distinguished by the way the heat is transported and released. The so-called central heating systems, which usually use oil or gas as a fuel, use one large furnace to heat water, which then is circulated through the building to release its heat in numerous decentralized radiators. These modern systems are typically highly efficient and fairly clean burning leaving little to no residue for disposal. The second type of heating system is mostly based on solid fuels (coal) and consists of individual stoves, which are located in each room of the building or inside the wall to provide direct access to several rooms at the same time. These stoves consist of fairly small furnaces but provide a system for air to circulate inside the stove around the furnace. These systems are typically older, less efficient and less clean burning. Also bottom ash resulting from the inert content of the fuel is generated and must be disposed of. Some of these systems are also capable of burning oil.

Three groups of emission factors were derived from studies done in Austria, Belgium, Denmark, Germany, The Netherlands, Sweden, Switzerland, and the UK. These are given in Table 41.

Table 41: Emission factors for fossil fuel based domestic heating

	Emission Factors - µg TEQ/TJ of Fossil Fuel Burned Air	Concentrations – ng TEQ/kg Ash Residue
1. Coal fired stoves	70	5,000
2. Oil fired stoves	10	NA
3. Natural gas fired stoves	1.5	NA

These default emission factors are also based on the assumption that only the coal burned leads to PCDD/PCDF releases associated with the disposal of ash.

6.3.5.1 Release to Air

Releases to air are the predominant vector for fossil fuel combustion. The default emission factor for class 1 was derived from mean values reported between 1.6 and 50 µg TEQ/t of coal burned. The value of 0.91 mg TEQ/t as reported in the Austrian study seems to be extraordinarily high. The Swiss value of 230 ng TEQ/GJ also seems to be somewhat on the high side. It is important to note that the values reported for domestic coal combustion are fairly consistent between 1 and 7 µg TEQ/t for all the other studies. Thus, an average value of 2 µg TEQ/t was chosen for coal. Based on an average heating value of 28–35 MJ/kg for coal, a default emission factor of about 150 µg TEQ/TJ can be calculated.

The default emission factor for class 2 was derived from values reported between 0.04 and 2 µg TEQ/t. The value of 0.04 mg TEQ/t as reported in the Austrian study seems to be extraordinarily high whereas the Swiss value of 0.5 ng TEQ/GJ is extremely low. Thus, an average value of 0.5 µg TEQ/t was chosen for oil. Based on an average heating value of 44–46 MJ/kg for heating oil, a default emission factor of 10 µg TEQ/TJ was calculated.

The default emission factor for class 3 was derived from values reported between 0.04 and 0.07 ng TEQ/m³. An average value of 0.05 ng TEQ/m³ was chosen for natural gas. Based on an average heating value of 32–35 MJ/m³ for natural gas, a default emission factor of 1.5 µg TEQ/TJ was calculated (LUA 1997, IFEU 1998, Environment Canada 1999).

6.3.5.2 Release to Water

No release to water is expected.

6.3.5.3 Release to Land

No release to land is expected.

6.3.5.4 Release in Products

The process has no product, thus no release to product occurs.

6.3.5.5 Release in Residues

PCDD/PCDF in the fly ash residue of coal combustion has been analyzed and concentrations between 4 and 42,000 ng TEQ/kg ash were detected (Dumler *et al.* 1995). For a first estimate, an emission factor of 5,000 ng TEQ/kg ash should be used in the Toolkit.

6.4 Main Category 4 – Mineral Products

This section summarizes high-temperature processes in the mineral industry. Raw materials or fuels that contain chlorides may potentially cause the formation of PCDD/PCDF at various steps of the processes, *e.g.,* during the cooling phase of the gases, at preheaters or in the heat zone. Due to the long residence time in kilns and the high temperatures needed to fabricate the product, emissions of PCDD/PCDF are generally low in these processes. In this Toolkit, the subcategories as shown in Table 40 will be included into the dioxin and furan inventory.

Table 40: Subcategories of Main Category 4 – Production of Mineral Products

			Potential Release Route				
No.		**Subcategories of Main Category**	**Air**	**Water**	**Land**	**Product**	**Residue**
4		**Production of Mineral Products**	**X**				**X**
	a	Cement production	X				x
	b	Lime production	X				x
	c	Brick production	X				x
	d	Glass production	X				x
	e	Ceramics production	X				x
	f	Asphalt mixing	X			x	x

Relevance to Article 5, Annex C

With relevance to the provisions of Article 5, sources in this category can be classified as follows:

Annex C, Part II source categories include:

	Source category	Section in Toolkit
(b)	Cement kilns firing hazardous waste	6.4.1

6.4.1 Cement Production

Principal raw materials are clay and limestone. Cement manufacture begins with calcination, which is the decomposition of calcium carbonate ($CaCO_3$) at about 900 °C to leave calcium oxide (CaO, lime) and carbon dioxide (CO_2). Afterwards, lime reacts at temperatures typically around 1,400-1,500 °C with silica, alumina, and ferrous oxide to form silicates, aluminates, and ferrites of calcium (= clinker). The clinker is then ground or milled together with gypsum ($CaSO_4$) and other additives to produce cement (BREF 2000d).

There are four main process routes for the manufacture of cement: the dry, semi-dry, semi-wet and wet processes. In the dry process, the raw materials are ground and dried to raw meal, which is fed to the pre-heater or pre-calciner kiln (or more rarely into a long dry kiln). The dry process requires less energy than the wet process. The majority of the European kilns use the dry process. In the wet process, the raw materials (very often with high

moisture content) are ground in water to form a pumpable slurry, which is fed directly into the kiln or first into a slurry dryer. Most of the U.S. cement kilns use the wet process.

The process: the raw materials are first brought to site, are then mixed, crushed and ground to produce a raw meal of the correct particle size and chemical properties. The raw meal is converted into cement clinker by pyroprocessing in rotary kilns (50 m in length and more than 5 m in diameter). These consist of a refractory lined cylindrical steel shell slightly inclined to the horizontal and rotating at 1–3 rpm. Raw material is fed in at the upper end and gradually moves downward towards the lower end where a burner provides counter-current heating. The rotary kilns in the cement manufacture are different from the classic firing processes as feed materials and off-gases pass each other counter-currently thus leading to a thoroughly mixing, high temperatures (>1,400 °C at the hot end where clinker is formed), and long residence times (5-7 s) of the gases. These conditions will result in the destruction of any organic contaminants introduced with the fuel at the primary burner.

Modern cement kilns often use the dry process, in which raw mill material may be pre-heated in a vertically arrayed multi-cyclone pre-heater, in which the rising hot gases exiting the kiln contact the downward flowing raw materials. Some dry processes also employ a pre-calciner stage beneath the pre-heater, just before the raw material enters the kiln. The use of the wet process, where the ground meal is mixed with water and fed into the kiln as a slurry uses about 40 % more energy than the dry process.

The last stage involves cooling the clinker. As the hot clinker comes off the end of the lower end of the kiln it is rapidly cooled by ambient air in a clinker cooler, *e.g.* a travelling grate with under-grate fans that blow cool air through the clinker (EMEP 1999).

Finally, the cooled clinker is then mixed with gypsum and, for composite cements, other materials such as blast furnace slag, and ground to a fine homogeneous powder to produce the final product, which is then stored in silos prior to bulk transportation or bagging.

Typical fuels used are coal, oil, gas or petroleum coke. In many cases a variety of waste fuels are also used to supplement the fossil fuel. The wastes used may include: waste oils, solvents, certain industrial wastes, and in some cases hazardous wastes. Most of these will be fired at the burner (hot) end of the kiln. Tires are often used and may be added to the kiln some distance from the hot end as whole tires or chipped.

In the USA tests have indicated that higher emissions were found for some kilns where hazardous wastes were fired (EPA 1998). More detailed investigation has suggested that, provided combustion is good, the main controlling factor is the temperature of the dust collection device in the gas cleaning system, the plants equipped with low temperature electrostatic precipitators appear to have well controlled emissions with or without waste fuels. It is thought that the raw materials themselves can have a considerable influence on the emissions and the presence of high levels of organic matter in the raw materials has been associated with elevated emissions of PCDD/PCDF. It should be noted that the higher emissions measured in the USA were from wet kilns whereas the lower emissions (more than 150 measurements) from European cement kilns (mainly Germany and Switzerland) were obtained from plants using the dry process. Off-gases from dry kilns cannot be quenched to temperatures and thus enter the flue gas cleaning system at relatively high temperatures (>300 °C). From European plants, no elevated PCDD/PCDF concentrations have been reported from cement kilns with ESP.

The low results found in most of the modern European plants have been confirmed by the dioxin sampling and analysis program in Thailand, where PCDD/PCDF samples were taken and analyzed from two rotary kilns at a modern and well-operated cement plant. The samples were taken from two kilns under normal operation (full load and fired with a blend of lignite and petroleum coke as primary and secondary fuels) and with co-firing of (a) used tires and (b) industrial wastes including waste oils (UNEP 2001, Fiedler *et al.* 2002).

Kilns usually have a device to reduce emissions of particulate matter and to capture particles, which may be valuable as cement product. The pollution control system may be a simple dust collector (cyclone), electrostatic precipitators or fabric filters. In some plants other pollution controls may be fitted such as gas scrubbers. The following classes of emission factors were developed (Table 43).

Table 43: Emission factors for cement production

Classification	Emission Factors – µg TEQ/t of Cement				
	Air	Water	Land	Product	Residue
1. Wet kilns, ESP temperature >300 °C	5.0	ND	ND	ND	1.0
2. Wet kilns, ESP/FF temperature 200-300 °C	0.6	ND	NA	ND	0.1
3. Wet kilns, ESP/FF temperature <200 °C Dry kilns with APC (all types)	0.05	ND	NA	ND	0.003

6.4.1.1 Release to Air

Emissions to air in terms of PCDD/PCDF produced per unit production will be influenced by the concentration of the PCDD/PCDF in the flue gas and the amount of gas produced per unit production. A larger volume of flue gas is generated in wet kilns per unit output than in dry kilns (4,000 m³/t versus 2,500 m³/t, HMIP 1995).

German measurements at 16 cement clinker kilns (suspension pre-heater kilns and Lepol kilns) during the last ten years gave an average concentration of about 0.02 ng TEQ/m³ (Schneider, 1996).

Very low concentrations of PCDD/PCDF were found in the sampling campaign in Thailand at a cement plant utilizing the dry process. During normal operation (lignite/petroleum coke and full load), the stack emissions were all below 0.02 ng I-TEQ/Nm³ and as low as 0.0001 ng I-TEQ/Nm³; the means were 0.0105 ng I-TEQ/m³ and 0.0008 ng I-TEQ/m³ for the normal operation conditions and 0.003 ng I-TEQ/Nm³ and 0.0002 ng I-TEQ/Nm³ for the tests performed with substitute secondary fuels, respectively. The resulting emission factors were at a mean 0.02 and 0.001 µg TEQ/t of clinker for the normal operation and 0.005 and 0.003 µg TEQ/t of clinker in the case of co-firing alternative fuels/wastes. Thus, all test results were far below the orientation value of 0.1 ng I-TEQ/Nm³. The results demonstrated that the addition of tires and/or liquid hazardous waste had no effect on the emission results keeping in mind that the dry cement kiln process employed in the cement plant is state-of-the-art technology and the plant is well-managed (UNEP 2001, Fiedler *et al.*, 2002).

Concentration of PCDD/PCDF in the flue gases seems to be influenced by the temperature of the dust collection device. Low temperatures (<200 °C) seem to indicate that typical concentrations will be under 0.1 ng TEQ/Nm³, temperatures over 300 °C increase the likelihood of

finding higher emissions, typical concentrations would be 0.3 ng TEQ/Nm³ and above. In some cases much higher emissions may be found. These seem to be linked to high dust collector temperatures, high levels of organic matter in the raw materials and may be linked to use of certain wastes under inappropriate conditions.

An average emission factor of 5 µg TEQ/t of product (clinker) is applied to kilns with dust collectors over 300 °C. An average emission factor of 0.6 µg TEQ/t of product is applied where the dust collector is between 200 and 300 °C. An emission factor of 0.05 µg TEQ/t of product is applied where dust collector temperature is held below 200 °C.

Examples of cement kilns, where raw materials have unusually high concentrations of organic matter and dust collector temperatures are high, should be noted for further consideration. The use of wastes should be recorded noting the wastes used, the means used to introduce them to the kiln and any controls on operation (*e.g.,* prevention of feeding during combustion upsets, *etc.*).

6.4.1.2 Release to Water

Releases to water are not expected. However, if effluents are identified these should be noted and the origin in the process described.

6.4.1.3 Release to Land

Some residues may be spread on land, in some cases the use of cement kiln dust to increase alkalinity and add lime has been reported. Any use of cement kiln dust (CKD) in this manner should be noted.

6.4.1.4 Release in Products

Releases in the cement product are expected to be small since the product has been exposed to very high temperatures.

6.4.1.5 Release in Residues

It should be mentioned that the dusts collected in air pollution control systems, typically electrostatic precipitators (ESP) or cyclones, mainly consist of raw materials fed into the kiln (at the end of the secondary burner). The remainder of the dust consists of emissions from the kiln that has passed the hot zone. Typically, the dusts from the ESPs/cyclones are re-introduced into the kiln.

The principal residue to be disposed off is cement kiln dust (CKD), which is the dust collected in pollution abatement systems. A range of concentrations of PCDD/PCDF has been reported in the CKD and the rate of production will vary depending on plant specific factors and the degree to which the CKD may be reused in the process.

To provide an initial estimate of release of PCDD/PCDF in CKD an average rate of production was 0.4 million tons CKD from 13.5 million tons of clinker/cement production (Dyke *et al.* 1997) – approximately 30 kg of CKD per ton of clinker (0.3 % of clinker production).

Concentrations of PCDD/PCDF in the CKD are expected to vary. Insufficient data are available to accurately estimate levels of PCDD/PCDF from all kilns. A wide range of concentrations has been reported 0.001-30 ng TEQ/kg (Dyke *et al.* 1997) for UK kilns, 1-40 ng TEQ/kg for German tests (SCEP 1994). US tests indicated that on average kilns burning hazardous waste had higher levels (35 ng TEQ/kg) than kilns not burning hazardous waste (0.03 ng TEQ/kg) (EPA 1998). These results were strongly influenced by very high levels in one sample, the range is reported as 0.045-195 ng TEQ/kg.

To make an initial estimate of releases in CKD, three classes of emission factors as outlined in Table 43 are proposed.

6.4.2 Lime Production

Lime is used in a wide range of products. Quicklime (or burnt lime) is calcium oxide (CaO) produced by decarbonization of limestone ($CaCO_3$). Slaked lime is quicklime with water content and consists mainly of calcium hydroxide ($Ca(OH)_2$) [13]. Major users of lime are the steel industry, construction, pulp and sugar industries.

The lime making consists of the burning of calcium and/or magnesium carbonate at a temperature between 900 and 1,500 °C. For some processes, much higher temperatures are needed. The calcium oxide product (CaO) from the kiln is generally crushed, milled, and/or screened before being conveyed into a silo. The burned lime is either delivered to the end user for in the form of quicklime or reacted with water in a hydrating plant to produce hydrated lime or slaked lime.

Different fuels - solid, liquid, or gaseous - are used in lime burning. The fuels provide the energy to calcine the lime but also interact with the process. Most kilns can operate on more than one fuel. The lime burning process involves two phases (BREF 2000d):

1. Providing sufficient heat at above 800 °C to heat the limestone and cause decarbonization, and
2. Holding the quicklime at sufficiently high temperatures (around 1,200-1,300 °C) to adjust reactivity.

Most of the kilns are either shaft or rotary design. Most kilns are characterized by the counter-current flow of solids and gases. Fluidized bed kilns and rotary hearths may also be found. The typical kiln sizes lie between 50 and 500 tons per day (BREF 2000d).

Raw materials or fuels that contain chlorides may potentially cause the formation of PCDD/PCDF in the combustion process of the lime kiln. Data reported from Europe, obtained from seven kilns, of which four were rotary kilns and three were shaft kilns, showed PCDD/PCDF concentrations below 0.1 ng TEQ/Nm³. Measurements at two annular shaft kilns in Germany were all below 0.05 ng I-TEQ/Nm³. However, the scarcity of

[13] Very often, the term “lime” is incorrectly used for describing limestone products.

measurements means it cannot be ruled out that individual plants may be found in Europe and elsewhere, which may have a local impact (LUA 1997).

High concentrations of PCDD/PCDF have been measured at three kilns, 2 rotary kilns and one shaft kiln, in Sweden. The measurements made between 1989 and 1993 gave concentrations between 4.1 and 42 ng N-TEQ/Nm³ . All measurements of high dioxin levels have been explained either by the raw material and/or fuel content, or the less than optimum burning conditions, underlining the importance of controlling the kiln inputs and maintaining a stable kiln operation (BREF 2000d).

The following classes were established along with emission factors (Table 44):

Table 44: Emission factors for lime production

Classification	Emission Factors – µg TEQ/t of Lime Produced				
	Air	Water	Land	Product	Residue
1. Cyclone/no dust control	10	NA	ND	ND	ND
2. Lime production using dust abatement	0.07	NA	ND	ND	ND

Class 1 factors are to be applied to plants with poorer combustion and simple or no gas cleaning systems. The class 2 factor should be used where kilns are highly energy efficient and fitted with fabric filter gas cleaning.

6.4.2.1 Release to Air

Emissions have been measured from a number of German kilns (SCEP 1994). An emission factor of 0.07 µg TEQ/t of lime produced is to be used where lime kilns are well controlled and fitted with dust abatement equipment (typically electrostatic precipitator or fabric filter).

However, individual plants found in Europe (3 kilns, 2 rotary kilns and 1 shaft kiln in Sweden n the years between 1989 and 1993) showed measured concentrations between 4.1 and 42 ng N-TEQ/Nm³. All measurements of high PCDD/PCDF emissions were explained either by the raw material and/or fuel content, or the less than optimum burning conditions, underlining the importance of controlling the kiln inputs and maintaining a stable kiln operation (BREF 2000d). Considerably higher emissions were also quoted for limited tests (LUA 1997), an emission factor of 10 µg TEQ/t of lime produced is to be applied where control of the kilns is limited and dust control is basic (cyclone) or absent.

6.4.2.2 Release to Water

No release to water is expected. Any effluent identified should be recorded and it's source in the process identified.

6.4.2.3 Release to Land

Lime product or gas cleaning residues may be used on land. No information was available on levels of PCDD/PCDF in these to allow an estimate to be made of releases to land.

6.4.2.4 Release in Products

No information was available on PCDD/PCDF in lime products. Levels are expected to be low due to the high temperatures used in processing.

6.4.2.5 Release in Residues

A residue in the form of dust from gas cleaning operations may arise although this may be reused in the process or may have a product value. No information was available on PCDD/PCDF in such dust.

6.4.3 Brick Production

Bricks are predominantly made from clay with some additional materials added to achieve desired porosity and other characteristics. Industrial production typically uses tunnel type kilns with firing temperatures of around 1,000 ºC. Fuels for such systems would be oil or gas and attention is paid to gas cleaning with fluoride removal in some cases.

More basic brick firing may be carried out with a variety of kiln types and different fuels. In some cases there will be little in the way of gas cleaning technology.

The following classes of emission factors were selected (Table 46):

Table 43: Emission factors for brick production

Classification	Emission Factors – µg TEQ/t of Brick Produced				
	Air	Water	Land	Product	Residue
1. Cyclone/no dust control	0.2	NA	NA	ND	ND
2. Brick production using dust abatement	0.02	NA	NA	ND	ND

Class 1 factors would be applied to smaller less well-controlled kilns with no gas cleaning technology. Class 2 factors should be applied to production in modern facilities with high standards of combustion control and energy efficiency.

6.4.3.1 Release to Air

The emissions from brick kilns can vary depending on the type or process, the nature of the raw materials and any gas cleaning used. Few data are available on releases of PCDD/PCDF from brick making.

Tests in Germany showed emissions to air to vary from 0.002 to 0.23 µg TEQ/t of product. All tests were on relatively well-controlled plants.

An emission factor of 0.02 µg TEQ/t of product is to be applied to brick making processes with good control, consistently high temperatures and controls over the fuels used. Higher emissions may occur if poor controls are in place and wastes or poor quality fuels burned.

6.4.3.2 Release to Water

No release to water is expected. Any effluent should be noted and its source recorded.

6.4.3.3 Release to Land

No release to land is expected.

6.4.3.4 Release in Products

No data were available on levels of PCDD/PCDF in bricks. The levels are expected to be low as the bricks have been subject to high temperatures.

6.4.3.5 Release in Residues

PCDD/PCDF may be present in residues from the process. No information was available to estimate releases from this source.

6.4.4 Glass Production

Furnaces used for glass manufacture may be continuously or intermittently operated. Typical fuels are oil and gas. The raw materials are principally sand, limestone, dolomite and soda. In addition a wide range of other materials may be used to achieve desired properties such as color, clarity, and for purification. Chlorinated and fluorinated compounds may be added (SCEP 1994).

In some modern glass furnaces gases are cleaned with sorbents and electrostatic precipitators or fabric filters.

Very few tests are available and those that are come from Germany where pollution control is usually very good. It is possible that where standards of pollution control are weaker emissions could be higher. A lack of control over the fuels used, cleaning of recycled glass or pollution controls applied could all result in much higher emissions.

The following classes of emission factors were selected:

Table 46: Emission factors for glass production

Classification	Emission Factors – µg TEQ/t of Product				
	Air	Water	Land	Product	Residue
1. Cyclone/no dust control	0.2	NA	ND	ND	ND
2. Glass production using dust abatement	0.015	NA	ND	ND	ND

6.4.4.1 Release to Air

Tests in Germany on three glass producing furnaces showed low concentrations of PCDD/PCDF (SCEP 1994). The plants tested were fitted with dry sorption or wet scrubbing or electrostatic precipitators. Emissions factors for two plants were 0.005 and 0.022 µg TEQ/t of product, for the third plant concentrations were about a factor of 8 higher but an emission factor could be calculated.

An emission factor of 0.015 µg TEQ/t of product should be applied to plants with pollution control systems and careful control over combustion conditions and material inputs to the kiln.

An emission factor of 0.2 µg TEQ/t of product should be used where no gas cleaning is used and controls on plants may be less stringent.

6.4.4.2 Release to Water

Releases to water may occur where wet scrubbers are used. There is not enough information to estimate an emission factor in this case. The presence and source of effluents should be noted.

6.4.4.3 Release to Land

No release to land is expected.

6.4.4.4 Release in Products

Releases of PCDD/PCDF into glass products are expected to be very low due to the high processing temperatures.

6.4.4.5 Release in Residues

PCDD/PCDF may be present in residues from gas cleaning systems used in glass manufacture. No information was available to estimate an emission factor.

6.4.5 Ceramics Production

There is not enough information available to consider the production of ceramics as a source of PCDD/PCDF. It is likely that because it is a thermal process PCDD/PCDF will be released to air. It is proposed that an estimate be made by the application of the emission factors developed for brick making above.

6.4.6 Asphalt Mixing

Asphalt is used for road construction and generally would consist of rock chips, sand, fillers bound together in bitumen. Fillers can include fly ash from incineration or power plants.

The first stage of the process is generally an air-drying unit for the minerals. The hot minerals are then mixed with hot bitumen to obtain asphalt.

Asphalt mixing plants in industrialized countries may typically have gas cleaning consisting of fabric filters or wet dust control devices.

The following classes of emission factors were developed (Table 45):

Table 45: Emission factors for asphalt mixing

Classification	Emission Factors – µg TEQ/t of Asphalt				
	Air	Water	Land	Product	Residue
1. Mixing plant with no gas cleaning	0.07	NA	ND	ND	ND
2. Mixing plant with fabric filter or wet scrubber	0.007	NA	ND	ND	0.06

Class 1 factors would be applied to installations without gas cleaning systems, Class 2 factors would be applied to modern asphalt mixing installations fitted with fabric filter or wet scrubbers for gas cleaning.

6.4.6.1 Release to Air

Tests have been carried out on asphalt mixing installations in Germany (SCEP 1994) and the Netherlands (Bremmer *et al.* 1994). The plants tested all had fabric filters and some used cyclones as a pre-separator for dust. An average emission factor of 0.007 µg TEQ/t of product is to be applied to plants with this type of gas cleaning.

For plants without fabric filters an emission factor of 0.07 µg TEQ/t of product is applied (assuming fabric filters would capture approximately 90 % of PCDD/PCDF).

Emissions may be highly increased where contaminated materials are used as part of the asphalt – for example fly ash from an old incinerator could lead to increased releases. Any incidence where such materials are used should be noted.

6.4.6.2 Release to Water

No release to water is expected. If effluents are released, their source in the process should be noted.

6.4.6.3 Release to Land

It is assumed that the asphalt is used on land but no data are available on the levels of PCDD/PCDF in it.

6.4.6.4 Release in Products

There may be PCDD/PCDF in the asphalt although levels are unknown. It is expected this will be used on land for road construction.

6.4.6.5 Release in Residues

Flue gas cleaning residues are likely to have PCDD/PCDF in them. Amounts are unknown. An initial estimate can be made by assuming that 90 % capture of the PCDD/PCDF in the flue gas is achieved and assuming that the raw gas contains the same amount as for processes, which are uncontrolled giving an emission factor of 0.06 µg TEQ/t.

6.5 Main Category 5 – Transport

The major fuels used in transportation are gasoline, Diesel, and liquefied petroleum gas (LPG). In this Toolkit, emission factors are given for the sub-categories as shown in Table 46 with the guiding principles being the type of fuel and the type of combustion engine. So far, the occurrence of PCDD/PCDF has not been reported from aircrafts. No increase in concentrations or change in patters of PCDD/PCDF could be detected in a biomonitoring program on the Frankfurt International Airport with long-term exposure of kale at different locations, *i.e.,* along the runway or close to the terminals. Consequently, it was assumed that the combustion of kerosene in aircraft motors is not a source of PCDD/PCDF and this subcategory will not be addressed in this Toolkit (Fiedler *et al.* 2000, Buckley-Golder *et al.* 1999).

Table 46: Subcategories of the Main Category 5 - Transportation

			Potential Release Route				
No.		**Subcategories of Main Category**	**Air**	**Water**	**Land**	**Product**	**Residue**
5		**Transport**	**X**				
	a	4-Stroke engines	X				
	b	2-Stroke engines	X				
	c	Diesel engines	X				(x)
	d	Heavy oil fired engines	X				(x)

Relevance to Article 5, Annex C

With relevance to the provisions of Article 5, sources in this category can be classified as follows:

Annex C, Part III source categories include:

	Source category	Section in Toolkit
(h)	Motor vehicles, particularly those burning leaded gasoline	6.5 Special emphasis on 6.5.1, 6.5.2

6.5.1 4-Stroke Engines

Most gasoline powered internal combustion engines used today in cars, light trucks, motor-cycles and other vehicles are 4-stroke engines. These engines follow the thermodynamic combustion cycle invented by Nicolaus Otto, which consists of 4 strokes, namely the intake stroke, the compression stroke, the ignition and combustion stroke, and the exhaust stroke. These four strokes are completed during two full revolutions of the crankshaft. Like all combustion processes, internal combustion engines produce PCDD/PCDF as an unwanted byproduct. Higher emissions have been associated with the use of chlorinated scavengers used in leaded gasoline. However, when unleaded gasoline is used and a catalytic converter is installed for the removal of NO_x as well as unburned hydrocarbons, the emissions of PCDD/PCDF are negligible. The only release vector is into the air. All other release vectors

are not present. Thus, for the following categories default emission factors were established (Table 47):

Table 47: Emission factors for 4-stroke engines (*i.e.* passenger cars)

Classification	Emission Factors – µg TEQ/t of Fuel Burned				
	Air	Water	Land	Product	Residue
1. Leaded fuel [14]	2.2	NA	NA	NA	NA
2. Unleaded fuel without catalyst [14]	0.1	NA	NA	NA	NA
3. Unleaded fuel with catalyst [14]	0	NA	NA	NA	NA

Different emissions occur during different phases like start-up and engine warming. Here, steady state condition is considered.

6.5.1.1 Release to Air

The annual average mileage, type and level of maintenance of vehicles are different in different countries. The use of leaded fuels decreased dramatically in Europe, Japan, and North America as a result of legislation, however, leaded fuel is still used in some other countries. Phase out of leaded gasoline and adoption of catalytic converters as required in the EU Guideline 94/12/EG or similar US or Japanese legislation will mean that 4-stroke gasoline engines will become an almost negligible source of PCDD/PCDF emissions to air.

The emission factors are based on a German and Belgian study. Other countries, like North America and Asia, have very limited data on vehicle emissions.

6.5.2 2-Stroke Engines

Most small gasoline powered internal combustion engines used today in boats, jet-skis, mopeds, small motorcycles, tuk-tuks, lawnmowers, chain saws, and other vehicles are 2-stroke engines. These engines follow the same thermodynamic combustion cycle as the 4-stroke engines, however, it consists of only 2 strokes, namely the combined exhaust and intake stroke, and the compression, ignition and combustion stroke. The most striking difference to the 4-stroke engine is the fact that all strokes occur during only 1 full revolution of the crank shaft. Lubrication is usually by oil added with the fuel. Therefore, higher amounts of pollutants may be released and efficiency may be lower compared to 4-stroke engines. However, the simplicity and low production cost of 2-stroke engines make it an ideal motor especially for small engines. Like all combustion processes, 2-stroke engines also produce PCDD/PCDF as an unwanted byproduct. The only release vector is into the air. All other release vectors are not present. Thus, for the following categories default emission factors were established as shown in Table 48.

[14] if consumption data are given in liters (L), note that 1 L of gasoline has a mass of 0.74 kg; thus, a conversion factor of 0.00074 must be used to convert liters into tons

Table 48: Emission factors for 2-stroke engines (*i.e.* small mopeds)

Classification	Emission Factors – µg TEQ/t of Fuel Burned				
	Air	Water	Land	Product	Residue
1. Leaded fuel [14]	3.5	NA	NA	NA	NA
2. Unleaded fuel without catalyst [14]	2.5	NA	NA	NA	NA

Different emissions occur during different phases like start-up and engine warming. Here, steady state condition is considered. Since 2-stroke engines are mostly used for smaller engines, catalytic converters are hardly ever used.

6.5.2.1 Release to Air

The annual average mileage, type and level of maintenance of vehicles are different for different countries. In many cases, small engines are not very well maintained. This may result in higher emissions of PCDD/PCDF. Unfortunately, no data is available which relates age and level of maintenance to the level of PCDD/PCDF emissions. All data used was derived from various European studies.

6.5.3 Diesel Engines

Diesel engines are used in heavy trucks, light trucks, passenger cars, heavy construction equipment, boats, Diesel generators, pumps, and farm equipment including tractors and other large equipment. They usually use Diesel (light oil) and a 4-stroke cycle. Compression is used for ignition rather than a spark. Air is taken into the cylinder and compressed. Diesel fuel is added at high pressure and burned. This results also in a more efficient use of fuel and lower specific emissions. Unfortunately, particle emissions in form of soot are also associated with the operation of Diesel engines due to incomplete combustion especially during start-up, warming and load changes. Deposition of this soot can lead to releases *via* residues. Particulate emissions from Diesel engines are well known to contain high concentrations of polycyclic aromatic hydrocarbons (PAH). However, no PCDD/PCDF concentrations in Diesel soot are available. There is only one class of emission factor for Diesel engines.

Table 49: Emission factors for diesel engines (*i.e.* trucks)

Classification	Emission Factors – µg TEQ/t of Fuel Burned				
	Air	Water	Land	Product	Residue
Diesel engines[15]	0.1	NA	NA	NA	ND

Different emissions occur during different phases like start-up and engine warming. Here, steady state condition is considered.

[15] if consumption data are given in liters (L), note that 1 L of Diesel has a mass of 0.85 kg; thus, a conversion factor of 0.00085 must be used to convert liters into tons

6.5.3.1 Release to Air

Few data are available to base an evaluation of the PCDD/PCDF emission from Diesel-fueled vehicles. So far, only passenger cars and trucks have been measured; there are no data for off-road diesel uses (*i.e.*, construction vehicles, farm vehicles, and stationary equipment). From the USA, there are two tailpipe studies where the Californian Air Resources Board reported a relatively high emission factor of 676 pg I-TEQ/km; corresponding to 3.2 µg I-TEQ/t of Diesel [16] (CARB 1987); whereas for one tested heavy-duty truck Gullett and Ryan (1997) determined a range of emission factors from 3.0 to 96.8 pg I-TEQ/km (mean of 29.0 pg I-TEQ/km); corresponding to between 0.014 and 0.453 µg I-TEQ/t of Diesel with a mean of 0.14 µg I-TEQ/t of Diesel [16].

Marklund *et al.* (1990) could not quantify any PCDD/PCDF emissions at a detection limit of 100 pg I-TEQ /L when they tested a truck. Schwind *et al.* (1991) and Hutzinger *et al.* (1992) reported emission factors between 32 and 81 pg I-TEQ/L (or 6-15 pg I-TEQ/km assuming a fuel economy of 5.5 km/L) for a truck engine run under various simulated driving conditions. Hagenmaier (1994) reported no emissions from a bus at a detection limit of 1 pg/L of fuel consumed for individual congeners. For diesel-fueled cars, Hagenmaier et al. (1990) reported an emission factor of 24 pg I-TEQ/L for one tested car.

From the above, an emission factor for Diesel-fueled vehicles of 0.1 µg TEQ/t of Diesel will be applied. If efficient soot filters are employed, emissions from consumption of Diesel fuel are negligible.

As a result of concerns about heavy duty Diesel trucks, US-EPA will soon require all heavy duty vehicles to be equipped with particle filters, which will reduce emissions significantly and will result in emissions comparable to those from catalytic converters in gasoline powered cars.

6.5.3.2 Release in Residues

Particulate emissions from Diesel engines are likely to have PCDD/PCDF in them. Amounts are unknown, thus, more research is needed to determine actual PCDD/PCDF concentrations.

6.5.4 Heavy Oil Fired Engines

Heavy fuel oil (HFO) fired engines are used for ships, tanks, stationary power generators, and other very large quasi-stationary motors. The availability of emission factors is very limited and presently no distinction can be made with respect to composition of the fuels with respect to *e.g.,* chlorine content, type of catalytic metals present, *etc.* Based on very limited data, only one default emission factor to air was determined.

Waste oils are often burned in motors (stationary or in ships); they will be included in this subcategory.

[16] assuming a consumption of 1 L Diesel for a 5.5 km distance driven

Table 50: Emission factors for heavy fuel and waste oil fired engines (*i.e.* ships)

Classification	Emission Factors – µg TEQ/t of Fuel Burned				
	Air	Water	Land	Product	Residue
All types	4	NA	NA	NA	ND

Different emissions occur during different phases like start-up and engine warming. Here, steady state condition is considered.

6.5.4.1 Release to Air

Heavy oil fired engines cause PCDD/PCDF emissions to air. Unfortunately, very limited data is available from isolated measurements in Europe and North America. Typically numbers between 3 and 6 µg TEQ per ton of fuel are reported from studies in Canada, the Netherlands, Sweden, and the US.

Measured data from the burning of recycled waste oils are available from Austria, where emissions from a small incinerator gave a concentration of 0.02 ng TEQ/Nm³ (@11 % O_2) equivalent to an emission factor of 0.37 µg TEQ/t of waste oil burned (LUA 1997). Dutch data from two small firing installations and a ferry determined a minimum of 0.1 ng TEQ/m³ and a maximum of 0.3 ng TEQ/m³ equivalent to emission factors of 2 µg TEQ/t and 6.5 µg TEQ/t, respectively. The mean of the measurements was 0.2 ng TEQ/m³ (= 4.25 µg TEQ/t) and the median was 0.17 ng TEQ/m³ (= 2.9 µg TEQ/t) (LUA 1997). Based on these data, an emission factor of 4 µg TEQ/t of oil burned is suggested in this Toolkit.

6.5.4.2 Release in Residues

Heavy oil fired engines residues, especially emitted soot, are likely to have PCDD/PCDF in them. Unfortunately, amounts are unknown and further research is needed in order to determine exact concentrations.

6.6 Main Category 6 – Uncontrolled Combustion Processes

Uncontrolled combustion processes considered in this section are the burning of harvest residues, trees or bushes in the open air where no incinerator, stove or boiler is used. This category also includes the informal "disposal" of waste in barrels or in the open air as well as landfill fires, or accidental fires in buildings, vehicles, *etc.* In general, none of these combustion processes and fires is controlled resulting in poor combustion conditions due to inhomogeneous and poorly mixed fuel materials, chlorinated precursors, humidity, or catalytically active metals. This Toolkit differentiates between two major sub-categories (Table 51).

Table 51: Subcategories of Main Category 6 – Uncontrolled Combustion Processes

			Potential Release Route				
No.		**Subcategories of Main Category**	**Air**	**Water**	**Land**	**Product**	**Residue**
6		**Uncontrolled Combustion Processes**	**X**				**X**
	a	Biomass burning	X	(x)	X		(x)
	b	Waste burning and accidental fires	X	(x)	X		(X)

Relevance to Article 5, Annex C

With relevance to the provisions of Article 5, sources in this category can be classified as follows:

Annex C, Part III source categories include:

	Source category	Section in Toolkit
(a)	Open burning of waste including burning of landfills	6.6.2

6.6.1 Biomass Burning

This category is to cover the burning of biomass where it occurs in the open (*i.e.* excluding controlled combustion in appliances such as stoves, furnaces and boiler plants). This sub-category includes forest fires (deliberate and accidental) as well as burning of grassland or harvest residues such as straw, in the field. Post-harvest field burning is a common practice to remove residues, control weeds, and release nutrients for the next crop cycle.

The following process classes were established along with emission factors (Table 52).

Table 52: Emission factors for biomass burning

Classification	Emission Factors – µg TEQ/t of Material Burned				
	Air	Water	Land	Product	Residue
1. Forest fires	5	ND	4	NA	NA
2. Grassland and moor fires	5	ND	4	NA	NA
3. Agricultural residue burning (in the field), not impacted	0.5	ND	10	NA	NA
4. Agricultural residue burning (in the field), impacted, poor conditions	30	ND	10	NA	NA

Emission factors are expressed per ton of material burned. In this subcategory the emission factor is given for "Land" since due to the lack of containment, the ashes are disposed on land and typically are not collected for further disposal. Within this sub-category the hardest step may be to estimate the amount of material burned in any of these classes.

Appropriate texts on agriculture, forestry and land management may supply indications of the amount of material expected to be involved in a fire based on the land area involved. In the UK the figures were derived as follows:

- Heather moorland – material consumed in fires – 8 tons per hectare.
- UK forest – material consumed in fire – 23 tons per hectare.

For comparison, New Zealand (NZ 2000) reported 10 t/ha material lost in forest fires, 20 t/ha in scrub fires and 2.5 t/ha for grass fires. US-EPA suggested a figure of 23 t/ha for forest fires (EPA 1998). From Southeast Asian experience, it can be assumed that harvest residues of 25 % w/w are being generated from rice (in other words: 250 kg of rice straw are generated per ton of (polished) rice produced).

These are only examples and forest and moorland vegetation will vary considerably depending on the geographic location of a country. The Philippines gave 43 t/ha to be consumed in their typically forest fires. The degree to which vegetation will burn is highly influenced by the climatic conditions.

It is recognized that vegetation varies between regions depending on species, geography, and climate. Consequently, depending on these local conditions, the way a forest or biomass fires proceeds may be different from country to country. Since presently, no measured data are available from, e.g., typical fires in tropical regions and the influence of their vegetation, no differentiation can be done in this Toolkit according to different tree species or crop species. Further data generated by combustion experiments of such biomasses need to be performed.

The best source of information on where fires occur in a country may be fire departments. Departments and research institutions for agriculture and forest may be the best sources for the estimation of biomass grown in a given region.

6.6.1.1 Release to Air

No data were found that gave direct measurements of PCDD/PCDF released from forest fires. Only limited data are available for burning of wood in open fire places (most tests relate to closed wood stoves). Forest fires are likely to consume a variety of materials including

branches, leaves, living and dead wood whereas most fire place tests will be using specifically cut and dried logs – conditions are likely to be different.

Tests in the Netherlands gave emission factors of 13-28.5 µg TEQ/t (Bremmer *et al.* 1994) which were higher than factors the authors found in the literature from Germany (0.7-1.2 µg TEQ/t). Swiss work reported an emission factor of 0.77 µg TEQ/t for a wood stove with the door open to simulate an open fireplace (Schatowitz *et al.* 1994).

Mahnke and Krauss (1996) presented results of tests on smoke trails from open burning of sugar cane leaves in Brazil, they found levels of PCDD/PCDF were elevated compared to urban areas – emission factors are not available.

An emission factor of 5 µg TEQ/t is suggested to make an initial estimate for forest fires, taking into account the tests on open burning of leaves from Japan (Ikeguchi *et al.* 1999).

A range of agricultural residues may be burned in the field or to dispose of the wastes. Those materials burned for energy (*e.g.,* heating) are excluded from this Section (see Section 6.3). This Section is to estimate emissions from open burning, generally in the fields. Gullett *et al.* (2002) performed biomass burns in an open burn simulation facility and determined emission factors for wheat straw (containing ~0.8 % Cl for spring straw and 0.08 % for winter straw), rice straw (containing 0.33 % Cl), stubble (0.33 % Cl). The wheat straw emission factors ranged from 0.337 to 0.602 µg TEQ/t of straw burned and the one for rice straw was 0.537 µg TEQ/t of straw. The ten-fold difference in chlorine content did not affect the emission factors. These measured emission factors were higher than those used by US-EPA for their Dioxin Reassessment (US-EPA 2000). Much higher emission factors were determined in open burn trials in Japan (Ikeguchi *et al.* 1999), which included tests on emissions from leaves, bundles of straw and rice husks. These emission factors were 4.6, 20.2 and 67.4 µg TEQ/t, respectively.

It is expected that the emissions will vary considerably depending on the conditions under which the materials are burned, the nature of the crop or residue (*e.g.,* composition), humidity, or the possible presence of contaminants (presence of salt water residues or heavy pesticide treatment could conceivably alter the emissions). From the above, biomass burning will be devided into two classes whereby class 3 assumes that relatively clean harvest residues are burned under favorable conditions. Class 4 represents the burning of harvest residues in the field under less favorable conditions such as prior use of pesticides that contain precursors or catalysts for the formation of PCDD/PCDF, poor burning conditions (smouldering rather than an open flame), high humidity or wet ground. For the favorable conditions, an average emission factor of 0.5 µg TEQ/t will be applied and for the bad conditions, an emission factor of 30 µg TEQ/t is used to make an initial estimate of releases. More experiments are needed to better reflect harvest residues commonly burned in tropical countries such as sugar cane, rice husks, *etc.*

6.6.1.2 Release to Water

No direct release to water is expected but rainfall can be expected to wash away residues and some of this may enter water courses. Inputs to water courses may be highly relevant.

6.6.1.3 Release to Land

PCDD/PCDF are expected to be present in residues, which may be left on the land or incorporated into the field surface constituting a release to land.

PCDD/PCDF may be expected to be present in the ashes from fires. In some cases, these ashes may be used for their mineral content in agriculture. Ash production from these fires will vary with the conditions and the nature of material combusted.

A few studies have been carried out on levels of PCDD/PCDF in soils after open burns (as discussed in EPA 1998) and generally only small changes in soil concentrations of PCDD/PCDF have been found. Studies on levels of PCDD/PCDF in ash and soot from open fires showed very wide ranges of concentrations. Ash content of wood is usually low (compared to wastes or coal). An initial emission factor of 4 µg TEQ/t of material burned is suggested based on an average ash production of 2 % of mass burned and concentration in ash of 200 ng TEQ/kg.

6.6.1.4 Release in Products

No product is expected.

6.6.1.5 Release in Residues

Residues are assumed to be releases to land since they are typically left in place.

6.6.2 Waste Burning and Accidental Fires

This is a broad and poorly quantified sector. This Toolkit includes the deliberate combustion of waste materials for disposal where no furnace or similar is used – for example the burning of domestic and other waste in piles in the open, the burning of waste in landfills – both deliberate or accidental - fires in buildings, cars and similar vehicles. The following categories as shown in Table 53 were selected for consideration,

Table 53: Emission factors for waste burning and accidental fires

Classification	Emission Factors – µg TEQ/t of Material Burned				
	Air	Water	Land	Product	Residue
1. Landfill fires	1,000	ND	NA	NA	ND
2. Accidental fires in houses, factories	400	ND	See residues	NA	400
3. Uncontrolled domestic waste burning	300	ND	See residues	NA	600
4. Accidental fires in vehicles	94 (per vehicle)	ND	See residues	NA	18 (per vehicle)
5. Open burning of wood (construction/demolition)	60	ND	ND	NA	10

Uncontrolled domestic waste burning should include all instances where waste is burned with no pollution controls and therefore includes burning in the open in piles, in barrels or in home fires. The burning of waste in landfills is considered as a separate category. An estimate of the amount of PCDD/PCDF remaining in solid residues can be derived for this practice and is expressed in terms of PCDD/PCDF per unit of waste burned.

Accidental fires are very variable and the emissions will depend strongly on the materials burned and on the nature of the fire. There is limited information on emissions from these fires and a single indicative figure is given to cover all accidental fires excluding fires in vehicles. PCDD/PCDF will be present in residues that may be disposed of or left on the ground.

Chemical fires may lead to very high releases where certain precursor chemicals are involved, there is insufficient information to assess releases from chemical fires as a distinct category and releases are included in the subcategory of accidental fires. It should be noted that specific incidences could give rise to local contamination and a potential "hot spot".

Vehicle fires can release PCDD/PCDF, limited data are available to give emission factors for such events and these are presented. The vehicles involved can vary considerably and emissions are expected to vary also – figures here are for initial estimates only.

In some countries a considerable amount of wood used in construction and demolition is burned for disposal. Emission factors for this are given.

6.6.2.1 Release to Air

Emissions to air from burning of domestic and similar wastes in uncontrolled conditions have been measured in the US from trials where domestic waste was combusted in a barrel (EPA 1997, Gullett *et al.* 1999, Lemieux *et al.* 2003). Emissions to air seem to vary considerably depending on the conditions of combustion (highly variable) and the composition of the waste, from under 9 µg WHO-TEQ/t of waste to over 6,655 µg WHO-TEQ/t. Repeatability showed that the six repetitions of burning the baseline waste under the same conditions gave emission factors from 9 µg WHO-TEQ/t to 148 µg WHO-TEQ/t (factor of 16 between the experiments, whereby twice almost the same lower and the same higher emission factor was obtained). Highest emissions were found when either the content of organic chlorine (PVC; up to 7.5 % in the waste) was increased (3,543 and 6,655 µg WHO-TEQ/t) or high copper contents (Cu acts as a catalyst) were present (2,725 µg WHO-TEQ/t). On the other hand, poor combustion conditions obtained by doubling the load, increasing the humidity of the waste to be burned, compressing the waste before burning, as well as a high inorganic chlorine content (as $CaCl_2$) also generated quite high PCDD/PCDF emissions (up to 992 µg WHO-TEQ/t). One of the 0 % PVC experimental burns gave higher concentrations than one of the two high copper experiments. The mean value from the 25 experiments gave 706 µg WHO-TEQ/t and the median gave 148 µg WHO-TEQ/t. Interestingly, the share of a total WHO-TEQ from dioxin-like PCB was only 5 % on average. A value of 300 µg TEQ/t is used here for open burning where a wide range of wastes including items such as household hazardous wastes and chemicals may be burned.

Comparatively few studies are available on releases of PCDD/PCDF from landfill fires. High levels of PCDD/PCDF have been associated with landfill fires, which is to be expected with poor combustion conditions and mixed wastes. An emission factor of 1,000 µg TEQ/t is

applied (based on Swedish work reported by EPA 1998).

Materials burned and conditions experienced in accidental fires vary enormously. Limited data are available giving emissions from such fires. It is hard to measure emissions and studies tend to use laboratory simulations or measure soot and residues left after a fire. Emission factors developed here are indicative and more work is required to study fires of all types to improve estimates of releases. Some studies have considered emissions from the burning of PVC only and provided emission factors based on soot production in the range 40-3,500 µg TEQ/t (based on summary by Carroll 1996). These factors were based on results from laboratory and real fire samples and assume that 20 % of the PVC remains unburned and that all emissions to air are captured in the soot. Merk *et al.* (1995) burned wood and PVC in a closed room and measured levels of PCDD/PCDF in the air/flue gas in the room as well as in wipe samples from the walls. Assuming all the air in the room was contaminated at the levels measured an emission factor of 560 µg TEQ/t of PVC or 51 µg TEQ/t of the wood/PVC mixture is obtained. Further it was assumed that deposited soot is additional to this a further 2,200 µg TEQ/t PVC or 200 µg TEQ/t PVC/wood mixture was produced. Ikeguchi *et al.* (1999) provide emission factors for the open burning of various wastes (220 µg TEQ/t for scrap tires, 1,000 µg TEQ/t for electric wire tube and 6,600 µg TEQ/t for agricultural plastics (PVC)). Testing in Denmark of PCDD/PCDF released from burning chemicals (Vikelsoe and Johansen 2000) showed an enormous range of emission factors (at 500 °C) from 1 µg TEQ/t for dichlorobenil up to 740,000 µg TEQ/t for pentachlorophenol (PCP), PVC produced 100 µg TEQ/t in these tests. At 900 °C yields were greatly reduced. After a review of accidental fire data emission factors for residential fires of 83 µg TEQ/t to air, 83 µg TEQ/t in locally deposited soot and for industrial fires 500 µg TEQ/t to air and 500 µg TEQ/t in locally deposited soot were developed for Germany (LUA 1997).

Given the wide range of materials considered under accidental fires and the wide range of possible emission factors an initial estimate can be made by applying an emission factor of 400 µg TEQ/t to accidental fires.

Limited testing has been carried out on the release of PCDD/PCDF from fires in vehicles. Tests were carried out in a tunnel with an old car (1974), a new car (1988), a subway car and a railway carriage (Wichmann *et al.* 1995). Emissions to air were estimated from PCDD/PCDF deposited inside the tunnel and no estimate was made of PCDD/PCDF, which may not have been deposited. Emissions were 32 µg TEQ for the old car, 44 TEQ µg for the new car, 2,000 µg TEQ for the subway car and 9,200 µg TEQ for the railway wagon. For the purposes of making an initial estimate a composite emission factor is developed assuming 49.5 % of vehicle fires involve "old" cars, 49.5 % involve new cars and 0.5 % each of vehicles represented by subway cars and railway wagons giving a factor of 94 µg TEQ per incident (NB this emission factor is per incident not per ton of material!).

It is relatively common to see fires used to dispose of wastes from construction and demolition – these are often predominantly burning wood but may also be used to dispose of other materials. Again little information is available either on the amounts burned or on emissions. Studies in Japan can be used to make an initial estimate of a suitable emissions factor to be applied – 60 µg TEQ/t (Ikeguchi *et al.* 1999).

6.6.2.2 Release to Water

There is little information available on the release of PCDD/PCDF to water from these types of fires. The releases will vary considerably but highest releases may result from the use of water to extinguish a fire or rain falling on a fire site and washing material into water courses. Since these processes will depend on local circumstances it is not possible to provide emissions factors but the issue may be important.

6.6.2.3 Release to Land

For many of the fires considered a release to land will occur because residues from the fire are left in place on land.

6.6.2.4 Release in Products

No product is made in these processes – therefore there are no releases by this route.

6.6.2.5 Release in Residues

Residues from all types of fires considered in this Section are likely to contain PCDD/PCDF. The amounts will vary depending on the conditions in the fire and the nature of the materials. The residues may remain in place or be removed.

An indicative emission factor of 600 µg TEQ/t of material burned is used for open burning of domestic wastes based on results from US barrel burns (Lemieux *et al.* 1997).

For accidental fires there is little information on levels of PCDD/PCDF in residues. A wide range of concentrations has been measured but there is often insufficient information to estimate an emission factor since the amounts of ash produced are not known. In Germany, an estimate was made that gave emission factors in residues (including deposited soot) of 1,000 µg TEQ/t for industrial fires and 350 µg TEQ/t for residential fires (LUA 1997). As an approximation and to make an initial estimate, an emission factor of 400 µg TEQ/t is used giving equal PCDD/PCDF in air emissions and in residues on average from the fires considered.

For vehicle fires the limited testing in Germany (Wichmann *et al.* 1995) gave amounts of PCDD/PCDF left in residues, a composite emission factor is used to make an initial estimate – 18 µg TEQ per incident (using the same assumptions as above). Note, this emission factor is per incident not per unit mass.

For fires involving construction and demolition wood, no emission factors were found. To make a preliminary estimate, an emission factor of 10 µg TEQ/t wood burned is suggested (from UK work on industrial wood combustion, Dyke *et al.* 1997). Note that treated wood, mixed fire loads and poor conditions may increase the amount of PCDD/PCDF in residues considerably.

6.7 Main Category 7 – Production and Use of Chemicals and Consumer Goods

This Section 6.7 describes the potency of the chemicals and consumer goods production sector to generate PCDD/PCDF and gives findings from measured data and information on characteristics to estimate/quantify release of PCDD/PCDF from the various activities in this sector. This Section 6.7 also gives brief descriptions of the processes addressed here to gain a general understanding of the industries. They might help to better understand the relationship between the industrial processes and subsequent releases with or without dioxin and furan relevance. For details, more specialized information and literature should be consulted.

As can be seen from Table 54, there are five major subcategories. It can also be seen that releases of PCDD/PCDF may occur *via* various pathways resulting in contamination of air, water, and soil or in the product. In addition, the residues may contain dioxin and furan contamination as well. For all the activities listed in this sector, the major emissions are not into he atmosphere but into other compartments.

Table 54: Subcategories of Main Category 7 – Production and Use of Chemicals and Consumer Goods

7	Subcategories of Main Category	Air	Water	Land	Product	Residue
a	Pulp and paper production	x	X		x	X
b	Chemical industry (chlorophenols, halogenated organics, Cl_2 production, oxychlorination processes)	x	X	(x)	X	X
c	Petroleum industry (refineries)	x				x
d	Textile production		x		x	
e	Leather refining		x		x	

Relevance to Article 5, Annex C

With relevance to the provisions of Article 5, sources in this category can be classified as follows:

Annex C, Part II source categories include:

	Source category	Section in Toolkit
(c)	Production of pulp using elemental chlorine or chemicals generating elemental chlorine for bleaching	6.7.1

Annex C, Part III source categories include:

	Source category	Section in Toolkit
(f)	Specific chemical production processes releasing unintentionally formed persistent organic pollutants, especially production of chlorophenols and chloranil	6.7.2
(j)	Textile and leather dyeing (with chloranil) and finishing (with alkaline extraction)	6.7.4, 6.7.5

6.7.1 Pulp and Paper Production

In general terms, paper is a sheet of fibers with a number of added chemicals that affect the properties and quality of the sheet. Besides fibers and chemicals, manufacturing of pulp and paper requires large amounts of process water and energy (as steam and electricity).

Pulp for papermaking may be produced from virgin fiber by chemical or mechanical means or may be produced by re-pulping of recovered paper. A paper mill may utilize pulp made elsewhere (= non-integrated pulp mills) or may be integrated with the pulping operations at the same site (= integrated pulp mills). Kraft pulp mills can be both non-integrated and integrated operations whereas sulfite pulp mills are normally integrated with paper production. Mechanical pulping and recycled fiber processing is usually an integrated part of the papermaking but has become a stand-alone activity in a few cases.

Pulp and papermaking is a complex field that consists of many processes with different stages and different products. For the sake of the Toolkit and due to common parameters, such as raw materials, processes can be broken down into a number of classes.

The production of pulp is the major source of environmental impacts from the pulp and paper industry. In general terms, the process to make paper and paperboard [17] consists of three steps: pulp making, pulp processing, and paper/paperboard making.

From pulp and paper mills releases of PCDD and PCDF may occur *via* the following vectors:

- Emissions to air (from burning of lignin and black liquor to generate energy);
- Emissions to air from burning wood or bark to generate energy;
- Emissions with process water (modern pulp mills operate totally effluent free);
- Emissions into the pulp sludge, which may be applied on land, be incinerated or land-filled;
- Emissions into the products (= pulp, paper), which enter the market as a valuable product.

Pulping

During the pulping process, the cellulose fibers are separated from the lignin of the wood, known as delignification. Most commonly, hardwood and softwood are used, however other starting materials such as coconut shells, bamboo, papyrus, straw, *etc.* can be pulped as well. To achieve this goal either mechanical pulping or chemical pulping can be employed.

[17] Paperboard is thicker than 0.3 mm

In **mechanical pulping** the wood fibers are separated from each other by mechanical energy applied to the matrix; *e.g.*, where logs are pressed against a rotating grinder stone with simultaneous action of water or by defiberizing wood chips between disc refiners. If chemicals are added to pre-treat the wood chips, the process is named chemo-thermo-mechanical pulping (CTMP). For high quality paper grades, the pulp needs to be delignified or bleached. For this purpose, two processes are employed:

a) the Sulfite Process

This is an acidic cooking liquor process and is based on aqueous sulfur dioxide (SO_2) and a base, calcium [18], sodium [19], magnesium [18] or ammonium. Its importance has decreased over the years and today only 10 % of the world's pulp is produced by this method. The sulfite process requires high quality fibers, while the products are of lower tensile strength. It is more frequently used for softwood.

b) the Kraft or Sulfate Process

It is an alkaline cooking liquor process and is the dominating pulping process worldwide (80 % of the world pulp production). It is applicable to all kinds of woods/fibers and produces cellulose of high tensile strength. The Kraft process uses a sodium-based alkaline pulping solution (liquor) consisting of sodium sulfide (Na_2S) and sodium hydroxide (NaOH) in 10 % solution. Unreacted pulping chemicals (= black liquor) will be recovered to generate white liquor for the first pulping step.

Bleaching

To remove the color associated with remaining residual lignin, the pulp is bleached in three to five bleaching stages, alternating between acid and alkaline conditions.

The most commonly used chemicals are chlorine, hypochlorite, chlorine dioxide, oxygen, ozone and peroxide. Lately, peracetic acid has become commercially available as bleaching chemical. Increasing the chlorine dioxide substitution decreases the formation of chlorinated aromatic substances and eliminates the formation of PCDD/PCDF. There are four basic approaches to bleaching:

1. Elemental Chlorine Bleaching
   It uses chlorine (Cl_2) and hypochlorite to brighten the pulp. When elemental chlorine and hypochlorite react with the lignin, chlorinated compounds including PCDD/PCDF are formed.

2. Elemental Chlorine Free Bleaching (ECF)
   ECF bleaching is a bleaching sequence, which usually uses chlorine dioxide (ClO_2) as the main bleaching agent. Elemental chlorine (chlorine gas, Cl_2, also hypochlorite) is no longer used. ECF results in reduced levels of PCDD/PCDF. In October 1998, 54 % of the world market was supplied by ECF pulp.

3. Totally Chlorine Free (TCF)
   Uses no chlorinated bleaching agents to bleach the pulp; instead oxygen (O_2), peroxide (H_2O_2) or peracetic acid are used. The effluents are almost chlorine-free. In October

[18] cheaper, but cooking chemicals cannot be recovered (outdated in Europe)

[19] dominating processes in Europe; chemical recovery allowed

1998, the TCF pulp totaled 6 % of the world market.

4. Bleaching of Mechanical Pulps
   The bleaching of mechanical pulp is completely different from chemical bleaching as it is based on lignin-saving methods instead of lignin-removing ones. The effect is not permanent and the paper yellows with time. The lignin-saving is carried out in 1-2 stages using sodium dithionite ($Na_2S_2O_3$), peroxide (H_2O_2) or a combination of the two.

Paper Making

Primary fiber paper: All paper and board machines are based on the same basic process, where a 99 % aqueous solution of fibers and chemicals is mechanically dewatered by a press and finally run through a set of cylinders at a temperature of slightly over 100 °C. At the end, the paper is smoothed with hot roll pairs (calendars or soft-calendars) and finally, the paper is rolled on a so-called parent reel.

Recycling paper: Secondary fiber pulping is a relatively simple process, which utilizes pulping chemicals such as NaOH. Recycled fiber (RCF) processes are either processes with exclusively mechanical cleaning, *e.g.,* without de-inking or processes with mechanical cleaning and de-inking. The recovered paper is dissolved in hot water in a pulper, separated from non-fiber impurities and progressively cleaned to obtain pulp. For some uses, *e.g.,* graphical papers, the pulp is de-inked to increase whiteness and purity.

Chemical Recovery Systems

The Kraft chemical recovery process has not changed a lot since 1884. Residual weak black liquor is concentrated by evaporation to strong black liquor, which is burned in a recovery boiler for energy and the process chemicals are removed from the mixture in molten form. The recovery boilers can be augmented with fossil fuel-fired or wood-waste boilers (hogged fuel) to cover the energy demand of the plant. The emissions from these boilers are subject to releases of PCDD and PCDF.

For the Toolkit we will follow the common approach and report data for pulp based on Air Dried tons (ADt), which refers to pulp at 90 % dryness or 900 kg of bone dry pulp. For paper, the basis is the finished paper at the dryness that results, typically 94-96 % dryness.

For the pulp and paper industry emission factors should be chosen as shown in Table 55 and Table 57.

Table 55: Emission factor for the pulp and paper industry: boilers

	Emission Factor	
	µg TEQ/t Feed Air	µg TEQ/t Ash Residue
1. Black liquor boilers, burning of sludges and wood	0.07	1,000
2. Bark boilers only	0.4	1,000

Annual emissions with wastewater effluents and pulp and paper sludges (= residues) will calculated by multiplying the concentration in the effluent (in pg TEQ/L) or the concentration in the sludge (in µg TEQ/t dry matter) with the annual discharge or production volume, respectively. To assist in estimating releases typical values in terms of µg TEQ/ADt are given in

the tables along with typical concentrations in effluent and solids – these can be used if mass flow data are unavailable. The PCDD/PCDF concentrations for different classes are provided in Table 56. These emission factors assume all plants have effluent treatment facilities producing sludge and effluent low in suspended solids.

Table 56: Emission factors for effluents and pulp and paper sludges

	Emission Factors			
	Water		Residue = Sludge	
Classification	µg TEQ/ADt	pg TEQ/L	µg TEQ/ADt	µg TEQ/t in Sludge
1. Kraft process, old technology (Cl_2)	4.5	70	4.5	100
2. Kraft process, modern technology (ClO_2)	0.06	2	0.2	10
3. TMP pulp	ND	ND	ND	ND
4. Recycling pulp	ND	ND	ND	ND

Table 57: Emission factors for pulp and paper products

Classification	Emission Factors µg TEQ/t of Product
1. Kraft pulps and papers from primary fibers, free chlorine bleaching	8
2. Sulfite papers, old technology (free chlorine)	1
3. Kraft papers, new technology (ClO_2, TCF), unbleached papers	0.5
4. Sulfite papers, new technology (ClO_2, TCF)	0.1
5. Recycling paper	10

6.7.1.1 Release to Air

The major emissions to air from pulp and paper mills originate from energy generation and not from the manufacturing process itself.

Pulp and paper mills burn lignin (from the pulping process) for generation of energy utilized in the mills. In addition, residual wood chips bark chips, *etc.* can be burned in the boilers. For both, sulfite and Kraft mills, average volumes are 6,000-9,000 m³/t of pulp and concentrations around 0.41 ng I-TEQ/m³ (range: 0.036-1.4 ng I-TEQ/m³) (CEPA-FPAC 1999). The higher emissions are based on measurements from coastal areas in British Colombia where salt-loaded wood enters the pulp mills.

Kraft liquor boilers are used by the pulp and paper industry to burn the concentrated black liquor. Most are equipped with some simple flue gas cleaning devices, *e.g.,* cyclones, wet scrubbers or electrostatic precipitators (ESP). Average concentrations are between 0.004 and 0.008 ng I-TEQ/m³ (CEPA-FPAC 1999). For the Toolkit, the emission factor as determined by NCASI and used in the US-EPA Reassessment of 0.007 µg TEQ/t of black liquor will be used (US-EPA 2000, Volume 2, 5-26).

US-EPA (1998) reported emissions from pulp mills burning sludge and wood residues in wood boilers (stoker with ESP) between 0.0004 and 0.118 µg I-TEQ/t of sludge or wood,

respectively. The default emission factor for pulp mills burning sludge or wood residue is 0.06 µg TEQ/t of feed (*i.e.*, sludge or wood residue). There will be no differentiation between different technologies, *e.g.,* flue gas cleaning devices.

Kraft pulp mills have lime kilns to reburn the calcium carbonate formed during the recausticizing process. The rotary kiln operate at temperatures from 800 °C at the start of the calcination reaction and 1,000-1,100 °C to complete the reaction. The gas flow in the lime kiln is around 1,000 Nm^3/t of pulp. Emission factors for lime kilns should be used, see Section 6.4.2.

The default emission factor for wood burning at pulp mills will be the same as determined for wood burning, see Section 6.3.

6.7.1.2 Release to Water

The pulp and paper industry is one of the largest water users. Sulfite mills discharge more water than Kraft mills. A modern bleach plant discharges between 15 and 20 cubic meters of water per ton of Air-dried pulp (15-20 m^3/t ADt).

In 1988, in the USA, a typical pulp and paper mill used 16,000 to 17,000 gallons of water per ton of pulp produced (60-64 m^3 of water/t pulp); in the EU water consumption varied between 15 and 100 m^3/t. Water consumption can be reduced by increasing internal water recirculation. Typical figures for wastewater discharge are 20-40 m^3 per ton of pulp. For the Toolkit, 30 m^3 of water per ton of pulp produced will be used.

Concentrations in effluents ranged from 3 pg TEQ/L to 210 pg TEQ/L with a median of 73 pg TEQ/L (US-EPA 1998a). The default emission factor for Kraft bleached pulp using old bleaching sequences is 4.5 µg TEQ/t of pulp. Alternatively, the concentration in the effluent can be used and multiplied with the total mass of water discharged per year to calculate the annual release.

Replacement of Cl_2 in the first bleaching stage by ClO_2 will dramatically reduce the formation of 2,3,7,8-Cl_4DD and 2,3,7,8-Cl_4DF (below detection limits of 0.3-0.9 pg/L).

Data generated and published by NCASI [20] (1998) in the USA from 20 bleach lines at 14 U.S. Kraft mills that use complete chlorine dioxide substitution for chlorine gave 119 data pairs for 2,3,7,8-Cl_4DD and 2,3,7,8-Cl_4DF in pulp mill effluents. The results showed that 2,3,7,8-Cl_4DD was not detected in any sample above the proposed guideline concentration of 10 pg/L. 2,3,7,8-Cl_4DF was detected in two samples from the acid stage at concentrations in the range of 15-18 pg/L and in the alkaline stage at concentrations in the range 11-18 pg/L.

The default emission factor for releases from modern pulp mills utilizing either chlorine dioxide or totally chlorine-free bleaching agents will be set to 60 ng TEQ/t of bleached pulp using a conservative approach. The emission factor will be applied only if there is direct discharge into the environment. If sludges are generated, the dioxin freight will be collected in the sludges and the effluents leaving from the effluent treatment plant will have non-accountable concentrations of PCDD/PCDF.

[20] National Council of the Paper Industry) for Air and Steam Improvement, Inc.

A special case of higher concentrations has been detected in effluents from pulp mills located in coastal areas of British Columbia in Canada. Here, special operating conditions occur where salty hog is burned and where ashes are disposed in the effluent treatment plant. Any similar occurrence should be notified; at present no default emission factor for these pulp mills can be given.

Pulping of pentachlorophenol treated wood may increase the concentrations in the effluent although no data have been published. Any use of PCP or of PCP-treated wood in the pulp and paper industry should be notified.

In mechanical pulp and paper mills (integrated mills, TMP), the water systems are usually quite closed in order to maintain high process temperatures. Consequently, wastewater volumes are small – 5-10 m^3/ADt.

6.7.1.3 Release in Products

Products from the pulp and paper industry can be contaminated with PCDD and PCDF. The degree of the contamination depends on the technology used in the bleaching. High concentrations of PCDD/PCDF have been reported when elemental chlorine bleaching sequences have been applied. Modern technologies result in lower concentrations in the products. Replacing Cl_2 with ClO_2 results in a reduction of 2,3,7,8-Cl_4DD and 2,33,7,8-Cl_4DF concentrations to non-detectable levels. However, complete elimination of PCDD/PCDF in ECF bleached effluents and products is a question of kappa-number and purity of ClO_2. With high kappa numbers and impure ClO_2 (*i.e.* high impurities of Cl_2) the probability of forming PCDD/PCDF increases.

Concentrations in **pulp** can be in the range from 0.6 ng TEQ/kg pulp to 200 ng TEQ/kg bleached pulp (US-EPA 1998a, Table 8-1). The median concentrations applying "old technology" has been calculated to be 9 ng TEQ/kg Kraft bleached pulp. The default emission factor is 10 µg TEQ/t of Kraft bleached pulp.

TMP [21] pulp had concentrations of around 1 µg TEQ/t pulp (de Wit 1989). The emission factor for TMP pulp is 1 µg TEQ/t pulp.

Unbleached sulfite pulps have low concentrations of PCDD/PCDF (0.1 µg TEQ/t pulp). The emission factor for sulfite pulp is 0.1 µg TEQ/t pulp.

Recycled pulp has a emission factor of 4 µg TEQ/t recycled pulp.

Replacement of Cl_2 in the first bleaching stage by ClO_2 will dramatically reduce the formation of 2,3,7,8-Cl_4DD and 2,3,7,8-Cl_4DF and to 0.1-0.3 pg/g bleached pulp corresponding to 0.1-0.3 µg/t of bleached pulp.

The disposal of the ash should be monitored and potential releases into the environment included (uncontrolled, land spreading) or excluded (landfill).

Concentrations of PCDD/PCDF in Kraft bleached **papers** using free chlorine and the respective default emission factors are 5 µg TEQ/t for cosmetic tissues, shopping bags and other

[21] Technical mechanical pulp

consumer papers and 2 µg TEQ/t for filter papers and newspapers from primary fibers. If chlorine dioxide or total chlorine-free bleaching is utilized, the emission factor will be 0.5 µg TEQ/t.

Sulfite papers using old technologies have an emission factor of 1 µg TEQ/t paper. Applying new technology will lower the emission factor to 0.1 µg TEQ/t.

Unbleached papers have an emission factor of 0.5 µg TEQ/t.

Recycling paper will have an emission factor of 10 µg TEQ/t.

6.7.1.4 Release in Residues

The major and dioxin-relevant residues from pulp and paper mills are the pulp sludges from the wastewater treatment. Sludge production is between 14 and 140 kg of sludge produced per ton of pulp (US-EPA 1998a). The EU reports 30-60 kg of organic wastes per ton of Kraft bleached pulp [22]. Unbleached pulp produces 20-60 kg dry solids per to of pulp. For the calculation of the emission factor, it is assumed that production of one ton of pulp generates 50 kg of sludge (dry matter).

Release vectors into the environment will be determined by the way the sludges are handled. Common disposal practices include landfill and surface impoundment, land application, recycling (compost, animal bedding) or incineration.

The concentrations in pulp sludges using old bleaching sequences are in the range from 2 ng TEQ/kg d.m. to 370 ng TEQ/kg d.m. with a median of 93 ng TEQ/kg sludge. The emission factor for bleached Kraft sludges is 4.5 µg TEQ/t of bleached Kraft pulp. Alternatively, the concentration in the sludge of 100 ng I-TEQ/kg sludge can be used and multiplied with the total mass of sludge disposed of per year to calculate the annual release.

Almost no difference in the concentrations of the sludges from wastewater treatment systems was found between mills using conventional delignification and those mills using oxygen delignification. The sludges have been analyzed for 2,3,7,8-substituted Cl_4DD and Cl_4DF as well as for all 17 2,3,7,8-substituted PCDD and PCDF congeners. The concentrations ranged from 3.8 ng TEQ/kg d.m. to 5.2 ng TEQ/kg d.m. for conventional delignification and from 1.8 ng TEQ/kg d.m. to 4.5 ng TEQ/kg d.m. for ED or ED/OD delignification (see also section 6.9.3).

With an estimated average of 4 ng TEQ/kg d.m., the default emission factor for pulp sludges using modern technology will be 0.2 µg TEQ/t of pulp.

At a recovered paper mill, Santl *et al.* (1994) found between 24.9 and 44.37 ng TEQ/kg in the deinking sludge. Upon treatment of the effluents, the contamination in the sludge was reduced to 11.01 ng I-TEQ/kg,

Especially the recovered pulp and papermaking generates a number of wastes with a high organic carbon content (*e.g.,* paper rejects, de-inking sludge, bio-sludge). This waste can be landfilled or incinerated. In Europe, there is an increasing number of large plants on-site for

[22] In addition, 40-70 kg of inorganic wastes per ton of pulp are generated

generating steam or co-fire the sludges in power plants. The emissions from a stand-alone incinerator equipped with active carbon or zeolite injection are low in PCDD/PCDF in the range of 0.1 ng I-TEQ/m³; also co-firing of pulp sludges in large, well-operated fossil fuel power plants gave results below 0.1 ng I-TEQ/m³ (BREF 2000a). As there is no effect of the alternative fuel observed, the emission factors for sludge burning as shown in Section 6.1.5 or for power plants co-firing sludges – Section 0 - should be applied.

Concentrations in ash are in the range from 10 to 3,700 ng I-TEQ/kg. For the Toolkit, an average of 1,000 ng TEQ/kg ash will be used.

6.7.2 Chemical Industry

Historically, the first observations of contamination with dioxins and furans were from the manufacture of chlorinated phenols and their derivatives. In particular, pesticides such as 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) and pentachlorophenol (PCP) were found to be contaminated with PCDD and PCDF. High PCDF contamination was also found in polychlorinated biphenyls (PCB).

PCDD and PCDF can be formed in chemical processes where chlorine is involved. The following processes have been identified as sources of PCDD and PCDF with a decreasing probability of generating PCDD/PCDF from top to bottom:

- Manufacture of chlorinated phenols and their derivatives,
- Manufacture of chlorinated aromatics and their derivatives,
- Manufacture of chlorinated aliphatic chemicals,
- Manufacture of chlorinated catalysts and inorganic chemicals.

For some of the processes the formation of PCDD and PCDF is implicit from the manufacturing process, *e.g.,* through direct chlorination of phenols when purified by distillation or through chlorophenate condensation.

The production of chlorine from alkali salts or brine utilizing graphite anodes has been shown to result in high contamination of the residues mainly by PCDF with lower concentrations of PCDD. Contamination in the µg TEQ/kg range has been reported in electrode sludges.

For chemical manufacturing processes, the generation of PCDD and PCDF is favored if one or several of the conditions below apply (for further information on formation mechanisms of PCDD/PCDF see UNEP Chemicals 2003, NATO/CCMS 1992b)[23]:

- High temperatures (>150 °C)
- Alkaline conditions (especially during purification)
- UV radiation or other radical starters.

The following subsections list products, which have been found to contain PCDD and PCDF or the process of their manufacture has been associated with the formation of PCDD/PCDF. It should be noted that some countries have published lists of chemicals that must be tested for PCDD/PCDF before being placed on the market. Such lists include many chemicals that

[23] The conditions, which favor the formation of PCDD/PCDF in wet chemical processes are different from those that favor the formation of PCDD/PCDF in thermal processes

were or are suspect of containing PCDD/PCDF concentrations above certain limits. For most of the chemicals, the PCDD/PCDF concentrations are below the threshold. Several chemicals are intermediates in the manufacture of other chemicals; the PCDD/PCDF contamination of these intermediates is either transferred to the final product (*e.g.*, in the case of the chloranil-based dye pigments, old process) or will be found in production residues (and then mostly associated with the residues from the oxychlorination process).

In all cases where plants are identified to manufacture the chemicals listed in the following subsections, it is recommended to characterize the processes in place by starting with the raw materials and conditions applied through purification steps applied and ending with amounts and treatment of residues from the process (*e.g.,* what type of treatment is applied to effluents and how much residue is produced – where does it go). The main uses and customers for the products and any available data on levels of PCDD/PCDF in products, residues and effluents will help in compiling the inventory.

Since the design of the processes and the handling of effluents and residues has such a profound effect on the formation of PCDD/PCDF and any releases to the environment, it is not possible to provide default emission factors for the different processes discussed in this Section. Each Section discusses the principal relevant features of the chemical production processes and, where possible, provides data on concentrations found in products. The suggested approach for assessing releases from the chemical industry is to identify production facilities for the chemicals listed, to detail the processes used, the purification applied, the production and treatment of residues and by-products. Further, it is important to know about the fate of the residues (landfill, by-product recovery, incineration, *etc.*). As many of these chemicals may be used in formulations, these should be identified as well as the uses for each product. It may be possible to assess in general terms the flow of PCDD/PCDF in the product and also to identify entry points to the environment. Any information on the disposal of materials treated with the chemicals will be valuable, too.

Some of the chemicals may not be produced in the country but may be imported as final products (*i.e.* formulations) or intermediates. In other cases, products maybe imported which have been subject to treatment with one of the chemicals (*e.g.,* wood treated with PCP). Imports should be noted and quantified if possible and the uses noted. On the other hand, there may be plants in a country, where chemicals listed in this Section are synthesized for export (only). Whereas the potential PCDD/PCDF releases occurring during the production phase should be accounted in the country's inventory, the PCDD/PCDF releases associated with the use or the disposal of these chemicals should show up in the recipient country.

Release to Air

Most studies on the chemical industry have shown that only minor releases of PCDD/PCDF to the air result from manufacture of the listed products.

In general, air releases of PCDD/PCDF will be of concern at the local level. It is usually an issue of occupational exposure/worker hygiene, workplace design, and provision of suitable protective clothes – eventually including filter masks - to potentially exposed workers.

Higher air release may result from chemicals in use but these are hard to quantify and will depend on local conditions. Other air releases may occur from incineration of residues from the chemical production processes. These are likely to be accounted for as hazardous waste incineration and dealt with in Section 6.1.2).

Release to Water

Releases of PCDD/PCDF to water and to sewer can result where effluents are discharged and not recycled within the process. The PCDD/PCDF are likely to be strongly bound to solid material or associated with oily phases of the effluents. The release of PCDD/PCDF will depend on the process used, the amount of effluent produced and effluent treatment in place.

It is not possible to provide emission factors for releases to water as they are dependent on site-specific factors.

For each process it is important to identify effluent releases, to note where in the process they come from, to identify treatment applied and to note where the effluent is released to (sewer, river, settling pond, *etc.*). If data is available on the amount of effluent and on composition this is valuable also.

Releases may also occur where products are used. In the case of product use it may be possible to estimate the amount of product released to water and therefore estimate the release of PCDD/PCDF. In other cases it is valuable to note where releases to water may be occurring from product use.

Release to Land

Releases of PCDD/PCDF to land are only likely from production processes where residues from the production processes are disposed by simple dumping on land. No emission factors can be given and any such practice should be noted with information gathered on the amount and source of the residue where possible.

Releases to land from product use are possible, especially for pesticides. If good information is available on the use of contaminated chemicals it may be possible to estimate the releases to land. In other cases note the possible releases to land and gather data on the product uses.

Release in Products and from Product Use and Disposal

For each of the chemicals listed in the Sections below data is provided on concentrations of PCDD/PCDF in the products (where these are available). This can be combined with production data and import/export information to estimate a flow of PCDD/PCDF in the product.

The releases from the product to the environment will depend on the uses of the chemical and disposal of materials treated with the product. Where possible data should be gathered on the main uses, the amounts used, the nature of the industry or domestic uses and the handling and treatment of materials, which have been treated.

Release in Residues

Residues from chemical production may contain PCDD/PCDF. The levels will depend on the process used and purification applied. There are many possible residue streams. Those of interest will include by-products (especially the denser oily residues from purification), sludges from effluent treatment, *etc.* Concentrations of PCDD/PCDF can vary widely from ng TEQ/kg to mg TEQ/kg. No general factors can be provided.

It is useful to gather data on residues produced at chemical production sites. It is also helpful to note how the residues are treated and disposed of.

Residues may also arise from product use or formulation. It may be possible to estimate the amount of a contaminated product ending up in a residue.

6.7.2.1 Pentachlorophenol (PCP) and Sodium Pentachlorophenate (PCP-Na)

Pentachlorophenol (PCP) and sodium pentachlorophenate (PCP-Na) are pesticides and used as a preservative for *e.g.,* wood (indoor and outdoor), leather, textiles (including cotton or wool). Pentachlorophenol (PCP) is a chlorinated hydrocarbon insecticide and fungicide. It is used primarily to protect timber from fungal rot and wood-boring insects. PCP products are very toxic to plants and are used as pre-harvest defoliants and general herbicides. Technical mixtures containing PCP or PCP-Na have been marketed under numerous trade names.

The predominant use of PCP was as wood preservative at least until the end of the 1980s. In the USA, 95-98 % of American PCP production is used directly or indirectly in wood treatment. Data from Canada (95 %) and Germany (61 %) confirm the main use of PCP as a wood preservative. In Germany, however, considerable amounts of PCP were used by the textile (13 %), leather (5 %), mineral oil (6 %), and glue (6 %) industries in 1983 (WHO 1987).

The sodium salt of pentachlorophenol (PCP-Na) is utilized primarily in aqueous solution. It is used as an antifungal and antibacterial, and has applications in the following areas:
- a wood preservative (fungicide and anti-blueing agent),
- an agent for the impregnation of industrial textiles (fungicide),
- bactericide in tanning and the paper pulp industry,
- a molluscicide in the treatment of industrial water, in particular cooling water,

and sometimes as
- a sterilizing agent.

Because of its toxicity, PCP has been made subject to various restrictions in more than thirty countries.

Pentachlorophenol contains dangerous impurities including up to 0.1 % of polychlorodibenzodioxins/polychlorodibenzofurans and 1-5 % of polychlorinated phenoxyphenols. PCDD/PCDF are emitted when products treated with PCP are exposed to the sun and when they are improperly burned at the end of their useful life. PCP in sewage sludge is also a source of PCDD/PCDF (EC 1996).

There are three major processes for the commercial production of pentachlorophenol (NATO/CCMS 1992a):

- The most common method is the direct chlorination of phenol with chlorine gas in the presence of a catalyst. The reaction results in the formation of byproducts such as hydrogen, hydrogen chloride and PCDD/PCDF.

- Hydrolysis of hexachlorobenzene with sodium hydroxide. PCDD/PCDF are formed as unwanted byproducts. This process was used only in Germany.

In China, PCP is manufactured *via* thermolysis of hexachlorocyclohexane (HCH) (Wu 1999).

Overall, there are two processes to manufacture PCP-Na:

(1) Hydrolysis of hexachlorobenzene (HCB) with sodium hydroxide. This process was applied in Germany until 1984 (then, method (2) with PCP as the starting material has been used).

(2) Dissolution of PCP in sodium hydroxide. After filtration, the PCP-Na solution is being concentrated.

Normally, the PCDD/PCDF contamination in PCP-Na is lower as in the PCP as some contamination is eliminated through the filtration process.

The contamination of PCP and PCP-Na with PCDD and PCDF varies from some µg I-TEQ/kg to 1-2 mg I-TEQ/kg depending on the manufacturing process and the compound. Today many countries have banned the use of pentachlorophenol and its sodium salt. In the EU, Directive 91/173/EEC prohibits the marketing and use of pentachlorophenol and its salts and esters in a concentration equal to or greater than 0.1 % by mass in substances and preparations [24]. In any event, PCP used as such or as a constituent of preparations must have a total Cl_6DD (hexachlorodibenzo-*para*-dioxin) content of less than four parts per million (4 ppm). Remaining principal uses are the high-pressure treatment of (telephone) poles, railroad ties, and wooden fences (see Main Category 10, Section 6.10).

A considerable flow of PCP into a country may occur through the imports of the chemical substance itself as well as of PCP-treated products such as wood (also as furniture) or textiles and leather. Tracing these flows can be very difficult.

The default emission factor for PCP manufactured *via* processes (1) or (2) is 2,000,000 µg TEQ/t (200 µg TEQ/kg). The Chinese production line will give an emission factor of 800,000 µg TEQ/t.

The default emission factor for PCP-Na is 500 µg TEQ/t. Note: Santl *et al.* (1994) detected 3,400 µg TEQ/kg in a PCP-Na sample from France in the year 1992.

Emissions of PCDD/PCDF to air from materials treated with PCP are difficult to quantify and may be controlled by site-specific factors and releases from the disposal of PCP-containing materials by combustion can lead to high emissions of PCDD/PCDF, which cannot be adequately addressed here. However, the impact on the emission factors when combusting PCP-contaminated wood can be seen in Section 6.3.4 and also contributes to higher emissions in uncontrolled burning processes (see Section 6.6.2).

[24] However, four exceptions are given. The use of pentachlorophenol and its compounds in industrial installations is permitted:
(a) for wood preservation;
(b) for the impregnation of fibers and heavy-duty textiles;
(c) as a synthesizing and/or processing agent in industrial processes;
(d) for the in situ treatment of buildings of cultural and historic interest (subject to individual authorization by the Member State concerned)

6.7.2.2 Polychlorinated Biphenyls (PCB)

Polychlorinated biphenyls (PCB) have been widely used in electrical applications (transformers, capacitors) as sealants and in carbonless paper. Since 1995, worldwide the production of PCB seemed to have stopped but there is still much PCB-containing equipment in use and materials and wastes containing PCB are either being used or awaiting their disposal.

PCB were manufactured commercially by the progressive chlorination of biphenyl in the presence of a suitable catalyst, *e.g.,* iron chloride. Depending on the reaction conditions, the degree of chlorination varied between 21 % and 68 % (w/w). The yield was always a mixture of different congeners and isomers, which were further purified by filtration or distillation. In general, commercial PCB contained impurities, mainly polychlorinated dibenzofurans (PCDF) in the µg/kg to mg/kg range but no polychlorinated dibenzo-*p*-dioxins (PCDD). Although there are 209 different PCB congeners possible, only about 130 are likely to occur in commercial mixtures (EHC 1993, Fiedler 1998).

PCB are exclusively contaminated with PCDF through the production process. When subject to thermal stress (high temperatures), the levels of PCDF in the commercial PCB will increase. Note: there is no formation of PCDD. Depending on the degree of chlorination, the contamination of the unused products ranges from low to high µg I-TEQ/kg.

To UNEP's knowledge, presently there is no PCB production in any part of the world; therefore no emission factor is given for PCB production.

Releases of PCDF will result from uses of PCB or recycling operations where PCB are removed from equipment, stored or disposed of. Sites, where PCB are used or PCB-containing equipment is stored, dismantled or disposed of can give rise to local contamination and potential Hot Spots (see Main Categories 9, Section 6.9.5, and 10, Section 6.10.6).

As a first step to estimating releases of PCDF associated with the use of PCB equipment is to compile an inventory of the PCB equipment in a country. Assembling such an inventory is discussed in separate UNEP guidance (UNEP 2000) and beyond the scope of this Toolkit. During the use phase, PCB equipment can leak and older out-of-use equipment, which is poorly stored or maintained, can release PCB and PCDF to the air, water and land. PCB equipment may release PCB through evaporation and fluid loss in normal use. General estimates of leakage rates have been made in the USA. The PCB inventory should be able to improve estimates of potential rates of leakage by consideration of the condition of plant items.

PCB leaking from equipment may evaporate (a release to air), be collected in suitable containment around the equipment and disposed of or may be a release to water or land. For the purposes of this inventory, example concentration data are provided, which can be used to estimate the rate of release of PCDF *via* identified or estimated leakage. The ultimate fate of the leaked PCB and PCDF will depend on local circumstances (release to air, water, land or disposal/destruction).

PCB fluid can also enter the scrap metal industry if inadequate treatment occurs. Releases may occur *via* evaporation from contaminated scrap, releases from scrap processing, from leakage from disposal sites. Estimates for these releases have not been made.

The PCB can serve as an indicator as especially the higher chlorinated PCB show a similar behavior (*esp.* stability and mobility) in the environment as the 2,3,7,8-substituted PCDF.

The concentration of PCDF in PCB products will be grouped according to the chlorine content and are as shown in Table 58:

Table 58: Concentrations of PCDF in PCB products

PCB Type	New PCB (µg TEQ/t)	Used PCB (µg TEQ/t)
Low chlorinated, *e.g.,* Clophen A30, Aroclor 1242	15,000	No numbers available but thought to be higher than in the new product
Medium chlorinated, *e.g.,* Clophen A40, Aroclor 1248	70,000	
Medium chlorinated, *e.g.,* Clophen A50, Aroclor 1254	300,000	
High chlorinated, *e.g.,* Clophen A60, Aroclor 1260	1,500,000	

Annema *et al.* (1995) used US data to estimate the following leakage rates for PCB filled capacitors and transformers (Table 59):

Table 59: Leakage statistics for PCB equipment

	Leakage Frequency (% of Installed Units)	Average Quantity Leaked per Unit and Year	Average Loss by Leakage of Fluid Present in Total per Year
Transformers	2 %	30 kg	0.06 %
Capacitors	3 %	8 kg	1.6 %

As there is no production of new PCB, there will be no emission for releases with new products in the dioxin inventory. However, releases with products could be estimates for PCB in existing equipment as described above. Releases can also occur with inadequate disposal of used PCB-containing equipment. These releases cannot be quantified without a case by case assessment and thus, an emission factor cannot be given. Releases of PCDF caused by leaking of PCB are dependent on the local conditions and will be subject to assessment and management under hazardous waste or toxic chemicals regulation.

6.7.2.3 2,4,5-Trichlorophenoxy Acetic Acid (2,4,5-T), 2,4,5-Trichlorophenol and Other Chlorophenol Derivatives

Chlorophenol derivatives known to be contaminated with PCDD and PCDF are:

- 2,4-D = 2,4,-dichlorophenoxy acetic acid and 2,4-DB = 2,4,-dichlorophenoxybutyric acid
- Sesone = 2-(2,4-dichlorophenoxy) ethyl sodium sulfate
- DMPA = 0-(2,4-dichlorophenyl) 0-methyl isopropylphosphoramidothiolate
- 2,4,5-T = trichlorophenoxy acetic acid
- Silvex (acid) = 2-(2,4,5-trichlorophenoxy) propionic acid (also known as Fenoprop, 2,4,5-TP, 2,4,5-TCPPA)
- Erbon = 2,2-dichloropropanoic acid 2-(2,4,5-trichlorophenoxy) ethyl ester
- Ronnel = 0,0-dimethyl 0-(2,4,5-trichlorophenyl) phosphoroate (also Fenchlorfos)

2,4,5-Trichlorophenoxy acetic acid (2,4,5-T) is a herbicide with the major use as a defoliant. Large amounts of the butyl esters of a 50:50 mixture of 2,4,5-T and 2,4-D (2,4-dichlorophenoxy acetic acid) – known as Agent Orange - were sprayed over Vietnam during the Vietnam War. Today, there are only a few production sites of 2,4,5-T. 2,4,5-T was found to be highly contaminated with 2,4,7,8-Cl_4DD; no other PCDD or PCDF congeners have been identified. The highest concentration reported in a product from Germany was 7,000 ng I-TEQ/kg 2,4,5-T [25]. 2,4,5-Trichlorophenol was mainly used as intermediate for the manufacture of 2,4,5-trichlorophenoxy acetic acid and hexachlorophene. A single measurement gave 680,000 ng I-TEQ/kg.

2,4,5-T is the most important derivative of 2,4,5-trichlorophenol (2,4,5-TCP). Commercially, 2,4,5-trichlorophenol is reacted with chloroacetic acid under alkaline conditions. Subsequent addition of sulfuric acid produces 2,4,5-T, which can then be reacted with a variety of alcohols or amines to produce 2,4,5-T esters and amine salts. Although, there have not been too many manufacturers of 2,4,5-T, there was a much higher number of companies marketing more than 400 formulated pesticide products containing 2,4,5-T (Esposito *et al.* 1980).

Hotspots in soil may exist at former 2,4,5-T production and handling sites.

The emission factor for commercial (technical product) 2,4,5-T is 7,000 µg TEQ/t.

The emission factor for 2,4,6-trichlorophenol is 700 µg TEQ/t.

The emission factor for dichlorprop is 1,000 µg TEQ/t.

The emission factor for 2,4-D is 700 µg TEQ/t (US-EPA 1998a, p 8-74). Concentrations in may vary considerably: random samples from American brands gave 3 µg TEQ/t and Asian and Russian brands had around 200 µg TEQ/kg (US-EPA 1998a, p 8-77). The ultimate fate of PCDD/PCDF in these products will depend on their use and be controlled by local conditions.

6.7.2.4 Chloranil

2,3,5,6-Tetrachloro-2,5-cyclohexadiene-1,4-dione (*p*-chloranil) is the precursor for the production of dioxazine dyes [26] (for cotton, leather, and synthetics) and other chemicals (*e.g.,* seeds and fungicides). Depending on the production process, *p*-chloranil can contain high contamination with PCDD/PCDF.

Two production processes are known:

(1) The old Hoechst AG process *via* chlorination of phenol (used until 1990 in Germany). Utilizing this old process, *p*-chloranil was contaminated in the range of several hundred µg I-TEQ/kg with PCDD/PCDF (mostly PCDF). The contamination of the *ortho* congener was much lower (around 60 µg I-TEQ/kg).

[25] Present as 2,3,7,8-Cl_4DD

[26] Synthesis of pigments is from reaction of chloranil (or other halogenated benzoquinones) with aromatic amines to diarylaminochloroquinones and oxidative cyclization in high-boiling solvents, such as *o*-dichlorobenzene, in the presence of acyl chlorides or sulfuric acid

(2) The process developed by Rhône-Poulenc Chimie and used today by *e.g.* Clariant (Germany) *via* chlorination (with HCl) of hydroquinone. This process results in much cleaner products (*p*-chloranil: ~7 µg I-TEQ/kg) [27].

In the USA, chloranil has been used as a fungicide and seed-dressing agent between 1937 and 1977. After 1977, all uses of chloranil in agriculture were banned. In Europe, chloranil has not been used as a fungicide nor as a seed protectant. In Africa, chloranil has been used as a fungicide and seed-dressing agent at least until 1984.

Of the approximately 400 t of chloranil produced per year until 1989, 300 t/a were processed to pigments and 100 t/a to dyestuffs (BUA 1992). In the last year of its production 1990, Hoechst AG produced 300 t/a. Until 1989, 150-200 t/a have been exported and approximately 50-100 t/a have been imported by the Hoechst AG from India. It is known that in India the same process has been applied for the production of chloranil until the mid of 1990. Further imports into Germany have been estimated to be around 50-100 t/a (BUA 1992). Since 1990, the only producer in Western Europe and probably the largest producer of chloranil worldwide is Rhône-Poulenc Chimie of France. Smaller production sites of chloranil have been found to exist in India, which may still use the traditional phenol process. No information could be obtained for productions in Eastern Europe and the Russian Federation. However, it is known that chloranil has been produced in the Russian Federation and has been imported into Russia as well. There is no domestic production of chloranil in the United States of America (BUA 1992).

PCDD/PCDF contamination in the final products made from chloranil, such as dyestuffs and pigments, finally will end in wastes of polymers/plastics, textiles and packaging materials (paper, tin cans, *etc.*) to be disposed of as municipal solid waste or re-entering recycling processes. In the case of paper recycling and textile dyeing, the PCDD/PCDF will be released into water or found in the sludges.

The most important dioxazine pigment is C.I. Pigment Violet 23 (of Hoechst AG), which is used for lacquers, polymers, and printing inks. A similar use is for C.I. Pigment Violet 37 (of Ciba Geigy AG).

The emission factor for *p*-chloranil manufactured *via* the old Hoechst Farben process is 400,000 µg TEQ/t. The emission factor for *o*-chloranil is 60,000 µg TEQ/t. Dyestuffs on chloranil basis of this old production pathway can have 1,200 µg TEQ/t.

The emission factor using the hydroquinone process for the manufacture of *p*-chloranil is 100 µg TEQ/t.

Dioxazine dyes and pigments using the old process had concentrations between 20,000 and 57,000 µg TEQ/t (for Blue 106) and between 1,000 and 19,000 µg TEQ/t (Violet 23) (Williams 1992). In the USA, concentrations in chloranil were between 263,000 µg TEQ/t and 3,065,000 µg TEQ/t. The Carbazole Violet (dye-pigment) had 211,000 µg TEQ/t.

Quantitative information on discharges of PCDD/PCDF into the environment cannot be given due to lack of reliable analytical data. Releases into the hydrosphere are to be expected from the downstream industries such as the production of dyestuffs, from textile dyeing with the liquor bath, and from paper recycling (BUA 1992). Utilizing the Hoechst process, generation

[27] The same quality is obtained by Tokoyama Soda (Japan)

of 20 m³ of wastewater per ton of product has been reported, however PCDD/PCDF concentrations in the wastewater have not been published. The synthesis of dioxazine pigments is done in closed systems, so that normally, no effluents are generated. PCDD/PCDF contamination might be dissolved in the solvent, *e.g.,* dichlorobenzene, and would be concentrated in the distillation residues. The fate of these solid residues should be notified (*e.g.* if landfilled or incinerated).

Further, active carbon used in the production of the dyestuffs may contain PCDD/PCDF (in Germany, disposal is by hazardous waste incineration in rotary kilns) (BUA 1992).

6.7.2.5 2,4,6-Trichlorophenyl-4'-nitrophenyl Ether (CNP)

2,4,6-Trichlorophenyl-4'-nitrophenyl ether (CNP) or chloronitrofen has been used as an alternative for pentachlorophenol with intensive applications in rice paddies in Japan. CNP has been found to contain high concentrations of PCDD and PCDF. Especially, batches produces in the 1970s and early 1980s had contamination in the range of 240 to 540 µg TEQ/kg; later productions showed lower concentrations in the range of 400 ng TEQ/kg (Masunaga and Nakanishi 1999). There is no further information on the synthesis and what might have caused the decrease in the contamination level in the more recent batches.

The emission factors for CNP is 300,000 µg TEQ/t using old technologies and 400 µg TEQ/t with new technology.

6.7.2.6 Chlorobenzenes

PCDD/PCDF formation concerns only trichlorobenzene, in a specific process, which does not exist any longer today (Source: EUROCHLOR). Mono- and dichlorobenzenes are produced commercially by the direct chlorination of benzene in the liquid phase in the presence of a Lewis catalyst such as ferric chloride ($FeCl_3$) or oxychlorination of benzene with HCl in the presence of oxygen (NATO/CCMS 1990, EHC 1991).

The formation of PCDD/PCDF is not obvious from the reaction mechanisms mentioned above but probably occurs during purification where alkaline conditions are often used.

PCDD/PCDF contamination in chlorobenzenes is relatively low. As no measured data of congener-specific analyses were found, no emission factor can be given.

6.7.2.7 Chlorine Production

Chlorine gas is produced by passing an electric current through brines (common salt dissolved in water). Essential co-products are caustic soda (sodium hydroxide, NaOH) and hydrogen (H_2). There are three major processes in use: the mercury process, the diaphragm process, and the membrane process. PCDF can be formed in the chlorine cells; concentrations of PCDD are very low.

PCDD and PCDF formation can be relevant when graphite anodes are used. Many industrialized countries replaced the graphite anodes at the beginning of the 1970s, however, the old process using graphite anodes can be a significant source of PCDD/PCDF. Due to the

low costs and easy operation, graphite electrodes are commonly used in China, the second largest chloralkali producing country in the world (Wu 2000). Historical production by this method can lead to Hot Spots (see Section 6.10). Limited data shows that PCDF may also be present where titanium anodes are used. The source of the organic carbon may be in rubber sealing rings used in the process.

It has been reported in the literature (Kannan *et al.* 1997) that the commercial mixture Aroclor 1268 has been used to lubricate the electrodes. Disposal of process wastes has caused severe environmental contamination.

6.7.2.7.1 Release to Air

From the process, no release of PCDD/PCDF to air is expected.

6.7.2.7.2 Release to Water

Releases of PCDD/PCDF to water will depend on the effluent treatment applied. PCDD/PCDF are likely to be tightly bound to particles and the efficiency with which these are captured is likely to influence any release to water. No general emission factor can be provided. Information on the sources, quantities and treatment applied to effluents should be gathered.

6.7.2.7.3 Release in Products

Chlorine gas does not contain PCDD/PCDF. Thus, the emission factor for chlorine is zero.

6.7.2.7.4 Release in Residues

Most PCDD/PCDF contamination will be found in the residues. For this Toolkit and in a first step, the evaluation of this source will be restricted to identifying production sites of chlorine utilizing graphite electrodes. Where these are used, the disposal pathway of the residues should be followed in order to identify potential hotspots. No general emission factor can be given for this vector and further evaluations are subject to a case study (see Section 6.10.2). In sludges from graphite electrodes, concentrations between 13,500 and 30,000 µg TEQ/t of sludge have been reported.

6.7.2.8 Ethylene Dichloride or 1,2-Dichloroethane (EDC)

Ethylene dichloride (EDC) is an important intermediate in the manufacture of PVC. In the USA, >90 % of the total EDC production is used to produce vinyl chloride monomer (VCM). Most PVC production uses dehydrochlorination (cracking) of ethylene dichloride (EDC)

Production of EDC (two different methods)

a) **Direct chlorination** of ethylene with chlorine in the presence of a catalyst [28]. The process has a high conversion rate. Typically, direct chlorination is carried out in a liquid-phase reactor at temperatures between 50 °C and 70 °C and pressures around 400-500 kPa. The HCl formed in the process can be recycled into the oxychlorination process.

b) **Oxychlorination** of ethylene with hydrochloric acid (HCl) and either air or oxygen is carried out in the presence of a catalyst (usually copper) in a fixed-bed reactor or a fluidized-bed reactor. Temperatures should not exceed 325 °C, as higher temperatures will increase formation of by-products (mostly chlorinated C_1- and C_2-compounds). The first step of the EDC purification process is usually a water quench followed by caustic scrubbing. The water is returned to the process or is steam stripped prior to discharge (see emission factor for discharge water).

Production of VCM

VCM is produced by thermal dechlorination from EDC. The so-called cracking furnace typically operates at around 2,000 kPa at temperatures between 450 °C and 650 °C. Unreacted raw material is recycled back into the process. VCM (boiling point: -13 °C) is separated from byproducts by distillation. High boiling materials may contain various condensation products including PCDD/PCDF. These materials are typically thermally decomposed; in some cases, HCl from the process is recovered and recycled.

Production of PVC

There are the following processes to produce PVC resins:

Suspension

Dispersion (emulsion)

Bulk (mass,) and

Solution.

Within the EDC/VCM/PVC industry, the most critical step for PCDD/PCDF generation is the manufacture of EDC *via* oxychlorination of ethylene. Generation of PCDD/PCDF in VCM pyrolysis is unlikely due to the low concentration of oxygen. Chemical conditions for generation of PCDD/PCDF do not exist in PVC polymerization.

Streams that may contain PCDD/PCDF include any combustion streams, including liquid, liquid/gas or vent gas combustors. In addition, some PCDD/PCDF may reside on catalyst support. Releases of that material differ with the production process.

Fluidized bed catalysis will be accompanied by the catalyst's particle size distribution. Small particles can be carried over in product vapor and washed out with quench water. The catalyst in fixed bed systems is replaced on approximately an annual basis. As a result, particles from fluid bed systems are typically isolated in solids from wastewater purification. Spent fixed bed catalyst, if discarded, represents an explicit waste stream.

[28] Chlorides of iron, aluminum, copper, antimony

Emission factors for the EDC/VCM and PVC industry are displayed in Table 60. There will be two classes of emission factors splitting between old and modern technology. As can be seen, for old technologies, no emission factors to air are available at present.

Table 60: Emission factors for the EDC/VCM/PVC industry

	Emission Factor – µg TEQ/t (of Product)			
	Air	Water	Product	Residue [1]
1. Old technology, EDC/VCM, PVC	ND	1	ND	3
2. Modern plants				
EDC/VCM (vents only)	0.91 [2]	0.015	0.03	2
EDC/VCM liquids and vents)	0.66 [2]			
PVC only (vent gas combustion)	0.00084 [3]	0.03	0.1 [3]	0.02

[1] includes spent catalyst and wastewater treatment sludge
[2] per ton of EDC.
[3] per ton of PVC product

6.7.2.8.1 Release to Air

Emissions to air from these processes come mainly from incineration. Incineration is used to control exhaust gases from the various steps of the process with various furnace types such as thermal oxidizers, rotary kiln, liquid injection incinerators and fluidized-bed incinerators. Due to the HCl content in the exhaust gases, it is expected that the incinerators are equipped at least with a cooling system and a caustic quench to neutralize HCl.

The US survey of EDC/VCM and PVC plants (US-EPA 2000, Vinyl Institute 1998) evaluated results from 22 incinerators within the industry. The emissions were lowest for vent gases from combustors at PVC only production sites (note: no liquid residue streams). The emission factors for vent and liquid/vent combustion were highly variable and varied four orders of magnitude for similar combustors. For the Toolkit, the average emission were taken to calculate the emission factors for the combustion of vent gases only and liquid and vents based on EDC production as shown in Table 60.

The data in Table 60 are based on EDC or PVC production data from the U.S. industry: the best estimate was 0.00135 g TEQ/a from production of 5,215,000 tons of PVC, resulting in an emission factor of 0.00027 µg TEQ/t of PVC product. The EDC production of 11,115,000 tons gave total emissions to air of 10.6 g TEQ/a. This would result in an emission factor of 0.95 µg TEQ/t of EDC (US-EPA 2000, Vinyl Institute 1998).

An alternative approach would be to use emission factors based on the amount of waste fed. Also in this case, releases from vent gas and liquid waste/vent gas incinerators at combined EDC/VCM plants showed variable emissions, which ranged from 1.3 and 14 µg TEQ/t of waste feed.

Since the combustor design and operation is most critical it is suggested that an estimate of the amount of waste burned is made and this is treated as hazardous waste incineration – see Section 6.1.2.1.

6.7.2.8.2 Release to Water

The manufacture of EDC/VCM and PVC uses considerable amounts of process water, which either leaves the plant or is recycled as far as possible back into the EDC/VCM/PVC manufacturing process. The process water that cannot be recycled may be discharged without further treatment or directed into a wastewater treatment process [29].

At modern US facilities PCDD/PCDF concentrations in wastewaters from PVC sites only were close to detection limit. The overall mean concentrations were 0.88 pg I-TEQ/L (ND=0) and 4.7 pg I-TEQ/L (ND=½ DL). At EDC/VCM plants, all samples had quantifiable concentrations with mean values of 0.42 pg TEQ/L (ND=0) and 4.4 pg TEQ/L (ND=½ DL). An emission factor of 0.03 µg TEQ/t of PVC has been derived for wastewaters from modern PVC plants and an emission factor of 0.015 µg TEQ/t of EDC for wastewaters from EDC/VCM plants (US EPA 2000, Vinyl Institute 1998).

For old and poorly controlled systems formation of PCDD/PCDF may be higher and releases to water will depend on the effectiveness of the water treatment system. For an initial estimate for these plants without wastewater solids removal, an initial emission factor of 1 µg TEQ/t of EDC should be applied.

6.7.2.8.3 Release in Products

PCDD/PCDF concentrations in PVC products are low; most samples showed no detectable PCDD/PCDF. An overall mean concentration of 0.3 ng I-TEQ/kg should be used for the Toolkit. In EDC, only in one sample 0.03 ng I-TEQ/kg (ND=0) could be detected. Emission factors for old PVC and EDC products cannot be given due to the lack of authentic samples.

6.7.2.8.4 Release in Residues

The main residues of interest are: heavy ends from EDC purification, spent catalyst (from fixed bed plants) and wastewater treatment sludges. Each of these residues may be handled and disposed of in a number of ways, which will affect releases to the environment.

For combined EDC/VCM plants concentrations in wastewater treatment sludges ranged from 100 to 5,900 µg I-TEQ/t of product (VI 1998). Sites using fixed-bed technology were usually lower but these sites produced spent catalyst (in fluidized bed processes, this is released with the water and is being collected in the wastewater treatment sludge). Overall average emission factors were approximately 2 µg I-TEQ/t (EDC production). For fixed bed plants most PCDD/PCDF may be expected to be associated with the spent catalyst.

For older plants or those not based on licensed technology an initial estimate of releases in wastewater treatment sludge and spent catalyst is 3 µg I-TEQ/t of EDC.

Sludges from sites where PVC only is being produced have an emission factor of 0.02 µg TEQ/t of PVC. Solid emissions, as spent catalyst and wastewater treatment solids taken together at EDC and combined EDC/PVC sites will be ca. 2.0 µg TEQ/t of product (US-EPA

[29] that typically reduces BOD (biological oxygen demand) and total suspended solids as well as adjustment of the pH to meet water guidelines

2000, Vinyl Institute 1998).

Concentrations of PCDD/PCDF can be much higher in some residue streams, such as heavy ends from EDC purification. For example, Stringer *et al.* (1995) reported concentrations from 3,000 ng TEQ/kg to 5,000,000 ng TEQ/kg in wastes from PVC manufacture. Clearly the potential for releases from these streams depends on the way the materials are handled and disposed of. The amount of residue produced should be estimated if possible. In many cases these residues are incinerated on-site or by commercial hazardous waste incinerators to make an estimate of releases from this activity see Section 6.1.2.1 - Hazardous waste incineration. In a few cases residues have been either disposed of in underground stores (Dyke *et al.* 1997) and in some cases may be used as feedstock for solvent production.

If the residues are disposed of by dumping or are used as a feedstock for another process this should be noted. UK data showed that halogen-organic wastes contained 100 µg I-TEQ/t (expressed per unit of EDC production). This factor can be used to make initial estimates of the amount of PCDD/PCDF in these streams – the fate of the residue streams must be identified.

6.7.2.9 Chlorinated Aliphatic Compounds

Many processes producing chlorinated aliphatic compounds would produce little or no PCDD/PCDF (recent measurements of perchloroethylene gave results below detection limits). However, if residues from processes such as the production of EDC (see above) or other mixed residues are used as a feedstock there may be formation and releases of PCDD/PCDF.

At one time in the UK residues from EDC production were fed to an oxychlorinator to produce per- and trichloroethylene (solvents). This process produced significant quantities of PCDD/F in the residue streams (350-630 g TEQ in the residues from the production of 130,000 tons of tri- and perchloroethylene produced approximately 4,000 µg I-TEQ/t of product – Dyke *et al* 1997). The handling and fate of these residues will determine actual releases to the environment. An emission factor for the residues cannot be given. When these production residues occur within chemical production processes and are being recycled into the *e.g.,* oxychlorination process, they will show up in the residues from oxychlorination.

6.7.2.10 Summary

Within the sub-sector of the chemical industry, the most critical parts in the manufacturing processes are the oxychlorination process to manufacture ethylene dichloride (EDC), which is usually found as part of the manufacture of chlorinated organics.

At some locations, there may be some stand-alone operations that would recycle HCl back to Cl_2. However, such process would be much more expensive compared to the electrolysis of KCl, NaCl or brine. If such operations will be identified, a case-by-case evaluation needs to be performed to evaluate potential formation and releases of PCDD/PCDF.

The most critical process within the chemical industry is the oxychlorination of ethylene to manufacture EDC. Further down the production chain of any chlorinated or non-chlorinated chemical, there are no more critical emissions.

In 1995, the European Council of Vinyl Manufacturers (ECVM) set voluntary emission targets as a means of promoting environmental performance. The ECVM Charter, which is a form of self-regulation, includes dioxin emission guidelines based on Best Available Techniques. For the emission of vent gases to the atmosphere the ECVM guideline for dioxin-like components is 0.1 ng I-TEQ/Nm³ [30] and 1 µg I-TEQ/t of EDC in water effluents. These numbers can be taken as rough estimates for calculating PCDD/PCDF releases from state-of-the-art EDC/VCM plants.

6.7.3 Petroleum Industry

Crude oil is a mixture of many different hydrocarbons and small amounts of impurities. The composition of crude oil can vary significantly depending on its source. Petroleum refineries are a complex system of multiple operations and the operations used at a given refinery depend upon the properties of the crude oil to be refined and the desired products.

Within the petroleum refining industry, so far, only one potential source for PCDD/PCDF has been reported: re-generation of the catalyst used during catalytic cracking of the larger hydrocarbon molecules into smaller, lighter molecules (Beard *et al.* 1993).

Feedstock to catalytic reforming processes is usually low octane naphtha. Catalytic hydroreforming uses platinum-based catalysts. In the continuous process, aged catalyst is continuously removed from the bottom of the reactor and sent to a regenerator where the carbon is burned from the catalyst with hot air/steam. Trace quantities of a promoter, normally organochlorines, such as tri- or perchloroethylene, are added to retain catalytic activity. Moisture is removed and the regenerated catalyst is returned to the first reformer bed. In the cyclic or semi-regenerative units, the regeneration of the catalyst is discontinuous as well as the resulting emissions. In this process, PCDD/PCDF have been detected.

PCDD/PCDF may be emitted to air or captured in scrubbing systems and transferred to effluents. Ultimate releases will depend on the pollution controls and handling of residues. No emission factors can be given at this time due to lack of data. For this subcategory measured data are urgently needed.

6.7.3.1 Release to Air

No data were available to provide emission factors.

6.7.3.2 Release to Water

The amount of wastewater generated in the catalytic reforming process is around 190 kg/t of feedstock. The wastewater contains high levels of oil, suspended solids. Emissions of PCDD/PCDF to water may occur upon discharge of the wastewater. However, no data are available at present. Any discharge of wastewater should be noted.

[30] (European) normal conditions: 11 % O_2, 0 °C, 103.1 hPa

6.7.3.3 Releases in Residues

Spent catalyst fines may be generated from the fine particle abatement systems. Spent catalyst generated is around 20-25 tons per year for a 5 million tons per year refinery. Typically, spent catalyst is sent back for recycling or regeneration.

From the wastewater treatment, sludges can be generated. There are no PCDD/PCDF concentrations available at present; however, concentrations of pyrene and benzo[a]pyrene in the low mg/kg range have been detected (BREF 2000b).

6.7.4 Textile Production

The textile industry is comprised of a diverse, fragmented group of establishments that produce and/or process textile-related products, which include fiber, yarn, fabric for further processing into finished goods. These may range from small "back street" operations with few controls to large-scale highly sophisticated industrial operations with comprehensive pollution controls. The process of converting raw fibers into finished textile products is complex; thus, most textile mills specialize (EPA 1997). The textile industry is being targeted as a potential source of PCDD/PCDF as:

- Pesticides such as pentachlorophenol, known to be contaminated with PCDD/PCDF, can enter the plant *via* raw materials, *e.g.,* cotton, being treated with PCP;
- Dyestuffs on the basis of chloranil can be used to color the textiles;
- Finishing processes may utilize chlorinated chemicals contaminated with PCDD/PCDF and washing processes at alkaline media are part of the textile finishing processes; and
- Large volumes of effluent water are released into the environment.

Woven and knit fabrics cannot be processed into finished goods until the fabrics have passed through several water-intensive wet-processing stages (also known as finishing) such as fabric preparation, dyeing, printing, and finishing. Natural fibers typically require more processing steps than manmade fibers. Relatively large volumes of wastewater are generated, containing a wide range of contaminants that must be treated prior to disposal. Significant quantities of energy are used heating and cooling chemical baths and drying fabrics and yarns.

Fabric Preparation requires de-sizing[31], scouring[32], and bleaching as well as singeing[33] and mercerizing[34]. Dyeing operations are used at various stages of production to add color and intricacy to textiles and increase product value. Dyes used by the textile industry are largely synthetic. Finishing encompasses chemical or mechanical treatments.

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[31] to remove size materials applied prior to weaving

[32] a cleaning process that removes impurities from fibers, yarns, or cloth through washing. Typically, alkaline solutions are used for scouring

[33] eliminates unwanted colored matter from fibers, yarns, or cloth. The most common bleaching agents include hydrogen peroxide, sodium hypochlorite, sodium chlorite, and sulfur dioxide gas. Hydrogen peroxide is the most commonly used bleaching agent for cotton and cotton blends

[34] designed to chemically or physically alter the fabric by passing through a 15-20 % solution of caustic soda

Wastewater is, by far, the largest waste stream for the textile industry. Large volume wastes include washing water from preparation and continuous dyeing, alkaline waste from preparation, and batch dye waste containing large amounts of salt, acid, or alkali.

Of the 635,000 metric tons of dyes produced annually worldwide, about 10-15 % of the dye is disposed of in effluents from dyeing operations. However, dyes in wastewater may be chemically bound to fabric fibers. The average wastewater generation from a large, centralized industrial U.S. dyeing facility is estimated at between 3.8 and 7.5 million liters per day (one and two million gallons per day). Dyeing and rinsing processes for disperse dyeing generate about 100-140 L of wastewater per kg of product (12-17 gallons of wastewater per pound). Similar processes for reactive and direct dyeing generate even more wastewater, about 125-170 L of wastewater per kg of product (15-20 gallons per pound of product) (EPA 1997).

Based on the analyses of 16 samples from Germany, it was concluded that, the PCDD/PCDF concentration will not increase significantly during these finishing processes: mean concentrations found in finished cotton were at 0.21±0.10 ng I-TEQ/kg with a median of 0.20 ng I-TEQ/kg (Horstmann 1994). These results were confirmed by random sample analyses of raw and pre-treated cotton arriving at the Hamburg harbor, which contained 0.03-0.2 ng I-TEQ/kg (Hutzinger *et al.* 1995, FHH 1995).

Sources of PCDD/PCDF in the final products can be due to:

- Use of chlorinated chemicals, *esp.* PCP, to protect the raw material (cotton, wool or other fibers, leather, *etc.*)
- Use of dioxin-contaminated dye-stuffs
- Formation of PCDD/PCDF during finishing.

Whereas there are many data for PCDD/PCDF concentrations in final products (textiles), there are no data for residues and wastewater. Therefore, emission factors canl be given only as upper bound and lower bound limits for the final product.

Table 61: Emission factor for the textile industry

Classification	Emission Factors – µg TEQ/t of Textile				
	Air	Water	Land	Product	Residue
1. Upper limit	NA	ND	NA	100	ND
2. Lower limit	NA	ND	NA	0.1	ND

6.7.4.1 Release to Air

There is no indication of relevant PCDD/PCDF emissions to the air from textile plants and thus, no emission factor will be given. The emissions from the generation of steam and power should be accounted for under Section 6.3.

6.7.4.2 Release to Water

There are no data available and no emission factors could be generated. When German finishing processes were investigated, no quantifiable concentrations have been found.

Releases to water will depend on the materials and chemicals used or applied, both in the process and to the raw materials and also on the water treatment. There is evidence for potential releases where there are poor controls on the discharges and large quantities of certain chemicals.

6.7.4.3 Release in Products

There is no simple indicator to identify dioxin-contaminated fibers, wools or textiles: whereas in most samples of raw textiles, concentrations below 1 ng I-TEQ/kg were detected (means around 0.2 ng I-TEQ/kg), there were also highly contaminated samples found. For example, 244 ng I-TEQ/kg were detected in bleached polyester, 370 ng I-TEQ/kg in blue cotton (Horstmann 1994), and 86 ng I-TEQ/kg in wool (Mayer 1998). The homologue profiles of all highly contaminated samples were dominated by the higher chlorinated PCDD and PCDF (Cl_7 and Cl_8). These are indicators for either the biocide pentachlorophenol or chloranil-based dyestuffs as the source of the contamination. However, several analyses confirmed that there is no correlation between PCP and PCDD/PCDF concentrations in textiles although the dioxin patterns gave strong indications that PCP should be the source. These findings make sense as PCP is water-soluble and will be removed in the finishing process and final washing processes whereas the PCDD/PCDF adsorb to the fiber and will stay in the textile (Horstmann and McLachlan 1995b, Klasmeier and McLachlan 1998).

6.7.4.4 Release in Residues

Depending on the factors described above, sludges from water treatment or from process steps may contain PCDD/PCDF. At present, there are no measured data available.

6.7.5 Leather Refining

So far, there are no reports on PCDD/PCDF contamination at or around leather plants. However, contamination of commercial leather products has been reported and based on the PCDD/PCDF pattern, it can be assumed that PCP is the source for the contamination. This assumption is underlined by the fact that since the ban of PCP in Germany in the year 1989 [35], the PCDD/PCDF concentrations in leather goods decline.

In contrast to textiles, PCP once applied on leather is not so easily removed by washing processes. In leather "breast-wallets" concentrations of PCDD/PCDF up to 430 ng I-TEQ/kg, in leather shoes up to 6,400 ng I-TEQ/kg were found (Malisch 1994b). Although in many countries, the use of PCP has decreased, at least in shoes, the PCDD/PCDF concentrations did not decrease: in Germany, peak concentrations of 2,100 and 3,000 ng I-TEQ/kg, respectively, were detected in leather shoes bought in 1991. In the year 1996, highly elevated

[35] Which sets a maximum concentration of 5 mg PCP/kg in the final product

concentrations continued to exist (Klasmeier and McLachlan 1997). For leather goods, the PCP concentrations correlate with PCDD/PCDF concentrations at least qualitatively. The homologue and congener profiles and patterns strongly indicate that PCP is the source of the dioxin contamination.

For this Toolkit, only emission factors for the final product can be provided presently. There are no data available for effluents or wastes. Emissions to air are expected to be negligible. Releases to water and with residues could be high.

Table 62: Emission factors for the leather industry

Classification	Emission Factors – µg TEQ/t				
	Air	Water	Land	Product	Residue
1. Upper limit	NA	ND	NA	1,000	ND
2. Lower limit	NA	ND	NA	10	ND

6.8 Main Category 8 – Miscellaneous

This category comprises eight processes that could not be classified in the other Main Source Categories. The sub-categories are shown in Table 63.

This Section also includes two processes (drying of green fodder, smoke houses), which may be considered to be combustion processes, *e.g.,* waste wood combustion – Section 6.1.6 or household heating and cooking - 6.3.4). They are dealt with here because green fodder drying can have a severe impact on PCDD/PCDF concentrations in feedstuffs and foods and therefore for human exposure as was shown recently in Germany. Also, although not well investigated, smoking of meat and fish can result in higher concentrations of PCDD/PCDF in the foodstuffs and consequently directly impact human body levels.

Table 63: Sub-categories of Main category 8 - Miscellaneous

No.		Categories and Subcategories	Air	Water	Land	Product	Residue
8		**Miscellaneous**	**X**	**X**	**X**	**X**	**X**
	a	Drying of biomass (green fodder, wood chips)	x			x	
	b	Crematoria	x				X
	c	Smoke Houses	x			x	X
	d	Dry cleaning residues		x		x	x
	e	Tobacco smoking	x				

Relevance to Article 5, Annex C

With relevance to the provisions of Article 5, sources in this category can be classified as follows:

Annex C, Part III source categories include:

	Source category	Section in Toolkit
(g)	Crematoria	6.8.2

6.8.1 Drying of Biomass

Drying of biomass, *e.g.,* wood chips or green fodder, occurs either in drums or in the open without containment. In the absence of measured data, copra and other local biomass (very often for export) will be included under this category as Subcategory a.

Under controlled conditions, clean fuels such as wood will be used. In a recent accident in Germany, it has been shown that contaminated wood has been used as the fuel resulting in very high concentrations of PCDD/PCDF in the green meal. There have been three categories established as shown in Table 64.

The drying of green fodder using poor fuels, *e.g.,* treated wood, used textiles, carpets, *etc.*, may lead to the contamination of the product. This can transfer PCDD/PCDF contamination into feedingstuffs and in the human food-chain. It is a management issue to feed appropriate fuel into the process to ensure that contamination does not occur.

Table 64: Emission factors for drying of biomass
* after drying

Classification	Emission Factors – µg TEQ/t of Product *				
	Air	Water	Land	Product	Residue
1. Clean wood	0.007	NA	ND	0.1	ND
2. Green fodder	0.1	NA	ND	0.1	ND
3. PCP- or otherwise treated biomass	10	NA	ND	0.5	ND

6.8.1.1 Release to Air

Measured concentrations in air ranged from 0.005 ng I-TEQ/Nm³ to 3.51 ng I-TEQ/Nm³ with a median of 0.16 ng I-TEQ/Nm³ (LUA 1997). The very high concentration was found when PCP-treated wood was used as a fuel for drying of green fodder.

6.8.1.2 Release in Products

Concentrations in the product, *e.g.,* virgin wood are close to detection limit, around 0.1 ng I-TEQ/kg and for fodder, concentrations as being found in biomonitoring studies with Welsh rye grass can be used. The concentrations found in the dried product, when contaminated wood was used as a fuel, was between 0.3 and 0.8 ng I-TEQ/kg d.m. An emission factor of 0.5 µg I-TEQ/t should be applied if PCP-treated wood is the fuel and an emission factor of 0.1 µg I-TEQ/t will be applied if clean fuel is used.

6.8.2 Crematoria

Cremation is a common practice in many societies to destroy human bodies by burning. The essential components for cremation are the charging of the coffin (and the corpse), the main combustion chamber, and where applicable the afterburning chamber. In some cases, a dust separator or more sophisticated gas treatment are present. Finally, gases leave through the stack. Most furnaces are fired using natural oil or natural gas; some run on electricity. Crematoria are usually located within cities and close to residential areas and normally, stacks are relatively low. Both facts result in relatively immediate impacts on the environment and humans.

Facilities may have no flue gas cleaning systems at all, more advanced facilities have secondary combustion chambers to ensure good burn-out of the gases and may be equipped with dust abatement systems (cyclones, electrostatic precipitators). The modern crematoria have sophisticated APC equipment such as adsorbent injection or catalysts to remove or destroy PCDD/PCDF. With the latter techniques, the emission concentrations of 0.1 ng I-TEQ/Nm³ can be met (the legal limit in Germany, 27th BImSchV). Emissions from crematoria without any air pollution controls can range up to 50 ng I-TEQ/Nm³ (@11 % O_2). Capacities vary

between 2 and 70 cremations per day. On average, 70 minutes are needed per cremation. Flue gas volumes range from about 2,000 m³/h to 10,000 m³/h. Concentrations between 1,000 and 2,500 ng I-TEQ/kg multi-cyclone ash or filter dust have been reported (LUA 1997; Belgian data). Dutch data report that 75 g of fly ash is generated per cremation with a concentration of 35,000 ng TEQ/kg.

The sampling and analysis project in Thailand measured the flue gas concentrations and bottom ashes from a crematory, which consisted of a refractory lined primary combustion chamber and a secondary combustion chamber with an afterburner. Both were fired by light fuel-oil. Subsequent followed a refractory lined flue gas duct, which discharged through an underground brick flue gas duct into a brick lined stack, which is about 15 meters away from the furnace (UNEP 2001, Fiedler *et al.* 2002).

Table 65: Emission factors for crematoria

Classification	Emission Factors – µg TEQ per Cremation				
	Air	Water	Land	Product	Residue
1. No control	90	NA	NA	NA	ND
2. Medium control	10	NA	NA	NA	2.5
3. Optimal control	0.4	NA	NA	NA	2.5

6.8.2.1 Release to Air

Class 1 emission factors should be chosen if the combustion conditions are poor, *e.g.,* temperatures below 850 °C, uncontrolled combustion air flow, *etc.*, if plastic or other decoration materials are burned together with the coffin, the wood of the coffin has been treated with wood preservatives or if there is no flue gas cleaning system in place. Class 2 factors should be applied if the combustion conditions are better – temperatures securely above 850 °C, controlled combustion air flow, no plastics or other problematic input materials - and some dust removal is in place. The class 3 emission factor should be applied if there is a state-of-the-art APCS in operation.

The PCDD/PCDF concentrations at the stack from the crematory in Thailand ranged from 10.5 to 28.6 ng I-TEQ/m³ with an average of 17.6 ng I-TEQ/m³ (@11 % O_2). These concentrations would have given an emission factor of 18 µg TEQ/body cremated. Since the crematory had an afterburner, it would have been classified into class 2 with an emission factor of 10 µg TEQ/body cremated; and therefore fall into the range of the estimated emission. The actual measured emission factor was somewhat higher than expected what can be explained by the fact that the crematory had a long underground flue gas duct, which favored the recombination of PCDD/PCDF at temperatures of the "reformation window" of PCDD/PCDF and thus, increased the PCDD/PCDF concentrations in the flue gas (UNEP 2001, Fiedler *et al.* 2002).

6.8.2.2 Release to Water

Normally, wet scrubbers or water quenching are not used at crematoria and thus, no discharges to water will occur. If wet scrubbers are used, the wastewater may end up in local sewer systems or being discharged without any prior collection. Examples from Western

Europe show, commonly wastewater-free APC systems with the wastewater being evaporated internally.

6.8.2.3 Release to Land

There are no releases to land.

6.8.2.4 Release in Products

There are no products generated.

6.8.2.5 Release in Residues

Poor combustion conditions will result in poor burn-out of the organic carbon and in higher concentrations in the fly ash and in the furnace ash. The PCDD/PCDF concentrations in the bottom ashes collected from a crematory in Thailand were 44 and 48 ng I-TEQ/kg of bottom ash (UNEP 2001, Fiedler *et al.* 2002). However, insufficient data are available to provide an emission factor.

6.8.3 Smoke Houses

Smoking food for preservation of meat and fish is common practice in many countries. As smoke houses are normally relatively small installations, combustion conditions may not be optimal and from the fuel – wood in most cases – there is a dioxin formation potential.

Table 66: Emission factors for smoke houses

Classification	Emission Factors				
	Air µg/t	Water	Land	Product ng TEQ/kg	Residue µg TEQ/t Residue
1. Treated wood used as fuel	50	NA	NA	ND	Same as wood combustion
2. Clean fuel, no afterburner	6	NA	NA	ND	
3. Clean fuel, afterburner	0.6	NA	NA	ND	

6.8.3.1 Release to Air

PCDD/PCDF concentrations in off-gases from smoke houses have been published from Germany (LAI 1993). A conventional smoke curing chamber emits about 300 m³/h and produces about 50 kg product her hour. The flue gas volume will be 6,000 m³/t product. With the measured data of 1.02 ng TEQ/m³ for a smoke house without thermal afterburning and 0.1 ng TEQ/m³ for a smoke house with thermal afterburning, the emission factors for class 2 and class 3 have been generated. Class 1 emission factors should be applied if treated wood is being used. Class 2 emission factor should be used if clean wood is being used.

6.8.3.2 Release to Water

Normally, wet scrubbers are not used at smoke houses and thus, no discharges to water will occur.

6.8.3.3 Release to Land

There are no releases to land.

6.8.3.4 Release in Products

There are systematic measurements on smoked meat and fish. An increase in the dioxin concentration of the foodstuff has been found in a few measurements. However, the concentration in the foodstuff is determined by the origin of the foodstuff (with higher concentrations in beef and sheep, lower concentrations in pork; highly variable with eventually very high concentrations in fish).

6.8.3.5 Release in Residues

The emission factors are the same as those for wood combustion.

6.8.4 Dry Cleaning

PCDD/PCDF have been detected in the distillation residues from dry cleaning (cleaning of textiles with solvents – not washing with water). The contamination of the textiles with PCDD/PCDF, *i.e.* from use of PCP as a biocide to protect the textile or the raw material – wool, cotton, *etc.* – or from dyestuffs, was identified as the source of the contamination. The dry cleaning process itself does not generate any PCDD/PCDF. During the dry cleaning process, the PCDD/PCDF contamination is extracted from the textiles and transferred into the solvent. The solvent is distilled for recovery and reuse and consequently, the PCDD/PCDF are concentrated in the distillation residues, which normally are disposed of. Detailed research has shown that the PCDD/PCDF concentrations in the distillation residues do not depend on the solvent present in the dry cleaning process. Therefore, the influence of the solvent used is negligible; typical solvents are perchloroethylene, petrol, or fluorocarbons.

Table 67: Emission factors for dry cleaning residues

Classification	Emission Factors – µg TEQ/t of Distillation Residue				
	Air	Water	Land	Product	Residue
1. Heavy textiles, PCP-treated, *etc.*	NA	NA	ND	ND	3,000
2. Normal textiles	NA	NA	ND	ND	50

6.8.4.1 Release to Water

No release to water is expected.

6.8.4.2 Release to Land

No release to land is expected.

6.8.4.3 Release in Products

There are no products generated (concern is with the distillation residues only).

6.8.4.4 Release in Residues

Class 1 emission factor should be applied if highly contaminated textiles have been cleaned in the process; *e.g.,* carpets or heavy curtains suspect to be treated with PCP (the country of origin may be an indicator) or cloths from workers from dioxin-polluted environments. The class 2 emission factor should be used if normal cloths are being cleaned in the system.

The treatment of the residues should be noted.

6.8.5 Tobacco Smoking

As any other thermal process, "combustion" of cigarettes and cigars produces PCDD/PCDF. Investigations of the ten most popular brands smoked in Germany gave "emissions" of 0.1 pg I-TEQ/cigarette. There are no results from cigars. Only releases to air are addressed; any other releases will be insignificant.

Table 68: Emission factors for tobacco smoking

Classification	Emission Factors – pg I-TEQ/Cigar or Cigarette				
	Air	Water	Land	Product	Residue
1. Cigar	0.3	NA	NA	NA	NA
2. Cigarette	0.1	NA	NA	NA	NA

6.8.5.1 Release to Air

The emission factors are self-explanatory. The emission factor for cigars has been derived from the greater amount of tobacco being smoked. A cigar can be anywhere from 2 to 20-times the amount of tobacco compared to cigarettes.

6.8.5.2 Release to Water

Does not apply.

6.8.5.3 Release to Land

Does not apply.

6.8.5.4 Release in Products

There are no products generated.

6.8.5.5 Release in Residues

Not relevant.

6.9 Main Category 9 – Disposal/Landfill

The way in which waste is handled and disposed of can have severe effects on the formation and release of PCDD/PCDF. In the precedingsSections many processes have been described, which give rise to residues containing PCDD/PCDF. The fate of these residues, *e.g.* containment in secure landfills, destruction (thermally or chemical decontamination) or release into the environment, i.e. effluents simply dumped into rivers, lakes or oceans, can result from negligible to major releases of these contaminants. Any disposal practices of dioxin-containing residues should be noted. In extreme cases the handling of residues can give rise to a high exposure to PCDD/PCDF. Recent examples are the Belgian chicken accident where a small volume of used PCB oil (contaminated with PCDF) was recycled into fats used by the feedingstuff producing industry or the use of contaminated lime in the animal feed production (EU SCAN 2000).

This Section addresses some disposal options other than incineration or thermal recycling. The cause for the presence of PCDD/PCDF is that dioxins and furans have been formed in other processes but the contamination will be concentrated or dispersed by the management options listed in Table 69. Examples of products contaminated with PCDD/PCDF have been addressed earlier – especially in Section 6.7. The presence of PCDD/PCDF in the general human environment as consumer goods and in residues, including house dust, results in the fact that "normal" household waste contains PCDD/PCDF. There are a few data available on PCDD/PCDF concentration in municipal solid waste: the numbers range from relatively low concentrations around a few ng I-TEQ/kg to concentrations above 100 ng I-TEQ/kg with peak concentrations orders of magnitude higher (especially when dust fractions are present). In Germany, a mean concentration of 50 ng I-TEQ/kg was estimated in the early 1990s and in the UK a mean concentration of 6 ng I-TEQ/kg was measured in the mid 1990s. As the waste composition will vary highly from country to country and during the year (with higher amounts of green materials during summer time) and as emissions or product use changes, variations with time have to be considered. Time trends will occur if waste management plans are altered; *e.g.,* installing a recycling system for used paper and cardboard (*e.g.,* newspapers, office papers, packaging papers) or for glass, cans, *etc.,* or promotion of composting to remove these fractions from the waste to be landfilled or dumped. On the other hand, economic growth may increase the amount of plastic materials of all kinds and composite materials to be disposed of at the end of their use phase. Lastly, it is very difficult or almost impossible to take a representative waste sample and determine its PCDD/PCDF concentration.

Table 69: Subcategories of Main Category 9 - Disposal

No.		Categories and Subcategories	Air	Water	Land	Product	Residue
9		**Disposal**		**X**	**X**	**X**	
	a	Landfills and waste dumps		x			
	b	Sewage/ sewage treatment	(x)	x	x	x	x
	c	Open water dumping		x			
	d	Composting			x	x	
	e	Waste oil treatment (non-thermal)	x	x	x	x	x

Relevance to Article 5, Annex C

With relevance to the provisions of Article 5, sources in this category can be classified as follows:

Annex C, Part III source categories include:

	Source category	Section in Toolkit
(g)	Waste oil refineries	6.9.4

6.9.1 Landfills and Waste Dumps

For the purposes of the Toolkit landfills and waste dumps are places where waste is disposed of by burying in the ground or piling on the surface. For purposes of the Toolkit, a landfill is a controlled engineered waste storage site with respect to inputs/types of wastes, location of different types of waste and management (gas and water collection, etc.) whereas a dump is largely unregulated and typically contains mixed waste that was disposed of without any pollution prevention devices.

Degradation of organic materials takes place in a landfill and in a dump, which results in the formation of gases (with methane as a major constituent). The passage of water through the waste results in a leachate. When no collection systems are installed, landfill gases and leachates escape from the landfill in an uncontrolled manner.

Care has to be taken when calculating emissions from burning landfills or dumps. The Toolkit differentiates between the use of the landfill gas (methane generated through decomposition of the waste) for energy generation, and burning of the landfill caused by ignition. In the first case, when the gases are collected and burned in a torch or simple device, the burning of the landfill gas is considered to be energy production and therefore will fall into Subcategory 6.3.3. For the Toolkit it does not matter if the "energy" is being used or not. Landfill or waste dump burning under category 6.6.2 describes the situation when the body of the waste is under fire. In this context it does not matter if the fire is initiated through self-ignition of methane gas, *etc.* (= spontaneous combustion at landfill sites) or the landfill was set under fire intentionally, *e.g.,* in order to create more space for new incoming wastes. The length of the time the waste is under fire and the amount of waste that burned will determine the level of the emission.

Table 70: Emission factors for landfills and waste dumps

Classification	Emission Factors – pg TEQ/L for Water Release and of Leachate Released				
	Air	Water	Land	Product	Residue
1. Hazardous wastes	0	200	NA	NA	NA
2. Non-hazardous wastes	0	30	NA	NA	NA

6.9.1.1 Release to Air

On average, 1 ton of normal municipal waste in a landfill generates 150 m³ of landfill gas (European waste) during a period of 10-20 years (or even longer). The highest gas production takes place in the early years after disposal. Measurements of landfill gas have not produced any quantifiable PCDD/PCDF concentrations. After flames and in gas motors PCDD/PCDF concentrations have been detected (see Chapter 6.3.3). In native landfill gas, no PCDD/PCDF could be quantified. No measurable emission to air is expected from this activity.

6.9.1.2 Release to Water

The leachate or seepage from landfills and dumps can contain PCDD/PCDF. Limited data are available on concentrations of PCDD/PCDF in leachates. PCDD/PCDF is likely to be concentrated in any oily phase of the leachate (the oily phase can be found either above or below the aqueous phase). So far, analysis of the aqueous phase of seepage water did not find any PCDD/PCDF neither in the waters from municipal, mixed nor hazardous landfills.

Data from five landfills in New Zealand ranged from 7.5 to 221 pg I-TEQ/L. The New Zealand inventory (NZ 2000) subdivided the range into 14-48.3 pg I-TEQ/L for small and medium landfills and 7.5-221 pg I-TEQ/L for large landfills. The highest concentration came from a landfill with significant industrial and potentially hazardous wastes.

For the Toolkit two categories are suggested: class 1 with an emission factor of 200 pg I-TEQ/L for landfills, which may contain hazardous wastes and 30 pg I-TEQ/L in class 2 for landfills containing non-hazardous municipal wastes.

6.9.1.3 Release to Land

Contamination of land can result from poorly controlled dumps and landfills.

6.9.1.4 Release in Products

There is no product.

6.9.1.5 Release in Residues

There is no residue being produced in general. The PCDD/PCDF present in the landfill acts are a reservoir and a potential source for the future. The amount of PCDD/PCDF present in landfills or waste dumps will be determined by the level of dioxin sources in the country. Countries with little dioxin-generating activities should apply an emission factors of 6 µg TEQ/t for domestic waste disposed of in landfills, whereas an emission factor of 50 µg TEQ/t for domestic waste should be applied for countries with relevant PCDD/PCDF sources. In this sub-category, only the historic load can be quantified.

6.9.2 Sewage and Sewage Treatment

This section includes aqueous releases that are collected in a central system. The final discharge may be with or without treatment of these effluents, with or without generation of sludges. The direct discharge into the environment is addressed in section 6.9.3.

Sewage sludge considered here is the solid residue from treatment of wastewater – in particular wastewater arising from human sanitation and households. Wastewater can include human wastes (sewage), water from washing of people and clothes, in some cases storm water run-off, and industrial effluents released to sewer. Since most of the contamination present in the sludge has its origin in other processes or products [36], sewage sludges may be considered to be sinks for PCDD/PCDF formed and emitted previously by other sources. However, the handling of the sludge can cause releases of PCDD/PCDF. Concentrations of sewage sludge have been studied in several countries. Further, countries such as Germany and Austria, with legislation in place, routinely analyze sewage sludges for PCDD/PCDF. In this Section, domestic sewage sludge is considered only. Sludges from production processes such as the pulp and paper industry are listed in the respective subcategories (mainly in Section 6.7.1)

The amount of PCDD/PCDF entering a sewage system or treatment works will depend on the sources of the wastewater. Sewage treatment systems can have different configurations ranging from simple transport of the effluent to a dumping ground (perhaps out at sea) with no treatment, simple removal of large solids (by settling ponds or coarse screening) and biological treatment and settling. In some cases further stages of treatment can be applied.

The amount of PCDD/PCDF entering a sewage system or treatment works will depend on the sources of the wastewater. Inputs to wastewater may be highly variable and thus, estimates are difficult to make. The lowest concentrations are expected in areas with no industry and in remote or undeveloped environments. In such cases concentrations of PCDD/PCDF in run-off are low (with no atmospheric deposition). Low concentrations may be expected also in countries with stringent controls on discharge of industrial effluents to sewer and effective controls on PCP, *etc.* on textiles and no use of chlorine-bleached toilet paper. Higher levels can be expected in urban areas with mixed industry and use of dioxin-containing consumer

[36] We are aware that biogenic formation of PCDD/PCDF in sewage sludge has been reported by some authors. However, the contribution from biological formation is very small and cannot be quantified in terms of emission factors. Further, biodegradation of PCDD/PCDF during fermentation is not been considered as well. PCDD/PCDF may also be produced where sludge is thermally dried.

goods. Occasionally, direct discharges of industrial effluents (for reference, see Section 6.7.2) without any treatment can cause very high levels of PCDD/PCDF in sewage sludge.

With more advanced treatment – such as biological treatment - where a sludge is produced most of the PCDD/PCDF is likely to be concentrated in the sludge produced. The amount of PCDD/PCDF in the effluent is likely to be influenced by the amount of suspended solids remaining in the effluent.

PCDD/PCDF concentrations in sewage sludge have been measured since the late 1980s, when Hagenmaier found an average concentration of 200 ng TEQ/kg d.m. from 43 German sewage sludge treatment plants (Hagenmaier 1988). Subsequently, about 300 plants were analyzed to give an average of 50-60 ng TEQ/kg d.m. (Butzkamm-Erker and Mach 1990). In 30 Swiss sewage plants Rappe *et al.* (1994) found concentrations between 6 and 4,100 ng TEQ/kg d.m., whereby four samples were above 1,000 ng I-TEQ/kg d.m. Typically, in industrialized countries, concentrations in sewage sludge show downward trends due to source controls.

Potential sources of PCDD/PCDF in sewage sludge may include microbial formation, runoff from lands or urban surfaces contaminated by product uses or deposition of previous emissions to air, household wastewater, industrial wastewater, *etc.*. However, in a series of studies demonstrated that wastewater generated by laundering and bathing could be the major source at many, if not all, sewage plants that serve primarily residential populations (for summary see, US-EPA 2000 and references therein).

PCDD/PCF concentrations in household effluents ranged between 0.8 pg I-TEQ/L and 15 pg I-TEQ/L. Some fractions such as the effluents from washing machines have higher concentrations (17-25 pg I-TEQ/L) and others such as effluents from showers or bath-tubs were lower (2-16 pg I-TEQ/L) (Horstmann and McLachlan 1995, Horstmann *et al.* 1993c).

Table 71: Emission factors for sewage sludge
(Note: the emission factors are given in pg I-TEQ/L of sewage water effluent and in µg I-TEQ per ton of sewage sludge (dry matter = d.m.) generated)

Classification	Emission Factors			
	Air	Water pg I-TEQ/L	Land	Product = Residue µg TEQ/t d.m.
1. Mixed domestic and industrial inputs (with chlorine relevance)	NA NA	5 [a] 0.5 [b]	NA NA	1,000 1,000
2. Urban environments	NA NA	2 [a] 0.5 [b]	NA NA	100 100
3. Remote environments or input control (and here treatment systems in place)	NA	0.1	NA	10

a = no sludge removal, b = with sludge removal

6.9.2.1 Release to Air

Emissions to air – other than from incineration or other thermal treatment of sewage sludge – are not relevant.

6.9.2.2 Release to Water

Effluents from sewage treatment plants are normally very low and the removal of the particles results in an almost complete elimination of PCDD/PCDF as dioxins and furans bind tightly to organic carbon of the sludge particles. The higher class 1 emission factor should be applied where no sludge is being generated and the class 2 emission factor should be used where sludge removal is in place.

6.9.2.3 Release to Land

Sludge from sewage treatment may be applied to land to improve the soil quality. If so, the concentrations of the product will be used.

6.9.2.4 Release in Products

Sludge may be considered a product where it is applied to land as a soil improvement. In these cases it will be considered a release to land (see above). Sludge otherwise disposed of is a residue.

Here, sewage sludge is the product and there is no residue generated. Class 1 concentration should be applied if besides the normal domestic effluents, industrial effluents with a potential to contain dioxin and furan contamination are collected in the same sewer system or if run-offs from roofs and contained land with high loads of fine particulates are entering the sewer plant. The class 2 factors should be applied for urban, industrialized areas and the class 3 factors should be used for remote areas with no known dioxin source nearby (Rappe *et al.* 1996). Class 3 emissions factors should also be chose in areas/countries where regulations are in place to prevent contaminated effluents to enter into the sewer plants (this explains why relatively low concentrations are found in the sludges of large European cities).

6.9.2.5 Release in Residues

The residue is the sewage sludge (from biological treatments or settling ponds) and coarse materials removed by gravity. No residue is produced where no treatment is carried out. Where sludge is applied to land this should be considered a release to land. If sludge is dumped at sea this should be noted.

An Asian country calculated the PCDD/PCDF releases in sludges assuming that sludge generation at wastewater treatment plants typically is at 0.4 % of raw sludge in effluent water. The effluent typically contains 3 % of dry matter. Depending on the degree of industrialization and the presence of PCDD/PCDF-contaminated consumer goods and input of potentially contaminated effluents into the treatment plant either the higher or the lower emission factor should be applied (Asia Toolkit Workshop 2002).

6.9.3 Open Water Dumping

Open water dumping is a waste or wastewater management practice and the tail-end of other industrial or domestic activities. In this section, only effluents or other wastes directly discharged into the environment are considered. In most cases, discharges occur into receiving waters, *i.e.* rivers, lakes or oceans.

As in the previous section 6.9.2, this section 6.9.3 does not address industrial effluents, which are covered under the respective industries. Therefore, the same classification of wastewaters will be applied resulting in the PCDD/PCDF concentrations discharged. will be assumed as in section 6.9.2. we attempt to characterize and quantify discharges from households, offices, and other small businesses as well as run-offs from contained land, *e.g.,* parking lots, streets, *etc.*

Table 72: Emission factors for open water dumping

Classification	Emission Factors – pg TEQ/L				
	Air	Water	Land	Product	Residue
1. Mixed domestic and industrial inputs	NA	5	NA	NA	NA
2. Urban environments	NA	0.5	NA	NA	NA
3. Remote environments or input control	NA	0.1	NA	NA	NA

6.9.3.1 Release to Air

Not relevant.

6.9.3.2 Release to Water

Not relevant.

6.9.3.3 Release to Land

Not relevant.

6.9.3.4 Release in Products

Not relevant as there is no product.

6.9.3.5 Release in Residues

Not relevant.

6.9.4 Composting

Composting is a popular method of disposal for wastes originating from kitchen activities, gardening, park and other public/private area maintenance, agriculture, and forestry. Basically, any organic material can be composted and this disposal process generally has a high degree of acceptance in the public. The composting process results in a loss of about 50 % on a weight basis of the input material. The average water content of compost is 30 %.

Data from Europe have shown that contamination with PCDD/PCDF in compost can be high if the total organic fraction is being composted. Fractions, which may enter the composting process and which may have high concentrations of PCDD/PCDF. Such materials are *e.g.,* the content of vacuum cleaners or any fine particles such as house dust, soil from contaminated land entering with vegetable and other plant's leftovers, leaves from alleys impacted by traffic using leaded gasoline, greens from cemeteries or other pesticide treated organic wastes. This practice will result in an unacceptable contamination of the final product not suitable for use in horticulture. Concentrations above 100 ng I-TEQ/kg have been detected in these composts.

Table 73: Emission factors for composting

Classification	Emission Factors - µg TEQ/t d.m			
	Air	Water	Land	Product = Residue
1. All organic fraction	NA	NA	NA	100
2. Garden, kitchen wastes	NA	NA	NA	15
3. Green materials from not impacted environments	NA	NA	NA	5

6.9.4.1 Release to Air

Emissions to air are very low (few pg per m^3) and are not relevant.

6.9.4.2 Release to Water

The composting process generates water, however, the concentrations are normally very low and the water is being recycled into the compost during the process.

6.9.4.3 Release to Land

The usual use of finished compost is application on land, therefore the concentrations of the product will be used.

6.9.4.4 Release in Products

In the case of compost, product equals residue. The class 1 concentration should be applied when the whole organic fraction is being composted and eventually the content from vacuum cleaners, ashes from chimneys or stoves or from barbecues/grills are included. Class 2 emis-

sion factor should be used if kitchen and garden greens together with foliage or spruce needles from parks, *etc.* are being composted. Class 3 emission factor should be applied in cases vegetable and plant residues are being composted that have not been treated with chlorinated pesticides and no fine particles are included.

6.9.5 Waste Oil Treatment (Non-Thermal)

The estimate for waste oil treatment in the dioxin inventory may be difficult for several reasons. First, there is no clear definition of "used" oil or "waste" oil. The oil or fat fraction collected in oil filters from canteens, restaurants, businesses, *etc.,* can be collected and be recycled. Oils from *e.g.,* cars, other motors, *etc.,* would represent another category and finally oils from transformers, potentially containing PCB have to be considered as well. Whereas the latter will be dealt with in Main Category 10 (see Section 6.10.6), the oils from the two first former uses will be addressed in this Section.

The first difficulty arises in obtaining activity data, in other words how much waste oil is being collected and processed in the country. It can be assumed that the illegal part may have a big share of the total (and will remain unknown). Some of the waste oil will be used as alternative fuel in other processes and has to be accounted there, *e.g.,* asphalt mixing stations, cement kilns, brickworks, *etc.*). Some can be - with or without prior refining – blended with heavy fuel oil and used in motors for, *e.g.,* in ships. The Toolkit addressed such use in Section 6.5.4; some emission concentrations are given therein as well.

The management of PCDD, PCDF or PCB contaminated oils may cause human exposure of personnel collecting or otherwise handling the oils. During storage and handling, diffuse emissions may occur. Contamination of the environment may result from spills of the contaminated oil. Residues from recycling operations may contain high concentrations of PCDD/PCDF. Improper disposal may result in contamination of land or water. It can be assumed that site- or process-specific evaluation has to be performed.

Presently, no emission factor can be given with respect to any of the release vectors.

6.10 Main Category 10 – Hot Spots

This Section 6.10 gives an indicative list of activities that might have resulted in the contamination of soils or sediments with PCDD/PCDF. If one of the activities listed below has been performed or is being practiced, there is a high probability to detect PCDD/PCDF contamination. Quantitative numbers cannot be given but in many cases concentrations will be several orders of magnitude higher than background concentrations. Each of such potential hot-spots needs a site-specific evaluation starting with a historic evaluation if the suspected activities have been taken place or are presently performed. In this context, it is important to obtain an estimate of the magnitude of *e.g.,* chemicals produced or used, time-scale of the activities (months, years, decades).

6.10.1 Production Sites of Chlorinated Organics

There is a high probability for pollution of buildings and soil at present or former production sites of chlorinated organics. Highest concentrations of PCDD/PCDF are expected to be associated with the production of chlorinated phenols and their derivatives. If there has been wastewater discharge into receiving waters, sediments below the discharge pipe can be contaminated with PCDD and PCDF. If wastewater has been allowed to settle in ponds, these sediments or the sludges from these settling ponds can contain high concentrations of PCDD/PCDF.

6.10.2 Production Sites of Chlorine

The manufacture of chlorine using the mercury cell and graphite anodes leaves PCDD/PCDDF contamination in the residues. Contamination up to 30 mg TEQ/kg residue has been found. Graphite anodes were used almost exclusively for chlorine production before being replaced in the 1970s by metal anodes. The graphite anode was composed of various types of particulate coke mixed with a pitch binder. Some oxygen was liberated at the anodes with the chlorine, and this oxygen attacked the graphite forming carbon monoxide and carbon dioxide. This electrode wear was the cause of a graphite consumption of about 2 kg per ton of chlorine produced from sodium chloride and 3-4 kg per ton of chlorine from potassium chloride. The graphite residue produced was contaminated with PCDD/PCDF compounds, mainly from the reaction between chlorine and the pitch binder containing polycyclic aromatic hydrocarbons (PAH) (Ullmann 1996).

An emission factor for PCDD/PCDF cannot be given for these locations and each site needs its own evaluation. Primary targets will be soil and if leaching has occurred neighboring compartments and eventually sediments of nearby rivers can be affected as well. A strong indicator for contamination by PCDD/PCDF will be high concentrations of mercury, which is a concern by itself. Unfortunately, a correlation factor between the concentrations of mercury and PCDD/PCDF cannot be established.

6.10.3 Formulation Sites of Chlorinated Phenols

These are sites where chlorinated phenols have been formulated into *e.g.,* pesticides for agricultural or other application. Normally, the contamination will be found in the buildings where the chlorinated phenols have been stored or formulated. Consequently, there is a high potential for soil contamination.

6.10.4 Application Sites of Chlorinated Phenols

These sites include locations where chemicals, *e.g.,* pesticides have been applied. According to the use pattern, dioxin-containing herbicides such as 2,3,4-T, 2,4-D or others (see Section 6.7.2.3, 6.7.2.5 or 6.7.2.6) have been applied in agriculture or for right-of-way purposes. Besides the usage as shown in Section 6.10.5 contamination with pentachlorophenol and its salts may occur in rice paddies or on farmland when PCP-treated poles are being used in fences or around telephone poles, *etc.*

6.10.5 Timber Manufacture and Treatment Sites

Saw mills and timber manufacturing sites are often associated with the use of pentachlorophenol. Soils and sediments can be contaminated with PCDD/PCDF as these industries use a lot of water and often are located at rivers. As PCP and PCP-Na have a much higher water solubility and shorter half-lives, the concentration of PCP in soils or sediments cannot give more than indications for PCDD/PCDF contamination. Quantitative correlation between concentrations of PCP and PCDD/PCDF cannot be established as both classes of compounds have different physical, chemical behavior and undergo different fate under environmental conditions.

6.10.6 PCB-Filled Transformers and Capacitors

Wherever a PCB-containing transformer or capacitor is detected, there will be PCDF present since through the production process of PCB, contamination by PCDF occurs (chlorination of biphenyl with chlorine gas in the presence of a catalyst). With increasing age and time of operation, the concentrations of PCDF in the transformer fillings will increase. As long as the transformers and the capacitors are in a good shape – no leakages – there will be no release of PCDF (and PCB) into the environment. Once leakages have been determined, the PCDF together with the PCB will subsequently be released into the surroundings, *e.g.,* soil, surfaces, sediments. The PCB can serve as an indicator as especially the higher chlorinated PCB show a similar behavior (*esp.* stability and mobility) in the environment as the 2,3,7,8-substituted PCDF.

In this section and for the purposes of the dioxin/furan inventory, releases of the PCDF (as TEQ) will be estimated. It should be noted that with the release of the commercial mixture of the PCB, dioxin-like PCB and non-dioxin-like PCB are released as well. However, the latter two groups of POPs are not covered under the scope of the present Toolkit (see chapter 1 – Introduction). For further information on dioxin-like PCB in commercial mixtures of PCB, see Schmitz *et al.* 1996).

Emission factors for PCB products will be grouped according to the chlorine content and are as shown in Table 74. It is known that under thermal stress, PCB will transform into PCDF and thus increase in TEQ. No correlation can be established but it can the assumed that the used PCB will have higher concentrations than the new PCB. As presently, all PCB discovered in any equipment will be "used" PCB, the concentrations given below should be considered as lower limits.

Table 74: Emission factors for PCB

PCB Type	New PCB (µg TEQ/t)
Low chlorinated, *e.g.,* Clophen A30, Aroclor 1242	15,000
Medium chlorinated, *e.g.,* Clophen A40, Aroclor 1248	70,000
Medium chlorinated, *e.g.,* Clophen A50, Aroclor 1254	300,000
High chlorinated, *e.g.,* Clophen A60, Aroclor 1260	1,500,000

Due PCB regulation in place in many countries, PCB containing equipment has to be inventoried anyhow and be treated as hazardous waste (for disposal). Such activities will help identify PCB for the dioxin inventory and also to identify potential hot-spots where PCB may have leaked into the environment.

6.10.7 Dumps of Wastes/Residues from Categories 1-9

Wherever, PCDD/PCDF containing products or residues have been disposed of, there is a probability that these contaminants will be released into the environment. The dump or land-fill itself is the reservoir. PCDD/PCDF are relatively immobile in these dumps as long as there is no seepage water capable of mobilizing the PCDD/PCDF contamination. Once released, PCDD/PCDF will concentrate in the oily layers (organic phases in the water/organic phase mixture). For analytical purposes, only the organic phase should be analyzed for PCDD/PCDF. All experiences have shown that the aqueous phases contained non-detectable concentrations of PCDD/PCDF.

Indicators for PCDD/PCDF-containing dumps are when there is a record that one or more of the following wastes have been disposed:

- Residues from chemical production, *esp.* chlorophenols;
- Residues from combustion and incineration processes, *e.g.,* fly ashes;
- PCB-containing equipment (*e.g.,* capacitors, transformer or other utilities);
- Sludges from pulp mills where chlorine gas (free chlorine) has been used in chemical bleaching;
- Timber industry where PCP or other chlorinated aromatic wood preservatives have been applied.

In addition hot-spots will be generated when
- plastic-coated copper cables have been burned on the ground;
- when incidental or accidental landfill fires have occurred.

6.10.8 Sites of Relevant Accidents

Accidents such as fires can produce soot and residues with elevated concentrations of PCDD/PCDF (see also Section 6.6.2). Such accidents very often result from fires, *e.g.,* PCB transformer fires, fires at storage rooms, houses (especially if treated wood, plastics, carpets or brominated flame retardants are involved). Normally, the PCDD/PCDF contamination will be concentrated in the soot. The soot should be collected and disposed of properly as hazardous waste.

6.10.9 Dredging of Sediments

Sediments from harbors or below industrial discharge pipelines of any of the above-listed industrial activities can be contaminated with PCDD/PCDF. Very often, to maintain shipment, these sediments are being dredged and placed on land. This activity only removes the PCDD/PCDF contamination from its present location and from the aquatic pathway but does not more than transfer the same level of contamination to another location with potentially new exposures (→ residential or agricultural soils). Therefore, care is required in deciding on the best way to handle contaminated sediments to reduce any risk of inadvertent exposure.

6.10.10 Kaolinitic or Ball Clay Sites

In recent years, an increasing number of observations indicate that PCDD/PCDF may have been present in the environment for considerably longer than the onset of the chlorine industry, and that they may – in fact – be formed through non-anthropogenic activities. High concentrations of mainly PCDD were found in mined ball clay from the USA, kaolinitic clay from Germany, deep soil samples from Great Britain, in dated marine sediment cores from Queensland/Australia and in man-made lake sediment cores from Mississippi/USA. Typical for all samples is the almost total absence of PCDF and the nearly identical congener/isomer distribution throughout all geographies. All studies provide a strong indication that PCDD/PCDF were formed by natural processes. These observations should lead to intensive investigations to assess how widespread the phenomena of naturally formed PCDD/PCDF and might be, and to investigate the mechanism of formation that could account for these observations. Presently, there are no indicators to identify such sites. Any finding of this kind should be notified.

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8 ANNEX 1: COMPILATION OF ALL EMISSION FACTORS

This Annex contains a compilation of all emission factors for the ten main Source Categories and their subcategories. These sheets are also available as EXCEL files to be used directly for calculation of the annual releases *via* all vectors.

In the following Tables the majority of the emission factors are given as μg TEQ per ton of feed material or product, respectively. In a few exemptions, *e.g.,* residues from coal fired stoves in domestic heating (Sub-category 3e) as well as for water and residues (wastewater and sludges) in the pulp and paper industry (Sub-category 7a), the annual emission are estimated on basis of residues generated.

Care should also be taken that annual releases are not counted twice; *e.g.* the residue from one process may be feed material for another process or activity. Examples are ashes from the ferrous and non-ferrous metal industry, which may be utilized in secondary processes. Further, wastewater from industrial processes normally should be accounted to the respective industry where they are generated. However, occasionally, statistics may provide data at the disposal site, for example the amount of wastewater discharged at a specific location may be known; *e.g.* for open water dumping or discharges at sewer plants. Thus, special care should be taken when numbers are being filled in, especially for sector 9.

In the following Tables
"NA" denotes that the vector is not expected

"ND" denotes that presently there is no suitable emission factor available. This means that this vector can be of importance to note but presently, releases along this vector cannot be calculated.

Emission Factors for Category 1 – Waste Incineration

Cat.	Subcat.	Class		Air	Water	Land	Products	Residues	
								Fly Ash	Bottom Ash
1			**Waste incineration**						
	a		**Municipal solid waste incineration**						
		1	Low technol. combustion, no APC system	3,500		NA	NA	0	75
		2	Controlled comb., minimal APC	350		NA	NA	500	15
		3	Controlled comb., good APC	30		NA	NA	200	7
		4	High tech. combustion, sophisticated APCS	0.5		NA	NA	15	1.5
	b		**Hazardous waste incineration**						
		1	Low technol. combustion, no APC system	35,000		NA	NA	9,000	
		2	Controlled comb., minimal APC	350		NA	NA	900	
		3	Controlled comb., good APC	10		NA	NA	450	
		4	High tech. combustion, sophisticated APCS	0.75		NA	NA	30	
	c		**Medical/hospital waste incineration**						
		1	Uncontrolled batch combustion, no APCS	40,000		NA	NA		200
		2	Controlled, batch, no or minimal APCS	3,000		NA	NA		20
		3	Controlled, batch comb., good APC	525		NA	NA	920	ND
		4	High tech, continuous, sophisticated APCS	1		NA	NA	150	
	d		**Light fraction shredder waste incineration**						
		1	Uncontrolled batch comb., no APCS	1,000		NA	NA	ND	ND
		2	Controlled, batch, no or minimal APC	50		NA	NA	ND	ND
		3	High tech, continuous, sophisticated APCS	1		NA	NA	150	
	e		**Sewage sludge incineration**						
		1	Old furnaces, batch, no/little APCS	50		NA	NA	23	
		2	Updated, continuously, some APCS	4		NA	NA	0.5	
		3	State-of-the-art, full APCS	0.4		NA	NA	0.5	
	f		**Waste wood and waste biomass incineration**						
		1	Old furnaces, batch, no/little APCS	100		NA	NA	1,000	
		2	Updated, continuously, some APCS	10		NA	NA	10	
		3	State-of-the-art, full APCS	1		NA	NA	0.2	
	g		**Animal carcasses burning**						
		1	Old furnaces, batch, no/little APCS	500		NA	NA		ND
		2	Updated, continuously, some APCS	50		NA	NA		ND
		3	State-of-the-art, full APCS	5		NA	NA		ND

Emission Factors for Category 2 – Ferrous and Non-ferrous Metal Production

Cat,.	Subcat	Class	Source Categories	Potential Release Route (µg TEQ/t)				
				Air	Water	Land	Products	Residues
2			**Ferrous and Non-Ferrous Metal Production**					
	a		**Iron ore sintering**					
		1	High waste recycling, incl. oil contamin. materials	20	ND	ND	ND	0.003
		2	Low waste use, well controlled plant	5	ND	ND	ND	0.003
		3	High technology, emission reduction	0.3	ND	ND	ND	0.003
	b		**Coke production**					
		1	No gas cleaning	3	0.06	ND	ND	ND
		2	Afterburner/ dust removal	0.3	0.06	ND	ND	ND
	c		**Iron and steel production plants and foundries**					
			Iron and steel plants					
		1	Dirty scrap, scrap preheating, limited controls	10	ND	ND	NA	15
		2	Clean scrap/virgin iron, afterburner, fabric filter	3	ND	ND	NA	15
		3	Clean scrap/virgin iron, BOS furnaces	0.1	ND	ND	NA	1.5
		4	Blast furnaces with APC	0.01	ND	ND	NA	ND
			Foundries					
		1	Cold air cupola or rotary drum, no APCS	10	ND	ND	ND	ND
		2	Rotary Drum - fabric filter	4.3	ND	ND	ND	0.2
		3	Cold air cupola, fabric filter	1	ND	ND	ND	8
		4	Hot air cupola or induction furnace, fabric filter	0.03	ND	ND	ND	0.5
	d		**Copper production**					
		1	Sec. Cu - Basic technology	800	ND	ND	ND	630
		2	Sec. Cu - Well controlled	50	ND	ND	ND	630
		3	Sec. Cu - Optimized for PCDD/PCDF control	5	ND	ND	ND	300
		4	Smelting and casting of Cu/Cu alloys	0.03	ND	NA	NA	ND
		5	Prim. Cu – including thermal steps	0.01	ND	ND	ND	ND
	e		**Aluminum production (all sec.)**					
		1	Processing scrap Al, minimal treatment of inputs, simple dust removal	150	ND	ND	ND	400
		2	Scrap treatment, well controlled, good APCS	35	ND	ND	ND	400
		3	Shavings/turning drying	5	NA	NA	NA	NA
		4	Scrap treatment, well-controlled, fabric filter, lime injection	4	ND	ND	ND	100
		5	Optimized process, optimized APCS	0.5	ND	ND	ND	400
	f		**Lead production**					
		1	Sec. lead from scrap, PVC battery separators	80	ND	ND	ND	ND
		2	Sec. from PVC/Cl2 free scrap, filters	8	ND	ND	ND	ND
		3	Sec. Lead, PVC/Cl2 free scrap in modern furnaces, with scrubber	0.5	ND	ND	ND	ND
	g		**Zinc production**					
		1	Kiln with no dust control	1,000	ND	ND	ND	ND
		2	Hot briquetting/rotarry furnaces, basic control	100	ND	ND	ND	ND
		3	Comprehensive control	5	ND	ND	ND	ND
		4	Melting (only)	0.3	ND	ND	ND	ND
	h		**Brass and bronze production**					
		1	Simple melting furnaces	10	ND	ND	ND	ND
		2	Sophisticated equipment, e.g. induction ovens with APCS	0.1	ND	ND	ND	ND
	I		**Magnesium production**					
		1	Using MgO/C thermal treatment in Cl2, no effluent treatment, poor APCS	250	9,000	NA	ND	0
		2	Using MgO/C thermal treatment in Cl2, comprehensive pollution control	50	24	NA	ND	9,000
		3	Thermal reduction process	3	ND	NA	NA	ND
	j		**Thermal Non-ferrous metal production (e.g., Ni)**					
		1	Contaminated scrap, simple or no dust control	100	ND	ND	ND	ND
		2	Clean scrap, good APCS	2	ND	ND	ND	ND
	l		**Shredders**					
		1	Metal shredding plants	0.2	NA	NA	ND	ND
	m		**Thermal wire reclamation**					
		1	Open burning of cable	5,000	ND	ND	ND	ND
		2	Basic furnace with after burner, wet scrubber	40	ND	NA	ND	ND
		3	Burning electric motors, brake shoes, etc., afterburner	3.3	ND	NA	ND	ND

Emission Factors for Category 3 – Power Generation and Heating/Cooking

			Source Categories	Potential Release Route (µg TEQ/TJ)				
Cat.	Subcat.	Class		Air	Water	Land	Products	Residues
3			**Power Generation and Heating**					
	a		**Fossil fuel power plants**					
		1	Fossil fuel/waste co-fired power boilers	35	ND	NA	NA	ND
		2	Coal fired power boilers	10	ND	NA	NA	14
		3	Heavy fuel fired power boilers	2.5	ND	NA	NA	ND
		4	Light fuel oil/natural gas fired power boilers	0.5	ND	NA	NA	ND
	b		**Biomass Power Plants**					
		1	1. Other biomass fired power boilers	500	ND	NA	NA	ND
		2	2. Wood fired power boilers	50	ND	NA	NA	15
	c		**Landfill and biogas combustion**					
		1	Biogas-fired boilers, motors/turbines and flaring	8	ND	NA	NA	NA
	d		**Household heating and cooking - Biomass**					
		1	Contaminated wood/biomass fired stoves	1,500	ND	NA	NA	2,000
		2	Virgin wood/biomass fired stoves	100	ND	NA	NA	20
	e		**Domesting heating - Fossil fuels**					ng TEQ/kg Ash
		1	Coal fired stoves	70	ND	NA	NA	5,000
		2	Oil fired stoves	10	ND	NA	NA	ND
		3	Natural gas fired stoves	1.5	ND	NA	NA	ND

Emission Factors for Category 4 – Production of Mineral Products

			Source Categories	Potential Release Route (µg TEQ/t)				
Cat.	Subcat.	Class		Air	Water	Land	Products	Residues
4			**Production of Mineral Products**					
	a		**Cement kilns**					
		1	Wet kilns, ESP temperature >300 °C	5	NA	ND	ND	1
		2	Wetkilns, ESP/FF temperature 200 to 300 °C	0.6	NA	ND	ND	0.1
		3	Wet kilns, ESP/FF temperature <200 °C and all types of dry kilns	0.05	NA	ND	ND	0.003
	b		**Lime**					
		1	Cyclone/no dust control	10	ND	ND	ND	ND
		2	Good dust abatement	0.07	ND	ND	ND	ND
	c		**Brick**					
		1	Cyclone/no dust control	0.2	NA	ND	ND	ND
		2	Good dust abatement	0.02	NA	ND	ND	ND
	d		**Glass**					
		1	Cyclone/no dust control	0.2	NA	ND	ND	ND
		2	Good dust abatement	0.015	NA	ND	ND	ND
	e		**Ceramics**					
		1	Cyclone/no dust control	0.2	NA	ND	ND	ND
		2	Good dust abatement	0.02	NA	ND	ND	ND
	f		**Asphalt mixing**					
		1	Mixing plant with no gas cleaning	0.07	NA	ND	ND	ND
		2	Mixing plant with fabric filter, wet scrubber	0.007	NA	ND	ND	0.06

Emission Factors for Category 5 – Transport

			Source Categories	Potential Release Route (µg TEQ/t)				
Cat.	Subcat.	Class		Air	Water	Land	Products	Residues
5			**Transport**					
	a		**4-Stroke engines**					
		1	Leaded fuel	2.2	NA	NA	NA	ND
		2	Unleaded fuel without catalyst	0.1	NA	NA	NA	ND
		3	Unleaded fuel with catalyst	0.00	NA	NA	NA	NA
	b		**2-Stroke engines**					
		1	Leaded fuel	3.5	NA	NA	NA	ND
		2	Unleaded fuel without catalyst	2.5	NA	NA	NA	ND
	c		**Diesel engines**					
		1	Diesel engines	0.1	NA	NA	NA	ND
	d		**Heavy oil fired engines**					
		1	All types	4	NA	NA	NA	ND

Emission Factors for Category 6 – Uncontrolled Combustion Processes

			Source Categories	Potential Release Route (µg TEQ/t)				
Cat.	Subcat.	Class		Air	Water	Land	Products	Residues
6	**6**		**Uncontrolled Combustion Processes**					
	a		**Fires/burnings - biomass**					
		1	Forest fires	5	ND	4	NA	ND
		2	Grassland and moor fires	5	ND	4	NA	ND
		3	Agricultural residue burning (in field), not impacted	0.5	ND	10	NA	ND
		4	Agricultural residue burning (in field), impacted, poor combustion conditions	30	ND	10	NA	ND
	b		**Fires, waste burning, landfill fires, industrial fires, accidental fires**					
		1	Landfill fires	1,000	ND	NA	NA	ND
		2	Accidental fires in houses, factories (per event)	400	ND	See residu	NA	400
		3	Uncontrolled domestic waste burning	300	ND	See residu	NA	600
		4	Accidental fires in vehicles (per vehicle)	94	ND	See residu	NA	18
		5	Open burning of wood (construction/demolition)	60	ND	ND	NA	10

Emission Factors for Category 7 – Production and Use of Chemicals and Consumer Goods

			Source Categories	Potential Release Route (µg TEQ/t)				
Cat.	Subcat.	Class		Air	Water	Land	Products	Residues
7			**Production of Chemicals, Consumer Goods**					
	a		**Pulp and paper mills**					
			Boilers (per ton of pulp)					
		1	Black liquor boilers, burning of sludges, wood	0.07				1000
		2	2. Bark boilers only	0.4				1000
			Sludges	Water		Residue		
				µg TEQ/ADt	µg TEQ/L	µg TEQ/ADt	µg TEQ/t sludge	
		1	Kraft process, old technology (Cl2)	4.5	70	4.5	100	
		2	Kraft process, modern technology (ClO2)	0.06	2	0.2	10	
		3	TMP pulp					
		4	Recycling pulp					
			Pulp and paper	Air	Water	Land	Products	Residues
		1	Kraft pulps/papers from primary fibers, Cl2				8	
		2	Sulfite papers, old technology (Cl2)				1	
		3	Kraft papers, new technology (ClO2, TCF), unbleached papers				0.5	
		4	Sulfite papers, new technology (ClO2, TCF)				0.1	
		5	Recycling paper				10	
	b		**Chemical industry**	Air	Water	Land	Products	Residues
			PCP					
		1	European, American production (chlorination of phenol with Cl2)				2,000,000	
		2	Chinese production (thermolysis of HCH)				800,000	
		3	PCP-Na				500	
			PCB	Air	Water	Land	Products	Residues
		1	Low chlorinated, e.g., Clophen A30, Aroclor 1242				15,000	
		2	Medium chlorinated, e.g., Clophen A40, Aroclor 1248				70,000	
		3	Medium chlorinated, e.g., Clophen A50, Aroclor 1254				300,000	
		4	High chlorinated, e.g., Clophen A60, Aroclor 1260				1,500,000	
			Chlorinated Pesticides	Air	Water	Land	Products	Residues
		1	Pure 2,4,5-Trichlorophenoxy acetic acid (2,4,5-T)				7,000	
		2	2,4,6-Trichlorophenol (2,4,6-PCPh)				700	
		3	Dichlorprop				1,000	
		4	2,4-Dichlorophenoxy acetic acid (2,4-D)				700	
		5	2,4,6-Trichlorophenyl-4'-nitrophenyl ether (CNP = chloronitrofen)					
			Old technology				300,000	
			New technology				400	
		6	Chlorobenzens				ND	ND
		7	Chlorine production with graphite anodes				NA	ND
			Chloranil	Air	Water	Land	Products	Residues
		1	*p* -chloranil *via* chlorination of phenol				400,000	
		2	*p* -chloranil *via* hydrochinone				100	
		3	Dyestuffs on chloranil basis (old process, Class 1)				1,200	
		4	*o* -chloranil *via* chlorination of phenol				60,000	
			ECD/VCM/PVC	Air	Water	Land	Products	Residues
		1	Old technology, EDC/VCM, PVC		1			
		2	Modern plants					
			EDC/VCM and/or EDC/VCM/PVC	0.95	0.015		0.03	2
			PVC only	0.0003	0.03		0.1	0.2
	c		**Petroleum refineries**	Air	Water	Land	Products	Residues
		1	All types	ND	NA	NA	NA	ND
	d		**Textile plants**	Air	Water	Land	Products	Residues
		1	Upper limit	NA	ND	NA	100	ND
		2	Lower limit	NA	ND	NA	0.1	ND
	e		**Leather plants**	Air	Water	Land	Products	Residues
		1	Upper limit	NA	ND	NA	1,000	ND
		2	Lower limit	NA	ND	NA	10	ND

Emission Factors for Category 8 – Miscellaneous

Cat.	Subcat.	Class		Air	Water	Land	Products	Residues
8			**Miscellaneous**					
	a		**Drying of biomass**					
		1	Clean wood	0.007	NA	ND	0.1	ND
		2	Green fodder	0.1	NA	ND	0.1	ND
		3	PCP- or otherwise treated biomass	10	NA	ND	0.5	ND
	b		**Crematoria**					
		1	No control	90	NA	NA	NA	ND
		2	Medium control	10	NA	NA	NA	2.5
		3	Optimal control	0.4	NA	NA	NA	2.5
	c		**Smoke houses**					
		1	Treated wood, waste fuels used as fuel	50	NA	ND	ND	see wood
		2	Clean fuel, no afterburner	6	NA	ND	ND	com-
		3	Clean fuel, afterburner	0.6	NA	ND	ND	bustion
	d		**Dry cleaning residues**					
		1	Heavy textiles, PCP-treated, etc.	NA	NA	NA	NA	3,000
		2	Normal textiles	NA	NA	NA	NA	50
	e		**Tobacco smoking ***					
		1	Cigar (per item)	0.3	NA	NA	NA	NA
		2	Cigarette (per item)	0.1	Na	NA	NA	NA
8			**Miscellaneous**					

Emission Factors for Category 9 – Disposal / Landfill

			Source Categories	Potential Release Route (µg TEQ/t)				
Cat.	Subcat.	Class		Air	Water	Land	Products	Residues
9			**Disposal/Landfill**					
	a		**Landfill leachate**					
		1	Hazardous waste *	NA	200	NA	NA	
		2	Non-hazardous waste *	NA	30	NA	NA	
	b		**Sewage/sewage treatment**					
		1	Industrial, mixed domestic with chlorine relevance					
			No sludge removal		5	NA	NA	1,000
			With sludge removal		0.5	NA	NA	1,000
		2	Urban environments					
			No sludge removal		2	NA	NA	100
			With sludge removal		0.5	NA	NA	100
		3	Remote and residential or modern treatment plant		0.1	NA	NA	10
	c		**Open water dumping**					
		1	Mixed domestic and industrial inputs	NA	5	NA	NA	NA
		2	Urban environments	NA	0.5	NA	NA	NA
		3	Remote environments or input control	NA	0.1	NA	NA	NA
	d		**Composting**					
		1	All organic fraction	NA	ND	NA	100	NA
		2	Garden, kitchen wastes	NA	ND	NA	15	NA
		3	Green materials,not impacted environments	NA	ND	NA	5	NA
	e		**Waste oil disposal**					
		1	All fractions	ND	ND	ND	ND	ND
9			**Disposal/Landfill**					

Emission Factors for Category 10 – Identification of Hot Spots

Class		Product (µg TEQ/t)	Occurrence (t)	g TEQ identified				
				Air	Water	Land	Product	Residue
	Identification of Hot Spots			x indicates need for site-specific evaluation				
	Production sites of chlorinated organics							
1	Chlorophenols and derivatives or PCB				x	x		
2	Other chlorinated organics					x		
	Production sites of chlorine							
1	with graphite electrodes				x	x		
2	without graphite electrodes				x	x		
	Formulation of chlorinated phenols/pesticides				x	x		
	Application sites of dioxin-contaminated pesticides					x		
	Timber manufacture							
1								
	Using pentachlorophenol, other dioxin-containing preservatives				x	x		
2	No use of PCP, not open to the environment				x	x		
	PCB containing equipment		**0**				**0**	
	Low chlorinated, e.g., Clophen A30, Aroclor 1242	15,000					**0**	
	Medium chlorinated, e.g., Clophen A40, Aroclor 1248	70,000					**0**	
	Medium chlorinated, e.g., Clophen A50, Aroclor 1254	300,000					**0**	
	High chlorinated, e.g., Clophen A60, Aroclor 1260	1,500,000					**0**	
1	Leaching				x	x		
2	Not leaching				x	x		
	Dumps of waste/residues from categories 1-9				x	x		
	Sites of relevant accidents				x	x		
	Dredging of sediments				x	x		

9 ANNEX 2: QUESTIONNAIRES

This Chapter presents sample questionnaires, which can be used to compile plant, process or activity specific data. The questionnaires will also be provided in electronic form on UNEP's Web Page for download. The purpose of the questionnaires and how to work with the questionnaires are explained in Chapters 4.3 and 4.4.

Category-specific questionnaires should be accompanied by a cover sheet clearly stating the sender (with all necessary coordinates), context with, *e.g.*, reference year, and return date for the questionnaire.

Questionnaires have been designed for each category (for some categories, the same questionnaires can be used).

Sample cover sheet for questionnaire

PCDD/PCDF (Dioxin and Furan) Release Inventory **Reference Year 20___** (January 1-December 31)	
Requested by:	[Institution's name with street address; contact person with phone and fax number; e-mail address]
To:	[Institution's name with street address and other coordinates]
Please return the completed questionnaire to the above sender not later than	_____ (Date)

Questionnaire 1: Category 1 - Waste Incineration

Type of Plant	Municipal solid waste Industrial waste Hospital waste Light shredder Sewage sludge Waste wood and waste biomass Animal carcasses	[ ] [ ] [ ] [ ] [ ] [ ] [ ]
Name of Plant		
Location (City/Province)		
Address		
Contact (Name, position, phone and fax numbers, e-mail)		
Number of Furnaces		
Type of Operation	Batch (*e.g.*, 100 kg per batch) Semi-continuous (*e.g.*, 8 hours per day) Continuous (24 hours per day)	[ ] [ ] [ ]
Annual Operational/Capacity (per Unit)	t/h (tons per hour) h/d (hours per day) d/w (days per week) t/d (tons per day) d/a (days per year) h/a (hours per year) t/a (tons per year)	
Annual Operation/Capacity (total)	t/h (tons per hour) h/d (hours per day) d/w (days per week) t/d (tons per day) d/a (days per year) h/a (hours per year) t/a (tons per year)	
Type of Furnace	Mass burn waterwall (grate) Fluidized bed Stoker Rotary kiln Other (please specify)	
Temperature in Furnace	Main furnace (°C) Afterburner/second chamber (°C)	

Type of Air Pollution Control System (APCS)	Electrostatic precipitator	[ ]
	Cyclone	[ ]
	Bag filter	[ ]
	Wet scrubber	[ ]
	Dry scrubber	[ ]
	Lime injection	[ ]
	NaOH/alkali injection	[ ]
	Active carbon/coke injection	[ ]
	Active carbon filter	[ ]
	Catalytic converter (SCR)	[ ]
	Induced or forced draft fan	[ ]
	Other (please specify)	
	None	[ ]
Heat Recovery System	Yes [ ]	No [ ]
Temperature of Gases	At entry to APCS (°C) [ ]	At exit from APCS (°C) [ ]
Flux of Exit Gases	(m^3/h) (dry gas)	

Residues		Disposal of these Residues	
Generation of Bottom Ashes	t/a [ ]	Recirculation [ ]	Landfill [ ]
Generation of Fly Ashes	t/a [ ]	Recirculation [ ]	Landfill [ ]
Generation of (Waste)Water	t/a [ ]	Disposal	
Generation of Sludges (as dry matter)	t/a [ ]	Recirculation [ ]	Landfill [ ]

Final classification and evaluation (to be filled out by the data evaluator)

	Emission Factor (µg TEQ/t)				
Class	**Air**	**Water**	**Land**	**Product**	**Residues**
	Annual Release (g TEQ/a)				
Annual Activity (t/a)	**Air**	**Water**	**Land**	**Product**	**Residues**

Questionnaire 2: Category 2 – Ferrous and Non-Ferrous Metal Production

Type of Plant	Sinter	[ ]	
	Coke	[ ]	
	Iron and/or steel	Primary [ ]	Secondary [ ]
	Foundry	Primary [ ]	Secondary [ ]
	Copper	Primary [ ]	Secondary [ ]
	Aluminum	Primary [ ]	Secondary [ ]
	Lead	Primary [ ]	Secondary [ ]
	Zinc	[ ]	
	Brass/Bronze	Primary [ ]	Secondary [ ]
	Magnesium	[ ]	
	Other non-ferrous metal	Primary [ ]	Secondary [ ]
	Shredder	[ ]	
	Other	Primary [ ]	Secondary [ ]
Address			
Contact (Name, position, phone and fax numbers, e-mail)			
Number of Furnaces			
Type of Operation	Batch (*e.g.*, 100 kg per batch) Semi-continuous (*e.g.*, 8 hours per day) Continuous (24 hours per day)		[ ] [ ] [ ]
Annual Operational/Capacity (per Unit)	t/h (tons per hour) h/d (hours per day) d/w (days per week) t/d (tons per day) d/a (days per year) h/a (hours per year) t/a (tons per year)		
Annual Operation/Capacity (total)	t/h (tons per hour) h/d (hours per day) d/w (days per week) t/d (tons per day) d/a (days per year) h/a (hours per year) t/a (tons per year)		
Type of Furnace	Blast furnace Induction furnace Electric arc furnace (EAF) Cowper Rotary kiln Reverberatory Other (please specify)		
Temperature in Furnace	Main furnace (°C) Second chamber/afterburner (°C)		
Primary Fuel	Type		t/a
Secondary/Alternative Fuel	Type		t/a or %

Type of Air Pollution Control System (APCS)	Electrostatic precipitator Cyclone Bagfilter Wet scrubber Dry scrubber Lime injection NaOH/alkali injection Active carbon/coke injection Active carbon filter Catalytic converter (SCR) Induced or forced draft fan Other (please specify) None	[ ] [ ] [ ] [ ] [ ] [ ] [ ] [ ] [ ] [ ] [ ] [ ]
Heat Recovery System	Yes [ ]	No [ ]
Temperature of Gases	At entry to APCS (°C) [ ]	At exit from APCS (°C) [ ]
Flux of Exit Gases	(m^3/h) (dry gas)	

Final classification and evaluation (to be filled out by the data evaluator)

	Emission Factor (µg TEQ/t)				
Class	**Air**	**Water**	**Land**	**Product**	**Residues**
	Annual Release (g TEQ/a)				
Annual Activity (t/a)	**Air**	**Water**	**Land**	**Product**	**Residues**

Questionnaire 3: Category 3 – Power Generation and Heating

Type of Plant	**Power plants**	
	Coal Lignite Bituminous coal Anthracite Other	[ ] [ ] [ ] [ ]
	Natural gas	[ ]
	Wood	[ ]
	Landfill gas	[ ]
	Sewer gas	[ ]
	Biomass (please specify)	
	Industrial Combustion units (small)	
	Coal (please specify) Lignite Bituminous coal Anthracite Other	[ ] [ ] [ ] [ ]
	Natural wood	[ ]
	Combustion of other kinds of biomass Sugar cane Tapioka Cotton Bamboo Banana Harvest residues Other (please specify)	 [ ] [ ] [ ] [ ] [ ] [ ] [ ]
	Other (please specify)	
Address		
Contact (Name, position, phone and fax numbers, e-mail)		
Type of Operation	Batch (*e.g.*, 100 kg per batch) Semi-continuous (*e.g.*, 8 hours per day) Continuous (24 hours per day)	[ ] [ ] [ ]
Annual Operation/Capacity (per Unit)	t/h (tons per hour) or TJ/h (Terajoule per hour) h/d (hours per day) d/w (days per week) t/d (tons per day) or TJ/h (Terajoule per day) d/a (days per year) h/a (hours per year) t/a (tons per year) or TJ/h (Terajoule per year)	
Annual Operation/Capacity (total)	d/a (days per year) h/a (hours per year) TJ/a (Terajoule per year)	
Type of Furnace/Combustor	Boiler Process heater Flare Turbine (internal gas) Combustion engine (internal) Other (please specify)	

Temperature in Furnace	Main furnace (°C) Second chamber/afterburner (°C)	
Type of Abatement Pollution Control System (APCS)	Electrostatic precipitator Cyclone Bughouse filter Wet scrubber Dry scrubber Lime injection NaOH/alkali injection Active carbon/coke injection Active carbon filter Catalytic converter (SCR) Other (please specify) None	[ ] [ ] [ ] [ ] [ ] [ ] [ ] [ ] [ ] [ ] [ ]
Heat Recovery System	Yes [ ]	No [ ]
Temperature of Gases	At entry to APCS (°C) [ ]	At exit from APCS (°C) [ ]
Flux of Exit Gases	(m^3/h) (dry gas)	

Final classification and evaluation (to be filled out by the data evaluator)

	Emission Factor (µg TEQ/t)				
Class	**Air**	**Water**	**Land**	**Product**	**Residues**
	Annual Release (g TEQ/a)				
Annual Activity (t/a)	**Air**	**Water**	**Land**	**Product**	**Residues**

Questionnaire 4: Category 4 – Mineral Production

Type of Plant	Cement Lime Brick Glass Ceramics Asphalt mixing	[ ] [ ] [ ] [ ] [ ] [ ]
Address		
Contact (Name, position, phone and fax numbers, e-mail)		
Number of Furnaces		
Feed Materials (type, quantity = t/a)		
Primary Fuel (type, quantity = t/a)		
Secondary/Alternative Fuel (type, quantity = t/a)		
Type of Process	Dry [ ]	Wet [ ]
Type of Operation	Batch (*e.g.*, 100 kg per batch) Semi-continuous (*e.g.*, 8 hours per day) Continuous (24 hours per day)	[ ] [ ] [ ]
Annual Operational/Capacity (per Unit)	t/h (tons per hour) h/d (hours per day) d/w (days per week) t/d (tons per day) d/a (days per year) h/a (hours per year) t/a (tons per year)	
Annual Operation/Capacity (total)	t/h (tons per hour) h/d (hours per day) d/w (days per week) t/d (tons per day) d/a (days per year) h/a (hours per year) t/a (tons per year)	
Type of Furnace	Rotary kiln Shaft kiln Tunnel furnace Other (please specify)	
Temperature in Furnace	Main furnace (°C) Second chamber/afterburner (°C)	

Type of Air Pollution Control System (APCS)	Electrostatic precipitator Cyclone Bagfilter Wet scrubber Dry scrubber Lime injection NaOH/alkali injection Active carbon/coke injection Active carbon filter Catalytic converter (SCR) Induced or forced draft fan Other (please specify) None	[ ] [ ] [ ] [ ] [ ] [ ] [ ] [ ] [ ] [ ] [ ] [ ]
Heat Recovery System	Yes [ ]	No [ ]
Temperature of Gases	At entry to APCS (°C) [ ]	At exit from APCS (°C) [ ]
Flux of Exit Gases	(m^3/h) (dry gas)	

Final classification and evaluation (to be filled out by the data evaluator)

	Emission Factor (µg TEQ/t)				
Class	**Air**	**Water**	**Land**	**Product**	**Residues**
	Annual Release (g TEQ/a)				
Annual Activity (t/a)	**Air**	**Water**	**Land**	**Product**	**Residues**

Questionnaire 5: Category 5 – Transport

Region/Province/Nation.			
Address			
Contact (Name, position, phone and fax numbers, e-mail)			
Type of fuel	**Leaded Gasoline**	**Unleaded Gasoline**	**Diesel/Light Fuel Oil**
Annual national fuel consumption in liter per year (L/a)			
Passenger Cars			
Number of vehicles			
Annual road performance per vehicle and kilometer (km/a)			
Fuel consumption (L/km; L/a)			
Total annual consumption (L/a)			
APCS* (Yes/No)			
Busses			
Number of busses			
Annual road performance per vehicle and year (km/a)			
Fuel consumption (L/km; L/a)			
Total annual consumption (L/a)			
Annual consumption in tons per year (t/a)			
APCS (Yes/No)			
Busses and Trucks			
Number of busses			
Annual road performance per vehicle and year (km/a)			
Fuel consumption (L/km; L/a)			
Total annual consumption (L/a)			
Annual consumption in tons per year (t/a)			
APCS (Yes/No)			
Ships			
Number of ships			
Annual performance per vehicle and year (km/a)			
Fuel consumption (L/km; L/a)			
Total annual consumption (L/a)			
Annual consumption in tons per year (t/a)			
APCS (Yes/No)			

Trains			
Number of trains (on any of the above fuels)			
Annual railroad performance per vehicle and year (km/a)			
Fuel consumption (L/km; L/a)			
Total annual consumption (L/a)			
Annual consumption in tons per year (t/a)			
APCS (Yes/No)			

Final classification and evaluation (to be filled out by the data evaluator)

	Emission Factor (µg TEQ/t)				
Class	**Air**	**Water**	**Land**	**Product**	**Residues**
	Annual Release (g TEQ/a)				
Annual Activity (t/a)	**Air**	**Water**	**Land**	**Product**	**Residues**

*APCS: means catalyst for gasoline and particulate removal for Diesel

Questionnaire 6: Uncontrolled Combustion Processes

Region/Province/Nation.						
Address						
Contact (Name, position, phone and fax numbers, e-mail)						
Biomass burning						
Type of biomass, *e.g.,* pine, sugarcane, *etc.*	Amount of biomass per hectare burned (t/ha)		Area burned per hectare and year (ha/a)		Amount of biomass burned in tons per year (t/a)	
1.						
2.						
3.						
4.						
5.						
Total						
Open Waste Burning and Accidental Fires						
General waste statistics						
Tons of waste generated	Per capita and day		Per capita and year		Nationally per year (t)	
Type of source	Amount of waste burned per capita (t/a)		Number of inhabitants		Amount of waste burned per year (t/a)	
	(%)	(t/a)	(%)	(t/a)	(%)	(t/a)
1.) Landfill fires						
2.) Uncontrolled domestic waste burning						
3.) Open burning of wood (construction/ demolition)						
Region/Province/Nation-wide						
	Number of houses burned per year (No/a)		Number of vehicles burned per year (No/a)			
4.) Accidental fires in houses, factories						
5.) Accidental fires in vehicles						

Final classification and evaluation (to be filled out by the data evaluator)

	Emission Factor (µg TEQ/t)				
Class	**Air**	**Water**	**Land**	**Product**	**Residues**
	Annual Release (g TEQ/a)				
Annual Activity (t/a)	**Air**	**Water**	**Land**	**Product**	**Residues**

Questionnaire 7: Category 7 – Production and Use of Chemicals and Consumer Goods (releases into air and into water)

Chemical Industry: Type of Plant	Pulp and paper industry: Pulp Pulp and paper industry: Paper (primary or recycling) Pulp and paper - integrated Organochlorine production Ethylene dichloride PVC Pesticides (PCP, 2,4,5-T, 2,4-D) Production of chlorine gas (graphite electrodes) Petroleum industry refineries	[ ] [ ] [ ] [ ] [ ] [ ] [ ] [ ]
Address		
Contact (Name, position, phone and fax numbers, e-mail)		
Capacity: Consumption of Raw Materials (type, quantity = t/a)		
Capacity: Final Product of Raw Materials (type, quantity = t/a)		
Type of Process	Fixed-bed Fluidized bed Other	[ ] [ ] [ ]
Type of Operation	Batch (*e.g.*, 100 kg per batch) Semi-continuous (*e.g.*, 8 hours per day) Continuous (24 hours per day)	[ ] [ ] [ ]
Annual Operation/Capacity (per Unit)	t/h (tons per hour) h/d (hours per day) d/w (days per week) t/d (tons per day) d/a (days per year) h/a (hours per year) t/a (tons per year)	
Annual Operation/Capacity (total)	t/h (tons per hour) h/d (hours per day) d/w (days per week) t/d (tons per day) d/a (days per year) h/a (hours per year) t/a (tons per year)	
Operation/ Production Temperature	(°C)	
Water discharge (L/h, m^3/a)		

Water treatment	Settling pond Aerated lagoon Secondary treatment Tertiary Treatment Others (please specify)	[ ] [ ] [ ] [ ] [ ]
Sludge generation	t/a (tons per year)	
Sludge disposal	Landfill (t/a) Land farming (t/a) On-site (t/a) Incineration (t/a) Others (please specify) (t/a)	
Type of Air Pollution Control System (APCS)	Electrostatic precipitator Cyclone Bag filter Wet scrubber Dry scrubber Lime injection NaOH/alkali injection Active carbon/coke injection Active carbon filter Catalytic converter (SCR) Induced or forced draft fan Other (please specify) None	[ ] [ ] [ ] [ ] [ ] [ ] [ ] [ ] [ ] [ ] [ ] [ ]
Temperature of Gases	At entry to APCS (°C) [ ]	At exit from APCS (°C) [ ]
Flux of Exit Gases	(m^3/h) (dry gas)	

Final classification and evaluation (to be filled out by the data evaluator)

	Emission Factor (µg TEQ/t)				
Class	**Air**	**Water**	**Land**	**Product**	**Residues**
	Annual Release (g TEQ/a)				
Annual Activity (t/a)	**Air**	**Water**	**Land**	**Product**	**Residues**

10 ANNEX 3: PRESENTATION OF THE INVENTORIES

10.1 Example Tables for the Inventory

Table 75 shows an example with numbers filled into the EXCEL sheet and the annual release data generated by the spreadsheet. In this hypothetical country, there exist facilities to burn municipal, hazardous and medical waste but there is none for light fraction shredder waste, sewage sludge, waste wood or animal carcasses. But note, the Table displays that there is no activity in this sector; in other words the country is aware that these activities are potential dioxin and furan sources, the country has looked into these sources and found out that they do not exist. The country is somewhat advanced in its technology as there is no plant that is operated at the lowest technical standard. The major release vectors are to air with a total of 150 g TEQ per year and with residues, which account for 552 g TEQ per year. The majority of PCDD/PCDF in the residues is due to contamination in the fly ashes. The data for releases to air clearly indicate that the largest contribution to the annual releases is caused by the incineration of 250,000 tons of municipal waste combusted in (perhaps only one) MSWI without state-of-the-art technology. This incinerator emitted 87.5 g TEQ in the reference year whereas the state-of-the-art incinerator that applies BAT and burns twice the mass (500,000 t/a), only releases 0.25 g TEQ in the reference year.

The final product after all steps of the Toolkit have been performed will be a summary table with all release data compiled for the reference year and the country. Such examples are given for countries that have successfully applied the Toolkit from Table 76 to Table 85.

Table 75: Copy of an example table generated by the EXCEL program showing input and output data for releases to air, water, land, in products and residues

Source Categories	Potential Release Route (µg TEQ/t)						Production	Annual release g TEQ/a	Annual release g TEQ/a	Annual release g TEQ/a	Annual release g TEQ/a	Annual release g TEQ/a
					Residues		t/a					
Waste incineration	Air	Water	Land	Products	Fly Ash	Bottom Ash		Air	Water	Land	Fly ash	Bottom Ash
Municipal solid waste incineration							**2750000**	**147.75**	**0**	**0**	**532**	**18.5**
Low technol. combustion, no APC system	3500		NA	NA	0	75					0	
Controlled comb., minimal APC	350		NA	NA	500	15	250000	87.5			125	3.75
Controlled comb., good APC	30		NA	NA	200	7	2000000	60			400	14
High tech. combustion, sophisticated APCS	0.5		NA	NA	15	1.5	500000	0.25			7.5	0.75
Hazardous waste incineration							**1000**	**0.075**	**0**	**0**	**0.414**	**0**
Low technol. combustion, no APC system	35000		NA	NA	9000		0	0			0	0
Controlled comb., minimal APC	350		NA	NA	900		200	0.07			0.18	0
Controlled comb., good APC	10		NA	NA	450		500	0.005			0.225	0
High tech. combustion, sophisticated APCS	0.75		NA	NA	30		300	0.000225			0.009	0
Medical/hospital waste incineration							**2000**	**2.026**	**0**	**0**	**0.995**	**0.01**
Uncontrolled batch combustion, no APCS	40000		NA	NA		200		0			0	0
Controlled, batch, no or minimal APCS	3000		NA	NA		20	500	1.5			0	0.01
Controlled, batch comb., good APC	525		NA	NA	920		1000	0.525			0.92	0
High tech, continuous, sophisticated APCS	1		NA	NA	150		500	0.0005			0.075	0
Light fraction shredder waste incineration *							**0**					
Sewage sludge incineration *							**0**					
Waste wood combustion *							**0**					
Animal carcasses incineration *							**0**					
											534	**18.5**
Waste Incineration							**2753000**	**150**	**0**	**0**	**552**	

* to save space, subcategories are omitted

10.2 National PCDD/PCDF Inventories Made with the Toolkit

Since the release of the DRAFT Toolkit in January 2001, the Toolkit methodology has been applied in many countries. Some of them have finalized work on their inventories. The summary of the results are given from Table 76 to (please note the different units!):

Table 76: PCDD/PCDF release inventory for Uruguay (DINAMA 2002)

	Category	Air	Water	Land	Product	Residue
1	Waste incineration	4.8	0.0	0.0	0.0	0.03
2	Ferrous and non-ferrous metal production	1.25	0.0	0.0	0.0	1.60
3	Energy production	1.14	0.0	0.0	0.0	0.15
4	Mineral products	0.91	0.0	0.0	0.0	0.12
5	Transport	1.36	0.0	0.0	0.0	0.0
6	Uncontrolled combustion	7.65	0.0	1.8	0.0	6.10
7	Chemicals/Pulp	0.004	0.17	0.0	0.6	0.01
8	Miscellaneous	0.016	0.0	0.0	0.0	0.004
9	Waste disposal	0.0	0.2	0.0	0.015	0.075
	Total	17.1	0.4	1.8	0.6	8.1

Table 77: PCDD/PCDF release inventory for Jordan, reference year 2000 (MoE Jordan, 2003)

	Source Categories	Annual Release (g TEQ/a)					
		Air	Water	Land	Product	Residue	Total
1	Waste incineration	4.04	0.0	0.0	0.0	0.3	4.3
2	Ferrous and non-ferrous metal production	0.79	0.0	0.0	0.0	1.9	2.7
3	Power generation and heating	0.46	0.0	0.0	0.0	0.0	0.5
4	Production of mineral products	0.74	0.0	0.0	0.0	0.1	0.8
5	Transport	0.77	0.0	0.0	0.0	0.0	0.8
6	Uncontrolled combustion processes	46.8	0.0	0.0	0.0	3.1	49.9
7	Production of chemicals and consumer goods	0.0	0.0	0.0	0.34	0.0	0.3
8	Miscellaneous	0.001	0.0	0.0	0.0	0.0	0.001
9	Disposal/Landfill	0.014	0.64	0.0	0.0	11.2	11.9
	Total	**53.6**	**0.64**	**0.1**	**0.3**	**16.5**	**71.1**

Table 78: PCDD/PCDF release inventory for Philippines, reference year 1999 (ITDI 2003)

	Source Category	Annual Releases (g TEQ/a)					Total/ Sector
		Air	Water	Land	Product	Residue	
1	Waste Incineration	37.8	0.0	0.0	0.0	3.72	41.6
2	Ferrous and non-ferrous metal production	8.7	0.0	0.0	0.0	1.89	10.6
3	Power Generation, cooking	142.8	0.0	0.0	0.0	14.39	157.2
4	Production of mineral products	2.5	0.0	0.0	0.0	0.04	2.6
5	Transportation	0.12	0.0	0.0	0.0	0.0	0.1
6	Uncontrolled combustion processes	135.5	0.0	46.9	0.0	4.73	187.1
7	Production of chemicals and consumer goods	0.0	0.605	0.0	77.6	13.32	91.6
8	Miscellaneous	0.23	0.0	0.0	0.0	0.001	0.23
9	Disposal/Landfilling	0.0	43.20	0.0	0.0	0.0	43.2
10	Identification of potential hot-spots						
	Total	**327.7**	**43.80**	**46.9**	**77.6**	**38.1**	**534.1**

Table 79: PCDD/PCDF release inventory for Brunei Darussalam; reference year 2001 (DEPR 2003)

Cat.	Source Categories	Annual Release (mg TEQ/a)					
		Air	Water	Land	Product	Residue	Total/All media*
1	Waste Incineration	585.0	-	-	-	3.9	588.9
2	Ferrous and non-ferrous metal production	0.09	0.002	0	0	0	0.09
3	Power generation and heating	23.0	-	-	-	-	23.0
4	Production of mineral products	18.9	-	-	42.80	-	61.7
5	Transport	67	-	-	-	-	67.0
6	Uncontrolled combustion processes	48.5	-	30.9	-	0.8	80.2
7	Production of chemicals, consumer goods	0	0	0	0	0	0
8	Miscellaneous	6.7	-	-	-	0.01	6.8
9	Disposal/Landfill	-	23.0	-	0.050	550.8	573.8
10	Identification of Hot Spots						
1- 9	**Total**	**749.2**	**23.0**	**30.9**	**42.85**	**555.0**	**1401**

* Total of all releases from each subcategory

Table 80: PCDD/PCDF release inventory for Lebanon; reference year 1999/2001 (MoE Lebanon 2003)

	Source Categories	Annual Releases (g TEQ/a)					
Cat.		Air	Water	Land	Products	Residue	Total
1	Waste Incineration	11.6	0.0	0.0	0.0	0.1	11.6
2	Ferrous and non-ferrous metal production	1.9	0.0	0.0	0.0	4.0	5.90
3	Power generation and heating	0.35	0.0	0.0	0.0	0.0	0.35
4	Production of mineral products	0.52	0.0	0.0	0.0	0.0	0.55
5	Transportation	2.46	0.0	0.0	0.0	0.0	2.46
6	Uncontrolled combustion processes	21.0	0.0	0.055	0.0	33.0	54.04
7	Production of chemicals and consumer goods	0.70	0.0	0.0	0.024	0.0	0.75
8	Miscellaneous	0.0	0.0	0.0	0.0	0.0	0.0
9	Disposal/Landfilling	0.035	0.964	0.0	0.781	0.0	1.78
10	Identification of potential Hot-Spots						
1-9	**Total**	**38.5**	**1.0**	**0.1**	**0.8**	**37.1**	**77.5**

Table 81: Preliminary PCDD/PCDF release inventory for Thailand, reference year 1999 (PCD 2002)

Cat.	Source Categories	Annual Releases (g TEQ/a)				
		Air	Water	Land	Product	Residue
1	Waste Incineration	247.2	0	0	0	30
2	Ferrous and non-ferrous metal production	20.4	0	0	0	1
3	Power generation and heating	40.2	0	0	0	0
4	Production of mineral products	10.0	0	0	0	0.14
5	Transport	7.3	0	0	0	0
6	Uncontrolled combustion processes	632.3	0	0	0	292
7	Prod. of chemicals, consumer goods	0.4	1.35	0	8.4	382
8	Miscellaneous	27.2	0	0	0	0
9	Disposal/Landfill	0	0	0	0	0
1- 9	Total	985	1.4	0	8.4	705

Table 82: PCDD/PCDF release inventory for Poland, reference year 2000 *. ** (Lassen *et al.* 2003)

Cat.	Source Categories	Annual Releases (g TEQ/a)				
		Air	Water	Land	Product	Residue
1	Waste Incineration	140				86
2	Ferrous+non-ferrous metal production	80	0.05?	?		140?
3	Power generation and heating	62		?	?	55
4	Production of mineral products	18				0.63?
5	Transport	3.6				?
6	Uncontrolled combustion processes	180		6.6?		2101.1??
7	Prod. of chemicals, consumer goods	0.07	0.04?		11	0.1?
8	Miscellaneous	1.7			0.14?	35
9	Disposal/Landfill	?	1.1?		0.03	?
1- 9	Total	490	1.2?	6.6?	11?	530?

- * Most of the estimates were obtained through application of the Toolkit; a few base on own measured data

** only medians given; original publication lists ranges for releases to air, water and product.
an empty field indicates that the release route is considered to be insignificant
? indicates that the release route may be significant, but no emission factor was available
? behind a number indicates that the number may be underestimated as some subcategories have not been quantified

Table 83: PCDD/PCDF release inventory for Estonia, reference year 2000 (Lassen *et al.* 2003)

Cat.	Source Categories	Annual Releases (g TEQ/a)				
		Air	Water	Land	Product	Residue
1	Waste Incineration	0.19				0.47
2	Ferrous and non-ferrous metal production					
3	Power generation and heating	4.9				5.8
4	Production of mineral products	0.39			?	0.06?
5	Transport	0.04				?
6	Uncontrolled combustion processes	8.1	?	0.12?		4.4?
7	Production of chemicals, consumer goods	0.004?	0.15		0.03	0.6?
8	Miscellaneous	0.04			0.002	0.009?
9	Disposal/Landfill					3.9
10	Identification of Hot Spots	?				
1- 9	Total	14?	0.15?	0.12?	003?	15?

* only medians given; original publication lists ranges for releases to air, water and product
an empty field indicates that the release route is considered to be insignificant
? indicates that the release route may be significant, but no emission factor was available
? behind a number indicates that the number may be underestimated as some subcategories have not been quantified

Table 84: PCDD/PCDF release inventory for Latvia, reference year 2000 (Lassen *et al.* 2003)

Cat.	Source Categories	Annual Releases (g TEQ/a)				
		Air	Water	Land	Product	Residue
1	Waste Incineration	0.98				0.28
2	Ferrous + non-ferrous metal production	1.5	?	?	?	7.0?
3	Power generation and heating	3.1				0.72
4	Production of mineral products	0.51	?	?	?	0.01?
5	Transport	0.05				?
6	Uncontrolled combustion processes	16	?	0.24		22
7	Prod. of chemicals, consumer goods					0.004
8	Miscellaneous	0.02		?		2.0
9	Disposal/Landfill		0.18			2.0
10	Identification of Hot Spots	?	?	?		
1- 9	Total				?	32?

* only medians given; original publication lists ranges for releases to air and water
an empty field indicates that the release route is considered to be insignificant
? indicates that the release route may be significant, but no emission factor was available
? behind a number indicates that the number may be underestimated as some subcategories have not been quantified

Table 85: PCDD/PCDF release inventory for Lithuania, reference year 2000 (Lassen *et al.* 2003)

Cat.	Source Categories	Annual Releases (g TEQ/a)				
		Air	Water	Land	Product	Residue
1	Waste Incineration	0.36?				
2	Ferrous + non-ferrous metal production	0.09	?		?	
3	Power generation and heating	2.6				
4	Production of mineral products	0.38	?		?	
5	Transport	0.07				?
6	Uncontrolled combustion processes	14	?	0.29?		
7	Prod. of chemicals, consumer goods	?	?		0.42	?
8	Miscellaneous	0.08			0.00004?	
9	Disposal/Landfill		0.1?		0.02?	
10	Identification of Hot Spots	?	?	?		
1- 9	Total	17?	0.1?	0.29?	0.43?	18?

* only medians given; the original publication also lists ranges for releases to air, water and product

an empty field indicates that the release route is considered to be insignificant

? indicates that the release route may be significant, but no emission factor was available

? behind a number indicates that the number may be underestimated as some subcategories have not been quantified

11 TECHNICAL ANNEXES

11.1 Toxicity Equivalency Factors (TEFs)

Many regulatory agencies have developed so-called Toxicity Equivalency Factors (TEF) for risk assessment of complex mixtures of PCDD/PCDF. The TEFs are based on acute toxicity values from *in vivo* and *in vitro* studies. This approach is based on the evidence that there is a common, receptor-mediated mechanism of action for these compounds. However, the TEF approach has its limitations due to a number of simplifications. Although the scientific basis cannot be considered as solid, the TEF approach has been developed as an administrative tool and allows to convert quantitative analytical data for individual PCDD/PCDF congeners into a single Toxic Equivalent (TEQ). TEF particularly aid in expressing cumulative toxicity of complex PCDD/PCDF mixtures as one single TEQ value. It should be noted that TEFs are interim values and administrative tools for order of magnitude estimates. They are based on present state of knowledge and should be revised as new data gets available.

Today there are two schemes applied: the older one are the TEFs established by a NATO/CCMS Working Group on Dioxins and Related Compounds as International Toxicity Equivalency Factors (I-TEF) (NATO/CCMS 1988, Kutz *et al.* 1990) and the most recent scheme established by a WHO/IPCS working group, who re-evaluated the I-TEFs and established a new scheme. The two schemes are found in Table 86. Here, we only show the TEFs for human and mammalian risk assessment although the WHO/IPCS group also included *non-ortho* and *mono-ortho* substituted polychlorinated biphenyls (PCB) into the TEF and established separate TEFs for fish and birds (van Leeuwen and Younes 1998).

Table 86: Toxicity Equivalency Factors (TEFs) – comparison of the two most commonly used schemes

Congener	I-TEF	WHO-TEFs
2,3,7,8-Cl_4DD	1	1
1,2,3,7,8-Cl_5DD	0.5	**1**
1,2,3,4,7,8-Cl_6DD	0.1	0.1
1,2,3,7,8,9-Cl_6DD	0.1	0.1
1,2,3,6,7,8-Cl_6DD	0.1	0.1
1,2,3,4,6,7,8-Cl_7DD	0.01	0.01
Cl_8DD	0.001	**0.0001**
2,3,7,8-Cl_4DF	0.1	0.1
1,2,3,7,8-Cl_5DF	0.05	0.05
2,3,4,7,8-Cl_5DF	0.5	0.5
1,2,3,4,7,8-Cl_6DF	0.1	0.1
1,2,3,7,8,9-Cl_6DF	0.1	0.1
1,2,3,6,7,8-Cl_6DF	0.1	0.1
2,3,4,6,7,8-Cl_6DF	0.1	0.1
1,2,3,4,6,7,8-Cl_7DF	0.01	0.01
1,2,3,4,7,8,9-Cl_7DF	0.01	0.01
Cl_8DF	0.001	**0.0001**

For all non-2,3,7,8-substituted congeners, no TEF has been assigned.
Numbers in bold represent TEFs, which have been changed by WHO from the I-TEFs.

11.2 Usage of Units in Air Emissions

When reporting air concentrations care must be taken with respect to the base units given. The following definitions apply:

m^3	Cubic meter: is the SI unit of volume and may be used to express the volume of any substance, whether solid, liquid, or gas
Nm^3	Normal cubic meter: refers to the volume of any gas at 0 °C and 1 atm (101.325 kPa) In European countries and for emissions from municipal waste incinerators (also co-combustion of waste): Nm^3 is defined at the following conditions: 101.325 kPa (= 1 atm), 273.15 K, dry gas, and 11 % oxygen. For emissions from other types of combustion/thermal plants, there is no requirement to normalize to 11 % oxygen.
Rm^3 in Canada:	Reference cubic meter. When using R, the conditions are 25 °C, 1 atm, dry. The need for oxygen correction should be explicitly stated, although it sometimes is not. The Canada-wide standard utilizes are correction to 11 % oxygen for incinerators and coastal pulp and paper mill boilers burning salt-laden wood residue. For others sectors such as sinter plants, they have decided to use no oxygen correction.
Sm^3 in U.S.A.:	Is the dry standard cubic meter (represented as dscm) at 1 atmosphere of pressure and 20 degrees Celsius (68 degrees F). The contaminant concentration is corrected to some standard percent oxygen or carbon dioxide in the combustion gases, usually 7 % oxygen and 12 % carbon dioxide.

11.3 Heating Values – For Main Category 3

In the Main Source category 3, the basis for reporting default emission factors is the energetic output. For this, the Toolkit refers to TJ (Terajoules) and not to the mass of 1 ton of feed material. In cases, only mass consumption data will be available, the following tables have been generated to provide an indicative list to relate masses (in kg) to heat outputs (in MJ).

Table 87: Heating values for coal

Type of Coal	Heating Value
Anthracite, Germany	27–35 MJ/kg depending on the mine
Bituminous coal, France	32–34 MJ/kg
Bituminous coal, USA	31–32 MJ/kg
Anthracite, Russia	30 MJ/kg (Donez Bay)
Bituminous coal, Germany	29–32 MJ/kg
Bituminous coal, China	25–27 MJ/kg
Sub-bituminous coal, Spain	16–17 MJ/kg
Sub-bituminous coal, Croatia	13–15 MJ/kg
Sub-bituminous coal, Turkey	12–14 MJ/kg
Lignite/brown coal, Central Germany	10–12 MJ/kg
Lignite/brown coal, Czech Republic	9–11 MJ/kg
Lignite/brown coal, West Germany	8–10 MJ/kg
Lignite/brown coal, Australia	8–9 MJ/kg
Lignite/brown coal, East Germany	7–9 MJ/kg
Lignite/brown coal, Greece	4–6 MJ/kg

Table 88: Heating values for coke

Type of Coke	Heating Value
Swell coke, Czech Republic	31–32 MJ/kg
Anthracite coke, Germany	28–30 MJ/kg
Lignite coke, Germany	27–28 MJ/kg
Swell coke, Germany	23–25 MJ/kg

Table 89: Heating values for oil

Type of Oil	Heating Value
Gasoline	44–47 MJ/kg
Light fuel oil/Diesel fuel	43–46 MJ/kg
Heavy fuel oil	40–43 MJ/kg
Lignite tar oil	38–40 MJ/kg
Anthracite tar oil	37–39 MJ/kg
Methyl alcohol	20–23 MJ/kg

Table 90: Heating values for gas

Type of Gas	Heating Value
Methane	50–55 MJ/kg
Natural gas, North Sea – Great Britain	48–53 MJ/kg
Natural gas, North Sea-Germany	47–52 MJ/kg
Propane	46–50 MJ/kg
Natural gas class H	44–49 MJ/kg
Natural gas class L	40–45 MJ/kg
Natural gas, The Netherlands	38–44 MJ/kg
Methanol	20–23 MJ/kg
Carbon monoxide	10–11 MJ/kg
For a first estimate, mean values should be applied as follows	
Natural gas	48 MJ/kg
LPG (mean heating value)	46 MJ/kg

Table 91: Heating values for wood

Type of Wood	Heating Value
Spruce, air dry	14–17 MJ/kg
Poplar, air dry	15–16 MJ/kg
Beech, air dry	13–15 MJ/kg
Beech, green	12–13 MJ/kg
Beech bark	11–13 MJ/kg
Spruce bark	10–12 MJ/kg

Table 92: Heating values for biomass

Type of Biomass	Heating Value
Coconut shells	17–19 MJ/kg
Almond shells	17–19 MJ/kg
Peat Pellets	15–18 MJ/kg
Peat, Germany	15–17 MJ/kg
Straw (wheat)	15–17 MJ/kg
Coconut fibers	14–16 MJ/kg
Rice husks	14–15 MJ/kg
Coffee roasting residue	9–11 MJ/kg
Peat, Finland	9–11 MJ/kg
Bagasse	8–10 MJ/kg
Peat, Spain	1–3 MJ/kg

11.4 Conversion Factors for Liquid and Gaseous Fuels – For Main Categories 3 and 5

Very often, consumption numbers for gasoline and Diesel in transportation or crude oil in the energy sector may be given in liters (L). Further, consumption numbers for gaseous fuels, such as natural gas, may be given in cubic meters (m^3). For the Toolkit, these volumes have to be converted into tons or heating values; these are provided in Section 11.2. To assist in the use of the Toolkit, mean heating values are also given in this section. For the purpose of the Toolkit:

1 L of gasoline has a mass of about 0.74 kg; thus, a conversion factor of 0.00074 must be used to convert liters of gasoline into tons;

1 L of (normal) Diesel fuel (for automobiles, trucks, *etc.*) and/or light fuel oil (including heating oil) has a mass of about 0.85 kg; thus, a conversion factor of 0.00085 must be used to convert liters of Diesel and/or light fuel oil into tons;

1 L of heavy duty fuel has a mass of about 0.970 kg; thus, a conversion factor of 0.00097 must be used to convert liters of heavy duty fuel into tons;

1 m^3 of natural gas has a mass between 0.77 and 0.85 kg; with a mean of 0.8 kg; thus, a conversion factor of 0.0008 must be used to convert m^3 of natural gas into tons; a conversion factor of 0.0000008 must be used to convert liters of natural gas into tons;

1 m^3 of LPG (mixture of propane and butane) has a mass of about 2 kg; thus, a conversion factor of 0.002 must be used to convert m^3 of LPG into tons and a conversion factor of 0.000002 must be applied to convert liters of LPG into tons.

11.5 Bleaching Sequences – For Main Category 7

Code letters and chemical formulas for bleaching stages are designated as shown in Table 93.

Table 93: Symbols used in bleaching stages

(Bleaching) Chemical	Chemical Formula	Code Letter
Sodium hydroxide	NaOH	E
Extraction step using sodium hydroxide with subsequent addition of gaseous oxygen or hydrogen peroxide as reinforcing agent(s)		Eo, Ep or E/O, E/P
Elemental chlorine	Cl_2	C
Chlorine dioxide	ClO_2	D
Hypochlorite	HClO, NaOCl, $Ca(OCl)_2$	H
Oxygen	O_2	O
Hydrogen peroxide	H_2O_2	P
Sulfur dioxide	SO_2	S
Sulfuric acid	H_2SO_4	A
Ethyldiamine tetra-acetic acid (acid stage to remove metals)	EDTA	Q
Washing step		W
Ozone	O_3	Z

In Europe, sulfite bleaching sequences are:
EOP-Q-EP-EP (HC) EOP-EP (HC) EOP-Q-EP-EP

The most common Kraft bleaching sequences in the USA in 1991 (= old technology) were based on elemental chlorine and have been as follows (EPA 1995):

C-E-D-E-D	C-E-H-D-E-D
C-E-H-E-D	C-E-H, C-E-H-P

The ECF bleaching is different for softwood and hardwood. Normally hardwood requires fewer chemicals than softwood to reach a certain brightness, which usually means that the number of bleaching stages can be shorter. Examples for light ECF sequences are (DZ)(EOP)D, (DQ)(PO), D(EOP)D(PO), which can be applied for both hardwood and soft-wood depending on the brightness target

Nowadays, oxygen delignification has become more and more common followed by bleach-ing sequences such as (ECF plants):

D-E-D-E-D	D-EOP-D-E-D
D-E-D-D	QP-DQ-PO

Depending on market demands, some ECF mills have the possibility to produce Totally Chlorine Free pulps (TCF). TCF mills have developed technologies such as:

Q-E/P-E-P	OP-ZQ-PO
Q-Z-P-E-P	OP-Q-PO.